SESTEC 2026

12TH DAE-BRNS BIENNIAL SYMPOSIUM ON EMERGING TRENDS IN SEPERATION SCIENCE AND TECHNOLOGY

February 11-14, 2026
DAE Convention Centre
IGCAR, Kalpakkam

BOOK OF ABSTRACTS

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१२वाँ डीएई–बीआरएनएस द्विवार्षिक संगोष्ठी कार्यवृत्त

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डी ए ई सम्मेलन केंद्र, अनुपुरम
इंदिरा गांधी परमाणु अनुसंधान केंद्र, कल्पक्कम

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आयोजक
भाभा परमाणु अनुसंधान केंद्र, मुंबई

सह- आयोजक
इंदिरा गांधी परमाणु अनुसंधान केंद्र, कल्पक्कम
एवं
एसोसिएशन ऑफ सेपरेशन साइंटिस्ट्स एंड टेक्नोलॉजिस्ट्स
(ऐ एस एस इ टी)

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Title:

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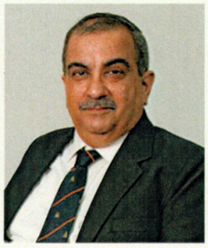

MESSAGE

It gives me great pleasure to know that the Association of Separation Scientists and Technologists (ASSET), along with BARC and IGCAR, is organizing the 12thDAE-BRNS Symposium on *Emerging Trends in Separation Science and Technology* (SESTEC-2026) at IGCAR, Kalpakkam, during February 11-14, 2026.

Since its inception in 2004, SESTEC series of symposia has been providing excellent forum for scientists and engineers to exchange the latest developments in the field of separation science and technology, particularly in areas relevant to nuclear fuel cycle activities.

It is heartening to note that the SESTEC-2026 will be attended by a wide spectrum of participants, including young researchers and faculties from universities and research institutes, and scientists and engineers from national laboratories from India and abroad. The symposium will cover diverse themes such as Separations in the Nuclear Fuel Cycle, Radiochemical Separations, Green Separations, Membrane Science and Technology, Treatment of Industrial Effluents, Computational Chemistry in Separation Science, and Speciation Studies.

The scientific programme of SESTEC-2026 will include a keynote address, plenary lectures, invited talks, presentations by research scholars, and poster sessions spread across 14 technical sessions. .I am confident that SESTEC-2026 will provide an excellent platform for fruitful deliberations and will significantly enrich the knowledge of young researchers in addressing current challenges in separation science related to industry, water treatment, and overall improvement in quality of life.

I wish SESTEC-2026 every success.

Vivek Bhasin
(Vivek Bhasin)

03.02.2026

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Outstanding Scientist & DIRECTOR

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Message

February 2, 2026

I am pleased to note that the 12th DAE–BRNS Symposium on "Emerging Trends in Separation Science and Technology (SESTEC-2026)" is being organized by the Bhabha Atomic Research Centre (BARC) in association with the Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, and the Association of Separation Scientists and Technologists (ASSET), with full support from BRNS, at the DAE Convention Centre, Anupuram, during February 11–14, 2026. The symposium will bring together researchers from nuclear and academic institutions, faculty, and students to deliberate on advances in separation science and technology relevant to the nuclear fuel cycle, including actinide, lanthanide, and fission-product separations and speciation.

The return of SESTEC to IGCAR after a gap of 15 years is noteworthy, reaffirming Kalpakkam as a key centre of excellence in nuclear separation science. I am particularly pleased that a half-day special session is devoted to reprocessing of spent fuel, with special emphasis on fast reactor spent fuel, a topic of significant scientific and technological relevance.

As envisioned by Dr. Homi Jehangir Bhabha, India's energy security rests on the three-stage nuclear power programme, now progressing through fast breeder reactors in Stage-II and towards thorium-based systems in Stage-III. IGCAR has a pivotal role in this national mission, with its leadership in sodium-cooled fast breeder reactor technology and the operation of the Fast Breeder Test Reactor (FBTR) using U-Pu mixed carbide fuel. Reprocessing of fast reactor fuels, closely integrated with BARC's Kalpakkam facilities, remains central to this effort, making SESTEC-2026 a timely and relevant forum for the Kalpakkam scientific community.

Future challenges in separation science call for novel extractants, advanced process concepts, and robust technologies for Pu- and U-233-based fuels, along with safe and efficient management of high-level radioactive waste. The concept of "wealth from waste", through recovery of valuable radioisotopes, highlights the broader societal impact of advances in this field. In parallel, pyrochemical reprocessing is gaining importance for metallic fuels envisaged for future fast reactors. IGCAR's ongoing work in metal-fuel fabrication and pyroprocessing further enhances the relevance of discussions on both aqueous and pyrochemical routes at SESTEC-2026.

In the broader context of Amrit Kaal, the 2047 national vision, and net-zero carbon goals, progress in separation science and technology is of strategic importance for sustainable energy development, resource efficiency, and waste minimization. SESTEC-2026 thus serves as a valuable platform to strengthen India's leadership in this domain, foster inter-institutional collaboration, and translate research outcomes into practical solutions for the nuclear fuel cycle and radioactive waste management.

I convey my best wishes for the grand success of SESTEC-2026.

(Sreekumar G Pillai)
Director

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Board of Research in Nuclear Sciences

Dr. R. B. Grover
Chairman

Government of India
Department of Atomic Energy (DAE)
Board of Research in Nuclear Sciences (BRNS)

02 February 2026

MESSAGE

I am pleased to know that the 12th DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2026) is being organised at IGCAR, Kalpakkam, during February 11-14, 2026.

The Separation Science and Technology play a critical role in various stages of nuclear fuel cycles, viz., the recovery of uranium and thorium and their purification, retrieving fission products and fissile materials from spent fuel, and partitioning of minor actinides for safe management of nuclear waste. Besides nuclear industries, Separation Science and Technology play a key role in sectors such as pharmaceuticals, petrochemicals, water purifications, etc. Innovations in Separation Science and Technology are important to all these sectors to make the processes efficient, selective, cost-effective, environmentally benign and commercially viable.

As in any symposium, SESTEC-2026 will provide a platform to scientists and engineers working in Separation Science and Technology to interact and share their ideas. Given the importance of reprocessing spent fuel for the nuclear programme in India, I am delighted to note that a special session is dedicated to reprocessing. I hope the researchers working in this field will benefit from deliberations in the symposium and will move forward to overcome various challenges in the back-end of the nuclear fuel cycle.

I am happy to know that a large number of researchers from India and some from abroad are expected to participate in the symposium. I compliment the organisers, and I must say that this symposium will benefit scientists, researchers, and students through deliberations and possible collaborations.

I extend my best wishes for the grand success of SESTEC-2026.

RB Grover

(R B Grover)

PREFACE

This proceedings presents the peer-reviewed abstracts to be presented in the 12th Biennial DAE–BRNS Symposium on Separation Science and Technology (SESTEC-2026), being held during 11–14 February 2026 at the DAE Convention Centre, Anupuram, Indira Gandhi Centre for Atomic Research (IGCAR), Kalpakkam, India. The contributions reflect recent developments and emerging trends in separation science and technology, as presented by researchers and technologists from diverse scientific backgrounds.

The abstracts compiled in this volume encompass a wide range of scientific themes, underscoring the central role of separation science in areas such as the nuclear fuel cycle, membrane science and technology, treatment of industrial effluents, chromatographic, electrochemical and pyrochemical separations, radiochemical separations, speciation studies, computational chemistry applied to separation processes, and the development of green and sustainable separation technologies for environmental protection. These themes represent rapidly evolving and scientifically stimulating areas of research and provide a forum for discussing future strategies, key objectives, and emerging challenges at the frontiers of advancing separation science.

The proceedings contain approximately 200 abstracts, selected through a single-blind critical peer-review process conducted by a panel of expert reviewers. The content is intended to cater to a broad audience, ranging from researchers to budding scientists.

SESTEC-2026 seeks to promote interdisciplinary interaction, facilitate effective exchange of scientific knowledge, and encourage novel thoughts through technical sessions and poster presentations. The symposium also provides an inclusive platform for young researchers to interact with experts, share ideas, and gain exposure to emerging research directions. It offers opportunities for delegates to exchange experiences, establish research linkages, and identify potential national and international collaborators for future scientific endeavours.

The symposium includes a special technical session on the reprocessing of spent nuclear fuels, with particular emphasis on fast reactor spent nuclear fuel. This session will address key challenges in the reprocessing sector and highlight significant advancements achieved to date, and are expected to be of considerable relevance to separation scientists and engineers engaged in this area. The inclusion of this session is appropriate in view of Kalpakkam's long-standing expertise and extensive experience in nuclear fuel reprocessing facilities.

The symposium is organized by the Bhabha Atomic Research Centre (BARC) in association with IGCAR, Kalpakkam, and the Association of Separation Scientists and Technologists (ASSET). Since its inception in 2004, SESTEC symposium has been held biennially at several premier institutions across India and has evolved into a recognised forum for the international separation science community. Details of SESTEC-2026, including the symposium programme and proceedings, are available on the symposium website.

ASSET has played a pivotal role in organizing the SESTEC symposium series and in ensuring its continued success. During SESTEC-2026, ASSET will confer the two awards: Dr. P. N. Pathak Memorial Award on a distinguished Indian researcher in recognition of outstanding contributions to the field of separation science and technology and THERMAX-ASSET awardfor the best Ph.D. & M. Tech. / M. Phil. thesis in the area of separation science and technology. An evening lecture by the awardees will be a special feature of the symposium.

The organizers are pleased to host eminent scientists from India and abroad, who will deliver invited and short invited talks and share their innovative research outcomes and perspectives. We record our sincere appreciation to Dr A. K. Mohanty, Chairman, Atomic Energy Commission, for his encouragement and continued support to SESTEC-2026, and to Dr. R. B. Grover, Chairman, BRNS, DAE, for being the Patron of the symposium. We extend our gratitude to Shri Vivek Basin, Director, BARC, for his wholehearted support and guidance as Chairman of the National Advisory Committee and Symposium Organizing Committee.We record our sincere thanks to Shri Sreekumar G. Pillai, Director, IGCAR, for hosting the symposium. We acknowledge BRNS for the financial support extended to the symposium. The constant support of the members of the National Advisory Committee and the Symposium Organizing Committee, the dedicated efforts of the Technical Committee in the timely evaluation of abstracts, and the valuable contributions of all authors are gratefully recognized. Special thanks go to the SESTEC-2026 Secretariat members for their diligent efforts to ensure smooth execution of the technical event. We put on record our sincere thanks to Shri Dharmendra Sharma, Shri Sapath Bhandari and Shr Atanu Das for their dedicated efforts towards preparation of the “Book of Abstracts”.

It is hoped that the participants and readers of this proceedings volume will derive significant scientific benefit from the contributions and find the compilation both informative and stimulating.

The symposium is being held at Anupuram, a Department of Atomic Energy township near Kalpakkam and in proximity to the historic coastal town of Mamallapuram. The location offers a calm setting for scientific interaction and enables comfortable participation in the technical programme during February.

Have a Pleasant Stay and Scientifically Stimulating Interactions!

With Best Wishes

Editors

प्रस्तावना

इस कार्यवाही शोधपत्र में पृथक्करण विज्ञान और प्रौद्योगिकी पर १२वें द्विवार्षिक डीएई-बीआरएनएस संगोष्ठी (सेस्टेक-२०२६) में प्रस्तुत किए जाने वाले सहकर्मी-समीक्षित सारों का संग्रह है, जो ११ – १४ फरवरी २०२६ के दौरान परमाणु ऊर्जा विभाग के सम्मेलन केंद्र, अनुपुरम, इंदिरा गांधी परमाणु अनुसंधान केंद्र (आईजीसीएआर), कल्पक्कम में आयोजित किया जा रहा है। ये योगदान पृथक्करण विज्ञान और प्रौद्योगिकी में हाल के विकास और उभरते रुझानों को दर्शाते हैं, जिन्हें विभिन्न वैज्ञानिक पृष्ठभूमियों के शोधकर्ताओं और प्रौद्योगिकीविदों द्वारा प्रस्तुत किया गया है।

इस शोधपत्र में संकलित सारांश वैज्ञानिक विषयों की एक विस्तृत श्रृंखला को समाहित किया गया है, जो परमाणु ईंधन चक्र, झिल्ली विज्ञान और प्रौद्योगिकी, औद्योगिक अपशिष्टों के उपचार, क्रोमैटोग्राफिक, इलेक्ट्रोकेमिकल और पायरोकेमिकल पृथक्करण, रेडियोकेमिकल पृथक्करण, स्पीसिएशन अध्ययन, पृथक्करण प्रक्रियाओं में लागू कम्प्यूटेशनल रसायन विज्ञान और पर्यावरण संरक्षण के लिए हरित और टिकाऊ पृथक्करण प्रौद्योगिकियों के विकास जैसे क्षेत्रों में पृथक्करण विज्ञान की केंद्रीय भूमिका को रेखांकित करते हैं। ये विषय तेजी से विकसित हो रहे और वैज्ञानिक रूप से प्रेरक अनुसंधान क्षेत्रों का प्रतिनिधित्व करते है, और पृथक्करण विज्ञान को आगे बढ़ाने के क्षेत्र में भविष्य की रणनीतियों, प्रमुख उद्देश्यों और उभरती चुनौतियों पर चर्चा करने के लिए एक मंच प्रदान करता है।

इस शोधपत्र में लगभग २०० सार-संक्षेप शामिल हैं, जिनका चयन विशेषज्ञ समीक्षकों के एक पैनल द्वारा संचालित एकल-अंधा आलोचनात्मक सहकर्मी-समीक्षा प्रक्रिया के माध्यम से किया गया है। इसकी सामग्री शोधकर्ताओं से लेकर नवोदित वैज्ञानिकों तक, व्यापक दर्शकों की आवश्यकताओं को पूरा करने के उद्देश्य से तैयार की गई है।

सेस्टेक-२०२६ का उद्देश्य अंतःविषयक संवाद को बढ़ावा देना, वैज्ञानिक ज्ञान के प्रभावी आदान-प्रदान को सुगम बनाना और तकनीकी सत्रों और पोस्टर प्रस्तुतियों के माध्यम से नवीन विचारों को प्रोत्साहित करना है। यह संगोष्ठी युवा शोधकर्ताओं को विशेषज्ञों के साथ संवाद करने, विचारों को साझा करने और उभरती अनुसंधान दिशाओं से अवगत होने के लिए एक समावेशी मंच भी प्रदान करता है। यह प्रतिनिधियों को अनुभवों का आदान-प्रदान करने, अनुसंधान संबंध स्थापित करने और भविष्य के वैज्ञानिक प्रयासों के लिए संभावित राष्ट्रीय और अंतर्राष्ट्रीय सहयोगियों की पहचान करने के अवसर प्रदान करता है।

संगोष्ठी में प्रयुक्त परमाणु ईंधनों के पुनर्संसाधन पर एक विशेष तकनीकी सत्र शामिल है, जिसमें विशेष रूप से तीव्र रिएक्टरों के प्रयुक्त परमाणु ईंधन पर जोर दिया गया है। यह सत्र पुनर्संसाधन क्षेत्र में प्रमुख चुनौतियों का समाधान करेगा, और अब तक प्राप्त महत्वपूर्ण प्रगति को उजागर करेगा तथा इस क्षेत्र में कार्यरत पृथक्करण वैज्ञानिकों और इंजीनियरों के लिए अत्यंत प्रासंगिक होने की उम्मीद है। परमाणु ईंधन पुनर्संसाधन सुविधाओं में कलपक्कम की दीर्घकालिक विशेषज्ञता और व्यापक अनुभव को देखते हुए इस सत्र का समावेश उचित है।

यह संगोष्ठी भाभा परमाणु अनुसंधान केंद्र (बी ए आर सी) द्वारा इंदिरा गांधी परमाणु अनुसंधान केंद्र (आईजीसीएआर), कलपक्कम और पृथक्करण वैज्ञानिकों और प्रौद्योगिकीविदों के संघ (ए एस एस इ टी) के सहयोग से आयोजित की जाती है। २००४ में अपनी स्थापना के बाद से, सेस्टेक संगोष्ठी भारत भर के कई प्रमुख संस्थानों में द्विवार्षिक रूप से आयोजित की जाती रही है और अंतरराष्ट्रीय पृथक्करण विज्ञान समुदाय के लिए एक मान्यता प्राप्त मंच के रूप में विकसित हुई है। सेस्टेक-२०२६ का विवरण, जिसमें संगोष्ठी कार्यक्रम और कार्यवाही शामिल हैं, संगोष्ठी की वेबसाइट पर उपलब्ध हैं।

ए एस एस इ टी ने सेस्टेक संगोष्ठी श्रृंखला के आयोजन और इसकी निरंतर सफलता सुनिश्चित करने में महत्वपूर्ण भूमिका निभाई है। सेस्टेक-२०२६ के दौरान, ए एस एस इ टी दो पुरस्कार प्रदान करेगा: पृथक्करण विज्ञान और प्रौद्योगिकी के क्षेत्र में उत्कृष्ट योगदान के लिए एक प्रतिष्ठित भारतीय शोधकर्ता को डॉ. पी.एन. पाठक स्मारक पुरस्कार तथा पृथक्करण विज्ञान और प्रौद्योगिकी के क्षेत्र में सर्वश्रेष्ठ पी.एच.डी. और एम.टेक. / एम.फिल. शोध प्रबंध के लिए थर्मैक्स- ए.एस.एस.इ.टी. पुरस्कार। पुरस्कार विजेताओं द्वारा दिया जाने वाला एक संध्याकालीन व्याख्यान संगोष्ठी का एक विशेष आकर्षण होगा।

आयोजक भारत और विदेश के प्रख्यात वैज्ञानिकों की मेजबानी करके प्रसन्न हैं, जो आमंत्रित और संक्षिप्त व्याख्यान देंगे और अपने नवोन्मेषी शोध परिणामों और दृष्टिकोणों को साझा करेंगे। हम परमाणु ऊर्जा आयोग के अध्यक्ष डॉ. ए.के. मोहंती के प्रति सेस्टेक-२०२६ को प्रोत्साहन और निरंतर समर्थन देने के लिए हार्दिक आभार व्यक्त करते हैं, और संगोष्ठी के संरक्षक होने के लिए बीआरएनएस, डीएई के अध्यक्ष डॉ. आर.बी. ग्रोवर के प्रति भी आभार व्यक्त करते हैं। राष्ट्रीय सलाहकार समिति और संगोष्ठी आयोजन समिति के अध्यक्ष के रूप में अपने पूर्ण समर्थन और मार्गदर्शन के लिए हम बीएआरसी के निदेशक श्री विवेक भसीन के प्रति कृतज्ञता व्यक्त करते हैं। संगोष्ठी की मेजबानी करने के लिए हम आईजीसीएआर के निदेशक श्री श्रीकुमार पिल्लई को हार्दिक धन्यवाद देते हैं। संगोष्ठी को वित्तीय सहायता प्रदान करने के लिए हम बीआरएनएस के आभारी हैं। राष्ट्रीय सलाहकार समिति और संगोष्ठी आयोजन समिति के सदस्यों के निरंतर समर्थन, समय पर मूल्यांकन में तकनीकी समिति के समर्पित प्रयासों और सभी लेखकों के बहुमूल्य योगदान को हम कृतज्ञतापूर्वक स्वीकार करते हैं। तकनीकी कार्यक्रम के सुचारू संचालन को सुनिश्चित करने के लिए सेस्टेक-२०२६ सचिवालय के सदस्यों के अथक प्रयासों के लिए हम विशेष धन्यवाद देते हैं। श्री धर्मेंद्र शर्मा, श्री सपथ भंडारी और श्री अतनु दास को "सार पुस्तिका" तैयार करने में उनके समर्पित प्रयासों के लिए हम हार्दिक धन्यवाद देते हैं।

आशा है कि इस कार्यवाही संकलन के प्रतिभागी और पाठक इसमें प्रस्तुत लेखों से महत्वपूर्ण वैज्ञानिक लाभ प्राप्त करेंगे और इसे ज्ञानवर्धक एवं प्रेरक पाएंगे।

यह संगोष्ठी कल्पक्कम के निकट और ऐतिहासिक तटीय शहर मामल्लापुरम के पास स्थित परमाणु ऊर्जा विभाग के अनुपुरम नगर में आयोजित की जा रही है। यह स्थान वैज्ञानिक संवाद के लिए शांत वातावरण प्रदान करता है और फरवरी के दौरान तकनीकी कार्यक्रम में सुगम भागीदारी सुनिश्चित करता है।

आपका प्रवास सुखद हो और वैज्ञानिक ज्ञानवर्धक संवादों का लाभ लें!

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PL-1

Radio-Cesium Separation Strategies for Nuclear Fuel Cycle Applications

Prof. P.K. Mohapatra, Former Director, RC&IG, BARC, Mumbai

Dr. P. K. Mohapatra, Former Director, Radiochemistry and Isotope Group, BARC, joined Radiochemistry Division, BARC in 1987 after graduating from the 30th Batch of the Bhabha Atomic Research Centre (BARC) training school. His research interests include separation of actinides and fission products using novel extractants, in ionic liquid based solvents and novel separation techniques including liquid membranes. A recognized guide of Mumbai University and Homi Bhabha National Institute (Deemed University), Dr. Mohapatra was an Associate Editor of Separation Science and Technology and one of the Editors of Radiochimica Acta. He was also on the advisory board of several prestigious journals including Solvent Extraction and Ion Exchange. He has over 450 publications in reputed international journals with over 9600 citations.

PL-2

Separation Technologies in Advanced Nuclear Fuel Cycle

Shri Kalyan Bhanja, Associate Director, ChEG, BARC

Shri. Kalyan Bhanja graduated in Chemical Engineering and joined BARC in 1990 through 34th Batch of BARC Training School. At present he is involved in proof-of-concept demonstration, process scale up, project planning and execution for production, separation and purification technologies. For the last three decades, he has been very active in the field of emerging technologies, including Hydrogen Energy, specifically Electrolytic Hydrogen production, Separation & Purification technologies involving Isotopes & Hazardous chemicals and High purity mono-crystalline Silicon preparation from metallurgical grade Silicon, under Atma Nirbhar Bharat initiative. He is currently the Associate Director, Chemical Engineering Group, BARC.

PL-3

Radioisotope Production in Fast Breeder Test Reactor

Dr K Sundararajan, IGCAR

Dr. K. Sundararajan obtained B.Sc (Chemistry) degree from Madras University (A.M Jain college, Chennai (1985-1988)); M.Sc (1988-1990; Physical Chemistry) from Pune University and joined 34th batch training school at BARC. He obtained his Ph.D degree in 2003 from Madras University and took one year postdoctoral position (2005-2006) at National Chiao Tung University, Taiwan. His specialization is in the area of Low temperature Matrix isolation Infrared technique, Fluorescence spectroscopy, Computational chemistry and Analytical and Radioanalytical chemistry. He has over 100 publications in international journals. He is currently heading the Analytical and Spectroscopy Division, MC&MFCG. He has guided four students under HBNI to obtain their PhD degree.

PL-4

Separation Science and Technology at Backend of Fuel Cycle: Current Status and Way Forward

Dr. G. Sugilal, Director, NRG, BARC

Dr. Sugilal Gopalakrishnan is an Outstanding Scientist at BARC. He is from 33rd batch of BARC Training School. He is a gold medalist in Chemical Engineering from University of Kerala and earned his MTech & PhD from IIT Bombay. He did his post-doctoral research in TUI, Germany. He is a Fellow of Indian National Academy of Engineering and a Senior Professor of Homi Bhabha National Institute, Mumbai. He has made significant contributions to the fields of spent fuel reprocessing and radioactive waste management. He is a member of several committees including BARC Safety Council. He is a recipient of several awards including DAE-Homi Bhabha Science and Technology Award. Currently he is the Director, Nuclear Recycle Group, BARC.

Pl-5

Advanced Process Flow-Sheet for Fast Reactor Fuel Reprocessing

Dr. K.A. Venkatesan, Associate Director, Reprocessing Group, IGCAR, Kalpakkam

K A Venkatesan obtained MSc Degree from University of Madras in the year 1991, and joined BARC training school. After completion of training school, he joined BARC 1992 and moved to IGCAR in 1998. At present he is the Associate Director of Reprocessing Design and R&D Group, Reprocessing Group, IGCAR, Kalpakkam. His field of Interest is chemistry of fuel reprocessing and waste management. He has several publications in peer-reviewed journal and national conferences, guided a number of research scholars and staff members to obtain PhD. He is one of the key members in commissioning DFRP, implementation of advanced processes at CORAL and DFRP plants, aiming at waste minimization strategy, building of facilities at DFRP (head end facility) and head end equipment at FRP/FRFCF

PL-6

The Vital Role of Radioisotope Separation Science in Nuclear Medicine

Dr. Madhav B. Mallia, Head, RCS, RPhD, BARC, Mumbai

Dr. Madhava B Mallia completed his MSc in Applied chemistry from Cochin University of Science and Technology. After a brief stint in National Chemical Laboratory, Pune, he joined BARC Training School in 2001. He was awarded with Homi Bhabha gold medal for securing 1st rank in BARC Training School in Chemistry discipline. After successful completion of the training program, he joined Radiopharmaceuticals Division, BARC. His research interest includes development of diagnostic/therapeutic radiopharmaceuticals employing in-silico methods for oncology applications and exploring the use of nanoplatforms for chemo-radiotherapy. Development of freeze-dried kits for the preparation of radiopharmaceuticals for various clinical applications is a significant contribution to radiopharmaceuticals program in India. He is the recipient several awards including the DAE-Scientific and Technical Excellence Award (2015) for his contributions to radiopharmaceuticals development and deployment in India. He is Professor (Chemistry) in Homi Bhabha National Institute and served as subject expert in overseas IAEA Regional Training Programmes. He is also serving as the Associate Editor of the international journal Cancer Biotherapy and Radiopharmaceuticals

Pl-7

Engineering of Solvent Extraction Process Development

Shri K.T. Shenoy, Former Director, ChEG, BARC

K. T. Shenoy joined Chemical Engineering Division of Bhabha Atomic Research Centre in 1988 after completing one-year Orientation Course (31^{st} Batch) in Nuclear Science and Engineering. His professional expertise is in the applied research related to process and equipment development of nuclear fuel cycle. His significant technological contributions are development of solvent extraction contactors, nitrate remediation through thermal denitration, alkaline leaching of Tummalapalle uranium ore, etc. Later, he spearheaded the in scaling up and technology deployment of green hydrogen production and desalination technologies. He superannuated from BARC as Director, Chemical Engineering Group in Oct. 2025. Currently, he holds the prestigious DAE-Homi Sethna Chair.

PL-8

Application of Ion Exchange Chromatography to Establish SI Traceability in Certified Reference Materials (CRMs) of Bio-molecules

Dr. K. Dash, Head, NCCCM, Hyderabad

Dr K. Dash, Scientist, Grade-H, and presently heading National Centre for Compositional Characterization of Materials (NCCCM), Hyderabad, which is a Division of Bhabha Atomic Research Centre (BARC). He passed out M.Sc (Chemistry) in 1989 from Ravenshaw University, Cuttack, Odisha and joined in the 34th batch of BARC Training School in 1990. In 2009, he obtained PhD degree from Osmania University, Hyderabad.

His field of specializations are in Liquid and Gas Chromatography, Atomic Absorption and Emission Spectroscopy techniques and research interests include Trace Analysis in high purity materials and production of Certified Reference Material (CRMs). Dr Dash's group at NCCCM-BARC has specialised in the analysis of high purity silicon dioxide which are exported from the country since last 30 years using spectroscopic techniques. His group at NCCCM-BARC has produced many high-end Certified Reference Materials (CRMs like high purity silicon dioxide, Bauxite, Alumina and Dolomite. Dr Dash is the project leader for the production of CRMs of High Strength Low alloy steels, which are used in naval ships including aircraft carriers and Preesure Vessel Steel (BARC-APURVA-01) in collaboration with Reactors Project Group-BARC. These two steel CRMs shall be shortly released by DAE authorities. Under his guidance Indias's first CRM of Rare Earth Elements (REEs) in Ferrocarbonatite (BARC-B1401) has been produced, a collaboration project between NCCCM-BARC & AMDER-Hyderabad. Presently Dr Dash is the project co-ordinator for the production of three high end CRMs of national importance (Enriched Boron Carbide, Intermediate enriched Boron carbide and natural boron carbide) where established laboratories from various DAE units like BARC, IGCAR and HWB are actively involved. Dr Dash has more than 100 publications in peer-reviewed international journals and symposiums.

PL-9

Polymer Inclusion Membranes and Beads in Environmentally Friendly Chemical Separation

Prof. S.D. Kolev, School of Chemistry, The University of Melbourne, Australia

Spas D. Kolev is currently serving as a Professor of Chemistry at the University of Melbourne, Australia. He is recognized for his research in flow analysis, polymer inclusion membranes, and environmental analytical chemistry. He has received numerous awards, including the Ronald Belcher Memorial Award, Lloyd Smythe Medal, JAFIA Medal, Environmental Chemistry Medal, and Max O'Connor Prize. He is the Editor in Chief of multiple journals viz. Talana, Membrane.

PL-10

Novel Reactions and Separations for Actinide Halides and Their Implications for the Nuclear Fuel Cycle

Prof. K.R. Czerwinski, University of Nevada Las Vegas, USA

Ken Czerwinski joined the University of Nevada Las Vegas Radiochemistry Program as an associate professor in 2004 and currently holds the rank of full professor of chemistry. He has conducted radiochemistry research since 1986, with his first faculty appointment beginning in 1996 in the Department of Nuclear Engineering at the Massachusetts Institute of Technology. He earned a PhD in nuclear chemistry from the University of California Berkeley in 1992, where his doctoral research focused on the chemistry of rutherfordium. At UNLV, Professor Czerwinski founded and served as the first director of the Radiochemistry PhD program, establishing a nationally recognized center for graduate education and research in radiochemistry. He previously held a joint appointment with TerraPower LLC from 2014 to 2021 and maintains an affiliate professorship with the University of Washington. His instructional portfolio spans undergraduate and graduate in numerous radiochemistry related courses. Professor Czerwinski's research focuses on actinide and technetium compounds in actinide separations chemistry, nuclear forensics, isotope production, fuel cycle related processes, and fundamental research. His work is closely integrated with graduate and undergraduate student training and emphasizes experimental laboratory investigations involving radioelements. He is a Fellow of the American Association for the Advancement of Science and provides technical consultation to industry, federal agencies, and international organizations with more than 240 peer reviewed publications and patents.

Molecular-Level Understanding of Sorption and Extraction Processes: Ionic Liquids and Deep Eutectic Solvents for Advanced Separation Science

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Efficient and selective separation of metal ions remains central to challenges in nuclear fuel cycle operations, waste management, and environmental remediation. In this context, ionic liquids (ILs) and deep eutectic solvents (DESs) have gained significant attention as designer solvents and functional additives owing to their tunable physicochemical properties, negligible vapor pressure, and rich intermolecular interaction landscapes.

This invited talk will present molecular-level insights into the role of ILs and DESs in enhancing sorption and solvent extraction processes relevant to separation science and technology. Emphasis will be placed on how specific interactions, such as hydrogen bonding, coordination chemistry, π–π interactions, and electrostatic effects, govern metal-ligand complexation, solute speciation, and phase transfer phenomena. Case studies will highlight the separation of strategically important metal ions, with broader implications for actinide, lanthanide and fission product analogues in aqueous and mixed-solvent systems.

Computational approaches, including density functional theory (DFT) and COSMO-RS, will be integrated with experimental observations to elucidate solvation thermodynamics, selectivity trends and structure–property relationships. These insights enable rational solvent design and improved predictability of separation performance under complex chemical environments.

Key physical chemistry aspects, such as solvation structure, thermophysical properties, phase behavior, and solvent recyclability, will be discussed in the context of wastewater remediation and critical metal recovery, with relevance to nuclear and non-nuclear separation challenges alike. Overall, the talk highlights how molecular-scale understanding can inform the development of efficient, sustainable, and next-generation separation technologies.

Key words: *Ionic liquids, Deep eutectic solvents, Solvent extraction, Solvation thermodynamics, Separation science*

Functionalized Polyurethane Foams - Promising Applications in Separation Processes

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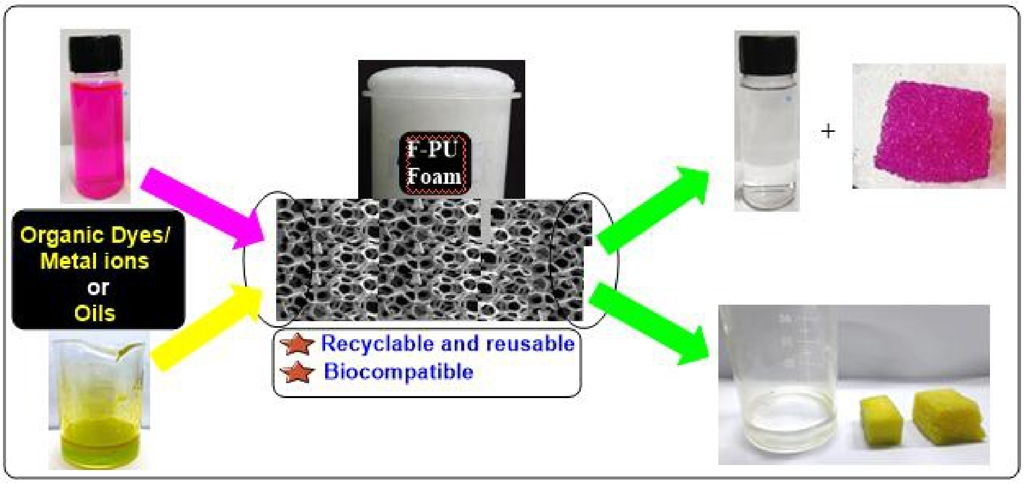
Polyurethane (PU) foams exhibit remarkable properties such as high porosity, lightweight, low density, high specific strength, electromagnetic shielding and excellent thermal and sound insulation compared to other polymeric materials. These important properties make them extensively used in different types of civil and industrial applications including insulation, packaging, automotive, medical, and aircraft fields. The presence of a chemical blowing agent facilitates excellent microcellular foaming with finer cells displaying specific properties required. Recently, research on PU foams has focused on the development of new materials with improved properties for a wide range of applications. In this regard, our research team at VIT-Vellore designed and prepared several new functionalized polymeric foams derived from the reactions of biomaterials and diisocyanates. These task-specific polymeric foams loaded with active metal species have been employed in a variety of catalytic organic transformations [1, 2]. Also, the selected PU foams have been used successfully in the efficient separation of various dyes (cationic and anionic) [3], metal ions, and oils from water [4] (Fig.1). Studies indicate that these materials possess recyclability and reusability for more than 10 cycles. The factors influencing the properties of these synthesized PU materials associated with additional phosphoryl [5] and terpyridyl moieties and their applications will be highlighted.



Key words: *Functionalized PU foams, Synthesis, Separation of cationic and anionic dyes, Metal ions from solutions, Oils from emulsions*

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Extraction of Critical Minerals - Breaking the Bottleneck

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Critical minerals form strategic foundation for the nation's goal towards vikshit Bharat to transform India into a developed country by the 100th year of independence through sustainable development, high-end infrastructure, and skilled workforce. The ambitious target to make India as a $30 trillion economy can be realized by addressing vulnerability in the supply chain of critical minerals. Ministry of mines, Government of India identified 30 prominent minerals crucial for green energy transition, low carbon economy, advanced manufacturing, security, healthcare and communication. A dramatic shift in Policy, Strategy and Science is the need of the hour to address accessibility of critical minerals.

The launch of National Critical Minerals Mission (NCMM) in the year 2025 with a financial outlay of ₹ 16,300 crores and amendment in the Mines and Minerals Development and Regulation Act marked the beginning of Policy shift. Establishment of (Khanij Bidesh India Limited) KABIL, expansion of field projects by Geological Survey of India (GSI) and waiver of Basic Customs Duty for imported critical minerals marked the beginning of Strategy shift. Now it is time for the researchers to make scientific shift on the extraction of critical minerals.

Current focus has been on establishing separation technology of critical metals from primary resources and now the focus has to shift towards sustainable urban mining. Hydrometallurgical and pyrometallurgical separation approaches with green methodologies on the urban resources such as smartphones, laptops, electronic/electrical appliances, batteries, capacitors and construction debris promotes a circular economy by recycling materials, reducing environmental impact, and securing supply chains for critical resources. This talk highlights the recent progress on the extraction of some of the critical minerals/metals through advanced recycling techniques.

Diffusion and Sorption behavior of tracers on Fe-montmorillonite relevant to deep geological disposal of HLW

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Bentonite clay is a candidate engineered barrier material in the deep geological disposal of HLW. Montmorillonite (**Mt**, 2:1 smectite group clay) is the major clay mineral of bentonite with high capacity for swelling and adsorption, low hydraulic conductivity and self-healing properties. The interaction of Mt with the overpack (carbon steel) and its corrosion products can provide potential pathways for the alteration of Mt. In addition to structural alteration leading to many thermodynamic phases, the most probable reaction under reducing conditions is the release of Fe ions from the overpack followed by the conversion of Na-Mt to Fe-Mt. The impact of such an alteration on the basic properties of clay mineral should be clarified. Therefore, we have carried out some basic studies using Fe(III)- and Fe(II)-Mt samples [1-4].

The results on swelling, hydraulic conductivity, thermal stability and diffusion behavior of tracers viz., $^{22}Na^{+}$, HTO and ^{36}Cl in compacted and water-saturated Fe(III)-Mt will be presented here. The apparent diffusion coefficient values for Fe(III)-Mt were found to be marginally different from that of Na-Mt [3]. The sorption of $^{152+154}Eu$(III), ^{137}Cs(I) and ^{133}Ba(II) on Fe-Mt are observed as a function of time (kinetic study), ionic strength and pH [5-7]. The isotherm sorption behavior is explained based on ion-exchange and surface complexation modeling. The diffusion of ^{22}Na, ^{137}Cs, ^{133}Ba, $^{152+154}Eu$ and ^{131}I in compacted, water-saturated Fe–montmorillonite. In general, the Da values were slightly higher in Fe(II)-Mt when compared to Fe(III)-Mt. Nevertheless, all these Da values (except Eu^{3+}) are comparable with those reported for Na-Mt [8]. The effect of temperature was found to be similar to that of γ-irradiation, particularly on the reduction of interlayer Fe(III) ions in Fe(III)-Mt. Recovery of Mo(VI) from simulated HLLW by solvent extraction and adsorption on Fe-oxides were also studied [9].

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Radiometallic Isotopes Such as ^{64}Cu, ^{89}Zr, ^{45}Ti and ^{68}Ga: Production, Purification And Quality Assurance: Our Experience

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The future of Radiometal-based Radiopharmaceuticals as theranostics appears to be strong modalities in health care. These will be necessary tools to identify the most promising strategies to tackle upcoming challenge in diagnosis and treatment for human health and its care. It is interesting to note that although a plethora of potentially medically useful metal radionuclides has been explored over the last decades, only a few have made their way towards frequent application or even into clinical routine studies. The foremost challenges are first, their production and secondly developing the feasible separation chemistry to get the purified radiometal to be clinically usable. We are focused on such of them for example ^{64}Cu, ^{89}Zr, ^{45}Ti and ^{68}Ga radio-metallic isotopes. We at our centre experienced the production of these radiometals via solid target methodology and developed their isolation/separation chemistries in order to have purified desired radionuclide. The purified radionuclide was further explored to be used as radiopharmaceuticals via chelation chemistry conjugated to different pharmacophores such as bio-molecules, metal chelators conjugated with bio-molecules, proteins, or peptides.

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Experimental and Theoretical Studies on Lanthanide and Actinide Speciation in Aqueous Environments – A Thermodynamic Prospective

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Lanthanide and actinide ions being hard acids prefer binding with hard Lewis donors (F, and O); and encapsulated with high coordination numbers. The use of multidentate ligands chelating through O and N donors, have been extensively utilized for the formation of thermodynamically and kinetically stable complexes with lanthanides and actinides; and have shown a dynamicity of bonding modes leading to their extensive applications in separation, sequestration, decontamination, decorporation and sensing applications [1]. Actinides need to be contained and concealed to minimize the environmental as well as biological hazards posed by its radio and chemical toxicity. Aquatic contamination is a major concern as it facilitates migration and transportation of the radionuclides from source [2]. Depending on the prevailing conditions around these nuclides, they can undergo various kinds of interactions like complexation, sorption, precipitation and colloid formations [3]. Chelating moieties significantly influences the migration of actinides in the aquifer through strong chemical interaction via forming aqueous soluble species. The behaviour of actinides in aquatic environment is dependent upon their chemical form viz. ions, polymeric forms or as colloids which in turn may affect their chemical interaction as well as their migration. Thus, the accountability of colloids is always essential to determine the solubility limits accurately which are required as inputs in geochemical model.

Determination of the thermodynamic quantities is of prime importance in understanding the basic chemistry behind the complexation reactions such as the feasibility, stability, the enthalpy and entropy of formation of various kinds of species that may probably form during the course of reaction. Thermodynamic parameters are used to predict speciation, enthalpy-entropy compensation and the coordination properties. In multi-component systems, such as natural waters, the stability constants of all the known complexes and the concentrations of each component are used to predict the resultant species [4]. Therefore, the inclusion of all relevant species is crucial for obtaining accurate predictions and experimental speciation data are required as input in these models.

The present report details the complexation of lanthanides (Eu, Nd) and actinides (U, Th, Np, Pu, and Am) with environmentally relevant anthropogenic chelates and associated thermodynamic and coordination behaviours. Potentiometry, absorption spectrophotometry, and fluorescence spectroscopy are very common techniques employed to determine the stability (log K) and speciation, while isothermal titration calorimetry is the widely accepted methodology to deduce formation enthalpies. The stoichiometry and coordination numbers are determined by the luminescence lifetime spectroscopy. It is important and interesting to understand at the molecular level that how the metal ion complexation proceed with change in the ligand concentration. Experimental determination corroborated and/or directed by theoretical elucidations can provide insight into the thermodynamically favored pathways of complex formation. Hence, to support the experimental determinations, theoretical calculations using density functional theory can predict the optimized geometries for the proposed complexes with various possible coordination modes of ligand moieties with metal ion. The free energies calculated for the optimized geometries help to trace the complexation mechanism. In addition to energetic evaluations, the bond distances and charges on individual atoms in bare ligand and on complex formation also provides detailed understanding of the modes and the atoms involved in the coordination during complexation process.

Key words: *Lanthanide, Actinide, Speciation, Complexation, Thermodynamics;*

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Pyrochemical Reprocessing Technology for Metal Fuel Fast Reactors: Development Status and Deployment Plans

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Pyrochemical reprocessing technology is being developed for the treatment of spent metal fuel from fast reactors as a part of closed fuel cycle strategies. The process flowsheet being pursued at IGCAR consists of head end steps (dis-assembly, chopping, sodium distillation), molten salt electrorefining, cathode deposit consolidation, spent electrolyte recycling, and waste treatment. Laboratory and engineering-scale studies for major process steps have been carried out to demonstrate the feasibility. Experience gained from these experimental studies has brought out several important aspects governing process performance and operability. While significant maturity has been achieved in a number of unit operations, challenges related to electrochemical behavior in multicomponent systems, long-duration operation, control of product characteristics, materials performance in corrosive environments, and limitations in process monitoring have to be overcome to ensure predictable operation under conditions relevant to fast reactor spent fuel reprocessing.

In view of the projected metal fuel fast reactor programme, planning activities for the deployment of pyrochemical reprocessing facilities are being initiated in parallel with continued technology development. The transition from development to deployment planning introduces additional considerations related to throughput scaling, remote operation and maintainability, integration with fuel fabrication and waste management systems, and compliance with safety, safeguards, and regulatory requirements specific to non-aqueous reprocessing technologies.

The present talk reviews the current development status of pyrochemical reprocessing technology for metal fuel fast reactors, discusses the key technical challenges identified through experimental and engineering experience, and outlines the major considerations influencing deployment.

Key words: *Non-aqueous reprocessing, pyrochemical reprocessing, pyroprocess, molten salt electrorefining, metal fuel reprocessing.*

IT-08

Current Strategies for Americium Recovery from High-Level Waste: International Scenario

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Americium, particularly the isotope ^{241}Am, is a minor actinide of considerable technological importance owing to its potential applications in radioisotope thermoelectric generators (RTGs) and advanced nuclear power systems. Globally, interest in americium recovery is increasing in response to the expansion of the nuclear energy sector and the emergence of new markets for long-lived radioisotopes. International initiatives, such as collaborations between Orano (France) and Perpetual Atomics (USA/UK), highlight ongoing efforts to establish sustainable americium supply chains through spent nuclear fuel recycling for use in RTGs and deep-space exploration missions.

The global inventory of americium is predominantly secondary in nature, arising from the radioactive decay of aged plutonium stocks. However, the primary source of americium is the raffinate generated during spent nuclear fuel reprocessing, that is high-active waste (HAW) or high-level waste (HLW). In conventional reprocessing schemes such as the PUREX process, uranium and plutonium are first separated, leaving minor actinides, including americium, in the highly radioactive raffinate. This raffinate contains a complex mixture of transuranic elements and fission products, particularly lanthanides, making the selective separation of americium a significant technological challenge. The chemical similarity between trivalent americium and lanthanides further complicates this task. Consequently, americium recovery is generally pursued through a two-step strategy: initial co-extraction of americium and lanthanides via actinide partitioning processes, followed by selective separation of americium using specially designed processes based on soft-donor ligands.

Countries adopting a closed nuclear fuel cycle, such as India, are actively pursuing the integration of americium recovery with high-level waste (HLW) management strategies. Such integration has the potential to reduce the volume of solid vitrified waste by a factor of 30–40. Since americium is a major contributor to the long-term radiotoxicity and decay heat of HLW, its partitioning and recovery are key elements of advanced waste management approaches aimed at reducing disposal hazards while enabling actinide recycling or transmutation. A significant volume of R&D work has been carried out at RCD, BARC on the recovery of high-purity americium from high-level waste (HLW) through integrated actinide partitioning and lanthanide–actinide separation cycles. More recently, several demonstrations have been conducted on advanced actinide partitioning strategies in collaboration with NRB, in which americium can be recovered in a single cycle of solvent extraction and stripping.

Despite substantial progress, americium recovery from HLW remains complex and resource-intensive, with ongoing challenges related to process selectivity, scalability, safety, and economic viability. This presentation provides an overview of the global status and recent developments in americium recovery technologies. In addition, current R&D efforts at the Radiochemistry Division, BARC, aimed at the clean and selective separation of americium from HLW, will be discussed.

Advancements in Separation Science and Technology in Nuclear Fuel Cycle and its Implications on Sustainability and Circularity of the Nuclear Power and Waste Management Program

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Closed nuclear fuel cycle adopted by India is the important cornerstone on which rests the edifice of India's thee stage nuclear power program, from natural-uranium fueled heavy-water reactors through fast breeder systems to a Thorium-U-233 closed cycle. Separation science and technology is the fulcrum of sustainability, energy security, and circular resource use within the nuclear fuel cycle. Efficient and customized technologies for the extraction of radionuclides at every stage enables fuel reuse, minimisation of secondary wastes, recovery of industrially important radionuclides thereby improving the overall safety and economics of the closed fuel cycle.

Recent developments in ligand development, selective solid sorbents, and functionalized resins, have increased selectivity for targeted radionuclides in complex, high-activity matrices. Advancements in the field of remote handling, process monitoring and automation have resulted in reduced man-rem exposure and increased the reliability of the process. These innovations have ushered in new pathways not only for recovery of strategic actinides (Pu, U, and Th) but also for the targeted extraction of industrially valuable fission products and transuranics like ^{137}Cs and ^{241}Am. These radionuclides have well established use in industry, instrumentation, and research.

Recovery of ^{137}Cs and americium from spent fuels and wastes is beneficial for various other reasons. Removal of heat-generating fission products and highly radiotoxic actinides not only reduces the thermal load but also long-term radiotoxicity of final wasteforms thereby lowering repository footprint and easing capital demand on disposal systems. Recovered isotopes can be conditioned and supplied for industrial and societal applications, supporting a circular-economy model that turns “waste into wealth”.

However, extraction of these radionuclides poses significant scientific and operational challenges. Selectivity in the presence of competing species, radiolytic and corrosion stability of separation media and remote operation and management of highly active waste streams are the challenges that hamper the full scale deployment of separation technologies. Economical production of speciality solvent systems and the management of spent solvents are another area of concern affecting the viability and sustainability of process. Regulatory, safeguards, and public-acceptance frameworks must evolve to enable reuse and ensure environmental protection.

In conclusion, leveraging separation technology as a strategic enabler of India's three-stage program and a route to a safer, lower-waste, circular nuclear future will require focused research in advanced separations, materials science, and systems integration, as well as clear regulatory pathways.

IT-10

Process Chemistry of Fast Reactor Fuel Reprocessing and Recovery of Valuables from Fast Reactor Waste

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The success of the fast reactor programme is fundamentally dependent on closing of nuclear fuel cycle and therefore, reprocessing of spent nuclear fuel is integral component of the sustained growth of nuclear energy in India. This presentation outlines a comprehensive overview of operational experience in the process chemistry of fast reactor fuel reprocessing, and a brief overview of research activities focusing on wealth from fast reactor waste. The mixed carbide fuel of 70% plutonium and 30% uranium is being used as the driver fuel in the Fast Breeder Test Reactor (FBTR) at Kalpakkam, India. The operational experience demonstrated the use of high-concentration nitric acid under reflux conditions was essential for the quantitative dissolution and complete destruction of soluble organic species formed during the dissolution of mixed carbide fuel. In the case of MOX fuel containing plutonium oxide more than 30%, the dissolution of MOX in pure nitric acid was quite difficult, and consequently, the electro-oxidative dissolution technique (EODT) was required for achieving complete dissolution of MOX fuel with plutonium oxide content more than 30%. The radiolytic degradation of the organic solvent (1.1 M TBP/n-DD) was significant in case of fast reactor fuel reprocessing due to the high burn-up and plutonium concentration. To address these issues, the process flow-sheet was modified to include the uranous nitrate stabilized with hydrazine nitrate. Later a procedure was also developed for the plutonium recovery from the lean organic phase. Considering the high level of fission product activity and plutonium concentration associated with irradiated fuel solutions, a UV–visible spectrophotometric method coupled with chemometric analysis was developed for the simultaneous determination of plutonium and free acidity in process samples. This approach aims to reduce the generation of alpha-bearing analytical waste, the use of corrosive reagents, and overall man-rem exposure. The presentation also covers the recovery of ^{237}Np, a strategically important target material for the production ^{238}Pu, and the recovery of ^{90}Sr from high level wastes (HLW), which decays to ^{90}Y, a pure beta emitter (β_{max}= 2.28 MeV, $T_{1/2}$= 64.1 h) with strong therapeutic potential in nuclear medicine applications.

IT-11

Processing of Uranium Ore at UCIL Mills of India

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Uranium Corporation of India Ltd (UCIL) plays a key role in the nuclear fuel cycle. UCIL works towards processing of the available lean ore grade uranium to sustain 3 stage nuclear power program of the nation. Ore is mined, crushed, ground, thickened, leached through atmospheric-acidic /pressurised alkaline route, filtered, clarified, concentration of U in liquor is increased through Ion exchange or re-dissolution of concentrate and precipitated with reagents to form different types of Uranium Concentrate and supplied to Nuclear Fuel Complex for further processing.

The ore mined from Singhbhum shear zone is consumed by Mills of Jaduguda and Turamdih and contains high SiO_2 content and low acid consuming gangue, thereby leading to selection of atmospheric acid leaching in Pachuca and CSTR with MnO_2 as oxidant and H_2SO_4, as lixiviant. Ion Exchange is used to increase the Uranium concentration in liquor and impurities in strong liquor such as ferric and sulphate ions are removed through addition of $Ca(OH)_2$ to form Iron Gypsum cake and subsequently Uranium is precipitated, washed, spray dried, calcined and dispatched. Magnetite is recovered and used for heavy media separation in collieries. Leached cake is repulped, neutralised with lime to increase pH of slurry and maintain in between 9.5-10.5 to prevent re-solubilisation of heavy metal. The solid settles and the liquor decant through spillway and gets collected in collection pond which is subsequently treated in Effluent treatment plant for fixing radium and other metallic ion through addition of $BaCl_2$ /$Ba(OH)_2$ and $Ca(OH)_2$ respectively. The precipitate thus obtained is removed in thickener and disposed in tailings dam. The effluent is discharged to the environment where the parameters are well within inland discharge limits. Tummalapalle (TMPL) mine and Mill operate with Zero discharge scheme. The host rock of TMPL deposit is siliceous dolomitic phosphatic dolostone, which contains 83% carbonate leading to excessive consumption of H_2SO_4, led for opting autoclave leaching in alkaline medium at elevated pressure and temperature with direct injection of gaseous O_2 and Na_2CO_3. Recently, technologies are being developed for removal of pyrites and Molybdenum separately through froth flotation and to process it separately at Tummalapalle. The Uranium ore concentrate (UOC) produced at Tummalapalle Mill possesses undesirable material (silica, zirconium, organic carbon, polyacryl amide and molybdenum), which are detrimental to NFC's existing process route for production of Nuclear Grade Uranium. For elimination, a new process has been developed by BARC for producing relatively pure UOC in the form of Heat-treated Uranium Peroxide.

Keywords: Uranium ore, Mill, Processing, drilling, Uranium Peroxide

From Ores to Wastes: Integrated Strategies for Sustainable Recovery of Rare Earth Elements

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Rare earth elements (REEs) are critical components of modern technology, vital for applications ranging from clean energy and defence to consumer electronics to medicines. However, their extraction from primary ores is environmentally intensive and concentrated in a few geographic regions, creating supply chain vulnerabilities. Simultaneously, the rapid growth of electronic waste (e-waste) represents a rich but largely untapped secondary source of these valuable materials, presenting an opportunity for a circular economy. This lecture explores the latest advancements in REE recovery from both primary ore deposits and end-of-life e-waste & other industrial wastes such as coal fly ash, phosphogysum and red mud, highlighting the scientific and engineering breakthroughs that are paving the way for a more sustainable and secure supply chain. Special emphasis will be placed on the challenges inherent to each source, such as the low concentration of REEs in some ores and the complex, heterogeneous nature of e-waste & industrial by-products. Emerging green technologies—including DES, ionic liquid extraction, and membrane separation—will be examined briefly for their potential to overcome current limitations. Ultimately, the recovery of REEs from both primary and secondary sources is crucial for ensuring a secure, sustainable, and environmentally responsible supply of these vital materials. The future of REE extraction and recycling depends on continued technological innovation, economic viability, and a coordinated effort to transition toward a circular economy. By integrating resource efficiency, waste valorization, and technological innovation, this lecture will provide a pathway towards a more resilient and sustainable supply of these critical materials for future generations.

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Innovative Approaches for Managing Complex Radioactive and Mixed Wastes

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Effective waste management is a critical pillar of the nuclear industry, particularly as facilities deal with increasingly complex waste streams arising from routine operations, research activities, and legacy programs. Of growing concern are mixed and radioactive wastes that were historically considered challenging, no-path-forward, or orphaned due to limited disposal options, prohibitive treatment costs, regulatory and cross-border logistics constraints. These challenges are not limited to large nuclear power plants but are equally relevant to small-scale research facilities and aging legacy waste inventories.

This paper focuses on real-world waste management challenges and highlights innovative, field-deployed solutions through a series of case studies developed and implemented by Kinectrics. These case studies demonstrate how innovative, yet operationally grounded technologies can be rapidly translated into deployable solutions for managing some of the most problematic waste streams in the nuclear sector:

- **Universal Separation Process (USEP) [1]**: An innovative chemical separation process designed to remove tritium and other alpha and beta-gamma emitting radionuclides from Mixed Liquid Wastes (MLW) to below unconditional clearance or free-release limits. USEP enables the disposal of treated waste as conventional chemical waste while isolating a small, concentrated radioactive secondary waste stream for licensed disposal.
- **Selective Carbon Extraction Process Through Exchange Reactions (SCEPTER™) [2], [3]**: A novel, low-temperature chemical process for the selective removal of C-14 from waste Pressurized Heavy Water Reactor (PHWR) Ion Exchange (IX) resins. By separating C-14 into a small, stable secondary waste stream, SCEPTER™ enables significant volume reduction and reclassification of the treated resin waste, addressing both disposal cost and long-term storage challenges.
- **Management of PCB-Contaminated Mixed Wastes [1]**: A practical technology for the destruction and decontamination of Polychlorinated Biphenyls (PCBs) in both liquid and solid radioactive mixed wastes, enabling compliance with federally mandated PCB management standards in Canada while avoiding cross-border shipment and reducing waste volume as well as disposal complexity.
- **Wastewater Treatment and Recycling at Kinectrics' Teeswater Laundry Facility (TLF) [3]**: Deployment of Kinectrics' licensed Teeswater Laundry Facility which integrates wastewater treatment and byproduct recovery systems involving a unique combination of well-known unit operations that enable up to ~80% water recycling, reducing wastewater generation, environmental impact, and operating costs.

Collectively, these case studies illustrate how practical innovation, driven by industry agility, enables effective solutions to real-world nuclear waste management challenges. A problem-solving mindset often described as a Jugaad Innovation, when combined with rigorous scientific tools such as factorial Design of Experiments (DOE) and disciplined engineering, allows companies such as Kinectrics to rapidly convert complex challenges into implementable, defensible, and scalable solutions. These experiences underscore the importance of applied innovation in sustaining safe, economical, and responsible nuclear operations.

Key words: Radioactive Waste Management, Universal Separation Process, Mixed Liquid Wastes, SCEPTER™, PCB Waste

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IT-14

Sea Bittern-Deriven Forward Osmosis; Exploiting High Osmotic Pressure for Dewatering of Coconut Water

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Coconut water is a nutritionally valuable natural beverage containing sugars, electrolytes, amino acids, and bioactive compounds. Despite its growing global demand, commercialization is constrained by its high-water content, short shelf life, and the degradation of nutrients and flavor associated with conventional thermal concentration methods. This study presents a non-thermal, energy-efficient forward osmosis (FO) process for concentrating coconut water feed solution using sea bittern as a high-osmotic pressure (π = 549–715 bar) draw solution. An Aquaporin Inside™ hollow fibre FO membrane module (0.6 m2 active area) was used for the study. Initial studies using deionized water as the feed and sea bittern as the draw solution demonstrated high salt rejection, with rejection efficiency is 99.8%, indicating excellent membrane selectivity against draw solute back-diffusion.

Fresh coconut water with an initial concentration of 4°Bx was concentrated up to 32°Bx through a three-stage continuous single-pass (CSP) FO operation. A hollow fibre FO membrane module coated with aquaporin proteins on the lumen side was employed to enhance water permeability and solute rejection. Sea bittern of 28°Bé density, a by - product of solar salt production, was used directly as the draw solution, providing a large osmotic driving force without the application of external hydraulic pressure. Experiments were conducted at ambient temperature (28–32 °C), ensuring preservation of heat-sensitive nutrients and natural flavor.

The process achieved an overall water removal of 88.7%, concentrating 3000 g of coconut water to 352 g of final concentrate. The observed water flux (J_w) decreased progressively from 6.39 kg m^{-2} h^{-1} in the first pass to 3.47 kg m^{-2} h^{-1} in the final pass, corresponding to the reduction in osmotic pressure difference as the system approached equilibrium. Experimental Brix values closely matched theoretical predictions, indicating minimal back diffusion of draw solutes and effective retention of coconut water constituents. Cleaning studies revealed restoration of membrane permeability, confirming that fouling was predominantly reversible and that the FO membrane was compatible with complex natural feed streams.

The study demonstrates that forward osmosis using sea bittern as a draw solution is a sustainable and scalable alternative to thermal concentration processes for coconut water. The technology offers significant advantages in terms of low energy consumption, high product quality, and reduced transportation volume. The findings highlight the potential of FO as a viable non-thermal processing platform for value addition to natural beverages and functional drinks while aligning with principles of resource recovery and process sustainability.

Density Functional Theory Studies on the Separation and Recovery of Lanthanides and Actinides

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Actinide separation and recovery is important at various stages of nuclear fuel cycle. The recovery of uranium and plutonium from the spent fuel is a vital step in the nuclear fuel cycle where in the major actinides are recycled. The most preferred method for this task is solvent extraction, where in tri-*n*-butyl phosphate (TBP) is used as an extractant for more than seven decades [1]. In this context, the development of new molecules (ligands) for actinide separation and recovery is an active field of research. The development of ligands finds its application in the removal of actinides from lean solutions, separation of actinides and lanthanides, and development of better ligands for fast reactor fuel reprocessing, etc. Experimental studies in the past were dedicated to synthesizing and studying many molecules for various applications. On the other hand, understanding the behavior of actinide extraction from a theoretical point of view and insights derived over time will help us tailor making an extractant for a specific application. In this regard, quantum chemical calculations are carried out to understand the complexation behavior of various ligands [2], understanding the electronic structure and bonding, [3] and establishing the relationship between the ligand geometries and their properties [4]. The talk will focus on the development and application of density functional theory methodologies in the context of research work carried out at IGCAR, Kalpakkam.

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Diverse Applications of Polyoxometalates (POMs) in the Field of Actinides

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Polyoxometalates (POMs) are a class of discrete, anionic metal–oxygen clusters composed mainly of early transition metals such as Mo, W, or V in their high oxidation states, linked through shared oxygen atoms to form well-defined molecular frameworks. In the field of actinide chemistry, POMs are widely used for the sequestration and selective separation of actinide ions due to their oxygen-rich surfaces and strong coordination ability [1]. They also serve as molecular hosts for the immobilization of actinides, which is important for nuclear waste management. Additionally, POMs serve as model systems for fundamental actinide studies, enabling structural characterization of complexes with americium and curium on the microgram scale and highlighting differences in coordination chemistry across the f-block. Recent work has also shown that POM-based materials, such as POM-encapsulated metal–organic frameworks (POM@MOFs), can enhance photocatalytic adsorption and reduction of U(VI) from aqueous solutions, improving removal efficiency for environmental and waste-treatment applications [2]. A recent publication on a lacunary polyoxometalate, PW_{11}, has demonstrated the reduction of Np(V) to Np(IV), which is subsequently stabilized within the POM matrix [3]. In another study, a lacunary POM, Se_6W_{45}, possessing a suitable coordination geometry to bind through the equatorial position of the actinyl ion, was shown to stabilize the unusual oxidation state of Am(VI) in aqueous medium [4]. Motivated by these findings, we have recently initiated systematic investigations on POM-based systems for the separation and stabilization of actinides in unusual oxidation states. The various intriguing applications and extensive studies on actinide–POM chemistry carried out in our laboratory will be discussed in detail.

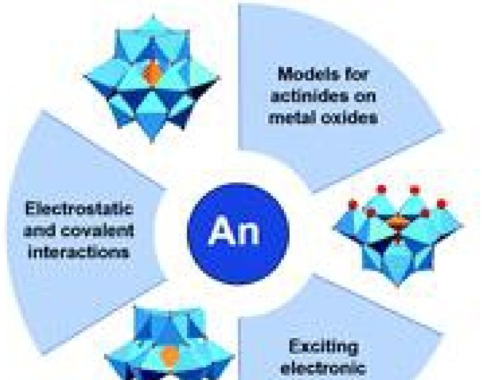

Fig. 1: *Polyoxometalate as ligands for actinide cations [1]*

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Advanced Functionalized Porous Monolithic Materials: Enabling Next-Generation Separation and Sensing Technologies

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Advanced porous monolithic materials have emerged as a versatile class of functional materials due to their continuous three-dimensional architecture, interconnected pore networks, high surface area, and superior mass-transport properties. Unlike conventional particulate systems, monoliths exhibit low flow resistance and high mechanical stability, enabling reliable performance under demanding analytical and industrial conditions. These attributes position porous monoliths as effective platforms across separation science, sensing, catalysis, environmental remediation, energy technologies, and biomedical applications. In catalysis, porous monoliths serve as efficient heterogeneous catalyst supports by immobilizing catalysts such as metal nanoparticles, enzymes, etc., within well-defined porous frameworks, thereby enhancing catalytic efficiency, improving stability, and enabling facile recyclability. Porous carbon and hybrid monoliths are also being explored as next-generation electrode architectures for supercapacitors and batteries, as well as catalyst supports in fuel cells and hydrogen storage systems. In environmental applications, functionalized monoliths serve as high-performance adsorbents for toxic metals, dyes, and organic pollutants. In contrast, in biomedical applications, they exploit their tunable porosity and surface chemistry for drug delivery, tissue engineering, and bioseparations.

In separation science, porous monolithic columns are widely used as stationary phases in HPLC, UHPLC, and capillary chromatography, enabling rapid, high-resolution separations at low back pressure. Among various monolithic formats, organic polymer monoliths have attracted increasing attention due to their synthetic versatility, broad pH stability, biocompatibility and ease of functionalization, enabling the rational design of application-specific stationary phases. Despite significant progress, the selective separation of metal ions, particularly lanthanides and actinides, remains a considerable challenge requiring tailor-made, highly selective monolithic materials. This talk focuses on the design and fabrication of customized functionalized polymer-based monolithic columns for the selective separation of UO_2^{2+}, Th^{4+}, and lanthanide ions. Rigid, highly porous monoliths bearing amide, organophosphorus, carboxylic acid (–COOH), and sulfonic acid (–SO_3H) functionalities display potent and selective analyte–stationary phase interactions under HPLC operating conditions. Organophosphorus-based monoliths, in particular, exhibited enhanced selectivity toward actinides and were successfully extended to solid-phase extraction formats. The talk will also discuss the fabrication of customized polymer- and hybrid-monolith-based optochemical sensors for ultra-trace detection of UO_2^{2+}, Th^{4+}, and selected platinum-group elements. Integration of chromoionophoric imine- and azo-based probes within engineered porous monolithic templates enabled rapid response, high sensitivity, and visible colorimetric detection. The structural tunability, robustness, and multifunctionality of porous monoliths offer promising opportunities for next-generation separation and sensing platforms relevant to nuclear reprocessing, environmental surveillance, and advanced analytical technologies.

Synthesis and Evaluation of Novel Functionalized Metal-Organic Frameworks for the Recovery of Metal Ions

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Over the last three decades, the science of porous solid materials has become one of the most intense areas of study for chemists, physicists, and material scientists. These materials have found many applications in various fields, such as adsorption, separation and purification, as well as catalysis, *etc*. Metal-organic frameworks (MOFs), a new class of porous solid materials, emerged approximately two decades ago and within a short span, investigation of MOF became an important research field. With extremely high porosity and large interior surface areas, MOFs have become a diverse class of crystalline materials. Owing to their regularity, rigidity/flexibility, variety, and design ability in both structure and properties, MOFs are being regarded as advanced porous materials capable of reaching or surpassing a number of current technologies.

This talk delivers designing of various functionalized metal-organic frameworks (MOFs) using post-synthetic modification (PSM) methodologies, and employ them as adsorbents for the recovery and sensing of metal ions (U(VI), Th(IV), and Pd(II)) for the nuclear materials processing applications. All pristine MOFs were functionalized with 2-pyridine carboxaldehyde (PC/PCA), glutaric anhydride (GA), sulfamic acid (SA/SMA), maleic anhydride (MA), diphenyl phosphoryl chloride (DPC), and diphenyl phosphonic chloride (DPC/DPPC) at amino pendent *via* PSM strategy. The pristine MOFs and their functionalized MOFs were characterized using different characterization techniques *viz*., FTIR, Powder XRD, TGA, NMR, BET surface area analysis, UV-Vis absorption spectroscopy, SEM, and EDX analysis. The resultant functionalized MOFs displayed the same structural topology, but varying porosity, surface area, stability, and binding affinities towards particular metal ions compared to their parent MOFs.

The talk explains the facile synthesis of highly chemical/thermal/radiation resistant, highly porous, high binding affinities, and large surface area MOFs for desired applications. Grafting with suitable functional moieties will enable the development of new materials for efficient sorption of metal ions for potential applications of environmental concern especially in the nuclear fields.

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Recent Advancement in the Chemical Characterization of $(U,Pu)O_2$ MOX fuel

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$(U,Pu)O_2$MOX fuels of different PuO_2 compositions and types have been developed and fabricated at Fuel Fabrication, Integrated Nuclear Recycle Plant (Operation), FF-INRP(O), NRB BARC Tarapur. The composition of plutonium oxide in MOX varies from 0.4 to 44%. The conventional powder metallurgical route is used for fabrication of $(U, Pu)O_2$ MOX sintered pellets. The purpose of the chemical quality control is to check different process parameters of MOX fabrication and certify that the product $(U,Pu)O_2$ meets the specifications. These specifications are laid down mainly for fissile content, homogeneity, isotopic composition, trace metallic and non metallic constituents , total gas content and cover gas analysis which in turn affect the properties and performance of the nuclear fuel. Development of new analytical methodologies are being pursued with a view to meet certain essential requirements such as high sample throughput, small sample size, good precision and accuracy, better sensitivity, minimum generation of waste solid sample analysis for covering the entire concentration range of elements, say major to trace level .

Chemical characterization of $(U,Pu)O_2$ becomes more challenging due to associated risk of radiotoxic dust hazard. All the operations have to be carried out inside the glove boxes & fume hoods. This paper describes basic concept and recent developments in chemical quality control related to MOX fuel fabrication in FF- INRP(O). Non destructive methodologies based on neutron counting using $_{2}He^{3}$, BF_3 and phoswich detector $Gd_3Ga_3Al_2O_{12}$:Ce and CsI:Tl, Wave length Dispersive X-ray Fluorescence (WDXRF) and Calorimetery have been developed to determine Plutonium in UO_2 and PuO_2 MOX blend for the process control of $(U,Pu)O_2$ MOX fabrication. Conventionally U and Pu are determined by potentiometric or coulometric methods in sintered MOX pellets. These methods are time consuming, involves extensive sample preparation, cumbersome dissolution, use of corrosive chemicals HF and destructive in nature. Moreover, recovery of U and Pu from analytical waste is difficult due to presence of sulphate and phosphates in analytical waste. Hence a non-destructive WDXRF method have been developed for direct determination of U and Pu in as fabricated annular sintered $(U, Pu)O_2$ mixed oxide (MOX) pellets. The homogeneity of plutonium and uranium is one of key properties from the view point of local heating in reactor operation and dissolubility in reprocessing. Thus plutonium enriched zone (Pu spot) should be detected with an adequate method. Dissolution studies have been performed to check the macrohomogneity of MOX fuel. DC ARC AES, ICP AES and Ion chromatographic methods have been developed for the determination of metallic impurities in $(U,Pu)O_2$ samples. Very recently, a microwave-induced nitrogen plasma source (MICAP), which replaces conventional argon-based ICP systems and employs Cerawave technology to eliminate the need for chillers and reduce operating costs, has been installed in our laboratory. Important trace rare-earth impurities have been determined in natural UO_2 samples and analyses of MOX samples will be carried out after installation of the system in an alpha leak-tight glove box. Methods for the determination of Hydrogen, Nitrogen in direct solid MOX samples have been optimized. Ion chromatographic methodologies have been developed for the simultaneous determination of chlorine, fluorine in $(U, Pu)O_2$ MOX fuel. Our laboratory has also participated in inter laboratory comparison exercise for the preparation of Certified reference material for bulk uranium and trace metallic impurities in PuO2.

During fabrication of $(U,Pu)O_2$ MOX fuel, a small percentage of pellets gets rejected at various stages leading to generation of rejects. These rejects are broadly divided in to two categories clean reject oxide (CRO) and dirty reject oxide (DRO) depending on the chemical and physical characteristics of the pellets. Calorimetric method has been developed for the determination of Pu in these rejects. During fabrication of MOX fuel radioactive solid waste also generated. Management of alpha bearing solid waste is an important aspect to be dealt with during the fabrication of $(U,Pu)O_2$ MOX. Accordingly, monitoring systems for alpha-bearing solid waste packets and drums have been developed to characterize these wastes using gamma spectrometric measurements. Developmental work for the determination of plutonium content in these wastes using ^{3}He neutron detectors is currently in progress.

Application of Cloud Point Extraction (CPE) in Various Fields of the Nuclear Industry

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The accelerated pace of nuclear research and installations has increased the demand for research innovations in fields like actinide extraction, environmental monitoring of actinides, CQC of nuclear fuels, etc. The separation chemistry plays a big role in all these fields. Over the last two decades, cloud point extraction (CPE) has emerged as a simple, cost-effective, and environmentally friendly method for the separation and preconcentration of metal ions [1]. CPE is based on the phenomenon of the separation of two isotropic phases generated from a micelle solution. The clear and homogeneous aqueous solution of non-ionic surfactants becomes turbid at and above some particular temperature and separates into two immiscible phases, that is (i) bulk aqueous phase containing surfactants at critical micelle concentration (CMC) and (ii) the surfactant-rich phase (SRP) of very small volume. This temperature is referred to as the cloud point temperature (CPT) of that particular micellar system. Any analyte, whether organic or inorganic that can be trapped in the micellar core due to its hydrophobicity, can be separated and pre-concentrated in the SRP from the bulk. Compared to a hydrated metal ion, selective metal-ligand complexation, therefore, can easily preconcentrate metal ion(s) in the CPE method.

Uranium, being one of the most abundant naturally occurring long-lived actinides, is ubiquitously present in the environment [2]. The World Health Organization (WHO) and United States Environmental Protection Agency (USEPA) have set 30 ng mL^{-1} as the provisional guideline value of U in drinking water, and this value is solely based on its chemical toxicity aspect. In this respect, we had developed various CPE methodologies based on diglycolamide-capped quantum dot (QD), amidoxime-capped gold nanoparticles (AuNPs), and phosphoramidate bearing task-specific ionic liquid (TSIL) for fluorometric, UV-vis spectrophotometric, and X-ray fluorescence spectroscopic techniques for ultra-trace level detection of U in environmental samples [3-5]. These developed methodologies have come out as the simple and low cost alternatives to the well known mass spectrometric, atomic emission spectroscopic, and laser fluorometric techniques.

Uranium and its compounds are the most widely used fuels in nuclear reactors for the sustainable production of energy. Boron (B) is one of the major poison elements responsible for reducing the thermal neutron economy in the reactor core. Consequently, boron has a maximum specification of 0.3 and 1.0 µg g^{-1} in the fuel meat of PHWRs and LWRs, respectively. A micelle surface modified CPE procedure was developed for the determination of trace amounts of B in U-metal, UO_2, and U_3O_8 compounds using a simple UV-vis spectrophotometer [6]. Other than the CQC of nuclear fuel, a novel cloud point back-extraction (CPE_{back}) procedure was developed for the stripping of U from U-loaded tributyl phosphate (TBP)/diluent phase [7]. This method has the advantage of single-step quantitative back-extraction of U over the cumbersome multistep liquid-liquid extraction (LLE).

The higher efficiency of the CPE procedure, due to its monophasic extraction mechanism, makes it a better, eco-friendly alternative to the LLE in many areas of the nuclear industry. In the future, we are looking to develop CPE methodologies for ultra-trace level detection of plutonium and other minor actinides in environmental samples.

Key words: Uranium, Preconcentration, Actinide, Micelle

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Speciation of f-Elements for Sustainable Growth of Nuclear and Renewable Energy

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In the 21st century, energy cries is one of the most challenging global issues [1]. At present, hydrocarbon-based fossil fuels are the utmost dominating source of energy. However, its extensive utilization resulted in toxic and greenhouse gases emission, climate change, global warming etc. Thus, sustainable advancement of clean and renewable energy sources is important to replace the extensive use of fossil fuels. Nuclear energy and energy storage device (battery) are considered as the important clean and renewable energy resources, respectively. For their sustainable growth, the exploration of new solvent and chelate are strategically essential related to their various chemical activities. Over the conventional batteries, the Redox flow battery (RFB) considered as promising choice as an energy storage device due to its appealing structure, high energy, and power densities [2]. The f-elements (lanthanides and actinides), due to their unique physicochemical properties, work as promising active source (i.e., fuel) for nuclear energy and RFB. The various chemical activities of f-elements such as processing/reprocessing, redox dynamics, complexation, conductance, decorporation etc. mainly depend on the solvation environment, i.e., speciation, of the metal ion. Thus, the speciation of f-elements is a fundamental chemical aspect for sustainable growth of nuclear energy and RFB. Understanding about the speciation of f-elements at low concentration level is also important, however, there is lack of portable device in this regard.

Our research aims are (i) investigation on the new non-aqueous solvents and aqueous soluble chelate for their potential applications in processing/re-processing, speciation and decorporation of actinides, (ii) speciation of f-elements in aqueous and non-aqueous electrolytes for RFB, and (iii) development of portable device for speciation and detection of actinides at low concentration to know their mobility and reactivity. In our laboratory, malonic acid and ethylene glycol based hydrophilic Deep eutectic solvents (DES) were synthesized and explored for the direct dissolution and speciation of solid actinide compounds. The Tetra-butyl ammonium nitrate-Decanoic acid (1:2) hydrophobic DES was prepared and used for extraction followed by recovery of actinides from acidic media. The amidoxime containing functional group is a well-known chelator for uranyl ion. The aqueous speciation and decorporation of uranyl ion with Pyrazine-2-Amidoxime chelate was performed with varying pH using multi-techniques approach. Using electrodic materials such as γ-Graphyne and Carboxylate based Metal Organic Frameworks, the redox speciation of Uranium was performed with varying pH.

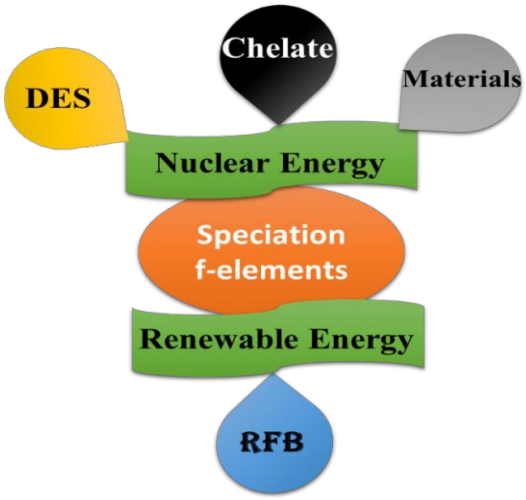

Figure 1. *Speciation of f-elements for potential applications in nuclear and renewable energy*

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SIT-03

Alternate Ligand – Solvent System for PUREX Process

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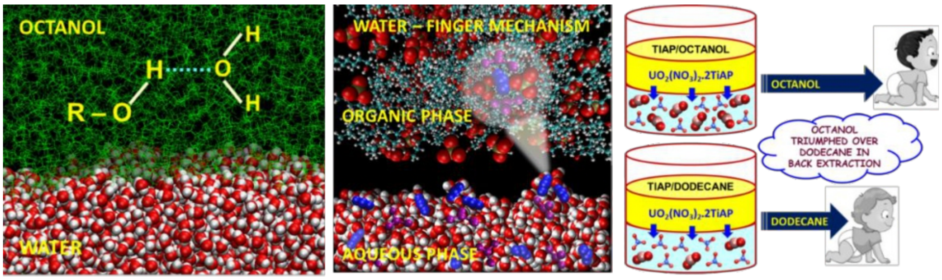
The design of efficient ligand–solvent system is the most challenging part in the liquid–liquid extraction processes. Tri-butyl phosphate (TBP) in dodecane is the widely used ligand–solvent system for widely popular PUREX (Plutonium Uranium Extraction) process [1]. In recent past a potential alternative of TBP namely tri-iso amyl phosphate (TiAP) is being used for spent fuel reprocessing applications because it overcomes the inherent limitations of TBP as aqueous solubility, third phase formation and degradation under thermal and radiological environment [2]. TiAP is normally diluted with dodecane to reduce the viscosity and to increase the diffusivity of TiAP for solvent extraction purposes. The polarity of the solvent may play an important role during interfacial ion transport. Dodecane as a nonpolar solvent does not have any influence on interfacial properties except changing the physical properties of ligand–solvent system. Therefore, it is of fundamental interest to study the effect of polar solvent as octanol in place of dodecane. How the molecular level structure and interactions due to the polar and non-polar nature of solvent dictates the interfacial mass transfer of metal ions. Hence, the objective of the study is not only to explore a potential replacement of dodecane but also to develop an understanding on the effect of polar solvent on the liquid–liquid extraction (LLE) process.

The extensive MD simulations studies have been carried out with octanol as a solvent to find out the advantages and disadvantages of such solvent in the field of spent fuel reprocessing. The octanol is normally used as phase modifier to reduce the aggregation of ligand in organic phase. Though the density of pure octanol is comparatively higher than dodecane but the diffusivity of pure octanol is quite impressive (~ 2.5 times higher than dodecane) which facilitates the ions movement. Further, the diffusivity of TiAP in octanol medium has been improved compared to dodecane medium which is favorable for LLE. Further, the simulation studies of simple biphasic system predict that the water–octanol system offers better mass transfer ability over water–dodecane [3] system because of higher total interface thickness (w_t) which is always favored for designing any solvent extraction system. Furthermore, the studies were extended to complex biphasic system where the w_t was found to be decreased with mole fraction of TiAP and increased with nitric acid molarity [4]. It can be noted that the polar solvent created a reverse trend of interfacial properties compared to nonpolar solvent because the H-bonding between water and polar solvent (octanol) plays an important role.

The distribution coefficient (K_D) of uranyl ion during extraction from aqueous phase using 30% TiAP/octanol [4] found to be lower than 30% TiAP/dodecane whereas the recovery of uranyl ion during back extraction from organic phase to aqueous phase is improved from 87.1% (TiAP/dodecane) [5] to 94.3% for TiAP/octanol [4] system. The water–finger formed at the interface plays an important role in extraction and back extraction of uranyl ions and the nature of water–finger depends on the ligand concentration and aqueous phase acidity. Hence, the present studies suggested that the extraction system can be designed in such a way that the dodecane and octanol both can be used as a solvent with an appropriate ratio which can improve both the extraction and back extraction of uranyl ion in the PUREX process.



Key words: *PUREX, TiAP, Polar solvent, Uranyl ion, total interface thickness, water – finger.*

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Role of DFRP in Closing the Fast Reactor Fuel Cycle

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Demonstration fast reactor Fuel Reprocessing Plant (DFRP) has been built and commissioned at Kalpakkam with the main objective of regular reprocessing of spent fuel discharged from Fast Breeder Test Reactor (FBTR) and demonstration of reprocessing of spent fuels discharged from Prototype Fast Breeder Reactor (PFBR). DFRP would demonstrate fast reactor fuel reprocessing on a plant scale after successful completion of R&D and pilot scale reprocessing in CORAL facility. The plant is equipped with several novel and first of its kind equipment that are unique to fast reactor fuel reprocessing. Demonstration of plant scale operation is vital for taking up the design and operation of large-scale reprocessing plants catering to the needs of the recycling the fuel for the fast breeder reactors, thereby effectively closing the fuel cycle. This presentation highlights the scope, present status & salient features of DFRP. Salient features during commissioning of radioactive liquid sampling system in DFRP is also covered.

Numerical Simulations to Predict Performance of Sparger for Xe Removal from Molten Salt

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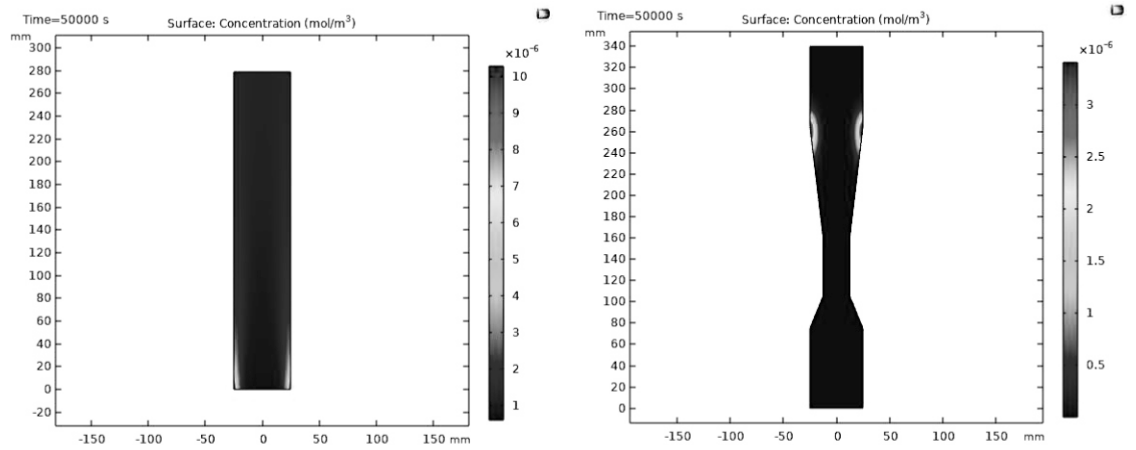
As a long-term program, in view of effective utilization of thorium in the third stage of Indian nuclear power program, BARC is working on the development of associated technologies for the molten salt reactor (MSR), which can breed fissile material effectively, and thus would provide a sustainable pathway for Th utilization **[1, 2]**. In MSR, the fissile and fertile materials circulate as molten fluoride salts, wherein fission continuously produces ^{135}Xe (strong neutron absorber). Periodic or online reprocessing of the circulating salt, especially the off-gas management for Xe removal, is therefore essential to maintain criticality of the reactor and achieve the desired burn-up **[3]**.

CFD simulation plays a vital role in understanding and optimizing helium bubbling through sparger for Xe removal in molten salt systems. The technique helps to optimize sparger design such as hole size, geometry, and gas flow distribution without the need for extensive physical trials, which are difficult and costly, especially in high- temperature molten-salt environment. In this work, a CFD model of sparger system for Xe removal from the molten salt has been developed and validated with reported data of ORNL. The model was used to predict the effect of bubble size, L/D and configuration (bubble column & venturi scrubber) on Xe extraction efficiency. It has been observed that venturi scrubber is more effective in Xe extraction than bubble column, which is due to better mass transfer (better mixing) in divergent section of venturi scrubber. Fig. 1 shows the contours of Xe concentration in molten salt for bubble column (a) and venturi scrubber (b). The off-gas management system is being designed based on the in-house CFD simulation studies.



(a) **(b)**

Fig.1*: Xe concentration in molten salt; (a) Bubble column; (b) Venturi scrubber*
[Velocity: 0.08 m/s, Initial concentration of Xe: 0.0794 mol/m^3, Temperature: 723 K, Time: 50000 s]

Key words: *Molten Salt Reactor, Off-gas management, He bubbling, Xe extraction, CFD simulations*

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Simultaneous Si Separation and Sample Decomposition for Accurate Analysis of Th, Nb, Zr and Hf in Granites of Siwana

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Silica (Si) rich peralkaline granites of Siwana, Rajasthan are known for Niobium-Zirconium (Nb-Zr) mineralization along with Thorium (Th) and Hafnium (Hf). Reported host minerals like zircon, gittinsite, monazite, thorianite, rutile etc. are refractory in nature and pose a challenge in complete decomposition of the sample for accurate analysis of Th, Nb, Zr and Hf. HF-HNO$_3$ acid treatment is inefficient in decomposing the refractories, whereas fusion methods using fluxes like Na_2O_2 and 1:1 Na_2HPO_4 & NaH_2PO_4 cause hydrolysis of Si in these peralkaline granites, leading to solution instability and making it unfit for instrumental analysis.

To overcome these challenges, we propose an effective fusion flux i.e. mixed hydroxide flux (NaOH+KOH) for decomposing the refractories and simultaneously separating the Si from the matrix. Addition of KOH in the mixed hydroxide flux is crucial as it is reported to have better decomposition effect on the refractory zircon **[1]**. After fusion, the fused mass is kept in contact with distilled water, where Si is converted into soluble alkali silicates and Th, Nb, Zr and Hf are precipitated as hydroxides. After filtration, the separated precipitates were dissolved in dilute HCl.

To achieve maximum possible separation of Si and maximum recoveries of Th, Nb, Zr and Hf, optimization of various parameters for the fusion method was carried out extensively. The optimum conditions are NaOH and KOH mixed in 3:1 ratio, sample amount 0.2 gm, flux amount 1.4 gm, 5 minutes of contact time of fused mass with distilled water, and 10% HCl concentration in final solution. Final solution of precipitates with dilution factor 250 was analysed for Th, Nb, Zr and Hf (wherever necessary, further dilutions were done); and filtrate solution with dilution factor 12500 was analyzed for Si by ICP-OES at interference free wavelengths (Si 288.158 nm) using matrix matched calibration standards.

The developed method was validated by Certified Reference Material 'REE-1' (CCRMP) and applied on five samples from different areas of Siwana. Si separation achieved was between 85.7 to 88.9 % and more than 90% relative recoveries for Th, Nb, Zr and Hf were obtained (Table 1). RSD values were found to be less than 5% (n=5) for all analytes. Limit of quantification for the developed method was 10 ppm for each analyte. The interference effect of un-separated Si was checked by standard addition method and 98.5 to 99.1 % recoveries were obtained for added Si standards. The developed method is quicker (saves 18-20 hours), consumes lesser chemicals, avoids explosive and hazardous chemicals and utilizes simple equipments like burner & nickel crucible, when compared with traditional methods. Thus this method is quite suitable for routine analysis of Th, Nb, Zr and Hf in Siwana samples for supporting and expediting the exploration program of AMD, DAE.

***Table 1**: Comparison between results obtained using the developed method and reported values by traditional method (HF-HNO$_3$ acid digestion followed by Na_2O_2 fusion of residue)*

Element & ICP-OES Wavelength		CRM REE-1*	SG-1	SG-2	SG-3	SG-4	SG-5
Th 401.913 nm	Obtained value (ppm)	691	302	1954	132	65	765
	Reported value (ppm)	719	310	2094	131	68	755
	% Recovery	*96.1*	*97.4*	*93.3*	*100.8*	*95.6*	*101.3*
Nb 309.418 nm	Obtained value (ppm)	4015	789	514	345	307	1032
	Reported value (ppm)	4050	790	550	376	335	1142
	% Recovery	*99.1*	*99.9*	*93.5*	*91.8*	*91.6*	*90.4*
Zr 343.823 nm	Obtained value (ppm)	18750	12450	11000	5960	18050	8520
	Reported value (ppm)	19100	12400	11200	6000	17900	8800
	% Recovery	*98.2*	*100.4*	*98.2*	*99.3*	*100.8*	*96.8*
Hf 264.141 nm	Obtained value (ppm)	480	285	270	167	410	200
	Reported value (ppm)	479	310	283	175	435	215
	% Recovery	*100.2*	*91.9*	*95.4*	*95.4*	*94.3*	*93.0*

Key words: *Siwana, peralkaline granites, refractory, mixed hydroxide flux, ICP-OES*

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A-3

Recovery of Technetium-99 from Iron Oxide based Radioactive Sludge

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Technetium (Tc, Z = 43), the first artificially produced element, is generated in significant quantities as the long-lived fission product ^{99}Tc ($t_{1/2}$ = 2.11 × 10^5 years) during the irradiation of ^{235}U, with nearly 20 kg produced annually in a single light-water reactor [1]. Accumulating to several hundred tons globally in spent nuclear fuel (SNF), technetium persists in reprocessing streams predominantly as the highly soluble pertechnetate ion (TcO $^{-}$), making it one of the most mobile and environmentally challenging radionuclides. Conventional immobilization strategies rely on the reduction of Tc(VII) to Tc(IV), stabilized as $TcO_2 \cdot 2H_2O$ or TcS_2 within iron oxide [2] or sulfide [3] matrices; however, the re-oxidation of Tc(IV) can compromise long- term containment [1].

In this study, the recovery of ^{99}Tc from iron-oxide–based radioactive sludge**,** generated by technetium sequestration from the Tc-rich intermediate-level liquid waste (ILW) treatment stream at WIP-K**,** was investigated. The sludge was first dissolved in warm nitric acid (40–60 °C)**,** followed by solvent- extraction–based recovery of technetium**.** The Fe-rich feed solutions containing ^{99}Tc and associated fission products were clarified and subjected to extraction using TBP and TEHDGA systems. Systematic variations in acidity (0.4–6 M HNO_3),uranium concentration (0–15 $g \cdot L^{-1}$), TEHDGA molarity (0.1–0.7 M), modifier content (0–45%), and eluent type were examined to optimize ^{99}Tc recovery, with TBP employed for comparative evaluation. Technetium concentrations were determined by tetra-phenyl-arsonium chloride (TPAC) extraction followed by β-counting, while fission products were quantified using HP Ge γ-spectrometry. Additionally, direct estimation of ^{99}Tc was performed by liquid scintillation counting. All experiments were conducted in triplicate, with uncertainties within ±5%. The experimental methodology for ^{99}Tc recovery from iron oxide–based radioactive sludge is illustrated in Figure 1.

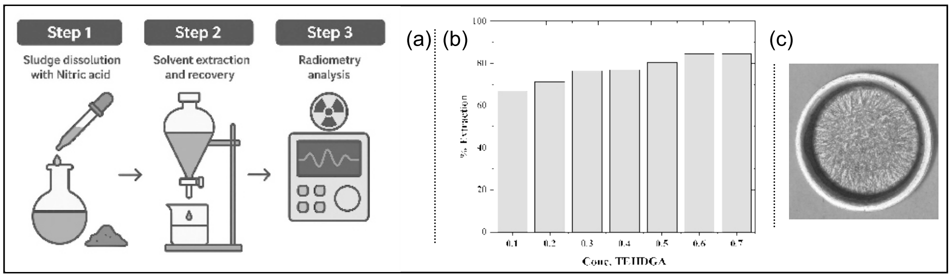

Figure 1. *(a) Experimental methodology adopted; (b) ^{99}Tc recovery as a function of TEHDGA concentration; (c) Dried ^{99}Tc product on aluminum planchette.*

The results (Figure 1b) demonstrated that TEHDGA systems exhibited superior ^{99}Tc recovery compared to TBP (42% at 1.4 M HNO_3), particularly at moderate acidity (1–2 M HNO_3). Increasing TEHDGA concentration enhanced ^{99}Tc uptake up to 0.7 M, beyond which no significant improvement was observed. Co-extraction of fission products such as ^{106}Ru and ^{137}Cs was partially suppressed under optimized conditions, highlighting the selectivity for ^{99}Tc. The recovery of ^{99}Tc from the loaded organic phase was successfully achieved using 10% NH_4OH solution, followed by solidification of the product under an IR lamp. These findings establish a practical route for recovering ^{99}Tc from Fe-rich sludge, offering dual benefits of (i) environmental risk reduction through vitrified immobilization and (ii) resource valorization via conversion to metallic ^{99}Tc for advanced technological applications.

Keywords: *Technetium-99; Solvent extraction; Di-glycol-amide; Liquid scintillation; Tetra-phenyl-arsonium chloride*

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Exploring Separation of Sr from Aqueous Solution using Raw and Alkali Activated Bentonite

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Separation of Sr from radioactive waste solution is very crucial step before its disposal to mitigate the radioactivity level for long term management. Many adsorbents were used for separation of Sr from the waste solution like zeolite, activated carbon, clays etc. The present study investigates the efficacy of bentonite clay for separation of Sr from the aqueous solution. Bentonite clay is abundant, cost effective and posseses high cation exchange capacity and thus a promising candidate for ion separation process. Its adsorption capacity for metal ion increases with acid or alkali activation. The aim of the study is to evaluate the adsorption capacity of alkali-activated bentonite for Sr from aqueous solution. Bentonite was activated by reacting with Na_2CO_3 (4 wt.% of BT) in aqueous media at 80°C for 6h.

The raw bentonite and alkali activated bentonite were characterized using XRD, EDXRF and TG-DTA. The X- ray diffraction pattern (Fig 1a) shows montmorillonite as the main crystalline phase along with quartz as impurity in the bentonite while intensity of some peaks of montmorillonite phase (Fig 1b) decreases for alkali activated bentonite. EDXRF result of raw bentonite shows that the major component is SiO_2 (~57 wt.%) followed by Al_2O_3 and Fe_2O_3 along with trace amount of TiO_2, CaO, MgO, Na_2O and K_2O. The ratio of amount of SiO_2 to Al_2O_3 is 2.5. TG-DTG-DTA plot (Fig 2) of raw bentonite represents ~5 % mass loss at 90℃ for removal of adsorbed water and ~4% mass loss at 696℃ for removal of interlayer moisture. Two endothermic peaks were observed in DTG and DTA plot at those temperatures supporting the TG curve. The batch adsorption studies were carried out with the adsorbents by varying pH of the solution, contact time, dose amount and initial concentrations of the Sr^{2+} ions. The solutions after adsorption experiments were analysed by ICP- OES to determine the removal efficiency. The adsorption studies shows that bentonite can effectively remove Sr from aqueous solution in the pH range 6 to 9 with 75% removal efficiency keeping solid to liquid ratio 4:1 (g/L) in 1 h of equilibration time. The adsorption capacity was found to be enhanced for alkali activated bentonite compared to raw bentonite as the number of reactive adsorption site as well as cation exchange capacity increases due to conversion of calcium bentonite to Na bentonite.

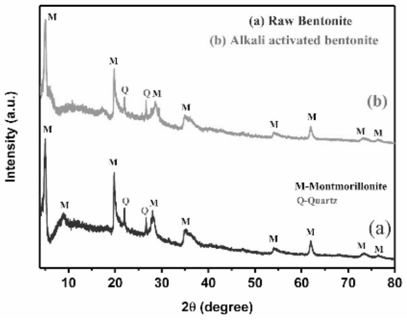

Fig 1: XRD patterns of (a) Raw bentonite (b) Alkali activated bentonite

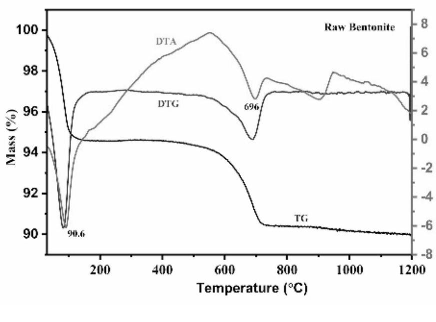

Fig 2: TG-DTG-DTA plot of raw bentonite

Key words: *Bentonite, Strontium, alkali activation, Adsorption capacity*

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Spectral and Thermal Characterization of Neutral and Acidic Extractants for High-Level Liquid Waste Treatment

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The separation of trivalent minor actinides (An^{3+}) and lanthanides (Ln^{3+}) from high-level liquid waste (HLW) demands extractants with strong structural and chemical stability under highly acidic and radiolytic conditions [1]. In this study, the molecular integrity, purity, degradation behaviour, and thermal stability of neutral extractants (TODGA, TEHDGA) and acidic extractants (TBP, D2EHPA, HEH[EHP]) were assessed through integrated spectral and thermal analyses. FT-IR confirmed characteristic vibrational signatures of phosphate/phosphinic groups and diglycolamide functional units, while ESI-MS verified molecular ions and major fragmentation pathways, including oligomeric species. Gas chromatographic analysis established extractant purity and revealed minor degradation products.

***Table 1**. ESI-MS fragmentations [M-H]$^+$*

	ESI-MS			ESI-MS	
Extractant	m/z	Fragment	**Extractant**	m/z	Fragment
TBP	98.97	$[H_4O_4P]^+$	**HEH[EHP]**	195.13	$[C_8H_{20}O_3P]^+$
	155.06	$[C_4H_{12}O_4P]^+$		**307.28**	$[C_{16}H_{36}O_3P]^+$
	211.11	$[C_8H_{20}O_4P]^+$		613.57 (100%)	$[C_{32}H_{71}O_6P_2]^+$
	267.21 (100%)	$[C_{12}H_{28}O_4P]^+$,		614.54	$[C_{32}H_{72}O_6P_2]^+$
	533.39	$[C_{24}H_{55}O_8P_2]^+$	**TODGA**	242.30	$[C_{16}H_{36}N]^+$,
D2EHPA	98.97	$[H_4O_4P]^+$		**581.65**	$[C_{36}H_{73}N_2O_3]^+$,
	211.12	$[C_8H_{20}O_4P]^+$		823.01 (100%)	$[C_{52}H_{108}N_3O_3]^+$
	323.27	$[C_{16}H_{36}O_4P]^+$	**TEHDGA**	242.30	$[C_{16}H_{36}N]^+$,
	645.57 (100%)	$C_{32}H_{71}O_8P_2]^+$		**581.65** (100%)	$[C_{36}H_{73}N_2O_3]^+$,
	646.55	$[C_{32}H_{72}O_8P_2]^+$		823.01	$[C_{52}H_{108}N_3O_3]^+$

Thermal stability assessed by TG-DSC revealed distinct decomposition patterns confirming their superior thermal endurance for solvent-extraction cycles (Figure 1). Preliminary solvent-extraction studies with simulated HLW further demonstrated strong affinity of TODGA/TEHDGA for An^{3+}–Ln^{3+} co-extraction, while D2EHPA and HEH[EHP] showed cation-exchange behaviour consistent with their acidic character. The integrated spectral, mass-spectrometric, chromatographic, and thermogravimetric results collectively establish the relative stability and extraction suitability of these extractants, supporting their application in advanced partitioning flowsheets for HLW management.

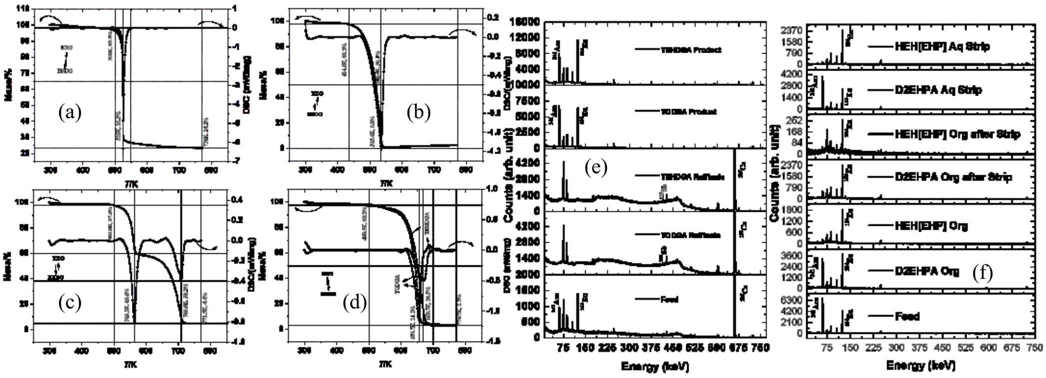

***Figure 1.** TG-DSC traces of extractans (a) TBP, (b) D2EHPA, © HEH[EHP], (d) DGA and HP-Ge spectra of extraction studies*

***Keywords**: Actinides; Diglycolamide; Acidic Extractant; HP-Ge gamma ray spectrometry; Thermogravimetry; Mass spectral analysis*

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A Simple Method for the Recovery of Uranium from Carbonate Wash Stream Resulted during Spent Solvent Clean-Up

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The carbonate effluent generated during the primary cleanup of lean solvent using hydrazine or sodium carbonate contains DBP along with residual uranium and plutonium. The DBP as well as the heavy metal (U & Pu) content may vary in the range 250-2500 mg.L^{-1} and 10-500 mg.L^{-1} respectively depending on the process flow sheet condition. Effective management of this waste prior to its disposal necessitates the near-complete removal of HDBP for the quantitative recovery of U and Pu. Although HDBP can be extracted from acidified waste using n-DD, this often leads to precipitate formation due to the poor solubility of HDBP–metal complexes in nitric acid [1]. Therefore, minimizing DBP content in the carbonate wash stream before acidification is essential. Instead of conventional ozonolysis for DBP reduction, the present study explores a simpler alternative for recovering retained metals as hydroxide precipitates using NaOH. Studies were carried out using a simulated solution of hydrazine carbonate containing U (as representative metal ion) and DBP. The NaOH concentration as well as the quantity of NaOH required under various experimental condition were optimized. For studying the effect of initial NaOH concentrations on U precipitation, 10 mL of stock solution (1.5 M hydrazine carbonate with 3 g.L^{-1} U(VI) and 2.91 g.L^{-1} DBP) were independently taken in 8 different centrifuge tubes. 10 mL of different concentrations (0.5 to 11.5 M) of NaOH were added respectively to the stock solutions. The solutions were mixed thoroughly for 15 minutes followed by gravity settling for 1day. The supernatant solution was analyzed for U and DBP content respectively. The precipitate wherever obtained were filtered and washed thoroughly with sodium hydroxide again to desorb the DBP, if any got adsorbed to surface of uranium precipitate. The resulting wash solution was analyzed for DBP as well as U and both were analyzed below their corresponding detection limit. To avoid the addition of large volume of NaOH, the minimum volume of 11.5 M NaOH that can quantitatively precipitate U leaving DBP as soluble N2H$_5$DBP in supernatant was also studied. The results are presented in figures 1 & 2 respectively.

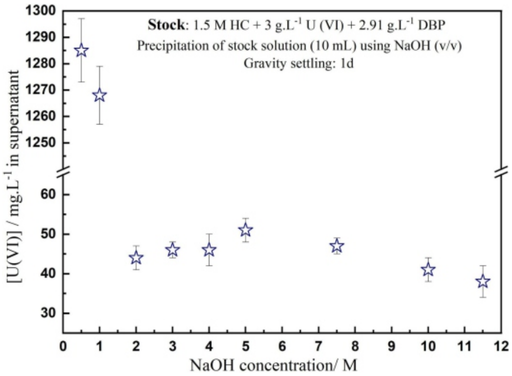

***Fig 1** Uranium (VI) in supernatant upon addition of different concentrations of NaOH*

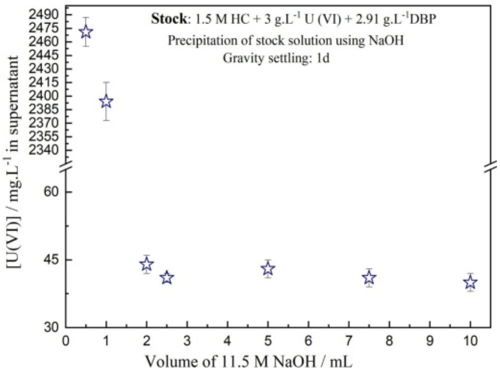

***Fig 2** Uranium (VI) in supernatant upon addition of different volumes of 11.5 M NaOH*

In both the cases it was observed that when the OH$^-$ concentration exceeds the total moles of carbonate ion, the metal got precipitated and the entitre DBP was present in supernatant as per IC analysis. The precipitate wherever formed was quantitatively dissolved using 10 M HNO$_3$ and the solutions were analyzed for uranium to account for the mass balance. The process was also validated for simulated hydrazine carbonate solution containing U, Pu and DBP.

***Key words:** Solvent wash, Precipitation, Ozonolysis, Supernatant*

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Functionalized Graphene Oxide-Polystyrene Composite Microspheres Synthesized through in situ Polymerization Route for Efficient Uranium Separation

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The monolayered allotrope of carbon, graphene, and its functional sibling—graphene oxide (GO)—have received widespread attention among separation scientists, particularly due to their large surface area, amenable surface properties, and enhanced mechanical, chemical, and thermal characteristics, which have fueled research into utilizing them as potential candidates for solid-phase separation–based metal ion recovery. Monolayered GO also exhibits sp^2-hybridized carbon domains characteristic of graphene sheets, along with an additional disrupted sp^3-hybridized framework due to extensive oxidation resulting from the presence of oxygen containing functional groups such as hydroxyl, epoxy, and carboxyl, which provides its flexibility to incorporate various functional groups [1]. The above feature of GO has been considered while designing the present adsorbent meant for separating uranium from dilute aqueous solutions such as contaminated mine water, seawater, etc., which is a compelling problem considering the huge strategic importance as well as the associated health hazards. The present work focuses on developing a GO-polymer composite, where the GO was initially functionalized with amine throughout its surface, and the in-situ preparation of the composite microspheres through the Pickering emulsion polymerization route has ensured the complete integrity of the matrix. A brief synthetic scheme is shown in Fig. 1. Use of polymeric microspheres containing the amine- functionalized GOs guarantees the stability of the adsorbent. Detailed characterization of the composite using SEM to identify morphology, XRD to monitor changes in crystallinity and interlayer distance during GO formation and subsequent modification with ligands and polymerization, as well as the amount of organic ligands present and their thermal decomposition behavior via TG-DTA, and FTIR analysis of the functional groups formed during chemical modification of GO supports the successful preparation of the composite adsorbent microspheres. The SEM image is shown in Fig. 2 which shows the spherical polymeric beads contains functionalized GO layers. Fig. 3 shows the adsorption behavior of uranium studied under acetate buffer and carbonate medium which showed an increase of uranium uptake up to pH 5 and a subsequent decrease. pH of the aqueous medium was adjusted by varying compositions of sodium acetate-acetic acid buffer (0.1 M each) or using 0.1 M sodium carbonate. A homogeneous Langmuir adsorption which revealed a uranium uptake capacity of approximately 106 mg/g, and validity of pseudo-second order kinetic model was deduced from the above studies. Various studies suggests that PS-GO-DETA is a promising composite adsorbent based on graphene oxide and styrene moiety for the removal of U from dilute aqueous solutions.

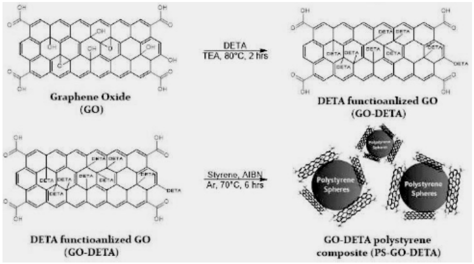

Fig. 1 Synthetic scheme for the for preparation of adsorbent

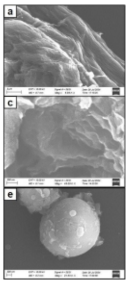

Fig. 2 *SEM images of GO (a), GO-DETA (c), PS-GO-DETA*

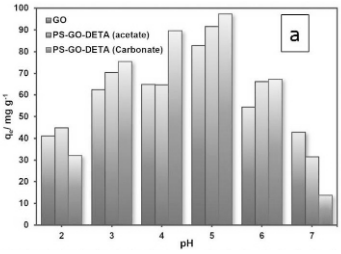

Fig. 3 *Amount of U extracted by GO in comparison withPS-GO-DETA in acetate and carbonate media*

Key words: *Graphene oxide, Composite adsorbent, Uranium, Adsorption, Diethylenetriamine*

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Fly Ash Based Geopolymers as Potential Adsorbents for Separation of Cesium from Aqueous Nuclear Effluents

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Geopolymers are potential and promising inorganic adsorbents for removal of radionuclides from radioactive waste solution due to their high surface reactivity and structural stability. The present study explores the synthesis of geopolymers from class-F coal fly ash which is an industrial byproduct and its adsorption performance for Cs which is one of the hazardous radioactive elements present in the nuclear waste. The chemical compositions of the fly ash (FA) was determined using EDXRF which shows SiO_2 to Al_2O_3 ratio (wt.%) is1.71. XRD (Fig. 1a) of FA shows the presence of mullite and quartz phases in it and Fig. 1b shows the XRD pattern of metabentonite (MBT) which was prepared from bentonite by heating at 800 °C for 6 h. It was observed that the peaks for quartz phase remained intact in the metabentonite. The geopolymers (GP) were prepared by reacting FA and MBT with NaOH and Na_2SiO_3 solutions for 15 min followed by curing at 80ºC for 24 h. Experimental parameters like concentration of NaOH, solid to liquid ratio, curing time and temperature have huge impact on the geopolymerization process. In this study, GPs were synthesized by varying NaOH concentration from 8-14 M and named as GP-8 to GP-14. Fig. 1(c-f) represents the diffraction pattern of the synthesized GPs which reflects that Quartz and mullite phases are present in the GPs. FTIR (Fig. 2) result shows the characteristics Si-O-Si and Si-O-Al stretching vibrations in FA and MBT at 1050 cm^{-1}. This intense peak shifted to lower wavenumber in the synthesized GPs. A new peak at 1454 cm^{-1} was observed in the GPs while it is absent in FA and MBT. This peak3is attributed to the stretching of O-C-O of CO^{2-} group which indicates the formation of carbonates during the curing process. XRD and FTIR analyses confirmed the successful synthesis of the geopolymers.

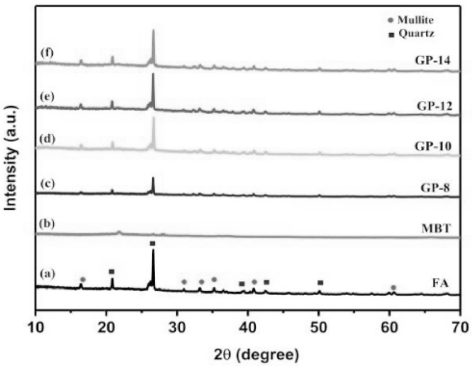

***Fig 1:** XRD patterns of (a) Fly ash (b) Metabentonite (c-f) GPs synthesized from 8, 10, 12 and 14 M NaOH*

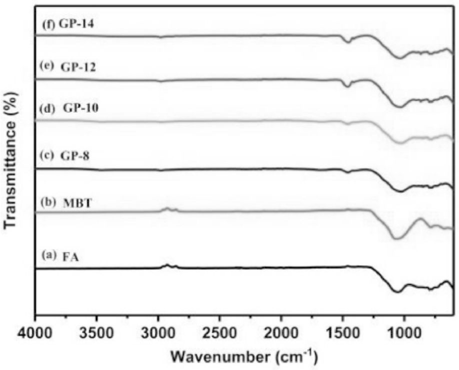

***Fig 2:** FTIR spectra of (a) Fly ash (b) Metabentonite (c-f) GPs synthesized from 8, 10, 12 and 14 M NaOH*

In batch adsorption experiments, GPs were equilibrated with Cs^+ solution keeping solid to liquid amount as 2mg/mL at ambient temperature for 6 h at different pH values ranging from 3 to 9. The Cs^+ solutions after adsorption experiments were analysed by Flame AAS to determine the adsorption capacity. The results demonstrated that adsorption capacity maximum in the pH range 6 to 7. The efficacy of different GPs were evaluated in terms of adsorption capacity of Cs^+ from aqueous solutions.

***Key words:** Fly ash, Metabentonite, Geopolymer, Cesium, Adsorption*

Acknowledgemnets: Authors gratefully acknowledge Dr. V. Jayaraman, Director, MC&MFCG and Dr. Rajesh Ganesan, Associate Director, FMCG, MC&MFCG for their support and encouragement.

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Palladium Removal from Simulated HLLW using Amine Modified Polystyene Copolymer

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Research on the separation of Pd produced in nuclear reactors through the nuclear fission reactions of U (or P u) is gaining significant attention within the scientific community, considering its low natural abundance on Earth and its extensive use in diverse industrial applications. present work is therefore to prepare a Pd selective adsorbent wherein an amine functional group is introduced to polystyrene copolymer, using diethylenetriamine (DETA) as a precursor by chemical modification. The resin was characterized using FTIR, SEM-EDX, XPS and TG-DTA. The IR spectrum (shown in Fig. 1) of the prepaared resin with reference to chloromethlated resin (PS- Cl) and DETA shows disappearance of characteristic band (1264 cm-1), attributed to the C-Cl stretching and emergence of doublet at 3353cm^{-1} and 3276cm^{-1} due to -NH_2 stretching. The amine functional group that is chemically bonded to the resin network is powerful due to its superior stability in the acidic environments. The adsorption results (Fig. 2) revealed that the initial uptake of Pd was sluggish up to 2 M nitric acid, followed by a sharp increase in Pd adsorption up to 5 M. However, the adsorption slightly decreased to 92% beyond this concentration. For practical Pd separation, the higher adsorption efficiency of PS-DETA at 4 M provides valuable insight into its practical utility for future applications. A synthetic feed solution was prepared based on the suggested feed corresponding to a burn-up of 80 Gwd/Te (Table 1)].Results of the study (shown in Table 4) indicated that PS-DETA did not exhibit any adsorption of lanthanides, Cr, Cd, Mo, Fe, Ba. The only interference was from Ag. The studies showed promising results on selective Pd uptake, even in the presence of large excess of metal ions present in radioactive waste that corresponded to the compositions of PUREX raffinate.

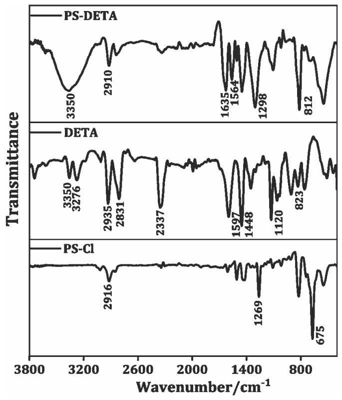

Fig. 1 *FTIR of PS-Cl, DETA and PS-DETA*

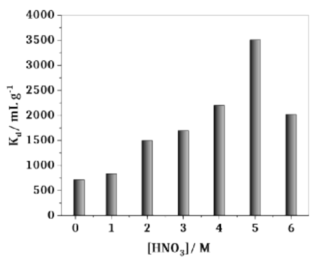

Fig. 1 *Pd adsorption as a function of nitric acid*

Fig. 3 *Selective adsorption of Pd from interfering elements present in the simulated high-level liquid waste*

Elements	**Concentration of elements (mg L^{-1})**	
	Before adsorption	**after adsorption**
Cr	10.4	10.3
Cd	8.3	8.1
Mo	46	46
La	48	48
Ce	76	76
Pr	37	37
Nd	115	115
Sm	35	34
Eu	3.4	3.4
Gd	7.6	7.4
Dy	1.1	1.1
Ni	11.9	11.8
Sr	16.4	16.3
Fe	62	62
Y	8.4	8.3
Ba	42	40
Ru	5.2	5.2
Rh	3.3	3.3
Pd	22.2	2.9
Zr	78	75
Ag	12.2	2.9
Tb	2.6	2.6

Key words: *Palladium, Polystyrene resin, Simulated High level waste, Adsorption, Imidazole*

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Selective Recovery of Zr(IV) from Hf(IV) and Ti(IV) in Nitric Acid Media Using Tri-n-Amyl Phosphate and Di-n-amyl-n-amyl Phosphonate

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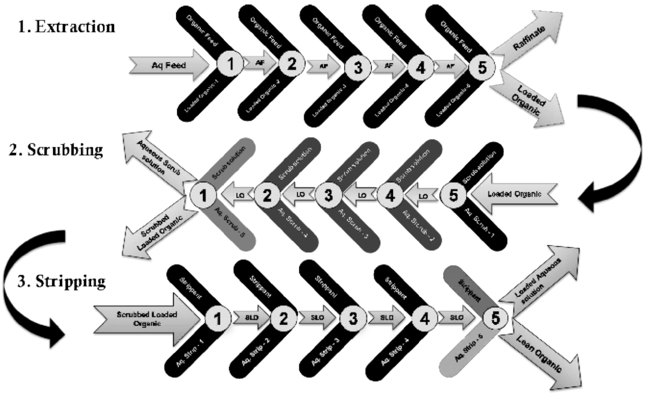
Zirconium is an essential structural material in nuclear reactors, particularly in PHWRs, owing to its high corrosion resistance and low thermal-neutron capture cross section.[1]. The production of nuclear-grade zirconium remains challenging due to the need to separate Zr(IV) from its tetravalent congeners, Hf(IV) and Ti(IV), which possess comparable ionic radii and chemical behaviour. Although TBP-based solvent extraction enables Zr–Hf separation under strongly acidic conditions, its performance is restricted by third-phase formation and reduced extraction efficiency in complex feed solutions.[2]. Higher homologues of TBP, such as Tri-*n*-Amyl Phosphate (TAP), along with phosphonate analogues such as Di-*n*-Amyl-*n*-Amyl Phosphonate (DAAP), exhibit superior third phase resistance and extraction efficiency. In this work, TAP and DAAP are evaluated independently to allow direct comparison of their performance in the selective recovery of Zr(IV).

The present study examines the solvent extraction behaviour of TAP and DAAP for the separation of Zr(IV), Hf(IV), and Ti(IV) from a simulated dissolver feed containing ~68 g/L Zr, 2020 mg/L Hf and 182 mg/L Ti in 4 M HNO_3. Cross-current extraction, scrubbing, and stripping were performed using five stages each, consistent with earlier work and to ensure uniform operating conditions(Scheme 1). All extractions were conducted at an O/A ratio of 5:1[3]. Scrubbing with zirconyl nitrate effectively removed co-extracted Hf and Ti, and dilute nitric acid quantitatively stripped Zr(IV) from the loaded organic phase. Overall, DAAP and TAP offer a robust alternative to TBP for processing tetravalent metal systems, delivering improved selectivity, phase stability, and efficient separations suitable for nuclear-grade Zr purification. DAAP demonstrated near-quantitative extraction of Zr(IV) with fewer stages and delivered superior Zr/Hf and Zr/Ti separation factors compared to TAP(Figure 1). The superior selectivity of DAAP over TAP is attributed to stronger steric and electronic contributions at the phosphoryl oxygen.



***Scheme 1:** Schematic representation of cross-current extraction, scrubbing and stripping of simulated zircon sand dissolver solution.*

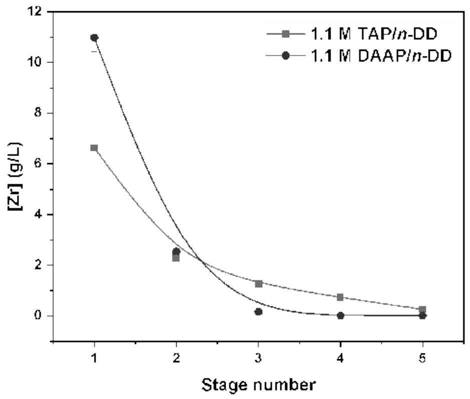


***Figure 1:** Extraction profile of Zr(IV) through stage-wise operation from the feed solution*

***Key words:** TAP, DAAP, Nuclear grade Zirconium, Zr/Hf separation, Zr/Ti separation.*

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A-11

Validation of ALSEP Concept for Separation of Am(III) from a Synthetic Mixture of Early Lanthanides

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The mutual separation of trivalent actinides, Am and Cm from the chemically similar lanthanides in high-level waste (HLW) solutions is one of the challenging problems faced by separation scientists working in the area of nuclear waste management. Among the various separation methods studied for this purpose, the 'ALSEP' process makes use of the better complexing ability of trivalent actinides with the soft donor ligand, di-ethylenetriaminepentaaceticacid (DTPA) in citric acid (CA) buffer medium [1]. The ALSEP process involves an extraction stage of trivalent actinides and lanthanides together from HLW followed by selective stripping of actinides using an aqueous formulation containing DTPA and CA.

The choice of solvent system used for the extraction stage is important in ALSEP process, as it is desirable to allow the quantitative extraction of actinides while minimizing the co-extraction of lanthanides in this step. A combined solvent containing both neutral and acidic extractants is used here. Diglycolamide extractants such as *N,N,N',N'*-tetraethylhexyldiglycolamide (TEHDGA) is considered as ideal choice for this step due to the moderate extraction and efficient stripping of lanthanides. In the current study, a synthetic mixture of early lanthanides (La: 250 ppm, Pr: 300 ppm, Nd: 1000 ppm, Sm: 200 ppm, Eu: 75 ppm) and Am (183 ppm) in 3 M nitric acid was prepared for evaluation of ALSEP methodology for the separation of Am from lanthanides. Different solvent systems containing either TODGA or TEHDGA extractants in combination with the acidic extractants, *N,N*-di-2-ethylhexyldiglycolamicacid (HDEHDGA) or mono-2-ethylhexyl(2-ethylhexyl) phosphonate (HEH(EH)P/PC-88A) were studied for the extraction step. Fig. 1 shows the percentage extraction of lanthanides in different solvents. The extraction of Am was more than 99% in all these solvents, except when 0.05 M TEHDGA was used. A combination of 0.075 M TEHDGA and 0.5 M PC-88A was found to have lower extraction of La and Pr in comparison to all other systems. Decreasing the concentration of TEHDGA further to 0.05 M reduced the extraction of both Am and lanthanides. The above solvent was reported in the recent study of ALSEP demonstration by Gelis et al. [2]. The stripping of extracted metals from this solvent using different combination of DTPA and CA at pH 3 was also studied and the results are compared in Fig.2. Stripping with 0.1 M nitric acid without any complexing agents was also studied for evaluating the holding effect of PC-88A for different lanthanides. A combination of 0.01 M DTPA and 0.1 M CA was found to have minimal stripping of lanthanides and nearly 80% stripping of Am in a single stage. Further studies were also carried out for optimizing the recovery of Am and minimizing the stripping of lanthanides in multi-stage stripping cycles. The studies established that Am can be successfully removed from the early lanthanide mixture in multi-stage extraction-cum stripping cycles by adopting to ALSEP process.

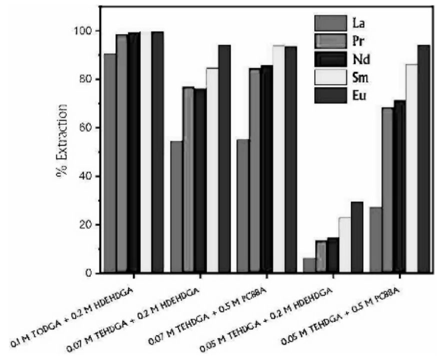

Fig.1 *Percentage Extraction of lanthanides during single stage extraction using different solvent systems*

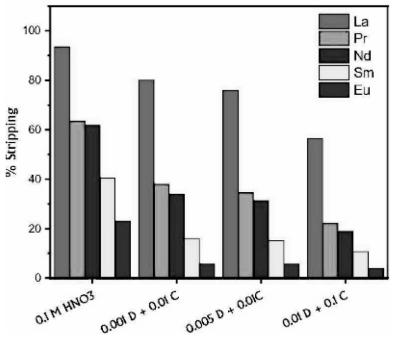

Fig.2 *Percentage stripping of lanthanides from 0.05 M TEHDGA+0.5 M PC88A solvent using different stripping formulations at pH 3*

Key words: *Americium, ALSEP Process, Diglycolamide, Group Separation, Mutual Separation*

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A-12

A Combined DFT–MD Investigation of Zr(IV) Selectivity in TAP and DAAP Organophosphorus Extractants

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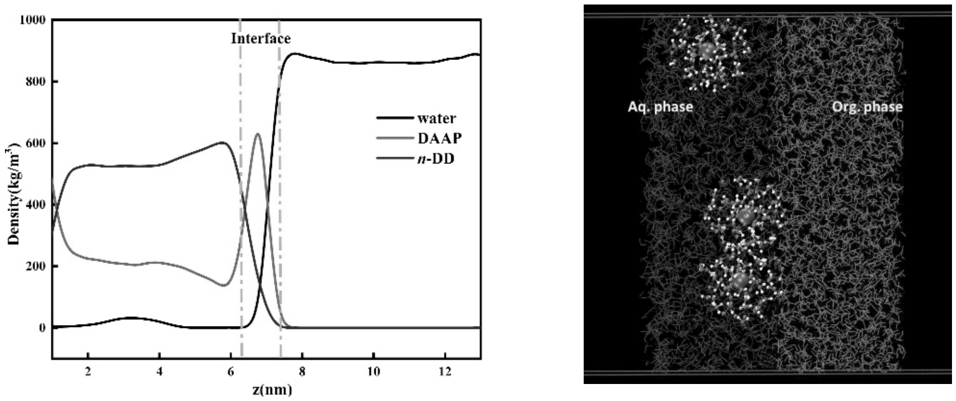
The efficient separation of zirconium from hafnium and titanium is a longstanding challenge in zircon processing and nuclear-materials purification.[1] Zirconium ores such as zircon ($ZrSiO_4$) naturally contain hafnium at the percent level and trace titanium, and because Zr(IV), Hf(IV), and Ti(IV) possess comparable ionic radii, coordination preferences, and hydrolysis behavior, traditional solvent-extraction strategies struggle to achieve the high selectivity required for nuclear-grade zirconium. Organophosphorus extractants— particularly tri-*n*-amyl phosphate (TAP) and diamyl amyl phosphonate (DAAP)—have emerged as promising alternatives to TBP owing to their improved phase behavior, higher third-phase limits, and potentially stronger interaction with tetravalent cations. In this work, we employ a combined density functional theory (DFT), Natural Bond Orbital (NBO), Energy Decomposition Analysis (EDA), and molecular dynamics (MD) approach to elucidate the molecular origins of Zr(IV) selectivity in TAP and DAAP systems. DFT calculations at the BP86/def2-TZVP level show that Zr(IV) forms markedly more stable complexes with TAP and DAAP compared to Hf(IV) and Ti(IV), with significantly more negative complexation energies for Zr—highlighting a clear thermodynamic driving force for preferential extraction. NBO analysis reveals stronger P=O → Zr donor–acceptor interactions and greater charge transfer in Zr–ligand complexes, while EDA confirms that both electrostatic and orbital-interaction components contribute more favourably to Zr binding relative to Hf and Ti. These bonding descriptors collectively demonstrate that the phosphoryl oxygen in TAP and DAAP coordinates Zr(IV) with greater covalent-electrostatic synergy, rationalizing the observed selectivity.

Interfacial properties were also examined, revealing moderately high interfacial tensions for the TAP ($44.35\ \mathrm{mN\cdot m^{-1}}$) and DAAP ($43.51\ \mathrm{mN\cdot m^{-1}}$) organic phases in contact with the aqueous feed. Despite this, MD simulations show that Zr–ligand complexes experience enhanced mobility at the aqueous–organic interface and diffuse more readily into the organic phase compared to Hf and Ti complexes. This behavior reflects a strong interplay between complex stability and interfacial transport: the highly favorable Zr–ligand complexation energy is sufficient to overcome the interfacial energy barrier, enabling efficient transfer into the organic phase even under high-IFT conditions. Overall, the combined DFT–MD analysis provides a mechanistic understanding of why TAP and DAAP preferentially extract Zr(IV) over Hf(IV) and Ti(IV).



(a) (b)

Fig. 1*: (a) Density profiles of water, DAAP, and n-dodecane along the z-axis (b) MD snapshot showing Zr(IV) (pink) migrating from the aqueous phase into the organic phase.*

Key words: *Zr/Hf/Ti separation, DFT, Molecular Dynamics*

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Extraction of Studies of Cesium from Aqueous Solution by a Synthetic Zeolite

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Zeolites are special type of inorganic ion exchangers which are considered as superior adsorbents for their ion exchange capacity and radiation in comparison with the organic based ion exchangers. Natural zeolites are formed in volcanic and sedimentary rocks, while synthetic zeolites are man-made and can be tailored for specific industrial applications [1]. In nuclear industry, the zeolites are used as the ion exchangers for cesium and strontium ions as well as the solid matrix for the immobilization of these ions for the purpose of the storing the waste in the location suitable for the disposal of the radioactive waste. The nuclear waste of the categories low level [2] and intermediate radioactive wastes can be treated by zeolites for the safe disposal. The main advantage of using zeolites is the stability of the solid matrix which will not allow the radioactive cesium or strontium to leach in to the nearby outer area or earth crust. The main objective of this paper is to develop suitable synthetic zeolites for the ion exchange and study the extraction behavior at various conditions and optimize the condition for better extraction.

The zeolite was synthesized using precursor materials mixed in the molar ratio NaOH : Al_2O_3 : SiO_2 : H_2SO_4 : H_2O = 4.3 : 1 : 10 : 2 : 180. The mixture was homogenized by ultrasonication, transferred to a Teflon- lined autoclave, and hydrothermally treated at 453 K for 24 h. The resulting sodium aluminosilicate was repeatedly washed with distilled water until the final wash reached pH 8.34, then dried in a fume hood for 48 h. FT-IR and XRD analyses confirmed the formation of the zeolite structure. XRD pattern (See Fig. 1) of the synthesized compound matched well with the standard JCPDS card no. JCPDS No. 39-1380. Batch adsorption experiments were performed using 50 mg of the adsorbent and 10 mL of cesium solution adjusted to the required pH, followed by equilibration for 6 h. Cesium concentrations were measured by atomic absorption spectroscopy. Fig. 2 shows a steady increase in the distribution ratio from pH 1 to 6, indicating improved cesium uptake at higher pH. This suggests that nuclear waste streams bearing Cs at pH close to neutral solutions can be effectively treated using the synthesized material. The synthesized zeolite effectively removes cesium from solution through a pH-dependent ion-exchange mechanism, demonstrating its suitability for treating the relevant nuclear waste streams.

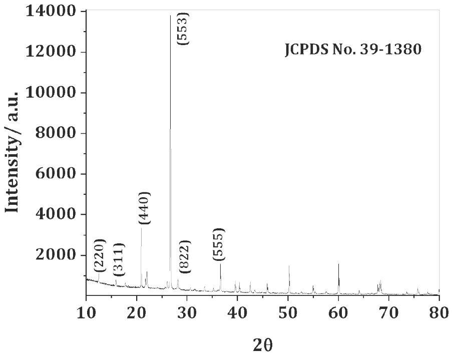

Fig.1 *XRD of synthetic zeolite, compared with JCPDS No. 39-1380*

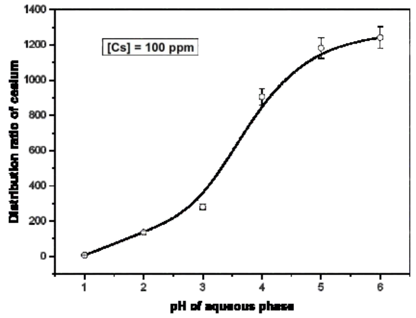

Fig.2 *Distribution coefficient of Cs as a function of pH*

Key words: *Synthesis, zeolites, cesium, distribution ratio, pH values after extraction*

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Sorption Studies of Strontium from Aqueous Solution by Zeolite y Sodium

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The removal of cesium and strontium radionuclides from nuclear waste streams is essential due to their long half-lives and significant heat generation. Zeolites are widely employed for this purpose owing to their high ion- exchange capacity, inherent selectivity, excellent thermal and radiation stability, and relatively low cost [1,2]. Beyond their ion-exchange abilities, zeolites also serve as effective matrices for the immobilization of radioactive waste. They are suitable adsorbents for extracting these nuclides from low- and intermediate-level liquid waste. Radionuclides such as ^{137}Cs and ^{90}Sr can be captured by zeolitic frameworks and immobilized through incorporation into solid matrices, which are subsequently stabilized with appropriate additives and disposed of in designated facilities. The general formula for zeolites is $Na_2Al_2Si_2O_8 \cdot xH_2O$. Numerous structural types exist, and their properties can be tuned by adjusting reactant concentrations and molar ratios during synthesis. Common classifications include zeolite A, P, X, and Y, with the Si/Al ratio in zeolite Y typically exceeding 1.5 [3, 4].

In this study, commercial sodium-form zeolite Y (Sigma-Aldrich) was used for Sr separation. The material was air-dried in a fume hood for two days before experimentation. Batch adsorption studies were conducted across a pH range of 2–6 using 50 mg of zeolite Y and 10 mL of aqueous strontium solution. Strontium concentrations before and after treatment were quantified via ICP-OES. Kinetic experiments indicated that equilibrium was reached within one hour. The distribution ratio was approximately 1400 at pH 2, increasing markedly to around 40000 between pH 3 and 6. The above pH range was considered to understand the Sr adsorption behavior with the intention of using the adsorbent for its recovery from ILW and LLW. The strong enhancement in distribution ratios at higher pH values demonstrates that sodium-form zeolite Y is highly effective for strontium extraction under mildly acidic to near-neutral conditions. Sodium-form zeolite Y exhibits rapid kinetics and exceptionally high distribution ratios at mildly acidic to neutral pH, demonstrating its strong suitability for efficient strontium removal from aqueous nuclear waste streams. Studies are underway in understanding the adsorption behavior in alkaline range also to understand applicability of zeolite Y sodium for Sr recovery from such feed solutions.

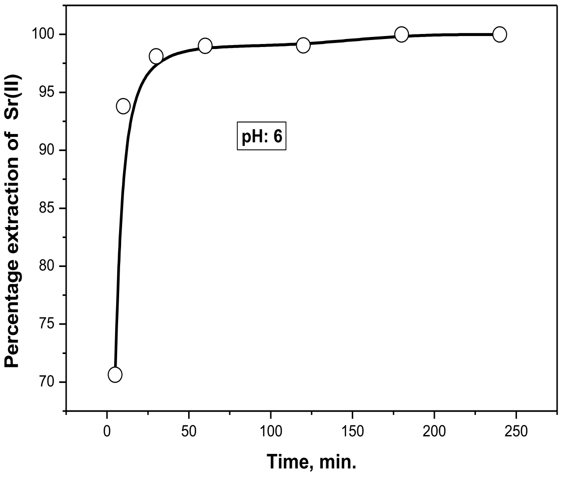

***Fig.1:** Kinetics of extraction for Sr from pH6.*

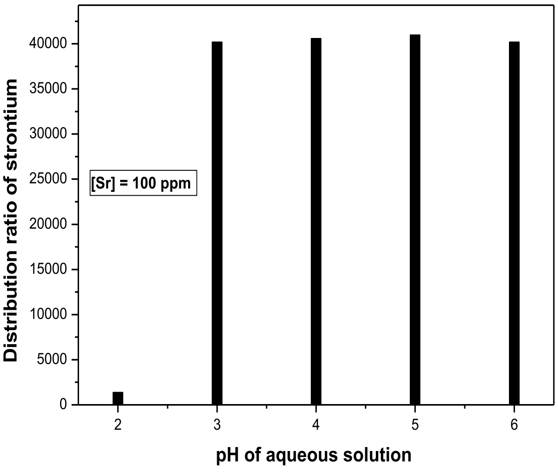

***Fig.2:** distribution ratio for Sr at various pH*

***Key words:** zeolite y sodium, strontium, batch extraction, distribution ratio, pH*

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Study on Hydrazine as a Reductant for Plutonium in Spent Fuel Reprocessing

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The spent nuclear fuel is reprocessed using liquid–liquid extraction, and the PUREX process is the method most widely used worldwide. In this process, 1.1 M tri n-butyl phosphate diluted in dodecane (TBP/n-DD) is employed as an extractant. In the PUREX process, the first step involves extraction of unused uranium (U) and plutonium (Pu) present in irradiated fuel solution leaving bulk of fission products into high level waste. In second step, separation of U and Pu is accomplished using suitable partitioning agent. In the reprocessing of spent fuel discharged from thermal reactor, the aqueous phase consisting $U(NO_3)_4$ stabilized with N_2H_4 in dilute HNO_3 (1.0-1.5 M) is contacted with loaded organic phase containing U and Pu for the selective stripping of Pu. This process is designated as organic partitioning and it demands a reagent which is capable of reducing the Pu in the organic phase. Usually $U(NO_3)_4/N_2H_4$ is used to achieve this and several times (~10 times) the stoichiometric amount of Pu in organic phase is required. The several fold excess uranous nitrate is admissible only for the partitioning of spent fuel containing Pu < 1 %. However, this organic partitioning with uranous nitrate is not feasible for the spent fuel from fast reactors (FR), where the Pu content is significantly higher. Therefore, aqueous partitioning was found to be promising method for mutual separation of U and Pu in FR spent fuel. In this method, U and Pu from loaded organic phase after first cycle extraction are co-stripped and the oxidation state of Pu is conditioned to Pu^{3+} by adding suitable reducing agent which can act in the aqueous phase. When, the resultant conditioned feed solution is on contact with TBP/n-DD, uranium is extracted into organic phase and Pu^{3+} remains in aqueous phase and partitioning of U and Pu was enabled. In this, the hydrazine is used as a HNO_2 scavenger to prevent the autocatalytic oxidation of Pu $^{3+}$ to Pu $^{4+}$. In the present study, hydrazine nitrate alone was investigated as both a reducing agent and a stabilizer for converting Pu^{4+} to Pu^{3+}. In this experiment, a solution mixture of 4.5 g/L Pu (0.0188 M), hydrazine nitrate (0.1 M) and nitric acid (2 M) was stirred continuously for hours and portion of sample from reaction mixture was drawn at different intervals of time and analyzed for Pu^{3+} concentration. The direct UV-Visible spectrophotometric method was employed to monitor Pu^{3+} concentration in the mixture. The UV-visible spectra obtained at different time intervals and the % of Pu converted to Pu^{3+} is provided in fig. 1 and in table 1 respectively. The optical density measured at 600 nm was employed for obtaining the concentration Pu^{3+} in the reaction mixture.

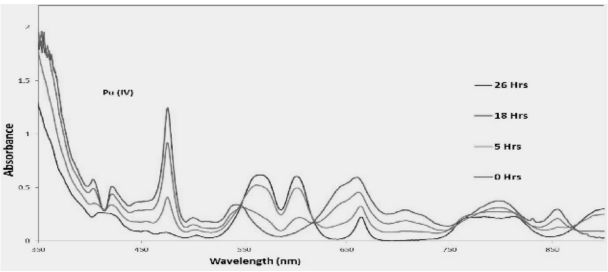

Fig 1: *Absorption spectra indicating the Progressive reduction of 4.5g/L Put (IV) to pu (III) with hydrazine in 2 M* HNO_3

Table 1: *% conversion of total initial Pu to* Pu^{3+} *at different time intervals*

S no	Time (h)	Pu (III) (M)	% of Pu as Pu (III)
1	0	< 0.001	< 1
2	5	0.0052	7.4
3	18	0.0141	72.3
4	26	0.0187	99.5

The result of this experiment indicates that hydrazine nitrate can reduce Pu (IV) to Pu (III), although the reaction proceeds with slow kinetics. The advantage of this approach is that it avoids introducing external metal-ion reductants and is therefore better suited for aqueous partitioning pertaining to the reprocessing of spent fuel from FR.

Key words: *Plutonium, uranium, hydrazine, partitioning, uranous*

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Separation of ^{237}Np from Fast Reactor Spent Fuel.

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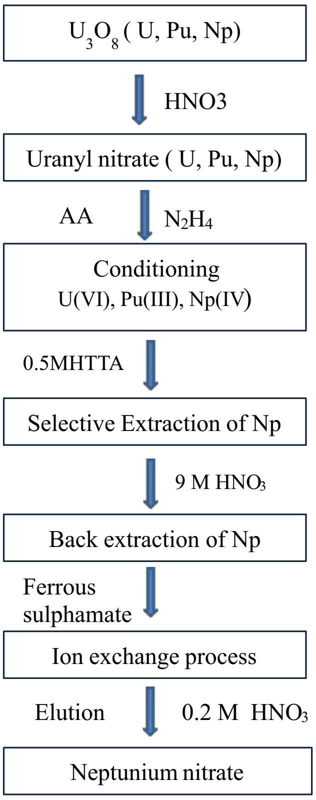
The abundance of ^{237}Np in nature is negligible and it is an artificially produced isotope formed in nuclear reactorsy means of various nuclear reaction such as neutron capture, (n, 2n) and alpha decay. In fast reactors, the formation of ^{237}Np is more as compared to thermal reactors primarily because of the higher neutron flux and the harder neutron spectrum, which significantly enhances the (n,2n) and successive neutron-capture reactions on uranium (U) isotopes. In view of its potential application as the target nuclide for the production of ^{238}Pu, an isotope employed as power source in space applications. Therefore, the separation of ^{237}Np has become a subject of significant interest.

The PUREX process is followed for the reprocessing of fast reactor spent nuclear fuel for the recovery of U and plutonium (Pu). The oxidation state of Np in the dissolver solution is crucial in determining whether Np enters the productstream or the effluent. For obtaining U and Pu product with better decontamination factor with respect to ruthenium, a high acid flow sheet is followed during reprocessing of spent fuel discharged from FBTR in CORAL and DFRP. In this condition, the oxidation state of Np is maintained in +4 and +6. Therefore, the typical route of Np as determined for fast reactor spent fuel reprocessing with high acid flow sheet is provided in fig 1. It is evident that maximum Np (>85%) is routed to the U product stream, therefore attempts were made to separate the Np from this stream. In the present work, U_3O_8 product was dissolved in nitric acid and acidity adjusted to 1M. Subsequently, the oxidation state of Pu and Np were maintained to be Pu (III) and Np (IV) respectively by adding ascorbic acid (AA) in presence of hydrazine nitrate followed by selective extraction of all Np in 0.5 M HTTA in xylene. The steps involved in separation and purification of Np from U_3O_8 dissolved product is shown Fig. 2.



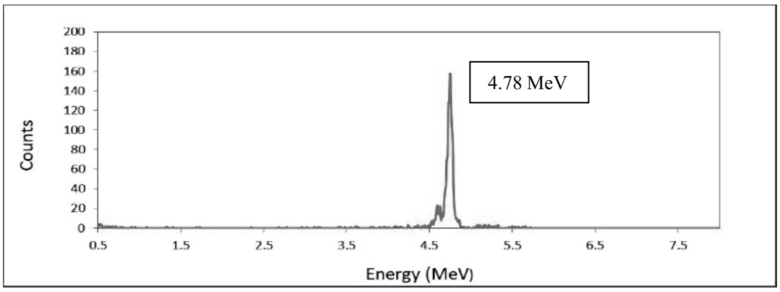


Fig 1: *Alpha spectrum of the purified ^{237} Np product*

Table 1: *U_3O_8 and Np product composition*

Element	U_3O_8	Np-oxide
U	99.68 %	< 0.2%
Pu	0.21 %	<0.07%
Np	0.045 %	99.8 %
Fe	0.03 %	< 0.001%

The concentration of Np in loaded organic phase and final product were confirmed by alpha spectrometry and the alpha spectrum of purified ^{237} Np is given in figure 1. Overall cumulative decontamination factor obtained with respect to Pu and U in the final Np product by following this separation scheme is 6.64 x 10^3 and 1.10 x 10^6 respectively.

Key words: *Neptunium, uranium, extraction, ion exchange etc*

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Extraction Behavior of U(VI) in Centrifugal Contactor in the Recovery Cycle of Fast Reactor Fuel Reprocessing

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PUREX process is employed for the recovery of uranium and plutonium from spent nuclear fuels of thermal as well as fast reactors. The recovery cycle in PUREX process aims the separation and recovery of actinides from dilute solution streams. In the present study, the extraction behavior of uranium (360 mg/L) from 4 M HNO_3 was studied in an organic phase consisted of 0.55 M Tri-n-butyl phosphate in *n*-dodecane (TBP/n-DD) and stripping of uranium from the loaded organic phase. The experiments were performed in a centrifugal contactor. Fig 1 and Fig 2 represents stage concentration profile of uranium during extraction and stripping in the centrifugal contactor respectively. The extraction results showed that 3 to 4 stages were adequate for quantitative extraction (> 99.9%). The dual acid stripping was conducted using 4 M and 0.01 M HNO_3 for recovery of uranium from the loaded organic phase. The stripping results showed unusual accumulation of uranium due to the introduction of 4 M HNO_3 in the extractor bank, due to the re-extraction of uranium in the bank. The steady state in the dual stripping procedure was found to be achieved only after 450 minutes.

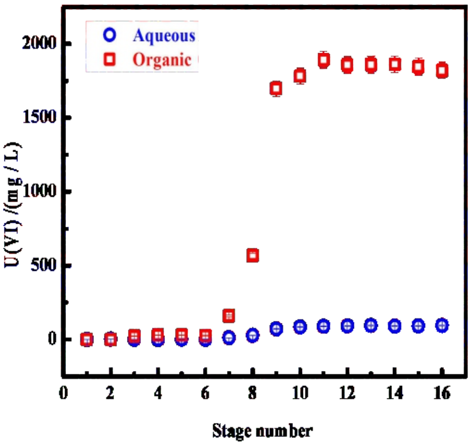

Fig.1. *The stage concentration profile of U(VI) in aqueous and organic phases during the extraction of uranium in 0.55 M TBP/n–DD from 4 M nitric acid*

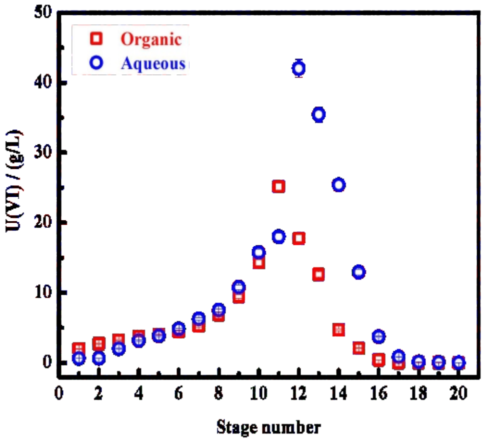

Fig. 2. *The stage concentration profile of uranium in aqueous and organic phases during the stripping of uranium from 0.55 M TBP/n-DD using 0.01 M and* 4 M HNO_3

Key words: *Uranium; Tri-n-butyl phosphate; nitric acid, solvent extraction; centrifugal extractor*

Processing of Analytical Wastes with Sulphate and Phosphate Content for Plutonium Recovery

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The Redox titration method is followed for sample consisting Pu as part of nuclear material accounting. In this method, an aliquot consisting Pu of 5-10 mg of is used [1]. As a result, the analytical waste produced contains a substantial amount of Pu in the concentration range of 25–30 µg/mL as Pu(IV) along with corrosive chemicals such as phosphates and sulphates. Consequently, this waste from Redox titration cannot be combined with plant waste streams due to its corrosive nature, nor can it be transferred to the waste management unit because its alpha activity exceeds 4000 Bq/mL. Hence, it is essential to treat this waste to bring alpha activity < 4000 Bq/mL. Therefore, efforts were made to recover Pu from these analytical wastes by solvent extraction method so that resulting effluent is suitable for disposal. The organic phase consisting 0.2 M tri n-Octyl Phosphine Oxide diluted with xylene (TOPO/xylene) was used as an organic extractant. And analytical wastes generated during Redox titration after adjusting acidity from 1.0 -8.0 M was used as aqueous feed for solvent extraction. During equilibration, A/O ratio was maintained to be 1.0 and mixing of two phases were carried out for 20 minutes using a vortex shaker. The concentration of Pu in organic and aqueous phases was determined after centrifugation and the results are given in Table 1. The percentage of extraction was maximum if feed acidity was above 5.2 M HNO3 as shown in Fig 1. In this experiment, quantitative stripping of Pu from loaded organic phase was also studied using oxalic acid of different concentrations, oxalic acid of 0.2 M was optimized and stripping efficiency was found to be > 98 % in a single contact and results are shown in Table 2. Therefore, solvent extraction method using organic phase consisting TOPO is found to promising method for the recovery of Pu from analytical wastes consisting strong complexing agents such as sulphate and phosphate.

Table 1. *Amount of plutonium in the sample feed and in the raffinate after extraction with 0.2M TOPO in xylene*

Sample No	Feed H+, M	Pu in Feed, µg	Pu in Raffinate µg
1	1.2	204	43.8
2	2.2	204	21.4
3	3.2	204	10.2
4	4.2	204	2.7
5	5.2	204	1.2
6	6.2	204	1.3
7	7.2	204	1.2
8	8.2	204	1.3

Table 2. *The concentration of Pu in loaded and lean TOPO after stripping with oxalic acid*

oxalic acid, M	Pu in loaded TOPO, ppm	Pu in lean TOPO, ppm
0.1	150.3	11.5
0.2	159.0	2.46
0.4	160.0	1.3
0.7	161.0	0.3

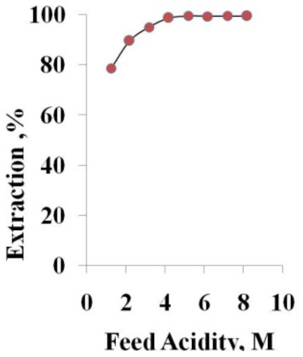

Fig 1 *Plot of % extraction of Pu from sulphate and phosphate waste solution against feed acidity.*

Ke words*: Plutonium, TOPO, sulphate, phosphate, waste*

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Novel Organo H-phosphonate-Based DES for Nuclear Fuel Cycle Applications: Synthesis and Exceptional Uranium Extraction Behavior.

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A new organophosphorus-based deep eutectic solvent (DES) was synthesized by mixing tri-n-octyl phosphine oxide (TOPO) and di-amyl hydrogen phosphonate (DAHP) in different molar ratios, with the 1:2 composition forming a stable eutectic liquid at room temperature. FTIR analysis confirmed DES formation through strong hydrogen bonding between the acidic P–OH group of DAHP and the P=O oxygen of TOPO, evidenced by the red shift and broadening of the P=O stretch and the significant broadening of the O–H band. Changes in the P–O fingerprint region further indicated rearrangement of the phosphate environment, while the unchanged C–H stretching region showed that alkyl chains do not participate in primary interactions. Thermal studies demonstrated excellent stability: TGA showed minimal degradation up to 180–200°C, with major decomposition occurring only beyond 250 °C, and DSC indicated a depressed melting point just below 0 °C, confirming the DES remains liquid at ambient conditions. The DES exhibited outstanding uranium extraction efficiency, maintaining >95% extraction across a wide acidity range. Maximum extraction (~97.8%) was achieved at 6 M HNO_3, attributed to the formation of neutral uranyl–nitrate species that are strongly extracted by TOPO-based systems [1]. Overall, the TOPO–DAHP (1:2) DES combines strong hydrogen bonding, good thermal stability, and high extraction performance, making it a promising candidate for uranium separation applications.

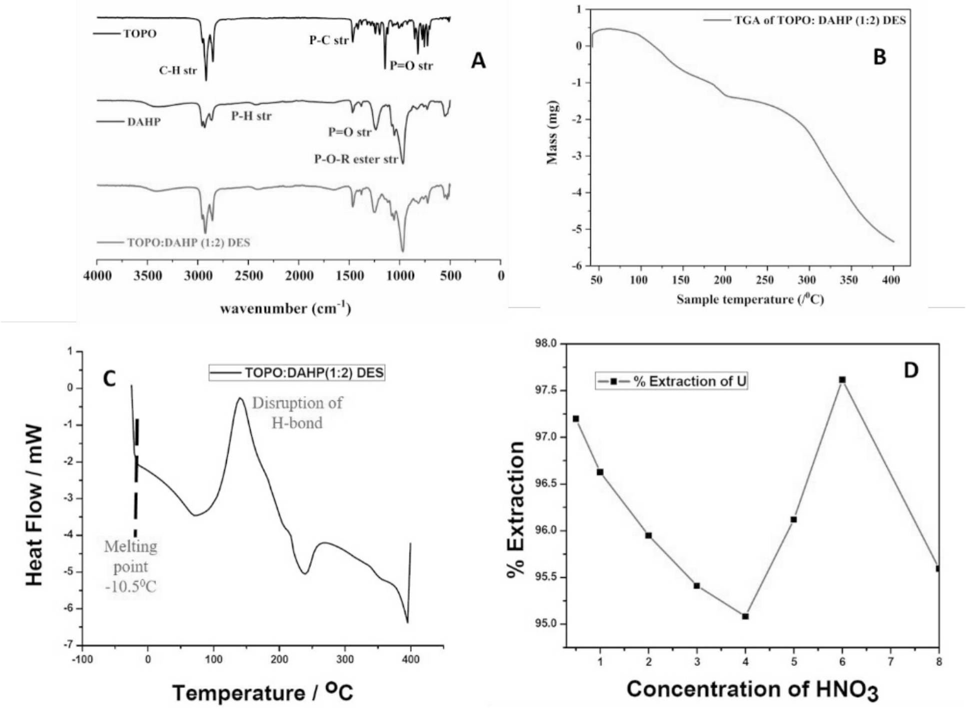

Figure 1. (A)FTIR spectra of TOPO, DAHP and TOPO: DAHP (1:2) DES (B)TG curve of TOPO: DAHP (1:2) DES (C) DSC curve of TOPO: DAHP (1:2) DES (D) extraction profile of uranium in DES with varying HNO_3

Key words: *DES, uranium, organophosphonates*

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Optimization of Process Conditions for Quantitative Recovery of Plutonium from Spent Solvent Employing Uranous Nitrate

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The PUREX (Plutonium Uranium Extraction) process is a widely employed aqueous reprocessing technique for the recovery of uranium and plutonium from spent nuclear fuel. In the case of fast reactor spent fuel reprocessing, after uranium and plutonium are recovered from the loaded organic solution, the lean organic phase still contains a significant amount of plutonium due to extensive solvent degradation. Among the degradation products, dibutyl phosphate (HDBP) is the major species responsible for retaining plutonium in the organic phase. Therefore, it is essential to recover plutonium from the lean organic phase (contains >10 mg/L of plutonium) before the solvent is subjected to further treatment and final disposal.

In the present work, a simulated lean organic solvent (1.1 M TBP/n-dodecane) containing HDBP was loaded with the desired amount of plutonium varying from 100 to 1000 mg/L (In general, the concentration of plutonium in lean organic varies from 10 to 250 mg/L, however in special conditions where the solvent is severely damage, under these the concentration of plutonium in lean organic may go even up to 1000 mg/L).The plutonium present in this lean organic phase was then recovered by contacting it with uranous nitrate solution under various experimental conditions. The effects of four process parameters, namely the concentrations of HNO_3, U(IV), Pu(IV), and HDBP, on plutonium recovery were studied in detail. Overall;27 batch experiments were conducted according to Box–Behnken design. The level of each parameter and the concentrations assigned to each parameter are shown in Table 1. The amount of plutonium recovered in each experiment was measured. The experimental results were optimized using response surface methodology and derived a model equation. The model was validated by conducting five random experiments, which showed that it could reproduce the experimental data with an error of less than 10%. Under the optimal experimental conditions identified, more than 85% of the plutonium could be recovered in a single contact. Figure 1 presents the contour plot of the percentage of plutonium recovered as a function of different levels of U(IV) and Pu(IV). From this optimization study, the optimum experimental conditions and the number of contacts required to reduce the plutonium concentration in the lean organic phase to less than 5 mg/L were determined.

Factor	level		
	-1	0	+1
HNO_3 / M	0.1	0.5	1
HDBP/(mg/L)	1000	2000	3000
Pu(IV)/(mg/L)	100	500	1000
U(IV)/(mg/L)	100	500	1000

Table .1. *Level of process parameter and the concentration assigned in Box- Behnken design.*

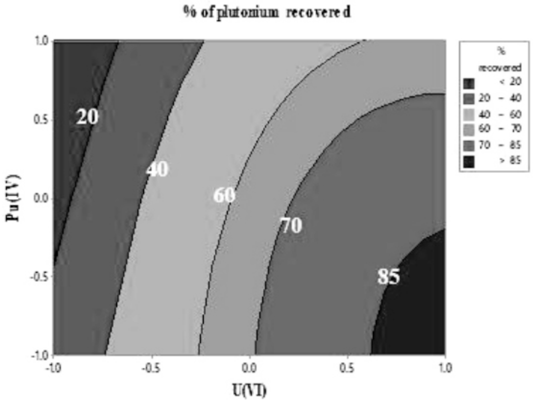

Fig.1 *Contour plot for % of plutonium recovery versus levels of Pu (IV) and U(IV).*

Key words: *Plutonium, Uranous nitrate, Dibutyl Phosphate, Optimization*

A-21

Development of a Common Digestion Cum Matrix Separation Methodology for Determining Critical Trace Impurities in Various Uranium Fuels by ICP-OES

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Uranium and its compounds are the most widely used fuels in nuclear reactors for the sustainable production of energy. The production of uranium metal and its compounds from the ore involves various steps like crushing, leaching, precipitation, solvent extraction, etc. The final product coming out after all these processes may contain various trace impurities. These impurities are likely to come from the ore itself, mechanical wear and tear of the machinery used in the process, and the various reagents used in the U-extraction process. Depending upon the fuel and reactor type, stringent trace impurity specifications were imposed on these materials. Trace impurities like boron (B), cadmium (Cd), samarium (Sm), europium (Eu), gadolinium (Gd), and dysprosium (Dy) affect the neutron economy of the rector due to their high neutron absorption cross section (σ_a). The equivalent boron content (EBC) limit for U-metal in a research reactor and UO_2 in a LWR is 4 ppmw. However, for UO_2 fuel in PHWR, the EBC limit is 2.5 ppmw. The EBC limit for U_3Si_2 fuel in APSARA-U is 7.5 ppmw. The individual specification limits are reported elsewhere [1,2].

In this work, we have proposed a common digestion procedure for various uranium fuels, including U-metal, UO_2, and U_3Si_2. Approximately 0.5 g of the sample was dissolved in 4 mL of 6 mol L^{-1} HCl and 1 mL of 30% H_2O_2 in a screw-capped Nalgene tube under ultrasonication. U-metal and UO_2 get completely dissolved, whereas U_3Si_2 gets dissolved, leaving a white solid at the bottom. The solid was characterized as SiO_2 after heat treatment in the Muffle furnace. The dissolved sample was directly used for one-step selective separation of U(VI) and quantitative recoveries of trace analytes of interest. To do the job, the well known tributyl phosphate (TBP) and a literature reported task specific ionic liquid (TSIL), viz., N-propyl(diphenylphosphoramidate)tri-methylammonium bis(trifluoromethane-sulfonyl)imide ([phamdNMe$_3$][NTf$_2$]), were compared [3]. The TSIL viz., [phamdNMe$_3$][NTf$_2$] was previously reported from our laboratory for its high affinity towards U(VI) in high acidic medium, but never tested for this type of application [3]. It was found that 30% (v/v) TBP in CCl_4 phase extracted almost 80% of the U(VI) in a single (1:1) equilibration. Whereas the 30% (w/w) [phamdNMe$_3$][NTf$_2$] in [C$_4$mim][NTf$_2$] phase extracted 99% of U(VI) in a single (1:1) equilibration. The interference of the remaining U in solution onto the emission signals of B, Cd, Sm, Eu, Gd, and Dy were studied (Fig. 1 a & 1b). The interference for the TBP separated fraction was found to have huge interference onto the analyte signals which cannot be corrected. On the other hand, the same for [phamdNMe$_3$][NTf$_2$] separated fraction was found to be low and corrected by the standard addition method for determining the trace analyte concentrations in U-metal, UO_2, and U_3Si_2 samples (Table 1) employing ICP-OES. The method was validated by a spike recovery study. The method had a linear dynamic range of 0.25-50 µg g^{-1} with an RSD of ≤ 8%.

***Table 1:** Analysis of U-metal, UO_2, and U_3Si_2 samples (n=5)*

Sample	Element conc. in µg g^{-1} (%RSD)					
	B	Cd	Sm	Eu	Gd	Dy
U-metal	0.75(6)	0.92(4)	0.85(5)	0.68(4)	0.43(6)	0.38(8)
U-metal#	1.70(4)	1.95(3)	1.88(5)	1.77(3)	1.45(5)	1.40(6)
UO_2	<0.25	0.77(5)	0.76(6)	0.84(4)	0.32(7)	0.30(8)
UO_2#	1.14(5)	1.72(4)	1.72(4)	1.80(2)	1.33(5)	1.31(6)
U_3Si_2	0.70(6)	0.95(3)	0.55(6)	0.76(4)	0.46(6)	0.35(8)
U_3Si_2#	1.72(5)	1.92(3)	1.58(4)	1.75(3)	1.44(5)	1.32(7)

***Note:** #Spiked with 1 µg g^{-1} of individual analytes. The RSD is given in the paranthesis.*

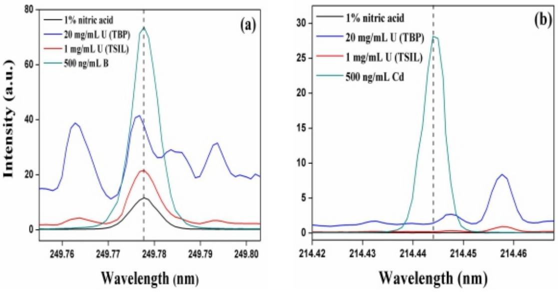

***Fig.1** ICP-OES spectra of (a) boron and (b) cadmium with interference study*

***Key words:** Uranium, Uranium dioxide, Uranium silicide*

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Instantaneous Aqueous Iodine Sorption using Silver-Incorporated Aluminosilicate Synthesized from Fly Ash

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Nuclear energy is widely considered as a low-carbon or clean energy source and is currently contributing to 10% of global electricity supply [1]. However, the production of radioactive gaseous fission products, particularly $^{129/131}$I, necessitates highly efficient remediation strategies due to their long-term environmental and health risks [2]. Therefore, developing highly selective adsorbents for radioactive iodine is a paramount goal in minimizing the environmental footprint of nuclear facilities. In this study, we report the synthesis of a novel silver-incorporated aluminosilicate composite (Ag-AAS) designed to leverage the strong Ag^+-iodine affinity. X- ray Diffraction (XRD) confirmed the formation of a highly crystalline silver aluminosilicate matrix upon Ag incorporation (Fig. 1). Scanning Electron Microscopy (SEM) and Energy-Dispersive X-ray Spectroscopy (EDX) verified a uniform distribution of silver throughout the matrix. Liquid phase sorption studies demonstrated exceptional performance of the composite. The Ag-AAS exhibited a exceptionally fast kinetic behavior, reaching ~ 95% adsorption within minutes (Fig: 2). The material achieved a remarkable liquid phase adsorption3 4capacity of 0.5 g I_2 g^{-1} for a simulated I_2/KI solution. Crucially for real-world application, a comprehensive interference study confirmed the superior selectivity of Ag-AAS. In the presence of common competing anions present in waste water stream (NO $^-$, Cl^-, SO $^{2-}$) at equimolar concentrations that of iodine ion, Ag-AAS showed negligible impact on iodine uptake. This result confirms Ag-AAS as a highly effective and selective material for radioactive iodine sequestration from aqueous waste streams.

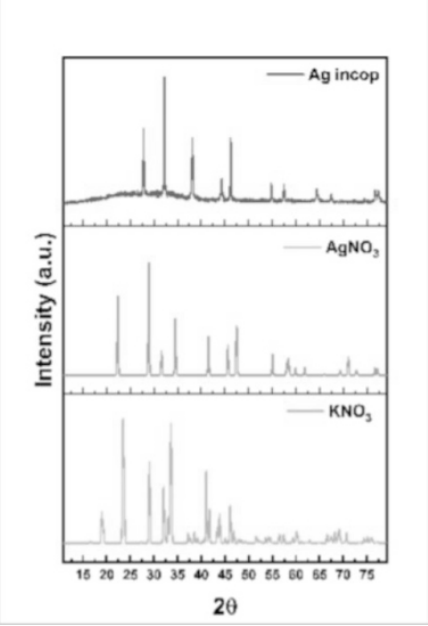

***Fig.1:** XRD spectra of Ag- AAS*

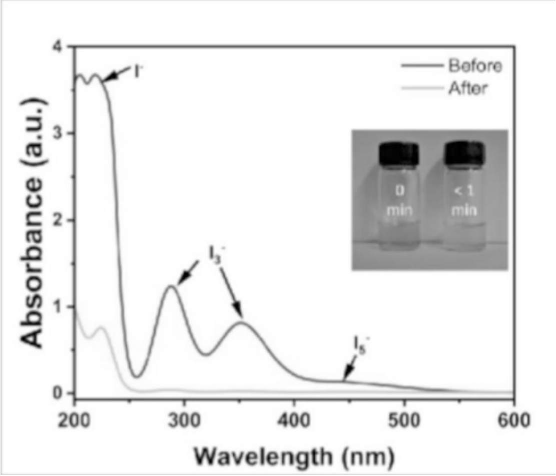

***Fig. 2:** UV-Vis spectra of iodine aqueous solution before and after contacting with Ag-AAS.*

***Key words:** Iodine, Sorption, Aluminosilicate, Nuclear waste remediation, Spectrophotometry*

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February 11-14, 2026
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Estimation of Absorbed Dose during the First Co Decontamination and Stripping Cycles of Fast Reactor Fuel Reprocessing

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The reprocessing of high burnup fast reactor fuel associates with the handling of high radioactivity. The high activity is due to the alpha, beta and gamma radiation. The exposure of high radioactivity to the organic phase leads to the degradation. The formed degradation product is Di butyl phosphoric acid (HDBP) which interferes in the stripping operation of PUREX process. The retention of Pu in the lean organic solution is mainly due to the HDBP.The amount of HDBP generated due to the radiation exposure is important to understand the stripping behavior of Pu and taking remedial measures to reduce the retention of Pu in the lean organic phase [1,2]

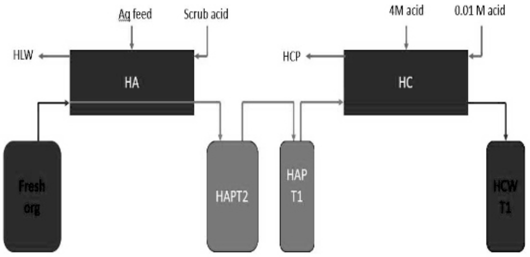

***Fig 1:** Typical flow sheet of HA and HC cycle in Demonstration Fast fuel reprocessing plant (DFRP)*

***Table 1:** The calculated dose during various cases*

S. No	Description	Absorbed dose, KGy
1	During the running of HA contactor	2.33
2	During the storage in HAP tank	3.22
3	During the running of HC contactor	6.66
4	Dose due to dead volume in Tank & vent pot	300

In this study, the observed radiation dose due to alpharadiation during the first co decontamination (HA) and stripping cycle (HC) is presented. The majority of alpha dose received by the organic phase is due to the extraction of Pu in the HA contactor and its storage as shown in fig 1. The organic phase continues to receive Pu till the stripping of Pu in HC contactor. The formula for estimating the alpha dose during the collection of loaded organic in the tanks (HAPT 2 & T1) and drawing of loaded organic during the running of HC contactor is presented. The dead volume of organic solution in the tanks and vent pots are continued to receive alpha dose proportional to the concentration of Pu in the solution. The typical value of dose received from various sources in the DFRP plant during campaign V is listed in Table 1. The values listed in the table 1 were estimated for the processing of 100 L of aqueous feed solution containing Pu concentration of 18 g/L. The flow rate in the HA and HC contactor is maintained at 6 L/hr and 2 L/hr respectively. The organic holdup in the HA contactor is assumed as 2 L. The dead volume in the HAPT1, HAPT2 and vent pot were assumed to be 6.22 L. The time interval between campaign IV and V is approximately 78 days. The HDBP generation is calculated by taking the value of 0.09 µmol/J of absorbed dose[3]. Therefore, for the total absorbed dose of 312 KGy, HDBP generated is 50 g. The loss of HDBP due to the solubility in aqueous phase is 7.35 g. Therefore, total HDBP is 42.65 g which corresponds to the HDBP concentration of 387 ppm in the lean organic solution by considering the total lean organic volume is 110 L. However the observed value is 650 ppm in the lean organic solution of DFRP campaign V. The difference in the value is due to the beta/gama radiolysis and also due to the acid hydrolysis effect. The uncertainty in the estimation of tank dead volume, holdup in the pipeline and vent pot also contributes to the difference in the estimation of HDBP and observed value.

***Key words:** Reprocessing, Plutonium, PUREX, Di butyl phosphoric acid*

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A-24

Remediation of Plutonium from Laboratory Analytical Waste by Electrochemical Reduction Followed by Precipitation Route

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Plutonium (^{239}Pu) is an important strategic nuclear material and its recovery and purification from laboratory waste is essential for its further use as a fuel in nuclear reactor [1]. In our laboratory, large amount of Pu aqueous waste was generated by the routine chemical quality control of nuclear fuel samples and associated research activities [2]. Therefore method development related to the robust, easy and reagent free separation method for the efficient recovery of Pu is essential. In the present work, an attempt has been made to recover and purify the Pu from pre-concentrated laboratory analytical waste solution which contains impurities Ag,Ti, Fe and Cr resulted from the redox titrimetric determination of plutonium through electrochemical reduction followed by the precipitation route. The pre-concentration of Pu from analytical waste was carried out by ammonium hydroxide precipitation. Afterwards the precipitate was dissolved in 1M HNO_3 and the cyclic voltammetry (CV) was performed to know the stable oxidation state and the corresponding redox potential of Pu. The Pu(IV)/Pu(III) redox couple was found to be stable and its redox potential value obtained to be 0.450 V. Using the CV results, the electrolysis (at 0.1 V) on Pu solution was performed using Pt-gauge electrode for 1 hour for complete and selective reduction of Pu(IV) to Pu(III) in presence of stabilizer hydrazine nitrate. The formation of Pu(III) was confirmed by intense blue colour of the solution and also by UV-Vis absorption spectra Fig. 1a. Pu (III) was now selectively precipitated as Pu(III) oxalate by adding 0.2M oxalic acid without maintaining any stringent conditions normally followed for oxalate precipitation. The impurities in the analytical waste before and after precipitation were determined by ICP-OES and by TXRF. The oxalate supernatant was found to be with negligible amount of Pu as confirmed by Liquid Scintillation Counting. The bright green Pu(III) oxalate was washed several times with 0.2M oxalic acid. Through this method the recovery of Pu was found to be ~99% in a single step. In situ spectroelectrochemical study Fig. 1b authenticates the conversion of Pu(IV) to Pu(III) followed by its precipitation using 0.2 M oxalic acid. The main advantage of the present method is direct precipitation of Pu in presence of impurities such as Ag, Fe and Cr.

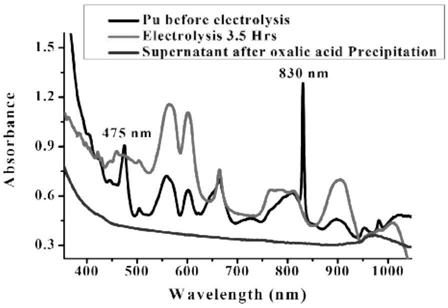

Fig.1(a) *Effect of electrolysis and precipitation on Pu spectra.*

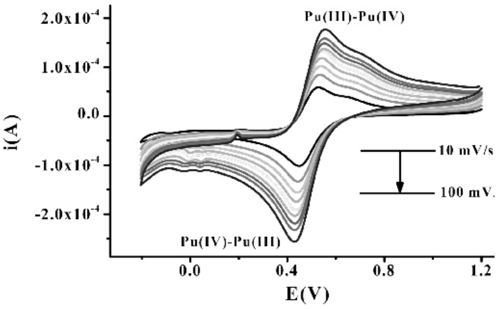

Fig.1(b) *CV plot of Pu(IV)*

Key words: *Plutonium, Recovery, Chemical quality control, Electrolysis*

References:

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Amino-Imidazole Modified Polystyrene Copolymer for Efficient Palladium Removal from Acidic Waste Solutions

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Palladium (Pd) is a critical and economically valuable metal, indispensable in catalysis, electronics, and energy technologies, yet its limited natural abundance and high cost necessitate efficient recovery from secondary sources [1]. High-level liquid waste (HLLW) and industrial effluents represent potential reservoirs of Pd, but recovery under strongly acidic conditions is challenging due to its complex speciation and competition from coexisting elements. In the current paper, we report the design and development of a novel imidazole-functionalized macroporous polystyrene resin (named as PAMI resin), prepared by chemical modification with 4(5)-amino-1-methylimidazole, to exploit the strong donor ability of imidazole nitrogen atoms for selective coordination with Pd(II). A brief synthetic scheme is shown in Fig. 1. The resin was comprehensively characterized by XPS, FT-IR, solid-state NMR, SEM-EDX, and TG-DTA analyses, confirming successful functionalization and thermal stability. The FTIR spectra of chloromethylated polystyrene resin and imidazolium functionalized resin are showed in Fig. 2. Batch adsorption studies revealed rapid uptake kinetics, excellent chemisorption behaviour, and a maximum Pd(II) adsorption capacity of ~258 mg g-1. Across the entire acidity range tested, the resin consistently exhibited high adsorption efficiency, with greater than 94% Pd uptake observed in all cases. The extraction behavior remained nearly constant up to 3 M nitric acid, beyond which a maximum was reached at 4 M. Mechanistic insights from XPS showed a coordination-type interaction between Pd(II) ions and the imidazolium moiety as the dominant uptake pathway. Fixed-bed column experiments further validated the material's practical utility, with dynamic capacities of 121 mg g-1 and efficient recovery of Pd using thiourea eluents. To assess the performance of PAMI resin in realistic conditions, adsorption studies were carried out with simulated HLLW prepared to mimic the composition of waste expected from nuclear fuel irradiated to a burn-up of 80 GWd/Te. The uptake profile of various elements on PAMI resin is shown in Fig. 3. It can be seen that the only possible interference is from silver. The resin exhibited strong selectivity for Pd(II) even in the presence of competing ions typical of nuclear waste matrices, underscoring its robustness. Since the studies are conducted with the intention of application to simulated waste streams, any potential interference from uranium is minimal; moreover, uranium is expected to be complexed with amine moieties. These findings demonstrate that the imidazole-functionalized resin offers a scalable and efficient route for Pd separation and recovery under harsh acidic conditions, with direct implications for nuclear waste remediation and sustainable resource recovery.

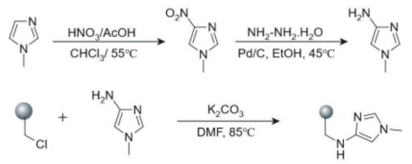

***Fig. 1** Synthetic scheme for the for preparation of PAMI resin*

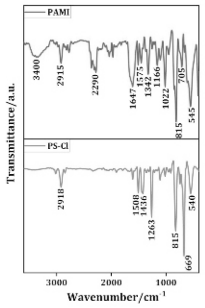

***Fig. 2** FT-IR spectra of NMI, NMI-NO$_2$, AMI*

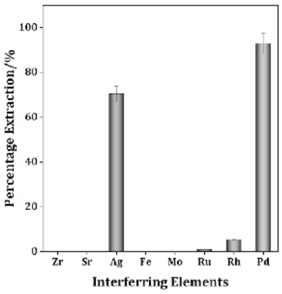

***Fig. 3** Selective adsorption of Pd from interfering elements present in the simulated high-level liquid waste*

Key words: *Palladium, Polystyrene resin, Simulated High level waste, Adsorption, Imidazole*

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Extraction of Major Actinides using Phosphonium Based Anion Functionalized Ionic Liquid

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The appropriate functionalized groups attached to the cationic moiety of the ionic liquid displayed superior extraction properties for actinides in various oxidation states [1]. Nonetheless, there is a lack of literature demonstrating the use of anion functionalized ionic liquids for the extraction of actinides. In this study, trihexyl tetradecyl phosphonium dodecylsulphate, an anion functionalized ionic liquid [Fig 1 (a)], was utilized for the extraction of major actinides from an aqueous hydrochloric acid medium. The distribution ratios $D_{M(IV)}$ and $D_{M(VI)}$ were observed to increase with the acidity of the aqueous feed, with plateau values of approximately $D_{M(IV)}$~ 8.4 and $D_{M(VI)}$ ~ 2.3 noted at 8 M HCl and beyond[Fig 1 (b)]. The higher D values for M(IV) compared to M(VI) can be attributed to the greater ionic potential of M(IV). The D values for both actinides were found to increase with longer equilibration times, up to 90 minutes, after which there was almost no change [Fig 1 (c)]. The sluggish mass transfer can be attributed to the slower diffusion in the highly viscous ionic liquid phase. The extraction processes were found to be exothermic [Fig 1 (d)], yet spontaneous in nature. The ionic liquid phase demonstrated good radiolytic stability up to 200 kGy of gamma exposure. However, a gradual reduction in D values with increasing gamma exposure was observed [Fig 1 (e)]. The ionic liquid phase loaded with M(IV) was effectively back extracted using 0.1 M oxalic acid, while 0.1 M sodium carbonate was effective for the back extraction of M(VI). However, multiple contacts with the stripping agent were necessary to achieve more than 99.9% back extraction [Fig 1 (f)].

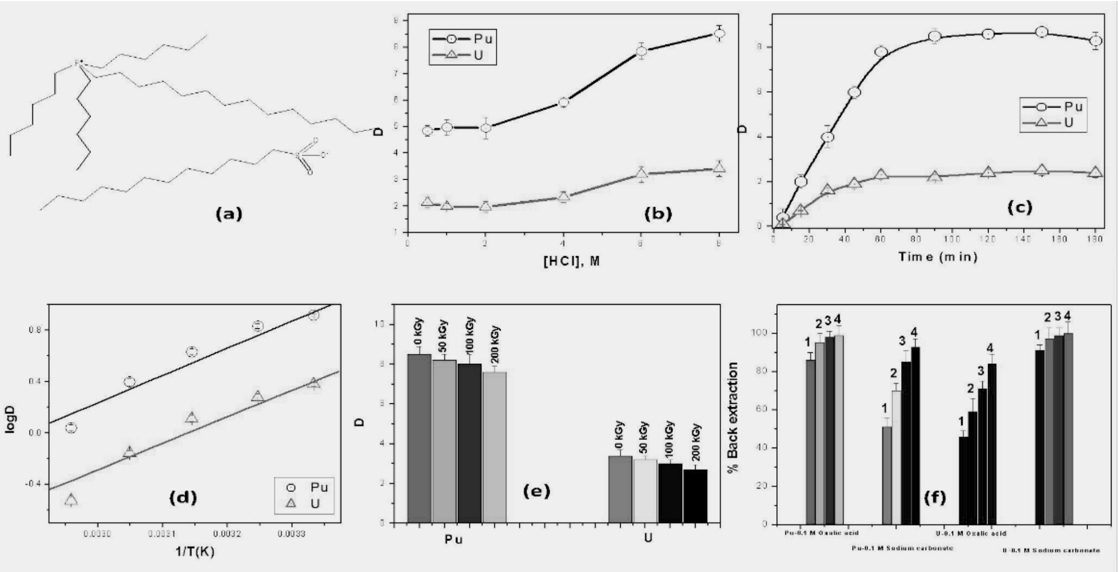

Fig.1 (a) *Synthesis scheme; (b) FTIR spectra for TSILs; (c) M(VI) Dissolution into TSIL; UV-Vis spectra for M(VI) into TSIL as a function of (d) time ; (e) temperature*

Reference

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Exploration of Dissolution of Uranium Compounds in Acidic Media by in-situ DPV Approach

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For the routine chemical quality control and physical inventory verification exercise for nuclear material accounting purposes of fuel matrices and waste management, the advancement of a sensitive method for understanding dissolution of uranium compounds is essential [1-2]. Exploration of the dissolution kinetics of uranium compounds in acidic solution is important to gain knowledge about mechanism and factors which contribute to faster dissolution. As the first stage in the reprocessing of nuclear fuels, the dissolution of uranium compounds (oxides, salts, alloys, etc.) in nitric acid is very fascinating. Reagent-free sensitive methods that can provide information about the dissolution mechanism and kinetics at a single location and time (i.e., in-situ mode) are lacking, even though many processes have been developed to understand nitric acid dissolution and assay by spectrophotometry and redox titrimetric methods [1-2]. Our aim is to develop reagent free differential pulse voltammetry (dpv) method for understanding the dissolution mechanism of UO_3 and Ammonium diuranate (ADU) in nitric acid medium. Approximately 20 mg was taken in 3 ml of 0.1 M nitric acid medium and dissolution was carried out with varying temperatures and the corresponding differential pulse voltammetry (DPV) plots are shown in Fig. 1(a). Also, the calibration plot was obtained using DPV method to evaluate the dissolved amounts of above compounds. The variation of dissolved amounts of uranium compound with varying time is shown in Fig. 1b, which indicates the equilibration time for dissolution is 24 minutes. The rate of dissolution was fit second order model and its corresponding rate constant value is evaluated.

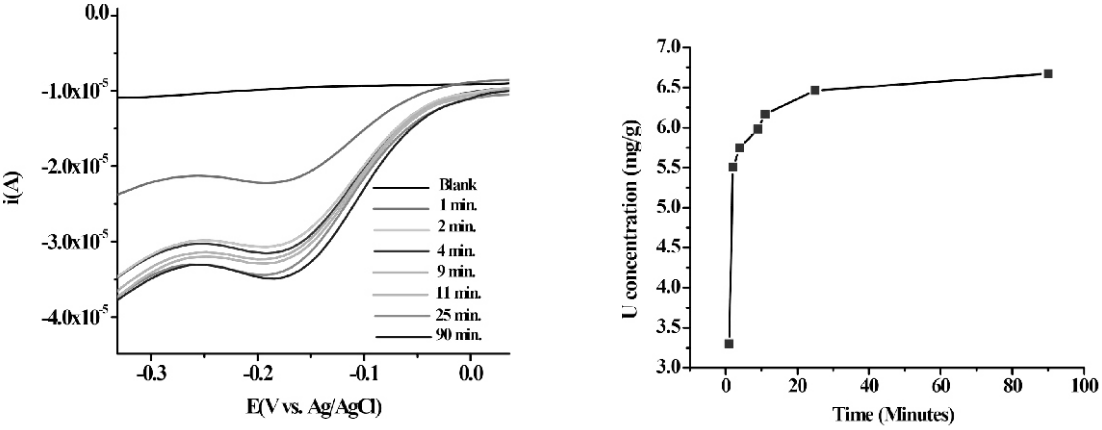

***Fig. 1**: (a) Differential pulse voltammetry plots with varying time obtained during dissolution (b) Dissolved amount of uranium compound with varying time*

Key words: Dissolution, DPV approach, Kinetics

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Mutual Separation of Am (III) and Eu(III) from SHLW using Mixed Ligand Polymeric Beads

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In light of the limited research on polymeric beads impregnated with combined ligands and their potential for synergistic extraction behavior, a series of beads with varying compositions of TODGA and D2EHPA were synthesized, characterized, and evaluated for the extraction of Am (III) from acidic feed solutions. The synthesized beads were characterized using Fourier Transform Infrared (FTIR) spectroscopy, scanning electron microscopy (SEM), thermo gravimetric analysis (TGA) and photoluminescence (PL) spectroscopic techniques. The effect of nitric acid concentration on the extraction efficiency of Am (III) was studied. Furthermore, the maximum sorption capacity of the beads was determined, and the equilibrium sorption data were fitted using different isotherm models. The stripping behavior of the beads was also systematically investigated. Finally, the beads were used for mutual separation of Am(III) and Eu(III) from a simulated high level waste (SHLW).

The beads were subjected to uptake Am (III) from a wide range of concentration of nitric acid. A synergistic extraction behaviour was noticed at 0.1 M and at above 3 M HNO_3 with the bead containing 30% TODGA+70% D2EHPA (bead 4) and 70% TODGA+30% D2EHPA (bead 5) respectively (Fig. 1a). The equilibrium uptake data were fitted with Langmuir, Freundlich and Dubinin–Radushkevich (DR) isotherm model equation and the maximum uptake was found to be around 23.5(±1.1) and 14.2(±0.5) mg/g Eu(III) with bead 4 and bead 5 respectively. The desorption study suggest HEDTA can strip more than 99% Am (III) from the beads with two times contact. The extraction data were found to be highly promising for the extraction of Am (III) in a wide range of nitric acid concentration. The mutual separation of Am(III) and Eu(III) was carried out with bead 5 from SHLW at 3 M HNO_3 followed by stripping of Am(III) selectively using 10 mM BTP in the aqueous phase at 0.1 M and 1 M HNO_3 indicated promising results (Fig. 1b). The decontamination factor of Am(III) over Eu(III) was found to be 300(±10) and 22(±0.9) at 1 M HNO_3 and 0.1 M HNO_3 respectively.

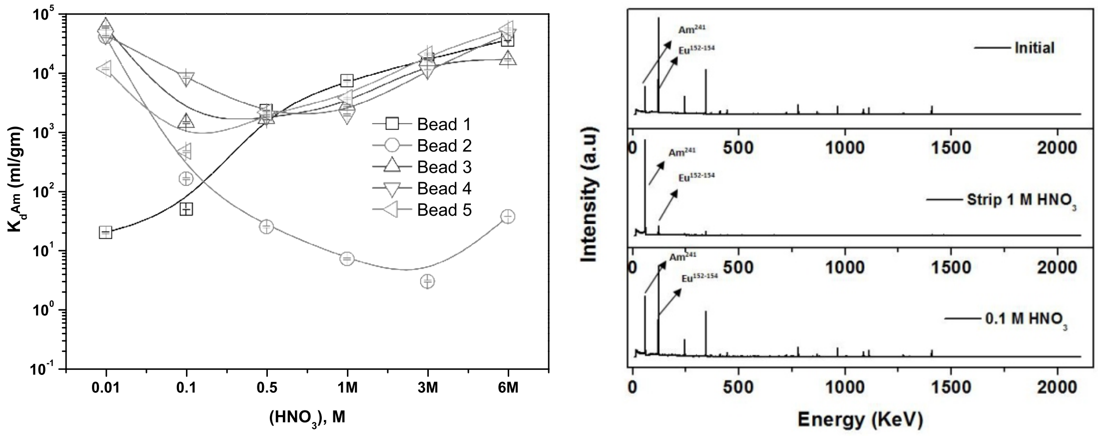

Fig. 1 *(a) $K_{d,Am(III)}$ with HNO_3(M), (b) Am(III)/Eu(III) separation, gamma spectrum,*

Key words: Americium, Europium, FTIR, synergistic

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A-29

Efficient Uptake of Lanthanides and Actinides from Aqueous Streams using Functionalized Multiwall Carbon Nano-Tubes

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Radioactive waste is generated primarily as a result of reprocessing of spent nuclear fuel and the decontamination of process equipment. Radioactive waste contains various actinides having half-lives ranging from a few hundred years to several thousand years or more. Migration of these radionuclides to the environmental matrices results in contamination of environment. Such contamination leads to radiological exposure of humans via food chain. Therefore removal of these long-lived radioisotopes from waste solutions is of importance for effective nuclear waste management.

The simultaneous extraction of trivalent lanthanides and actinides from various aqueous streams is essential for both partitioning and decontamination purposes. Thanks to the nano porous structures and high surface area, multiwall carbon nanotubes (MWCNTs) demonstrate a strong affinity for different cations; additionally, functionalized MWCNTs enhance selectivity among them [1-2]. In this study, MWCNTs with amidothiol functional group, Fig.1(a), have been utilized for the decontamination of Eu^{3+} and Am^{3+} from acidic aqueous solutions by solvent extraction method. Within the pH range of 1 to 4, the uptake values for both metal ions were observed to increase; reaching a plateau beyond pH ~3, with maximum uptake values ~99% [Fig.1 (b)]. The extraction values for both metal ions were also found to rise with prolonged equilibration time, up to 180 minutes, after which a plateau was reached Fig.1(c). The recyclability of the extraction process was also evaluated over five consecutive extraction cycles [Fig.1(d)].

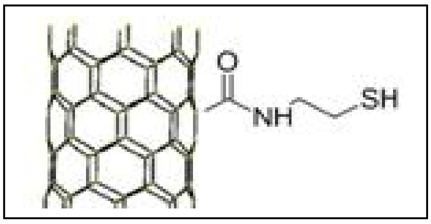

Fig.1(a)

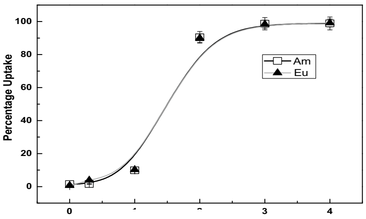

Fig.1(b)

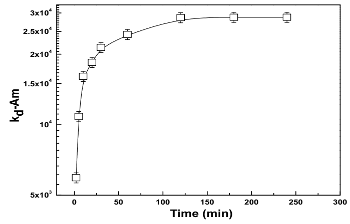

Fig.1(c)

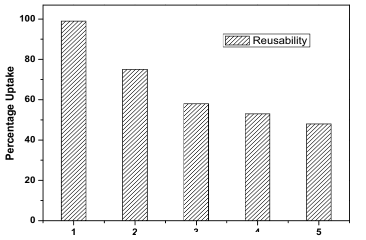

Fig.1(d)

Fig. 1 *(a) Structure of amidothiol-MWCNT; (b) Influence of aqueous pH; (c) time of equilibration on Kd; (d) Recyclability of sorbent*

<u>Reference</u>

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A-30

Polyoxotungstate (POT) mediated stabilzation of U(IV) in aqueous medium

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The stabilization of uranium (IV) in aqueous solutions remains a significant challenge due to its tendency to undergo oxidation to the more stable uranium (VI) species. The work focuses on understanding the redox behavior and stabilization mechanism of U(IV) using electrochemical and spectroscopic techniques. This study provides a fundamental basis for controlled uranium redox chemistry and its conversion to its unusual oxidation state (IV). In this study, we investigate the stabilization of uranium (IV) by a polyoxotungstate (POT) clusters in presence of iron(II) sulfate using cyclic voltammetry (CV) and UV-Vis spectroscopy at pH 3.0. The lacunary POT which have a large size, highly charged anionic structures, suitable geometry demonstrated strong coordination properties that facilitate the stabilization of U(IV) in presence of Fe(II) ion. The lacunary PW_{11} was formed by dissolving commercially available PW_{12} at pH 3.0 [1]. Here high stabilization of U(IV) and Fe(III) by the lacunary PW_{11} drives the reduction of U(VI) by Fe(II) which otherwise not feasible thermodynamically. From CV study it can be seen that both U(VI)/U(V) and U(V)/U(IV) reduction peak of uranium disappears and a new reduction peak corresponding to U(VI)/U(IV) appears in presence of POT at slightly more positive potential compare to that of U(V)/U(IV) couple indicating stabilization of U(IV) in presence of POT (Fig. 1a). Similarly a negative shift of Fe(III)/Fe(II) reduction potential has been observed in presence of POT indicating stabilization of Fe(III) in presence of POT (PW_{11}) (Fig. 1a). When both U(VI) and Fe(II) are present in POT solution, the corresponding U(VI) to U(IV) reduction peak is not observed whereas Fe(III) to Fe(II) reduction peak is observed indicating complete reduction of U(VI) to U(IV) by Fe(II) in presence of POT at pH 3.0 (Fig. 1a). The corresponding UV-Visible spectra indicates a peak at 690 nm indicating the formation of U(IV) as the complex with the PW_{11} (Fig. 1b) [2]. The stability of U(IV) over longer period was checked by UV-Visible spectroscopy which indicated more than three months stability. The uses of POT as effective ligands for the stabilization of U(IV), offering insights into their use in nuclear chemistry, waste-management, particularly in controlling uranium speciation, reducing mobility in aqueous environments, and designing inorganic matrices for actinide immobilization.

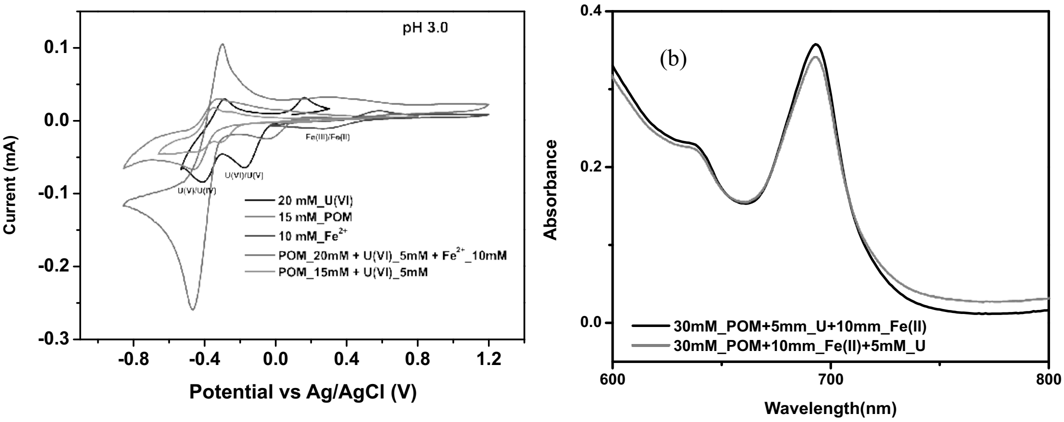

Fig. 1: *(a) CV with GC as W.E., Pt as CE, Ag/AgCl as RE (b) UV-Visible spectra of U(IV) in presence of POT and Fe(II) at pH 3.0*

Key words: *POT, Uranium*

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Synthesis and Characterization of Hydrophobic Deep Eutectic Solvent Based on TOPO and Octanoic Acid (1:1) for the Extraction of Actinides (Pu, and Am).

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The extraction of actinides such as plutonium (Pu), uranium (U), and americium (Am) from nuclear waste streams is of paramount importance for radioactive waste management and recycling. Deep eutectic solvents (DESs) have emerged as promising alternatives to conventional organic solvents due to their tunable physicochemical properties and low volatility. In this study, we report the synthesis and characterization of a hydrophobic DES based on Tri-n-octylphosphine oxide (TOPO) as the hydrogen bond acceptor (HBA) and octanoic acid as the hydrogen bond donor (HBD) in a 1:1 molar ratio, specifically tailored for actinide extraction. The formation of TOPO:OA (1:1) DES was confirmed using Fourier Transform Infrared Spectroscopy (FTIR), which revealed significant spectral shifts indicative of strong hydrogen bond interactions between TOPO and octanoic acid. The characteristic P=O stretching frequency of TOPO exhibited a downward shift due to hydrogen bonding with the -OH group of octanoic acid. Additionally, the carbonyl stretching frequency of octanoic acid shifted upward, further confirming DES formation. Differential Scanning Calorimetry (DSC) analysis demonstrated the unique thermal behavior of the DES, including a lower melting point compared to its individual components, a hallmark of eutectic formation. The synthesized hydrophobic DES was evaluated for its efficacy in the extraction of Pu, and Am under varying HNO_3 concentrations and contact time. The results highlight its potential as a selective and efficient extraction medium. This study underscores the advantages of hydrophobic DESs in nuclear waste reprocessing and lays the groundwork for further exploration of DES-based extraction methodologies

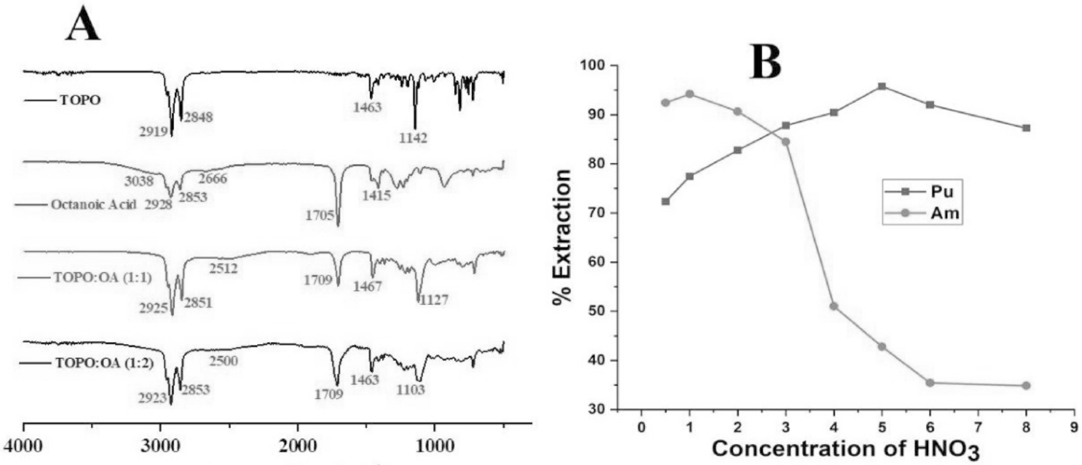

Fig 1: *A) FTIR spectra of TOPO:OA B) Extraction profile of Pu and Am in the TOPO:OA DES.*

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Tunable Nitrogen Sites in COFs Enable High-Efficiency Palladium Recovery in Acidic Media

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Palladium (Pd), a critical platinum-group metal used in catalysis, energy conversion, and hydrogen storage, must be efficiently recovered from high-level liquid waste (HLLW) to ensure resource sustainability and environmental safety. This study compares two nitrogen-rich covalent organic frameworks (COFs)—melamine–terephthalaldehyde (MA–TP) and 2,4,6-triaminopyrimidine–terephthalaldehyde (TAP–TP)—to elucidate how nitrogen donor hybridization influences Pd(II) adsorption in 4 M HNO_3. Figure 1 represents adsorption isotherm of MA-TP COF and TA-TP COF determined in 4 M HNO_3. It can be observed that, the triazine-based MA–TP COF, with tertiary nitrogens, exhibited a higher adsorption capacity (134 mg g^{-1}) than the pyrimidine-based TAP–TP COF (60 mg g^{-1}), owing to stronger N–Pd coordination and greater acid tolerance. Langmuir and pseudo-second-order models confirmed monolayer chemisorption governed by donor site density and pore accessibility. PXRD, FTIR, SEM/EDX, and BET analyses verified framework stability and selective Pd coordination, underscoring nitrogen-site engineering as an effective route for designing acid-stable COFs for scalable precious metal recovery from nuclear waste.

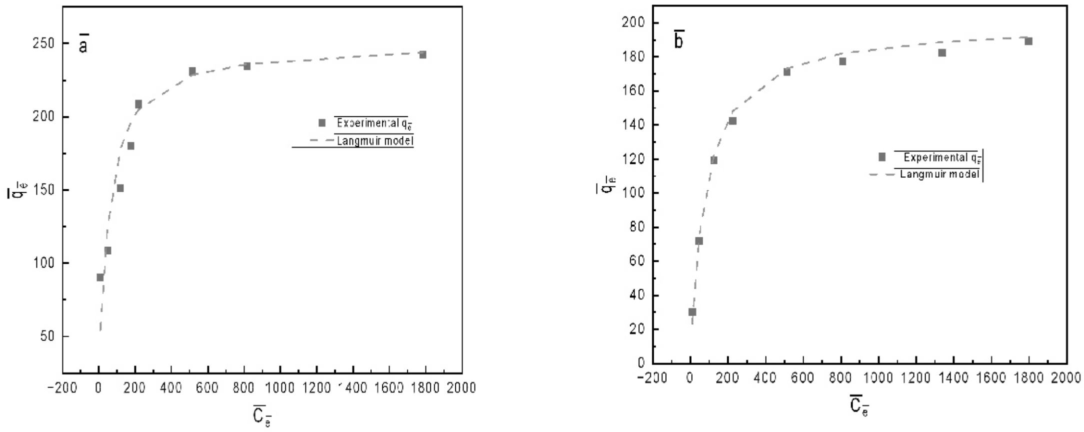

Fig1: *Adsorption isotherm of a) MA-TP COF b) TA-TP COF fitted with Langmuir model.*

Key words: *Covalent Organic Frameworks, Pd Adsorption, Nitrogen donor sites, High level liquid waste*

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Effect of H_2SO_4–HNO_3 Composition on the Dissolution and Analytical Performance of FBTR Mixed Carbide Fuel

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Mixed carbide fuel is used as a driver fuel for the Fast Breeder Test Reactor (FBTR) at Kalpakkam. To meet the stringent specifications laid down by the fabricator, accurate and precise determination of U and Pu content of the fuel is an essential part of fuel CQC. The fuel can be dissolved in conc. HNO_3 alone, but it leads to the formation of various organic acids such as mellitic and oxalic acids. These acids affect the precise determination of the U and Pu by redox titrimetry method. Therefore, various methods were developed for destroying these organic acids, the most useful being the use of 1:1 mixture of H_2SO_4 and HNO_3 by volume **[1]**. Here, H_2SO_4 acts as a heat sink and destroys the various organic acids in-situ during the dissolution process itself. Building upon prior experience, the present study systematically evaluates varying proportions of H_2SO_4 and HNO_3 to identify optimal conditions for quantitative dissolution and high-precision analysis for U and Pu employing the redox titrimetry method with biamperometry end point detection for the dissolved samples.

Seven samples of FBTR mixed carbide fuel, each weighing approximately 300 mg and taken from the same batch, were used for dissolution studies. The proportion of H_2SO_4 was varied from 50% to 0% keeping the total volume constant as 50 mL. The various compositions of the acid mixture taken is tabulated in the Table 1. Each weighted sample was transferred into a conical flask along with the mixture of H_2SO_4 and HNO_3. Dissolution was carried out by refluxing the mixture for 1 to 2 hours on a heating mantle inside a glove box until a clear transparent solution is obtained. The dissolved solution is then quantitatively transferred using dilute HNO_3 to a pre-weighed PVC bottles. Five (5) aliquots from each dissolved sample were analyzed for their U and Pu content by employing BARC modified Davies-Gray and BARC modified Drummond-Grant method respectively with biamperometric end point detection. The obtained results are tabulated in Table 1.

It was observed that the quantitative dissolution was achieved for all the compositions except for 1:1 & 1:2 H_2SO_4 : HNO_3 mixtures, where undissolved suspended particles persists even after repeated heating. For the rest five composition, the results for U and Pu content are precise for the dissolved samples. From the point of precision of analysis the best result were obtained for 1:10 composition. The poor precision in case of the 1:16 composition may be due to the interference by the presence of organic acids in the titrimetric analysis as reported in literature **[1]**. The same can be corroborated in the results obtained for the samples dissolved in pure conc. HNO_3 where there was sluggish endpoint for the U analysis.

The study clearly show that the 1:10 composition is the best from the point of precision of analysis with complete quantitative dissolution. The optimized dissolution strategy minimizes organic acid interference and offers a reliable, reproducible approach suitable for routine quality-control analysis of mixed carbide fuels in fast reactor fuel cycle operations.

Table1. *% U and % Pu in samples dissolved in various proportions of* H_2SO_4 *and* HNO_3

Sample No.	H_2SO_4:HNO_3	% U	% Pu	Remarks
1	1:1	---	---	Sample not dissolved
2	1:2	---	---	Sample not dissolved
3	1:4	26.54± 0.25	67.73± 0.26	
4	1:8	26.68± 0.27	69.46± 0.29	
5	1:10	26.46± 0.19	68.84± 0.21	
6	1:16	26.34± 0.73	68.66± 0.45	
7	0:1	---	67.79± 0.52	Sluggish endpoint for U determination

Key words: *Uranium, Plutonium, Biamperometry*

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Bi(0)- Nano Composite for Iodine Capture: An Effort Towards Radioactive Iodine Management.

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The inherent properties of radioactive iodine such as its long half-life, strong toxicity, and high diffusion, pose a serious threat to the environment, making the capture of radioactive iodine gas produced from nuclear power plants and spent fuel reprocessing plants essential [1]. The management of iodine involves two steps one is capture and other one is converting it into stable forms suitable for storage. Two typical techniques for iodine gas capture, solid-phase adsorption and wet scrubbing, are commonly employed. The former has been widely studied due to its simplicity and reliability. Various adsorbents have been developed based on this method among these, Ag-based composites have been popular and commercially used as iodine adsorbents, though they suffer from the drawbacks of high cost and toxicity [2]. Bi-based materials have emerged as an alternative, gaining widespread attention due to their low toxicity, high capture capacity, good stability, and low cost. To date, numerous Bi-based composites have been successfully prepared and shown to exhibit high iodine capture capacity. In all studies reported in literature highlights that the support material of the Bi based composite markedly influence the capture and stability of the captured iodine. In this study, we have made an effort to explore the iodine capture behavior of two Bi-based composite prepared with two different support material viz Zeolite 4A and activated charcoal namely $Bi^{(0)-}$ Zeolite 4A and $Bi^{(0)}$- C. The synthesis of these two composite has been carried out through reduction of Bi^{3+} to $Bi^{(0)}$ at pH medium of 7-9 by L-ascorbic acid in presence of hydrazine hydrate as the nitrate suppressor. The synthesis scheme is shown at Figure 1. The obtained $Bi^{(0)}$-Zeolite 4A and $Bi^{(0)}$-activated charcoal ($Bi^{(0)}$-C) composites were characterized by Energy Dispersive X-ray (EDAX) and the percentage of $Bi^{(o)}$ present in each of the composite were found to be in the range of 35 to 40%. Iodine capture experiment were carried out in a sealed glass tube containing 1.0g of the inactive iodine crystal fitted with glass column containing 0.1 g of the composites and heated at 200°C for 6h. The capture capacity (q_e (mg/g)) was calculated from the initial weight (m_1) and final weight (m_2) of the composite before and after iodine capture from the equation (i). q_e (mg/g) = $(m_2\text{-}m_1)\text{x}1000/m_1$ (i) The retention experiment was carried out by using the composite used in the capture experiment in a two neck flask connected to air supply with heating at 150°C for 6h. Both $Bi^{(0)}$- Zeolite 4A and $Bi^{(0)}$-C the composite material exhibited the iodine adsorption capacity of 911 and 1334 mg/g, with the iodine retention of 90.9, 85.9% respectively results shown in Figure 2 and are higher compared to other reported Bi-based nanomaterials. The $Bi^{(0)}$- Zeolite 4A showed the highest iodine retention compared to $Bi^{(0)}$-C because the clay support have no affinity for iodine and the adsorption is mainly due to the chemical reaction of $Bi^{(0)}$ with I_2 ($2Bi + 3I_2 = 2BiI_3$). While the $Bi^{(0)}$- C exhibited the highest capture capacity due to the synergistic adsorption effect between C supports and Bi(0) sites in combination with chemical reaction of $Bi^{(0)}$ with I_2.

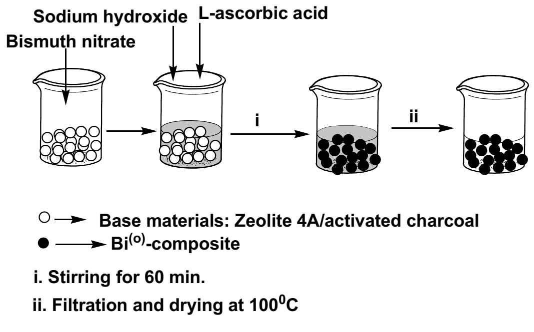

Fig 1: *Synthesis scheme of the* $Bi^{(o)}$*- composites*

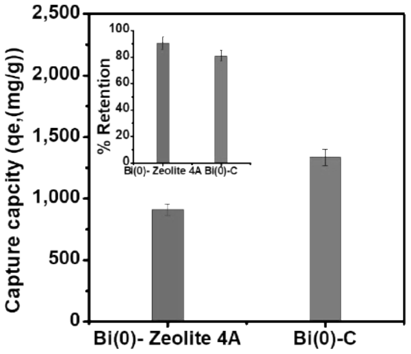

Fig 2: *capture capacity and %retention (inset)*

Key words: *Iodine, Nanoparticle, Composite, Reduction, Radioactivity*

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Hydrophilic BTP Assisted Lanthanide-Actinide Separation from SHLW

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Spent fuel reprocessing generates high level liquid radioactive waste (HLLW) containing un-extracted U and Pu from the PUREX cycle, bulk of minor actinides (An) (Am, Np, Cm), fission products (Tc, Pd, Zr, I, Cs, Sr and lanthanides (Ln)). Partitioning and transmutation (Separation of An followed by their transmutation) is adapted for efficient management of nuclear waste [1]. However, due to chemical similarity between lanthanides and actinides, it is difficult to separate these elements from each other. Thus, development of extractants and methods of separation of lanthanides and actinides from each other is necessary for effective nuclear waste management. Ligands containing soft donor atoms such as S or N binds preferentially to An due to diffused 5f-orbitals of An compared to 4f-orbitals of Ln. Amongst various reagents used for An/Ln partitioning, aqueous soluble BTP derivatives are found promising for actinide partitioning [2]. Considering this fact, a strategy to separate Ln and An from the simulated high level waste (SHLW) is developed using N,N,N′,N′-tetra-2-ethylhexyl diglycolamide (T2EHDGA) and aqueous soluble 2,6-bis(5,6-di(sulphophenyl)-1,2,4-triazin-3-yl)-pyridine (SO_3-Ph-BTP). Am^{3+} and Eu^{3+} were used as representatives of An and Ln respectively. Quantification of elements were done by gamma spectrometry.

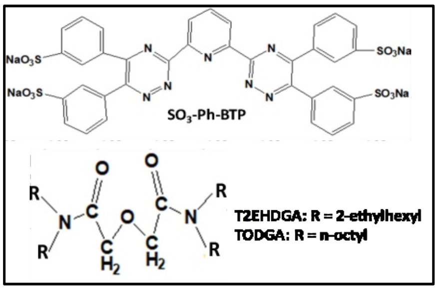

***Fig. 1** Structures of ligands used*

Am^{3+} and Eu^{3+} were extracted together from SHLW into T2EHDGA in n-dodecane containing isodecanol (IDA) as phase modifier. Batch experiments involving different compositions of extractants indicted 0.2 M T2EHDGA in n-dodecane containing 15% IDA as optimum composition for extracting Am^{3+} and Eu^{3+} from the SHLW. The loaded organic phase is then subjected to stripping of Am^{3+} selectively using 20 mM SO_3-Ph-BTP in HNO_3 as strippent. Stripping studies carried out at different nitric acid concentrations indicated optimum composition of strippent as 20 mM SO_3-Ph-BTP in 2 M HNO_3. Under this condition, the separation factor (D_{Am}/D_{Eu}) was found to be 91.3. To strip Am^{3+} from the loaded organic phase completely, three stripping cycles were required. However, under these conditions, Eu^{3+} contamination (~ 11% of initial value) in product (aq. phase containing Am) was observed. Hence washing of the product with fresh organic phase was done in order to remove the Eu contamination. Different compositions of the washing phase were studied for Eu removal from the product (Table 1). It was observed that T2EHDGA alone was incapable of removing Eu form the product. Hence combination of T2EHDGA with N,N,N′,N′-tetraoctyldiglycolamide (TODGA) was used for purification of product. Amongst different combinations, the washing phase containing 0.02 M T2EHDGA and 0.02 M TODGA in n-dodecane containing 15% IDA was found optimum for removal of Eu from the product. However, to remove Eu from the product quantitatively (>99%) three washing cycles were required. Based on above results, a flow sheet for separation of Am^{3+} and Eu^{3+} from HLLW is proposed.

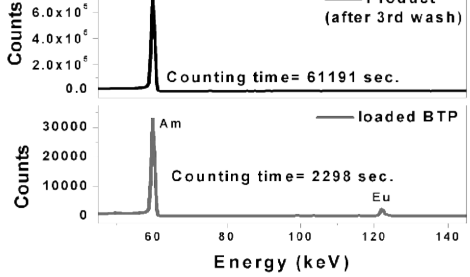

***Fig. 2:** HPGe spectrum of product before and after washing*

***Table 1:** organic Phase compositions for product washing*

Organic phase for washing (in n-dodecane)	D Am(III)	D Eu(III)
T2EHDGA (0.1 M), IDA (5%)	0.04	3.9
T2EHDGA (0,1 M), IDA (10%)	0,04	3,5
T2EHDGA (0,1 M), IDA (15%)	0,04	3,2
T2EHDGA (0.2 M), IDA (10%)	0.2	10.7
T2EHDGA (0.2 M), IDA (15%)	0.2	10.2
T2EHDGA (0.2 M), IDA (30%)	0.2	9.6
T2EHDGA (0,05 M), IDA (7.5%)	0,01	0,8
T2EHDGA (0,075 M), IDA (5%)	0,02	1,4
T2EHDGA (0.02 M), TODGA (0.005 M), IDA(15%)	0.00	0.5
T2EHDGA (0.02 M), TODGA (0.01 M), IDA(15%)	0.01	2.3
T2EHDGA (0,02 M), TODGA (0,02 M), IDA(15%)	0,03	12.6

***Key words:** Actinide partitioning, T2EHDGA*

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Metakaolin Derived Geopolymers as Efficient Adsorbent for Separation of Strontium from Aqueous Solution

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Geopolymers as alternate to ordinary portland cement are studied extensively as it exhibits high mechanical strength, excellent thermal and chemical resistance and the ability to immobilize hazardous ions. The present study aims to synthesize geopolymers (GP) from kaolin which is a naturally available clay mineral. The study reveals the adsorption performance of the synthesized GP for Sr^{2+} removal which is one of the hazardous radioactive elements present in the nuclear waste. The chemical compositions of the kaolin (K) was determined using EDXRF which shows SiO_2 to Al_2O_3 (wt.%) ratio is 1.14. XRD analysis (Fig 1 a) shows the presence of mineral phases like kaolinite and quartz in it. Metakaolin (MK) was prepared by heating kaolin clay at 600°C for 3h and the XRD (Fig 1b) result shows broad hump reflecting its amorphous nature with trace crystalline impurity. The geopolymer (GP-MK) was prepared by reacting MK with 8M NaOH and Na_2SiO_3 solutions keeping solid to liquid ratio as 1: 0.5 for 15 min followed by curing at 80ºC for 24 h. XRD plot (Fig. 1c) shows the shift in signature broad hump of the synthesized geopolymer (GP-MK) from MK indicating the geopolymerization process. FTIR (Fig 2a) spectra of kaolin shows the characteristics Si-O-Si stretching vibrations. The band at 1024 cm^{-1} in fig. 2b for metakaolin is attributed to the stretching of Si–O bonds in amorphous SiO_2. Fig. 2c shows that there is a shift in Si-O-Si stretching vibration in GP-MK to a lower wavenumber compared to kaolin and metakaolin indicating the formation of geopolymer.

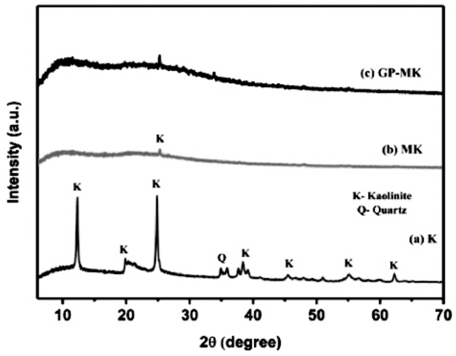

Fig 1: XRD patterns of (a) kaolin (b) Metakaolin (c) GP-MK

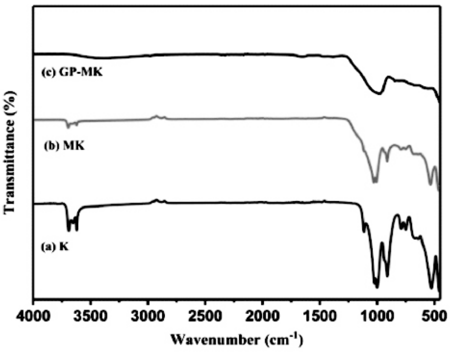

Fig 2: FTIR spectra of (a) Kaolin (b) Metakaolin (c) GP-MK

to study the adsorption behavior of GP-MK, it was equilibrated with 100 mgL^{-1} Sr^{2+} solution keeping solid to liquid amount as 1mg/mL at ambient temperature for 6 h at different pH values ranging from 3 to 9. The solutions were centrifuged and then filtered. The Sr^{2+} solutions after adsorption experiments were analysed by ICP-OES to determine the adsorption capacity (Q_e). The value of Q_e increases from 56.9 mg/g at pH = 3 to 94.9 mg/g at pH = 7 and remains constant upto pH = 9. The results demonstrated that the adsorption capacity is highly dependent on pH of the solutions.

Key words: *Kaolin, Metakaolin, Geopolymer, Strontium, Adsorption capacity*

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Advancing Nuclear Forensics through Imogolite Assisted Actinide Sequestration and Direct Alpha Spectrometry Coupled with Computational Response Modeling and Analysis.

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Nanomaterials continue to display promises for improving actinide sequestration, pre-concentration, and analytical definition in nuclear forensics [1]. In our earlier work, the hybrid aluminosilicate nanotubes, commonly known as methyl imogolite (Imo-CH_3), was demonstrated as an efficient substrate for arresting uranium and plutonium ions from dilute aqueous medium by a simple one-pot chemical pathway and radiometric analysis using -scintillation counting and -spectrometry [2]. Building on prior single-actinide studies, the present work reveals that Imo-CH_3 nanotubes can sequester actinides from a mixed actinide sample, offering a valuable tool for nuclear forensic investigations. Complexation of actinides on the external surface of Imo-CH_3 nanotubes at alkaline condition has been the basis for the actinide sequestration without selectivity. This study advances the work by the optimization of the Imo-CH_3 layer thickness to improve -spectrum energy resolution, alongside computational modeling of detector response, representing a novel nuclear forensic approach through response function analysis.

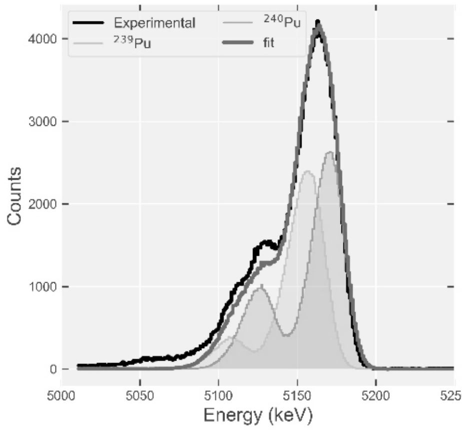

Fig. 1. *Response function fitting of plutonium alpha spectrum at 5.1 MeV region.*

Fig. 1 shows the 5.1 MeV region of the measured -spectrum showing ^{239,240}Pu peak for a sample containing a mixture of power reactor grade Pu (about 1 μg), ^{229}Th and its daughters anchored with Imo-CH_3 nanotubes backed by PES membrane filter. Owing to the advantage of ultrathin film formation characteristics of Imo-CH_3 nanotubes, the spectrum shows improved energy resolution compared to traditional stainless steel planchet source of the same radionuclide mixture while also preserving the elemental and isotopic signatures. Due to the close proximity of -particle energies, spectral overlap among different isotopes poses a significant challenge for straightforward isotopic analysis in -spectrometry. In this study, the Si semiconductor detector response has been simulated for different isotopes of Pu, and ^{241}Am using Monte Carlo approach for a PES supported Imo-CH_3 substrate. Detector parameters, including dead layer thickness and energy resolution, has been iteratively optimized in our earlier work using an in-house Monte Carlo code developed in Python-3.8 [3]. In this work, ^{229}Th has been spiked as an internal monitor for energy calibration as well as parameter optimizations related to the detector deadlayer and the source thickness. Response function analysis of the present PR grade Pu spectrum gives the ^{240}Pu/^{239}Pu mass ratio as 0.40 ± 0.08; which is within 20% of the expected mass ratio of 0.34. The present result highlights the potential of imogolite-based substrates to strengthen α-radiometry based nuclear forensic analysis at μg level where γ-ray spectrometry-based analysis is impossible and mass spectrometric analysis would involve costly instrumentation and sophisticated laboratory set-up. The present methodology offers a foundation for the design of next-generation separation materials, where in contrast to conventional selective extraction methods which can bias the analysis toward specific actinides, the non-selective surface complexation approach through Imo-CH_3 ensures complete retention of all actinides, preserving their elemental and isotopic ratios, which is critical for source attribution and determination of nuclear material origin.

Key words: *Nuclear forensics, Non-selective sequestration, Monte-Carlo Simulation, Response function analysis*

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Synthesis and Functionalization of UiO-66 (Ce)-NH2 for the Development of MOFs with Selective Adsorption of Lanthanides

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Lanthanides are crucial elements, finding widespread applications in fields such as medicine, communications, and nuclear technology. Given the rising global need for these elements, there is an urgent requirement to develop new adsorbents for lanthanide separation. This necessity stems from the inadequacies of traditional extraction techniques, like solvent extraction, in keeping up with current market demands. [1] Metal-Organic Frameworks (MOFs), which are formed by the coordination bonding of metal ions and organic ligands, create highly porous, periodic crystalline networks with large surface areas. These structures are valued for their exceptional properties, including vast internal surface area, versatility, and customizability.

To enhance adsorption performance and induce selectivity, UiO-66(Ce)-NH_2 synthesized via a room-temperature method was subsequently modified through Schiff base condensation reactions using various aldehydes (benzaldehyde, salicyaldehyde, and 2-hydroxy-3-methoxy benzaldehyde). This modification strategy successfully introduced different functionalities and tailored the pore sizes. The adsorption studies of La and Yb was done at different pHs and the quantification was carried out by EDXRF.

The synthesized MOF crystallized in UiO-66 kind of structure without any impurity as shown in Fig. 1. FT-IR confirms the successful coordination of 2-aminoterephthalic acid with Ce (IV) in UiO-66 (Ce)-NH_2, identifying characteristic vibrational modes like carboxylate and N-H stretching bands. Post-modification with aldehydes results in spectral changes, including diminished N-H bands, a new C=N peak at ~1620 cm^{-1}, and broadened -OH peaks, verifying successful MOF modification. TGA analysis reveals that both functionalized and unfunctionalized UiO-66 (Ce) MOFs exhibit high thermal stability and functionalized MOFs show a distinct hump at ~ 300°C, confirming successful incorporation of Schiff base-like functional groups.

All synthesized MOFs displayed strong lanthanide adsorption. The MOF functionalized with 2-hydroxy-3-methoxy benzaldehyde demonstrated superior simultaneous uptake of La (III) and Yb (III) at pH 4, a performance attributed to synergistic electrostatic and pore size effects. As shown in Fig. 2, all post-synthetically modified MOFs outperformed the virgin MOF across the tested pH range. At pH 6, the salicylaldehyde-based MOF showed promising selectivity, achieving approximately 78% uptake for Yb (III) compared to 64% for La (III), indicating its potential for targeted separation. Future experiments will involve detailed studies on adsorption isotherm, kinetics, selectivity, and reusability to optimize conditions for the selective removal of Yb (III) over La (III).

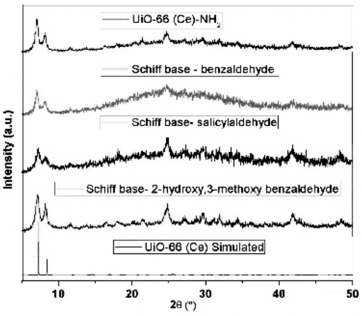

Fig. 1 *XRD patterns of Simulated UiO-66 (Ce); UiO-66 (Ce)-NH_2 and Schiff base MOFs after reacting UiO-66 (Ce)-NH_2 with benzaldehyde, salicyaldehyde, 2-hydroxy-3-methoxy benzaldehyde*

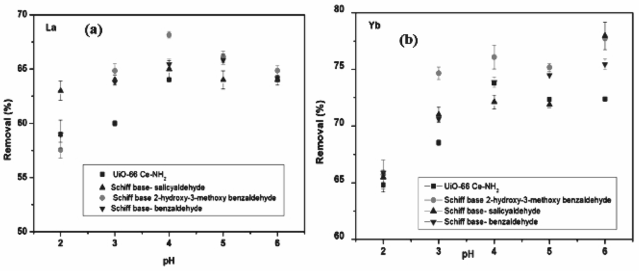

Fig. 2 *The effect of pH on removal efficiency of different MOFs for (a) La (III) and (b) Yb (III).*

Key words: *MOFs, Lanthanides, Adsorption, Functionalization*

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Solvent Extraction Studies of Pu Thiocyanate Complexes in DAAP

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Analytical laboratory waste containing U and Pu in ammonium thiocyanate medium is generated in reprocessing laboratories. Recovery of U from such analytical waste has been studied using the organophosphonate extractant diamylamyl phosphonate (DAAP) [1]. Thiocyanate also serves as an effective complexing agent in the separation of actinides and lanthanides using techniques such as ion-exchange and solvent extraction [2]. Recovery of Pu from this analytical waste is equally important for subsequent waste management. Since the waste matrix contains thiocyanate, understanding the behavior of Pu in this medium is essential. Pu(III) forms stable complexes with thiocyanate. Solvent extraction using organophosphorus extractants is widely used for the separation of uranium (U) and plutonium (Pu) in nuclear fuel reprocessing. In this context, solvent extraction studies on Pu were carried out using the phosphonate-based extractant DAAP. The extraction performance of DAAP depends on its selectivity toward Pu, the solvation of Pu in the extractant, the thiocyanate concentration $[SCN^-]$, and the pH of the medium. DAAP was synthesized, characterized, and dissolved in n-dodecane (DD) to prepare solutions of suitable concentrations (0.02, 0.1, 0.2, 0.3, 0.6, 0.75, and 1.1 M) for the experiments. Pu(III) solutions of various concentrations (7.29, 18.22, 32.8, 43.74, and 54.67 ppm) were prepared in 0.45 M thiocyanate solutions at pH 1 and 2.5 and used for all experiments.

Distribution studies are carried out in batch mode with 0.2 M DAAP/n-DD by taking equal volumes of Pu(III) solutions with varying amounts of plutonium (7.29, 18.22, 32.8, 43.74, 54.67 ppm) of 0.45M SCN^- of pH 2.5 and compared the same with 0.2M TBP/n-DD (Fig,. 1). D_{Pu} increases for [Pu] up to 18.2 ppm and further it decreases up to 54 ppm in both DAAP and TBP. The distribution ratio of Pu is higher in DAAP (31) than in TBP (7.8) therefore DAAP extracts Pu better than TBP (Fig. 1). Solvent extraction experiments are continued using Pu (III) solution of $[SCN^-]$ (0.45M, at pH 2.5) with each of [DAAP] extractant (0.02, 0.1, 0.2, 0.55, 0.75 & 1.1 M). Pu is estimated in aqueous and organic phase after allowing the phases to separate. D_{Pu} is calculated in each case and plotted against [DAAP] in logathimic scale and solvation number is evaluated from the slope of the line and found to be 1.85 (Fig. 2). Back extraction studies are carried out with Na_2CO_3 as strippant. Different molarities of Na_2CO_3 (0.15, 0.3, 0.6, 0.75, 1.5 & 2.25 M) are employed in 1:1 (Organic: Aqueous) ratio for stripping. Stripping of Pu is near complete with 2.25 M Na_2CO_3. Stripped Pu is brought into nitrate form from carbonate medium. These studies conclude that the Pu (III) can be completely extracted from thiocyanate medium in to DAAP and it forms a disolvate complex. Extracted Pu could be recovered by stripping with 2.25M Na_2CO_3. Future studies will be to ascertain the nature of the Pu(III) species extracted and reuse of Pu after recovery from actual waste.

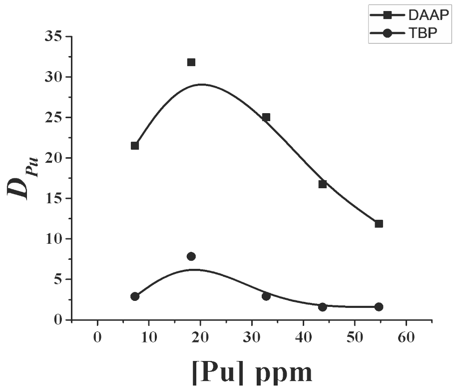

Fig. 1: D Pu in 0.45M [SCN] at pH 2.5; [DAAP] /n-DD - 0.2 M

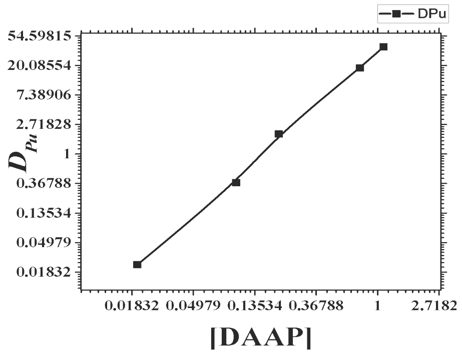

Fig. 2: ln D Pu vs ln [DAAP]

Key words: *Plutonium, solvent extraction, ammonium thiocyanate, solvation number, stripping.*

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Recovery of Plutonium from Ammonium Thiocyanate Analytical Waste Using Diamylamylphosphonate as Extractant

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Ammonium thiocyanate is widely employed as a chromogenic reagent for the spectrophotometric determination of uranium (ppm range) [1]. PUREX process samples are routinely analyzed for uranium using this method. However, this procedure generates plutonium-bearing analytical waste in a thiocyanate medium, necessitating the recovery of Pu from it. The analytical waste is typically at pH 2–3 and contains 15–20 ppm of plutonium. Thiocyanate (SCN^-) is an ambidentate ligand that can bind through either the nitrogen or sulfur atom. As plutonium is a hard acid, it preferentially binds through the nitrogen atom. Although Pu exists in both IV and III oxidation states in the sample aliquot, the presence of the reducing agent $SnCl_2$ in the waste solution converts it to the +III oxidation state. The recovery of Pu by solvent extraction depends on the choice of extractant, selectivity for the metal ion, pH of the solution, and the distribution ratio (*D*) for Pu. Organophosphorus compounds largely meet these criteria. In this context, the organophosphonate extractant diamylamylphosphonate (DAAP) was examined for the recovery of Pu from thiocyanate medium, and solvent extraction studies were carried out using Pu solutions (18.22 ppm) after reducing Pu to the +III state with hydroxylamine hydrochloride (5 M). Extraction was performed using 0.2 M DAAP in n-dodecane (n-DD) from thiocyanate solutions at various pH values and thiocyanate concentrations. DAAP was synthesized as reported in the literature [2] and characterized by IR and NMR spectroscopy. A 0.2 M DAAP solution in n-DD and thiocyanate solutions (0.45 M) at pH 1.0, 1.5, 2.0, 2.5, 3.0, 3.5, and 4.0 were prepared, along with solutions of varying thiocyanate concentrations (0.225–1.12 M) at pH 2.5, and used for all experiments.

Extraction was carried out in batch mode using 0.2 M DAAP and TBP in n-DD by mixing equal volumes of plutonium thiocyanate solution and equilibrating the phases for 30 minutes at each pH (1–4). After phase separation, Pu was estimated in both the aqueous and organic phases. The *D* value of Pu was found to be higher for DAAP than for TBP, with a maximum at pH 2.5, followed by a decrease with increasing pH. A similar trend was observed for TBP, but with lower *D* values, and maximum extraction also at pH 2.5 (Fig. 1). Equilibration studies were further conducted by fixing the concentrations of DAAP (0.2 M) and Pu (18.22 ppm), while varying the thiocyanate concentration from 0.22 to 1.12 M to evaluate ligand effects. The *D* values for both DAAP and TBP increased with ligand concentration up to 0.54 M and then showed a decreasing trend (Fig. 2). From these studies, we conclude that the *D* value of Pu depends on both pH and thiocyanate concentration, with maximum extraction at pH 2.5 up to 0.54 M thiocyanate using 0.2 M DAAP. These results indicate that Pu can be effectively recovered from thiocyanate-based analytical waste, with DAAP showing superior extraction performance. Future work will focus on the recovery of Pu from actual thiocyanate analytical waste.

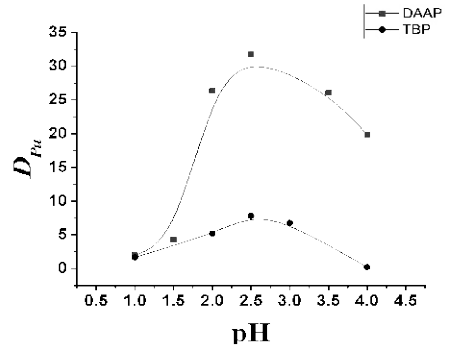

Fig 1: *Variation of* ***D Pu*** *as a function of pH of 0.45 M NH4SCN in 0.2 M DAAP/n-DD and 0.2 M TBP/n-DD. Initial [Pu] = 18.22 ppm.*

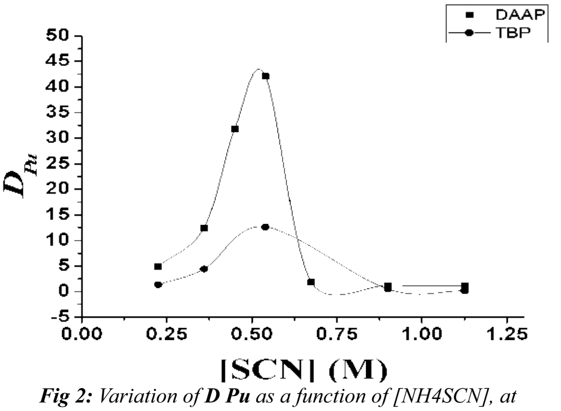

Fig 2: *Variation of* ***D Pu*** *as a function of [NH4SCN], at fixed pH 2.5 in 0.2 M DAAP/n-DD and 0.2 M TBP/n-DD. Initial [Pu] = 18.22 ppm.*

Key words: *plutonium, uranium, ammonium thiocyanate, solvent extraction, spectrophotometry.*

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Computational Investigation into Y/Sr Selectivity with TBP and TiAP Extractants

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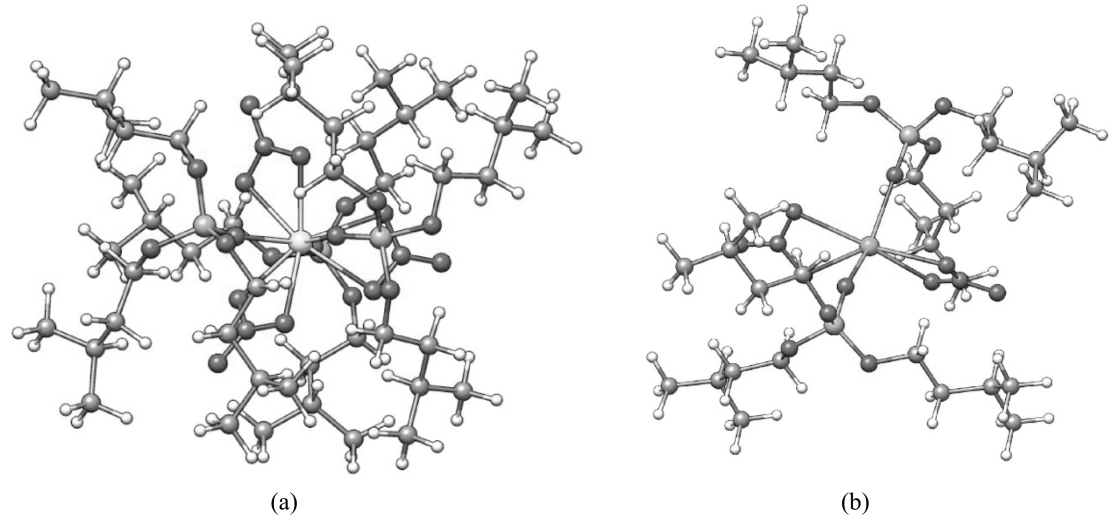
The selective separation of yttrium (Y^{3+}) from strontium (Sr^{2+}) is of major importance in nuclear waste processing, radiochemical purification, and the production of medical isotopes where efficient isolation of ^{90}Y from ^{90}Sr generators is required. [1] Neutral phosphoryl ligands such as tri-n-butyl phosphate (TBP) and tri-isoamyl phosphate (TiAP) are widely used in highly acidic extraction systems, yet the molecular origins of their differing affinity toward Y^{3+} and Sr^{2+} remain insufficiently understood. To address this, we employed density functional theory (DFT) calculations at the BP86/def2-TZVP level to investigate the structure, thermodynamics, and bonding characteristics of the solvated nitrate complexes extracted by TBP and TiAP.

The calculated complexation energies per ligand clearly demonstrate the much stronger stabilization of Y complexes: −254.74 kcal/mol (Y–TiAP) and −251.31 kcal/mol (Y–TBP), compared to only −21.65 kcal/mol (Sr–TiAP) and −17.15 kcal/mol (Sr–TBP). This energy difference confirms the greatly enhanced extractability of Y^{3+} relative to Sr^{2+}. To further elucidate the bonding nature, we performed Atoms-in-Molecules (AIM) analysis. The Y–O(P=O) coordination exhibits higher electron density at the bond critical point ($\rho \approx 0.05$ a.u.), a larger positive Laplacian ($\nabla^2\rho \approx 0.227$ a.u.), and a small positive energy density ($H \approx 2.76 \times 10^{-4}$ a.u.), consistent with a strong electrostatic interaction with partial covalent character. In contrast, the Sr–O(P=O) bonds show lower electron density ($\rho \approx 0.03$ a.u.), a smaller Laplacian (0.164 a.u.), and a higher energy density ($\approx 3.8 \times 10^{-3}$ a.u.), reflecting significantly weaker and more diffuse coordination. Complexation energies and AIM descriptors provide a coherent molecular-level rationale for the superior extraction of Y^{3+} by TBP and TiAP. This work offers both theoretical validation and mechanistic insight into Y/Sr separation chemistry, supporting the design of more efficient phosphoryl-based extractants for radiochemical and nuclear fuel cycle applications.



(a) (b)

***Fig. 1**: Lowest energy optimized geometry of (a) $Y(NO_3)_3{\cdot}3TiAP$ and (b) $Sr(NO_3)_2{\cdot}2TiAP$ at BP86/def2-TZVP level*

***Key words:** Y/Sr separation, DFT, TBP, TAP, AIM*

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Efficient Extraction of Uranium from Thiocyanate Waste Using Metal-Organic Frameworks (MOFs)

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Uranium plays a pivotal role as the principal fuel in nuclear power generation and strategic energy applications. However, the discharge of uranium-bearing waste poses severe radiological and ecological risks due to its long half-life and chemical toxicity. Consequently, the development of efficient, selective, and regenerable adsorbents for uranium recovery and environmental remediation has become an issue of critical importance for achieving sustainability in the nuclear industry.[1] [1] The efficient recovery of uranium from thiocyanate-containing waste streams is crucial for sustainable nuclear fuel cycle management and environmental protection. In the present study, a series of post-synthetically modified UiO-66–NH_2(Hf) frameworks were designed to enhance uranium(VI) extraction efficiency from aqueous solutions. UiO-66–NH_2(Hf) was functionalized using glutaric anhydride, diglycolic anhydride, and iminodiacetic acid, yielding UiO-66–GA, UiO-66–DGA, and UiO-66–IDA, respectively. These modifications introduced additional oxygen- and nitrogen-rich chelating groups, thereby increasing the number of potential coordination sites for uranyl ion binding. The adsorption performance of the pristine and modified MOFs was systematically investigated as a function of pH, contact time, and initial uranium concentration.The pH-dependent sorption studies revealed maximum U(VI) uptake in the mildly acidic region (pH 4–5), attributed to the deprotonation of functional groups and the favorable electrostatic interaction with the uranyl species. Kinetic experiments demonstrated rapid adsorption during the initial stage, reaching equilibrium within 180–200 minutes. The adsorption kinetics followed the pseudo-second-order model ($R^2 = 0.9944$), confirming a chemisorption-controlled mechanism involving surface complexation and electron sharing between uranium and donor atoms of the ligand. Among the tested materials, UiO-66–IDA exhibited the highest adsorption capacity ($q_e = 179.87$ mg g^{-1}), followed by UiO-66–DGA and UiO-66–GA. The superior performance of UiO-66–IDA is attributed to the synergistic interaction of its amine and carboxylate functionalities, which provide multiple binding sites for uranyl coordination. This study demonstrates that strategic post-synthetic modification of UiO-66–NH_2(Hf) is an effective route to tailor surface chemistry and enhance the uranium binding affinity of MOFs. The obtained results highlight the potential of UiO-66–IDA as a high-capacity, selective, and reusable sorbent for uranium(VI) recovery from aqueous waste streams, providing valuable insight into the rational design of functional MOF-based adsorbents for nuclear waste management and environmental protection.

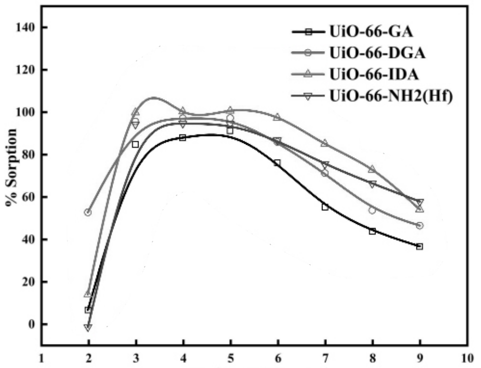

***Fig. 1:** Variation of % sorption of uranium with pH*

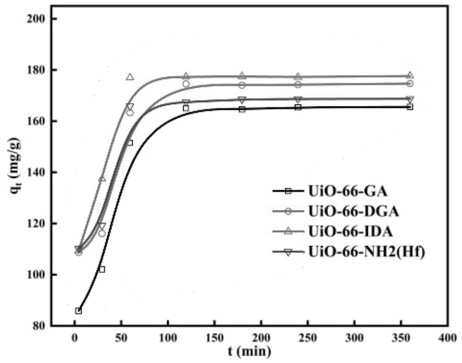

***Fig. 2:** Variation of sorption capacity with time*

***Key words:** Uranium, MOF, sorption, GA, DGA, IDA*

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A Comparative Study of Different Glycolamide Solvent Systems for the Group Separation of Trivalent Lanthanides from Simulated HLLW

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The high-level liquid waste (HLLW) solutions remaining after the aqueous reprocessing of spent fuel is identified as a rich source of several radioactive metals with potential applications in industrial and medical fields. Among them, minor actinides (the long lived radioisotopes of Np, Am and Cm) are identified as the major source of radiotoxicity of HLLW solutions, and partitioning of minor actinides from these waste solutions is considered as one of the essential steps before their final disposal in geological depositories. Several extractants and solvent extraction processes are studied in the literature for minor actinide partitioning, and the first step of the separation processes usually involve the group separation of trivalent actinides along with chemically similar trivalent lanthanides from HLLW [1]. The diglycolamide based extractants such as *N,N.N',N'*-tetraoctyldiglycolamide (TODGA), *N,N,N',N'*-tetradecyldiglycolamide (TDDGA) and the monoglycolamide extractant, *N,N*-di-octyl-2-hydroxyacetamide (DOHyA) were identified as ideal candidates for the group separation, even though all these solvents showed significant co-extraction of a few other fission products along with trivalent lanthanides and actinides.

The current study attempted a comparison of the extraction of different elements from a fast reactor simulated high-level waste (FR-SHLLW) solution in all the above solvents. The aim of the study was to quantify the extraction of interfering fission products such as Ru, Mo, Zr, Pd and Sr in different solvents under similar conditions. It was found that kinetic factors play a significant role in the extraction of interfering fission products such as Ru, showing complex aqueous chemistry. As all the studied glycolamides extracted trivalent actinides efficiently, minimal number of stages and contact periods ensured minimal co-extraction of other fission products. Even under these conditions, some of the fission products such as Zr and Y were quantitatively extracted along with lanthanides and actinides in all the solvents studied. The diglycolamide extractants, TODGA and TDDGA were found to show high extraction (> 95%) of Pd and moderate extraction (20%-40%) of Mo and Sr. On the other hand, the monoglycolamide extractant, DOHyA showed high extraction of Mo, but moderate to low extraction of Pd and Sr. An efficient modifier-free extraction system combining both TODGA and DOHyA was studied for group separation of trivalent elements from waste solutions [2]. In comparison to the solvent containing TODGA alone, the combined system showed reduced co-extraction of Pd and Sr, however, high extraction of Mo. A comparison of the results in different extraction systems is shown in Fig.1. The effects of different complexing agents in the feed solution for each extractant were further studied in detail for identifying the optimal extraction conditions for group separation of trivalent elements from HLLW solutions.

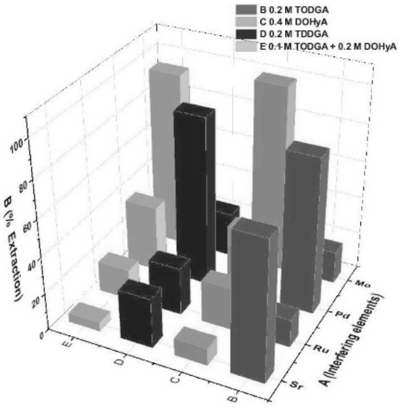

***Fig. 1** Percentage extraction of some of the major interfering elements of FR-SHLLW in different glycolamide extraction systems used in the study. Diluent: n-dodecane modified with 5 vol% 1-octanol for TODGA and n-dodecane alone for all the other extractants*

***Key words:** High-Level Liquid Waste, Diglycolamide, Hydroxyacetamide, Fission Products, Group Separation*

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Solvent Extraction Studies with U-Pu-Th Solutions towards the Development of a Flow Sheet for Spent Fuel Reprocessing using Phosphate Based Solvents

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The spent fuel from AHWR is expected to contain approximately 2–4% fissile materials, including ^{233} and plutonium [1]. Reprocessing this spent fuel poses a challenge in a closed fuel cycle, as it requires the separation of three key components namely uranium, plutonium, and residual thorium from the bulk of the fission products. A solution of 1.1 M TBP in n-DD forms the third phase with tetravalent metal ions such as Pu, Zr, and Th when the metal ion concentration in the organic phase exceeds certain limit called limiting organic concentration (LOC). TiAP has drawn considerable attention as an alternate solvent to TBP especially for processing of solutions containing tetravalent metal ions [2]. In the present study TiAP has been explored for the processing of solutions containing U, Pu and Th. TiAP has higher third phase limits for Th compared to TBP. In this context distribution ratios for U, Pu and Th by 1.1M solutions of TBP and TiAP in n-DD has been measured as a function of nitric acid concentration. The distribution ratios are in the following order; U>Pu>>Th for both TBP and TiAP solvents. The distribution ratios for all three metal ions are higher for TiAP than that of TBP indicating that it is possible to achieve higher extraction of metal ions through TiAP. In addition TiAP has higher third phase limits for Pu and Th than that of TBP. As reported in our earlier studies, TiAP has lower third phase formation tendency for Th compared to TBP. The limiting organic concentration for Th at 4 M HNO_3 with 1.1 M TiAP/n-DD and 1.1 M TBP/n-DD are 35 g/L and 76 g/L, respectively at 303 K. A feed solution containing U and Th about 2 g/L and 100 g/L in 4 M HNO_3, respectively was prepared. Cross-current experiments with U-Th solutions were performed using TBP and TiAP based solvents. Initially U was separated using 0.183M solutions of TBP and TiAP in n-DD in 4 stages followed extraction of Th by 1.1M solutions of TBP and TiAP in n-DD in 4 stages. Subsequently stripping of U and Th from organic phase was performed with 0.01M HNO_3 in 4 stages each. It was observed that 1.1M TBP/n-DD forms third phase with Th during the 1st stage of Th extraction. However third phase was not observed with 1.1M TiAP/n-DD during the extraction of Th. Quantitative extraction of U and Th was observed in all the cases. Similarly experiments were also carried out with U-Pu-Th feed solutions (U-2 g/L, Pu-2 g/L and Th-100 g/L in 4 M HNO_3). Results indicate that Pu follows U stream and in this case also third phase observed with Th by TBP based solvent. The present study demonstrates that TiAP based solvent can be employed for processing of three component systems containing U, Pu and Th without third phase formation.

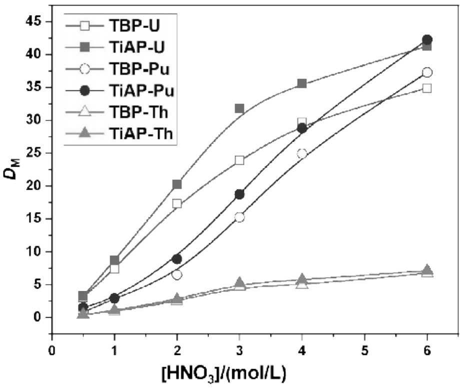

Fig. 1. Distribution ratios for U, Pu and Th by 1.1M solutions of TBP and TiAP in n- DD as a function of nitric acid concentration

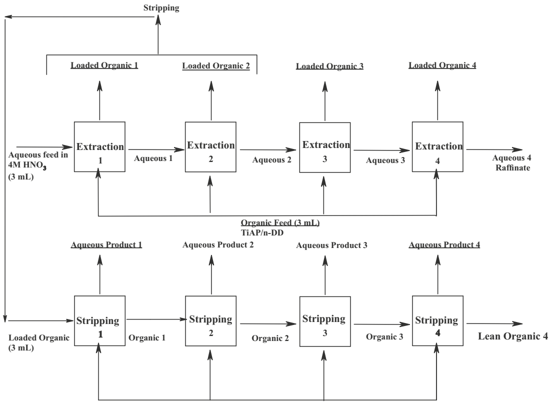

Fig. 2. Flow sheet for the separation of U, Th and Pu solutions of TBP and TiAP in n-DD in cross- current mode.

***Key words:** Uranium, Thorium, Plutonium, TBP, TiAP, Cross-current*

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Recovery, Purification and Reconversion of Uranium from Secondary Pyro Streams Produced during the Electrorefining

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Pyroreprocessing of natural U in bulk scales were demonstrated in high-temperature electro-refiner (HTER) setups at IGCAR [1, 2,]. During the engineering scale demonstration of the process (10 kg U per batch), several secondary matrices containing uranium were produced. These include graphite moulds (AM005), uranium particulates (AM007), electrode (anode) scrap (AM008). Graphite mouldwas used in during melting and consolidation steps to promote partition of the U ingot. Being in contact with the molten U, it would have picked some U on the exposed surfaces. AM007 includes the U particles or fines produced during handling of U bearing components in the glove box. These may be laden with salt and other particulates also. AM008 is an active solid material (salt +U) collected by scrapping the anode basket manually during cleaning works. Before disposal as solid waste, it is important to recover uranium present in these materials. The recovery of uranium from these pyro-secondary streams has been carried out by leaching in nitric acid medium and it was leached in nitric acid medium until U is completely recovered. These leeched nitric acid solutions contain notable quantities of uranium (~350-400 g) along with other impurities such as Li, K, Fe, Cd, Y, Zr. The acidity of the feed solutions were adjusted to around 4 M HNO_3 and the concentration of U in these feed solutions is found to be in the range of 25-100 g/L. Batch solvent extraction studies were performed with various organophosphorous compounds such as Tri-n-Butyl Phosphate (TBP), Tri-iso-Amyl Phosphate (TiAP), Dibutylbutyl phosphonate (DBBP) and Diamylamyl phosphonate (DAAP) in cross-current mode at 303 K. Extraction and stripping of uranium from nitric acid medium were performed using 1.1 M solutions of TBP, TiAP, DBBP and DAAP in n-DD (n- Dodecane) and the number of stages for quantitate extraction of U were decided based on the concentration of uranium in the feed solution. Extraction efficiency of U was found to be >85% with negligible extraction of other impurities. Subsequently stripping of U from loaded organic phase was performed with 0.01 M HNO_3 and stripping efficiency was found to be >89% in all the cases (Table 1). Bulk scale purification of U from AM007 and AM008 was carried out using 1.1 M TiAP/n-DD and the purified $UO_2(NO_3)_2$ was converted to ammonium-diuranate using ammonia solution followed by calcination at 700°C for 4 hrs. The calcined uranium oxide was characterized by XRD and its XRD pattern is found to be similar to XRD of U_3O_8 reported in literature (Fig.1). Conversion of U_3O_8 to U metal by direct oxide electro-reduction method is in progress. The present study demonstrates the feasibility of recycling uranium from pyro-secondary streams, material accounting and converting it into suitable form for further use in metallic fuel.

Table 1: *Extraction and Stripping of U (%) by organophosphrous compounds during the recovery of U from secondary matrices*

	Extractionandstripping(%)			
	TBP	TiAP	DBBP	DAAP
Extraction-AM005	96.77	97.03	98.76	99.09
Stripping-AM005	97.80	98.78	92.23	92.23
Extraction-AM007	-	90.91	-	85.24
Stripping-AM007	-	99.75	-	97.69
Extraction-AM008	-	97.39	-	96.36
Stripping-AM008	-	99.92	-	89.15

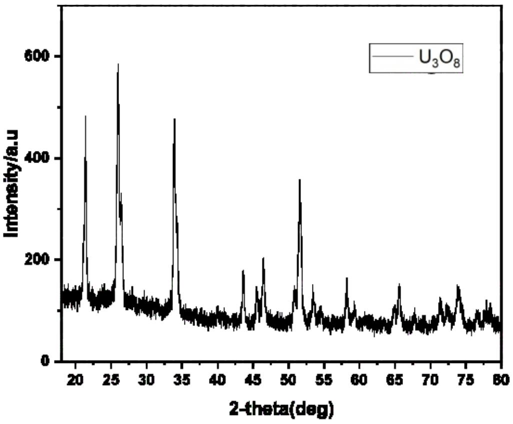

Fig.1 *XRD of uranium oxide obtained upon calcination at about 700°C*

Key words: *Pyro-secondary streams, Uranium, Recovery, Cross-current, Organophosphorus Compounds*

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Processing of Aqueous and Organic Radioactive Waste Solutions for the Safe Disposal

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Large quantity of aqueous liquid waste has been generated from various R&D activities such as solvent extraction experiments for the development of an alternate extractant to TBP for fast reactor fuel reprocessing, flow sheet development studies, evaluation of resins for the recovery of actinides etc. over a long period in our laboratory. In addition during the analysis of U and Pu by Davies-Gray and Drummond-Grant methods, a significant amount of analytical waste is produced, comprising plutonium in the range of mg/L in a sulfuric acid medium (1 M), together with other metallic impurities such as Fe, Ag, Cr, etc. The aqueous waste contain actinides (U, Pu, Am) and fission products in nitric acid, sulfuric acid and phosphoric acid medium [1]. Similarly large quantity of organic waste was also generated from various R&D activities in separation chemistry with radioactive materials in our laboratory. The composition of organic waste is as follows: Trialkyl phosphates such as TBP, Tri-iso-amyl phosphate (TiAP), Tri-2 methyl Butyl phosphate (T2MBP), Phosphonates, TTA/xylene, etc., diluents such as n-Dodecane, Heavy normal paraffin's (C10-C13), etc., dioxane based cocktail solvent, degradation products of all the above solvents generated due to radiolysis [2]. The alpha activity of the above liquid waste solution was found to be very high and is in the range of 10^4-10^5 Bq/mL which is higher than the acceptable limits of CWMF. The objective of this study is to reduce activity of the liquid waste solution containing mainly alpha bearing radionuclides, below the limits, acceptable for disposal. Various methods such as solvent extraction, ion exchange, precipitation etc. were examined for the processing of the waste. A suitable method has been developed to reduce the activity of the liquid waste generated. Initially different chemical reagents (precipitating reagents) were examined for reducing the activity of the waste such as $BaCl_2$, $CaSO_4$, NaOH. Precipitation by sodium hydroxide and sodium carbonate has been employed for the reduction of activity in the aqueous and organic liquid wastes, respectively. GM counting system and solid scintillation ZnS (Ag) counting system were used for estimation of gross β, γ and α activities, respectively. Average alpha activity of this aqueous liquid waste has been brought down to < 5000 Bq/mL. The treated solution is alkaline in nature ([OH-] = ~0.3 M) and it's activity is below the limit acceptable to CWMF (3.7×10^5 Bq/mL – β, γ and 5500 Bq/mL – α) as shown in Table 1 and the concentration of Pu was found to be very low (< 0.7 ppm) by radiometry. Analysis of treated aqueous sample by HpGe indicated the presence of trace quantities of ^{241}Am (~ 35 nCi/mL corresponds to ~ 10 ppb) and ^{137}Cs (~ 3 nCi/mL corresponds to ~ 0.03 ppb) in the aqueous waste. About 115 liters of aqueous liquid waste has been processed by precipitation method and gross α and β,γ activities were reduced below the acceptable limits and transported to CWMF for further disposal. Similarly radioactive organic waste was characterized by HpGe, α-spectrometry, plancehtting etc. The radionuclides present in the organic waste are ^{233}U, ^{239}Pu, ^{241}Am, ^{137}Cs, ^{60}Co etc. characterized by HpGe (Table 1). The initial activity of the organic waste determined LSC (Table 2) and planchetting and its α-activity was found to be 67.7x10^3 Bq/mL by Liquid Scintillation Counter which is higher than the acceptable limits of CWMF. The organic waste was treated in different batches with saturated sodium carbonate solution with organic to aqueous ratio of 1:10. The activity of the treated organic waste (supernatant solution) was analyzed for α and β, γ activity and it was found to be less than 1190 and 800 Bq/mL, respectively in all the batches. The present study demonstrates processing of radioactive liquid waste to reduce the alpha activity.

Table 1: *Gross α and β,γ activities of treated* aqueous liquid waste

S.No	Volume, Litres	Gross α activity, Bq/mL	Gross β,γ activity, Bq/mL
Carboy-1	27	2935	2002
Carboy-2	27	4900	5477
Carboy-3	29	4585	2863
Carboy-4	31	2626	1776

Table 2: *Radionuclides present untreated radioactive organic liquid waste characterized by HpGe*

Radionuclide	Activity, nCi
^{60}Co	2.68
^{137}Cs	1.08
^{239}Pu	5310
^{241}Am	140

Key words: *Radioactive liquid waste, Treatment, Precipitation, NaOH, Na_2CO_3*

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A Study on Significance of Settling Time in Separation and Deactivation Process of Rare Earth Chloride by use of Gamma Spectrometry at IREL (India) Limited, OSCOM, Chatarpur, Odisha

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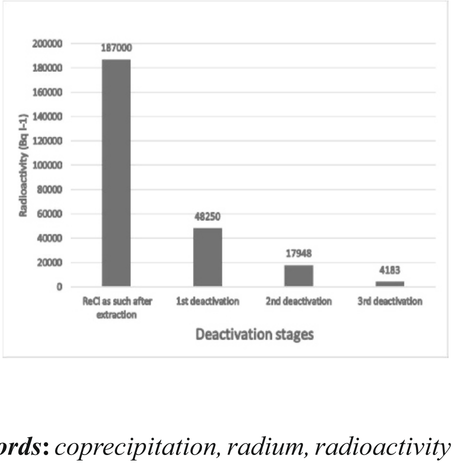
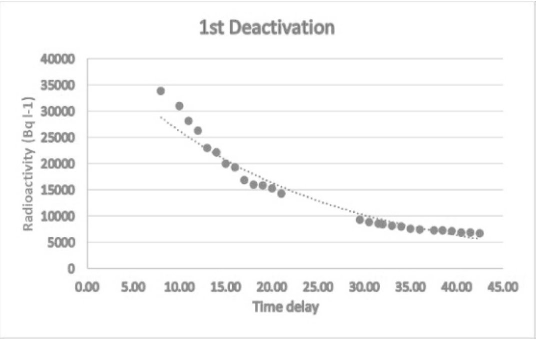
The Orissa Sand Complex (OSCOM), Chhatarpur, Odusha is the largest division of IREL for production of monazite heavy mineral that is a commercially suitable rare earth mineral. The presence of naturally occurring radioactive materials (NORM) in rare earth minerals in varying concentrations is quite often significant enough to result in occupational and environmental radiation exposures during their mining, milling and chemical processing for the extraction of the rare earth elements and compounds. The mining of the ores and further processing results in concentration/ redistribution of the NORM in the process streams, product intermediaries, products and effluent wastes as technically enhanced naturally occurring radioactive materials (TNORM). Rare earth elements (Ln (III)) are chemically rather similar to uranium (U) and thorium (Th) and are often found in conjunction with these radionuclides. The production of Ln (III) has been accompanied by the production of large volumes of thorium hydroxide and residues containing radioactive lead and radium-isotopes [1,2].The rare-earth chloride solution recovered from monazite milling followed by alkali digestion and HCL treatment shows a radioactivity of 1,87,000 Bq l^{-1}. The majority of the enhanced radioactivity in all RECl3 liquor was attributed mainly to γ-emissions of ^{228}Ra progenies (i.e., ^{228}Ac, ^{212}Pb, ^{212}Bi, ^{208}Tl), whereas the rest was due to ^{226}Ra radiation or its progenies (i.e., ^{214}Pb, ^{214}Bi) as well as radionuclides of ^{223}Ra and ^{210}Pb. In order to deactivate the solution, co-precipitation process by adding chemicals like BaCl2 and MgSO4 is being used. Thus, the Radium contained in the RE solution is co-precipitated along with barium sulphate as radium sulphate. The iron and lead present in the above solution is eliminated by adding sodium sulphide (Na_2S) solution. In this process radioactivity measurement plays a key role to monitor the deactivation process. Samples collected at different stages of deactivation were analyzed in a 2" X 2" NaI (Tl) detector. Fig.1 shows the batch wise reduction in radioactivity from 1,87,000 Bq l^{-1} to 4183 Bq l^{-1} in rare earth chloride deactivation process. After one deactivation usually 8hrs of settling time was being given. Here, the settling time after a deactivation process also a measure parameter as increased settling time after 1st deactivation allows auto reduction in radioactivity allowing the progenies to self-decay (Figure-2 and within 45 hours almost 85% reduction in activity was observed). Settling time has a significant role in reducing number of deactivation steps and most importantly in reducing the quantity of radioactive waste (lead barium cake) generated through the deactivation process.





Key words: *coprecipitation, radium, radioactivity*

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Distribution Characteristics of Pu (VI) in TBP/n-DD Mixtures

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The mixed (U,Pu)O_2 fuel containing a higher fraction of plutonium (Pu) is used as the driver fuel in fast reactors. As part of the fuel development program and to generate irradiation data for oxide fuels in a fast spectrum, fuel subassemblies with mixed oxide compositions containing more than 30% plutonium oxide are employed as test fuel subassemblies in nuclear reactors. A major challenge associated with such high-plutonium mixed oxide fuels is their slow dissolution kinetics during reprocessing. Hence, solution mixture of concentration nitric and hydrofluoric acid or nitric acid in presence of electrolytically generated cerium (IV) are employed for the quantitative dissolution of MOX fuel with higher Pu content. Since, fluoride is highly corrosive to stainless steel equipment, an electro-oxidative dissolution method in presence of cerium is considered to be a more promising option for such fuels. In this method, the oxidation state of all Pu in dissolver solution is completely oxidized to Pu (VI). Therefore, reduction of all PuO_2^{2+} to Pu^{4+} is essential prior to solvent extraction in view of minimizing the Pu loss in high level waste. During reprocessing, hexavalent plutonium is typically reduced to the +4-oxidation state by adding sodium nitrite or sparging NO_2 into the conditioner tank. However, these reagents do not fully convert Pu (VI) to Pu (IV), and about 5 % of the plutonium remains in the +6-oxidation state even after adding excess reagents beyond its stoichiometry requirement. Therefore, it becomes necessary to determine the distribution coefficient of Pu (VI) in 30% tri-n-butyl phosphate in n-dodecane (TBP/n-DD) in view of understanding the loss of Pu in raffinate. For this study, a feed solution containing 10.0 g/L of Pu in nitric acid at concentrations range from 2-6 M was prepared. The concentration of Pu in this sample is corresponding to concentration range envisaged in conditioner tank during reprocessing of spent fuel from fast reactor. And the oxidation state of Pu was maintained in the +6-by adding ceric (IV) nitrate. The oxidation state of Pu in resultant sample was further confirmed by recording UV-Visible spectrophotometric method. The typical UV-Visible absorbance spectrum is shown in Fig 1. The absorbance at 830 nm indicates that all Pu are in +6 oxidation state. A known volume of this feed solution was transferred to extraction vial consisting same volume of 30% TBP/n-DD and equilibrated for 10 minutes using a vortex shaker. After centrifugation of phases and separation, the Pu concentration and acidity in both the aqueous and organic phases were analyzed. The data shown in **Fig 2** indicates that distribution ratio of Pu in +6 oxidation state increases with increasing acidity. The distribution ratio of hexavalent Pu in nitric acid in the concentration range of 5-6 M is found to be 3.5-4.0 and 5 contacts in batch extraction are required to minimize loss of Pu in raffinate < 5mg/L.

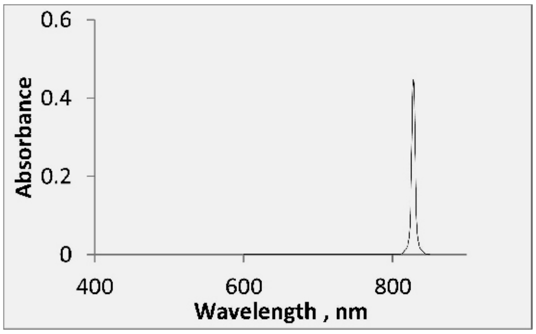

***Fig** 1Typical UV-Visible spectrum of feed samples*

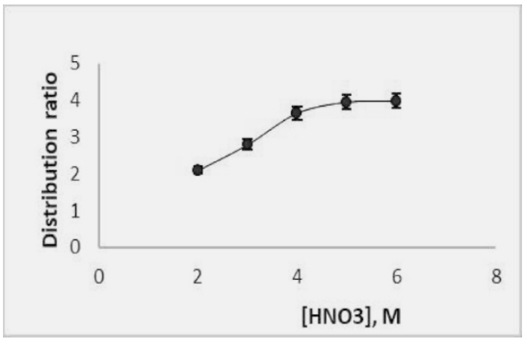

***Fig. 2** Plot of distribution ratio of Pu(VI)&[HNO_3]*

Key words: *Distribution ratio, hexavalent Pu, fast reactor*

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Exploring Anion Functionalized Ionic Liquids in Dissolution of UO_3

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Ionic liquids have been recently exploited for selective dissolution of oxides of f block elements for mutual separation and non-aqueous processing [1]. In the present case, dodecyl sulphate (DS^-) functionalized ionic liquids with tetraalkylammonium ($(C_8)_3C_1N^+$) and tetraalkylphosphonium ($(C_6)_3C_{14}P^+$) cations have been synthesized and chosen for the rapid dissolution of UO_3 followed by electrodeposition. An equi-molar amount of $(C_8)_3C_1N^+Cl^-$ *or* $(C_6)_3C_{14}P^+Cl^-$ and sodium dodecyl sulphate (SDS) in 1:1 water-toluene mixture was stirred for about 5 h at 27°C [Fig. 1 (a)]. A complete phase separation occurred and the straw yellow, highly viscous TSIL was separated. Both the ionic liquids thus formed were characterized by FTIR [Fig. 1 (b)] and NMR spectroscopy. The peak at 1220 cm^{-1} with a shoulder was ascribed to the -S=O functional group. The same functionality was also evidenced by the peak at 1049 cm^{-1}. The peaks at 721 cm^{-1}, 789 cm^{-1} and 857 cm^{-1} with the typical pattern were ascribed to the signature of $(C_8)_3C_1N^+$ ion. The peaks at 1112.68 cm^{-1} were attributed to $(C_6)_3C_{14}P^+$moiety. For $(C_8)_3$C1N+,$UO_3$was found to be dissolved to the higher extent compared to $(C_6)_3C_{14}P^+DS^-$ at room temperature [Fig. 1 (c)]. For both the ionic liquids, UO_3 dissolution enhanced with enhancement in time of biphasic equilibration [Fig. 1 (d)]. Quantitative dissolution was achieved within 150 min in case of former compared to 240 min for the later. The dissolution into $(C_8)_3C_1B^+Cl^-$ was found to be endothermic; while exothermic for $(C_6)_3C_{14}P^+DS^-$ [Fig. 1 (e)]. The electrodeposition from ionic liquid phase resulted a black deposit of $UO_{2\pm x}$.

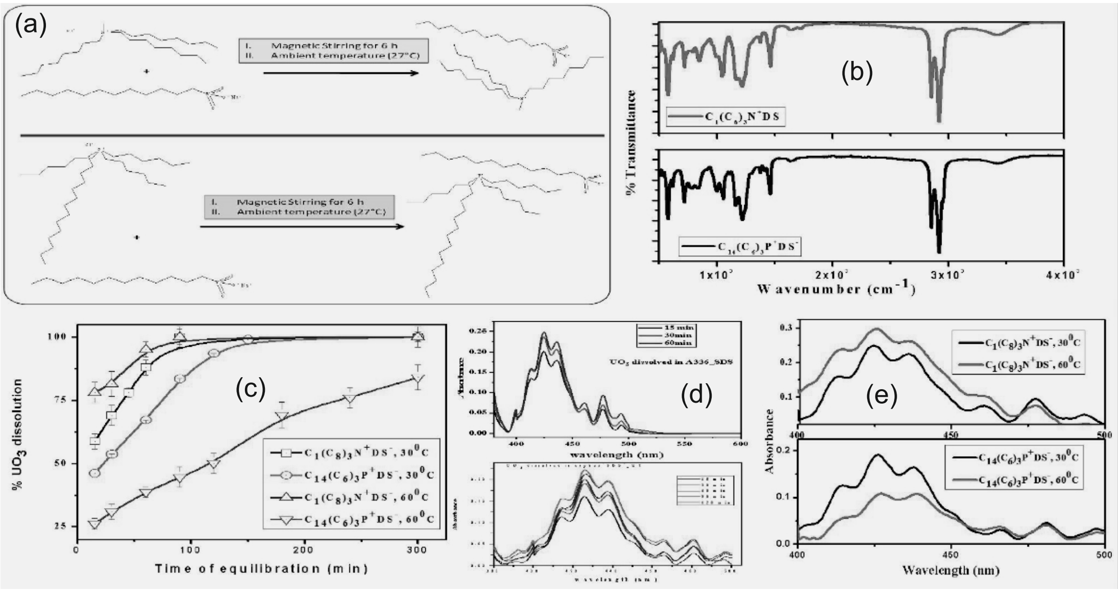

Fig.1 (a) *Synthesis scheme; (b) FTIR spectra for TSILs; (c)* UO_3 *Dissolution into TSIL; UV-Vis spectra for* UO_2^{2+} *into TSIL as a function of (d) time ; (e) temperature*

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Optimization of Process Parameters for Pyrolysis cum Incineration of Cellulosic and Polymeric Materials on Continuous Mode to Minimize Chlorine Content of Ashes

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A two-step process has been envisaged for processing of alpha bearing solid waste stored at interim facilities awaiting its treatment. The first step involves pre-treatment of cellulosic(C) and polymeric(P) alpha solid waste via pyrolysis cum incineration to obtain ashes achieving a significant reduction in waste volume and the second step involves catalyzed electrolytic SNM dissolution from obtained ashes followed by SNM recovery. A continuous process for pre-treatment was developed and demonstrated in a train of three glove boxes (GBs) with representative nonradioactive solid organic materials [1]. Though free flowing ashes were obtained for a feed rate of 0.5kg/h, the obtained ashes did not qualify for SNM dissolution step due to carbon and chlorine content each as high as 3% instead of desirable value of <1%carbon and <1%chlorine [2]. Higher chlorine contents in the ashes at a throughput of 0.5kg suggest the need of either higher residence time or higher heat flux for effective removal of chlorine. In the existing pyrolyser cum incinerator setup, it was not possible to increase the residence time beyond 90min. Therefore, a compromise was made with the throughput and studies were carried out at reduced feed rates and by increasing the temperature of incinerator from 500°C to 700°C. Since chlorine handling at elevated temperature leads to higher corrosion rate, only two temperatures were tried i.e. 400 and 500°C for pyrolyser. For a feed rate of 0.2kg/h, chlorine free ashes were obtained for all tried combinations of pyrolysis and incinerator temperature. The feed rates of 0.3 and 0.4kg/h were also tried with pyrolyser and incinerator temperature as 500°C and 700°C respectively. Chlorine free ashes were obtained for 0.3kg/h but not for 0.4kg/h. It could be attributed to chlorine removal by higher heat flux for 0.3kg/h as against 0.4kg/h. Process parameters optimized for continuous treatment of C and P material to obtain ashes with <1%chlorine are given in table-1. These experiments were carried out using a wet flue gas handling system for effective removal of HCl from generated off gases. Process schematic is given in fig.

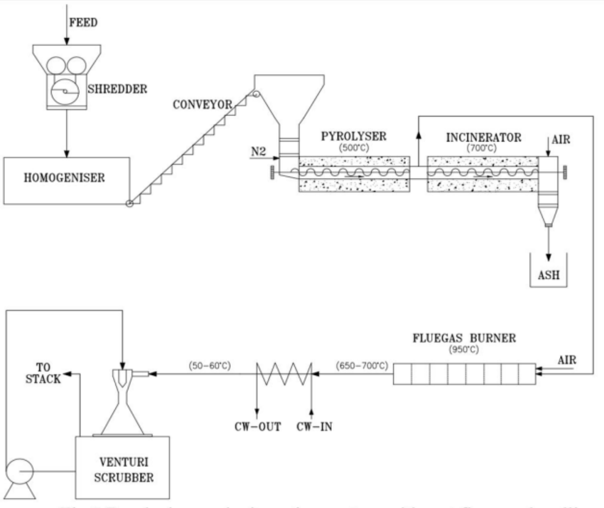
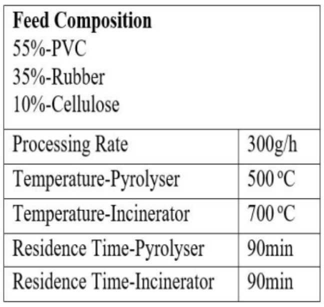


Fig.1 Pyrolysis cum incineration system with wet flue-gas handling

Table-1 Optimized process parameters to obtain ashes with <1%Chlorine



Feed Composition 55%-PVC 35%-Rubber 10%-Cellulose	
Processing Rate	300g/h
Temperature-Pyrolyser	500 °C
Temperature-Incinerator	700 °C
Residence Time-Pyrolyser	90min
Residence Time-Incinerator	90min

Key words: *Pyrolysis, Incineration, Continuous-Mode, Residence-Time, Heat-Flux*

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Evaluation of Some MOFs for Boron Adsorption and Isotope Separation from Aqueous Medium

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Boron, having two stable isotopes ^{10}B (~19.9%) and ^{11}B (~80.1%), is an important nuclear materials due to large neutron attenuation coefficient of ^{10}B. It is used in control rods to regulate fission and other nuclear related application. It is also used in boron neutron capture therapy (BNCT) for tumor-selective particle radiotherapy [1]. Several methods based on exchange distillation, adsorption, mass spectrometry and laser have been utilized [2]. Adsorption-based process have been proven to be more efficient, easier to operate and less costly. Various adsorbents such as anion exchange resin, chelating resin, metal oxide loaded resin, etc. have been studied for boron isotope separation. The glucamine modified resin has the up-to-date highest isotopic separation factor of 1.027, which is still far from satisfaction from the angle of industrial application [3]. Recently, metal-organic frameworks (MOFs), highly porous and larger surface area crystalline materials with good chemical stability, have also been investigated for boron isotope separation and adsorption showing very promising results [4]. In view of this, in this work two types of water stable MOFs, namely, UiO-66-NH$_2$ and MIL-101(Cr) were synthesized and tested for boron adsorption and isotope separation from aqueous medium. Boron adsorption studies were conducted in batch mode by varying pH, initial concentration, contact time, temperature and presence of other metal ions. Isotopic separation factor were calculated from the ^{10}B/^{11}B ratio in adsorbent and solution phase of the batch adsorption experiments.

UiO-66-NH$_2$ was synthesized using solvothermal method starting from zirconium oxychloride and 2-aminoterephthalic acid in DMF/HCl medium. MIL-101(Cr) was synthesized from chromium nitrate and terephthalic acid in H_2O/HF medium. After purification and activation, the MOFs, UiO-66-NH$_2$ and MIL-101(Cr), were characterized with FTIR, SEM and TGA analysis. The pH dependent boron adsorption data with the MOFs (Fig. 1) indicates strong dependence of pH on the binding of boric acid by MOFs. The maximum adsorption were found at pH 5 and 6 with MIL-101(Cr) and UiO-66-NH$_2$, respectively. The speciation of boric acid and surface charge of the adsorbents at different pHs are responsible for this behavior. The lighter isotope of B was seen to prefer MOF phase over aqueous phase as seen from the results shown in Table 1. It is also seen that higher adsorption capacity (Q) leads to lower isotope separation factor. The stronger interaction of B may results in lower rate of isotope exchange reaction. The interaction of boric acid and metal centers (Cr and Zr) through B-O bonds as well as Lewis acid base type interaction between boric acid and amine of UiO-66-NH$_2$ may be responsible for the binding of boron on the MOF structures [4,5].

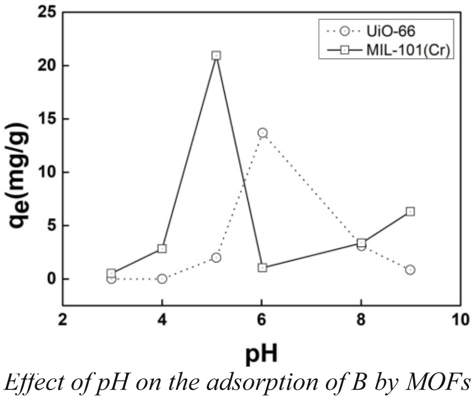

Fig. 1: *Effect of pH on the adsorption of B by MOFs*

Table 1. *Boron isotope separation factor results*

MOF	pH	Q (mg/g)	S(^{10}B/^{11}B)
UiO-66-NH$_2$	6	13.68	0.89
	8	3.09	2.04
MIL-101(Cr)	5	20.94	1.07
	4	2.81	1.94

Key words: *Boron adsorption, Boron isotope separation, MOF, UiO-66-NH2, MIL-101(Cr), Separation factor*

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Synthesis and Evaluation of Layered Bimetallic Sulfides for Strontium Removal

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Strontium-90 (^{90}Sr), along with its daughter product ^{90}Y; is considered as the third most harmful radioactive contaminant, after ^{137}Cs, due to its long half-life and high-energy beta emission. So, removal of radioactive strontium from nuclear waste and effluents is a matter of global concern and is actively being pursued by researchers worldwide. Thio stannate based layered metal sulfides; with anionic frameworks and easily replaceable interlayer cations, have demonstrated excellent ion-exchange properties towards Cs(I) and Sr(II). They can be utilized for the selective removal of Cs(I) and Sr(II) from matrices like freshwater and seawater; where the competition from cations like Na(I) and Ca(II) are very high. Presence of soft ligands like S makes them selective towards soft cations like Cs(I) and Sr(II); which is highly beneficial for their preferential removal in presence of hard cations like Na(I) and Ca(II).

Tin based bimetallic sulfides - potassium zin tin sulfide (PZTS) and potassium magnesium tin sulfide (PMTS) - were prepared as per reported procedures[1,2] using $MgCO_3$ as the Mg precursor, instead of metallic Mg or MgS. PMTS and PZTS were characterized using powder XRD and the layered structure formation was ascertained (Fig. 1). Both PZTS and PMTS exhibited sharp, distinct diffraction peaks, confirming their crystalline nature. Overall patterns strongly suggested the formation of layered compounds, consistent with potassium zinc tin sulfides and potassium magnesium tin sulfides. Both PMTS and PZTS samples showed comparable Sr(II) uptake capacities (0.55 and 0.67 mmol/g, respectively). Approximately two K(I) ions were released for each Sr(II) ion uptake indicating stoichiometric exchange of K(I) ions by Sr(II) as the uptake mechanism. Nearly 80% elution of the bound Sr(II) was possible with a single step of desorption using 1 M KCl as the eluent. This has ascertained the easy regeneration of the synthesized metal sulfides. Powder XRD of the regenerated samples showed identical diffraction patterns corresponding to the parent samples, which indicated a completely reversible ion exchange between Sr(II) and K(I) (Fig. 1). Sorption studies of PMTS and PZTS using freshwater samples (containing 0.11 mM Sr(II), 0.08 mM K(I), 0.53 mM Ca(II), 0.43 mM Mg(II) and 2.98 mM Na(I)) showed selective removal of Sr(II) with K_d values of 6053 L/kg (PMTS) and 21983 L/kg (PZTS). Decontamination factors achieved are 32 (PMTS) and 113 (PZTS).

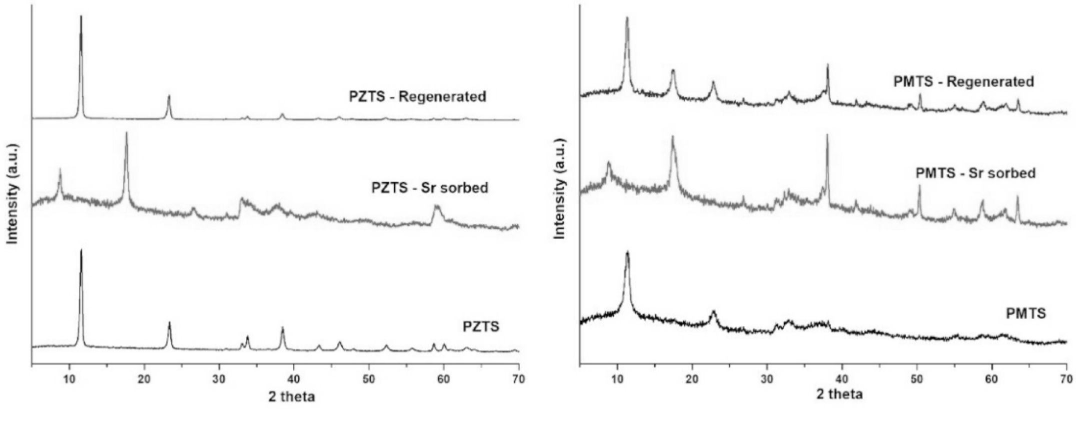

Fig 1. *Powder XRD of potassium zinc tin sulfide (PZTS) and potassium magnesium tin sulfides (PMTS): PXRD patterns of as prepared, strontium loaded and regenerated (elution using KCl) layered bimetallic sulfides*

Key words: *Layered metal sulfides, Potassium zinc tin sulfide, Potassium magnesium tin sulfide, Strontium, Ion exchange, Sorption*

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Scale-Up of Gaseous Sparging Experiments for Actinide Removal from Used Salts in Pyrochemical Reprocessing

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Pyrochemical reprocessing is particularly well-suited for the reprocessing of future fast breeder reactor (FBR) fuels, which are envisioned to be fueled by metallic fuell . The widely recognized Integral Fast Reactor (IFR) pyrochemical reprocessing method employs electrorefining (ER) conducted in a eutectic LiCl-KCl electrolyte. With consecutive runs of ER, the electrolyte gets loaded with fission products (FP) such as rare earth chlorides ($RECl_3$), alkali and alkaline earth metal chlorides. Such accumulations, in turn, are detrimental to the quality of electrodeposits of fuel elements. Hence, at particular intervals, the FPs need to be removed from the electrolyte. The well-known actinide drawdown process (ADDP), which utilises Li-assisted reductive extraction, has been employed thus far. However, the high reactivity of Li makes it non-selective, resulting in poor separation. In this context, the conversion of soluble chlorides to respective insoluble oxides/ oxychlorides was investigated earlier on a 30 g scale to achieve separation between actinides and other FPs[2] As the results of smaller-scale experiments were promising, the same process was taken up for scale-up.

In the present study, gaseous sparging experiments were carried out using (1) oxygen, (2) wet oxygen, and (3) wet argon at a 250 g scale. The aforementioned gases were passed through the LiCl-KCl-UCl_3 melt at 773K. The reaction and the products were analysed by cyclic voltammetry (CV), IR and UV-Vis Spectroscopy. Analysis of the results shows a nearly complete conversion for the UCl_3.

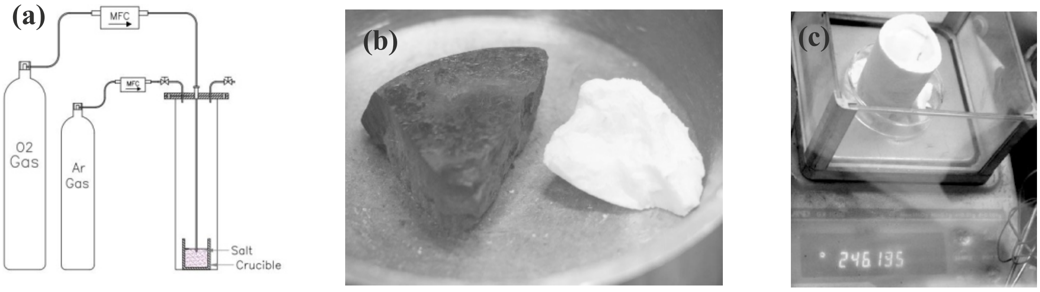

Fig. 1 (a) Schematic of oxygen sparging setup (b) Chlorinated LiCl-KCl eutectic salt (white) and UCl_3 loaded LiCl-KCl (purple) (c) UCl_3 loaded LiCl-KCl salt sparged with oxygen, showing conversion of purple salt to a yellow coloured salt

Keywords: *Pyrochemical process, ADDP, Gaseous sparging, Used Salt treatment*

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Mixer-settle runs with Y-Sr feed solutions using Tributyl Phosphate (TBP) and Tri-iso-amyl phosphate (TiAP)

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Yttrium has many useful applications and solvent extraction plays a key role in the separation and purification of Y from ore. ^{89}Sr (pure beta emitter; $T_{1/2}$ = 50.53 d) is used for palliative care of bone metastasis. ^{89}Sr is produced from ^{89}Y by (n, p) reaction in fast reactors [1]. Among the various extractants reported for the separation of Sr from Y by solvent extraction, tributyl Phosphate (TBP) and tri-iso-amyl phosphate (TiAP) are suitable solvents for effective separation [2]. In this context, measurement of distribution ratios of Y(III) as a function of nitric acid and extractant concentration for both TBP and TiAP based solvents has been carried out. The distribution ratios (D) for Y increases with increase in nitric acid as well as extractant concentration (Fig.1). D values were also measured for Sr as a function of nitric acid concentration and it was found to be negligible (<0.01). Mixer-settler runs were carried out with neat TBP and TiAP solvents. A feed solution containing Y around 99.25 g/L and Sr around 1 g/L was prepared in 8.7 M HNO_3. A sixteen stage ejector mixer-settler facility was employed for carrying out mixer-settler runs and the working mechanism of the ejector mixer-settler unit is presented elsewhere [2]. Separation of Y from Sr was carried out in extraction run with neat TBP and TiAP solvents. The concentration of Y in raffinate was found to be about 7.30 and 8.41 g/L, respectively in the case of TBP and TiAP and the extraction of Y by neat TBP and TiAP was found to be about 92.64 and 91.52%, after 16 stages indicating that some more stages are required for quantitative extraction of Y and the extraction of Sr is found to be negligible. The organic and aqueous stage profiles for Y are shown in Fig.2 and the concentration of Y decreases from stage 1 to 16 indicating transfer of Y from aqueous to the organic phase. The concentration of nitric acid in the aqueous and organic phase in about 7-8 M and 3 M, respectively from stages 1 to 13 and there is decline in acid concentration beyond this stage. Subsequently stripping of Y from loaded organic phase was carried out with 0.01M HNO_3 by feeding loaded organic phase at the 16th stage and 0.01 M HNO_3 at the 1st stage with flow rates of 6 mL/min. The concentration of Y in the loaded organic phase (feed to the strip cycle) was about 38.12 and 33.96 g/L in the case of TBP and TiAP and it was found BDL (0.2 g/L) after 16 stage of stripping. Quantitate stripping (>99.9%) of Y is achieved within 8 and 10 stages in the case of TBP and TiAP. The concentration of Y in the aqueous and organic phase decreases from stage 16 to 1 revealing that Y is back-extracted into the aqueous phase. The concentration of Sr is found to be BDL in all strip samples. These studies are useful for the development of flowsheets for separation of Y from ore and Y-Sr feed solutions.

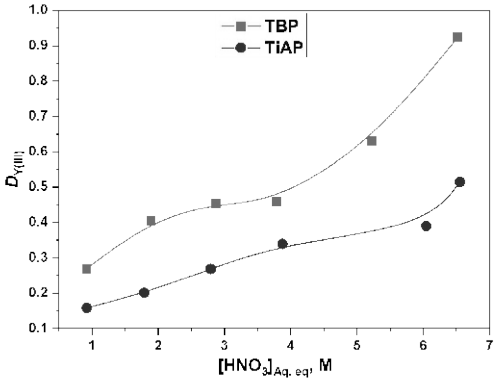

Fig.1 *Distribution ratios for Y(III) by TBP and TiAP as a function of nitric acid concentration (Y: 10 g/L and O/A: ~1)*

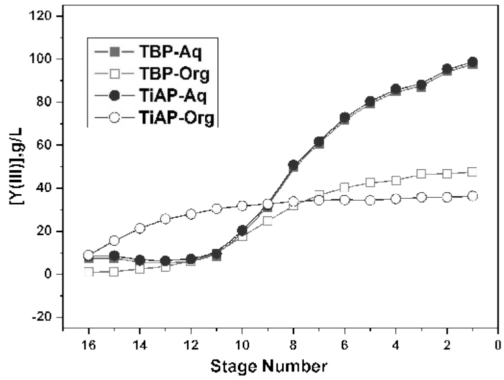

Fig.2 *Organic and aqueous stages profiles for Y(III) during the extraction run by neat TBP and TiAP in mixer-settler runs*

Key words: *Y(III), Solvent Extraction, TBP, TiAP, Mixer-settler*

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Synthesis and Chromatographic Studies of U, Th and Lns using TDDGA

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The separation of uranium (U), thorium (Th) and lanthanides (Lns) is important for experimental determination of burn-up in irradiated fuel samples. The chromatographic based methods are used for the separation of these elements from the complex matrices. The extraction chromatographic method offers selectivity for the elements and is a field of consideration for the better separation [1]. In view of this, chromatographic studies were carried out using N,N,N,N-Tetradecyl diglycolamide (TDDGA) as the column modifiers and compared with N,N,N,N-Tetraoctyl diglycolamide (TODGA). TDDGA was synthesized by reacting diglycolyl chloride (2,2-oxydiacetyl chloride) with didecylamine in the presence of triethylamine, yielding the product in the range of 60–70%.

TDDGA was subsequently used to modify a C18 reversed-phase column by passing a 0.1 mM solution of TDDGA in a 65:35 (v/v) acetonitrile–water mixture through a PRP-C18 column (150 mm × 4.6 mm) at a flow rate of 0.5 mL min^{-1}. After completion of coating, the column was washed with water at the same flow rate. Chromatographic studies show that decrease in retention of U and Th with decrease in pH of mobile phase, however, La and Lu does not show any retention at any pH (Fig. 1). As seen in Fig. 2, retention times of U, Th, La and Lu were reduced compared to those observed with TODGA-coated columns under identical experimental conditions. The difference in behavior between TODGA and TDDGA is helpful for the exploring the separation.

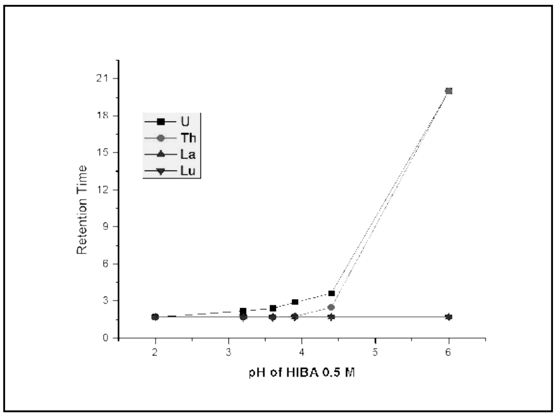

Fig. 1: *pH Study on TDDGA column*

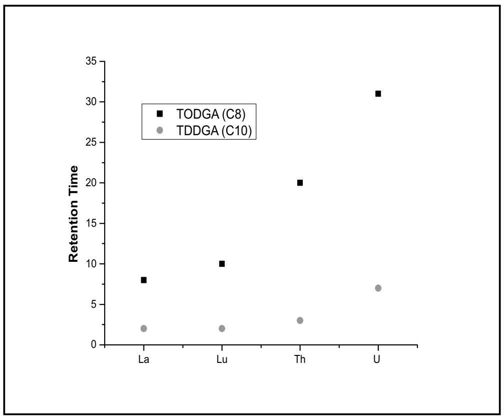

Fig. 2: *Comparison of retention of U, Th, La & Lu on TODGA and TDDGA coated column*

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Microwave based ICP-OES for Metallic Impurities Determination from U_3O_8 Matrices

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Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) is well established & widely used sensitive, accurate method for simultaneous determination of trace metallic impurities viz.; Al, Ag, B, Be, Cd, Dy, Gd, Sm, Ca, Mg, Co, Cr, Cu, Eu, Fe, Mn, Mo, Ni, Pb, Sn, Si, W, Zn (*abbreviated as metallic impurities hereafter)* in uranium matrices such as PFBR (U, Pu)O_2 MOX fuel samples [1]. Recently, microwave-sustained (cerawave technology based) inductively coupled atmospheric-pressure plasma has been proposed as an alternative to conventional ICP-OES for determination of elemental composition of complex samples [2, 3]. Cerawave; a kind of microwave; when applied with an alternating potential the material creates a bulk polarization current, resulting in a hundred times higher efficiency current producing hundred fold less heat in the oscillating coil which is air cooled eliminating the water chiller requirement for cooling. System has microwave plasma source of 1000W based on Cerawave technology, air cooled and runs on nitrogen. It has Echelle spectrometer which simultaneously measures the entire wavelength: 194 nm - 625 nm, simultaneous: up to 625 nm. Three carrier gases were utilized viz.; Nitrogen Gas, Argon Gas & Zero Air for different purposes. It's very compact unit with dimensions 74cm x 62cm x 50cm.

The aim of this study was to investigate, microwave based ICP-OES capabilities for the analysis of metallic impurities from uranium matrices. For this, calibration of instruments was carried out initially by five variable standard solutions of above mentioned metallic impurities. Typical calibration graph is presented in Fig. 1 while Fig. 2(a) & (b) presents typical sharp peaks obtained for same. From calibration data obtained; detection limits were calculated for different metallic impurities and obtained up to ppb level. By choice of suitable wavelength for elements Ag, Al, B, Ca, Cd, Cr, Cu, Dy, Eu, Gd, Mg, Mn, Ni, Sm detection limit calculated were 8.5, 12, 20, 62, 120, 8, 30, 12, 8, 63, 33, 101, 75, 28 ppb respectively. Relative standard deviation (RSD) obtained were ranging from 1% to 5% for elements Ag, B, Al, Ca, Cr, Cu, Dy, Eu, Mg,, Mn, Ni, Sm while it was 14% for Gd. Only for cadmium it was >50%.

Required powdered Certified Reference Materials (CRM) - U_3O_8 viz.; CRM-1 & CRM-2 were dissolved in the conc. HNO_3 medium and uranium matrix were removed by conventional method of TBP extraction using solvent extraction technique. Raffinate was subjected for microwave based ICP-OES analysis after acidity adjustment & dilution which was carried out on basis of detection limits calculations. Results obtained were satisfactory as accuracy in terms of expected concentration & obtained concentration were 90.9, 90.6, 12.5, 88.9, 9.5, 77.3, 94.1, 75.0, 51.0, 42.9, 82.0, 100.0, 98.3, 38.7% for elements Ag, B, Al, Ca, Cr, Cu, Dy, Eu, Mg, Mn, Ni, Sm respectively. The lower accuracy for some elements might be attributed to interferences obtained and may be improved by selection of non-interfering wavelengths. Typical 3mL solutions were required for the analysis. The advantages of new microwave ICP-OES were; simultaneous analysis of multiple elements at ppb level in lesser time as compared to conventional ICP-OES, air cooled plasma unit eliminating need of chilled water circulation inside glove box, compact size, etc. In future studies; analysis of nuclear fuel samples and respective more fine detection limits are envisaged after adaption of instrument for said analysis along with comparison of results with same standard and sample analysis with CCD-ICP and DC-Arc methods.

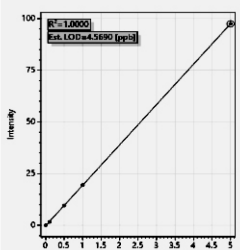

***Fig.1:** Calibration graph for silver.*

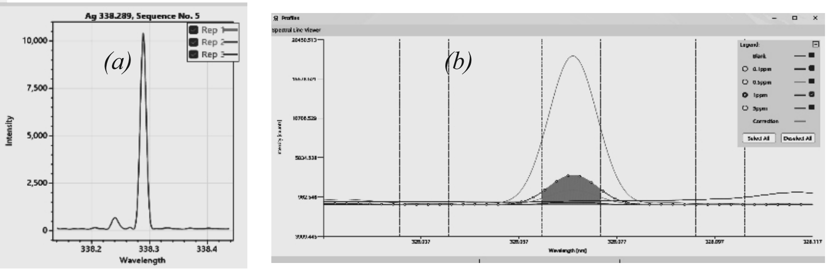

***Fig.2(a):** Typical peak for silver in Single standard, (b) Combine graph of different standards.*

***Key words:** Microwave Based ICP-OES, Metallic Impurities, Uranium Standards, Matrices.*

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Dissolution Behavior of $(U_{0.77}Pu_{0.23})O_2$ Mixed Oxide (MOX) Fuel in Nitric Acid

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FF-INRP(O) is currently fabricating (U, Pu)O_2 MOX fuel for upcoming prototype fast breeder Reactor (PFBR) at Kalpakkam, India. Studying the dissolution behavior of (U, Pu)O_2 MOX fuel in nitric acid is essential for optimizing parameters in aqueous reprocessing. Additionally, the bulk homogeneity of the (U, Pu)O_2 MOX fuel is critical, as any inhomogeneity in its composition can result in uneven dissolution. (U, Pu)O_2MOX up to 35% PuO_2 gets completely dissolved in HNO_3[1]. Typical challenges during dissolution of high Pu containing MOX fuel include slower dissolution rates due to the higher Pu content ensuring criticality safety and prevention of Pu hydrolysis. Typical chopping time for Pressurized Heavy Water Reactor (PHWR) fuel is 24-30hrs and strip acid (~0.01M HNO_3) is used to prevent the impact of chopped fuel pieces on the dissolver basket. While in fast reactor fuel reprocessing chopping time will be 7-8 days. Due to the high plutonium (Pu) concentration in the fuel, we cannot use a 0.01M strip acid, as it may lead to the hydrolysis of plutonium. Moreover, the dissolution of MOX fuel was carried out with 11.5M HNO_3 which leads to a huge dilution of the dissolved solution to maintain the final acidity from 9M to 4M. Hence, the dissolution behavior of (U, Pu)O_2 MOX at different nitric acid concentration and different temperature need to be investigated. Dissolution behaviour of dimensionally rejected MOX fuel pellets have been extensively carried out in 8-15.5M HNO_3 at different temperature under stirring condition of 600rpm [2]. Present study deals with the dissolution behavior study of $(U_{0.77}Pu_{0.23})O_2$ dimensionally accepted MOX pellets in 12M and 2M HNO_3 at room temperature, 80°C and 90°C. The annular MOX pellets employed for the studies were fabricated by the conventional powder metallurgy route. During the dissolution of MOX pellets, UO_2 and PuO_2 present in the sintered pellet gets converted to U(VI) and Pu(IV) ions respectively in the solution. Hence the extent of dissolution is determined by measuring the concentration of these actinide ions in the solution. In the present study, two annular $(U_{0.77}Pu_{0.23})O_2$ MOX pellets weighing 1.63± 0.05g were dissolved in 60mL HNO_3 at different acidity in each experiment. Samples were taken at regular intervals for the analysis of U and Pu by by Ti(III) reduction and Drummond & Grant potentiometric titration method. The concentration profiles of all these species were generated during the course of the reaction and displayed in **Fig 1**. Rate of dissolution of U and Pu is obtained almost same. In different experiments indicating that $(U_{0.77}Pu_{0.23})O_2$ pellets have complete solid solution. This behavior is different compared to previous study [2] where U was preferentially dissolved over Pu due to presence of Pu agglomerates in physically rejected pellets. Dissolution rate increases with the temperature. Two pellets got completely dissolved in 12M HNO_3 for 420min and 360 min at 80°C and 90°C respectively. At room temperature, 97.9% U & Pu dissolved in 220hrs in 12M HNO_3. If we decrease the acidity of nitric acid concentration to 2M, only 28% of U and Pu were getting dissolved in 220hrs. At 2M HNO_3 concentration, only 16.18% U & Pu gets dissolved in 8days at room temperature. During chopping of fuel, (U, Pu)O_2 should not get dissolved as it leads to breach of activity. So, further studies will be carried out at lower acidity of HNO_3(1M or 0.5M).

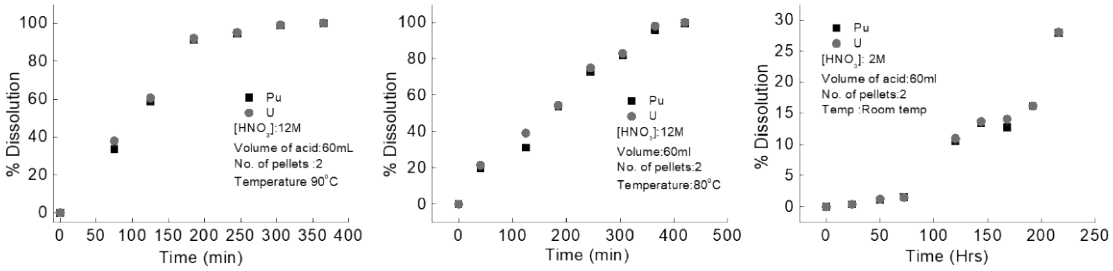

Fig1. *The percentage of Dissolution for U, Pu at different temperature (90^0C, 80^0C and room temperature) and at various acid molarity*

Key words: *Dissolution, $(U_{0.77}Pu_{0.23})O_2$MOX, nitric acid.*

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Spectrophotometric Evaluation of Zirconium with Substantial Uranium Content – Application to Zr-U

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Adopting the UV-Vis spectrophotometric technique, a method was developed to determine zirconium in the presence of large amount of uranium. The Zr(IV) is always in competition with the heavy metal ions and fluoride, particularly in U-Zr dissolution studies. Zr(IV) is often complexed with heavy metal ions, forming a stable complex, which presents a significant challenge in Zr(IV) estimation [1]. The primary objective of this work is to develop a method for estimating Zr(IV) in the presence of large amount of heavy metal ions like U(IV). For this purpose, various complexing agents have been employed for the spectrophotometric determination of Zr(IV), including thoron, alizarin Red S, arsenazo III, xylenol orange, PAR, and chrome azurol s [2]. The selection of a complexing agent is often challenging in a complex matrix, as there are always interfering ions, and no complexing agent is selective to Zr. In this work, a simple use of ascorbic acid as a suppressing reagent to eliminate the interference of U(VI) in the estimation of zirconium in both aqueous and organic media by Br-PADAP as a chromogenic agent was developed and validated. Ascorbic acid forms a stable 1:1 stoichiometric ratio complex with U(VI) at a specific pH 4.2-4.5, which effectively ties up the U(VI) ions, so that it does not interfere with the Zr(IV) determination and acts as a masking agent. To ensure that all U(VI) is effectively masked in a U-Zr sample for Zr(IV) estimation, a sufficient excess of ascorbic acid (10%) is used, masking the effective ratio in the solution at a 1:1 level. Linearity was acquired from absorbance at 585 nm, achieved over the concentration range of 0.1 to 1 ppm of Zr with a molar absorptivity of 89,574 L.mol^{-1}.cm^{-1} and Sandell's sensitivity of 0.003 µg.cm^{-2}. Zirconium is quantified in various Zr-U samples using spectrophotometric detection with a classical univariate calibration, suppressing uranium with ascorbic acid. The obtained results are compared with those from TTA extraction, followed by the spectrophotometric method and also with alternative techniques such as ICP-AES and are presented in the table.1. Fig. 1 & 2 represent the typical absorption spectra of Zr when complexed with Br-PADAP at pH 4.2 using a sodium acetate buffer. The developed methodology is applicable for estimating zirconium in U-Zr dissolution streams from reprocessing spent fuel.

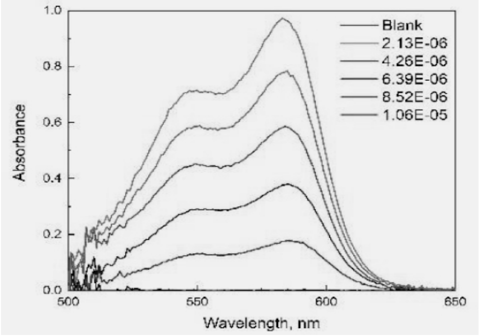	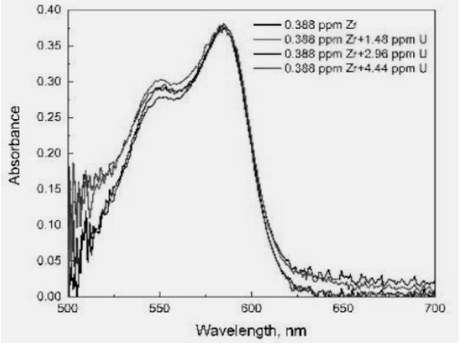
Fig 1: *Typical absorption spectrum of Zr-BrPADAP at pH 4.2*	***Fig 2:*** *Typical absorption spectrum of Zr+U-BrPADAP at pH 4.2*

Table 1. *Comparison of estimation of zirconium in U-Zr samples by three different techniques*

Sample ID	Concentration of Zirconium (g/L) in diff U Samples. S.No 1 (U 115 g/L), 2 (U 68.79 g/L) & 3 (U 126.4 g/L)		
	HTTA extraction, followed by Arsenazo III	ICP-AES	Present method
1	4.57±0.7	4.3	4.31±0.2
2	2.84±0.5	2.5	2.39±0.3
3	5.14±0.4	4.9	5.02±0.7

Keywords: Zirconium, Spectrophotometry, Br-PADAP, U-Zr dissolution, Uranium, Reprocessing

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Centrifugal Separation of Ammonium Diuranate

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Separation of ammonium diuranate (ADU) is a challenging. The morphology of ADU precipitate depends upon primary nucleation, crystal growth, aggregation and breakage. The ADU settling is time-consuming process and depends upon the morphology. Currently, gravity-based filtration methods for ADU separation is employed in DFRP plant. When the ADU contains traces of plutonium, filtration must be performed within a glove box, posing practical difficulties such as prolonged filtration times and increased manual intervention. To address these issues and reduce both filtration time and manual handling, the existing 50 mm centrifugal contactor design was modified to enable glove box compatibility. Preliminary experiments were conducted to evaluate the feasibility of the modified centrifuge bowl for ADU separation and filtration.

In this study, ADU slurry was generated by reacting ammonium hydroxide with 0.5 M HNO_3 containing 4g of uranium. The resulting slurry was fed into the 50 mm centrifuge and the outlet solution was recirculated three times. The entire experiment was completed in 30 minutes. Analysis of the final filtrate indicated a uranium concentration of less than 5 mg/L, while the ADU precipitate collected from the centrifuge, when dissolved in nitric acid, contained a total uranium quantity of 3.94 g. These experimental results demonstrate that ADU slurry can be quantitatively separated using the developed centrifuge, with less than 1.5% material loss. The study also confirms that the modified centrifuge is suitable for deployment in a glove box, effectively reducing filtration time and minimizing human intervention. Figure 1 shows a photographic view of the 50 mm centrifuge experimental setup, and Figure 2 displays the ADU precipitate settled inside the centrifuge.

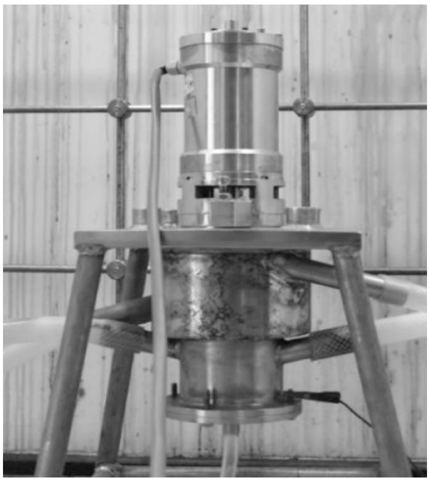

Fig 1: *Photographic view of 50 mm centrifuge experiemental setup*

Fig 2: *Photographic view of ADU precipitate collected in the centrifuge*

Key words: *Ammonium diuranate, Centrifuge, Slurry filtration*

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Development of T2EHDGA-impregnated Resin

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Solvent extraction process is used as separation technique in industrial scale processes wherein an organic based solvent plays vital role in separation of the solute of interest. Solvent extraction based partitioning flow-sheet is being deployed in the back-end of the fuel cycle for management of variety of radioactive liquid waste streams using novel solvents. One of the novel solvents, viz T2EHDGA [N,N,N',N'–tetra (2-ethylhexyl) diglycolamide], has been earlier synthesized indigenously for selective co-extraction of actinides and lanthanides from radioactive liquid waste[1]. In the Indian context, use of fixed bed sorbent-based processes has proven to be very successful in low and intermediate level liquid radioactive waste (LILW) treatment. To enable utilization of this solvent in a column mode for LILW, a process was developed. This involves impregnation of solvent on "Duolite^{TM}" sorbent beads as substrate. The duolite sorbent beads used were commercially available adsorbent grade non-functionalized resin with particle size 0.5 – 0.6 mm with surface area 610 m^2/g and pore volume 790 mm^3/g. The beads were washed thoroughly using acetone. Rotary evaporator was used for impregnation of T2EHDGA in different concentration such as 20%, 25% and 30%. The flow sheet of the procedure is shown in the fig.1 below. The T2EHDGA-impregnated beads were dried till it achieved free flow condition in evaporator. The beads were polymer coated in the laboratory with polyvinyl alcohol and sodium alginate solutions[2] with the help of mechanical stirrer. The polyvinyl alcohol and sodium alginate form a physically crosslinked network which enhances mechanical strength and better film forming property. A thin plastic like coating is formed over the loaded organic which protects the adsorbed solvent. After drying, the beads were stirred in boric acid solution using mechanical stirrer. Polyvinyl alcohol chemically cross links with borate ions. Treatment with boric acid increases the glass transition temperature of the polymer[3]. The polymer coating of polyvinyl alcohol, sodium alginate and boric acid gives acid and heat resistance to solvent beads. This leads to the enhanced life of the impregnated beads. The prepared beads are shown in Fig.2. Distribution coefficient (K_d) with respect to Am in nitric acid conditions was evaluated to assess their performance. For this 0.2 gm TEHDGA loaded resin beads were equilibrated with 10 mL of Am-241 in 3.5M nitric acid medium for 4 hrs and then the activity of initial and final solutions with respect to Am-241 were determined using gross alpha counter having ZnS (Ag) scintillation detector. Different concentrations of TEHDGA loaded resins Kd values were determined with respect to Am-241. As expected, it was observed that as the concentration of T2EHDGA increases, the K_d value increases. The values are indicated in the table-1 below. The stripping of loaded resin beads was observed 99% using 0.01M nitric acid solution. The results indicate, prima facie, the feasibility of use of these beads in column-mode. The studies are being continued to check the performance of prepared beads in column mode.

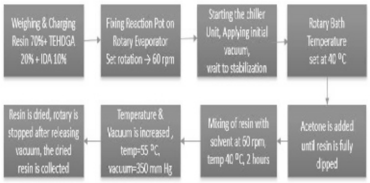

Fig.1 *Flow sheet of Resin Preparation*

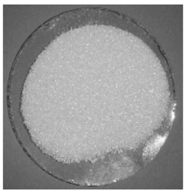

Fig.2 *T2EHDGA Resin*

Table.1 *Kd values of resin*

Sr No	TEHDGA concentration on resin bead (%)	Kd value (mL/g)
1	20	990
2	25	2000
3	30	2800

Key words: T2EHDGA*, polymer coating, column mode*

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Operating Region of 40 mm ID Annular Centrifugal Extractor

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Centrifugal extractor is the candidate equipment for solvent extraction operation in a Fast breeder reprocessing plant due to its low holdup, short contact time and compact size. 40 mm ID annular centrifugal extractor is selected and installed in the DFRP plant to process FBTR and PFBR fuels. In this work, the operating region for 40mm ID annular centrifugal extractor (back extraction bowl) was generated by conducting non-mass transfer flooding experiment at different O/A ratio (from 0.01 to 10) at constant rotating speed (3600 rpm). Flooding limit is defined as the throughput at which carryover of other phase approaches 1%. 0.01 N HNO_3 pre-equilibrated with 30% TBP in NPH is used as an aqueous phase. Similarly, 30% TBP in NPH pre -equilibrated with 0.01 N HNO_3 as an organic phase. Experimental results shows that the above bowl can be operated up to 72 L/h. The photographic view of single stage 40 mm ID ACE setup is show in Figure 1 and experimental result is shown in Figure 2.

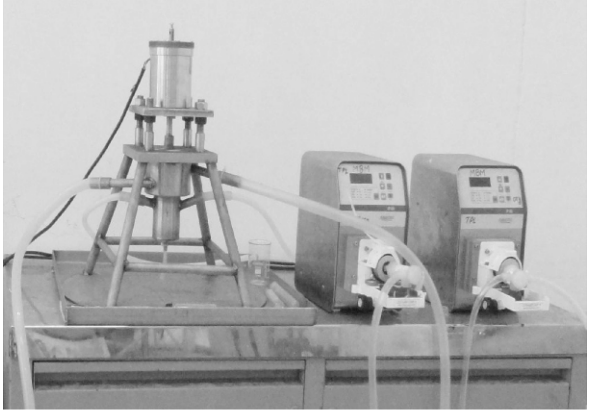

Fig. 1: *Photographic view of single stage 40 mm ID ACE setup*

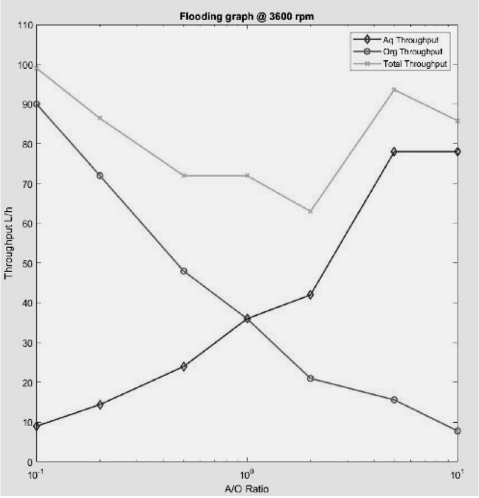

Fig. 2: *Operating region for 40 mm ID ACE at 3600 rpm w.r.t to A/O ratio*

Key words: *Nuclear Reprocessing, Annular Centrifugal Extractor, Flooding Curve, Solvent Extraction*

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Impact of Dissolved TBP on Plutonium Extraction in the Diluent-Wash Step of the Recovery Cycle

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The plutonium oxalate filtrate generated during reconversion operation, has a typical composition of 20–50 ppm Pu (IV), 100–200 ppm dissolved TBP, and 0.1–0.15 M oxalic acid in about 2.5–3.5 M nitric acid medium. In recovery cycle, the oxalate destruction is desired for the quantitative recovery of Pu. Oxalate destroyed using $KMnO_4$ can be carried out before the diluent-wash. In alternate method, catalytic oxalate destruction using Mn^{2+} can be carried out after the diluent-wash. In either of the cases, a critical concern is the potential formation of extractable Pu–TBP which can get transferred to n-DD during the diluent-wash. The present study systematically examines this possibility through experimentation.

1.1 M TBP/n-DD was equilibrated with an equal volume of 5M HNO_3 and 5 M HNO_3 with 0.1 M oxalic acid independently. The resultant aqueous phases containing dissolved TBP were spiked with 68 mg.L^{-1} of Pu(IV) and were subjected to diluent wash using n-DD at A/O ratios of 5:1and 1:1 respectively. After complete phase disengagement, both phases were analyzed for Pu content using radiometry. The results are summarized in Table 1.

Table 1 *Pu distribution during diluent wash*

Sample no.	$[H_2C_2O_4]_{Aq}$ / M	A/O ratio	[Pu] / mg.L^{-1} in org	[Pu] / mg.L^{-1} in aqueous	D value	% Pu Extracted
1	0	1:1	0.55	67.51	0.008	0.81%
2	0	1:5	1.19	67.93	0.018	1.72%
3	0.1	1:1	0.36	67.75	0.005	0.53%
4	0.1	1:5	0.11	66.85	0.002	0.16%

Based on the results, it can be concluded that irrespective of the experimental conditions studied, the maximum Pu removal through diluent wash was below 2%. In the absence of oxalic acid, a higher O/A ratio (1:5) slightly increases Pu extraction. However, the presence of 0.1 M oxalic acid markedly suppresses Pu extraction, as Pu–oxalate complexes remain predominantly in the aqueous phase and have negligible affinity for TBP. These findings confirm that the diluent-wash operation offers a high degree of process safety with negligible Pu contamination of the diluent stream.

Key words: *Diluent wash, Oxalate destruction, Supernatant*

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Alpha Degradation Study of Phosphate and Phosphonate Based Solvents

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The third phase formation is an important concern in the solvent extraction of tetravalent metal ions such as plutonium (IV), thorium (IV), and zirconium (IV) using tri-n-butyl phosphate (TBP). This unwanted phase hinders efficient metal recovery. Our earlier studies have shown that phosphonate-based solvents such as dibutylbutyl phosphonate (DBBP) and diamylamyl phosphonate (DAAP) exhibit a lower tendency to form third phase compared to TBP [1]. This reduced third phase tendency, along with their superior actinide extraction efficiency arising from the higher basicity of their phosphoryl oxygen, makes phosphonates promising alternatives to TBP for fast reactor fuel reprocessing [2]. In fast reactor fuel reprocessing, the solvent is exposed to extreme radiation from actinides and fission products, leading to the formation of various degradation products. Even at low concentrations, these metal ions can cause significant changes in physico-chemical properties resulting in reduced decontamination factors and increased phase disengagement time after organic–aqueous mixing. To evaluate the feasibility of phosphonate-based solvents for fast reactor fuel reprocessing, radiation-induced degradation studies of these solvents were carried out and compared with TBP. The objective of the present study is to understand the effect of alpha-induced degradation on the stripping of plutonium from 1.1 M solutions of DBBP, DAAP, and TBP in n-dodecane.

Solutions of 1.1 M DBBP, DAAP, and TBP were prepared in n-dodecane and pre-equilibrated with 4 M nitric acid prior to extraction of Pu. These organic phases were contacted with Pu feed solution (12 g/L), and the loaded organic phases were kept for alpha degradation. At different time intervals, aliquots of the organic phases were withdrawn, and plutonium was back-extracted using 0.5 M nitric acid at an aqueous-to-organic phase ratio of 1:1. This stripping was performed three times, followed by a final stripping using 1 M oxalic acid. Plutonium concentration was estimated by liquid scintillation counting after appropriate dilution. Figure 1 shows the amount of Pu retained in the organic phase after oxalic acid treatment as a function of time. As the degradation time increases, the alpha dose absorbed by the organic phase also increases, leading to the formation of degradation products that have a higher affinity for plutonium. Consequently, plutonium retention in the organic phase increases with time. Gamma-radiolysis studies of the phosphonates are also in progress, and the results will be compared with that of TBP under identical conditions.

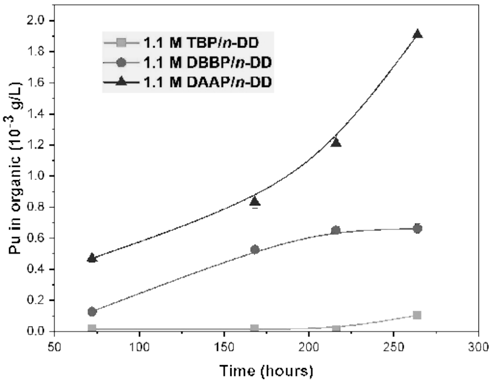

Fig. 1: *Pu in organic phase after oxalic acid treatment as function of time.*

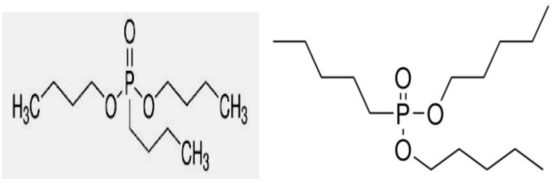

Fig. 2: *Structure of DBBP and DAAP respectively*

Key words: *DBBP, TBP, DAAP, Pu, Solvent Extraction.*

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Functionalized Metal Organic Frameworks for Efficient Extraction of Antimony from Aqueous Solution

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Antimony is a fission product generated during the irradiation of nuclear fuel having radionuclides such as ^{125}Sb ($t_{1/2}$ = 2.76 years) and ^{124}Sb ($t_{1/2}$ = 60.2 days). These isotopes are released into aqueous waste streams during spent nuclear fuel reprocessing, contributing significantly to the radiotoxicity of high-level waste. The efficient separation and recovery of antimony from such complex matrices are therefore essential for waste minimization and radiotoxic inventory reduction. In recent years, several studies have demonstrated that metal–organic frameworks (MOFs)—particularly Zr-based systems like NU-1000 and UiO-66 derivatives—are highly effective for Sb(III)/Sb(V) adsorption due to their tunable porosity and high stability.[1,2] In this study, a series of bimetallic Zr–Hf-based amino-functionalized metal–organic frameworks (Zr–Hf-MOF-1, 2, and 3) were synthesized via a solvothermal route using $HfCl_4$, $ZrOCl_2 \cdot 8H_2O$ in different ratios and 2-amino-1,4-benzenedicarboxylic acid (2-NH_2-BDC) as building units. The introduction of mixed Zr–Hf clusters enhanced framework stability and provided abundant Lewis acidic sites favorable for Sb(V) adsorption. The sorption performance was systematically evaluated as a function of pH and contact time. The maximum antimony(V) uptake was observed at pH ≈ 4, achieving ~98 % removal efficiency for Zr–Hf-MOF-2, markedly higher than that of UiO-66-NH_2(Hf) (~86 %). Adsorption equilibrium was reached within 40 min, and kinetic analysis revealed excellent fitting to the pseudo-second-order model (R^2 = 0.9998) with a maximum adsorption capacity (q_e) of 214.8 mg g^{-1} for Zr-Hf-MOF-2 where Zr:Hf molar ratio was 2:1. Further the kinetic data was fitted with pseudo-first order and pseudo-second order equation where pseudo-second order showed greater fit, indicating chemisorption as the rate-determining step. The superior performance is attributed to the synergistic effect of Zr–Hf cluster substitution and amino-functionalized linkers, which collectively promote strong coordination with Sb(V) oxyanions. These results demonstrate that mixed-metal functionalized MOFs represent a promising new class of sorbents for the selective extraction of antimony and other fission products from nuclear process streams.

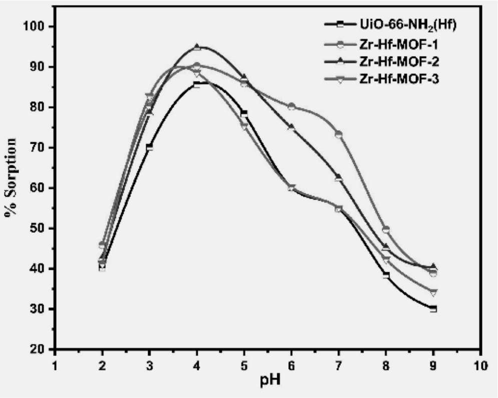

Fig.1: Variation of % sorption of Sb as a function of pH with parent and bimetallic MOFs

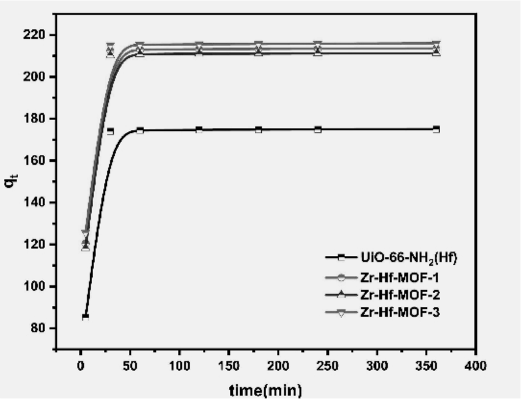

Fig 2. *Variation of Sorption capacity as a function of time*

Key words: *Bimetalllic MOFs, Synthesis, Characterization, Antimony, Sorption*

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Thermal Decomposition Behavior of N,N-didodecyl-N',N'-dioctyl diglycolamide

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The long half-lives and high decay heats of Am and Cm nuclides demand the long-term surveillance and large volumes at deep geological repositories for the vitrified high-level liquid waste (HLLW), generated from the reprocessing of spent nuclear fuels. In view of this, partitioning (P) of trivalent actinides from HLLW followed by transmutation (T) into stable or short-lived nuclides (P&T) is considered as the best strategy for the safe management of HLLW[1]. Among various solvents studied worldwide for the separation of trivalent f-ions from HLLW, diglycolamide (DGA) based extractants were proven as more promising. However, most DGAs including the well studied *N,N,N',N'*-tetraoctyl diglycolamide (TODGA) and *N,N,N',N'*-tetra-2-ethylhexyl diglycolamide (TEHDGA) form an undesirable third phase and demand for the addition of phase modifier-free during the separation of trivalent f-ions from HLLW, originated from fast reactor fuel reprocessing [2]. To overcome these challenges, *N,N*-didodecyl-*N',N'*-dioctyl diglycolamide (D^{3}DODGA) was developed as a modifier extractant for the separation of trivalent lanthanides and actinides from HLLW of fast reactors. Though the studies related to the extraction and third phase formation behaviors, and stability against radiation induced damage etc were studied in detail, its stability against the thermal decomposition has not been reported in the literature. Hence, the present work is aimed at studying the thermal decomposition behavior of D^{3}DODGA and comparing the results with that of well studied TODGA and TEHDGA.

The solvents, TODGA, TEHDGA and D^{3}DODGA were synthesized and purified by a similar procedure described elsewhere [3]. The thermal degradation of these compounds was studied using Setsys Evolution thermal analyzer. The study was conducted up to 900ºC with a heating rate of 10 K/min from room temperature in the presence of argon as a carrier gas. Figure 1 shows that the decomposition onset temperature of D^{3}DODGA, TEHDGA and TODGA are 140ºC, 170ºC and 200ºC respectively. All three DGAs undergoes complete decomposition with no residue above 465ºC. D^{3}DODGA undergoes decomposition in three stages, the first being 4.5% of decomposition in the temperature range of 140ºC to 230ºC, the second one with 9% decomposition at temperature below 325ºC and the remaining decomposes before 465ºC. On the other hand, TODGA and TEHDGA begin to decompose at 200ºC and 170ºC respectively, and undergo complete decomposition before 440ºC and 425ºC respectively. Differential thermal analysis of DGAs was carried out and the results are shown in figure 2, and were used to calculate the energy associated with the decompositions.

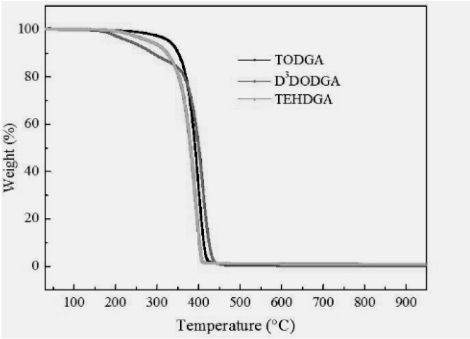

***Fig 1.** Thermogravimetric curves of DGAs.*

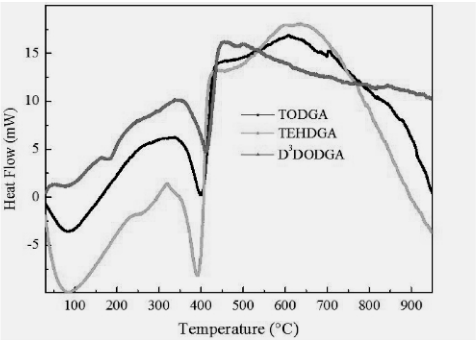

Fig 2. Differential thermal analysis of DGAs.

***Key words:** High-level liquid waste, Diglycolamide, Thermograimetry, Solvent extraction, Third phase, Actinide*

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Counter-Current Extraction and Stripping of Nd(III) into TEHDGA using Six Stage Annular Centrifugal Extractor

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N,N,N',N'-tetra-2-ethylhexyl diglycolamide (T2EHDGA) is one of the most widely studied solvents for the separation trivalent lanthanides and actinides from high-level liquid waste (HLLW) generated from the aqueous reprocessing of spent nuclear fuel [1]. The lower metal loading capacity and higher viscosity of T2EHDGA demands the addition of a phase modifier during the trivalent f-ions extraction from the HLLW of fast reactor fuels. In view of this, isodecyl alcohol (IDA) modified T2EHDGA was studied for the separation of target metal ions from HLLW. The annular centrifugal extractor (ACE) is the preferred solvent extraction equipment for the separation of actinides from the highly radioactive solutions of complex mixtures. In view of these, the present work is targeted to verify the possibility of employing a multistage ACE for the separation of trivalent f-ions from HLLW of fast reactor origin using 0.4 M T2EHDGA-10%IDA/*n*-dodecane.

Extraction of a trivalent f-ion representative, Nd(III), from 4 M nitric acid was carried out into the organic solution composed of 0.4 M T2EHDGA+ 10% IDA /*n*-dodecane using a six-stage ACE having a rotating bowl of 40 mm inner diameter. A solution of 0.05 M Nd(III) (the concentration equivalent to the highest expected concentration of total lanthanides and actinides in a typical HLLW) in 4 M nitric acid was used as the aqueous feed for the extraction. The aqueous and organic solutions were fed with equal flow-rates of 100 mL/min (A/O=1) in counter-current mode while the bowl was rotating at a speed of 3600 rpm. Both organic and aqueous samples were collected at regular intervals of time during all the extraction and stripping experiments. Similarly, samples from both aqueous and organic phases were collected from the bowls of each stage at the end of each experiment. The concentration of Nd(III) in both the phases was estimated by the titration against standard ethelene diamine tetraacetic acid (EDTA) using methylthymol blue indicator in the presence of hexamethelenetetraamine at pH 6. The acidity in each sample was determined by standard acid-base titration using standard sodium hydroxide in the presence of potassium oxalate.

The analytical results clearly indicated that the six-stage ACE setup reached steady state condition within ten minutes during all the extraction experiments under the operating flow-rate conditions. Data obtained from the stage-wise sample analysis shown that Nd(III) was extracted quantitatively within three stages of extraction. Subsequent to the extraction, the Nd(III) recovery from the loaded organic phase was carried out into dilute (0.03 M to 0.1 M) nitric acid using the same ACE under similar flow-rate conditions. The steady state was reached within 15 minutes of operation. Complete recovery of Nd(III) from the loaded 0.4 M TEHDGA-10%IDA/*n*-dodecane could not be achieved by the stripping solutions having the acidities above 0.1 M. This may be due to further increase in the concentration of nitric acid in the stripping solution, resulted from the release of extracted nitric acid by the loaded organic phase. Despite of this, a quantitative recovery of Nd(III) was achieved within 3 stages of stripping using the aqueous stripping solution with an acidity lower than 0.1 M. However, it is important to mention here that there was a milky white interfacial crud formation during the metal recovery into 0.03 M or lower nitric acid medium after the three stages of contact (4 to 6 stages), during the contact of lean organic phase with dilute acid medium. This may be due to the inappropriate interfacial tension and other physical properties of the system. Considering all these, the stripping was carried out using a solution of 0.03 M nitric acid. The studies clearly indicated that the quantitative recovery of Nd(III) from the loaded organic phase can be achieved by stripping with 0.03 M.

Thus, the current study indicates a multi-stage ACE is suitable to carry out the trivalent f-ion extraction and stripping by 0.4 M T2EHDGA-10% IDA/*n*-dodecane from nitric acid solutions in counter-current modes of operation.

Key words: *Diglycolamide, Minor actinides, Annular centrifugal extractor, Solvent extraction, Neodymium*

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Extraction of Trivalent Lanthanides and Actinides with Combined Extractant Impregnated Polysulfone Bead

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Extraction of trivalent lanthanides and actinides have been widely exploited with series of different ligands i.e., acidic extractants di-(2-ethylhexyl)phosphoric acid (D2EHPA), diamides, diglycolamides etc [1.] These ligands have shown promising results at different acidities with D2EHPA being acidic extractant works in pH range and diglycolamides being neutral extractants show high extractability at higher feed acidity. The presence of a neutral and an acidic extractant in a combined ligand system enhances the metal ion extraction efficiency and selectivity. A combined ligand containing an acidic extractant, D2EHPA and a neutral extractant, *N,N,N',N'*-tetrapentyl diglycolamide (TPDGA) were employed in the preparation of a polysulfone based polymeric beads. Five different beads were prepared by varying the concentration of D2EHPA and TPDGA in the bead. The beads were characterized using Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and photo luminescence (PL) spectroscopy. The beads were subjected to uptake Am(III) from a wide range of concentration of nitric acid. A synergistic extraction [2] behaviour was noticed at 0.1 M and 6 M HNO_3 (Fig. 1a) with the bead containing 30% TPDGA+70% D2EHPA (mmol%), 70% TPDGA+30% D2EHPA (mmol%) and 50% TPDGA+50% D2EHPA (mmol%) respectively. In view of the mutual separation of trivalent lanthanides and actinides , extraction studies were carried out in 10 mM BTP at 1 M HNO_3 as holding agent in the aqueous feed which selectively binds Am(III)in line with HAHB principle, BTP being soft donor binds preferentially with Am(III) over Eu(III). Trivalent lanthanides will be selectively extracted with the combined beads leaving trivalent actinides in the aqueous feed. Separation factor (144 ± 4.3) of Eu(III) over Am(III) has been achieved at 0.5 M HNO_3 when experiment was done with individual metal ion in presence of aqueous soluble BTP. Sorption isotherm studies with mixed beads (3:7) at 0.1 M HNO_3 revealed best fitting with Langmuir isotherm model (Fig. 1b) indicating monolayer sorption with 12.8 mg/g Eu(III) maximum sorption capacity.

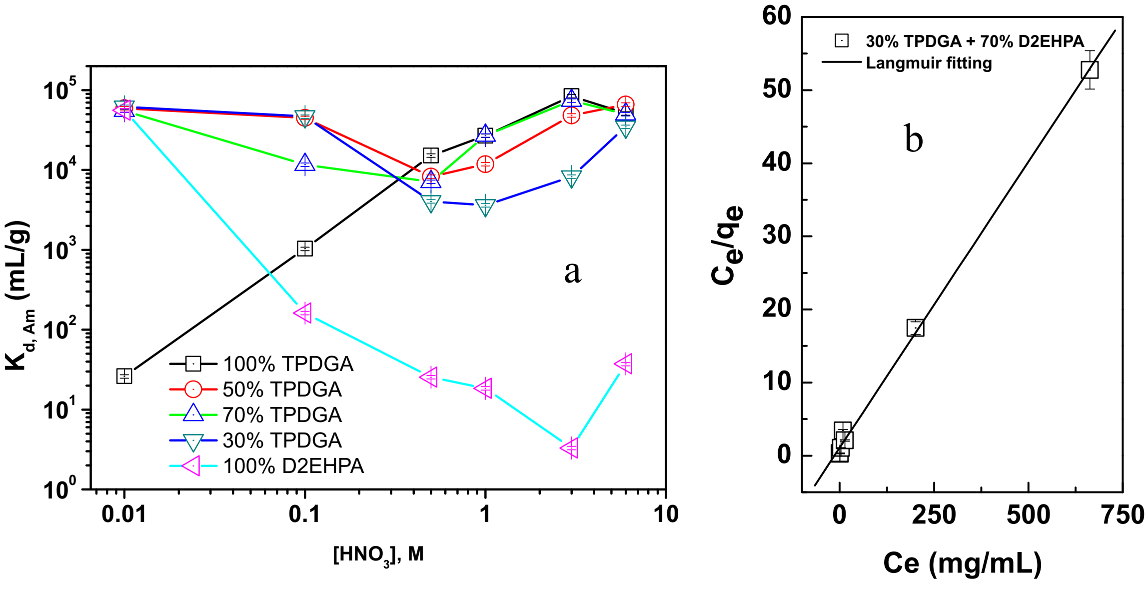

Fig 1. (a) *Am(III) uptake at different concentrations of nitric acid (b) Langmuir isotherm plot.*

Keywords: *Am(III), synergistic extraction*

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Solvent Extraction Study of Zr, Hf And Ti with Phosphonate and Phosphate Based Solvents using Simulated MK Feed Solution

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Owing to its low thermal neutron absorption cross section and excellent corrosion resistance zirconium is used as cladding for nuclear fuel, and as a structural material in thermal nuclear reactors [1]. Being a tetravalent metal ion, extraction of zirconium suffers from third phase formation with tri- n-butyl phosphate (TBP) based solvent; hence there is a need to develop alternative solvent. Our earlier studies revealed that phosphonate based solvents such as dibutylbutyl phosphonate (DBBP) and diamylamyl phosphonate (DAAP) exhibit lower third phase forming tendency than TBP [2]. Therefore the present study is about exploring the possibility of DBBP as an alternative to TBP for zirconium metal production. In India the production of zirconium metal was done by solvent extraction method by using zircon sand obtained from Manavalakurichi-Tamilnadu (MK grade).

Simulated MK feed solution was prepared in 4 M nitric acid concentration and having Zr, Hf, Ti concentration as 68 g/L, 1970 ppm, 166 ppm respectively. The organic solvents (1.1M TBP and DBBP diluted with *n*-DD) were pre-equilibrated with 4 M HNO_3 before giving contact with simulated MK feed solution. The organic to aqueous phase ratio was maintained to about 5:1 to avoid third phase formation. Extraction, scrubbing and stripping was done in cross current mode and each process was repeated for five times to ensure quantitative results. The study reveals that the quantitative extraction of Zr (>99%) was observed in the case of DBBP where as TBP shows only 93% extraction efficiency. Scrubbing was done to remove Hf and Ti from the loaded organic phase so that the zirconium product contain Hf<100 ppm and Ti<150 ppm. Stripping of Zr from the loaded organic was carried out using 0.01 M HNO_3 and the stripping efficiency was found to be 99.9% for both DBBP and TBP. Though the extraction of Hf and Ti is higher for DBBP as compared to TBP(figure 1) but the Hf and Ti contents in the final zirconium products were well below the acceptable limits. From the above observation it is clear that DBBP possess higher extraction efficiency for Zr as compared to TBP and also it have similar stripping efficiency as that of TBP and the final product contains Hf and Ti below the prescribed limits. DF of Zr(IV) with respect to Hf(IV) and Ti(IV) are 50 and 3 respectively. The structures of TBP and DBBP are shown in figure 2. Keeping all the aforementioned points in mind it can be concluded that DBBP has potential to replace TBP for Zr metal production.

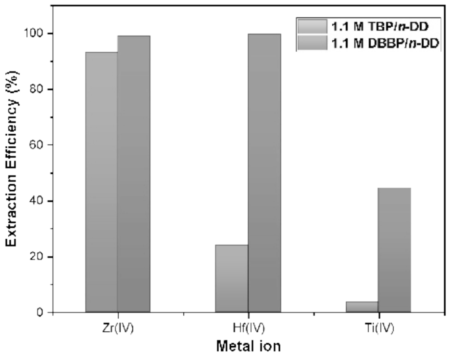

Fig. 1: *Extraction study of 1.1 M solvent/n-DD with simulated MK feed solution*

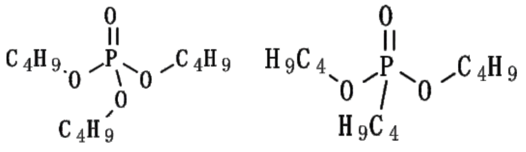

Fig. 2: *Structure of TBP and DBBP respectively*

Key words: *Zirconium, Hafnium, Titanium, Solvent Extraction.*

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Flow Sheet for Stripping of Pu (IV) with U(VI) in Presence of HDBP

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Solvent degradation presents a significant challenge in the Fast Breeder Nuclear Reprocessing Plant. To address this issue, an annular centrifugal extractor is employed. However, due to dead volume and other operational uncertainties, solvent degradation remains an unavoidable problem. In this process, a solvent composed of 30% (v/v) tributyl phosphate (TBP) in normal paraffin hydrocarbon (NPH) is used for the extraction of uranium (U) and plutonium (Pu). Radiation causes the TBP to degrade, resulting in the formation of dibutyl phosphate (HDBP) and monobutyl phosphate (MDBP). HDBP plays a crucial role during the back extraction of U and Pu. In the Fast Breeder Reactor (FBR) reprocessing, the concentration of Pu is higher than that of U, leading to observed losses of Pu in the organic phase during the stripping process. In CORAL facility, it has been observed that the retention of Pu in the organic phase exceeds the plant's specifications due to presence of HDBP formed by radiolysis of solvent. The reductive stripping of Pu with U(IV) is commonly employed in nuclear reprocessing plants. In this study, a novel flow sheet was developed for the stripping of Pu using U(VI) in the presence of HDBP. The details of the stripping flow sheet are illustrated in Fig. 1. During Pu stripping, the aqueous phase acidity was maintained to be 0.3-1.0 M in the Pu stripping stages (1^{st} stage to 9^{th} stage) to avoid Pu polymerization. The distribution ratio of U(VI) is much higher in Pu stripping stages due to high acidity. The concentration of U(VI) solution in 4M HNO_3 which results loading of uranium in organic phase to saturated condition enabling the release of Pu complexed by HDBP to aqueous phase. Based on above understanding, a stripping experiment as per novel flow sheet was conducted using a 16-stage annular centrifugal extractor over a three-hour period, achieving steady state within the first 30 minutes. The results indicate that the loss of Pu in the organic phase was less than 10 ppm. The results of this experiment will serve as key input to minimize plutonium retention in the operational plant during the reprocessing of fast-reactor spent fuel.

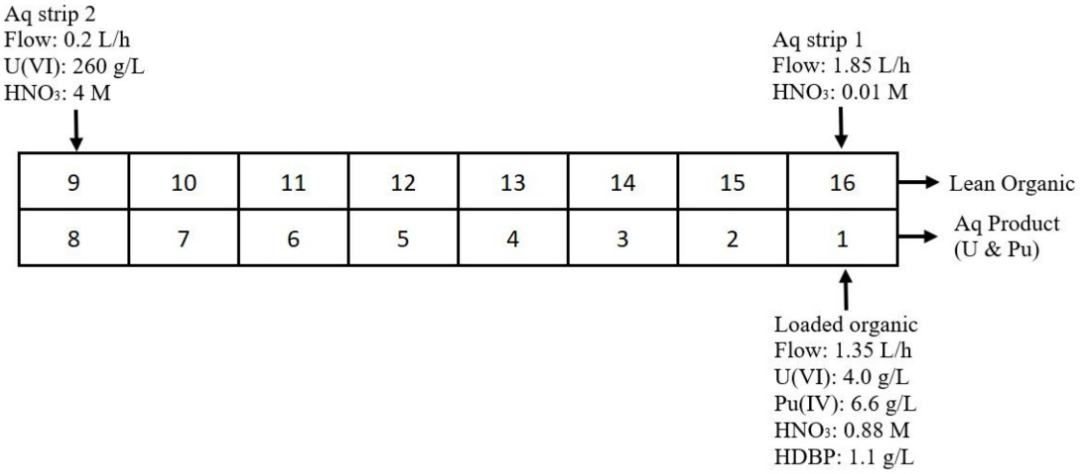

***Fig. 1:** The schematic view of novel flow sheet for the stripping of Pu using U(VI) in the presence of HDBP*

***Key words:** Nuclear Reprocessing, Annular Centrifugal Extractor, Plutonium stripping, Solvent Extraction*

Acknowledgements
The contributions of Smt T Selvi, V Ramya during analysis of samples are greatly acknowledged

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Extraction Behavior of Uranium by PS-EDTA Resin from Aqueous Solution

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The sustainability of nuclear energy-based power generation depends on the availability of uranium [1-2], the only naturally occurring fissile element, whose primary source in land-based igneous rocks is rapidly declining due to widespread exploitation. The separation of uranium from alternative sources such as seawater, contaminated mine water, etc., still requires technological advancements, particularly due to its low abundance and the presence of a variety of interfering ions. Nevertheless, the use of solid-phase adsorbents with chelating functional groups has demonstrated potential for uranium separation from seawater and similar solutions, where conventional methods fail to achieve separation.

In the present study, PS-EDTA was prepared by the procedure reported in literature [3]. The synthesis was achieved in two steps. In the first step, chloromethylated polystyrene divinyl benzene was refluxed with ethlenediamine (EDA) in the presence of sodium hydroxide solution and tetrabutyl ammonium bromide, PS-EDA was formed. This was converted to PS-EDTA by refluxing PS-EDA with sodium hydroxide solution, sodium chloroacetate and tetrabutyl ammonium bromide. The final product, PS-EDTA was washed with iso propanol, distilled water and acetone and dried. The dried PS-EDTA was used for the extraction studies. The structure of PS-EDTA is shown in Fig. 1. The resin was characterized by FT-IR and TG-DTA studies. The batch extraction was carried out by taking 50 mg of the PS-EDTA resin and 10 mL of the U(VI) solution of different pH, ranging from 1 to 8. The concentration of uranium was analyzed by spectrophotometry. The results shown in Fig.2, indicated the increase in uranium adsorption with the increase of pH of the aqueous solution and reached a maximum around pH 2, and a subsequent decrease. The adsorption was negligible after pH 6. PS-EDTA showed superior U uptake performance even with simulated U spiked sea water samples also. The adsorbent showed superior performance with respect to regeneration and reusability also. Overall, the studies indicated the feasibility of using the resin for uranium separation from lean aqueous solutions.

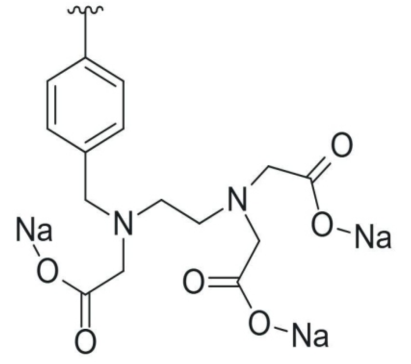

***Fig. 1** Structure of PS-EDTA resin*

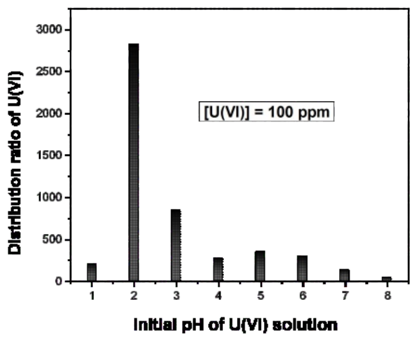

***Fig. 2** Distribution ratio of U (VI) by PS-EDTA resin*

***Key words:** PS-EDTA, separation, uranium, spectrophotometry, distribution ratio*

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Interphase Calculation using Weir Coefficient Studies in 40mm Diameter Annular Centrifugal Extractor

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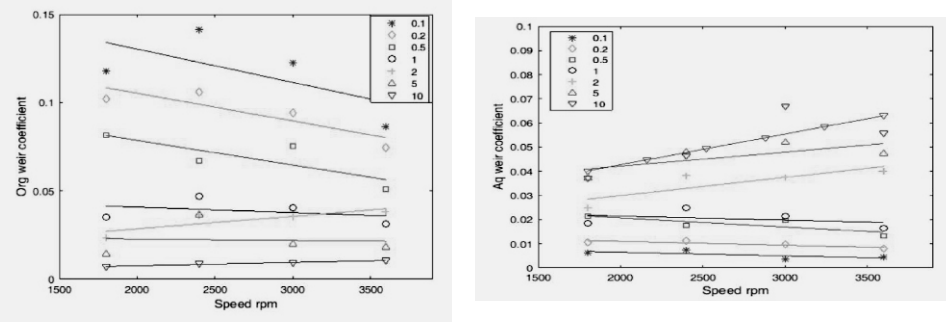
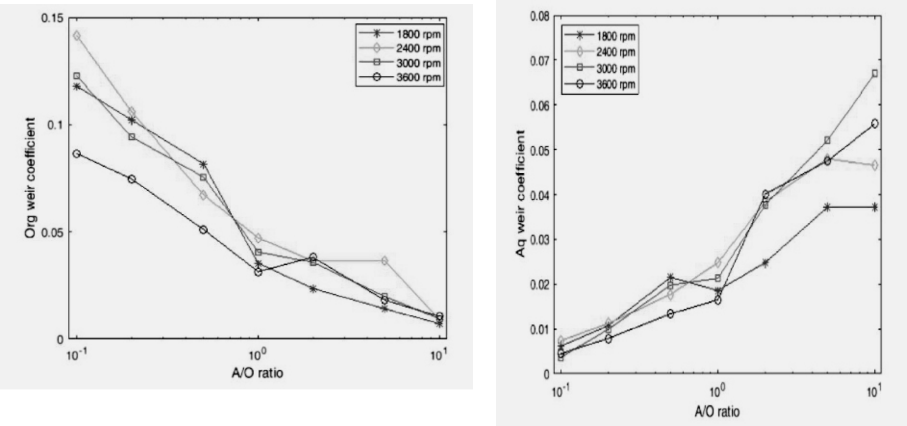
Annular centrifugal extractors (ACE) are process intensified contactors for extraction and separation. Due to small holdup, short residence time this contactor found application in fast reactor nuclear fuel reprocessing applications. Generally 4N HNO_3 and 30%TBP are the aqueous, organic phases used in nuclear fuel reprocessing. Holdup of the phases is important parameter for the mass transfer between phases. Weirs control the flow of liquid in settlers; weir coefficients are required for scale up studies. In this work, effect of flow ratios, flow rates and rotor speed on ACE holdup, ACE weir coefficients investigated.

Weir coefficient vs. rotor speed



Weir coefficient vs. A/O ratio



Key words: *ACE, Hold up, Weir coefficient*

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Monitoring of Distillation of N-Butanol in TBP Production Through Density Measurements

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Tri n-Butyl Phosphate(TBP) solvent is a work horse of reprocessing and other nuclear industries in front and back end of the nuclear fuel cycles in order to close the nuclear fuel cycle [1]. During TBP production, recovery of excess butanol is necessary. Distillation process is employed to recover the same. It is important to estimate percentage of moisture in distilled butanol and butanol traces in water in order to monitor distillation process. Karl Fisher coulometer which is present in heavy water plant, tuticorin estimates ppm level of moisture only. In order to overcome this limitation, density based method was developed. Since, water and butanol forms ideal solutions in ambient temperature, density can be given exact value of water or butanol in binary solution. Density measured at 25 degree Celsius using Anton-Par high accurate density meter. The results are tabulated in Table 1 and Table 2. Based on the values, linear fits were made and corresponding equations were arrived. We can estimate moisture in distilled butanol and traces of butanol in residue water using linear equations.

Table 1. *%of butanol in water*

Density g/cc at at 25°C	% butanol (V/V)	% butanol (W/W)
0.997	0	0
0.9951	1	0.8
0.9932	2	1.6
0.9913	3	2.4
0.9894	4	3.3
0.9875	5	4.1
0.9855	6	4.9

Density of ultrapure water=0.997g/cc at 25°C
If density of the sample more than 0.8404 g/cc,
n-butanol content % (w/w)=-428.18x+426.89
Where x=density of sample at 25°C

Table 2. *%of water in butanol*

Density g/cm3	% Moisture (V/V)	% Moisture (W/W)
0.806	0	0
0.8079	1	1.2
0.8156	5	6.1
0.8232	9	10.9
0.8308	13	15.6
0.8385	17	20.2
0.8442	20	23.6

Density of pure (99.995%) butanol=0.806 g/cc at 25°C
If density of the sample less than 0.8404 g/cc Moisture content% (w/w)=621.04x-500.42 Where x= density of sample at 25°C

Key words:*n- butanol distillation, butanol and moisture estimation , TBP production*

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Studies on the Uptake of Uranium(VI) from Acidic Feeds using Extraction Chromatography Resins Containing TBDGA-C_4mim.NTf_2 Extractant

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Solid phase extraction employing extraction chromatography (XC) is having advantages of both the solvent extraction and the ion exchange methods, has been widely used as a versatile analytical separation method [1]. Diglycolamide (DGA) extractants have been employed in XC resins for efficient uptake of trivalent *f*-cations from acidic feeds [2]. Also, in our previous study ionic liquid based XC resins were found to be superior to those with a molecular diluent as the solvent for uptake of tri as well as tetravalent *f*-cations [3]. So, It was of interest to study the extraction behaviour of hexavalent *f*-cation i.e. U(VI) with the same resin. XC resin containing *N,N,N',N'*-tetra-butyl (TBDGA) diglycolamide ligand was prepared using a room temperature ionic liquid (RTIL) C_4mim.NTf_2 as the diluent and Chromosorb-W as the solid support material.

In the present study, batch uptake of U(VI) was carried out from nitric acid feeds with an objective of analytical application of separation of U from laboratory wastes. The uptake of U(VI) from 3M HNO_3 was studied as a function of time and the results are presented in Fig. 1(a). The results suggested moderate uptake kinetic (takes ca. 20 minutes) for uranium. The obtained data were also fitted to pseudo-first order or pseudo- second order kinetic models and found to follow the pseudo-second order kinetic model, suggests chemisorption as the rate-limiting mechanism of the process. The U(VI) uptake was also studied as a function of nitric acid concentration and the results are presented in Fig. 1(b). Though a decrease in K_d values was seen at lower acidities (up to 1 M HNO_3), an increasing trend with nitric acid concentration was seen beyond 1 M. For RTILs, an initial decrease in K_d values with acidity was attributed to the predominance of a cation exchange mechanism in the lower acidity range followed by predominance of a solvation mechanism in the higher acidity range. The TBDGA-IL resin yielded very high K_d values at pH level (>5,000) while relatively moderate values at 3M HNO_3 (>400). A solution of 0.5 M Na_2CO_3 was used for the back extraction of the loaded metal ion. The resin was found to be satisfactory up to 6 cycles of extraction and back-extraction with marginal decrease in extraction efficiency, suggests the long-term reusability of the XC resin based on TBDGA-IL.

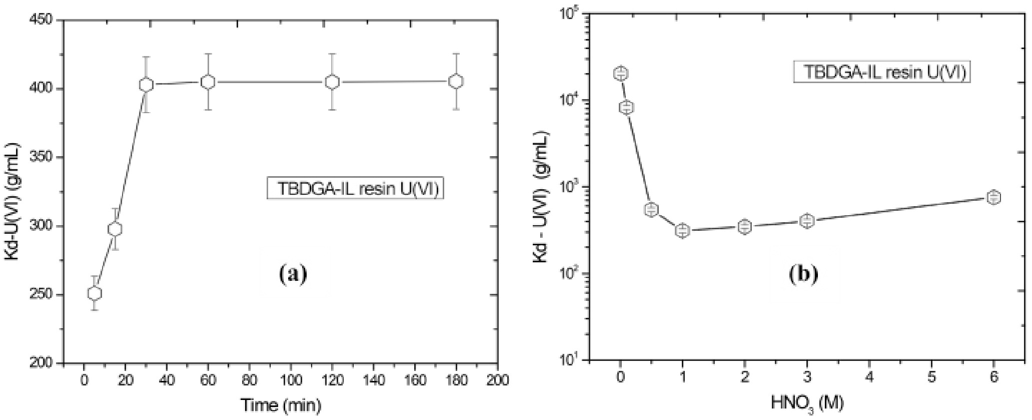

Fig. 1: *Uptake of U(VI) as a function of (a) time from 3 M HNO_3 and (b) nitric acid concentration*

Key words: *Extraction chromatography, Uranium, RTIL, TBDGA*

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Design and Application of a Green Platform of Co-Assembled Cyanobacterial Metallothionein and Magnetic Nanoparticles for Heavy Metal Removal

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The mitigation of increasing heavy metals from the environment needs sustainable remedial measures. In this context, we synthesized a nanocomposite comprising of a metal binding protein, metallothionein (NmtA) from *Anabaena* sp. strain PCC 7120 immobilized in magnetic nanoparticle (MNP) for heavy metal removal from aqueous solutions. Our previous studies had shown protective role of *Anabaena* NmtA against cadmium stress (1). The recombinant NmtA purified from *E. coli* was immobilized onto citrate functionalized Fe_3O_4 magnetic nanoparticles, namely CMNP-NmtA. Biophysical characterization of the synthesized nanocomposites was carried out by TEM, DLS and zeta potential studies. The protein loading onto the nanoparticles was confirmed by FT-IR studies (Fig. 1A & B). The CMNP-NmtA nanocomposites showed efficient removal of ~90% Cd and ~81% U from 10 µg/mL input solutions within 5 h (2). The metal adsorption onto the nanocomposites was confirmed by SEM-EDX analysis (Fig. 2). The maximum adsorptive capacities of the CMNP-NmtA nanocomposites for Cd and U were found to be 21.43 µg/mg and 43.32 µg/mg respectively (2). X-Ray Photoelectron spectroscopy (XPS) studies revealed that Cd and U interacted with CMNP-NmtA in the divalent Cd (II) and hexavalent U (VI) states respectively (2). Apart from Cd and U, CMNP-NmtA nanocomposites could also remove 82% Pb from 10 µg/mL input solutions within 5 h (2). Further, the usability of these nanocomposites in real wastewaters was assessed by removal of 51% Cd from industrial wastewater supplemented with 10 µg/mL Cd. CMNP-NmtA nanocomposites showed removal of other metals present like 58% of Fe, 44% of Zn and 57% of Mn from the wastewater. An efficient green platform for removal of both soft heavy metals like Cd, Pb and hard metal like U from contaminated solutions supported by its magnetically recoverable features was demonstrated.

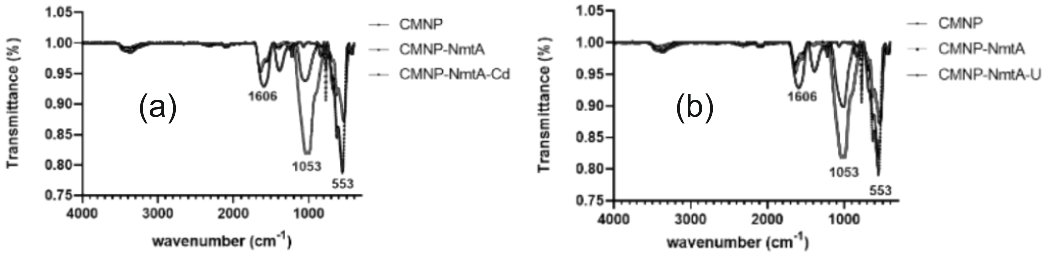

Fig 1. FT-IR spectra of CMNP, CMNP-NmtA with (A) CMNP-NmtA-Cd, (B) CMNP-NmtA-U nanocomposites. The peak at 1053 cm^{-1} obtained after NmtA immobilization corresponds to the C−N stretch from the aliphatic amine group present in the protein.

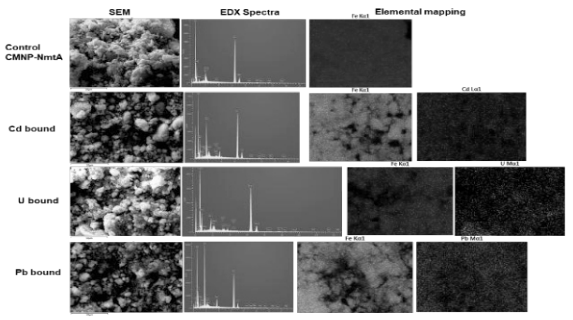

***Fig. 2.** SEM, EDX spectra and elemental maps of CMNP-NmtA nanocomposites before and after metal loading.*

***Key words:** Anabaena PCC 7120, metallothionein, magnetic nanoparticles, heavy metal*

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Investigating Novel CO_2-Phillic Extractant Aided Mineral Acid Free Matrix Dissolution-SC CO_2 Extraction of Rare Earth Nd From Solids

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Rare earth metal, neodymium (Nd) has been enlisted as critical mineral by Ministry of Mining, Government of India owing to supply chain risk and vast utility in assorted industries. In comparison to corrosive solvent-inten- sive hydrometallurgy or energy-intensive pyrometallurgy based conventional routes, Supercritical carbon diox- ide (SC CO_2) extraction [1] offers a scope for direct dissolution-extraction of metals from solid matrices result- ing in solvent inventory minimization, process simplification and compact extract collection. Eutectic solvents are an emerging area of separation where solids of desired properties can be mixed in specific mole ratios to obtain an effective liquid extractant media targeted for dissolution and/or extraction applications [2].

Current study explores feasibility of usage of novel CO_2-philic extractants, based on triphenyl phosphate, TPP (H-bond acceptor) and thenoyl trifluoro acetyl acetone, HTTA (H-bond donor) for mineral acid free dissolution- SC CO_2 extraction of Nd from solid matrices. The extractants were prepared by mechanical mixing and warm- ing of the solids at 313 K, with 1:1 and 1:2 mole ratios (designated as TT1 and TT2). TT1 and TT2 were char- acterized for their melting points, contact angle, ^{1}H NMR, IR spectra. Subsequently, dissolution and SC CO_2 extraction of neodymium from solid oxide was explored under various conditions. The extract and unextracted parts were analyzed UV-Vis spectrophotometrically (Arsenazo III, 690 nm) to establish mass balance. For TT1 and TT2, extraction efficiency was found to increase with pressure, following density trend with TT2>TT1. On the other hand, temperature enhancement led to sharp fall in extraction for TT2 than TT1, leading to a crossover at higher pressure. Also, extraction efficiency showed improvement with water spiking. Under optimised con- ditions (313 K, 200 atm., 60 min dynamic + 60 min static, in-situ complexation mode) Nd extraction efficiency of 89 ±2 % was obtained with TT2.

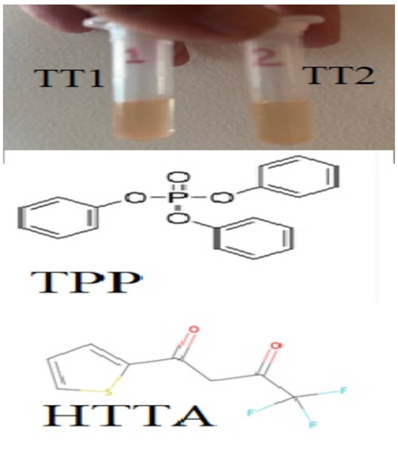

Fig. 1. SC CO_2 philic extractants

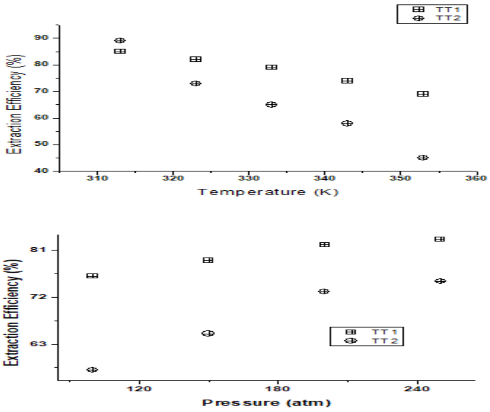

Fig.2. *Variation of extraction efficiency with temperature (at 200 atm) and pressure (at 323 K)*

Key words: *Supercritical Carbon dioxide Extraction; Neodymium; TPP; HTTA; Spectrophotometry*

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Online Solid Phase Separation Assisted Trace Impurity Characterization of U_3O_8 By Electrothermal Vapourization Inductively Coupled Plasma Optical Emission Spectroscopy

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Thermal power, the major source of global electricity, is facing issues such as depleting fossil-fuel reserves and a carbon-positive rating. In this context, nuclear power has emerged as an alternative potential source of energy with its negative carbon footprint. The nuclear reactors use uranium compounds as the primary fuel. The optimum purity of various uranium compounds like uranium dioxide (UO_2), uranium trioxide (UO_3), triuranium octoxide (U_3O_8), ammonium diuranate ($(NH_4)_2U_2O_7$) etc is needed for their specific applications [1]. In this work, U_3O_8 was chosen to develop a direct solid analysis procedure for the determination of trace impurities employing electrothermal vapourization inductively coupled plasma optical emission spectroscopy (ETV-ICP-OES). U_3O_8 was chosen because of its highest atmospheric stability among the uranium oxides, which will lead to precise trace impurity measurements. In ETV-ICP-OES procedure, the matrix interference needs to be overcome by using matrix-matched calibration standards (MMCSs), which are either commercially unavailable or inhomogeneous in the 1-5 mg range used for ETV. In order to overcome this problem, the U_3O_8 solid was fused with different mole ratios of ammonium bifluoride (NH_4HF_2) which resulted into the formation of $(NH_4)_3UO_2F_5.xH_2O$ and $UO_2F_2.xH_2O$. It was found that a (1:10) mole ratio of U_3O_8 and NH_4HF_2 is sufficient for the complete conversion (Fig.1). In the ETV furnace, when the solid was heated in a mixed flow of Ar and CF_4 gas, the analytes and the matrix were found to behave independently. The solid was evaporated in three different heating zones, viz., lower zone from 650°C to 1200°C for analytes Al, Ag, Hf, Mn, and Zr; middle zone from 1200°C to 1450°C for matrix U; and the higher zone from 1450 to 2600°C for analytes Ca, Cd, Cu, Dy, Eu, Gd, Mg, Sm, and Th. The quantification of the analytes was done by drop-casting a pure 10 multielemental standard solution on the sample boat. The method was validated by analyzing ILCE II (Table 1). The developed method had a linear dynamic range (LDR) of 1-100 µg g^{-1} and a relative standard deviation (RSD) of ≤ 10%. This direct solid analysis methodology can be applied to the chemical quality control of uranium based fuels without generating any solid or liquid waste.

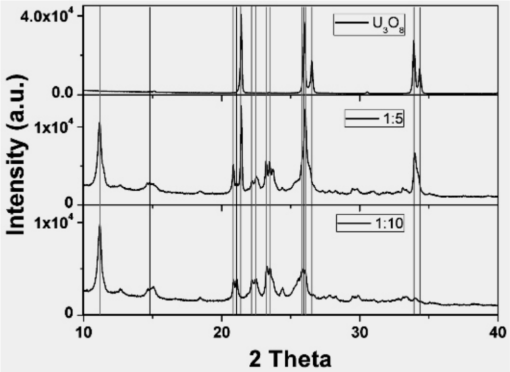

Fig. 1: *XRD pattern of pure U_3O_8 and its fused phases with 5 and 10 moles of NH_4HF_2. 2theta values: U_3O_8 (blue),* $(NH_4)_3UO_2F_5.xH_2O$ (red), and $UO_2F_2.xH_2O$ (black)

Table 1: *Analysis of ILCE II U_3O_8 (n=5)*

Ele.	Cert. value (µg g^{-1})	Obt. value (µg g^{-1})	Ele.	Cert. value (µg g^{-1})	Obt. value (µg g^{-1})
Ag	2.2	2.0±0.2	Cu	51	48±4
Al	53	55±4	Dy	2	2.1±0.2
Hf	---	< LDR	Eu	2.1	2.2±0.2
Mn	56	54±3	Gd	2.1	2.1±0.2
Zr	---	<LDR	Mg	61	58±4
Ca	96	98±3	Sm	2.3	2.4±0.2
Cd	2.1	2.2±0.2	Th	---	<LDR

Note: Linear dynamic range (LDR) for all the analytes was 1- 100 µg g^{-1}.

Key words: *Uranium, Ammonium bifluride, ETV-ICP-OES.*

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Investigation of Uranium–TBP Complex Solubility in Supercritical Phase: Experiments and Predictive Modelling

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Supercritical CO_2 based extraction technologies have recently gained significant attention for the recovery of metal ions from different matrices owing to their classification as clean and sustainable processes. A key factor in designing efficient extraction strategies for actinides is the solubility behavior of ligands and their corresponding metal–ligand complexes in $SCCO_2$ phase. This data is essential for modeling extraction performance and also for developing mechanistic insights into the extraction. Although the solubility of several actinide-specific ligands has been investigated, knowledge on solubility of actinide complexes in CO_2 remains limited. In the present study, we examined the solubility patterns of uranyl–TBP adduct, ($UO_2(NO_3)_2$2TBP) in $SCCO_2$ using a dynamic flow saturation technique.

The uranyl–TBP adduct was prepared using a procedure similar to that established for the synthesis of the triphenylphosphine counterpart [1]. About 10 g of $UO_2(NO_3)_2\cdot6H_2O$ and 2 molar equivalents TBP in 200 mL of hexane are placed in 500 mL round bottom flask and the mixture was stirred for 2 h at room temperature until the uranyl nitrate completely dissolved. The organic layer was subsequently separated, and evaporating the hexane resulted in a yellow, viscous liquid. The complex was purified by dissolving it in hexane, cooling the solution to ~ −20°C to initiate crystallization, and collecting the pure crystals via cold filtration. The crystallization and filtration sequence was carried out three times to remove any remaining TBP from the complex. The UV–visible spectrum of the prepared complex (in *n*-hexane) was recorded, and λ_{max} was observed at 415 nm (**Figure 1**) and is used for quantitative determination. The influence of the number of equilibrium cells, amount of compound loaded, and CO_2 flow rate were evaluated, and the conditions were optimized to achieve saturation solubility. For solubility measurements, about 8 g of the complex was loaded into twin 10 mL high-pressure equilibrium cells, arranged with alternating layers of glass wool to ensure uniform distribution. $SCCO_2$ was continuously passed through the vessels, and the saturated $SCCO_2$–complex stream was collected downstream via a back-pressure regulator. The solubility of the complex in supercritical CO_2 was investigated across a temperature interval of 313–333 K and pressures ranging from 10 to 20 MPa. The measurements revealed a strong pressure-dependent enhancement in solubility, whereas increasing temperature produced a noticeable decline in solubility (**Figure 2**). At 15 MPa and 313 K, the solubility reached approximately 55 $kg\cdot m^{-3}$. The experimental solubility data were internally consistent when evaluated with Mendez-Teja model, and further correlation using four semi-empirical models (Chrastil, Bartle, del Valle and Adachi-Lu) yielded an average deviation of less than 10%, indicating that these models are suitable for prediction of solubility behavior of the complexes at different experimental conditions. The solubility results demonstrate that the complex exhibits high pressure-dependent and retrograde behavior in supercritical CO_2, enabling efficient extraction even at relatively low pressures.

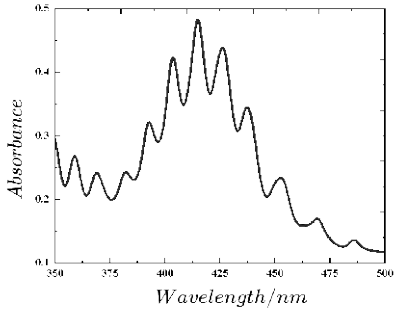

***Fig 1**. UV-Vis spectrum of ($UO_2(NO_3)_2\cdot$2TBP)/n-hexane*

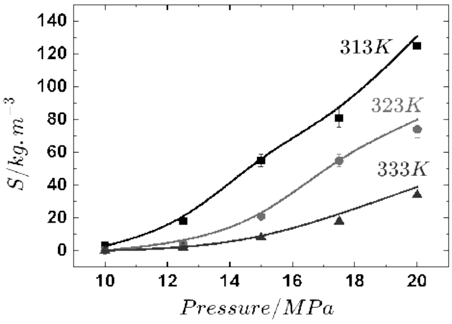

***Fig 2.** Solubility of ($UO_2(NO_3)_2\cdot$2TBP) in $SCCO_2$*

Key words: *Green solvent, Semi-empirical models, Supercritical fluid extraction, Tributyl phosphate, Uranium*

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Prediction of Thermodynamic Properties of Trialkyl Phosphates Using Group-Contribution Methods

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Conventional solvent-extraction methods used for recovery of actinides from different process of nuclear fuel cycle generate substantial secondary waste, rising environmental and sustainability concerns. Supercritical carbon dioxide ($SCCO_2$) with suitable ligands offers a cleaner alternative; however, its efficiency depends on ligands solubility patterns in $SCCO_2$ phase. Solubility patterns and extraction behavior in $SCCO_2$ can be predicted using various equation-of-state models, which require accurate thermodynamic properties of the ligands. Despite their importance, pure-component thermodynamic data for actinide-specific ligands is scarcely reported.

In this study, a comprehensive set of thermodynamic parameters (critical temperature, critical pressure, boiling point, acentric factor and molar volume) for a series of trialkyl phosphates was calculated using group- contribution methods. The compounds selected are trimethyl phosphate (TMP), triethyl phosphate (TEP), tributyl phosphate (TBP), triamyl phosphate (TAP) tri-*iso*-amyl phosphate (T*i*AP) and trihexyl phosphate (THP), for which solubility data in $SCCO_2$ phase is reported. Critical temperature, critical parameters and molar volume of these ligands are estimated using group contribution methods proposed by Fedor, Gani, Edmister and Chen [1,2,3] and are represented in Table 1. The critical temperature of TMP and THP is found to be 717.3 K and 865.6 K respectively. The critical temperature and boiling point increases with alkyl-chain length, as alkyl chain becomes longer, the molecular size and surface area increase, leading to stronger London dispersion forces and enhanced intermolecular interactions. The critical pressure of trialkyl phosphates decreases from TMP to THP due to the progressive increase in alkyl-chain length. As it increase, the molecular size and molar volume increase, leading to weaker effective intermolecular attraction per unit volume at the critical point. The acentric factors are calculated by the Edmister method [1] and Chen et al. method [3]. The data from these two methods differ significantly as each method is based on distinct correlations, assumptions, and reference states. The Edmister correlation tends to overestimate ω for complex, high-boiling, and strongly associative molecules and its methodology depends on extrapolated vapor-pressure patterns near the critical region. In contrast, the Chen et al. method correction factors intended to improve accuracy for polar and multifunctional compounds, which often leads to lower predicted ω values. The generated thermodynamic property data serve as an essential basis for interpreting solubility and extraction mechanisms in supercritical systems.

Table 1. *Thermodynamic properties of trialkyl phosphates*

Ligand	**Thermodynamic Properties**					
	Critical temperature (Tc, K)	**Critical pressure (Pc, bar)**	**Boiling point (Tb, K)**	**Acentric factor (ω)**		**Molar volume ($V, cm^3.mol^{-1}$)**
				Edmister	**Chen *et. al.,***	
TMP	717.3	62.8	410.1	0.0317	1.0257	128.5
TEP	755.5	37.6	475.1	0.1477	1.1383	176.8
TBP	817.0	20.8	566.3	0.2806	1.2790	273.4
TAP	842.6	17.0	600.9	0.3169	1.3206	321.7
TiAP	836.7	18.9	587.7	0.2976	1.2982	322.6
THP	865.6	14.5	630.8	0.3438	1.3526	370.0

Keyword: *Actinides, Equation of state models, Group contribution methods, $SCCO_2$, Trialkyl phosphates.*

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B-7

Development of Sustainable Supercritical Fluid Extraction Method for Recovery of Palladium from Nitric Acid Medium.

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The demand of platinum group metals (PGMs) continues to rise due to their extensive applications in industrial processes and medical fields. Palladium (Pd) is widely used as catalyst in variety of chemical reactions and is scarce in natural ores, making recovery from secondary sources essential. The recovery of Pd from different sources is carried out using solvent extraction, ion exchange, precipitation and electrochemical deposition etc. However these methods result in the production of large volume of hazardous liquid waste. To address this, greener alternatives are being explored without negative impact over environment. Supercritical fluid extraction has emerged as an alternative to conventional separation methods, providing key advantages including significant reduction in secondary waste volume. In the present study, recovery of Pd from nitric acid medium is carried out using supercritical carbon dioxide ($SCCO_2$) modified with different ligands (trialkyl phosphates, dialkyl hydrogen phosphonate and N,N- dialkyl amides). The concentration of Pd is estimated using ICP-OES. The extraction efficiency of Pd is systematically studied as a function of temperature (313 K to 343 K), pressure (10 MPa to 20 MPa) and extraction period, and the conditions are optimized accordingly. The optimal conditions for complete recovery of Pd are identified as 323 K, 15 MPa with static equilibration of 30 min followed by 120 min. dynamic extraction. Under these optimized conditions, the extraction efficiencies of Pd from 0.1 M nitric acid medium using tributyl phosphate (TBP), dibutyl hydrogen phosphonate, N,N-dihexyl octanamide are 98 %, 96 % and 94 % respectively with a RSD of 5%. The extraction behavior of Pd using $SCCO_2$+TBP phase is depicted in **Figure 1**. About 70% of Pd is extracted with in first 30 min., primarily due to rapid mass transfer that occurred during the static equilibration stage. The extraction efficiency increases to 92% at 90 min. Extending the dynamic extraction up to 2 h resulted in near complete extraction (97%), suggesting that final stage is governed by slow diffusion of metal-ligand complex from aqueous phase. The extraction behavior is analyzed using different models, with power-law model providing the most satisfactory fit to experimental data. The influence of matrix (nitric acid) on recovery process is also established using (TBP) and is depicted in **Figure 2**. These results indicated that a pronounced decrease in recovery with nitric acid concentration. Near-complete extraction at 0.1 M and 1.0 M nitric acid indicates that favorable Pd–ligand complexation and efficient transfer into the $SCCO_2$ phase. Beyond 1M, a pronounced decrease in recovery of Pd is observed and is attributed to the formation of anionic species of Pd in nitric acid medium. The percentage of anionic species increases with acidity that exhibit reduced affinity towards ligand–$SCCO_2$ phase and similar trend is also observed in liquid- liquid extraction [1]. This study demonstrates an effective strategy for recovering Pd from nitric acid medium and provides a roadmap for adopting green solvent–based extraction methods.

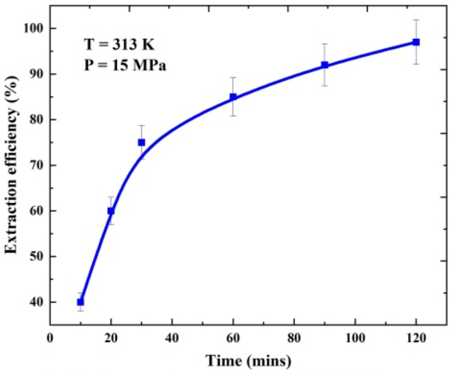

Fig 1. Extraction of Pd using TBP-$SCCO_2$ phase

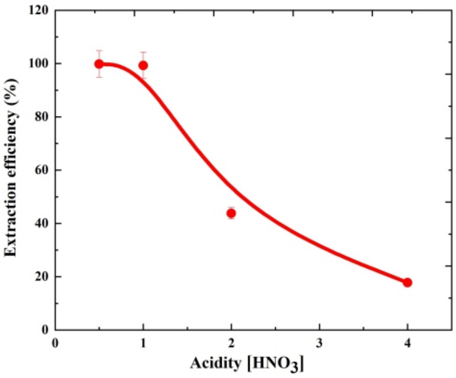

Fig 2. Extraction efficiency of Pd from HNO_3 media

Key words: *Green solvent, N,N-dialkylamides, Palladium, Supercritical fluid extraction, Tributyl phosphate*

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Development of New Association Theory Based Model for Correlating the Solubility of Actinide-Specific Ligands in $SCCO_2$

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Successful design and development of supercritical extraction of metal ions demand knowledge on solubility of ligands in $SCCO_2$. Different models are developed to predict the solubility of solutes across different temperature and pressure ranges. These models provide a theoretical framework to predict extraction behavior, thereby reducing the need for extensive experimental studies and also aiding in optimization of experimental conditions for efficient extraction. In this investigation, a new association theory based model for predicting solubility of actinide-specific ligands in $SCCO_2$ was proposed and is a modified form of well-known Chrastil equation [1]. Two modifications are implemented in existing model: (i) the association number "*k*" is expressed as a function of $SCCO_2$ density, and (ii) an additional term exhibiting a quadratic dependence on logarithm of density is also incorporated. The proposed model equation is represented as

$$\mathrm{In}\ S=(A_1+A_2 r)\mathrm{In}\ r + A_3(\mathrm{In}\ r)^2+\frac{A_4}{T}+A_5$$

The reliability of this model is evaluated by correlating solubility of different actinide-specific ligands available in literature and the ligands are listed in **Table 1**. The predictive performance of the modified model is evaluated through comparison with existing models, Chrastil (M1), del Valle (M2) [2] and Subashree (M3) [3]. Various statistical parameters, including average deviation (AARD), the Akaike information criterion, and R^2 values are employed to assess its accuracy and reliability. The new model is found to be reliable and better than existing models in predicting the solubility different class of actinide-specific ligands. The proposed model achieved lowest AARD of 5.4 %, among the models investigated. The model predictive capabilities are ranked as follows: the proposed model exhibited the highest accuracy, followed by Subashree, del Valle and Chrastil. The solubility predictions of N,N-dihexyl octanamide at various pressures, obtained using different models are represented in **Figure 1**, with the proposed model outperforming the existing models. These studies demonstrate that the proposed model provide an effective tool for predicting the solubility of ligands in supercritical phase.

***Table 1**. Performance of new model against existing equations*

Compounds	AARD% vs Models			
	M1	M2	M3	New
N,N-dihexylhexanamide	6.6	6.5	5.6	3.8
N,N-dihexyloctanamide	9.1	9.2	7.4	4.4
N,N-di-2-ethylhexylacetamide	17.4	17.3	13.7	8.1
N,N-di-2-ethylhexyl-*iso*-butyramide	9.8	8.6	11.2	6.0
2,2′-oxybis(N,N-diethylacetamide)	6.2	6.2	5.3	6.0
2,2′-oxybis(N,N-dihexylacetamide)	12.2	10.8	8.7	8.7
Dibutylhydrogen phosphonate	10.0	3.6	5.1	6.3
Dihexylhydrogen phosphonate	11.0	10.6	9.2	8.9
Dibutylbutyl phosphonate	4.0	2.3	0.9	0.9
Diamylamyl phosphonate	4.0	3.1	0.9	1.3
Global AARD	9.0	7.8	6.8	5.4

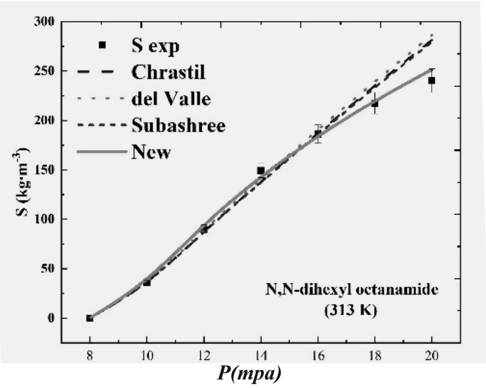

***Fig1.** Prediction ability of new model*

***Key words:** Density models, Actinide-specific ligands, Model predictions, Solubility, Supercritical CO_2*

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Dibenzoylmethane based Liquid–Liquid Extraction Method for Selective Extraction of Lithium from Secondary Sources

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Lithium (Li) is a vital metal for the production of Li-ion batteries used in electric vehicles and renewable energy storage systems. However, India relies predominantly on imports, making the lithium supply chain highly vulnerable to global price fluctuations. Developing Li production routes from indigenous primary and secondary resources is therefore of strategic importance. Seawater contains an estimated 200 billion tons of lithium— nearly 5000 times more than all land-based reserves combined [1]. Yet, its extremely low concentration in seawater (~0.18 ppm), along with the presence of chemically similar Na^+ at nearly 60,000-fold higher concentration, poses a major challenge for selective Li extraction. Recently, β-Diketone–based liquid–liquid extraction systems have demonstrated high efficiency and excellent selectivity for Li from aqueous matrices. Ligands such as dibenzoylmethane (DBM) and thenoyl trifluoroacetone (HTTA), typically dissolved in kerosene, form hydrophobic complexes that facilitate phase transfer in presence of Trioctylphosphine oxide (TOPO) [2]. However, kerosene is toxic and harmful to aquatic life with long lasting effects (GHS hazard-412), limiting its suitability for large-scale or field applications. Thus, there is a need to identify environmentally friendly solvents capable of supporting efficient Li extraction.

In the present work, DBM was dissolved in various non-toxic edible oils (mustard, coconut, groundnut and sunflower oils) and easily biodegradable methyl isobutyl ketone (MIBK) solvent to evaluate their suitability as greener organic substitues for Li extraction from seawater. The extraction mixtures were contacted with seawater at pH 12.5 for 5 min. At this pH, DBM exists predominantly in its deprotonated, resonance-stabilized enolate form, which selectively complexes Li^+ to form a hydrophobic Li–DBM chelate. This complex readily partitions into the organic phase, enabling liquid–liquid extraction. Lithium in organic phase was back extracted into dilute nitric acid and the organic phase was reused. Under optimized conditions, for 10 mL of seawater, 1 mL of edible oil or MIBK was used for the selective extraction of Li, corresponding to a tenfold pre- concentration of Li. As shown in Fig. 1, DBM dissolved in edible oils yielded upto 35% recovery of Li, whereas DBM in MIBK provided ~85% recovery. Spike recovery studies over a range of Li concentration validated the accuracy and robustness of the method.

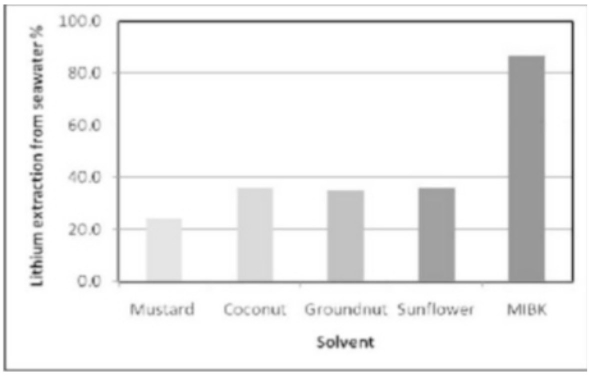

***Fig. 1** Recovery of Li using various biodegradable solvents.*

***Key words:** Lithium, β-diketone, DBM, extraction, MIBK*

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Preparation of Polymeric beads containing TOPO-DEHPA based DES for Extraction of Pu(IV) from Nitric Acid Medium

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Removal of plutonium from radioactive effluent generated at various stages of reprocessing operations in nuclear industry is crucial prior to its final disposal. Deep eutectic solvents (DESs) are emerging as a novel medium in the field of extraction and separation owing their low toxicity, biodegradability, sustainability and ease of synthesis. However, Deep Eutectic Solvents (DESs) grafted or incorporated into polymeric beads generates an efficient sorbent for metal ion extraction [1] as the polymeric structure helps to stabilize the DES onto solid support with enhanced surface area and chelation sites. This improved stability also enables their easier handling and reuse. In the present study, TOPO–DEHPA (1:4 molar ratio) based DES-impregnated polymeric beads were prepared by phase inversion method using polysulphone as base polymer [2].. Polysulphone (0.5g) powder was dissolved in NMP (n methyl pyrrolidone) under stirring condition and equal volume of DES was added for the preparation of polymer doped solution. This solution was then added drop wise into the water bath resulting in the production of soft polymeric beads (TDPB). These polymeric beads were employed for the extraction of Plutonium [Pu(IV)] in the nitric acid medium. The ^{239}Pu tracer solution in nitric acid was purified by 2% TTA in xylene ensuring Pu(IV) state for extraction experiments. The extraction experiments were carried out by equilibrating aqueous phase containing ^{239}Pu(IV) tracer in required nitric acid molarity with pre-weighed polymeric beads. Extent of extraction was monitored by assay of ^{239}Pu in aqueous phase by alpha liquid scintillation counting and ratio of activity in both the phases used for the computation of D value of the extraction.

Kinetics of uptake of Pu(IV) from 1M HNO_3 medium (Fig.1) shows a rapid uptake of Pu(IV) in the initial stage and more than 80% Pu(IV) is sorbed during the first 30 minutes of equilibration. However equilibration time of 4 hours was found to be sufficient (98%) for extraction. Influence of aqueous phase acidity (1-7M HNO_3) on D value of extraction (Fig. 2) reveals the uptake of Pu(IV) by TDPB increases with increasing acidity and reaches maximum at 4M and then follows decreasing trend at higher acidity. A solution of 0.2 M oxalic acid in 0.5M HNO_3 was found to be most suitable for the stripping of the loaded Pu(IV) from TDPB phase (~ 60% in single contact).

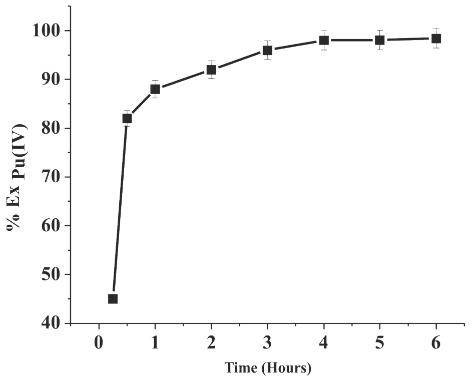

Figure 1: *Time of equilibration*

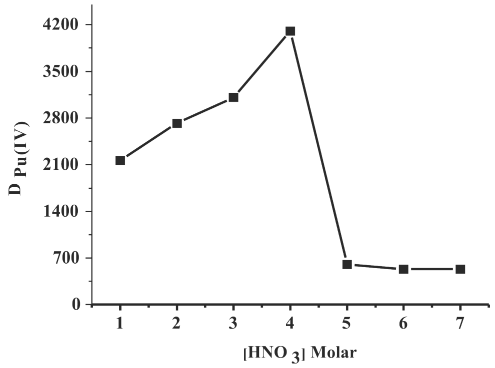

Figure 2: *Variation of D with acidity*

Key words: Plutonium, Extraction, Polymeric beads, Deep eutectic solvent

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Feasibility Study of Plastic Scintillation Microspheres as a Greener Technique for Alpha and Beta Response

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Conventional liquid scintillation counting (LSC) methods employ organic solvent–based cocktails, which pose challenges related to toxicity, handling, and radioactive waste management. To address these limitations, there is a growing interest in developing alternative greener approaches that reduce solvent usage while maintaining the analytical performance.

This study explores the feasibility of using plastic scintillation microspheres (PSm) as a sustainable, solvent free alternative for detecting alpha and beta radiations. The microspheres were synthesized by the extraction–evaporation method using polystyrene as the polymer matrix with suitable scintillating fluors. The solid-phase nature of the microspheres provides improved stability and handling convenience, making them suitable for routine laboratory analysis and field applications. A series of plastic scintillation microsphere formulations were synthesized incorporating polystyrene as the base matrix and varying concentration of additives (PPO, POPOP etc). Scanning electron microscopy (SEM) was employed to examine the morphological characteristics of the microspheres. The SEM images indicate that most particles exhibit a well- defined spherical geometry, with only a limited number showing irregular or fractured structures, suggesting controlled solvent removal under appropriate stirring conditions. The size of the synthesized microspheres span from tens to a few hundreds of micrometres. The detection efficiencies obtained with ^{241}Am and ^{90}Sr/^{90}Y is 57% and 143%, respectively, while the corresponding efficiencies for conventional cocktail is 97% for ^{241}Am and 195% for ^{90}Sr/^{90}Y. The quench parameter SQP(E) was calculated by the detector for each sample using ^{152}Eu (74 kBq) external standard source; it corresponds to the end-point channel that limits 99.75% of the total counts of the external standard spectrum. The SQP(E) obtained was 687, indicating comparable scintillation properties to conventional cocktails. Moreover, long-term stability and reproducibility studies will be conducted to validate the applicability of PSm in routine radiometric analysis. Ultimately, the development of plastic scintillation microspheres aligns with the global need for greener, safer, and more sustainable radiometric techniques, offering a promising alternative to conventional liquid scintillation methods.

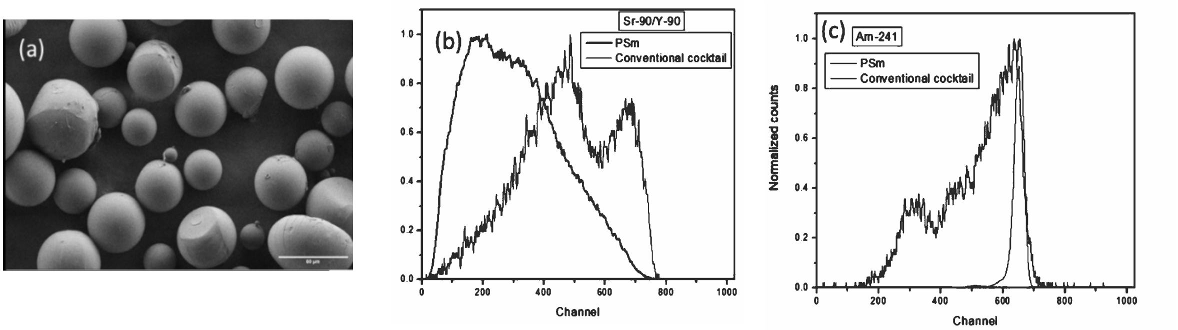

Fig: *(a) SEM image of the synthesized microspheres. (b) Comparison of spectral performance using ^{90}Sr/^{90}Y with PSm and cocktail systems. (c) Comparison of the corresponding spectra measured with an ^{241}Am source.*

Keywords: *Plastic scintillation microspheres, alpha–beta response, green separations, Conventional cocktail, solvent-free scintillation*

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Performance Evaluation of Amine-Functionalized PSEBS as a Sorbent for Direct Air Carbon Capture

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Direct air carbon capture (DAC) requires sorbent materials that are efficient, regenerable, and compatible with low-energy separation processes. In this study, poly(styrene-ethylene-butylene-styrene) (PSEBS) was investigated as a polymeric sorbent for carbon dioxide capture using a moisture swing approach. The polymer was chemically modified through chloromethylation to obtain CL-PSEBS, followed by amination to produce quaternary ammonium-functionalized PSEBS (AM-PSEBS). Hydroxide ions were introduced via ion-exchange to enable CO_2 adsorption. Structural and chemical modifications were confirmed using nuclear magnetic resonance (NMR) and Fourier transform infrared spectroscopy (FTIR). Scanning electron microscopy (SEM) revealed a rough and porous morphology favorable for gas adsorption, while energy-dispersive X-ray analysis (EDAX) confirmed uniform amine distribution and the absence of impurities. Contact angle measurements demonstrated a transformation of the polymer from hydrophobic to hydrophilic behavior upon functionalization, a critical requirement for moisture swing operation.

A custom experimental setup was designed and fabricated to evaluate CO_2 adsorption and desorption performance. The functionalized polymer demonstrated the ability to adsorb CO_2 directly from ambient air, confirming its suitability as a DAC sorbent. Adsorption experiments conducted using a desiccator showed a reduction in CO_2 concentration of approximately 2,100 ppm. Desorption studies indicated enhanced CO_2 release at elevated temperatures, with increased kinetics observed as temperature increased. An optimum desorption temperature of 60 °C was identified for effective CO_2 regeneration. The results suggest that sorbent performance can be further improved by increasing the degree of amination and by reducing particle size to enhance surface area.

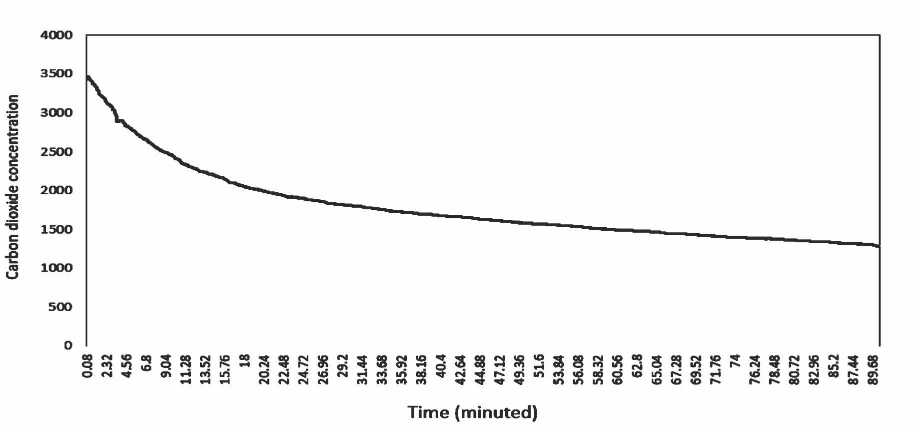

Figure 1 *CO_2 concentration decrease over time during adsorption by the amine-functionalized polymer.*

The developed experimental setup exhibited limitations, including CO_2 accumulation during desorption and inadequate humidity control. Future work will focus on designing a flow-based system with improved humidity regulation to better quantify adsorption capacity and fully evaluate moisture swing performance. Overall, the amine-functionalized PSEBS sorbent demonstrates promising potential for green separation technologies in direct air carbon capture applications.

Key words: Direct air carbon capture; Moisture swing adsorption; Amine-functionalized polymer

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DEHPA-Thymol based Deep Eutectic Solvent: Physico-chemical, Spectral Analysis and Extraction of Tb(III) from nitrate medium

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Conventional solvents tend to exhibit high melting and boiling points, evaporate rapidly, are often flammable, and can be harmful to the environment. In line with the principles of sustainable development and green chemistry, there has been growing efforts to design environmentally friendly alternatives that minimize ecological impact. Deep eutectic solvents(DESs) are a class of such solvents which have attracted attention of metallurgist in recent years owing to their distinguishing properties such as easy synthesis procedure, eco- friendly reagents, non-volatility and good solvent behavior[1]. Terbium (Tb) is one of the critical rare earth metals extensively used in NdFeB permanent magnets and fluorescent lamp phosphors with significant demand in modern electronic and energy-efficient technologies. With regard to the present scenario of its limited natural availability and growing industrial demand, an effective recovery of Tb(III) from secondary resources holds pivotal importance [2]. The present study deals with the synthesis and characterization of a hydrophobic DES (HDES) consists of DEHPA-Thymol(1:1 molar ratio) and its application to extract Tb(III).Physico-chemical properties such as density, dielectric constant (ε), refractive index (n_D) and viscosity of the HDES have been determined over a wide range of temperature 298.15K to 333.15K. The density, viscosity, and refractive index values steadily decreased as the temperature increased, reflecting the thermal expansion and structural relaxation of the components of DES, which results in enhanced molecular mobility and lower structural ordering at elevated temperatures. These trends confirm that the DES has thermal sensitivity and fluidity, supporting its application in temperature-driven extraction processes. The prepared hydrophobic DES has been further used for the solvent extraction of Tb (III) from nitrate medium. The effect of shaking time, aqueous phase pH, nitrate ion concentration and temperature on the extraction has been examined. Thermodynamic parameters like standard enthalpy and entropy changes have been calculated from temperature variation studies. From the solvent extraction studies, it has been observed that DEHPA–Thymol (1:1) HDES exhibited excellent performance, achieving 99.71% extraction efficiency for Tb (III) using 1M nitrate in aqueous phase. The UV- visible spectra of Tb(III) loaded HDES has been displayed in Fig.1.

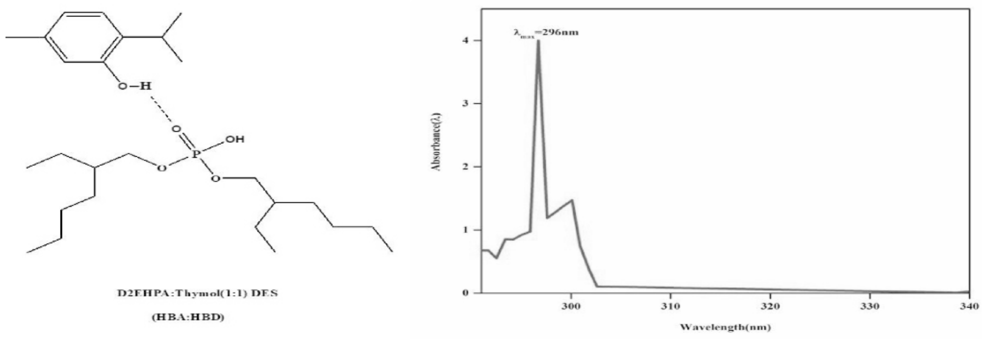

Fig.1.*(a)Structural representation of DES (b) UV-Vis. Spectra of Tb(III)-DES phase after extraction*

Key words: *DEHPA-Thymol DES, Physico-chemical properties, Terbium(III), Solvent extraction*

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Speciation and Extraction of Nd-Pr by D2EHPA-Thymol Deep Eutectic Solvent.

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Neodymium (Nd) and Praseodymium (Pr) are prominent rare-earth elements used in high-performance permanent magnets, cryogenic devices, lasers, and advanced optical technologies. These applications demand huge quantities of Nd and Pr with high purity. High-purity neodymium is a critical requirement for the manufacture of Nd–Fe–B permanent magnets, where even minor impurity contamination can significantly influence magnetic and thermal properties. However, as they are placed alongside in the lanthanide series with nearly identical ionic radii, mutual separation using conventional solvents remains a challenge. Deep Eutectic Solvent (DES) exhibits similar tunable properties to that of Ionic Liquids (ILs) and serves as a superior counterpart to conventional solvents owing to their low-cost precursors and ease of synthesis. So, in pursuit of sustainable and efficient alternatives to conventional solvents, herein we investigated a novel deep eutectic solvent (DES) composed of bis(2-ethylhexyl) phosphoric acid (D2EHPA) and Thymol (1:1 molar ratio) for the extraction of Nd^{3+} and Pr^{3+} ions in sulphate medium. FTIR spectra of precursors and product shown in Fig. 1 and 2 confirm the formation of the eutectic solvent. Analysis revealed that the prominent O–H stretching band of pure thymol at around 3181 cm^{-1} was significantly shifted in DES to 3352 cm^{-1}, indicating their mutual interaction, preferably due to hydrogen bonding. Moreover, the stretching vibration peak of the P–O bond shifted from 1010 to 1027 cm^{-1}. This indicates that when thymol was added to D2EHPA, the polar functional groups of OH in thymol weakens the hydrogen bonds connecting D2EHPA dimer molecules, and the consequent modification of electron density around the oxygen donor sites, favoring metal-extractant complex formation. Further extraction behavior of Nd^{3+} and Pr^{3+} was studied using optimized 30% (v/v) D2EHPA–thymol DES by varying aqueous phase acidity (equilibrium pH 0.8–2.6). Both ions exhibit increased extraction at higher pH values. A plot of log D versus pH as shown in Fig. 3 revealed a linear relationship for both metal ions. Slopes obtained from corresponding linear fits are close to 2 indicating a proton-exchange extraction mechanism with a metal ligand complex stoichiometry of 1:2 for both Nd^{3+} and Pr^{3+}. The enhanced extraction efficiency and observed spectral changes are fully consistent with established studies of D2EHPA–alcohol systems and recent analyses of organophosphorus-based deep eutectic solvents. Therefore, these results establish the D2EHPA–thymol deep eutectic solvent as a promising inexpensive solvent system for Nd–Pr extraction, with clear potential for advancing DES-based rare-earth recovery processes for sustainable future.

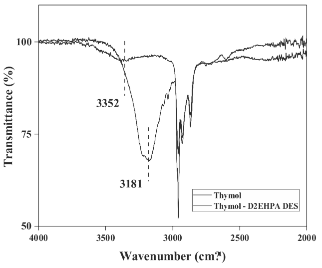

Fig. 1: *FTIR spectra of Thymol and Thymol – D2EHPA DES.*

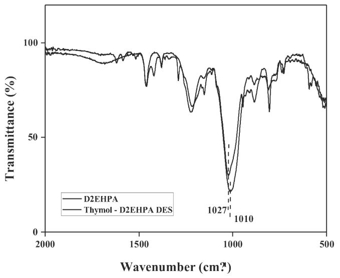

Fig. 2: *FTIR spectra of D2EHPA and Thymol – D2EHPA DES.*

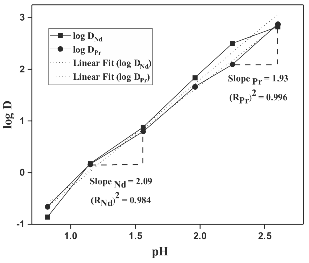

Figure.3: *Variation of log D as a function of pH.*

Key words: *FTIR, Deep eutectic solvent, rare earth elements, solvent extraction*
Acknowledgements: Authors acknowledge the funding from ANRF (CRG/2023/004477) and CSIR (OLP 134).

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Sequential Extraction of Rare Earth Elements, Strontium and Cesium: A Green Approach for Simulated Nuclear Waste

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The selective separation of fission-product ions such as rare-earth elements (REEs), strontium (Sr) and cesium (Cs) is critical for nuclear waste minimization, radionuclide partitioning, environmental surveillance, and radiochemical analysis. Graphene oxide, owing to its oxygen-rich functional groups and pH-responsive surface chemistry, provides a green and regenerable platform for aqueous-phase ion separation. In this study, the pH-dependent sorption behaviour of REE^{3+}, Sr^{2+} and Cs^{+} onto graphene oxide was systematically examined.

The extraction procedure involved dispersing graphene oxide in mixed REE–Sr–Cs solutions and exploiting the preferential interaction of partially deprotonated graphene oxide with high-charge-density REE^{3+} at pH 4. After a 10 min contact time, the graphene oxide surface charge was neutralized using KCl, promoting π–π stacking between graphene oxide sheets and inducing rapid coagulation. The resulting REE-loaded graphene oxide aggregates were removed by centrifugation, leaving Sr^{2+} and Cs^{+} in solution. The filtrate was then subjected to a second extraction at pH 8, where Sr^{2+} exhibited strong affinity for graphene oxide, enabling quantitative removal while Cs^{+} remained in the aqueous phase. Adsorbed REE and Sr were back-extracted separately using dilute nitric acid, and the regenerated graphene oxide was reused for at least five cycles with negligible loss of performance. The entire workflow avoided organic solvents, polymeric flocculants, and harsh reagents.

Batch sorption measurements over pH 1–11 revealed distinct selectivity regimes governed by the protonation state of graphene oxide and ion speciation. As shown in Table 1, REEs displayed strong uptake at pH >3 and reaching 95% at pH 6. Sr^{2+} showed negligible recovery at pH below 4 but near-quantitative recovery from pH >7. Cs^{+} exhibited negligible adsorption across the entire acidic range and only marginal uptake (<10%) even under high alkaline conditions (pH = 11). This preferential sorption behaviour originates from the strong complexation of multivalent REE^{3+} and Sr^{2+} with deprotonated graphene oxide functional groups (–COO^{-}), in contrast to Cs^{+}, which interacts weakly due to its low charge density, large ionic radius and inability to displace hydration water to form direct surface coordination.

These pH-dependent trends enable a practical sequential separation scheme in which REEs are isolated at pH 4, Sr at pH 8 and Cs remains in solution for downstream capture using a Cs-selective material. Overall, this work demonstrates that graphene oxide is a fast-responding, tunable and environmentally benign sorbent capable of sequentially separating REE, Sr and Cs from complex matrices. The pH-controlled adsorption windows established here provide a foundation for developing solvent-free, sustainable partitioning strategies for nuclear waste treatment.

Table 1. *Rapid (10 min) pH-controlled extraction of REE^{3+}, Sr^{2+} and Cs^{+} using graphene oxide*

Species	**Recovery (%) for 10 min. equilibration**		
	pH = 4	**pH = 6**	**pH = 8**
REE^{3+}	~65	~95	>95
Sr^{2+}	<10	<25	>95
Cs^{+}	<5	<5	<10

Keywords: *Graphene oxide, rare-earths, strontium, cesium, nuclear waste*

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B-16

Extraction of Bioactive Compounds from Electron Beam Irradiated Natural Honey from Diverse Region of Western Ghats

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Honey is rich reservoir of bioactive compounds like polyphenols and flavonoids but is often used in home remedies without understanding its nutritional benefits. This study explores a "Green Separation" method by evaluating the stability and bioactive potential of natural honey samples subjected to Electron beam irradiation (EBI) at doses from 0 to 40 kGy [1]. Bioactive compounds were extracted using two different techniques: conventional solvent extraction employing an acetone–petroleum ether mixture, and a novel Ultrasound-Assisted Extraction (UAE) method utilizing Natural Deep Eutectic Solvents (NADES) to enhance extraction efficiency and bioactive compound stability. [2] . The honey bioactive extracts after employing NADES were analyzed by NMR, FTIR, HPLC and LC-MS. Antioxidant activity, assessed by ABTS and DPPH radical scavenging methods, and antimicrobial activity was tested by disk diffusion assays.

Results revealed that UAE-NADES achieved 2.5-fold higher extraction efficiency (85.3 ± 2.1% yield) compared to conventional methods (34.2 ± 1.8% yield) for polyphenols and flavonoids. A 30 kGy EBI dose optimized bioactive release, with FTIR showing irradiation-induced shifts in O-H (3400 cm^{-1}) and C=O (1650 cm^{-1}) peaks indicative of hydrogen bond disruption and phenolic ring opening that correlating directly with a 68% rise in ABTS scavenging (IC_5 = 12.4 mg/mL) and 52% in DPPH (IC_5 = 15.7 mg/mL) at 50 mg/mL for N3 honey versus non-irradiated controls. NMR and LC-MS confirmed elevated HMF (up to 28 mg/kg) and polyphenols without degradation beyond 30 kGy, where higher doses (40 kGy) caused polyphenolic fragmentation and activity plateauing. Honey-derived bioactive compounds showed enhanced antimicrobial activity, with zones increasing from 15 ± 2 mm (0 kGy) to 22 ± 3 mm (30 kGy) against *S. aureus* and 11 ± 2 mm (0 kGy) to 21 ± 3 mm (30 kGy) against *E. coli*. Thus, 30 kGy EBI combined with NADES-UAE offers a sustainable method to unlock honey's bioactive compounds for medical applications and as biomarkers for authenticating Indian honey, supporting GI-tag status akin to Manuka honey.

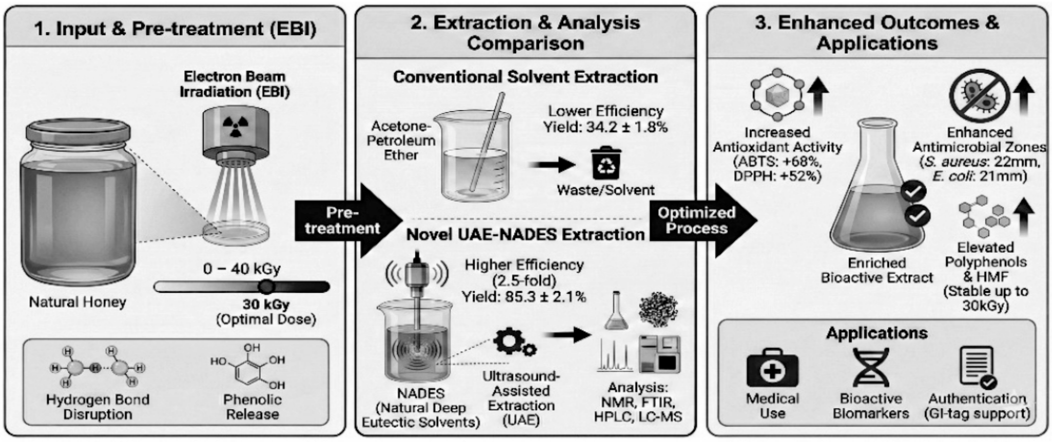

Figure 1 *Graphical Abstract of E-Beam Irradiation of Natural Honey*

Keywords: *Honey, NADES, ultrasound-assisted extraction, electron beam irradiation, antioxidant activity*

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Choline Chloride-Hexanoic acid based HDES –Synthesis, Spectral Characterization, Physico-chemical Properties and its use in Solvent Extraction of La(III)

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Deep eutectic solvents (DESs) have emerged as promising green solvents due to their advantageous physicochemical properties such as low melting points, non-volatility, non-flammability, and ease of preparation. They are also biodegradable, cost-effective, and exhibit low toxicity [1]. Typically, DESs are formed by mixing two or three components usually an HBD (hydrogen bond donor) and an HBA (hydrogen bond acceptor) in specific molar ratios [2]. These green solvents are showing good efficiency for retrieving valuable metals from diverse resources. In this present work, a hydrophobic DES (HDES) made up of Choline chloride (ChCl)-Hexanoic acid (HA) in a molar ratio of 1:4 has been prepared and characterized by FTIR (Fig.1(a)) and NMR studies.In FTIR spectra of DES ,O–H, C=O, and C–N stretching bands are observed at 2936, 1707, and 1092 cm^{-1}, respectively for changes in the electronic environment due to hydrogen-bond formation. In the NMR spectrum, a broad singlet peak assigned to the O–H group appears at 4.8 ppm, while a triplet corresponding to the N–CH_2 group appears at 3.4 ppm. Physico-chemical properties determination shows that density and refractive index decreased gradually from 0.973 g/cm^3 to 0.953 g/cm^3 and from 1.438 to 1.435, respectively, as the temperature was increased from 298.15 K to 328.15 K. The conductivity and dielectric constant values increased from 2.397 mS/m to 9.496 mS/m and from 4.970 to 10.384, respectively, in the same temperature range. The hydrophobicity of DES has been tested by shaking it with water and taking the FTIR spectra which showed no significant changes in the characteristic peaks between pure DES and DES after mixing with water (Fig.1(a)).The prepared hydrophobic DES has been further used for the solvent extraction of La (III) from its nitrate medium.Fig.1(b) illustrates effect of various parameters (HNO_3 molarity, DES/Aqueous phase volume ratio and temperature on La (III) extraction efficiency. All three parameters show positive impact on extraction efficiency and maximum of 62.01% La(III) extraction was achieved from 3M HNO_3..

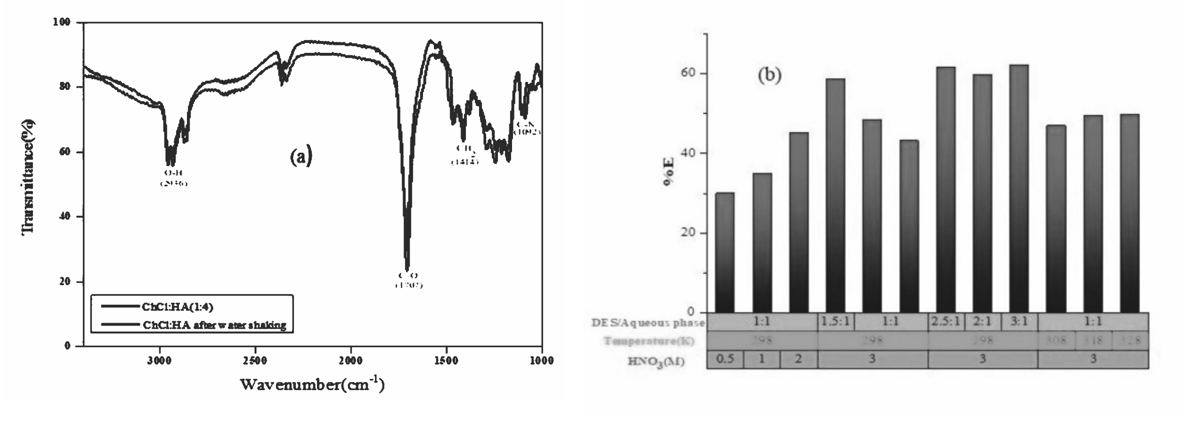

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Fig.1.(a)FTIR spectra of DES and Hydrophobicity test (b) %E versus HNO_3 molarity, DES/Aqueous phase volume ratio and temperature

Key words: *Choline Chloride-Hexanoic acid HDES, Physico-chemical properties, FTIR, Solvent Extraction Lanthanum (III).*

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Extraction of U(VI) from Aqueous Phase using Synthesized Menthol Based Eutectic Solvent.

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Hydrophobic eutectic solvents (HES) have been considered as green solvents owing to close resemblance of their properties with ionic liquids. HES have proven enormous application potential in several fields due to advantages like low cost and simple preparation. HES found to be effective as liquid-liquid extractants for organic pollutants dyes volatile fatty acids and nanoplastics [1-2]. Present work emphasized on the preparation of nonionic HES composed of simple monoterpene menthol and decanoic acid (DA) and its extraction ability for U(VI) from aqueous medium was examined. Synthesis of HES was carried out by mixing 1:2 mole ratio menthol and decanoic acid (DA).This mixture was kept at 60°C in an oven for about 30 minutes. This forms homogeneous hydrophobic eutectic solvent at room temperature as confirmed by IR spectra in Fig. 1a. This solvent was directly employed for liquid-liquid extraction of Uranium from nitric acid medium with varying pH. The stock solution of ^{233}U tracer (~10µg/ml) in nitric acid with required pH was used in extraction studies. The extraction experiments were carried out by equilibrating aqueous phase solution of required pH containing ^{233}U tracer with hydrophobic HES [1:2] solvent keeping HES: aqueous phase ratio 1:1. After extraction the solutions were centrifuged and the assay of ^{233}U in both the phases was carried out by using alpha liquid scintillation counting. Fast kinetic of extraction of U(VI) from aqueous phase (pH- 3) was observed (~10-15 minutes). The effect of pH on the extraction of U(VI) depicted in [Fig.1b] . It reveals steep increase in the extraction of U(VI) from pH 2 to 3. At pH 4–5, more than 90 % of U(VI) from aqueous phase was removed by HES. The presence of NaNO$_3$ as salting out agent exhibits a small increase in extraction efficiency as shown in [Fig.1b]. It is noteworthy that the Menthol:DA HES system still removes a substantial amount of U(VI) and its pronounced pH dependency, could found significant implications in the treatment of real wastewater streams.

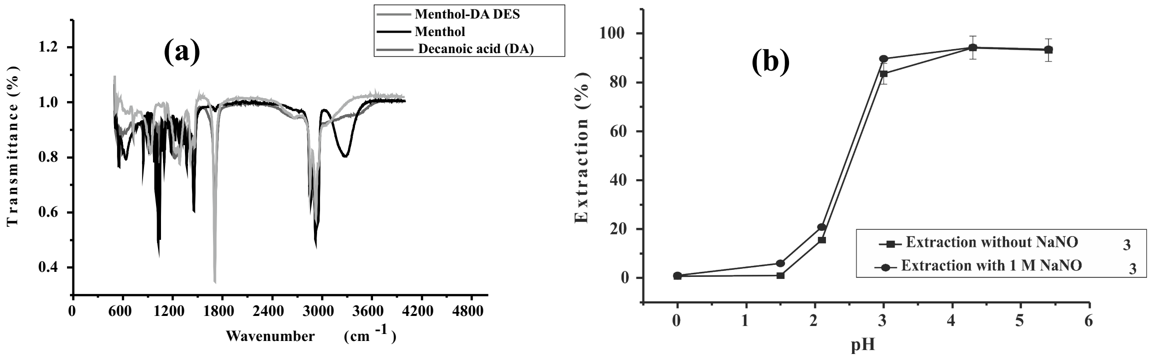

Figure 1: *(a) IR spectra of Menthol-DA, Menthol and DA (b) Effect of pH variaton on extraction of U(VI) into Menthol based HES.*

Keywords: *Hydrophobic eutectic solvent, Extraction, Menthol, Decanoic acid.*

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A Green Approach for Mineral Acid-Free Dissolution-Extraction of Uranium from Crude Yellow Cake Matrices Aided by Novel Supercritical CO_2-Philic Extractants

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The study reports exploiting novel eutectic CO_2-philic extractants, based on trioctyl phosphine oxide (TOPO) and penta decafluoro n-octanoic acid (HPFOA), for mineral acid free, direct dissolution-uranium extraction from crude matrices. Uranium is produced from different uranium ores as crude yellow cake of different chemical composition such as sodium diuranate (SDU), ammonium diuranate (ADU), magnesium diuranate (MDU), high temperature uranium peroxide (HTUP) etc. This depends on nature of ores and ore processing methods, availability of required facilities at processing site and other economic as well as environmental factors. These yellow cakes are further processed to produce pure uranium suitable for fuel fabrication facility by conventional solvent extraction process. Supercritical fluid extraction employing carbon dioxide is such a promising alternative [1]. Out of various available fluids, carbon dioxide is generally the preferred agent to carry out the extraction, majorly due to its mild operation conditions of temperature and pressure, easy availability as well as its easily tuneable density. TOPO, serving as H-bond acceptor, is a popular extractant for uranium and HPFOA, serving as H-bond donor, aids supercritical CO_2 extraction of metal ions due to multiple SC CO_2-philic C-F bonds. TH1 and TH2, having 1:1 and 1:2 mole ratio of TOPO and HPFOA, were prepared and characterized with respect to relevant properties viz. viscosity, density and melting point. Melting point of TH1 and TH2 were found to be similar and determined to be 205.3 K and 204.5 K, respectively by Differential Scanning Calorimetry. This was a significant depreciation from the pure components viz. TOPO (m.p. 327 K) and HPFOA (m.p. 329 K). Pressure and temperature were found to influence uranium extraction significantly by affecting the density of SC CO_2. TH2 yielded better extraction and under optimised conditions (200 atm., 323 K, 60 min. static and dynamic extraction time, 0.5 mL extractant), U extraction efficiency followed the order: HTUP (78; 87%) > SDU (75; 85%) > MDU (72; 82%) for TH1, TH2, respectively. The determination of uranium content in the extract post-SFE was carried out by biamperometric end point analysis using Ti(III) reduction method. The extracts were characterised by electrometry, UV-Vis spectrophotometry and IR spectroscopy, revealing presence of U(VI), independent of initial matrix. Electrochemical study (CV and DPV) of uranium extracts for this novel system, provided crucial diffusion coefficient (D_0) of U species in medium that was estimated to be 2.22×10-7 cm^2 sec^{-1}. Hence, employing dual functional media TH1 and TH2 dissolution-extraction of uranium was successfully demonstrated from matrices relevant to nuclear industry.

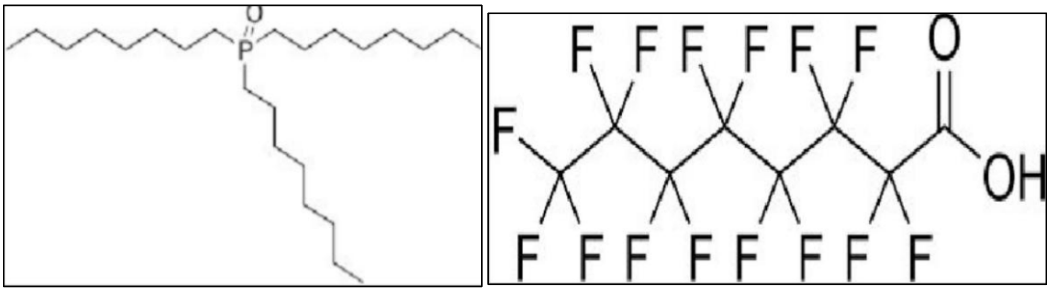

Fig. 1. *Structure of TOPO and HPFOA*

Key words: *Supercritical Carbon dioxide Extraction; Uranium; TOPO; HPFOA; Yellow cake; Bimperometry*

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Efficient Liquid-Liquid Extraction of Cobalt (II)\from Environmental Samples

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Cobalt is a hard, silvery gray in colour and ductile metallic element, of which the chemical properties are highly similar to iron and nickel. The compounds of cobalt mainly occur in two different oxidation states such as Co^{2+} and Co^{3+}, the former being most commercially and environmentally available [1 , 2]. A simple and selective spectrophotometric method was developed for the determination of cobalt (II) with 2- Bromobenzaldehyde thiocarbohydrazone [BBTCH] as a chromogenic reagent. The proposed method has been described on the basis of synergistic effective extraction of cobalt(II) in presence of pyridine at pH range 7.0 to 7.5, showed yellow coloured ternary complex having molar ratio 1:2:2 (M:L:Py). The equilibrium time is 2 min for extraction of cobalt (II) from organic phase at room temperature. The absorbance of coloured organic layer in ethyl acetate is measured spectrophotometrically at 420 nm against reagent blank. The Beer's law was obeyed in the concentration range 4.5–15 mol/L^{-1} of cobalt (II). The molar absorptivity and Sandell's sensitivity of [Co(II)- BBTCH -pyridine] complex in ethyl acetate are 3.079×10^3 $Lmol^{-1}cm^{-1}$ and 0.02061 µg/cm^{-2} respectively. The composition of [Co (II)-BBTCH -pyridine] complex (1:2:2) was established by slope ratio method. The ternary complex was stable for more than 48 h. The limit of detection (LOD) and limit of quantification (LOQ) of the method is 0.36 and 0.88 µg mL^{-1}. This method has been effectively applied for water samples, synthetic mixtures, cobalt oxide nano powder and alloy samples.

Water samples	Cobalt (II) mg L^{-1}		Relative Recovery	% R.S.D
	Added	Found		
Distilled water	100	99.48	99.48	0.52
Dam water	100	99.26	99.26	0.61
Lake water	100	98.75	98.75	0.24
River water	100	99.67	99.67	0.42
Municipal water	100	99.33	99.33	0.58

Key words: *cobalt (II), liquid-liquid extraction, environmental samples.*

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B-21

Extraction of Phytochemicals from Electron Beam-Treated Marigold (Tagetes erecta) Floral Waste

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Marigold (*Tagetes erecta*) flowers, rich in lutein and polyphenols, represent underutilized waste post-religious rituals in India. This study developed a "Waste-to-Wealth" strategy by subjecting marigold flower powder to electron beam (E-beam) irradiation (0–25 kGy), followed by bioactive extraction via conventional acetone:petroleum ether solvent and novel ultrasound-assisted extraction (UAE) using hydrophobic/hydrophilic natural deep eutectic solvents (NADES) embedded in nanofibers [1,2]. The extracts were characterized by using FTIR and LC-MS, while antioxidant potential was assessed via DPPH radical scavenging and antimicrobial disk diffusion assays.

The results of FTIR analysis revealed a broad peak at 3400 cm^{-1} corresponding to –OH groups in flavonoids and polysaccharides, C–H stretching at 2924 cm^{-1} (aliphatic) and 3976 cm^{-1} (aromatic), aromatic C=C vibrations at 1597–1609 cm^{-1} associated with polyphenols and lutein, C=O stretching at 1735 cm^{-1} attributed to esters and oxidized lutein, C–O–C ether vibrations at 1343 cm^{-1} indicating glycosidic bonds, and C–O stretching at 1027 cm^{-1} related to alcohols and ethers, collectively confirming post-irradiation bioactive stability. LC–MS analysis identified lutein at m/z 568 $[M+H]^+$ (RT 18.5 min) through standard library matching, calibrated with external standards of lutein (568.4 Da) and caffeine (195 Da), along with elevated polyphenols, including quercetin at m/z 303, without detectable degradation at 15 kGy. This optimal irradiation dose achieved a 2.8-fold higher extraction yield using NADES-UAE compared to conventional extraction methods, while avoiding discoloration observed at higher doses of 20–25 kGy. Environmental scanning electron microscopy (E-SEM) verified effective NADES embedment within the nanofiber matrix. The extract exhibited strong antioxidant activity with DPPH inhibition of 95.77% compared to 87–93% in controls, and enhanced antimicrobial efficacy, with inhibition zones increasing from 12 ± 2 mm (0 kGy) to 24 ± 3 mm (15 kGy) against *Staphylococcus aureus* and from 10 ± 2 mm to 22 ± 3 mm against *Escherichia coli*. Overall, the integration of 15 kGy E-beam irradiated marigold flower powder with NADES-nanofiber UAE enables sustainable lutein recovery from floral waste for nutraceutical applications, outperforming conventional methods through preserved structural integrity and scalable biomass valorization.

Keywords: *Tagetes erecta, NADES-nanofibers UAE, E-beam irradiation, lutein, antioxidant activity.*

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B-22

Rapid Spectrophotometric Determination Gold(III) by using of Novel 1-(Pyrimidine)-4, 4, 6-Trimethyl-1,4-Dihydropyrimidine-2-Thiol Extractant

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Day by day, consumption of gold is being increases due to its huge demand in the jewellery and electronic industries [1]. Subsequently, gold is widely used in the catalytic organic reaction [2], electroplating [3], and in the medicine as anti-inflammatory drugs [4]. However, e-wastes considered as an alternative source of the gold ore [5]. Hence, the development of low cost, rapid and selective extractive method is important with concerned to economic and environmental points of view. We have been synthesized novel chromogenic extractant, 1- (pyrimidine)-4, 4, 6-trimethyl-1,4-dihydropyrimidine-2-thiol [PTPT] which has been used for rapid extraction and spectrophotometric determination of gold(III). The PTPT ligand has been selectively forms stable complex with gold(III) in basic medium at pH 9, in presence of dilute pyridine. At the 5 min shaking time, the gold(III) is been extracted from aqueous phase to organic phase showing sky blue colour λ_{max} 505 nm against reagent blank. The developed method has been optimized by effect of pH, ligand concentration, type of the dispersive organic solvents, shaking time, pyridine concentration, etc. The Beer's law was obeyed in the concentration range 1-20 μg mL^{-1} of gold(III) and optimum concentration range is evaluated by Ringbom's plot and it is found that 2.5-25 μg mL^{-1}. The molar absorptivity and Sandell's sensitivity of gold(III)-PTPT complex is 2.80 x 10^3 L mol^{-1} cm^{-1} and 0.314 μg cm^{-2}, respectively in presence of pyridine while in absence of pyridine, molar absorptivity and Sandell's sensitivity of gold(III)-PTPT complex is 1.35 x 10^3 L mol^{-1} cm^{-1} and 0.469 μg cm^{-2}, respectively. The stoichiometry of the gold(III)-PTPT-pyridine complex was calculated by slope ratio method, mole ratio method and Job's method of continuous variation and it has been found as 1:2:2. The effect of interference ions also studied. The standard deviation (R.S.D.) is 0.11% for n = 5 repetition. The developed methods are applied for the determination of gold(III) from binary, synthetic mixtures and real samples and the obtained results were compared with Atomic Absorption Spectrophotometry (AAS).

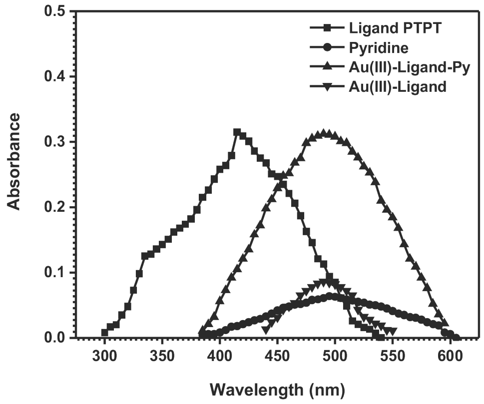

Fig.1. Absorption spectra of PTPT vs. Carbon tetrachloride blank; (B) Absorption spectra of Au(III)-PTPT-pyridine complex Vs. PTPT blank; (C) Absorption spectra of Au(III)-PTPT complex Vs. PTPT blank; (D) Absorption spectra of pyridine blank: Au(III) = 10 μg mL^{-1}; pH = 9.0; PTPT = 5 cm^3 of 0.01 mol L^{-1}; Pyridine = 5 cm^3 of 0.1 mol L^{-1}; Solvent = Carbon tetrachloride; Equilibrium Time = 5 min; Wavelength = 300 to 600 nm.

Fig. 2. Au(III)-PTPT-pyridine colored complex in CCl_4

Keywords: *Gold(III), Spectrophotometric determination; Real sample analysis*

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Preparation of Enhanced Hydrophobic Polyvinylidene Fluoride Membranes by Vapour/ Non-Solvent Induced Phase Separation for Membrane Distillation

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Membrane distillation (MD) is an emerging thermally driven membrane separation process for treatment of extremely high-salinity water where reverse osmosis (RO) is not feasible as RO is influenced by osmotic pressure of the feed. Commonly used MD membranes typically made from polymers like polypropylene (PP), polytetrafluoroethylene (PTFE) and polyvinylidene fluoride (PVDF) [1]. More hydrophobic PP & PTFE membranes are prepared through complicated melt casting technique which hinder its large-scale industrial application. In contrast, relatively less hydrophobic PVDF membranes are prepared by wet casting phase inversion techniques where controls of membrane preparation parameters are much easier to tailored the properties of the prepared membranes and are easy scalable [2].

In this study, we have attempted to develop the enhanced hydrophobic PVDF membranes by addition of gelling medium (water) soluble additives such as LiCl and $ZnCl_2$ in the casting solution with optimization of vapor-induced phase separation (VIPS) time followed by non-solvent induced phase separation (NIPS). As evident from the water contact angle values given in Table 1, the hydrophobicity increase on changing VIPS time is marginal for PVDF membranes prepared from casting solution with no additive but it is quite substantial at VIPS time of 2 min. and 3 min. for the membranes prepared using casting solution containing LiCl and $ZnCl_2$ respectively. Presence of additives in the casting solution results membranes with rougher surface (Fig.1) and the membrane surface roughness is found to be increased with increase in the VIPS time. The presence of additives in casting solution resulted more porous membranes as evident from the pure water permeability (PWP) data. PVDF membranes having water contact angle of >115deg. & PWP of >130litres/m^2.hr are tested in MD process.

Table 1: *Effect of additive & VIPS time on characteristics of PVDF membrane (casting solution: PVDF: 16% w/w in Dimethyl formamide (DMF)+ additive)*

Additive in casting sol.	VIPS time (min.)	Water contact angle (degree)	Surface roughness (nm)	PWP @ 2 kg/cm^2 (litres/m^2.hr)
Nil	0	71.4	43.43	31.4
	2	73.6	47.52	74.5
	3	75.0	52.02	121.5
4% LiCl	0	72.3	73.12	94.1
	2	**135.0**	**412.68**	**172.5**
	3	130.0	434.76	188.2
4% $ZnCl_2$	0	63.5	167.81	84.0
	2	78.5	166.74	78.9
	3	**115.9**	**182.02**	**134.8**

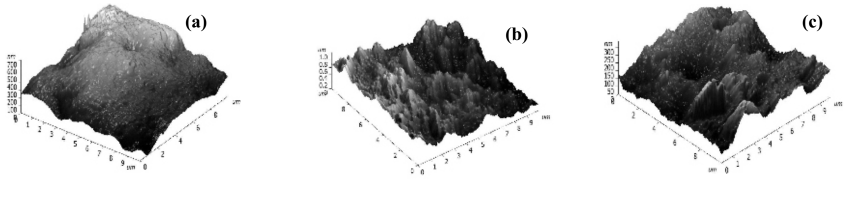

Fig. 1: *AFM images of* ***(a)*** *PVDF 16 wt.%,* ***(b)*** *PVDF 16 wt.% + 4% LiCl and* ***(c)*** *PVDF 16 wt.%+ 4 % $ZnCl_2$ at 3 min. of VIPS time.*

Key words: *Polyvinylidene fluoride, vapour induced phase-separation, non-solvent induced phase separation, enhanced hydrophobicity, membrane distillation*

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Electric Field Assisted Migration of H^+ and Cu^+/Cu^{++} Ions Through Nafion in Cu-Cl Electrolyzer for Hydrogen Generation: Molecular Dynamics Simulations.

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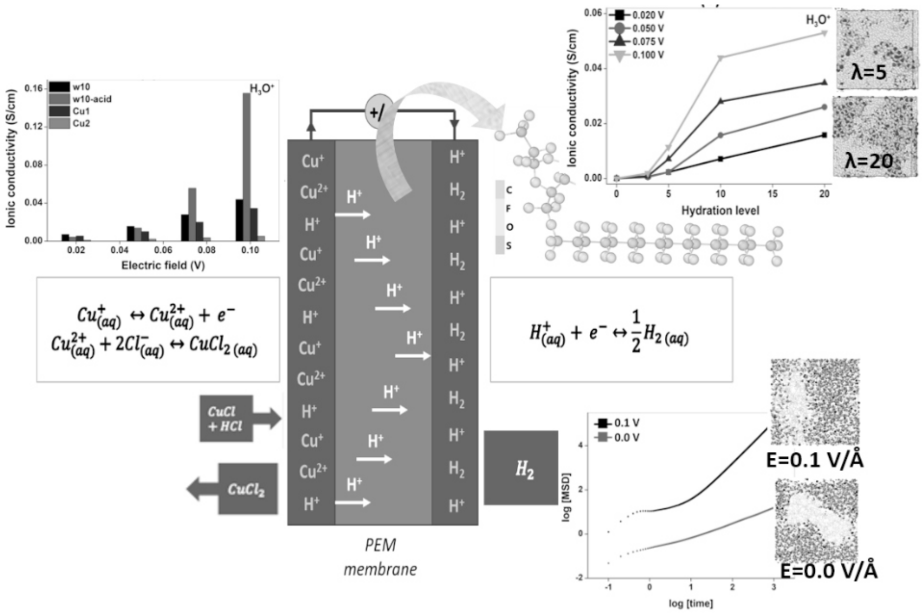
Hydrogen is widely regarded as a “fuel of the future” owing to its high energy density, and there is growing interest in developing cost-effective and energy-efficient green-hydrogen production technologies[1]. Among these, the Cu–Cl cycle offers notable advantages, including relatively low operating temperatures, stable hydrogen yields, and high current-conversion efficiency. In this cycle, electrolytic water splitting occurs in a Cu–Cl electrolyzer, which incorporates a membrane–electrode assembly with a Nafion-type proton-exchange membrane[2]. The efficiency of proton transport through the Nafion membrane is a key factor that governs the overall hydrogen yield. This study explores the transport of proton and copper ions in hydrated Nafion membranes within a Cu–Cl electrolyzer, a key component of hybrid Cu-Cl cycle for hydrogen production. Particular focus is given to the effects of membrane hydration level and applied electric field strength[3,4]. Molecular dynamics (MD) simulations reveal that electric fields enhance proton mobility by promoting water structuring and aligning hydronium ion trajectories, leading to a transition from diffusive to drift-dominated transport. Conversely, copper ions—especially Cu^{2+}—disrupt the hydrogen-bonding network through solvation shell formation; thereby significantly diminish the ionic conductivity. While both hydration and field strength improve transport, hydration exerts a stronger influence. Conductivity increases with both factors but saturates at high field strengths, suggesting a threshold beyond which water drag impedes ion mobility. The presence of acidic medium was found to boost conductivity, whereas copper ions were seen to suppress it—markedly by Cu^{2+}. This is first of one kind to reveal the microscopic mechanisms of hydronium transport and copper-induced nafion degradation, offering guidance for the design of advanced ionomer membranes in electrolyzers and energy conversion applications[5].



$$Cu^{+}_{(aq)} \leftrightarrow Cu^{2+}_{(aq)} + e^{-}$$
$$Cu^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \leftrightarrow CuCl_{2\,(aq)}$$
$$H^{+}_{(aq)} + e^{-} \leftrightarrow \frac{1}{2}H_{2\,(aq)}$$

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Fig. 1: *Transport of hydronium ions and Cu^+/Cu^{++} ions through nafion with influence of membrane hydration and Electric field strength.*

Key words: *Hydrogen, CuCl cycle, Nafion, Hydration, Membrane.*

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Studies on Performance of Reverse Osmosis Membrane for Treatment of Simulated Effluent from Solvent Production Plant of a Heavy Water Industry

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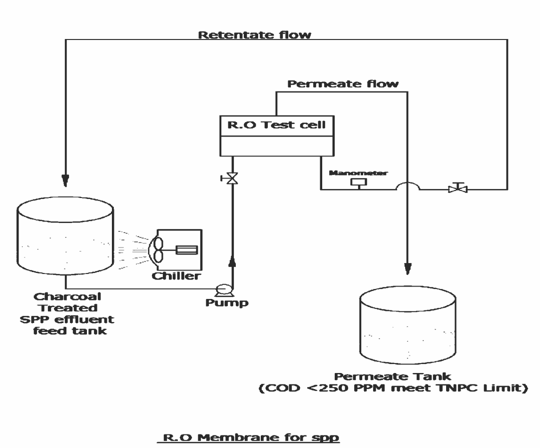
Reverse Osmosis (RO) membranes are widely employed for desalination and industrial wastewater treatment due to their high selectivity for dissolved solids and organic pollutants **[1]**. Their performance is strongly influenced by the structural and chemical characteristics of polyamide selective layer, which enables substantial removal of organic impurities even at varying strength of industrial effluents **[2]**. In this study the applicability of in-house developed both brackish water reverse osmosis (BWRO) and sea water reverse osmosis (SWRO) membranes was investigated for treatment of the simulated effluent generated at the Solvent Production Plant (SPP) of a Heavy Water Plant (HWP) Tuticorin. The experiments were performed using simulated feed composed of organic rich hypersaline solution [chemical oxygen demand (COD) within the range from 9520 ppm to 45070 ppm and total dissolved solids (TDS) in the range of 16450 to 16500 ppm] and determined the rejection rate of TDS & COD from the feed solution as a function of applied pressure. The results show that the permeate quality progressively improved with time and reached a saturated value after 2 – 3 hrs. Increased feed pressure significantly enhanced the rejection of both organics and salts. The experimental investigations proved that SWRO membrane at operating pressure of 35 bar excels than the counterpart BWRO in reducing the organic impurities to the minimal range of COD of 7680 ppm from the feed solution range up to 45070 ppm and the TDS in the range of 413.6 ppm from the feed solution up to16500 ppm. The outcome of this study confirms the RO treatment can reliably achieve the TDS level below 2100 ppm of reaching the Tamil Nadu Pollution Control Board (TNPCB) limit and emphasized the need for appropriate pre-treatment to reduce the organic load to minimum before processing through the RO membrane to facilitate compliance with the COD requirement of less than 250 ppm.



Schematic of test set-up for testing simulated SPP effluent using RO membrane

Time (min)	BWRO TDS (ppm)	SWRO TDS (ppm)	BWRO COD (ppm)	SWRO COD (ppm)
o	16500	16500	15825	7680
20	1215.38	516.10		
40	1173.84	501.83		
60	1195.95	501.42		
80	1245.53	487.30		
100	1538.32	474.89		
120	1431.79	450.44		
140	1280.571	418.48		
160	1243.52	415.20		
180	1240.84	413.60		

Applied Pressure: 35 Bar

Key words: *RO membrane, COD, TDS, SPP Effluent, HWP*

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Development of Graphene Oxide-b Cyclodextrin Composite Membranes for Separation of Strontium from Aqueous Solutions

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Graphene oxide (GO) is one of the extensively explored metal ion adsorbent materials in the past decade, owing to its phenomenally large surface area and abundant/tunable functional groups. Meanwhile, various micro-cyclic ligands were also investigated for metal ion entrapment, in view of host-guest interactions and tunable cavity dimensions, particularly for strontium (Sr) separation. However, conformation stability and toxicity have been few concerns with most of the micro-cyclic ligands. In this context, cyclodextrins are environmentally friendly, water-soluble cyclic oligomers and known to exhibit relatively stable host-guest interactions. Present work aims to prepare GO-β cyclodextrin (GO-βCD) composites, explore their characteristics and repercussions of such compositing on Sr separation ability of GO sheets. For this, GO (~0.5 mg/mL) and GO-βCD composite (~100 µg/mL βCD) dispersions were vacuum filtered (MCE filter, ~0.45 µm porosity) to prepare the membranes and Sr separation ability of obtained GO/GO-βCD membranes was examined. Compositing with βCD introduces substantial changes in GO vibrational features at ~2926 cm^{-1}, ~1430 cm^{-1} and ~1036 cm^{-1} (Fig. 1), which in turn suggest hydrogen bonding, electrostatic, nucleophilic substitution reactions among βCD molecules and GO functional groups and, their integration on GO sheets [1,2]. A schematic depicting all those possible interactions and a typical composite lamellar structure are shown in Fig. 2. To evaluate the Sr separation performance of GO/GO-βCD structures, aqueous Sr solutions (feed Sr:50 µg/mL) were percolated through GO as well as GO-βCD composite membranes under vacuum (15 min) and the filtrates were analyzed using Flame-AAS. Typical Sr adsorption performances of GO and GO-βCD composite membranes (0.1–0.6 mg) are shown in Fig. 3. In comparison with the precursor GO membranes (40-240 mg/g), composite membranes exhibited significantly escalated Sr adsorption capacity (70-420 mg/g), evidencing the synergistic Sr separation performance of GO sheets and βCD molecules in composite. Further, compositing with βCD enhances Sr adsorption ability of GO sheets nearly by two fold, irrespective of membrane mass conditions and an optimal Sr adsorption capacity of ~420 mg/g has been observed at ~0.1 mg. Despite such enhancement, even the GO-βCD composite membranes displayed deteriorating adsorption trend with the rise of membrane mass, due to degradation of composite layer surface area in lamellar structure and limited availability/accessibility of interaction sites/functionalities.

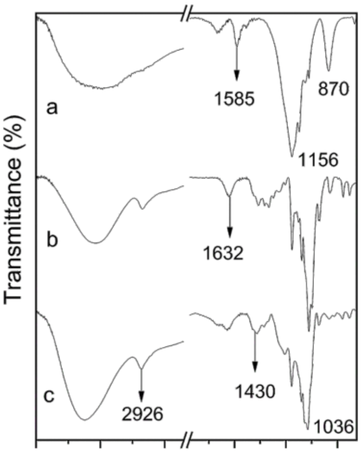

Fig. 1: *FT-IR spectra of (a) GO (b) βCD and (c) GO-βCD.*

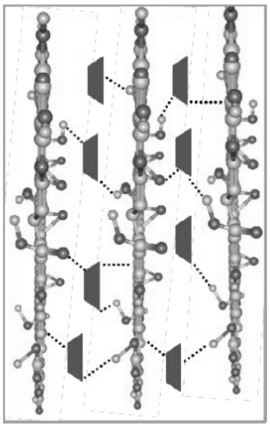

Fig. 2: *Schematic of GO-βCD composite layer structure.*

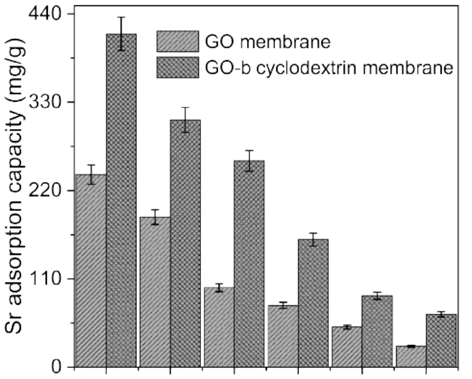

Fig. 3: *Sr adsorption capacity of GO and GO-βCD composite membranes at different mass.*

Key words: *Graphene oxide, β cyclodextrin, Strontium, Membrane, Adsorption*

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Effect of Phosphoric Acid Functionalization on Uranyl Adsorption Efficiency of Graphene Oxide Membranes

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Extraction of uranyl (UO_2^{2+}) ions from natural and nuclear aqueous resources has been widely investigated over decades, considering its importance in production of feedstock for nuclear plants and allied environmental issues [1]. Separation of uranyl ions via adsorption procedures was investigated using wide range of adsorbents, among which, GO based adsorbents have attracted substantial attention in recent years. Objective of the present work is to understand the effect of phosphoric acid (PA) functionalization on GO layers and explore the repercussions on uranyl adsorption ability of GO membranes. PA-functionalization of GO was carried out by preparation of GO-phosphoric acid (0.5–1.0 M H_3PO_4) composites and subsequent membrane fabrication. For the preparation of membranes, aqueous GO/GO-PA dispersions were spread on silicon substrate and dried enough under infrared lamp, where the formed free standing membranes (Fig. 1) get delaminated instantaneously. Interaction of GO layers with PA and subsequent changes in chemical composition, membrane structure and morphological characteristics of GO were examined. Compositing with PA brings up nominal changes in surface morphology of GO layers, reduces structural order of GO membranes and introduces multiple vibration features attributable to P-group incorporation (Fig. 2) including, possible formation of P-O and P=O functionalities [2]. Further, the uranyl adsorption ability of precursor and PA-functionalized GO membranes was evaluated by intercalation of these membranes in aqueous uranyl solution (feed uranyl: 50 µg/mL) and analysis of the supernatants collected at regular time intervals. Changes in uranyl (feed and supernatant) concentrations were analyzed by recording the absorption spectra of arsenazo III-uranyl complex solutions, where the absorbance value at ~650 nm was considered for the evaluation of uranyl concentration. The precursor GO membranes adsorb ~42% of feed uranyl ions in first 5 min of intercalation and in case of PA-functionalized GO membranes, the efficiency enhances up to ~72% (Fig. 3). Both precursor and PA functionalized membranes displayed optimum uranyl adsorption efficiency in first 5 min of intercalation, beyond which, their adsorption ability nearly saturates. In conclusion, functionalization of GO with phosphoric acid as P-source introduces additional functional groups on GO layers and enhances the uranyl adsorption ability of GO membranes significantly. Importantly, usage of such solid state GO/GO-PA composite membranes expedites the uranyl separation process and introduces an efficient method that mitigates the generation of secondary liquid wastes.

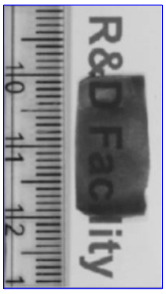

Fig. 1: Digital photograph of typical GOM.

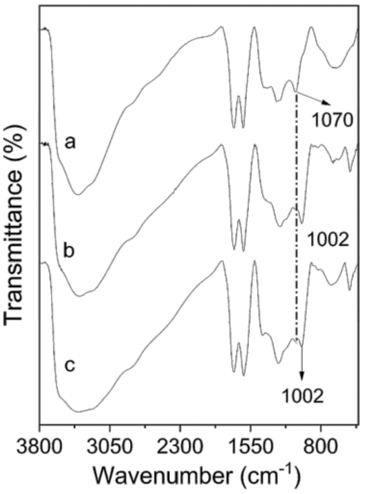

***Fig.2:** FT-IR spectra of (a) GOM and P-functionalized GOM prepared at (b) 0.5 M and (c) 1.0 M H_3PO_4.*

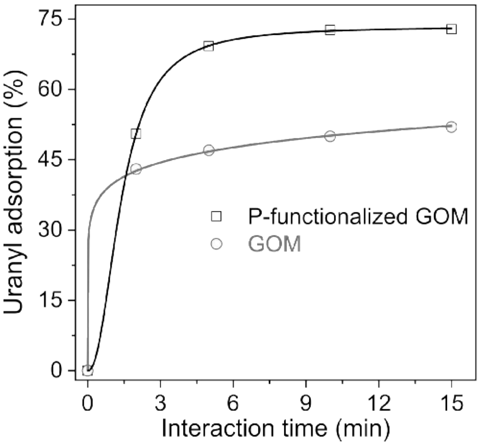

***Fig. 3:** Uranyl adsorption efficiency of GO and P-functionalized GOM as a function of interaction time.*

***Key words:** Graphene oxide, uranyl, P-functionalization, Membrane, Adsorption*

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Effect of Steam on Decomposition of Ammonia in Packed Bed Membrane Reactor

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Coke production, integral to the steel industry, generates coke oven gas that contains NH_3 (6-8 g/m^3) as an impurity. This NH_3, upon being stripped off, is often eliminated in the sulphur recovery unit to mitigate NOx formation. During this stripping operation, a gaseous stream containing NH_3 up to 50 vol% is generated, along with 20-40% entrained steam, with the balance composed of H_2S and CO_2 [1, 2]. Such NH_3-rich stream can be utilized for hydrogen production through thermal decomposition of NH_3. However, the decomposition is affected by presence of significant quantity of steam, which needs detailed investigation. Moreover, NH_3 decomposition is a mildly endothermic reaction that requires a temperature of ~900 °C to achieve industrial conversions greater than 95% [3]. To enhance the process efficiency, integrating membranes within the reaction chamber enables simultaneous reaction and product separation, providing a significant increase in conversion. Hence, in the present investigation, NH_3 decomposition studies in presence of steam were carried out in packed bed membrane reactor with porous clay alumina membrane and Pt-alumina catalyst. Fig. 1 shows the schematic of experimental setup.

The membranes were fabricated in-house using an extrusion-based process, which employed a slurry comprising alpha alumina, clay powder, water, and polyvinyl alcohol (serving as a binding agent), sintered at 1400 ºC. The membrane was found to have an average pore size of 0.85 µm (confirmed by image J analysis of SEM micrograph as shown in Fig. 2). The Pt-alumina catalyst was characterized using a surface area analyzer (BET), which revealed an average pore size of ~10 nm and a surface area of 195 m^2/g. An NH_3 to H_2 conversion of ~70% was obtained at 1 bar (g) and 700 ºC. To evaluate the influence of steam on ammonia decomposition, the ammonia-to-steam ratio was varied from 0.67 to 1.5, with an optimum found at 1.0, yielding a ~99% conversion of NH_3 (at same temperature & pressure). This could be attributed to the increased basicity of Pt- alumina catalyst in presence of steam that leads to enhanced NH_3 decomposition. Thus, membrane reactor, as a process intensification unit, offers a viable technology for hydrogen recovery from NH_3-rich streams obtained from coke production unit.

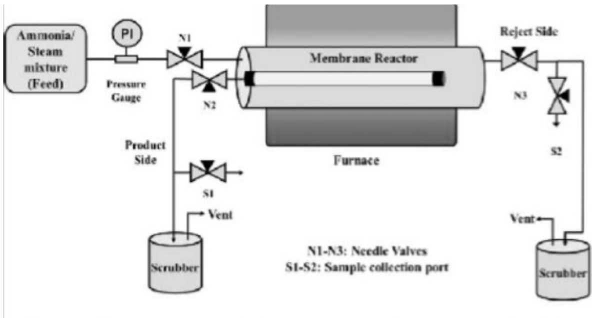

Fig.1: Schematic representation of experimental setup used for NH_3 decomposition studies

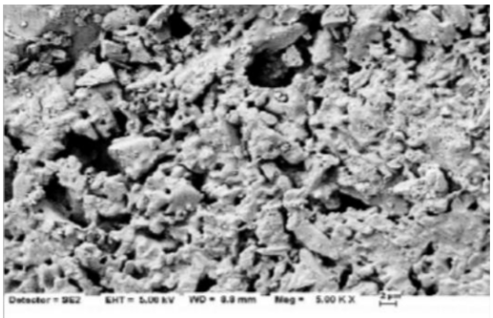

Fig.2: SEM image of the surface of clay alumina membrane

Key words: *Coke oven gas, Ammonia, Steam, Membrane reactor, Hydrogen*

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Studies on Process Parameters and Support Thickness on Extraction Performance of Supported Liquid Membrane for Chromium Removal from Aqueous Feed Solution

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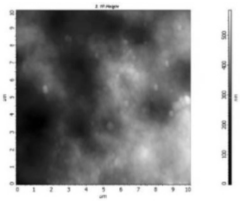
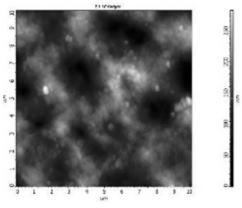
Chromium is extensively used in industries such as leather, steel and paint [1]. The effluent from such industries contains chromium which needs to be removed before discharge, keeping its concentration below 2 ppm [2]. Supported liquid membrane (SLM) based extraction of chromium from such effluents offer advantages of high surface area per unit volume, selective removal, simultaneous extraction and stripping among others [3].

In the present study, hydrophobic capillary polyvinylidene (PVDF) membrane were developed by vapor induced phase separation followed by non-solvent induced phase separation (VNIPS) process. These PVDF support membranes were prepared with different thickness and subsequently used as support in extraction of chromium. The liquid membrane held in the pores of the support consisted of Aliquat 336 as carrier in dodecane solvent. The aqueous feed used was 50 ppm chromium as potassium dichromate in HCl solution with pH of 1.5. Sodium nitrate with varying concentration was used as the stripping solution. The effect of carrier concentration, feed flow rate, strip flow rate, stripping solution composition and support thickness on the extraction performance of SLM was studied. Subsequently, mathematical model was used to compare the experimental data obtained with the extraction curve generated from the model equation.

The optimum concentrations of Aliquat 336 in liquid membrane and sodium nitrate in strip solution were found to be 0.1 M and 0.75 M respectively. The optimum feed and strip flow rates were 100 mL/min and 150 mL/min respectively. The optimum thickness of the PVDF support membrane was 90 µm. The optimum values were found for highest extraction achieved in 6 hours. The mathematical model predicted the results obtained experimentally with deviation less than 10%. The chromium extraction achieved in 6 hours with optimum process parameters and support thickness was ~91%.

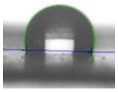


RMS roughness: 52.35 nm



RMS roughness: 57.47 nm

Fig. 1: Atomic Force Microscopy images of PVDF capillary support



Water contact angle: ~ 105.5°

Fig. 2: Images of water drop on PVDF capillary support to measure water contact angle

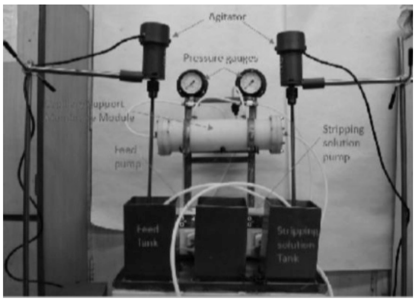


Fig. 3: SLM setup used

Key words: *chromium, polyvinylidene fluoride (PVDF), supported liquid membrane (SLM), support thickness, mathematical modelling*

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Development of Membrane for Concentration of Noble Gases

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Noble gas capture from ambient air is essential due to their extremely low natural abundance and high demand in medical, industrial, and scientific applications. Their efficient recovery enables a reliable supply of critical gases like xenon and krypton, supporting advanced technologies and reducing dependence on costly imports. Current commercial noble gas capture method, cryogenic distillation, requires large infrastructure and is energy intensive [1, 2]. Membrane-based separation, on the other hand, offers a low-energy, modular alternative with flexibility of continuous operation, tunable selectivity and reduced capital cost.

In this work, polysulfone (PSF) membrane which can selectively permeate O_2 and concentrate Xe in retentate is developed. The PSF flat-sheet asymmetric membrane was synthesized by dual phase inversion technique; the composition of the dope solution, gelling time and gelling media composition were optimized. Optimum dope composition was found to be 26% PSF in dimethyl acetamide with gelling time of 60 s in iso- propyl alcohol (1st gelling medium) followed by 24 h gelling in water (2nd gelling medium). The membranes were thermally treated (up to 80 °C) to densify their microstructure and improve separation performance. Membranes were characterized by SEM, AFM and gas permeation analysis. Cross sectional SEM image (Fig. 1) shows that membrane has top dense skin surface with finger-like structure at bottom. The AFM image (Fig. 2) indicates that the membrane prepared with a 60 s exposure to the first gelling medium exhibits low surface roughness of 6.5 nm, reflecting a smooth, dense, and uniform surface morphology. The permeabilities of pure O_2 & N_2 for flat sheet membrane were found to be 16 ± 2 & 3 ± 0.5 barrer, respectively, at 10 bar and 30°C (Fig. 3). It was observed that with increase in gelling time in iso-propyl alcohol (up to 60 s), there is an increase in O_2/N_2 selectivity due to pronounced dense skin layer as an outcome of delayed demixing. However, beyond 60 s, there is a decrease in selectivity due to defect formation. The membrane was utilized for xenon enrichment from a calibrated gas mixture comprising 5% Xe in air. Gas chromatography measurements demonstrated a 10% increase in xenon concentration in the retentate over an operational period of 150 min.

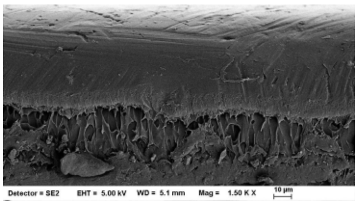

Fig. 1: *SEM image of PSF membrane*

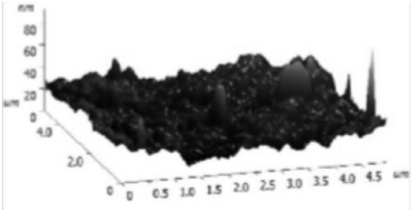

Fig. 2: *AFM image of PSF membrane*

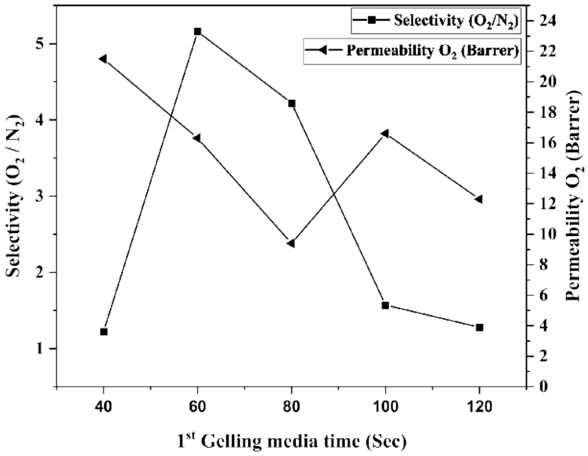

Fig. 3: *Gas permeation behavior of PSF membrane*

Key words: *Asymmetric membrane, O_2/N_2 separation, Polymeric membrane, Noble gases, Dual phase inversion*

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Effect of TiN Coating Thickness on Corrosion and ICR Behavior of AISI 316L Bipolar Plates for Proton Exchange Membrane Fuel Cells

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In polymer electrolyte membrane fuel cells (PEMFCs), the use of AISI 316L stainless steel as metallic bipolar plates is limited by two critical challenges: low corrosion resistance and high interfacial contact resistance (ICR). In this study, the corrosion behavior and ICR of AISI 316L specimens coated with titanium nitride (TiN) layers of varying thicknesses (1, 2, and 3 µm) were systematically investigated. TiN (titanium nitride) provides a good balance of corrosion resistance, electrical conductivity, and durability under the harsh PEMFC operating environment. The TiN coatings were applied using physical vapor deposition (PVD), a technique known for producing dense and adherent thin films suitable for fuel cell applications.

Electrochemical characterization of the coated specimens was performed under simulated PEMFC operating conditions at 80 °C using a pH 3 H_2SO_4 solution with 2 ppm HF, purged with either O_2 or H_2 to replicate cathodic and anodic environments, respectively. Potentiodynamic polarization, potentiostatic (PS) tests, and electrochemical impedance spectroscopy (EIS) were employed to quantify corrosion performance.

The Potentiodynamic polarization results indicated that the TiN-coated specimens exhibited significantly improved corrosion resistance compared to uncoated 316L. In the simulated cathode environment, corrosion potentials of coated specimens were higher than the bare substrate, indicating effective retardation of the corrosion process. The corrosion current densities (i_corr) of the TiN coatings were all below 1 $\mu A\cdot cm^{-2}$, with a clear trend of decreasing i_corr from 0.76 $\mu A\cdot cm^{-2}$ for 1 µm coatings to 0.43 $\mu A\cdot cm^{-2}$ for 3 µm coatings, demonstrating enhanced protective efficiency with increasing thickness. Under simulated anodic conditions, both coated and uncoated specimens exhibited negative current densities (-0.2 to -0.31 $\mu A\cdot cm^{-2}$), providing cathodic protection and confirming the passive nature of the coatings.

ICR measurements demonstrated that TiN coatings effectively reduced electrical resistance compared to bare 316L stainless steel. Specifically, the ICR increased in the order: graphite < TiN < TiN after PS < bare 316L < bare 316L after PS, indicating that the formed passive layers on TiN-coated surfaces improved conductivity relative to uncoated specimens.

In conclusion, TiN coatings applied via PVD significantly enhance the corrosion resistance of AISI 316L under simulated PEMFC conditions and provide moderate reduction of ICR. The protective efficiency improves with increasing coating thickness, and all coated specimens maintain current densities below the DOE corrosion target of 1 $\mu A\cdot cm^{-2}$. While TiN coatings represent a practical and effective approach to mitigating the limitations of stainless steel bipolar plates in PEMFC applications.

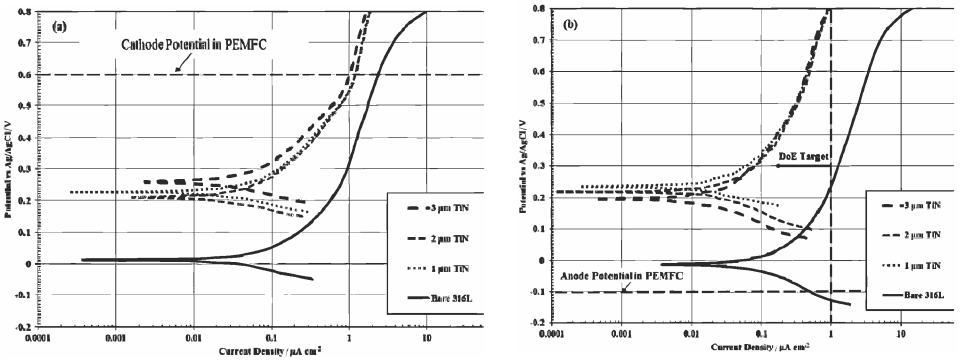

Figure 1: *Potentiodynamic polarization curves for uncoated and TiN-coated specimens in a pH3* H_2SO_4*+2 ppm HF solution at 80 °C with (a)* O_2 *purging and (b)* H_2 *purging.*

Key words: Proton Exchange Membrane Fuel Cell (PEMFC), AISI 316L Stainless Steel, Bipolar Plate

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Furan-Derived Pillar[4]Arene[1]Quinone Crystals for Efficient Adsorption of Iodine

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Nuclear reactors, through Uranium-235 fission, generate hazardous radioactive isotopes like ^{129}I and ^{131}I, which possess substantial volatility and a formidable half-life of 1.5×10^7 years, posing grave threats to both the environment and human health. Addressing the global focus on removing these isotopes, recent literature highlights non-porous adaptive crystals (NACs) as promising agents for iodine adsorption.[1] In this context, herein we report the synthesis of the furfuryl amine functionalized pillar[4]arene[1]quinone derivative[2] (BFP) using Michael-addition and characterized by various analytical techniques including ^{1}H-NMR, ^{13}C-NMR, ATR- FTIR, TGA, and single-crystal XRD.

BFP manifests an impressive iodine vapor adsorption capacity of approximately ~4.0 gg^{-1}. Within BFP, the cavity assumes a pivotal role, serving as a site for potential interactions with iodine during the adsorption process. The tailored nature of this cavity significantly influences BFP's adsorption capability, enabling the capture and release of iodine, as evidenced by its reversible adsorption behavior.[3] The manipulation of the cavity in pillar[4]arene[1]quinone not only showcases its versatility but also opens avenues for designing molecular systems with tailored host-guest interactions. This distinctive feature enhances the compound's potential applications in catalysis, sensing, and environmental endeavors, particularly in the realm of nuclear waste treatment.

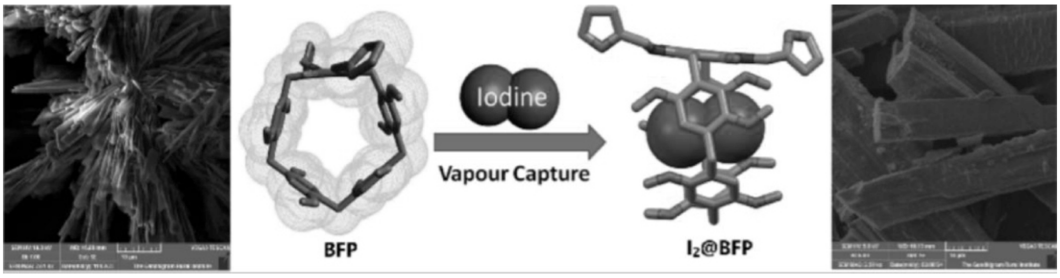

Figure 1: *cartoon representation of iodine adsorption of BFP along with SEM images*

Key words: *Iodine, sequestration, pillar[4]arene[1]quinone, non-porous, crystals*

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D-2

An Eco-conscious, Sustainable Schiff Base-Integrated Porous Polymer Monolith for Rapid and Sensitive Visual Quantification of Thorium Ions

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Thorium (Th^{4+}) ions pose significant environmental and occupational health risks due to their radiotoxicity, long-term persistence, and bioaccumulation in aquatic and terrestrial ecosystems [1]. At the same time, thorium is also an important strategic resource, widely utilized in advanced nuclear energy systems and in high- performance materials. Thorium improves the mechanical strength, creep resistance, and high-temperature stability of structural alloys, particularly magnesium–thorium alloys, which are employed in aerospace components and turbine engines. Therefore, the development of sensitive, selective, and cost-effective thorium detection systems is critical not only for environmental monitoring but also for efficient resource management and recovery. In this work, we synthesized a sustainable solid-state optical sensor for the detection, quantification, and potential recovery-related monitoring of Th^{4+} in aqueous solutions. A Schiff base probe, (Z)- N-(4-(diethylamino)-2-hydroxybenzylidene)-3-nitrobenzohydrazide (DHBH), was successfully immobilized on a porous polymer monolithic framework, poly(AMPH-co-EGDMA), which was prepared via thermal-assisted free-radical bulk polymerization using a functional monomer (AMPH), a crosslinker (EGDMA), and porogenic solvents. This yielded the sensor material poly(AMPH-co-EGDMA)DHBH, characterized by high structural stability, large surface area, tunable porosity, and excellent reusability. The material enables naked-eye detection of ultra-trace Th^{4+} concentrations in real-world aqueous samples [2]. Comprehensive characterization of both the monolithic template (poly(AMPH-co-EGDMA)) and the sensor material (poly(AMPH-co-EGDMA)DHBH) was performed using FT-IR, BET-BJH, FE-SEM, HR-TEM, EDAX, and XPS analyses. A distinct color transition from pale yellow to dark orange-brown is observed upon Th^{4+} binding. Optimization of key analytical parameters reveals a linear response range of 0–100 µg/L at pH 6.0, with detection and quantification limits of 0.68 and 2.26 µg/L, respectively. The rapid signal development within 60 seconds highlights the role of the macro-/mesoporous network in facilitating fast ion diffusion. The sensor shows high selectivity toward Th $^{+}$ over competing ions and maintains excellent reusability over seven consecutive sensing–regeneration cycles.

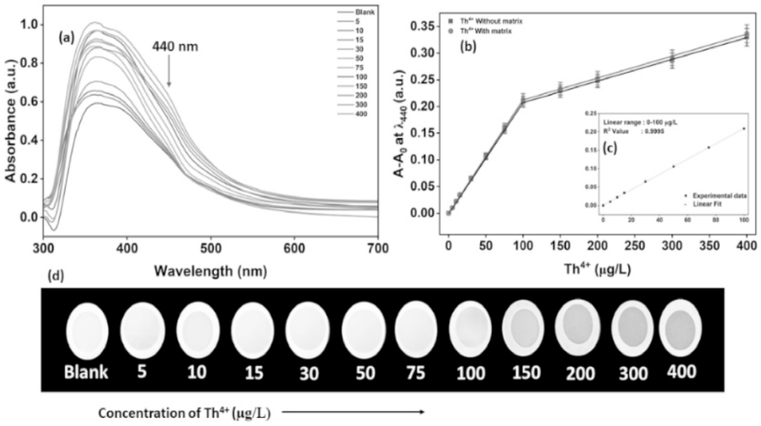

Fig: *(a) UV-Vis -DRS signal response profile, (b) calibration plot, (c) linear fit data, and (d) gradual naked eye colour shift of the sensor with an incremental concentration of* Th^{4+}.

Key words: *Polymer monolith, Schiff base, Thorium, Solid-state sensor, Mesoporous.*

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A Novel Three-Dimensionally Interconnected Porous Organic-Inorganic Hybrid Monolith as a Probe Anchoring Template for Solid-State Optical Sensing and Preconcentration of UO_2^{2+}

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Industrial operations such as uranium mining, nuclear fuel processing, and phosphate fertilizer production release significant quantities of uranium compounds, leading to severe contamination of soil and water resources [1]. The uranyl ion (UO_{2+}), the most mobile and soluble form, poses significant ecological and health risks, including nephrotoxicity, bone accumulation, and potential carcinogenic effects [2]. Conventional detection methods are often expensive, time-consuming, and unsuitable for rapid on-site monitoring. To overcome these limitations, this study presents a sensitive and selective solid-state colorimetric sensor for UO_{2+} detection and preconcentration from contaminated water samples. The sensor enables rapid visual detection through a distinct color transition, allowing trace-level monitoring without complex instrumentation. The sensing system employs the chromoionophoric properties of an azomethine probe, N'2-((Z)-4-(diethylamino)-2-hydroxybenzylidene)- N'6-(4-(diethylamino)-2-hydroxybenzylidene)dipicolinic-2,6-dicarbohydrazide (DHDPH), which changes from light yellow to dark orange upon binding UO_{2+}. Embedding the probe in a meso/macro-porous silica-polymer hybrid monolithic matrix, poly(VTEO-co-PETRA), enhances sensitivity, selectivity, and operational stability. Structural features are confirmed using p-XRD, FT-IR, BET/BJH, TGA, XPS, FE-SEM, and HR-TEM. Optimization of pH, probe concentration, sensor dosage, and metal ion concentration improves performance, while UV-DRS studies confirm minimal interference from other metal ions. The sensor achieves a detection limit of 0.28 ppb and a quantification limit of 1.12 ppb. The developed sensor was evaluated using a standard uranium solution prepared from uranyl nitrate $UO_2(NO_3)_2 \cdot 6H_2O$ (Sigma-Aldrich), which provides non- radioactive ('cold') uranium. The monolithic template's voluminous surface area and spacious porosity enhance receptor integration efficiency with constrained spatial orientation, offering exclusive UO_{2+}selectivity and maximizing the response kinetics (≤40 s). This work provides a robust and practical platform for rapid uranyl monitoring and preconcentration, supporting environmental surveillance and radiological safety efforts.

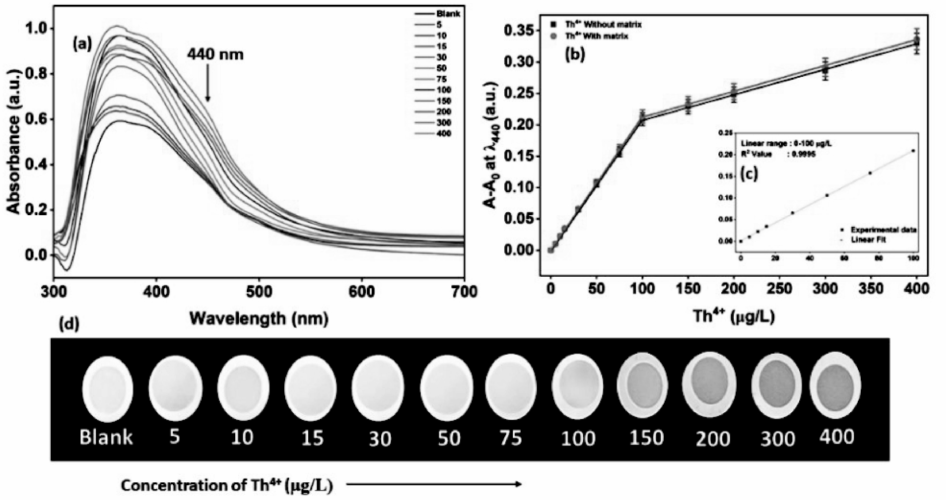

Fig (a) *Evaluation of cationic interference study using UV-DRS spectroscopy and* ***(b)*** *Naked-eye color response of fabricated sensor material upon interaction with heavy metal ions.*

Keywords: *Solid-state sensor, Hybrid monolith, Chromoionophoric, Meso/Macro-porous,* UO_2^{2+}.

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Characterisation of Cladding Hull Waste from Reprocessing Plant

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Management of metallic cladding hull waste generated during spent fuel reprocessing is a critical step in minimizing secondary radioactive waste and ensuring radiological safety [1, 2]. In this study, a representative hull sample from a single reprocessing batch was subjected to controlled chemical decontamination to quantify removable surface contamination and evaluate the residual matrix-bound activity using two complementary methodologies: surface etching and complete dissolution.

In the first approach, controlled chemical etching of hull samples was performed to selectively remove surface contamination and oxide layers. The resulting leachates were analyzed using High-Purity Germanium (HP-Ge) gamma spectrometry, alpha spectrometry, and gross radiometry. HP-Ge spectra revealed distinct signatures of fission products such as ^{137}Cs and ^{125}Sb, along with activation products including ^{60}Co, confirming both surface-deposited contamination and neutron-induced activation of the cladding material. Gross radiometry of the hull leachate showed significant removal of surface-bound activity, with measured gross β–γ activity of ~9.5×10^5 Bq·g^{-1} and gross α activity of ~3.0×10^4 Bq·g^{-1}, demonstrating the effectiveness of the chemical decontamination cycle in stripping fission-product contaminants from the cladding exterior.

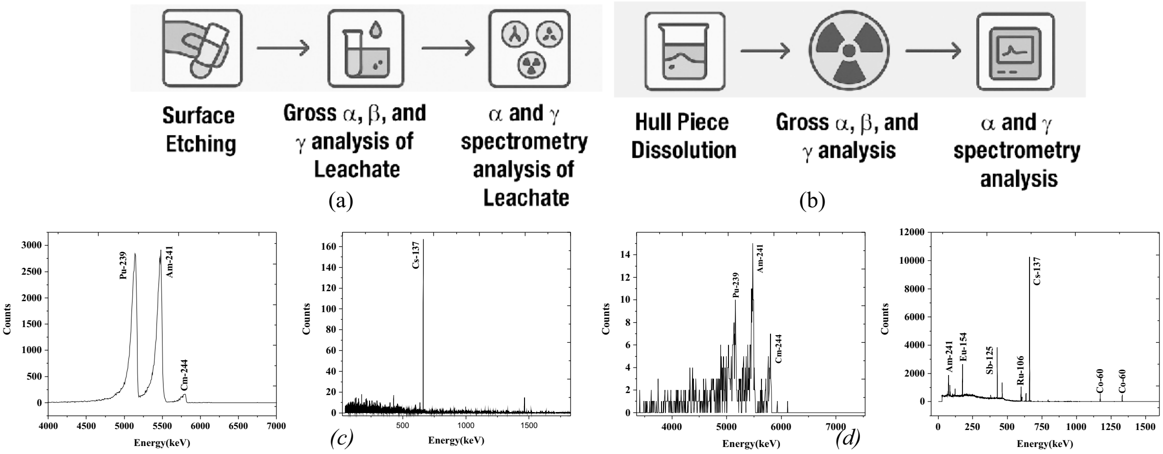

Fig 1. (a) Approach 1, (b) approach 2, (c) alpha and gamma spectrum of leachant (approach 1), and (d) alpha and gamma spectrum of hull dissolved (approach 2)

Alpha spectrometry complemented these findings by identifying transuranic radionuclides embedded in or adhering to the hull surfaces. Peaks corresponding to ^{239}Pu, ^{241}Am and ^{244}Cm were observed, indicating the persistence of alpha-emitting actinides even after mechanical and chemical cleaning during reprocessing. The presence of these isotopes highlights the long-term radiotoxicity potential of hull waste and underscores the importance of accurate isotopic characterization.

In the second approach, complete dissolution of hull samples in hydrofluoric acid was carried out to determine the total inventory of radionuclides within the cladding matrix. Radiometric and spectrometric analyses of the dissolution solutions confirmed the incorporation of both fission and activation products into the metallic lattice, differentiating matrix-bound activity from surface contamination. The comparative evaluation of surface etching and dissolution methodologies provided valuable insight into the distribution of residual activity in hull waste. This dual approach establishes a robust framework for waste characterization, supporting optimization of classification, conditioning, and safe interim storage strategies in reprocessing facilities.

Keywords: *Hull; Zircaloy-4; Alpha Spectrometry; HP-Ge gamma ray spectrometry; Actinides; Fission Products*

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High-Performance Iodine Adsorption using a Benzylated β-Cyclodextrin–Triazine-based Porous Organic Polymer

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Iodine sequestration has gained significant attention due to the environmental and health hazards posed by radioactive iodine released from nuclear waste. In this context, porous organic polymers (POPs) have emerged as promising adsorbent materials owing to their structural tunability, high surface area, and strong iodine- binding capability.[1-3] A one-pot reaction was employed to synthesize the β-cyclodextrin-based porous organic polymer (BCD), wherein the triazine backbone served as the crosslinking unit. Under identical reaction conditions, but in the absence of benzylated β-cyclodextrin, the corresponding 1,5-diphenylcarbazide-based triazine-crosslinked polymer (DT) was obtained. The iodine adsorption performances of both polymers were evaluated in aqueous and vapour phases. The DT polymer exhibited remarkable iodine uptake capacities, achieving 1258 mg g^{-1} in water (Fig. 1B) and 6.8 g g^{-1} in the vapour phase. In contrast, the BCD porous organic polymer exhibited comparatively lower adsorption capacities, with 684 mg g^{-1} from water (Fig. 1D) and 4.1 g g^{-1} from vapour. These results clearly demonstrate that the DT polymer possesses a substantially higher iodine adsorption capability than the BCD polymer under both experimental conditions. Furthermore, after five adsorption–desorption cycles (Fig. 1A), the polymer retained a significant fraction of its iodine uptake capacity. Dynamic adsorption studies also confirmed the reversible nature of iodine capture, highlighting the potential of the polymer for reuse and sustainable environmental and nuclear waste management applications.

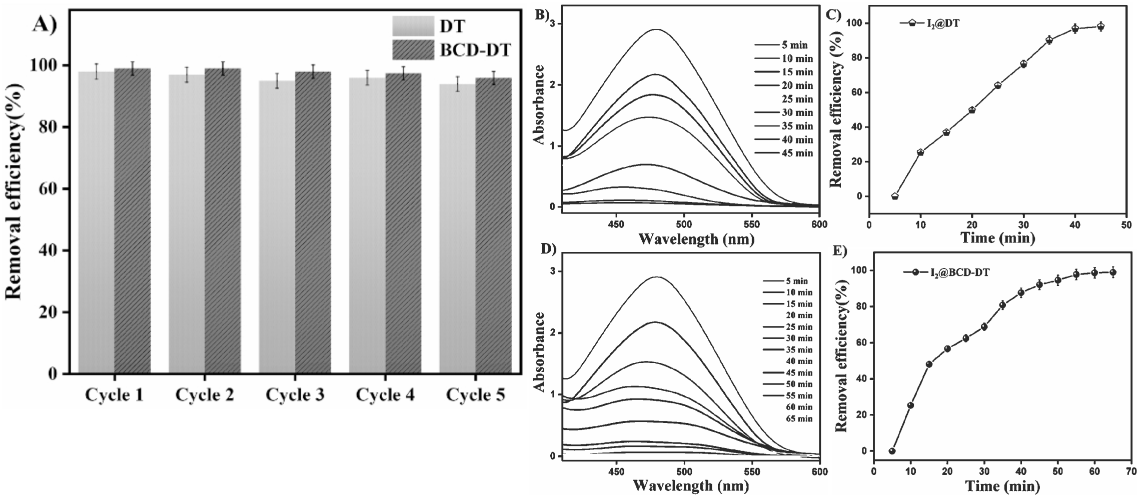

Fig 1. A) Polymer recyclability assessed by repeated iodine adsorption–desorption cycles. UV–vis spectra of aqueous iodine 1500 mg L^{-1} at 463 nm A, after addition of B) DT, D) BCD-DT at different sonication times and C) DT, E) BCD-DT corresponding iodine removal efficiencies

Keywords: *benzylated β-cyclodextrin, iodine, triazine, porous organic polymer*

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D-6

Dual-functional Zr-MOF for Rapid Chromogenic Detection and Highly Selective Recovery of Ru^{3+} from Industrial and Electronic Waste Leachates

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Ruthenium (Ru), a member of the platinum group metals (PGMs), is widely applied in electroplating, medicine, jewelry, and catalysis owing to its distinctive physicochemical properties. However, nearly 4% of precious metals remain unrecovered in waste residues, waste streams, and electroplating baths during processing **[1]**. To address this challenge, solid-state colorimetric sensors provide an efficient route for the detection and recovery of Ru^{3+}, while preconcentration strategies further enhance its recovery from E-waste leachates and industrial effluents. In this study, a novel, first-of-its-kind solid-state chromogenic chemosensor was developed by functionalizing NH_2-UiO-66(Zr) via Schiff-base condensation with vanillin, yielding the VNL=N-UiO-66(Zr) sensor for Ru^{3+} detection. The successful formation of both the parent MOF and the functionalized sensor was verified by PXRD. Furthermore, the materials were systematically characterized using FT-IR, FE-SEM, HR- TEM, XPS, and BET/BJH analyses. Among these, FT-IR and XPS provided conclusive evidence for Schiff- base formation and Ru^{3+} coordination with the binding sites. The sensor exhibited ultra-fast, selective, and pH- dependent recognition of Ru^{3+}, with a rapid response time of 40 s. Both naked-eye colorimetry and UV-Visible- DRS measurements confirmed its high sensitivity, affording a low detection limit of 0.36 $\mu g\ L^{-1}$ and excellent linearity over the concentration range of 0-100 $\mu g\ L^{-1}$ ($r^2 > 0.999$) at neutral pH. As shown in Fig. 1(a), pH- dependent sorption studies revealed maximum Ru^{3+} uptake at pH 7.0. Additionally, the sensor demonstrated strong preconcentration capability, enabling the complete recovery of Ru^{3+} from treated samples. The outstanding chemical and physical stability of the VNL=N-UiO-66(Zr) system underscores its promise for real- world applications. Overall, this work introduces a cost-effective and reliable sensor platform for the ultra-trace detection and recovery of valuable Ru^{3+} ions, offering significant potential for future commercialization.

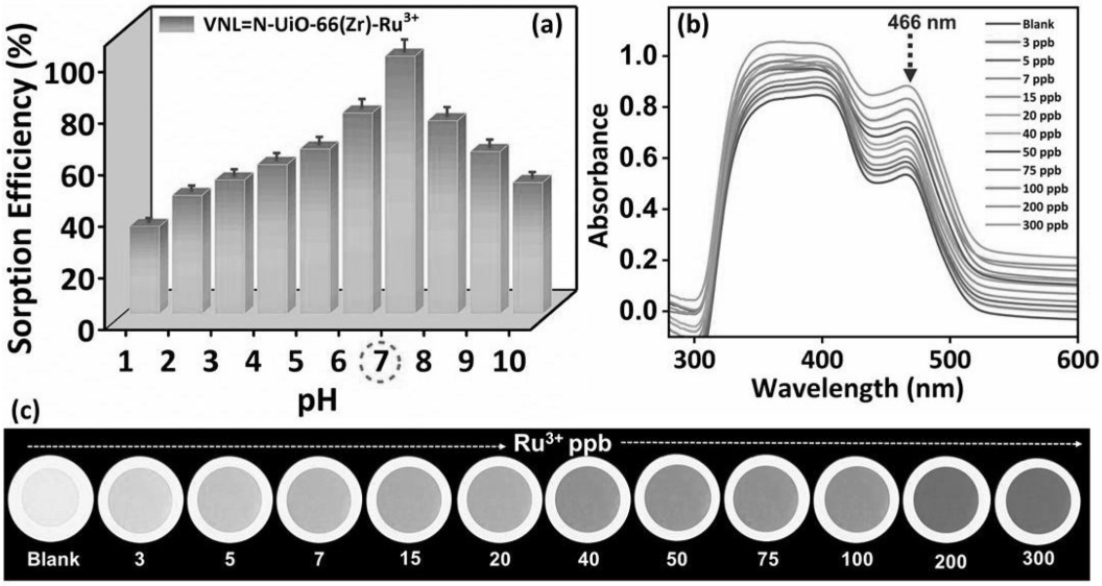

Fig. 1:(a) Sorption efficiency of VNL=N-UiO-66(Zr) with Ru^{3+} under varying pH, ***(b)*** *UV-Visible-DRS spectral patterns for increasing concentration of Ru^{3+}, and* ***(c)*** *visual solid-state colour transition images for the VNL=N-UiO-66(Zr)-Ru^{3+} complex during the concentration proportionate sensing process.*

Key words: *Zr-MOF, Ru^{3+}, Solid-state chemosensor, E-waste extractants, and Pre-concentrator*

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Advanced Porous Monolithic Sensors for Highly Selective Detection and Recovery of Palladium from E-Waste Streams

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Palladium (Pd), one of the rarest transition metals, is industrially indispensable in catalytic converters, petroleum refining, electronics, pharmaceuticals, jewellery manufacturing, and complex drug synthesis. However, trace amounts of residual palladium persisting in products and waste streams pose significant toxicological risks. Compelling evidence indicates that Pd^{2+} exhibits a strong affinity toward thiol-functionalized biomolecules, including amino acids, proteins, and DNA, thereby impairing cellular function and inducing apoptosis. Reported health effects include contact dermatitis, skin sensitization, lung inflammation, and hepatic and renal lesions [1]. To address these concerns, the present study develops a highly robust solid- state colorimetric sensor designed for the rapid detection, quantification, and recovery of Pd^{2+} ions. While previous research has explored diverse sensing approaches for heavy metals, solid-state platforms endowed with regimented mesoporous networks and large surface areas offer exceptional precision in metal-ion recognition. The sensor integrates a Schiff-base chromoionophore that functions as a colour-responsive probe, exhibiting a distinct visual transition upon interaction with Pd^{2+}. A bimodal macro-/mesoporous hybrid polymer monolith, poly(TMSPMA-co-PETRA), was synthesized to enable efficient and uniform incorporation of the ion receptor, (Z)-2-((2-hydroxynaphthalen-1-yl)methylene)-N-phenylhydrazine-1-carbothioamide (HMPC). Comprehensive structural and surface characterization—including morphology, surface area, pore distribution, and phase analysis—was conducted on both the template and the functionalized sensor using p-XRD, HR-TEM, FE-SEM, FT-IR, and BET/BJH techniques [2]. Critical sensing parameters, including pH, probe loading, sensor dosage, and analyte concentration, were systematically optimized. Potential interferences from common metal cations and anions in aqueous media were evaluated using UV-Vis spectroscopy. The stability of the developed sensor was systematically assessed under various working conditions, including pH tolerance and temperature variations. The sensor demonstrated robust reusability, retaining performance across eight consecutive cycles, and long-term durability for up to 8 months. Notably, it achieved a low limit of detection of 0.505 μg L^{-1}, enabling reliable quantification of analytes at trace concentrations. This work presents an innovative and cost- effective solid-state optical sensor that enables both selective recovery and sensitive detection of Pd^{2+}. By integrating precious metal reclamation with reduced environmental toxicity, the system contributes significantly to sustainable resource management, offering a valuable platform for economically and ecologically responsible applications.

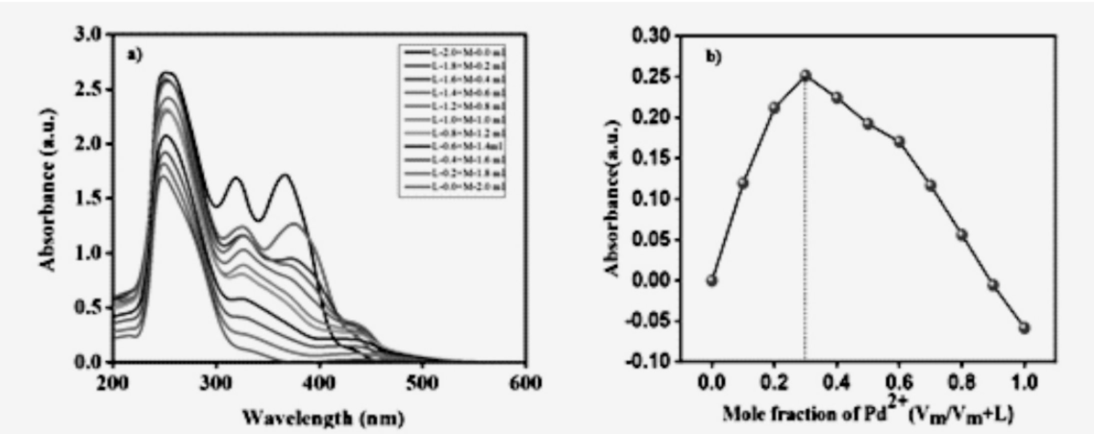

Fig. (a) *UV- Vis absorbance spectra for Pd^{2+} complex, and* ***(b)*** *Job's plot stoichiometric binding for (HMPC)- Pd^{2+} complex.*

Key words: *Schiff base, macro-/mesoporous, hybrid polymer monolith.*

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A Comparative Study on the Removal of Malachite Green Using Titanium Amino Tris (methylene phosphonic acid) (Ti-ATMP) and Zirconium Amino Tris-methylene Phosphonic Acid (Zr-ATMP) as an Adsorbents

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Industrial expansion and the widespread use of synthetic dyes in textile, leather, and printing industries have intensified the problem of water pollution, particularly due to the discharge of untreated dye-containing effluents. Among these pollutants, malachite green (MG), a cationic triphenylmethane dye, is of significant environmental concern owing to its high toxicity, carcinogenic nature, and resistance to degradation. The development of efficient and sustainable adsorbents for its removal is therefore an urgent need. Metal phosphonates, formed through organic–inorganic hybridization, have emerged as promising functional materials owing to their structural tunability, strong binding affinity, and excellent ion-exchange behaviour. It has been reported that, Ti-ATMP exhibits a good ion exchange capacity (4.01 $\text{mequiv}\cdot g^{-1}$) and exhibited good selectivity for the Cu^{2+} among the transition metal ions and Pb^{2+} among the heavy metal ions[1]. Further, this material was also explored as a solid acid catalyst for the esterification reaction of biomass-derived levulinic acid with n-butanol to synthesize n-butyl levulinate [2]. Similarly, Zr-ATMP also exhibits good selectivity for Cu^{2+} amongst the transition metal ions and Pb^{2+} amongst the heavy metal ions [3]. Further, from our research group a comparative study of proton transport properties of Zr-ATMP was explored [4]. The versatile performance of these materials motivates us to explore its application towards the removal of water-soluble dye like MG. Hence, in present study we investigated the effectiveness of Ti-ATMP and Zr-ATMP as an adsorbent for the removal of malachite green (MG) from aqueous solutions under varying conditions, including pH, temperature, contact time, and adsorbent dosage. The influence of pH range, adsorbent dose (m), temperature, MG concentration and contact time (t) on the adsorption efficiency was systematically examined. The term aqueous solution refers to a simulated effluent system prepared using malachite green dissolved in deionized water, without interference from competing ions or organic impurities. To elucidate the adsorption mechanism, various kinetic models namely pseudo-first-order, pseudo-second-order, Bangham, and intra-particle diffusion were applied to the experimental data. Additionally, the equilibrium sorption capacity of MG was evaluated using different isotherm models, and the best-fitting models were determined through comprehensive error analysis. This integrated approach provides a detailed understanding of the adsorption behavior of MG on both adsorbents. Both adsorbents demonstrated high MG uptake, confirming their strong affinity for cationic pollutants. The maximum adsorption capacities obtained for Ti-ATMP (169.49 $mg.g^{-1}$) and Zr-ATMP (117.64 $mg.g^{-1}$) were significantly higher than many previously reported adsorbents, underscoring the outstanding potential of metal phosphonates in dye remediation. Thermodynamic analysis further supported the feasibility of adsorption, with negative ΔG° values indicating spontaneity. The negative ΔH° values confirmed an exothermic adsorption process, while the decrease in entropy ($\Delta S^\circ < 0$) suggested strong physical interactions, likely electrostatic attraction or hydrogen bonding between the MG molecules and the phosphonate surface. Overall, the results establish Ti-ATMP and Zr-ATMP as highly effective, reusable, and structurally robust adsorbents for the removal of malachite green from aqueous media. This study contributes valuable insights into adsorption mechanisms, material performance, and the future potential of metal phosphonate-based hybrid materials in environmental remediation technologies. Regeneration and reusability studies indicate that after adsorption, the dye-loaded adsorbents were separated by simple filtration. The spent exchangers can be regenerated using 0.5 M nitric acid washing, allowing desorption of MG for safe collection and neutralization.

Key words: *Adsorbents, Removal of Malachite green, Titanium- amino tris(methylene phosphonic acid)(Ti- ATMP), Zirconium- amino tris(methylene phosphonic acid) (Zr-ATMP), Metal phosphonates as adsorbents*

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La^{3+}-MoS_2/PVDF Nanofiber As A Free-Standing Membrane For The Highly Efficient Continuous Flow Piezocatalytic Reduction of High Concentrations of Cr(VI) in Water

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Primary effluents generated from leather tannery operations contain a high concentration of toxic Cr(VI), a well- known carcinogenic species. Developing sustainable, environmentally friendly strategies for the remediation of Cr(VI)-containing water bodies is therefore a critical priority **[1]**. In recent years, piezocatalysts and their hybrid materials have emerged as promising candidates, offering chemical-free pathways for efficient treatment and decontamination of such pollutants **[2]**. Unlike photocatalysis, piezocatalysis provides more efficient energy transfer as ultrasonic waves penetrate the reaction medium with little loss, unlike light, which can be scattered or absorbed. Mechanical energy from ultrasonication is effectively converted into chemical energy via piezoelectric materials, which generate piezopotential to drive redox reactions without optical interference. Ultrasonic bath sonicators, a standard piece of equipment in industrial and lab environments, in combination with piezocatalysts, could be the future of Cr(VI) remediation. Herein, MoS_2 nanoflowers (NFs) with La^{3+} were synthesized by the hydrothermal method. The PXRD of varying wt% of La3+ shows an increase in the interlayer spacing of MoS_2 for loadings of 0.6%, 0.8%, and 1.0%. The Higher loadings 1.2% and 1.4% did not cause any increase in the interlayer spacing. Among the catalysts, the 1.0% La^{3+}-doped MoS_2 showed maximum efficiency in Cr(VI) reduction. At pH 2, 20mg of catalyst reduced 30 ppm of Cr(VI) to Cr(III) within 5 minutes under ultrasonication at 40kHz. The Cr(VI) concentration of the post-reaction aliquots was quantified with the diphenylcarbazide method. The Cr(VI) reducing property of the La^{3+}-MoS_2 was verified by the indirect quantification of Cr(III) by estimating the total Cr content with AAS. The AAS results showed a total Cr of 17.6 ppm, indicating that more than 58% of the Cr(VI) was reduced to Cr(III), with the remaining 42% adsorbed. We have adopted electrospinning to produce a PVDF-based nanofiber membrane, La^{3+}-MoS_2/PVDF, and have employed it in the continuous-flow treatment of Cr(VI)-contaminated water. La^{3+}-MoS2 and La^{3+}-MoS_2/PVDF were characterized by PXRD, FTIR, FE-SEM, HR-TEM, TGA, BET/BJH, EDAX, elemental mapping, and XPS. Further piezo-photocatalytic reduction of Cr(VI) by La^{3+}-MoS_2/PVDF was studied under ambient light conditions. The reaction parameters, including pH, catalyst dosage, initial Cr(VI) concentration, flow rate, and ultrasonic vibration frequency, were optimized to achieve peak La^{3+}-MoS_2/PVDF performance in Cr(VI).

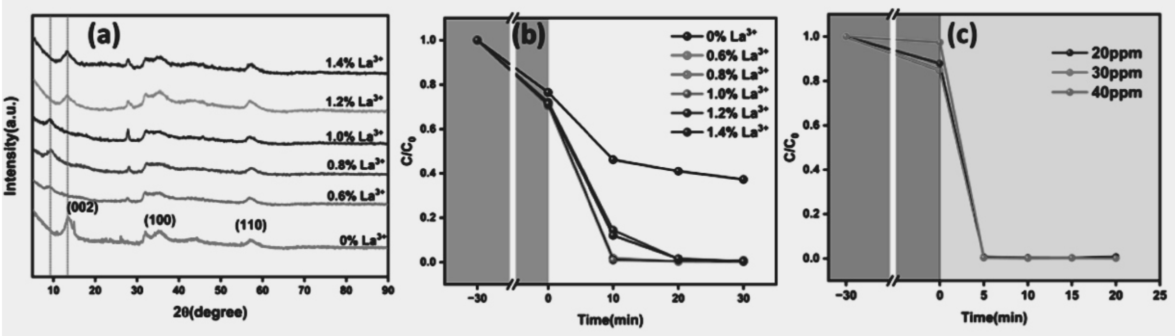

Fig 1 *(a) PXRD of the* La^{3+}*-*MoS_2*, (b) Comparison in the Cr(VI) reduction efficiency of the* La^{3+}*-*MoS_2 *piezocatalyst (10ppm Cr(VI), pH 2, 20mg of catalyst, and total volume 50mL), and (c) Reduction efficiency of* La^{3+}*-*MoS_2 *at various initial concentrations of Cr(VI)*

Key words: *Cr (VI) reduction,* MoS_2*, Piezocatalysis, Nanofibers*

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4E Parametric Industrial Effluent Treatment Method for optimizing the wastewater treatment processes of Solvent Production Plant of a Heavy Water Plant Tuticorin

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The Solvent Production Plant (SPP) at HWP Tuticorin generates hypersaline and organic contaminant effluents with elevated level of Chemical Oxygen Demand (COD) of 26,800 ppm, exceeding the regional Tamil Nadu Pollution Control Board (TNPCB) discharge limits at India. This research study presents an advanced 4E (Environment, Energy, Exergy, Economics) parametric method of $FeCl_3$ precipitation and activated charcoal adsorption in optimizing a feasible effluent treatment system for removal of organic contaminants from the feed water. The chemical based $FeCl_3$ precipitation method of treating effluent reduces COD to 540 ppm in average but requires two to three precipitation cycles to reach the TNPCB limit. In continuation with the same level of feed from $FeCl_3$ treated effluent, fixed-bed activated charcoal adsorption effluent treatment achieves a partial COD reduction to reach a TNPCB limit of less than 250 ppm. While $FeCl_3$ treatment correlates with increased TDS for dosage over time, due to dissolved ionic species **[1]** and charcoal maintains ionic stability with the TDS load in variation of effluent volumes **[2]**. The most remarkable regeneration studies using 0.3 M HCl concentration enables charcoal reuse economic and sustainable performance for post treatment to limit the level of COD with in prescribed limit of TNPCB. The salt content with high level of TDS in the integrated effluent treatment method of SPP was removed from a solar pond through evaporation process and the solid waste generated results in reuse for cement industrial operation processes. The novelty of this research lies in the new 4E method of approach in optimization of effluent treatment systems to match the statutory limit of pollution control agency. Thus, activated charcoal emerges as a viable polishing or post treatment option for reducing organic load with an integrated $FeCl_3$ Effluent treatment in fulfilment of sustainable and eco-friendly in operation for sustainable effluent management at SPP unit of HWP Tuticorin to comply with the TNPCB standards.

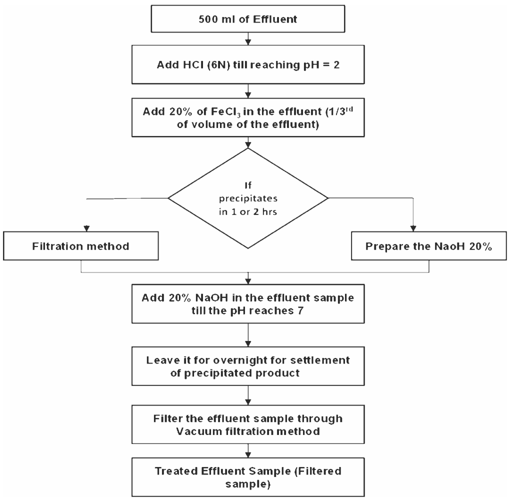

Fig.1: *$FeCl_3$ Precipitation mechanism*

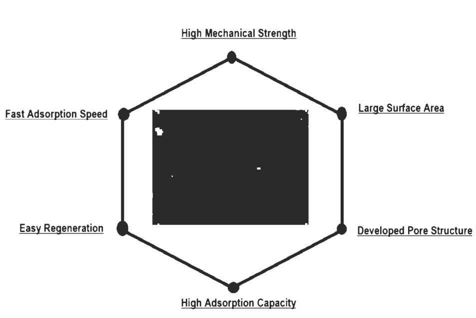

Fig.2: *Activated charcoal adsorption mechanism*

Key words: *COD, TDS, SPP, HWP Tuticorin, 4E Parameters*

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Acetonitrile Biodegradation by Aerobic Granular Biofilms

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Aerobic granular sludge (AGS) biofilms have been extensively investigated for the biodegradation of various organic pollutants due to its high degradation potential, compact structure, and potential applicability in both domestic and industrial wastewater treatment [1]. Despite wide scope of AGS for effluent treatment, studies are lacking on development AGS and biodegradation of organonitrile compounds. In this study, AGS was successfully developed using acetonitrile, an environmentally significant organic pollutant widely used in pharmaceuticals, agrochemicals, chemical synthesis, and laboratory analysis [2]. AGS cultivation in sequencing batch reactors (SBRs) was attempted using acetonitrile as the sole carbon and nitrogen source at an organic loading rate of 0.78 kg m^{-3} d^{-1}. The formation of well-defined granules within 12 days of start-up coincided with acetonitrile biodegradation (Fig. 1). Formation of acetamide intermediate and ammonium ions confirmed acetonitrile biodegradation. AGS system demonstrated stable and efficient biodegradation performance up to a loading rate of 1.56 kg m^{-3} d^{-1}, achieving nearly 95% COD removal efficiency within the 0.78–1.56 kg m^{-3} d^{-1} range (Fig. 2). However, when the organic loading rate was increased further to 2.34 kg m^{-3} d^{-1}, the process exhibited instability manifested by filamentous bacterial proliferation, granule disintegration, and incomplete acetonitrile degradation. Microbial community determined through 16S rRNA gene sequencing revealed a pronounced shift in bacterial population during AGS development, indicating enrichment of acetonitrile-degrading microorganisms. Two key bacterial strains, *Paracoccus versutus* ACN-BARC01 and *Rhodococcus pyridinivorans* ACN-BARC02 were isolated from the acetonitrile-degrading AGS, capable of utilizing acetonitrile as the sole carbon and nitrogen source. ACN-BARC01 and ACN-BARC02 have exhibited higher tolerance and degraded acetonitrile concentrations up to 3,900 mg L^{-1} and 7,800 mg L^{-1}, respectively. The combination of rapid granulation, robust microbial adaptation, and effective biodegradation underscores the potential of AGS as a promising biological treatment approach for acetonitrile-laden industrial wastewaters.

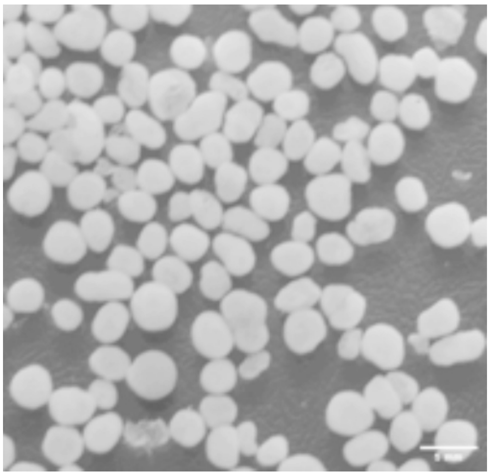

Fig.1. *Aerobic granularsludge cultivated in bioreactorfeeding acetonitrile*

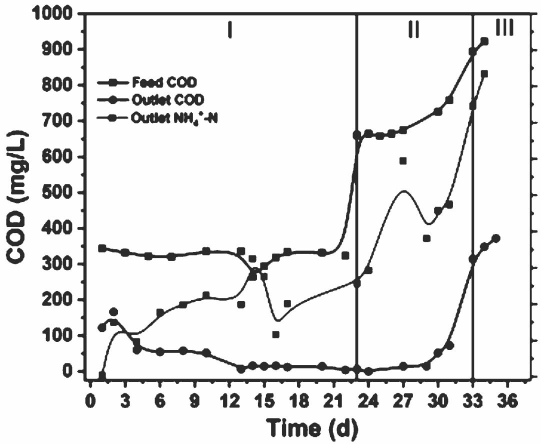

Fig.2. *Organic carbon (COD) and ammonium release in bioreactor at different feed concentrations of*

Key words: *Aerobic granular sludge, Organonitriles, Acetonitrile biodegradation, Sequencing batch reactors, Industrial wastewater*

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Development of Algal-bacterial Granular Consortium for Tributyl Phosphate Degradation

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Tributyl phosphate (TBP) is an organophosphorus compound used as an extractant, plasticizer and flame- retardant in industries. Due to its wide range of application, TBP has become a contaminant of emerging concern in recent years and requiring prompt remediation strategies. Bacterial or algal-bacterial granules are attractive for providing advanced biological treatment, sustainability and resource recovery in wastewater treatment plants [1.2]. Algal-bacterial system was chosen for evaluating bioremoval, as it can mineralize organic carbon and accumulate phosphate, key components of TBP. TBP biodegradation was attempted in three ways viz. with acetate as co-substrate, TBP as sole phosphate source and TBP as sole source of carbon (C) and phosphate (P). Algal-bacterial consortium was developed by inoculum-dependent and de novo granulation strategies. The photo-bioreactors were seeded with activated sludge, mixed algal culture or preformed algal- bacterial granules for inoculum-dependent approach. All the experiments were carried out in a 1-litre volume lab-scale photo-bioreactors operated in photo-sequencing batch reactor (SBR) mode with a 24 h cycle comprising of dark and light periods. The bioreactors were fed with synthetic wastewater containing 0.25 mM TBP under different conditions mentioned above. TBP degradation was monitored by phosphate release into the medium.

Development of algal-bacterial consortium was observed in the photo-SBR fed with SWW as co- substrate, sole P source or sole C and P source. However, supplying SWW with TBP as sole C and P source or sole P source exerted strong selection pressure for enrichment of TBP-degrading organisms. Stoichiometric amount of phosphate was released into the medium when TBP acted as sole P or sole C and P source for de novo granulation approach [Fig. 1]. During subsequent cycles, phosphate concentration has increased due to sustained TBP degradation in each cycle and also because of ineffective phosphate removal in photo-SBR. While, de novo granulation approach with TBP as sole P source led to phosphate release in the initial cycles. But, a decrease phosphate concentration in the effluent samples of subsequent cycles suggested both TBP degradation and phosphate removal capability of algal-bacterial consortium. Development of algal-bacterial granules was also evident in photo-SBRs inoculated either with enriched mixed algal culture or preformed algal- bacterial consortium and fed with TBP as sole P source. In these two systems, TBP degradation was evident in terms of phosphate release and phosphate accumulation in the initial cycles. Phosphate removal was observed in subsequent cycles. In general, TBP biodegradation and algal growth led to phosphate release and its uptake. This study provides first-time results on formation of algal-bacterial consortium, TBP biodegradation and phosphate removal in photo-bioreactors.

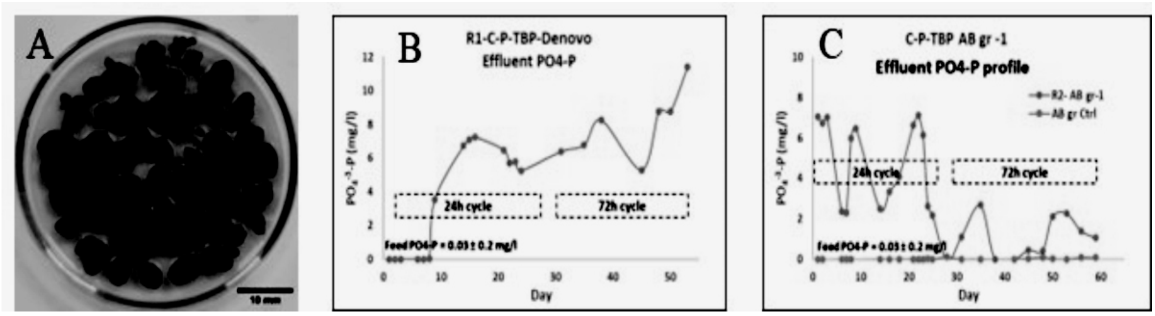

Fig 1. *Algal-bacterial granules for TBP biodegradation. A) Morphology of TBP-degrading algal-bacterial granules. B) Phosphate release and its accumulation. C) Phosphate release and its uptake by granules.*

Key words: *Algal-bacterial consortium, Bioremediation, Emerging contaminants. Wastewater, Tri-butyl phosphate.*

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Tailoring Silver Infusion in Faujasite for Enhanced Mercury Removal

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Silver-based adsorbents have shown considerable promise in enhancing the adsorption and catalytic properties of zeolites, particularly in environmental remediation applications [1,2]. In this study, we present the synthesis and detailed characterization of silver-modified X-type Faujasite, a material known for its structural stability and high surface area. The silver incorporation into the Faujasite framework was achieved using a wet impregnation method. Structural and morphological characterization of the resulting material was performed through various instrumental techniques, viz., XRF, AFM, FAAS FTIR, NMR and BET. BET analysis revealed slight reduction in surface area ranging from 433.65 m^2/g to 283.74m^2/g corresponding to different silver loadings (5-25%), indicating the impact of silver content on the zeolite's porosity. Flame Atomic Absorption Spectrometer (FAAS) was employed to quantitatively measure the silver content before and after adsorption experiments, confirming the successful incorporation of silver and its stability within the zeolite framework. XRF revealed the presence and distribution of silver on the zeolite surface, confirming the successful loading of silver nanoparticles onto the zeolite structure with partial capacity 758µg/g for 30LPM flow for 6hrs in 25gm of silver infused Faujasite and maximum absorption capacity was found to be 45000µg/gm of adsorbent. Amalgam formation and interparticle mass transfer diffusion was found to be the governing mechanism as confirmed by various characterizations. Inlet flow, Ag & Hg concentration, column height and diameter were the parameters that affected adsorption capacity. SEM images showed uniform distribution of silver nanoparticles on the zeolite surface, while FTIR and NMR spectra indicated characteristic changes in the Faujasite's framework upon silver loading. Adsorption studies demonstrated that the silver-modified Faujasite X-type zeolite exhibited enhanced adsorption capacities for heavy metals and organic pollutants, with significant improvements in selectivity and stability compared to unmodified zeolites. Synthesized material was characterized and tested against mercury adsorption and sample were analyzed using XRF (Fig. 1 and Table 1). Figs. 2 and 3 show the AFM images of control and silver loaded zeolite respectively.

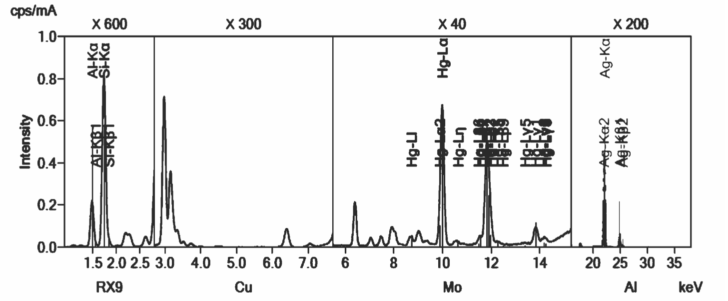

Fig. 1: *XRF intensity showing presence of silver and mercury*

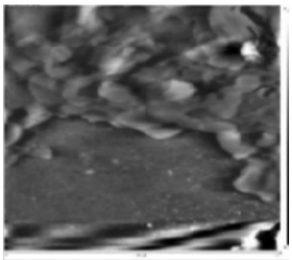

Fig. 2: *AFM image of control*

Table 1: *XRF intensity showing presence of silver and mercury*

Element	Mass%	Stat. error	LLD	Element line	Intensity (cps/mA)
Ag	72.8%	0.951	0.0458	Ag-Kα	3061.333
Si	17.9%	0.0285	0.0027	Si-Kα	4419.074
Al	8.57%	0.0283	0.0090	Al-Kα	1113.415
Hg	0.758%	0.0064	0.0031	Hg-Lα	452.270

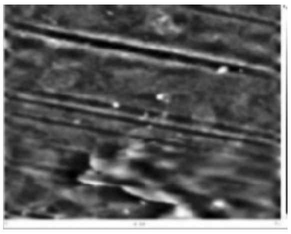

Fig. 3: *AFM image of silver loaded zeolite*

Key words: *Silver doping, Zeolite, Adsorption, Remediation, Mercury*

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Catalysed Destruction of Hydrazine in Nitric Acid Medium for PUREX process: A Comparative Study on Pt/SiO_2, Pd/SiO_2 & Ru/SiO_2S

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The compact reprocessing of advanced fuel in Lead shielded facility (CORAL) involves reprocessing a high burn-up and a rich content of plutonium. Hydrazine (salt-free) is employed in the partitioning step as a reducing agent to stabilize actinides or as a scavenger for nitrous acid during the electrochemical reduction of U(IV) in nitric acid medium [1]. However, the presence of residual hydrazine in radioactive waste streams necessitates its destruction to prevent unwanted side reactions and ensure environmental safety [2]. This study investigates the catalytic decomposition of hydrazine in nitric acid media using a PtSiO_2 catalyst, specifically exploring the impact of varying Platinum loading percentages and nitric acid concentrations to optimize the process, and comparing it with other catalysts, a critical safety measure. The Pt/SiO_2 catalyst is a well-established material for various catalytic destruction processes, including the decomposition of nitrate and oxalic acid in acidic solutions. The stability and recyclability of Pt/SiO_2 make it an attractive option for such applications, offering a robust alternative to conventional methods [3]. Furthermore, the dispersity of the active platinum component on the silica support has a significant impact on its catalytic activity in the reduction of various species. The decomposition of 1 M hydrazine was carried out in a 0.75 M nitric acid medium using a Pt-coated silica catalyst with a particle size of 35 microns in the temperature range of 80-100 °C on a laboratory scale. Different percentages of platinum loading on the silica support were utilized to investigate the optimal catalyst composition for enhancing the efficiency of hydrazine destruction. A 0.6% Pt content SiO_2 catalyst is more than sufficient for the destruction of hydrazine. If the % of Pt is around 1% & 1.5%, there is no significant change observed under the same experimental conditions. Fig.1 indicates that the amount of Pt/SiO_2 catalyst used for the destruction of hydrazine in 1M nitric acid, 85°C, 1000 RPM, and 0.6% Pt content. The obtained results were compared with those of the Pd/SiO_2 and Ru/SiO_2 catalysts and are presented in Fig2. The Pd catalyst is ineffective for the destruction of hydrazine, and the Ru-coated catalyst requires twice the amount of catalyst for the destruction of hydrazine under the same experimental conditions. The same experiment was repeated with activated carbon acting as a catalyst for hydrazine destruction, which took nearly an hour to decompose 100 milliliters of a 0.5 M hydrazine solution.

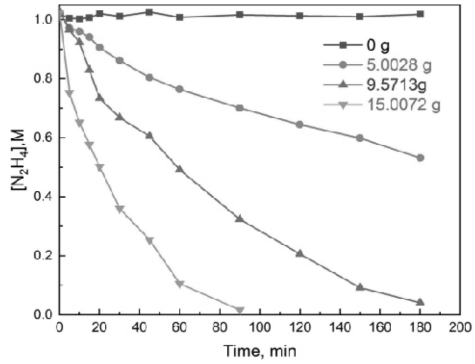

Fig. 1 *Effect of amount of catalyst on decomposition of hydrazine in nitric acid media on Pt/SiO_2*

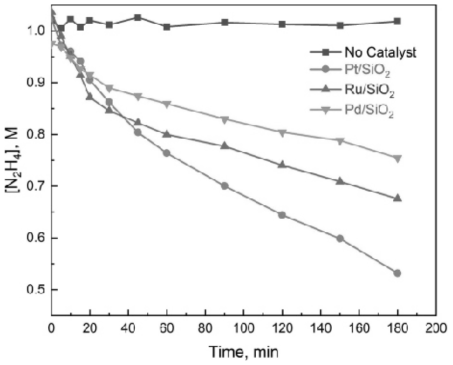

Fig. 2 *Effect of same quantity of different catalyst on decomposition of hydrazine in nitric acid media under same experimental conditions*

Keywords: Pt/SiO_2, hydrazine, decomposition, reprocessing

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Efficacy of Bare TiO_2 Nanoparticle in Adsorption of Uranium

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Uranium, one of the most important elements in the nuclear industry, can get easily released during mining, reprocessing and waste generation to the environment. The presence of uranium in the natural water becomes a serious concern owing to its chemotoxicity as well as radiotoxicity. In recent decades, scholars have paid increasing attention to the study of the sorption/desorption process of uranium at the solid/solution interface. In this regard metal oxide nanomaterials were studied extensively as a potential adsorbent of uranium from water bodies. The current work discusses the application of TiO_2 semiconductor oxide nanomaterials for effective removal of Uranium through adsorption. TiO_2 is considered suitable for sorption due to its chemical stability, high sorption capacity, radiation stability, wide availability and good recyclability. The sorption characteristic of TiO_2 depends on its crystallinity, morphology, surface area and grain size. In this study anatase phase TiO_2 nanomaterials developed without using any capping agent were characterized by using UV-visible, Raman spectroscopy and XRD. These as-prepared bare TiO_2 nanoparticles (NPs) of 5 nm size were used for adsorption studies of uranium where it was spectrophotometrically determined using Br-PADAP. In this experiment Uranium of known concentration was allowed to contact with the bare TiO_2 NPs at pH=6. At different intervals, the UV-Visible measurement was recorded to understand the kinetics of the adsorption experiment. The determination of Uranium adsorption is carried out spectrophotometrically using Br-PADAP which is highly sensitive method for U determination (ppm) with the characteristic λ_{max} at 578 nm. The percentage of sorption (%), distribution coefficient (K_d) and the solid phase concentration (q_e) were calculated. Adsorbent concentration was also varied to deduce the adsorption capacity. Importantly, as high as 30% sorption was recorded for bare TiO_2 NPs compared to only 8% sorption with commercial TiO_2. The Fig. 1 and 2 display the results. The observed adsorption capacity was 360 mg/g for the TiO_2 NPs. Thus the ultra small TiO_2, an environmental friendly wide band inorganic semiconductor, shows to be excellent uranium adsorbent. The underlying mechanism of adsorption is also discussed.

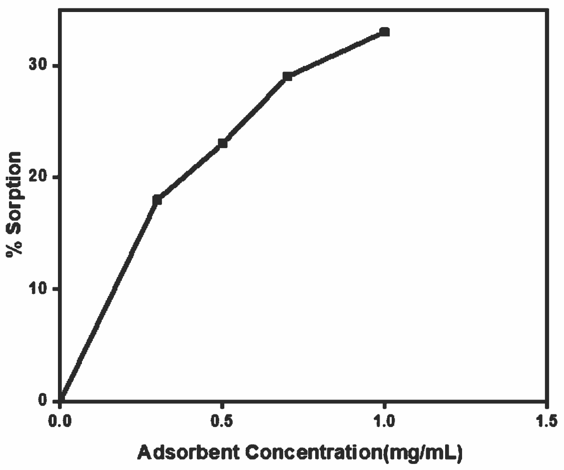

Fig 1: Effect of adsorbent concentration on adsorption of Uranium

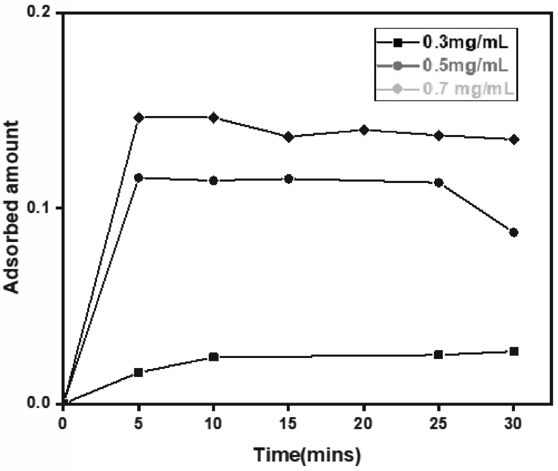

Fig 2: Amount of Uranium adsorbed with varying adsorbent concentration.

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Performance Evaluation of the Jaduguda ETP: Insights from Long-Term Radiological Monitoring

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Uranium ore processing produces large quantities of tailings & process effluents that contain residual radionuclides, heavy metals, sulphate & process reagents **[1].** At Jaduguda, India's oldest U production complex, ore is leached in conc. H_2SO_4 with pyrolusite (MnO_2) at pH ~1.7–1.8, oxidizing U(IV) to soluble U(VI). The clarified pregnant liquor is purified by IX & U is precipitated as $UO_4 \cdot 2H_2O$. The barren liquor, still containing Ra, Mn & trace U, is neutralized with lime to pH $\geq$ 9.5 & mixed with filter cake. Coarse solids are used as mine backfill, whereas fines (10–15% solids) are pumped to tailings ponds for containment. Although neutralization precipitates many metals as hydroxides & carbonates, the decanted tailings pond water equilibrates to near-neutral pH (6.8–7.7) due to dilution & CO_2 absorption. Under these oxidizing, carbonate- rich conditions, U persists as highly soluble uranyl-carbonate complexes. Ra remains mobile because homogeneous nucleation of $RaSO_4$ is kinetically inhibited despite of very low K_{sp} (4.2×10^{-11} at 25^0C). Mn remains as soluble Mn^{2+} at neutral pH & precipitates only at pH > ~9.5. Therefore, a secondary refining step, that is Effluent Treatment Plant (ETP), is essential to meet inland surface water discharge standards. Tailings overflow, combined with mine water, forms the ETP feed (~200 $m^3 \cdot h^{-1}$). Routine analysis of pH, U(nat.), ^{226}Ra, Mn, gross α & gross β to ensure regulatory compliance (table 1). Average ETP monitoring data (2020–25) show substantial reductions: ^{226}Ra from 435 to 77 $Bq \cdot m^{-3}$ (~82% removal), Mn from 8.3 to 0.4 $g \cdot m^{-3}$ (~ 95% removal) & U(nat.) from 68 to 8.6 $mg \cdot m^{-3}$ (~87% removal).

Table 1. *Mean Concentrations of Regulatory Parameters at ETP Jaduguda (2020-25)*

Sample	pH	^{226}Ra ($Bq.m^{-3}$)	Mn ($g.m^{-3}$)	U(nat.) ($mg.m^{-3}$)	Gross α ($Bq.l^{-1}$)	Gross β ($Bq.l^{-1}$)
ETP Inlet	7.0±0.5	435±87	8.3±2.7	68±17	2.5±0.8	5.0±1.6
ETP Outlet	8.2±0.6	77±24	0.4±0.17	8.6±3.2	1.2±0.5	2.0±0.6
Limits*	5.5-9.0	900	2.0	180	3.7	37

*Inland water discharge limits (The Environmental (Protection) Rules, 1986, Schedule-VI)

The primary removal mechanisms are governed by solution chemistry. After initial thickening, 2% $BaCl_2$ is added to induce instantaneous supersaturation with respect to $BaSO_4$, initiating rapid barite nucleation. $Ba^{2+}_{(aq)} + SO_4^{2-}_{(aq)} \rightarrow BaSO_4(s)$. Fresh barite crystals incorporate Ra^{2+} by isomorphic substitution, forming radiobarite ($Ba_{1-x}Ra_xSO_4$). This solid solution is extremely insoluble, & barite seeding is the only practical route for effective Ra removal, as pure $RaSO_4$ nucleation is very slow at environmental concentrations. Five reaction tanks in series provide the residence time needed for barite growth & diffusion-controlled Ra incorporation. Subsequent lime addition raises pH to ~10, precipitating $Mn(OH)_2$ & $Fe(OH)_3$. $Mn(OH)_2$ slowly oxidizes to MnO_2/MnO(OH), producing highly reactive surfaces that sorb trace metals (U). Because these precipitates are colloidal, a flocculant is added, forming dense, rapidly settling flocs in the secondary thickener. U removal occurs through adsorption onto $Fe(OH)_3$, association with Mn oxyhydroxides, & entrapment within flocs. The resulting sludge composed of radiobarite & metal hydroxides, is pumped back to the tailings pond for secure long-term immobilization. Overall, the Jaduguda ETP demonstrates robust performance driven by barite- mediated Ra co-precipitation, high-pH Mn precipitation, U adsorption & flocculation-enhanced settling— providing effective and stable immobilization of key contaminants.

Keywords: *Uranium mill, Effluents, Radium co-precipitation, Manganese, ETP performance*

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Development of an Analytical Method for the Quantitative Estimation of T2EHDGA in Spent Solvent

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N, N, N', N'- Tetra-2-ethylhexyl-diglycolamide (T2EHDGA) is a solvent which has been successfully deployed in Waste Immobilization Plant (WIP) Trombay, and Actinide Separation Demonstration Facility (ASDF) Tarapur for the treatment of high-level liquid waste (HLLW) emanating from spent fuel reprocessing [1]. The solvent T2EHDGA is used in both these Plants in a solvent extraction process to extract the trivalent minor actinides from the HLLW along with the lanthanides, and this leads to a substantial reduction in the radiotoxicity of the waste and in the final waste volumes for disposal. During this process, the T2EHDGA- Isodecyl alcohol-n-paraffin solvent system being used is exposed to high radiation levels at high aqueous acidity and thus undergoes radiolytic and hydrolytic degradation which eventually results in a poor stripping efficiency after many cycles. This solvent is then discarded as spent solvent to be incinerated. In the present work, an attempt was made to develop a process for the quantitative estimation of the undegraded T2EHDGA in the spent solvent so that the feasibility of any value recovery of the solvent could be determined before its final management. The quantitative analysis of T2EHDGA was attempted using GC-MS (Gas Chromatography – Mass Spectrometry) by the internal standard calibration method. The internal standard used during the analysis was DHOA (*N, N*-dihexyloctanamide). Both DHOA and T2EHDGA were analyzed individually using a 30 m GC column (Restek Rxi-5ms) and their retention times were obtained as ~ 21 min and ~ 37 min respectively indicating their complete separation in a mixture. Standard solutions consisting of varying concentrations of T2EHDGA and a constant 0.2 M concentration of DHOA were then analyzed and peak areas corresponding to both at each concentration were obtained. A typical chromatogram obtained during the analysis is shown in Fig. 1. The ratio of the peak areas corresponding to the individual standard concentrations were then plotted against the ratio of the concentrations to obtain a linear calibration curve as shown in Fig. 2. It is proposed to use this calibration curve for the analysis of undegraded T2EHDGA in the spent solvent. The presence of various degradation products in the spent solvent makes any quantitative determination of undegraded T2EHDGA challenging. However, the above method addresses this challenge as it allows for the separation of the various products in the spent solvent and isolation of undegraded T2EHDGA for an accurate analysis. Further studies are in progress.

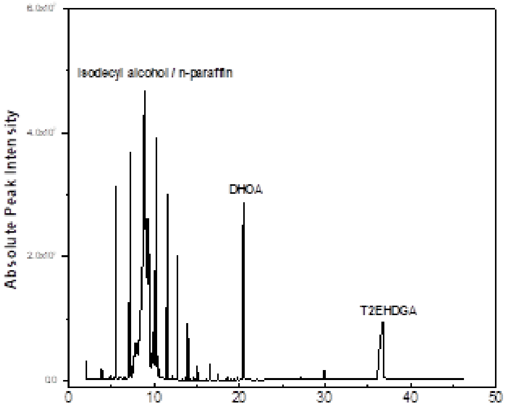

***Fig. 1**. Chro*
Analysis

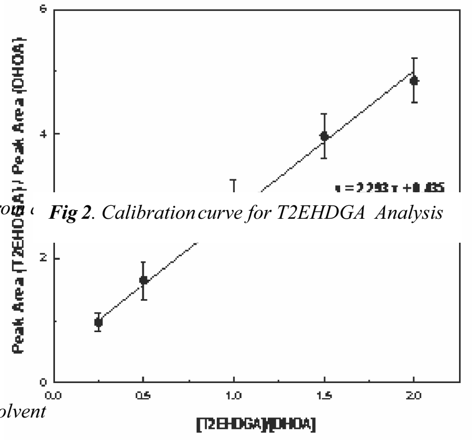

***Fig 2**. Calibration curve for T2EHDGA Analysis*

Key words: *Minor Actinides, T2EHDGA, DHOA, HLLW, Spent solvent*

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D-19

Acid-Resistant Magnetic Silica–Biochar Nanocomposites: Potential solution for Sustainable Recovery of Rare Earths and Uranium from Complex Aqueous Matrices

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The increasing demand for rare earth elements (REEs) and uranium in clean energy and nuclear sectors call for sustainable recovery technologies that can operate efficiently in complex and acidic environments. On the other hand, some studies evaluating toxicity of REEs' in soil, water, and organisms indicate persistent environmental impacts.[1]

In this study, acid-resistant magnetic silica–biochar nanocomposites were synthesized using sewage sludge–derived biochar as a sustainable substrate for extraction of uranium and rare earths from contaminated waters. The material was magnetized through integration of nanoscale zero-valent iron (nZVI), followed by silica coating to prevent iron leaching and enhance stability. The silica shell acted as a protective barrier that ensures environmental safety under both neutral and acidic conditions.

Initial results highlight that this synthesis route is both sustainable and effective. Batch adsorption experiments demonstrated that the BC–nZVI–Silica nanocomposite achieved extraction efficiency of approximately 25-27 mg/g for Ce, La, Nd, and U at pH 5. At lower pH (3), selective uranium removal was favored by BC–nZVI–Silica with an efficiency of 27 mg/g. Characterization of the materials through FTIR, XRD, and SEM confirmed the formation of stable, mesoporous, and magnetically responsive composites with good acid resistance. So, findings suggest a good approach for creating durable, eco-friendly adsorbents for recovering valuable metals.

Key Words: *Nanocomposites, REEs, Uranium, Acid Resistant Materials.*

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Removal of spectrophotometric waste from radioactive liquid waste by low-cost adsorbent XAD4

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The feasibility studies on the removal of chromogenic agents, such as Chrome Azurol S, Xylenol Orange, Arsenazo III, Br-PADAP, and Alizarin Red S, from synthetic spectrophotometric effluents generated during the determination of heavy metal ions, particularly uranium and zirconium, at the microgram level. It contains hydrophobic/non-ionic phenolic compounds, low nitric acid levels, and traces of U & Zr. The toxins and their discharge into the environment cause detrimental effects on human health. It requires management steps for the removal of radioactivity and hazardous chemicals for the safe disposal of effluents. Conventional methods for removing dyes from waste streams are categorized into three main types: physical, chemical, and biological treatments. The chemical and biological treatment was unsuitable due to incomplete dye removal, inefficiency, the generation of a large volume of secondary waste, limited operational conditions, and poor biodegradability of dyes in the matrices. The primary aim and objective of this study are to investigate the low cost, easy availability, and most importantly, the selectivity of different chromogenic agents with a single adsorbent. A 100-200 mesh size XAD4 was selected to achieve efficient disposal of analytical waste. Before the experiment, the XAD4 resin beads were pretreated with a 1:1 methanol-water solution for 12 hours to remove any residual monomers and other impurities that may have been present in the fabricated beads. The resin was rinsed with double-distilled water and placed in a drying oven at 323K for 30 min. From this, 0.1 g of dry resin was taken into glass stoppered tubes containing different concentrations of chromogenic agents, such as CAS & XO. The tubes were equilibrated for 3 hours to complete the impregnation process. It is then filtered. The filtrate was observed to be colourless, indicating that the chromogenic agent had been removed from the waste by the resin. The influence of parameters such as the weight of resin, contact time, metal concentration (particularly U(VI) & Zr(IV)), and concentration of dyes was also studied. A XAD4 resin gives better performance, with a maximum adsorption capacity of removing CAS of 72.4 mg/g of resin. The maximum adsorption capacities of the resin were calculated at a fixed weight of resin, and according to the standard experimental procedure followed for determining zirconium with different chromogenic agents as the feed solution, are shown in the table. 1. Comparison of resin capacity with the removal of other dyes and interference of U(VI) and Zr(IV) in CAS removal was shown in Figures 1& 2. The spent resin was decomposed by direct electrolytic destruction [3]. Based on the experiment, the total analytical waste was destroyed.

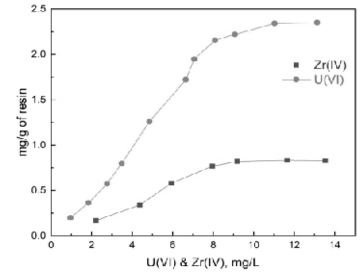

Fig 1: *Influence of U & Zr in removal of CAS*

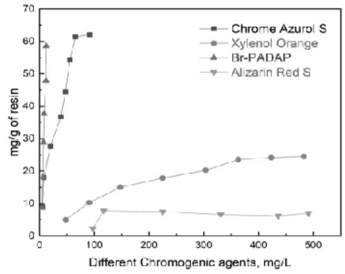

Fig 2: *Adsorption capacities of XAD4 (0.1 g) resin with removal of different dyes at 25°C*

Table 1. *Removal different dyes of spectrophotometric waste from radioactive liquid by XAD4*

	CAS	*Br-PADAP*	*XO*	*ARS*
Wavelength (nm)	*485*	*448*	*428*	*548*
Kd(mL/g)	*1000-2000*	*3000-5000*	*50-100*	*20-30*
Max. Resin Adsorption Capacity (mg/g)	*70*	*81*	*23*	*10*

Keywords: *XAD4, Chrome Azurol S, Xylenol orange, U(VI), Zr(IV), Analytical waste, Reprocessing*

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D-22

Cold Plasma Treatment on Recovery of Valuable Products from Coal Fly Ash

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This study demonstrates the effect of cold plasma treatment on significantly enhancing the physical and chemical properties of coal fly ash, making it more suitable for resource recovery. The XRF analysis of untreated fly ash confirmed that it is primarily composed of silicon dioxide (SiO_2) and aluminum oxide (Al_2O_3), indicating its classification as Class F fly ash. XRD analysis of untreated fly ash samples identified well-defined crystalline phases like quartz and sillimanite, while silica derived from plasma-treated samples showed additional peaks corresponding to halite (NaCl) and iron, along with a broad hump between 15° and 30°, indicating the formation of amorphous silica. The AAS and ICP-OES results showed that plasma treatment significantly increased the leaching efficiency of iron, aluminium, and silicon, confirming enhanced metal recovery potential. The iron concentration increased nearly fourfold after treatment, and silicon concentration also showed a substantial rise, suggesting plasma-assisted disruption of the aluminosilicate framework. FESEM analysis revealed that untreated fly ash particles were mostly smooth, spherical, and averaged 3.445 µm in diameter. Plasma-treated particles exhibited micropores and an increased average size of 5.026 µm, likely due to agglomeration during treatment. Silica extracted from both samples showed nano scale particle sizes, but the plasma-treated silica had a smaller average size (51.41 nm) compared to the untreated silica (99.27 nm), with both displaying uniform morphology. FTIR analysis of the silica confirmed the formation of amorphous SiO_2, with strong Si–O–Si stretching bands around 1025 cm^{-1}, O–H and H–O–H bands indicating surface hydroxylation, and additional features such as the 537 cm^{-1} rocking mode supporting a disordered silicate structure. In conclusion, plasma pre-treatment effectively modifies the surface, improves element accessibility, and enhances the extraction of nanosilica, highlighting its potential for waste valorisation and nanomaterial synthesis.

Key words: *Plasma treatment, coal fly ash, valuable products*
Acknowledgements: Authors acknowledge the funding from ANRF (CRG/2023/001114) and CSIR (OLP 132).

Highly Sensitive Liquid-Liquid Extraction Protocol for Pd(II): Analysis of Dental Alloys and Industrial Waste

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Palladium is a rare and lustrous silvery-white metal discovered in 1802 by the English chemist William Hyde Wollaston. He named it after the asteroid Pallas (formally 2 Pallas), which was itself named after the epithet of the Greek goddess Athena, acquired by her when she slew Pallas. Palladium, platinum, rhodium, ruthenium, iridium and osmium form together a group of elements referred to as the platinum group metals. They have similar chemical properties, but palladium has the lowest melting point and is the least dense of them.

A simple, rapid, selective and highly sensitive method has been developed for the extractive spectrophotometric determination of Pd(II) using 4-(4′-chlorobenzylideneimino)-3-methyl-5-mercapto-1,2,4-triazole, (CBIMMT), in hydrochloric medium. Pd(II) instantly forms stable orange coloured with CBIMMT at room temperature in presence of KI, which was well extracted (contact time: 2 min) in chloroform. The extracted 1:2:2 [Pd(II)- CBIMMT-I] species showed absorption maximum at 520 nm against reagent blank. The molar absorptivity and Sandell's sensitivity of Pd(II)-CBIMMT in chloroform were found to be 0.055 x 106 L mol-1 cm-1 and 0.01886 µg cm-2 respectively. The Beers law obeyed up to 3.5 to 14.5 µg mL^{-1} of Pd(II). To establish the optimum extraction conditions; various experimental parameters such as acidity, reagent and its concentration, solvents, shaking time, interference of cation and anions have been studied. The present method was successfully applied for the separation and determination of Pd(II) from synthetic mixture, separation and determination of metal ions and dental alloys.

Key words: *Pd(II), liquid-liquid extraction, dental alloy samples.*

Non-methane Volatile Organic Compounds (NMVOCs) in Biomass Fuel Combustion

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Indoor emissions from fuel combustion are classified as human carcinogens, while biomass fuel emissions are considered probably carcinogenic [**1, 2**]. In this study commonly used domestic biomass fuels like firewood, dung cake and LPG were tested for emission of non-methane VOCs during combustion. NMVOC emissions need specific investigation because they include compounds with known or suspected carcinogenicity and play a key role in forming secondary pollutants. Up to 5 replicate burns were conducted for each of the fuels studied. The experiment was conducted in a specially designed combustion chamber [**3**]. Dung cake and wood were burned with sufficient amount of oxygen supply in open and gas burner was used for LPG fuel combustion. The emitted air samples of fuel combustion were collected in 5-liter capacity tedlar bags using an air pump at a flow rate of 0.5 lpm. Subsequently, solid phase micro-extraction (SPME) fiber of DVB/CAR/PDMS type was exposed to the air samples for 10 mins to extract and preconcentrate the NMVOCs from the Tedlar bags. The SPME fibers were then analyzed by thermal desorption-gas chromatography flame ionization detection (GC- FID, Shimadzu 2010A). A standard mixture of NMVOCs (Restek make) diluted in gas phase was used for standardization and optimization of the chromatographic method. To the best of our knowledge, this is the first study in the literature to analyze NMVOCs across different burning phases of domestic fuels using SPME.

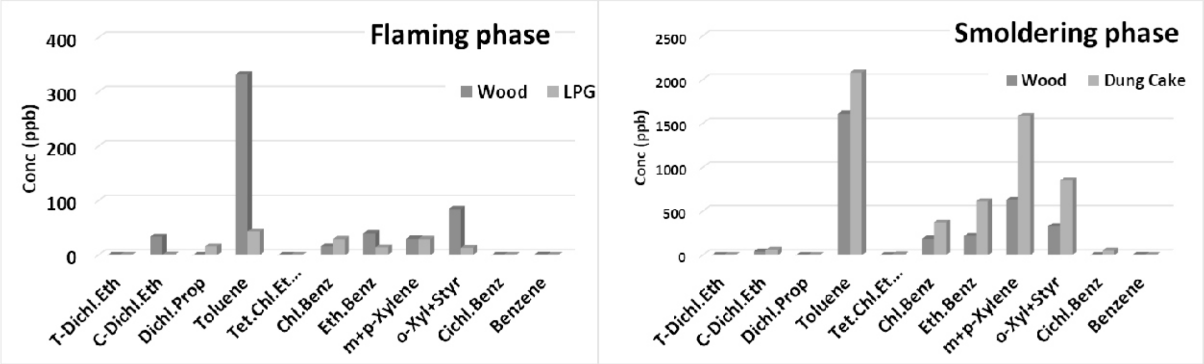

Fig 1: *Concentration of NMVOCs in emitted air in Flaming and smoldering phase of the fuel combustion*

Amongst the studied commonly used fuels, LPG burned only in flaming phase without any smoke whereas dung cake burned only in smoldering phase with lot of smoke. The firewood initially burned in flaming phase followed by a mixture of both smoldering and flaming phase and in later stage it burned in smoldering phase only. Total 11 non-methane VOCs were analysed in the emission air samples. We compared the results of NMVOCs in wood flaming phase with that of LPG and of wood smoldering phase to that of dung cake to assess whether fuel type or burning phase governs NMVOC emissions. Figure 1 represents the average concentration of all the tedlar bags in a given burning phase collected every 10 mins over a period of about half to one hour. It was observed that most NMVOCs were emitted in smoldering phase. Amongst the fuels, dung cake emitted highest quantity of NMVOCs followed by wood while LPG emitted the lowest. Amongst the NMVOCs, toluene showed highest concentration in the emissions from all the three fuels. This could be because incomplete combustion of lignin-rich biomass preferentially forms stable aromatic hydrocarbons. Benzene and chloro- benzene showed the lowest concentrations while trans-dichloroethane was not detected in any samples. Smoldering phase in wood showed increase of upto about 2 to 21 times more than flaming phase for different NMVOCs. The emissions of NMVOCs in dung cake were 13 to 87 times more than that of LPG emissions. LPG was observed to be the cleanest fuel amongst the three. The smoldering is a slow and incomplete combustion phase so it can be concluded that slow and incompletely burning fuels like dung cake and wood cause more pollution than the clean flaming fuels like LPG.

Key words: *NMVOCs, SPME, GC-FID, Biomass combustion.*

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High-Resolution Quantification of Trace Level Fluoroquinolone Antibiotics: An Enhanced RP-HPLC–FLD Approach for Environmental Matrices

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Fluoroquinolone antibiotics, primarily Ciprofloxacin (CIP), Norfloxacin (NOR), and Ofloxacin (OFL), accumulate in various environmental compartments due to their widespread use in multiple fields, including medicine, aquaculture, and veterinary, as well as incomplete removal during wastewater treatment. Their persistence at trace concentrations poses a significant ecological and public health risk, including the development of antimicrobial resistance. This study presents RP-HPLC strategies for the simultaneous separation of trace-level concentrations and environmentally sustainable extraction for environmental samples. During the method development process, a wide range of parameters was used for identifying an efficient separation process. The finalised method contained a mobile phase consisting of 26.5 mM formic acid (pH 2.5), acetonitrile, and methanol (v/v/v), with a ratio of 85:9:6. A C-18 column was used for the stationary phase, and a fluorescence detector was employed for sample analysis. The couple of excitation-emission wavelengths (λex= 290 nm; λem = 460 nm) was set for good separation of the selected FQs with a flow rate of 1 mL/min. The sample injection volume was 20 µL. A salting-out assisted liquid-liquid extraction technique, utilizing MgSO4 as a separating agent in the aqueous phase and acetonitrile as the organic phase, was employed during extraction. This method demonstrated linearity (r^2 = 0.99) over the range of 1000 ng L^{-1} to 18 µg L^{-1}, with extraction rates of approximately 90% to 92%, and precision with RSD from 3% to 12%. The lowest instrumental and method detection limits (LOD) and the lowest instrumental and method quantification limits (LOQ) were analysed and calculated after the development of the separation method. This method's intra-day and inter-day precision, as measured by the percentage relative standard deviation (% RSD), robustness study, number of theoretical plates (N), Tailing factor (T), Capacity factor (k′), Resolution (Rs), and Signal-to-Noise ratio (S/N), were also evaluated to validate the method. Our results underscore that the developed method demonstrates high sensitivity, allowing for the detection of selected FQs at trace levels, moreover, all the parameters permissible limits were checked and methods were followed according to the United States Environmental Protection Agency (U.S. EPA) Validation and Peer Review of U.S. EPA Chemical Methods of Analysis (2016 Revision; EPA/600/R-16/242) guidelines.

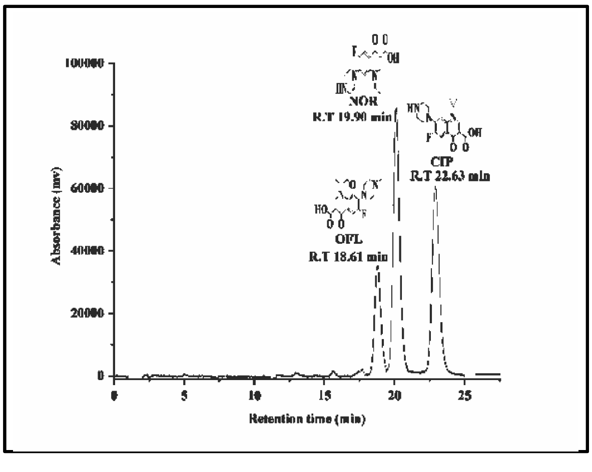

Fig.1: *RP-HPLC Separation CIP, NOR, and OFL*

Keywords: *Fluoroquinolones, Reverse High-performance liquid chromatography, Environmental matrix*

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Studies on Electrochemical Recovery of Zirconium from Zircaloy-4

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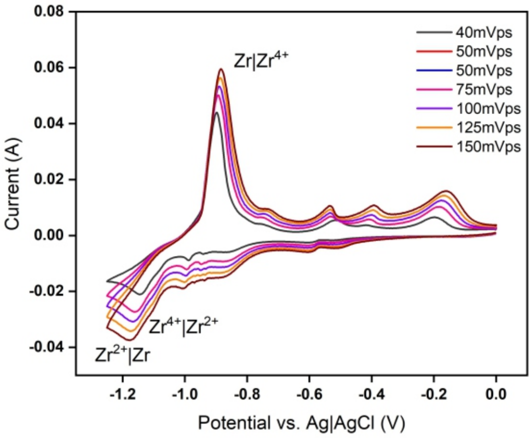
Molten salt electrorefining, employing a LiCl-KCl eutectic at 773 K, is considered a viable option for separating actinides from fission products in spent metallic fuel. It offers advantages over the conventional aqueous process, including radiation-resistant solvents, lower criticality hazards, reduced waste volumes, and proliferation resistance. Apart from spent fuel reprocessing, molten salt electrorefining can be adopted for the separation and purification of transition and rare-earth elements. Zircaloy-4 is primarily used for fuel cladding due to its low neutron absorption cross-section, good corrosion resistance, and mechanical stability under irradiation. It is proposed to recover zirconium from spent zircaloy to reduce the volume of high-level solid waste and to recycle the valuable material. This work investigates the separation of zirconium from zircaloy using the molten salt electrorefining technique.

The LiCl-KCl-CsCl molten salt has a lower eutectic temperature (535 K), which can be utilized for the electrochemical recovery of zirconium. The electrochemical behaviour of Zr^{4+} was examined in LiCl-KCl-CsCl containing 2 wt.% $ZrCl_4$ at 773 K. A three-electrode setup with tungsten as the working electrode, high-density graphite as the counter electrode, and Ag|AgCl as the reference electrode was employed. Cyclic voltammetry (CV) was used to evaluate the redox behaviour of zirconium tetrachloride. CV plots recorded for a scan rate ranging from 40-150 mV/s are shown in Figure 1. Two major cathodic peaks at -1.08 V and -1.14 V, corresponding to the reduction of Zr^{4+} to Zr^{2+} and the reduction of Zr^{2+} to Zr metal, respectively, were observed. A merged anodic peak at -0.90 V was also noticed. The peaks were assigned based on the literature [1.2]. The other minor redox peaks could be assigned to the existence of ZrCl and other Zr species. The varying peak potentials with the increasing scan rate indicated the irreversible nature of the redox couple.

Zirconium electrorefining was studied using zircaloy-4 as the anode and tungsten as the inert cathode. Zircaloy- 4 is a zirconium-rich alloy with tin, iron, and chromium added as alloying elements. To obtain pure zirconium, the potential of the zircalloy anode must be carefully controlled to prevent the dissolution of the alloying metals. The potentiostatic electrorefining in LiCl-KCl-CsCl-$ZrCl_4$ melts was conducted at -1.3 V vs Ag|AgCl with a 200 mV overpotential. The deposited zirconium was further analyzed for metallic impurities using ED-XRF. The deposit was washed with cold water to remove the adhered salt, and the resultant XRF plot is shown in Figure 2. The zirconium K alpha peak was observed at 15.6 keV, and a minor peak related to Fe K alpha was also detected.



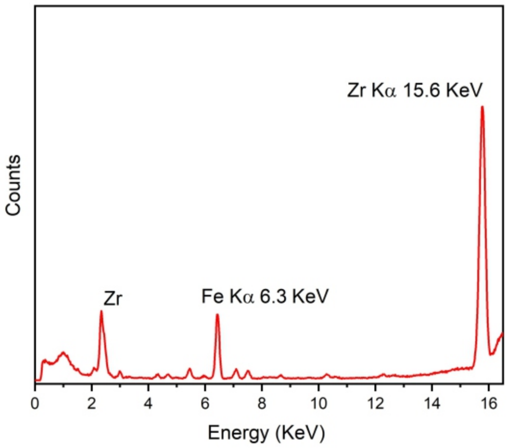


Fig.1: *Cyclic voltammograms of LiCl-KCl-CsCl-$ZrCl_4$ at W electrode*

Fig.2: *ED-XRF plot of electrodeposited Zr*

Keywords: *Zirconium, Zircaloy-4, Electrorefining*

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Voltammetric Investigations and Purification of Distilled LiCl-KCl Salt from PPRDF

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Pyroprocessing is considered as the most suitable method for reprocessing short-cooled, high-burnup metallic fuels. In this method, irradiated fuel is used as anode, SS430 or liquid Cd is used as cathode, LiCl-KCl-UCl_3 as electrolyte. During electrorefining at 773 K, uranium is selectively deposited on solid SS430 cathode, whereas U, Pu, and minor actinides are co-deposited at liquid cadmium cathode. As electrorefining progresses, concentration of fission products in the molten salt increases, necessitating purification once it reaches a threshold limit. Spent electrolyte is typically purified by Li/K-tagged zeolite-based ion exchange or by ADDP method using Li–Cd alloy. Consolidation of cathode deposit involves removal of occluded salt from SS430 cathode deposit or cadmium + salt from liquid Cd cathodes by vacuum distillation. The present work focuses on electrochemical characterization of LiCl-KCl salts obtained after vacuum distillation of liquid Cd and solid SS430 cathodes at PPRDF facility, PPED. The distillation was performed at 1223–1273 K under a vacuum of 1–5 Torr. The objective of the study is to assess the salt quality using cyclic voltammetry and quantify elemental composition using ICP-OES, thereby evaluating the feasibility of recycling the recovered salt back into the head-end stage of the pyroprocessing cycle.

A total of 150 g of vacuum-distilled salt was re-melted inside an argon atmosphere glove box, and cyclic voltammograms were recorded at a tungsten working electrode at 723 K, using AgCl|Ag as reference electrode and high-density graphite as counter electrode. The cyclic voltammograms (Fig. 1) exhibited multiple cathodic and anodic peaks. Redox couple ($E_p^{c1}|E_p^{a1}$) at -0.55 V was identified as $Cd^{2+}|Cd$, which was further confirmed by ICP-OES analysis of the salt. Redox couple at -2.351 V was assigned to $Li^+|Li$. Cadmium was found to be the major impurity (20.63 mg/g), along with trace amounts of other impurities: Fe (1.18 mg/g), U (2.83 mg/g), Co (0.09 mg/g), and Ni (0.01 mg/g). Additionally, four more redox couples ($E_p^{c2}|E_p^{a2}$, $E_p^{c3}|E_p^{a3}$, $E_p^{c4}|E_p^{a4}$ and $E_p^{c5}|E_p^{a5}$) were appeared in the potential range of -1.65 V to -2.2 V.

These peaks were attributed to the underpotential deposition of lithium due to formation of Li-Cd alloys. To purify the salt, pre-electrolysis was conducted on a tantalum foil applying cathode potentials of -0.6, -0.7, and -0.95 V for 3600 s. Purity of the melt was monitored by cyclic voltammetry (Fig. 2) after each pre-electrolysis run. It was observed that both the cathodic and anodic current intensities for $Cd^{2+}|Cd$ couple and other four redox couples gradually decreased. After eighth pre-electrolysis run, cyclic voltammogram showed no peaks except for the $Li^+|Li$ couple, indicating maximum separation of cadmium impurity from salt. Estimation of Cd and other metallic impurities in purified salt by ICP-OES is in progress.

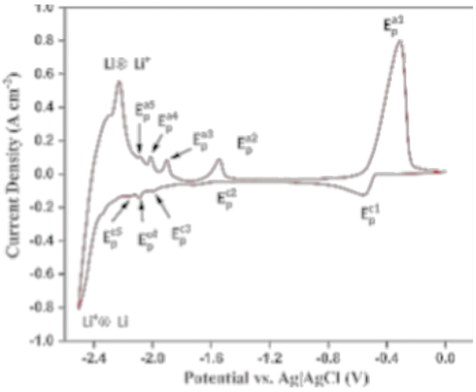

Fig. 1: *Cyclic voltammograms of distilled LiCl-KCl salt at tungsten WE at 723 K at 100mV/s scan rate.*

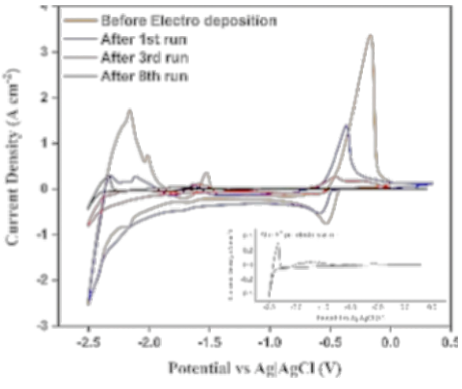

Fig. 2: *Cyclic voltammograms of distilled LiCl-KCl salt at tungsten WE before and after pre-electrolysis on Ta-foil at 773 K, Scan rate: 100mV/s.*

Key words: *Pyroprocessing, Eutectic LiCl-KCl, Li-Cd alloy, Cyclic Voltammetry, Pre-electrolysis*

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Performance Comparison Between Ceramic and Membrane Based Electrolyser For Treatment of Combustible Waste by Silver Mediated Chemical Dissolution

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Silver (II) mediated dissolution process was developed for the decontamination of alpha contaminated solid combustible wastes. Ag(II) was chosen as an electrocatalyst due to its higher electrode potential. Ag(II) was generated using porous ceramic separator between catholyte (16M) and anolyte (8M) in generator(electrolyser). Catholyte addition was to be done on hourly basis. Significant migration of Ag(II) ions and alpha activity were observed from the anolyte to the catholyte, leading to frequent catholyte replacement. To address this, a plate- and-frame type membrane-based electrolyser with reduced ion crossover and improved current efficiency was tried.

Ag(II)Conc(M) In the plate-and-frame electrolyser, a Nafion-324 membrane is used to separate the anolyte and catholyte, with platinized titanium as anode and titanium as cathode. The compact, sandwiched design reduces the required cell voltage to about 2.5 V for the same operating current of 100A and consequently lowers the likelihood of hydrogen generation. As a proton-exchange membrane, Nafion effectively reduces the permeation of Ag(II) ions and it may reduce the transfer of alpha activity from the anolyte to the catholyte, thereby decreasing secondary waste generation. Inactive experiments for the destruction of organic components in an ash generated from incineration of polymeric and cellulose material were carried out on 75-L scale in the plate-and-frame electrolyser which was operated at 100 A and 2.5 V is shown in Fig a. The corresponding Ag(II) generation which is an indication for destruction of organic compounds in ash is presented in Fig b. No catholyte addition was needed for 80 hours when experiments were performed with catholyte 12 M and anolyte 8 M nitric acid respectively. The modular and compact design of the plate-and-frame electrolyser enables easy maintenance and scale-up for continuous operations.

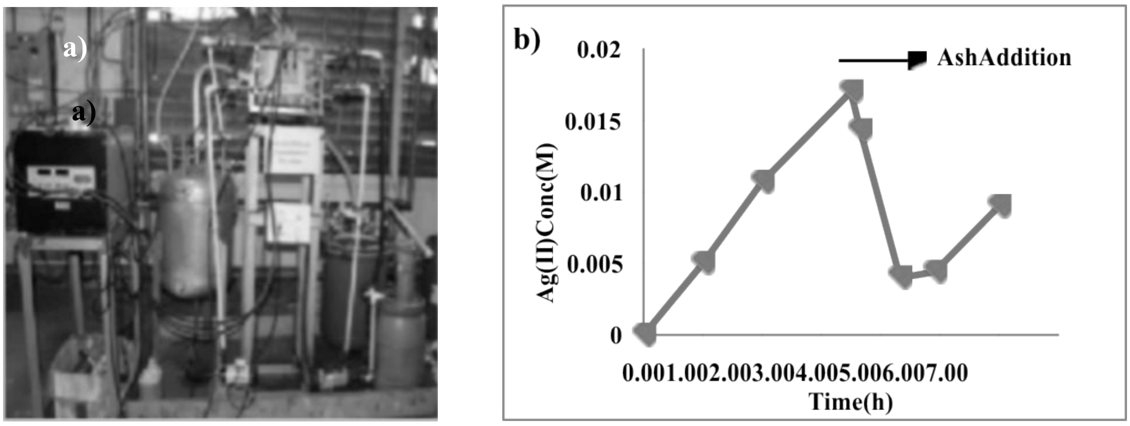

***Fig. a)** Experimental set up of Ash Dissolution in Plate and Frame Electrtolyser, **b)** Ag(II) generation vs time during Ash dissolution in Eletrolyser*

Key words: *Silver (II) mediated dissolution, Alpha Waste, Electrolyser, Membrane*

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Development of a Solvent Extraction Based Method for the Recovery of ^{90}Y from ^{90}Sr

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Yttrium-90 (^{90}Y) is a pure β-emitting radionuclide widely used in targeted radionuclide therapy owing to its favourable nuclear characteristics, including a 64.05 h half-life and 2.2 MeV maximum β energy. High-active waste (HAW) generated during FBTR spent-fuel reprocessing contains substantial quantities of ^{90}Sr ($T_{1/2}$ = 28.8 y), which remains in secular equilibrium with ^{90}Y and serves as an excellent long-lived parent for producing no- carrier-added (NCA) ^{90}Y. To meet domestic as well as international demand of carrier-free ^{90}Y, the most attractive technique is radiochemical separation from ^{90}Sr using a radionuclide generator to supply multi-Curie levels of ^{90}Y. ^{90}Y used for radionuclide therapy should be of very high radionuclidic purity (99.998%) as the most probable contaminant ^{90}Sr is a bone seeker with a maximum permissibble body burden of only 74 kBq (2 uCi). Consequently, 90Sr contamination in the clinical grade NCA 90 Y for targeted radionuclide therapy should be less than 20 ppm.Therefore efficient radiochemical separation of ^{90}Y from ^{90}Sr is essential. In this work, a solvent extraction based method was developed for the separation and purification of Y from Sr. Yttrium was selectively extracted from aqueous solution of Sr and Y in $Al(NO_3)_3$ using 1.1 M Tributyl phosphate in n- dodecane, followed by back-extraction into dilute nitric acid. The Sr–Y separation factor in the stripped phase was quantified via ion chromatography using a Nucleosil column with α-Hydroxy Isobutyric Acid (HIBA) and ethylene diamine as the mobile phase. With increasing nitrate ion concentration, distribution coefficient of Y is increasing whereas distribution co efficient of Sr is decreasing. The ion chromatogram of separated Y and Sr ion are shown in Figure 1. Experimental results (Figure 2) demonstrate that the Sr–Y separation factor increases with rising nitrate concentration in the aqueous phase, confirming the suitability of this method for radio chemically pure ^{90}Y production.

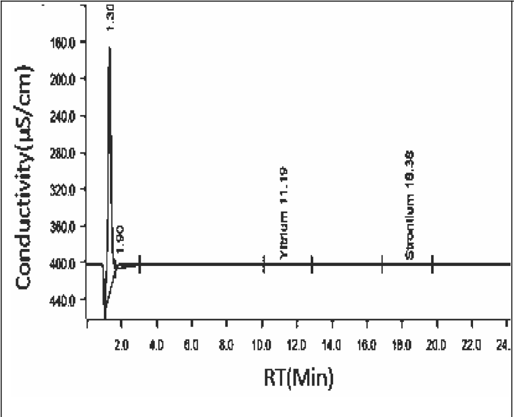

Figure1. *Ion chromatogram of separatedSr and Y ion*

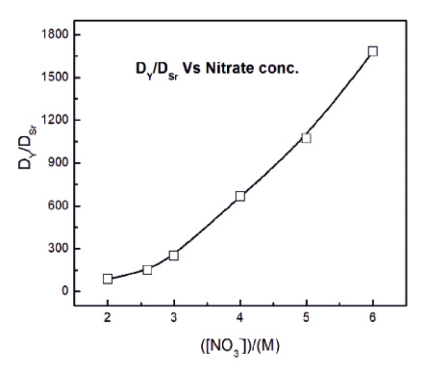

Figure 2*.Y-Sr separtion factor w.r.t. nitrate ion concentration*

Keywords: *Radioisotopes, Ion Chromatography, ^{90}Sr - ^{90}Y, Nuclear medicine, solvent extraction*

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Development of an Ion Chromatography Method for Determination of Boron in High Fluoride Pyrohydrolysis Distillate of Molten Salt

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The determination of boron in nuclear fuel is of critical importance because boron acts as a neutron absorber and directly influences the reactivity balance of reactor cores. Accurate quantification of boron is required to comply with the specifications laid down by the reactor physicist. Common analytical approaches for boron determination in nuclear fuel include spectroscopic techniques such as ICP-OES/ICP-MS, colorimetric methods (curcumin method) and pyrohydrolysis followed by ion chromatography (PH-IC). In pyrohydrolysis boron is directly separated from the solid matrix due to the effect of heat and moisture and subsequently trapped in NaOH solution.

In molten salt nuclear fuels, determining boron in such systems via PH-IC becomes challenging because the pyrohydrolysis distillate contains a very high concentration of fluoride. Boron determination in IC is generally carried out using a mannitol-NaOH eluent and under these conditions the B peak elutes in close proximity to the F peak. Given that fluoride constitutes the major matrix component in molten salt fuels, this approach was found to be unsuitable for boron determination. Therefore, it is essential to have a suitably optimized ion chromatography method to enable interference-free, high-sensitivity determination of boron in molten-salt fuel environments. An alternative strategy was developed in which boron obtained from pyrohydrolysis was converted to tetrafluoroborate (BF_4^-) [1] prior to IC analysis. The conversion of B to BF_4^- was studied with respect to the effect of acidity and temperature on formation of the desired species and reaction kinetics. Based on these investigations, the experimental parameters for the sample preparation were optimized. The complete conversion of B to BF_4^- requires to maintaining certain acidity and high fluoride concentration followed by heating. The anionic BF_4^- was determined using IC. Fig: 1 represents a typical chromatogram obtained with the developed IC method. Synthetic samples with known boron were compared with ICP-AES

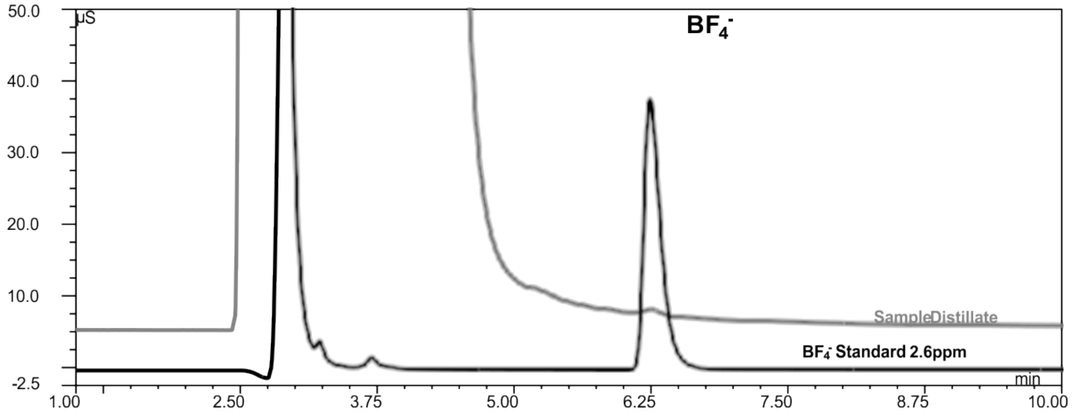

Fig.1: *Overlay of chromatograms of the 2.6 ppm BF_4^- standard and the sample. Column: AS16 along with AG16 guard column Eluent: 35mM NaOH.*

Key words: *Boron, Molten salt nuclear fuel, Pyrohydrolysis & Ion - Chromatography*

Reference:

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Removal of Arsenic from Drinking Water Using Zero-Gap Diaphragm Based Electrochemical Cell

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Safe drinking water is a basic criterion for good health and groundwater is the major source for drinking water. The contamination of ground water with arsenic is a serious environmental problem in many countries around the world and is considered one of the world's most severe cases of inorganic contamination of drinking water[1]. Arsenic remediation methodologies in water are largely based on the chemical methods of pre capitation /flocculation, adsorption, ion exchange, or reverse osmosis. The simultaneous removal of As (III) and As (V) is the prime requirement of As remediation methodology. Most of these methods work satisfactorily for As (V) but the efficient removal of As (III) has often proved to be difficult due to its existence as uncharged As (III) (H_3AsO_3) species. Therefore, the conversion of As (III) to As(V) by an oxidizing agent is the first step of remediation methods. The process of As removal from large volumes of water is generally performed by adding chemical coagulants such as aluminum or iron sulphate, using coagulation methods. In electro coagulation process, aluminum is dissolved by sacrificial anode followed by the coagulation of $Al(OH)_3$ for the adsorption of arsenate [2]. Aluminium is also one of the hazardous elements in drinking water with tolerance level of 30 ng/mL. Due to the amphoteric property of aluminium its solubility could not be controlled by adjustment of pH of water. Recently, we have developed zero gap electrochemical method for the removal of total dissolved solids (TDS) from water [3].

The sorption behavior of arsenate (As V) as a function of the solid:solution ratio was investigated by adding calcite in to a solution containing As (V) and As (III) [1]. It is reported that, arsenate adsorbs strongly on calcite with no significant adsorption of arsenite (As III). In this present work, we have developed a technology for the removal of arsenic using electrochemical method by generating calcite using diaphragm based electrochemical cell. The electrochemical cell consists of microfiber mesh as diaphragm with graphite electrodes as cathode and anode. Zero-gap between the electrodes generates hydroxyl and hydrogen ion on near the surface of the cathode and anode respectively. The in-situ generated OH^- ions on the surface of cathode converts bicarbonate into carbonate. The major concentration of bicarbonate present in the ground water is calcium bicarbonate. Hence, on the surface of the cathode calcium bicarbonate is precipitated as calcium carbonate along with the adsorption of arsenate. Initially the electrolysis was carried out for 10 minutes to convert As (III) into As (V) in anode compartment. Then, positive and negative terminals are interchanged to convert the respective half cells to adsorb As(V) with calcite precipitate in cathode compartment. Minimum required TDS of water is found to be ~400 mg/L to form sufficient precipitate of calcite for complete removal of arsenic (<10 ng/mL).

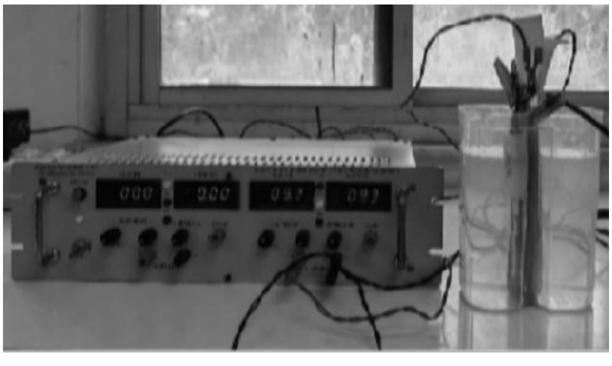

Figure1.*Zero-gap diaphragm based electrochemical set-up*

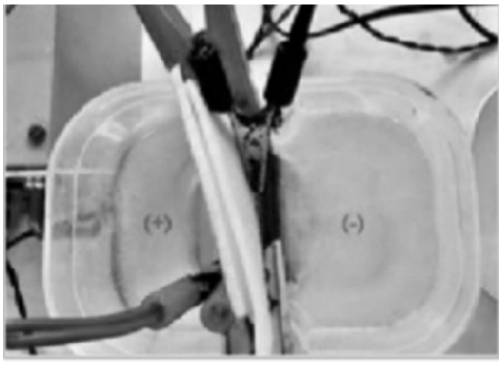

Figure.2.*Co-precipitation of As with* $CaCO_3$ *on cathode side*

Key words: *Arsenic, remediation, electrochemical, water-treatment*

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Electrorefining of U–10 wt.% (Zr+Mo+Pd+Nd) Alloy at Liquid Cd Cathode in LiCl-KCl-UCl_3 Electrolyte

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Molten salt electrorefining, a pyrochemical process, is ideally suited for reprocessing spent metallic fuels. In this process, a solid SS430 cathode is employed for electrodeposition of uranium, while a liquid cadmium cathode is used for codeposition uranium, plutonium, and minor actinides from spent metallic fuel, with LiCl-KCl-UCl_3 as electrolyte at 773 K. Separation of U, Pu, and minor actinides from the fission products in spent fuel is achieved due to the differences in the thermodynamic stability of their chlorides in the molten chloride medium. During electrorefining, noble metal fission products are retained in the anode basket, while alkali, alkaline earth, and rare earth metal fission products are dissolved into the electrolyte. The present work focuses on electrorefining studies of U-Zr-Mo-Pd-Nd alloys at liq. cadmium cathode. U–Zr–Mo–Pd–Nd alloy was prepared by vacuum arc melting using U, Zr, Mo, Nd, and Pd metals. Alloy composition was 90 wt% U, with 2.5 wt% each of Mo, Zr, Pd, and Nd. Prepared alloy was then analyzed using X-ray diffraction (XRD) to identify its phases.

Electrorefining experiments were conducted at 773 K using 2g of a U-Zr-Mo-Pd-Nd alloy in the anode basket, 13.4 g of cadmium at cathode, and LiCl-KCl-1.38 wt% UCl_3 as electrolyte. The cadmium cathode was prepared by melting cadmium metal in an alumina crucible, which was placed inside an SS430 electrode holder (Fig. 1). A 1 mm diameter tungsten wire served as the electrical lead for the cadmium electrode. AgCl|Ag (1 wt% AgCl) reference electrode was employed in the present work. The equilibrium potential of U-Zr-Mo-Pd-Nd alloy was measured to be -1.345 V at 773 K. The uranium deposition potential (peak potential) at the liquid cadmium cathode was recorded to be -1.374 V (Fig. 2). The potential of the cadmium cathode was measured to be -0.52 V prior to the electrorefining experiment. The electrorefining process was carried out in potentiostatic mode, applying a constant potential of -1.45 to -1.5 V at the cathode, with the resulting current varying between -10 and -150 mA. The variation in anode potential during the electrorefining runs is shown in Fig 3. A total charge of 738 C was passed during all electrorefining runs, corresponding to 607 mg of uranium deposited at the cathode. The uranium concentration in the electrolyte was measured to be 1.38 wt% prior to the experiment and 1.46 wt% upon its completion. Salt samples were analyzed for Nd, Zr, Pd, and Mo after the electrorefining experiment and were found to be absent in the salt. After electrorefining process, cadmium metal in the cathode basket was melted and poured into a silica dish. The cadmium metal was then cut at various locations, and 14 samples were collected. These samples were analyzed for U, Nd, Zr, Pd, and Mo using ICP-OES. The anode residue was dissolved in nitric acid, and U, Nd, Zr, Pd, and Mo were estimated by ICP-OES. A mass balance of uranium before and after the electrorefining process was demonstrated in the present study.

Fig.1: *Liquid Cd cathode*

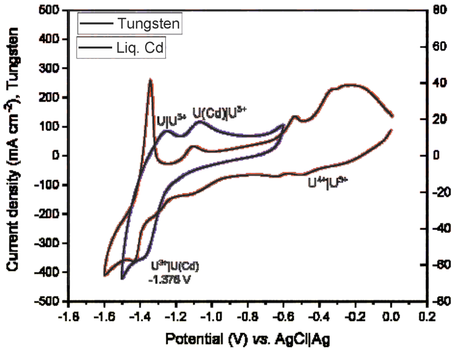

Fig. 2: *Cyclic voltammograms of LiCl-KCl-UCl_3 at W and liq. Cd electrode employing alloy as counter electrode at 773 K.*

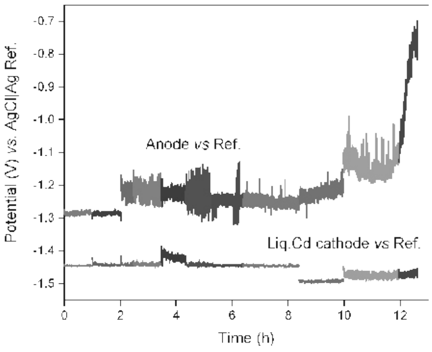

Fig. 3: *Variation of anode and cathode potential during electrorefining runs of U-10wt%(Zr+Mo+Pd+Nd) alloy at 773 K*

Key words: *Molten salt electrorefining, cadmium cathode, cyclic voltammetry, chronopotentiometry*

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Polyoxometalate (POM) Impregnated Chromatographic Resin for Am(III) Uptake from Aqueous Feeds

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Detection, preconcentration and estimation of radionuclides present in environmental matrices (Ground/surface water) is a challenging task considering their presence in low concentrations. Amongst the methods used for separation of radioelements from aqueous solutions such as solvent extraction, precipitation etc., extraction chromatography finds advantage over others due to lower solvent inventory, lower secondary waste generation and ease of operation [1]. Polyoxometalates (POMs) are well-known nanoscale clusters of inorganic metal-oxo compounds with controllable self-assembly in solution from MOx units (M = V, Mo, or W; x = 4−6) and are well known for radionuclide uptake [2, 3]. Considering the above facts, A polyoxometalate (Se_6W_{39}) composite chromosorb-W resin (Se_6W_{39}-R) was synthesized as per previously reported method [1], characterized (by single crystal XRD, FTIR, TGA and SEM) and studied for Am uptake from aqueous solutions. Am uptake studies were carried out by batch as well as column methods in aqueous solution containing PIPES buffer.

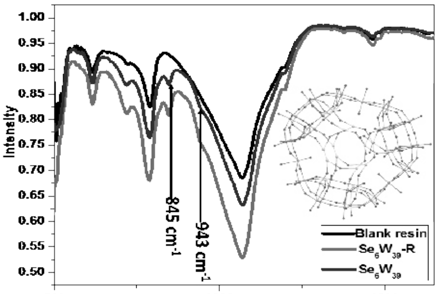

Fig. 2: a) *Am^{3+} uptake kinetics; b) selectivity of Se_6W_{39}-R*

The uptake of Am^{3+} by Se_6W_{39}-R follows fast kinetics indicating > 90% uptake within 5 min and reaches to >99% in 60 min. kinetic modelling indicate the uptake process follows pseudo 2nd order kinetics with rate constant 8.79 x 10^{-8} mg g^{-1} min^{-1}. Results from pH variation study indicate sharp increase in extraction efficiency from pH 1 to 3 (6.1 % to 99%) after which it remains nearly constant upto pH= 10. The lower sorption below pH 3 is may be due to excess protonation of Se_6W_{39} due to higher concentration of H$^+$ ions compared to the metal ion. The K_D values were observed to be increasing with increase in temperature indicating endothermic nature of sorption - process in present investigation. ΔH, ΔS and ΔG values were estimated to be 58.1 kJ mol^{-1}, 0.27 kJ mol^{-1} k^{-1} and –22.8 kJ mol^{-1} indicating the sorption of Am^{3+} on Se_6W_{39}-R is spontaneous, endothermic and entropy driven. Amongst different isotherm models, the present data fits into Langmuir isotherm indicating the maximum sorption capacity ($q_{max.}$) = 1.66 mg g^{-1}. The sorption energy calculated from D-R isotherm modelling was found to be 20.4 kJ mol^{-1}, indicating the uptake of Am^{3+} on Se_6W_{39}-R occurs through chemisorption. Stripping of loaded resin was carried out using 0.5 M α- Hydroxy iso-butyric acid (α-HIBA). Reusability study shows excellent extraction efficiency of the resin upto five cycles. Effect of radiological degradation on uptake efficiency of Se_6W_{39}-R was also studied and it was found that the material shows excellent efficiency upto 1000 kGy gamma dose. In order to evaluate the selectivity of Se_6W_{39}-R in presence of other cation, selectivity study was also carried out using sample containing mixture of different cations (inactive Eu^{3+} used as surrogate for Am^{3+}) . The results indicate good selectivity of the Se_6W_{39}-R for Eu^{3+} over other cation studied. Results from column studies shows efficient loading and fast elution of loaded Am^{3+}. Considering the above results, it may be concluded that the Se_6W_{39}-R resin is found promising for preconcentration/decontamination of aqueous systems from Am^{3+}.

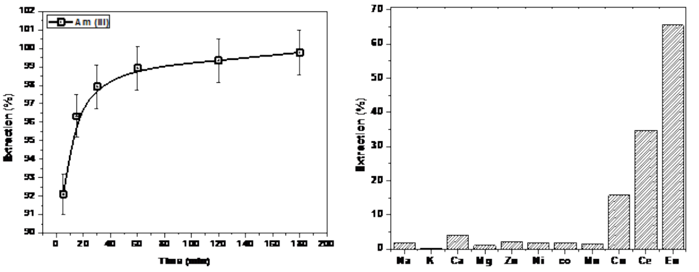

Fig. 2: a) *Am^{3+} uptake kinetics; b) selectivity of Se_6W_{39}-R*

Key words: *Polyoxometalate, extraction chromatography, Am(III).*

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Process for Production of High Purity Lithium Hydroxide Monohydrate from Spodumene Ore Concentrate Using A Chelating Cation Exchanger

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Lithium is primarily extracted for its application in energy storage batteries. An indigenous source of extractable lithium was found in the form of mineral spodumene, from which an intermediate product, lithium carbonate, of about ~85% purity, was obtained. Further hydrometallurgical processing and purification steps were carried out to obtain high purity lithium hydroxide. In this process, dissolution of Li-carbonate in sulphuric acid and subsequent treatment with barium hydroxide resulted in faster precipitation and easy solid-liquid separation. Complete removal of remnant Ba^{2+} from LiOH solution was carried out using chelating resin Indion BSR. From the purified LiOH solution, anti-solvent precipitation with binary mixture of ethanol and acetone showed increased salting out of $LiOH.H_2O$ along with faster settling. XRD confirmed $LiOH.H_2O$ as product and $BaSO_4$ as by-product respectively; further confirmation of $LiOH.H_2O$ and absence of carbonate was obtained from Raman spectra. Chemical analysis showed Na, Ca, Ba & K to be non-detectable (< 10 mg/l), indicating high purity (~99.9%) of the final product $LiOH.H_2O$.

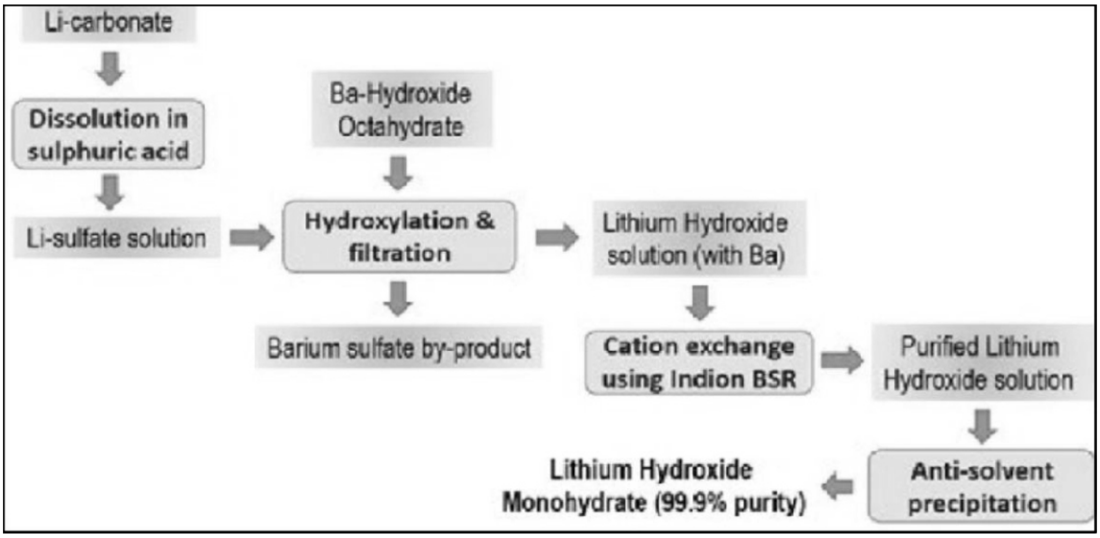

Figure 1 *Process flowsheet for conversion of impure lithium carbonate to purified lithium hydroxide monohydrate*

\References

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Development of Displacement Chromatography Setup For H/D Separation for Low Concentration Feeds

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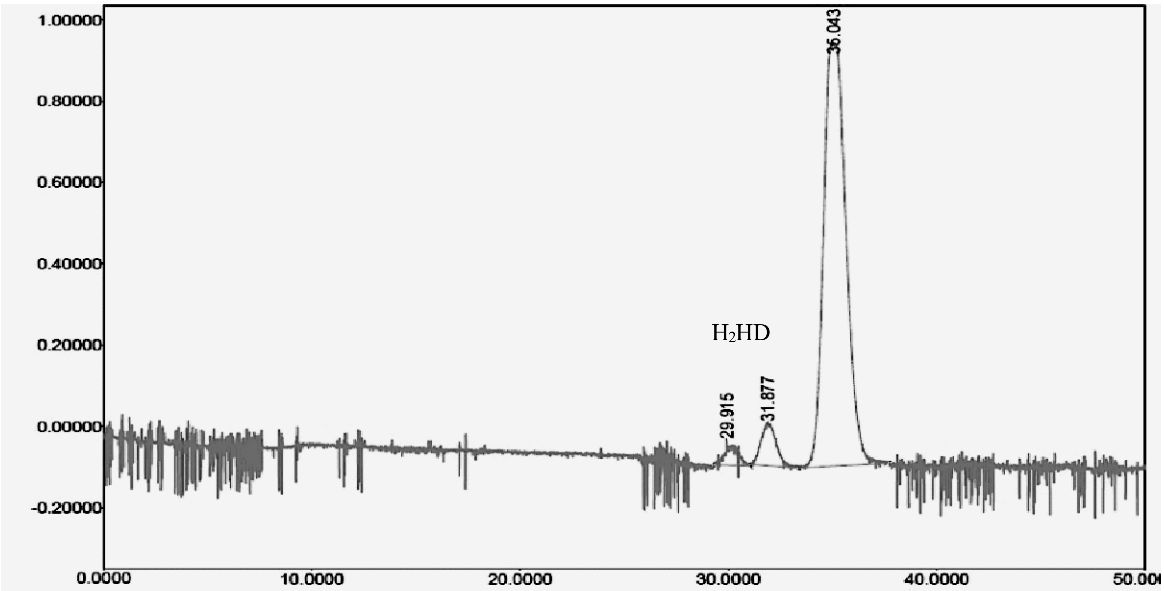
Deuterium is found to be extremely useful in the operation of Pressurized Heavy Water Reactors as a moderator [1]. Starting from its applications in the semiconductor industry to its applications in the medical sector, deuterium is useful in many different industries. In many cases, after use of this component, the deuterium concentration in the feed gas reduces, but still the deuterium content is high enough to be reused by increasing its D content. This can lead to a reduction in cost in many small-scale industries. As separation of H/D isotopes by the existing processes like vacuum distillation, cryogenic distillation, exchange process, etc. are normally energy intensive and suitable for large scale applications. Separation of the H/D isotopes in the small/laboratory scale can be achieved by the displacement chromatography process. The majority of data available for this process are for feeds of moderate concentrations in the literature. Very few studies are available for feed with low concentrations of deuterium. Experiments were conducted using columns filled with Pd black material using feeds of low concentrations. This study was done to establish the relation between recovery and purity at low concentrations of deuterium in the feed mixture. An unsteady state, one dimensional model has been developed validated using the experimental results to predict the recovery/ purity for various feed concentrations, length and diameter of columns, and packing material in the column. It was observed from the model and experiments that a single column is not sufficient for feeds of very low concentration (less than 10%), if reasonable amount of product is to be withdrawn from the setup. Based on the results obtained from the model, a two-stage cascade was used to produce gaseous mixture with D isotopic purity greater than 80%.



setup

Key words: *Deuterium Gas, Chromatography, Hydrogen, Palladium, Displacement Chromatography*

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Feasibility Studies of Using Laser-Induced Breakdown Spectroscopy Technique to Estimate Moisture in LiCl-KCl Salt

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Quantification of moisture in LiCl-KCl eutectic melt employed in pyroprocessing of metal fuels is essential for avoiding electrochemical side reactions that may deteriorate the melt [1]. Present work is focused towards employing Laser-Induced Breakdown Spectroscopy (LIBS) to quantitative estimation of moisture. Although moisture in salt can be accurately measured by titration method, developing spectroscopic techniques could reduce sample size and measurement time; the two criteria being important when sample sizes are large. If LIBS is coupled to an inert atmosphere glove box, it becomes easier to handle hygroscopic LiCl-KCl eutectic salt samples [2].

A set of calibration standards of purified LiCl-KCl eutectic melt containing LiOH in range 0.01 to 2 wt.% were prepared. Accurately weighed samples were taken in alumina crucible and heated to 450 °C under argon for 3 h, and samples were later drawn from condensed melt and sealed in transparent glass vial (Figure 1a) to subject them to LIBS analysis. Details of LIBS system is given elsewhere [2]. LIBS integration and delay time were set to 1.18 ms and 1.28 µs, respectively. Laser pulse energy, repetition rate and number of accumulation were 40 mJ, 10 Hz and 100, respectively. 10 measurements were carried out for each composition of melt containing LiOH. Non-interfering lines for H and O at 656.2 and 404.4 nm, respectively, were selected for calibration. Intensity ratio (IR) of these peaks with respect to Li peak at 670.6 nm are plotted against concentration of LiOH in LiCl-KCl melt in Figs. 1(b) and (c), respectively. As the Li concentration is same in all the samples, H and O peaks are normalized with respect to Li and this will minimize the variation in signal intensity due to pulse-to- pulse laser energy fluctuations. Figs. 1(b) and (c) fit linearly with good correlation coefficient (R^2) of 0.995 and 0.991 for both H and O, respectively. Hence, either H or O or both peaks can be used to quantify moisture in salt by LIBS. The limit of detection (LOD) and limit of quantification (LOQ) values are (0.044 and 0.145 wt.%) and (0.054 and 0.179 wt.%) for H and O, respectively. There is no significant change in IR observed at LiOH concentrations lower than 0.1 wt.% (insert of Fig. 1(b-c)) and the reason behind this is unknown. This could be due to interference from the free moisture.

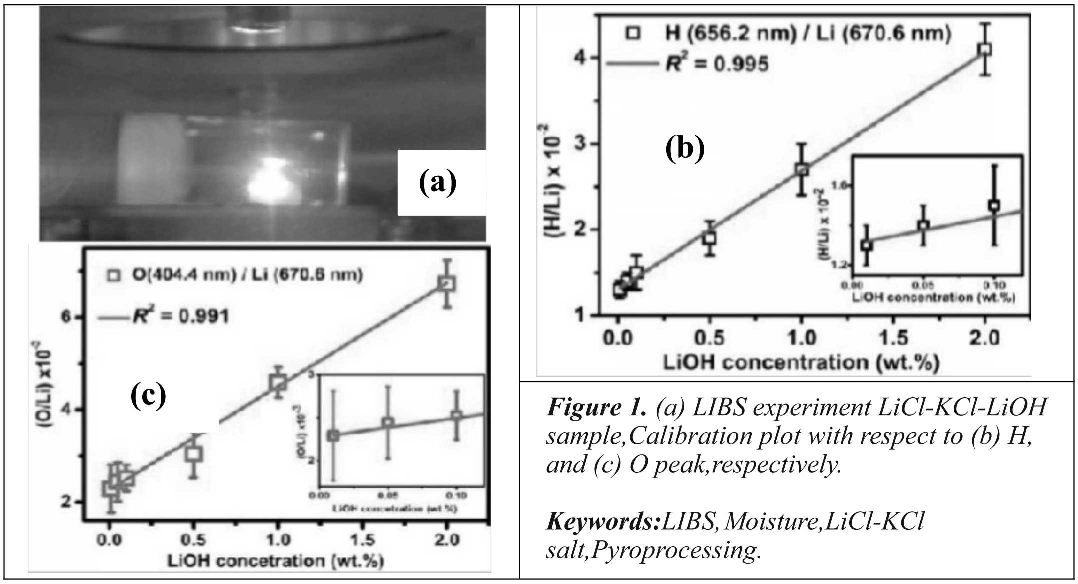

Figure 1. *(a) LIBS experiment LiCl-KCl-LiOH sample,Calibration plot with respect to (b) H, and (c) O peak,respectively.*

Keywords:*LIBS, Moisture,LiCl-KCl salt,Pyroprocessing.*

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Electro-refining of U and Gd from U-75wt%-Gd-19wt%-Zr-6wt% Alloy at 773K in the Presence LiCl-KCl-UCl_3-$GdCl_3$ Electrolyte and Modified Pool Type Liquid Cadmium Cathode

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Pyro-chemical reprocessing of spent metallic fuel is advantageous due to several reasons. Reprocessing of spent metallic fuel is not well established at industrial scale. Studies are in progress in several countries. Electro-refining (ER) is one of the important key process step in pyro-chemical reprocessing flow sheet [1, 2].ER experiments are mainly aimed at the separation of uranium, plutonium and minor actinides in the presence of LiCl-KCl-UCl_3 or UCl_3-$PuCl_3$ electrolyte at ~773K under inert atmosphere from spent metallic fuel. Initially uranium separation will be carried out by electrodepositing it at solid cathode (SS 430 or equivalent) followed by separation of uranium, plutonium and minor actinides at liquid cadmium cathode. ER separation of actinides from spent metallic fuel is based on thermodynamic stability of fission products (alkali and alkaline earth metal and rare earth elements) in molten salt electrolyte LiCl-KCl-UCl_3-$PuCl_3$, at solid cathode, at liquid cadmium cathode.

Present work deals with ER of uranium and gadolinium at 773 K in the presence of U-Gd-Zr alloy as anode, LiCl-KCl-$GdCl_3$ or $GdCl_3$-UCl_3 as electrolyte and liquid cadmium as cathode at 773 K in 2 m^3 argon glove box. U-75wt.%-Gd-19wt.%-Zr-6wt.% alloy was prepared and annealed. SEM-EDX analysis shows the presence of U-Zr and Gd-Zr separately. Mixing of U and Gd was not observed (Fig. 1c). U-Gd-Zr alloy was loaded in SS430 anode basket in the presence of LiCl-KCl-$GdCl_3$ electrolyte and liquid cadmium cathode for ER experiment in constant current mode at 773 K. All the potentials were applied and measured with reference to Ag-AgCl reference electrode. Potential profile of one of the ER run has been shown in fig. 1b. SEM-EDX analysis of liquid Cd cathode has confirmed the presence of uranium and gadolinium in cadmium after ER. It has also shown the uranium precipitate in liquid cadmium. It confirms that the presence of U is more than its solubility limit in Cd. ER experiments were demonstrated for uranium and gadolinium electro-transport to cadmium in the presence of LiCl-KCl-$GdCl_3$ electrolyte. These results have helped in understanding the electrolyte ratio ($GdCl_3$ and UCl_3) and potential profile required during ER of U-Gd-Zr in the presence of liquid cadmium cathode.

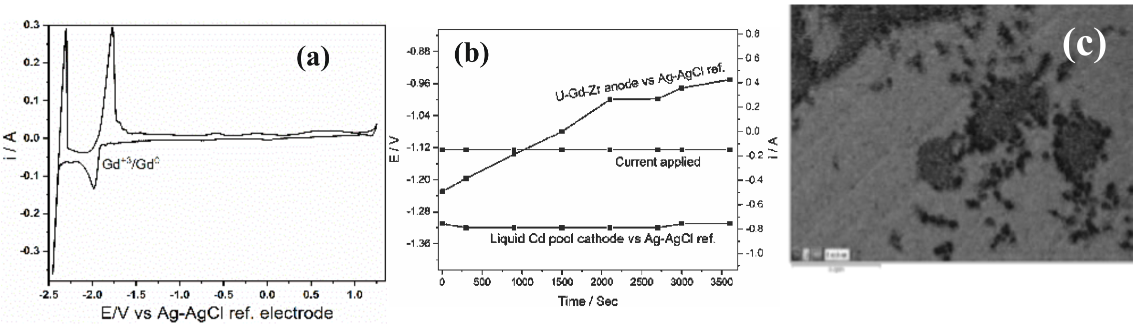

Fig. 1. *(a) Cyclic voltammogram for LiCl-KCl-$GdCl_3$ electrolyte, (b) Potential profile for U-Gd-Zr anode basket, liquid cadmium cathode and applied current during ER experiment, (c) SEM-EDX elemental mapping for U-Gd-Zr before ER*

Key words: *U-Gd-Zr alloy, Electro-refining, Pyrochemical reprocessing, SEM-EDX analysis*

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HPLC Separation of Derivatives of Amino Benzoic Acids

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Thorium based metal organic frame wok is a potential candidate for the separation and detection of radionuclides. Aminobenzoic acid–based moieties were used to increase the pore volume in a thorium MOF constructed from 2- aminobenzene-1,4-dicarboxylic acid (Th-ABDC) [1]. To characterize and quantify the successful incorporation of 4-amino Benzoic acid (ABA) in Th-ABDC an HPLC based separation method was developed.

The HPLC system equipped with DAD detector was employed for separation studies of MOF moieties. All the measurements were carried out at wavelength of 225 nm. Initial studies were carried out using a C18 reversed phase column of the dimension 150 x 4.6 mm, using the acetonitrile (ACN) and phosphoric acid as a mobile phase. Different chromatographic conditions were optimized and it was found that mixture of 10% ACN and phosphoric acid (0.05M) offered the maximum separation between ABDC and ABA. It was observed that ABDC was showing more retention than ABA onto the reversed phase column (Fig.1). The concentration of phosphoric acid was playing the crucial role for the separation of these linkers. For quantification of these linkers, a calibration plot (Fig. 2 and 3) was made of varying concentrations (0.01 M to 3.0 M). Under the optimized condition, quantification of ABDC and ABA in actual samples were carried out.

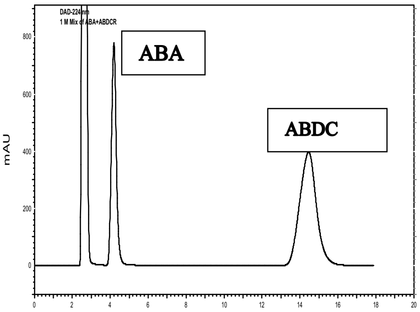

Fig.1. *Chromatographic Separation of ABA and ABDC*

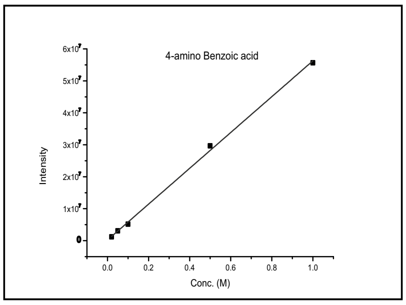

Fig.2. *Calibration Curve of ABA*

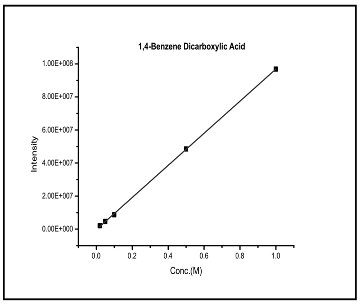

Fig. 3. *Calibration Curve of ABDC*

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Back Extraction of Uranium, Yttrium and Lanthanum from U-Cd, Y-Cd and La-Cd alloy to LiCl-KCl Salt Phase

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In pyro-chemical reprocessing flow sheet for spent metallic fuel, salt bath process is mainly aimed for reuse of electrolyte salt, cadmium metal and separation of actinides and fission products [1]. Salt bath process combines *actinide draw down* and *back extraction process* steps. Back-extraction is the process of transferring actinides from a liquid metal phase, typically molten cadmium, back into a molten LiCl-KCl salt phase.Cadmium chloride assisted oxidative step in back extraction process recovers the actinides along with traces of rare earth after they have been selectively extracted from molten chloride salts into the cadmium matrix in a preceding reductive extraction step. Back-extraction is an important process step for separating actinides from cadmium matrix and making it suitable for reuse [2].

***Table 1:** FactSage [3] based free energy estimation for uranium and rare earth (La and Y) separation in Cadmium and LiCl-KCl at 750K-773K*

Sl. No	ReactionsinLiCl-KClsalt	ΔGinKJ@ 773K
1	$UCl_{3(LiCl-KCl)} + 3Li_{(Cd)} \rightarrow U_{Cd} + 3LiCl_{(LiCl-KCl)}$	–341.96
2	$YCl_{3(LiCl-KCl)} + 3Li_{(Cd)} \rightarrow Y_{(Cd)} + 3LiCl_{(LiCl-KCl)}$	–243.19
3	$LaCl_{3(LiCl-KCl)} + 3Li_{(Cd)} \rightarrow La_{(Cd)} + 3LiCl_{(LiCl-KCl)}$	–148.41
4	$2U_{(Cd)} + 3CdCl_{2(LiCl-KCl)} \rightarrow 2UCl_{3(LiCl-KCl)} + 3Cd$	–574.53
5	$2La_{(Cd)} + 3CdCl_{2(LiCl-KCl)} \rightarrow 2LaCl_{3(LiCl-KCl)} + 3Cd$	–961.62
6	$2Y_{(Cd)} + 3CdCl_{2(LiCl-KCl)} \rightarrow 2YCl_{3(LiCl-KCl)} + 3Cd$	–772.07

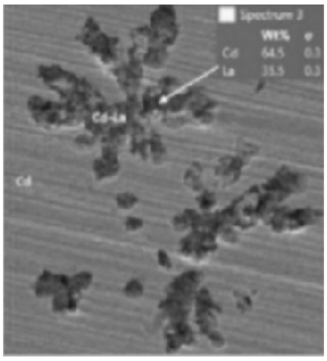

***Fig.1.**SEM-EDXanalysis mapping and elemental analysis for La-Cd alloy*

Present study explains about extraction of uranium, yttrium and lanthanum from U-Cd, Y-Cd and La-Cd alloy to LiCl-KCl salt phase by means of oxidation in the presence of dried cadmium chloride at 750K under argon atmosphere. Reactants in reaction 1-6 have been identified and used for present studies. Reaction 1-3 shows preparation of simulated feed for back extraction experiments by lithium-cadmium alloy assisted reductive extraction of uranium, yttrium and lanthanum to respective cadmium alloy. Reaction 4-6 shows back extraction experiments for recovery of U, La and Y to LiC-KCl salt phase in the form of respective chlorides. Table 1 shows thermodynamic feasibility by free energy estimation for reactions 1 – 6 by Fact Sage. Cadmium alloys were analysed by SEM-EDX analysis before and after back extraction experiments. LiCl-KCl salt was analysed by cyclic voltammetric electrochemical methods. Redox couple corresponding to U^{+3}/U, La^{+3}/La and Y^{+3}/Y confirms the extraction of U, La and Y from salt phase to cadmium phase.

Key words: *Uranium, Back extraction, Cadmium chloride, Oxidation, Pyrochemical reprocessing,*

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Rapid Analysis of Nitrosamines in Fresh Vegetables and Fruits Using Liquid Chromatograph

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Nitrosamines, such as N-nitrosodimethylamine (NDMA), N-nitrosomorpholine (NMOR), N-nitrosopyrrolidine (NPYR), N-nitrosodiethylamine (NDEA) and N-nitrosopiperidine (NPIP), are a class of chemical compounds formed from the reaction between nitrites and secondary amines, typically under acidic conditions. They are recognized for their potent carcinogenic properties and have been detected in a variety of environmental matrices, including food products like fruits and vegetables [1, 2]. Fruits and vegetables may contain nitrosamines due to several factors: high levels of nitrate and nitrite accumulated from fertilizer use, microbial activity that can convert nitrates to nitrites, and the presence of natural amines within plant tissues [1]. Routine surveillance of nitrosamines in fruits and vegetables is crucial because these food groups contribute significantly to dietary nitrate and nitrite intake, and thus, to human exposure to nitrosamines. Monitoring their concentrations is essential for public health risk assessment and to inform guidelines aimed at minimizing carcinogen intake through diet [3].

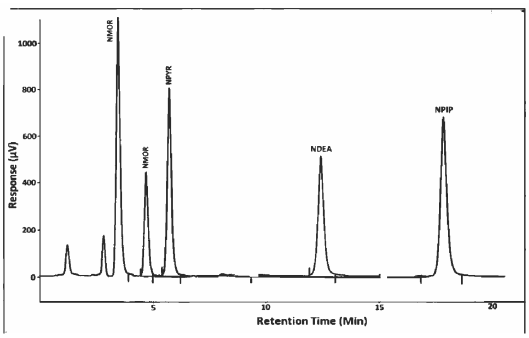

***Fig1:** ChromatogramofNitrosamineStandardMixture.*

***Table 1:** Concentration (ng/g) wet wt. of volatile N-nitrosamines in fruits and vegetable.*

		NDMA	NMOR	NPYR	NDEA	NPIP
Fruits	**Max**	5.07	0.88	0.15	0.00	1.57
	Min	1.67	0.00	0.00	0.00	0.00
	Avg	**3.04**	**0.38**	**0.03**	**0.00**	**0.42**
Fruity Veg	**Max**	18.79	2.75	1.57	9.51	1.29
	Min	0.00	0.00	0.00	0.00	0.00
	Avg	**5.69**	**0.49**	**0.32**	**0.86**	**0.17**
Under-Ground Veg	**Max**	6.07	1.17	2.42	0.00	1.46
	Min	0.65	0.00	0.00	0.00	0.00
	Avg	**2.55**	**0.37**	**0.68**	**0.00**	**0.29**
Leafy Veg	**Max**	24.49	1.04	3.39	8.47	3.15
	Min	0.00	0.00	0.00	0.00	0.00
	Avg	**11.58**	**0.37**	**0.86**	**1.98**	**0.63**
Flowery Veg	**Max**	5.19	0.00	0.31	0.00	0.21
	Min	1.13	0.00	0.12	0.00	0.00
	Avg	**3.16**	**0.00**	**0.21**	**0.00**	**0.10**

Approximately 25 grams of dried sample were finely homogenized with a mixture consisting of methanol, water, 1% sulfamic acid, and 1.5 M sulfuric acid in the ratio of 50:40:8:2, followed by vigorous shaking with n-hexane. The aqueous layer was then alkalized with 25 ml of 1 M potassium hydroxide before proceeding to extraction with dichloromethane (DCM). The extracted NAs in DCM were analysed. A high-performance liquid chromatography (HPLC) method was optimized to quantitatively determine five volatile nitrosamines in the samples. Separation was carried out on a Lichrosphere RP-18 column (25 cm × 4.6 mm, 5 µm particle size) using a polar mobile phase composed of acetonitrile and water (1:9 ratio). Nitrosamines were detected using a UV detector set at 230 nm wavelength, achieving detection limits from 0.2 to 0.4 ng/g for the target compounds. This refined technique was subsequently employed for quantifying nitrosamine concentrations in various fruit and vegetable samples. Figure 1 represents the chromatogram of all 5 analyzed nitrosamine standard mixture. Table 1 represents the summary of concentration of nitrosamine congeners in fruits and vegetable. NDMA levels are comparable to the upper range or slightly above typical reported values for fruits and vegetables in the literature, especially in leafy and fruity vegetables. For other nitrosamines, the results are largely consistent with global dietary surveys, though a few elevated values may reflect regional environment or cultivation practices.

***Key words:** Nitrosamines; HPLC-UV; Carcinogens; Food Analysis.*

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Distribution of Ionic Constituents in Particulate Matter (PM10) Collected from Ambient Air at Kalpakkam Site During 2024

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The ambient air quality assessment programme as part of the regular environmental monitoring is done at Kalpakkam site as per the Central pollution control board regulations. For this study, Particulate matter size fraction <10 micron along their water soluble ionic components were collected and analyzed for the period (2023- 2024) from one sampling location situated at the safety building inside the FRFCF site. Around 24 samples representing each season was collected. From the study it is found that the mean concentration of PM10 is much below the annual PM_{10} National Ambient Air Quality Standard (NAAQS) (60 µg/m^3) prescribed by the CPCB, India. The characterization of the ionic fraction of Particulate matter (PM_{10}) was carried out following the standard procedures, using Ion chromatography for the anions (Cl^-, NO_3^- and SO_4^{2-}) and for cations (Na^+, Mg^{+2}, Ca^{+2} and K^+). The distribution of these cations (Na^+, Mg^{+2}, Ca^{+2} and K^+) and these anions (Cl^-, NO_3^- and SO_4^{2-}) in three different seasons has been analyzed for the air dust samples collected from the site. The Seven ionic constituents were determined and has been found to be in the decreasing order of $SO_4^{2-} > Cl^- > Ca^{2+} > Na^+ > NO_3^- > K^+ > Mg^{2+}$. The total composition of PM_{10} particles shows that Ca^{2+} ions contribute to 49% of the cation concentrations followed by Na^+ at 31%, K^+ at 13%, and Mg^{2+} at 7%. Among secondary ions (i.e. sulphate^{2-} and nitrate$^-$), sulphate was the most abundant, followed by chloride and nitrate. The presence of both SO_4 and NO_3 concentrations may suggest secondary particulate formations and the photochemical reactions at the study site. As the site is very close to the sea, the influence of the marine sources is inevitable, also significant sources of atmospheric aerosols which are terrestrial sources and vehicular emissions are anticipated (Hong-Wei Xiao et al, 2018). The ionic concentrations were also seen to vary seasonally (Fig 1& 2). The Ionic composition followed a trend showing the least concentrations in monsoon and the highest in summer at the study area. Low concentrations of the atmospheric components particulates/aerosols are consequently anticipated to occur during and after precipitation events occurrences. This could be the attributing factor for lower cationic concentrations in monsoon as wet deposition is an effective natural scavenger for the removal of particles, especially in the size range of 0.1-10 microns. Likewise, higher wind speed conditions (2.6-3.5 m/s) as observed here at Kalpakkam during the summer season favour the influx of crustal deposits while the effective sea breeze conditions help transport discharge of sea salt ions by sea spray. It could also be linked that re-suspended road dust in the form of carbonates, bicarbonates, and silicates could have contributed to the presence of Ca^{2+},K^+, and Mg^{2+} in PM samples at the site as a result of on-going constructional activities in the vicinity (Gayathree et al,2023).

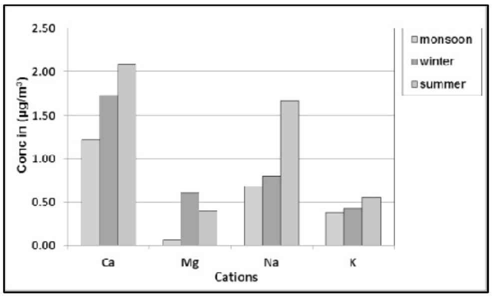

Fig 1: Seasonal cationic concentration in PM_{10}

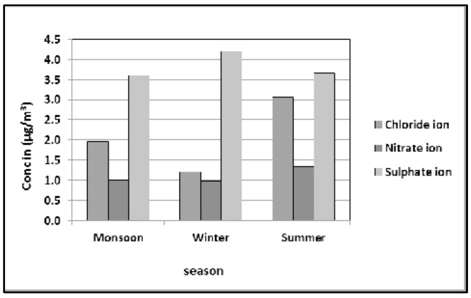

Fig 2: Seasonal anionic concentration in PM_{10}

Key words: *Particulate matter, cations, anions, ionic concentration.*

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Electrochemical Behaviour of U at SS430 Cathode in Molten LiCl-KCl-UCl_3 Electrolyte

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Molten salt electrorefining which is a pyroprocessing technique is used for reprocessing of spent metal fuels. Pyroprocessing of metal/alloy fuels is carried out in molten LiCl-KCl-UCl_3 electrolyte using SS430 or liquid Cd as cathode and spent fuel as anode. In electrorefining process pure uranium is electrodeposited at solid SS430 cathode and U, Pu and minor actinides are co-deposited at liquid cadmium cathode. It is reported that uranium forms UFe_2 and U_6Fe intermetallic compounds with iron. Under electrorefining conditions, electrodeposition of uranium at SS430 cathode may lead to partial formation of U-Fe alloy that may get strongly adhered to the electrode and scraping the deposit entirely may be difficult. This may result in losses in terms of overall recovery of uranium. The present work focuses on electrochemical behaviour of uranium at SS430 cathode in molten LiCl-KCl-UCl_3 electrolyte. Cyclic voltammetry technique was employed in the present studies.

Fig.1 compares cyclic voltammograms of LiCl-KCl eutectic melt at tungsten and SS430 electrodes at 773 K. Onset potential for Li^+ reduction was estimated at -2.37 and -2.36 V, respectively at tungsten and SS430 electrodes. Surge in anodic current at -0.46 V is due to Fe^{2+}|Fe couple. The redox couple observed near –0.773V (E |E) at the SS430 electrode could not be distinctly identified in this study. The relatively low anodi c current associated with lithium dissolution on SS430 may be attributed to inadequate retention of deposited lithium on the electrode surface, likely resulting in limited availability of reduced Li for subsequent oxidation. Fig. 2 shows cyclic voltammograms of LiCl-KCl-UCl_3 melt at SS430 working electrode and they are also compared with the voltammogram recorded at tungsten electrode. The voltammogram at tungsten electrode shows two redox couples $U^{4+}|U^{3+}$ and $U^{3+}|U$, respectively at -0.21 and -1.44 V. Voltammogram at SS430 V shows reduction of U^{3+} at -1.48 V and corresponding anodic peak at -1.34 V. Additional cathodic peak at -1.31 V, which appears at 170 mV more anodic than peak potential (-1.48 V) of $U^{3+}|U$ couple is associated with underpotential deposition of uranium with the formation of U-Fe alloy. Further characterization of the deposit at SS430 will be carried out employing XRD technique. Cyclic voltammograms of LiCl-KCl-UCl_3 melt at the SS430 electrode recorded at various scan rates at 773 K are shown in inset of Fig. 2. The redox peaks (Fe^{2+}|Fe) were analyzed and found to be two electron transfer single step quasi-reversible in nature. Cathodic and anodic limits of SS430 electrode was found to be -2.36 and -0.48 V, i.e. reduction of Li^+ and dissolution of Fe^{2+}, respectively in the melt. Since the anodic potential is controlled by onset potential of zirconium during electrorefining of spent fuel, anodic limit of SS430 is high enough to be used as anode basket. This study provides the electrochemical window of the system and to understand U3+|U electrochemical behavior of solid cathode during electrorefining.

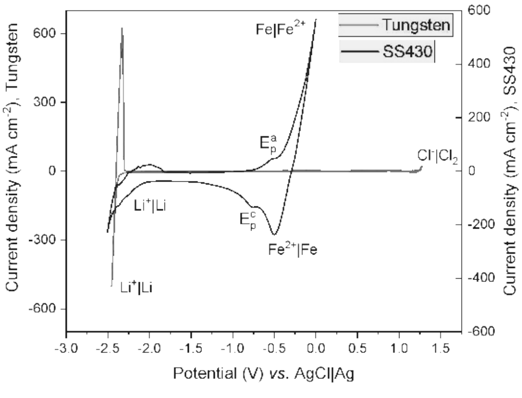

Fig. 1: *Cyclic voltammograms of LiCl-KCl eutectic melt at SS430 working electrode at 773 K.*

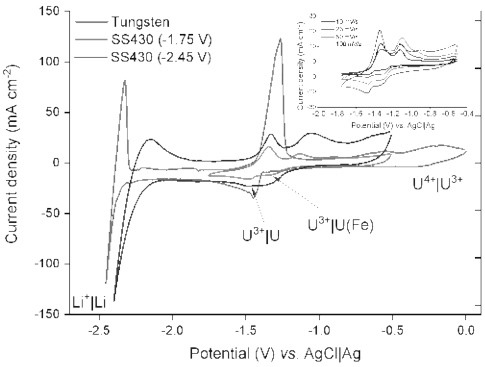

Fig. 2: *Cyclic voltammograms of LiCl-KCl-UCl_3 melt at SS430 working electrode at 773 K.*

Key words: *Pyroprocessing, molten salt, cyclic voltammetry*

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A Novel Approach for Rapid Screening of Heavy Metals in Forensic Casework-Bridging the Speciation Gap

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Heavy metals continued to be one of the most frequently encountered toxicants in forensic investigations, particularly in cases involving environmental contamination, deliberate poisoning and industrial exposures. Nevertheless, due to the lack of quick, portable and field-compatible analytical platforms, the rapid screening and species-level separation of heavy metals are still limited. This critically limits and misleads forensic investigations, as the bioavailability, toxic behavior and source identification of the heavy metals predominantly rely on their chemical form. For instance, if a water sample contains high levels of chromium speciation becomes indispensable. Elevated levels of Cr (IV), a well-established carcinogen are reflective of anthropogenic contamination. Conversely, the higher levels of Cr (III) are more consistent with natural leaching from chromium- rich geological resources.

Currently available high-end instrumentation exhibits inherent limitations with respect to the speciation analysis such as: AAS- highly sensitive but, limited to single-element analysis; ICP-MS- capable of muti-element analysis but highly expensive and required complex sample preparation; XRF- rapid but often fails in distinguishing chemical species. Traditional TLC methods have been reported to have a qualitative separation of metal ions such as Cu^{2+}, Ni^{2+}, and Co^{2+} using chelating reagents. According to the existing body of literature, no forensic literature has illustrated the systematic HPTLC for heavy metal speciation..

This paper aims to bridge the speciation gap by proposing a conceptual methodology grounded in a critical literature review. The proposal framework combines speciation-directed complexation, an optimized mobile phase, specific visualization techniques and the integration of densitometric analysis. Presented a conceptual model leveraging the use of ligand-specific reagents, which results in oxidation state (species) dependent calorimetric or fluorescent complexes. Additionally, this paper highlights the considerable potential HPTLC holds for preliminary on-flied screening of samples due to the low instrumental complexity.

Employing HPTLC can enhance the forensic workflow by enabling the rapid screening and prioritization of critical samples according to their metal species (high-risk) profile. Additionally, it can complement other high end sophisticated techniques which enhances the working efficiency of forensic laboratories.

Key words- *Heavy metal speciation, HPTLC, Differential, Rapid screening, complexation, Densitometric analysis.*

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Study on Leaching Behavior of Selected Metals in Coal Fly Ash and Bottom Ash Samples

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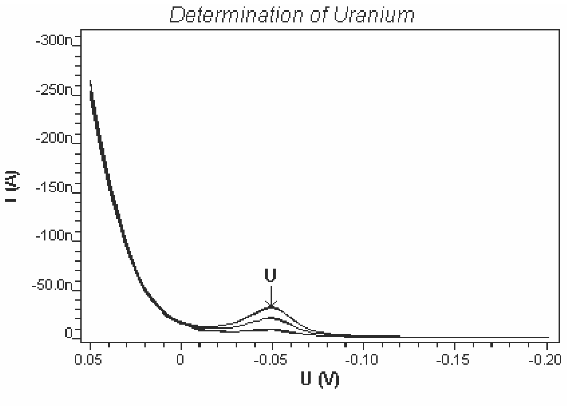
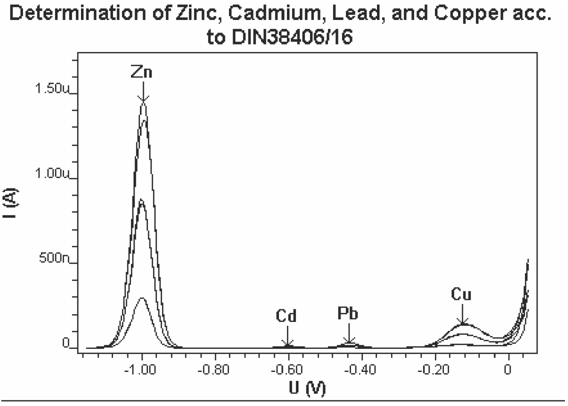
Coal combustion residues such as fly ash (FA) and bottom ash (BA) are known to contain environmentally significant trace metals, whose mobility depends strongly on ash chemistry and pH. Although the majority of fly ashes reported globally are alkaline due to elevated CaO and alkali oxide levels, the fly ash analysed in this study was remarkably acidic, indicative of its low calcium concentration (600 mg/kg in FA and 1924 mg/kg in BA). The pH of FA was found to be 5.75 while that of BA was 6.5. This study evaluates the leaching effects of specific metals associated with fly ash samples. In order to assess these effects, the leaching behaviour of zinc (Zn), cadmium (Cd), lead (Pb), copper (Cu), and uranium (U) was investigated in representative FA and BA samples collected from a coal-fired power plant. The total metal concentrations of Zn, Cd, Pb, Cu and U in FA were 331 mg/kg, 3.1 mg/kg, 27.2 mg/kg, 269 mg/kg and 9.4 mg/kg, and in BA were 135 mg/kg, 0.6 mg/kg, 8.3 mg/kg, 208 mg/kg, and 16.3 mg/kg respectively. The concentration of metals in both the solid and leachate samples were measured using voltammetry which is known for its high sensitivity, low detection limits and also for its ability to accurately quantify trace metals in complex matrices such as ash leachates. Leaching experiments were conducted with leachate solutions maintained at various temperatures (30°C, 40°C, and 50°C) at a shaking speed of 150 rpm for a period of 24hrs. The pH-dependent leaching tests were also performed on both FA and BA samples at different leachate solution pH ranging from 2 to 12. To verify the leachability of metals as a function of the L/S (Liquid to Solid, i.e., Water to Fly Ash/Bottom Ash) ratio, four parallel batch leaching tests with different L/S ratios (20, 30, 50, and 100) were carried out at room temperature using deionised water as the extractant. It was observed that leachability of metals decreases with increase in L/S ratio. pH of the leachate solution was observed to have a great influence on the leaching behaviour of metals associated with both FA and BA. In the present study, all metals except Uranium were observed to have their highest leachability at pH 2, compared to their leachability at other pH values. The highest values for leaching was observed for Cu at pH 2 (3.6 and 4.2%) while Uranium (2.1 and 1.5%) showed highest leaching in alkaline conditions at pH 12 for both FA and BA respectively. It was also observed that with the increase in temperature, the leachability of the five studied metals also increases. Very little literature is available on the leachability of acidic FA and BA. So we need to conduct more studies to understand the complete mechanism and leachability of metals in acidic coal ash residues.





Key words: *Fly ash, Bottom ash, leaching, Voltammetry*

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Electrochemical Separation of U at SS430 Cathode from U-Pd-Zr Alloys in Molten LiCl-KCl-UCl_3 Electrolyte

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Metal fuels are being considered for future fast breeder reactors, with pyroprocessing emerging as a promising method for reprocessing these fuels. In pyroprocessing, spent metal fuel serves as anode with stainless steel or liquid cadmium as cathode and LiCl-KCl-UCl_3 as electrolyte. During the process, uranium, plutonium and minor actinides are electrochemically dissolved from the anode into the electrolyte and are recovered at cathode. Fission products like alkali, alkaline earth and lanthanides remain in the electrolyte, and noble metals are retained at the anode. In order to assess behaviour of noble metals during electrorefining and to address further material balance issues, ternary U-Pd-Zr alloys were prepared and were investigated using electromotive force and cyclic voltammetric measurements. U-2Pd-4Zr and U-4Pd-2Zr (*wt.*%) alloys were prepared by vacuum arc melting and characterized using X-ray diffraction. Equilibrium phases were established to α-U, UZr_2 and UPd_3. Electrorefining was carried out at 773 K with 1.33 grams of the alloy as anode, SS430 as cathode and LiCl-KCl eutectic melt containing 2 *wt.*% UCl_3.

Equilibrium potential of U-2Pd-4Zr and U-4Pd-2Zr alloys was measured to be -1.344 V and -1.367 V (*vs.* AgCl|Ag), respectively at 773 K. Onset potential for dissolution of U, which is usually referred to as apparent equilibrium potential is measured by a transient technique such as cyclic voltammetry, was observed at -1.277 and -1.169 V, respectively for U-2Pd-4Zr and U-4Pd-2Zr. In the cyclic voltammogram of U-4Pd-2Zr alloy, anodic peak at -0.962 V (Fig. 1) is due to dissolution of U from the three equilibrium phases of alloy namely, α-U, UPd_3 and UZr_2. Beyond -0.962 V, diffusion current first decreases up to -0.90 V and remains more or less steady up to-0.40 V. In the reverse sweep from -0.20 V onwards, decrease in cathodic current beyond -1.0 V corresponds to reduction of U^{3+}. Electrorefining of U-2Pd-4Zr alloy at 773 K was carried out applying

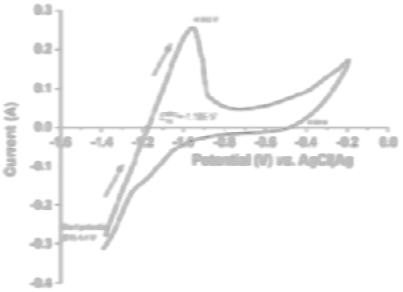

Fig. 1: *Cyclic voltammograms of U-4Pd-2Zr alloy in LiCl-KCl-UCl_3 electrolyte at 773 K.*

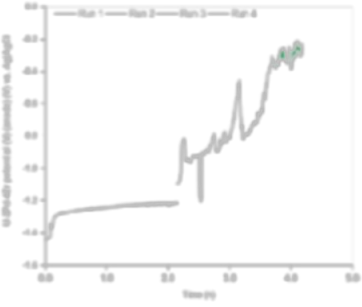

Fig. 2: *Variation of U-2Pd-4Zr alloy during ER runs at 773 K*

Key words: Pyroprocessing, molten salt, cyclic voltammetry, chronopotentiometry

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Orbital Interactions and Bonding Characteristics in Am(III) and Eu(III) Terpyridine Complexes

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Late 1990s studies demonstrated that *N*-donor ligands preferentially stabilize actinide complexes over lanthanide complexes due to the higher polarizability and softer nature of actinide ions. This selectivity arises from the stronger covalent interactions between *N*-donor ligands and the 5*f* orbitals of actinides, compared to the more core-like 4*f* orbitals of lanthanides. To illustrate this behaviour, terpyridine was employed as a representative ligand to examine its complexation with Am(III) and Eu(III) metal ions. The lowest-energy structures of the corresponding Am(III) and Eu(III) complexes were obtained using density functional theory (DFT) methods (cf. Figures 1a and 1b). Geometry optimizations were carried out both with and without dispersion corrections. For Am(III), the dispersion parameters defined for Eu(III) were used during geometry optimization. All calculations were performed using the Turbomole [1], NBO 6.0 [2], ORCA 4.2.1 [3], and ADF 2016 [4,5] program packages. To investigate the electronic structure of the complexes, an in-depth molecular orbital analysis was conducted at the DFT level. The analysis reveals ligand-to-metal charge-transfer (LMCT) interactions in both complexes, along with an additional metal-to-ligand charge-transfer (MLCT) component in the americium complexes. This bonding behaviour highlights a correlation between the ligand geometry and its enhanced binding affinity toward americium.

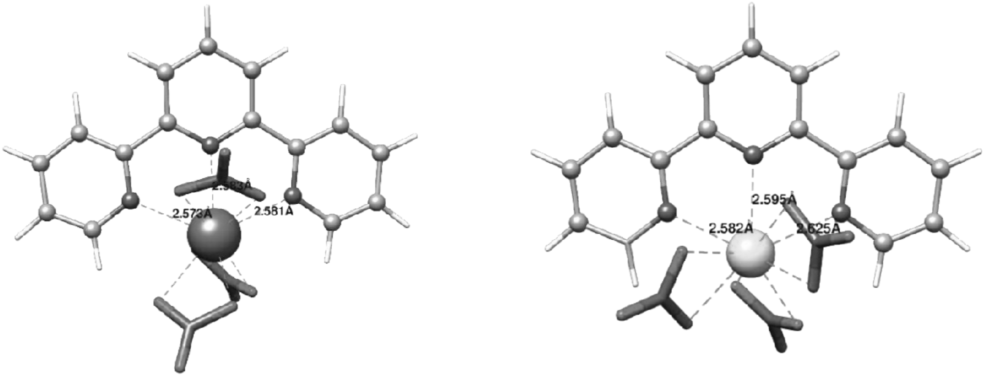

Fig.1: *Lowest energy geometries of* $Am(NO_3)_3$*·Terpy and* $Eu(NO_3)_3$*·Terpy complexes at RI-BP86-D3BJ/def2-TZVP-ZORA level of theory*

Keywords: *Americium, Europium, DFT, Molecular Orbital Analysis*

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Influence of Alkyl Chain Length on the Electronic Structure and Binding of Unsymmetrical Phosphate Complexes of U(VI) and Th(IV).

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Tri-*n*-butyl phosphate (TBP) has long served as the primary ligand in solvent-extraction process within the closed nuclear fuel cycle. Its effectiveness in separating uranium and plutonium from spent fuel, as well as in facilitating the partitioning of minor actinides from high-level liquid waste (HLW), has established it as the standard extractant. Nonetheless, TBP is not without limitations: it exhibits measurable aqueous solubility, undergoes radiolytic degradation, and can induce third-phase formation. These issues highlight the need for alternative ligands with enhanced chemical and physical robustness. Previous studies indicate that variations in alkyl chain length [1] do not substantially alter the basicity of the phosphoryl oxygen. However, the influence of symmetrical versus unsymmetrical alkyl substitution on coordination behaviour has received comparatively little attention, particularly from computational studies [2]. To address this gap, we performed a detailed quantum-chemical investigation of a series of unsymmetrical phosphate ligands in which the butyl groups of TBP were replaced with longer alkyl chains, extending up to heptyl. The derivatives examined-dibutyl pentyl phosphate (DBPnP), dibutyl hexyl phosphate (DBHeP), and dibutyl heptyl phosphate (DBHpP)-were studied in their complexes with uranyl nitrate (UO_2^{2+}, 1:2 metal-to-ligand ratio) and thorium nitrate (Th^{+4}, 1:3 ratio). All calculations were performed using ORCA [3], NBO[4], and Amsterdam Density Functional (ADF) [5] program packages. The net charge of the P=O group is similar, and the binding affinity of U and Th complexes is increasing with chain elongation of unsymmetrical phosphates.

Ligands	NBO Charges		
	P	**O**	**Net**
TBP	2.42	-1.06	1.36
DBPnP	2.42	-1.05	1.37
DBHeP	2.42	-1.05	1.37
DBHpP	2.43	-1.06	1.37

Fig.1: *Lowest energy geometry of $UO_2(NO_3)_2{\cdot}2DBPnP$ at RI-BP86-D3BJ/ZORA-def2-TZVP level of theory*

Keywords: *Phosphates, Uranium, Thorium, DFT, ADF, NBO.*

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Insights from DFT Studies on the Extraction of U/Pu/Zr Matrices Using Phosphonate Based Ligands

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Tri-*n*-butyl phosphate (TBP) has long served as the workhorse extractant in the solvent-extraction steps of the closed nuclear fuel cycle, enabling the efficient recovery of U and Pu from spent nuclear fuel and supporting the separation of minor actinides from high-level liquid waste (HLW). However, TBP suffers from several operational limitations - most notably its measurable aqueous solubility, pronounced susceptibility to radiolytic degradation under reprocessing conditions, and tendency to form third-phase at elevated metal and acid loadings. These issues motivate the development of next-generation ligands with enhanced chemical stability, reduced aqueous solubility, and improved extraction behaviour. Previous studies have shown that phosphonate-based ligands exhibit stronger orbital interactions than their phosphate analogues during complexation with actinides [1]. It is therefore of interest to examine their interaction patterns and complexation energetics with the U/Pu/Zr matrix. To address this, we conducted a detailed quantum chemical investigation of two phosphonate-based ligands - di-*n*-butyl butyl phosphonate (DBBP) and di-*n*-amyl amyl phosphonate (DAAP) - in their complexes with uranyl nitrate (UO_2^{2+}, 1:2 metal-to-ligand ratio), plutonium nitrate (Pu^{4+}, 1:3 ratio) and zirconium nitrate (Zr^{4+}, 1:3 ratio). All calculations were performed using the ORCA [2], NBO [3], and Amsterdam Density Functional (ADF) [4] program packages. Overall, DBBP exhibits more favourable complexation energies than DAAP.

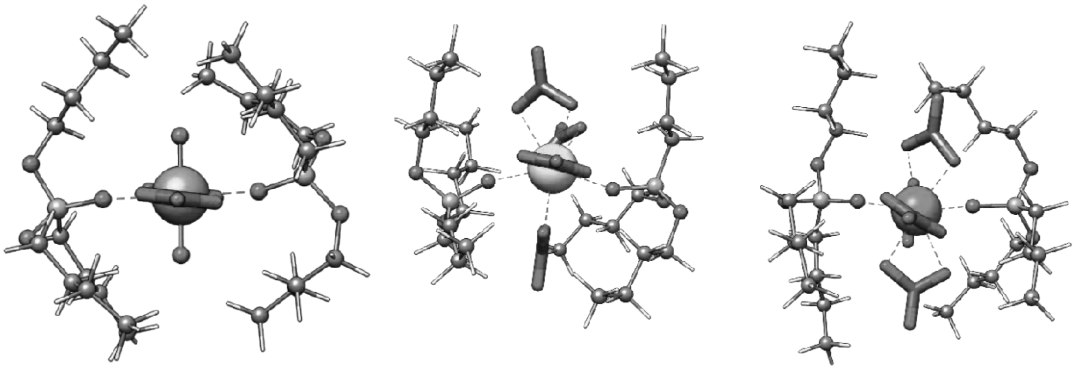

Fig.1: *Lowest energy geometries of $UO_2(NO_3)_2{\cdot}2DBBP$, $Pu(NO_3)_4{\cdot}2DBBP$ and $Zr(NO_3)_4{\cdot}2DBBP$ at RI-BP86D3BJ/def2-TZVP-ZORA level of theory. Colour code: white is hydrogen, grey is carbon, orange is phosphorus, red is oxygen, sky blue is uranium, cyan colour is plutonium, and dark pink is zirconium.*

Keywords: *Phosphonates, Uranium, Plutonium, Zirconium DFT, ADF, NBO.*

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Substituent Effects in Phosphinic Acids: Alkyl vs Aryl Variants in Uranyl Nitrate Extraction

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Spent nuclear fuel reprocessing commonly employs tri-*n*-butyl phosphate (TBP) in *n*-dodecane for the selective extraction of uranium and plutonium from fission products. Previous studies have shown that substituents near the phosphoryl group significantly influence metal-ligand interactions [1,2] following the trend: phosphine oxides > phosphinates > phosphonates > phosphates[3]. In this work, density functional theory (DFT) calculations were performed on a series of alkyl- and aryl-substituted phosphinic acids to investigate their complexation behavior with uranyl nitrate in a 1:2 metal-ligand stoichiometry. Three alkyl ligands (PA, EPA, DEPA) and three aryl ligands (PPA, DPPA, EPPA) were examined at the RI-BP86-D3BJ/def2-TZVP level using the ORCA quantum chemistry package [4]. Our results indicate that the phenyl-substituted ligand DPPA exhibits the strongest complexation among all studied ligands. The computed complexation energies (kcal/mol) for alkyl phosphinic acids were: PA (-66.2), EPA (-73.0), and DEPA (-78.6); and for aryl phosphinic acids: PPA (-72.4), DPPA (-80.8), and EPPA (-78.4). These results highlight the enhanced binding affinity associated with phenyl substitution in phosphinic acid ligand towards the uranyl ion.

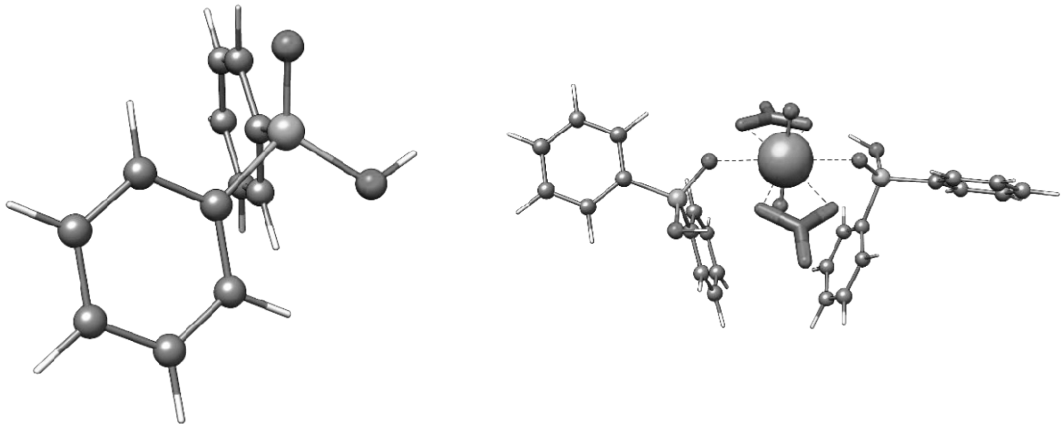

Fig.1: *Lowest energy geometries of DPPA ligand and* $UO_2(NO_3)_2\cdot 2DPPA$ *complex at RI-BP86-D3BJ/def2TZVP-ZORA level of theory. Colour code: white is hydrogen, grey is carbon, blue is nitrogen, red is oxygen, orange is phosphorous and sky-blue sphere is uranium.*

Key words: *Uranium, Phosphinic acids, DFT.*

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Metal Ligand Interactions in the Unsymmetrical Branched Alkyl Phosphate with Uranyl Nitrate and Thorium Nitrate Complexes

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Tri-*n*-butyl phosphate (TBP) is widely recognised as the cornerstone extractant in the closed nuclear fuel cycle, playing a central role in the separation of U and Pu from spent nuclear fuel and in facilitating the recovery of minor actinides from high-level liquid waste (HLW). Despite its extensive use, TBP exhibits several wellknown limitations, including significant aqueous solubility, susceptibility to radiolytic degradation, and the tendency to form third phase, all of which collectively motivate the search for next-generation ligands with improved performance. Previous investigations have shown that the basicity of the phosphoryl oxygen remains essentially unaffected either by increasing alkyl chain length [1] or by progressing along the series phosphate → phosphonate → phosphinate → phosphine oxide [2]. However, relatively few experimental or theoretical studies have examined how symmetrical versus unsymmetrical ligand-substitution patterns influence metal– ligand binding characteristics[3]. Motivated by this gap, we employed quantum chemical calculations to explore the electronic structure and complexation behavior of unsymmetrical, branched phosphate ligands derived by modifying the butyl substituents of the symmetrical tri-*n*-butyl phosphate framework. Representative examples include dibutyl *iso*-butyl phosphate (DBiBP) and dibutyl *sec*-butyl phosphate (DBsBP), evaluated in their complexes with uranyl nitrate (1:2 stoichiometry) and thorium nitrate (1:3 stoichiometry). All quantum chemical calculations were performed using ORCA quantum chemistry package [4], NBO program [5] and Amsterdam Density Functional (ADF) suite [6]. Our results indicate that the net charge on the phosphoryl group in all ligands are positive, and that it exhibits a stronger binding affinity towards U(VI) compared to Th(IV).
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Ligands	NBO Charges		
	P	**O**	**Net**
TBP	2.42	-1.06	1.36
DBiBP	2.41	-1.05	1.36
DBsBP	2.42	-1.05	1.37
TsBP	2.43	-1.05	1.38

Ligands	Binding Energies (g*as phase*) of various uranyl nitrate complexes (in kcal/mol)	
	Uranyl Nitrate (1:2)	**Thorium Nitrate (1:3)**
TBP	-77.3	-114.2
DBiBP	-77.8	-115.2
DBsBP	-77.4	-115.0
TsBP	-79.2	-115.5

Keywords: *Phosphates, Uranium, Thorium, DFT, ADF, NBO*

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F-6

Effect of Alternate Ligand – Solvent System in PUREX Process

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The design of efficient ligand–solvent system is a challenging part in the liquid–liquid extraction processes. Tributyl phosphate (TBP) in dodecane is the widely used ligand–solvent system for well-known PUREX (Plutonium Uranium Extraction) process.[1] In recent past a potential alternative of TBP namely tri-iso amyl phosphate (TiAP) is being used for fuel reprocessing applications because it overcomes the inherent limitations of TBP as aqueous solubility, third phase formation and degradation under thermal and radiological environment.[2] TiAP is diluted with dodecane to reduce the viscosity and to increase the diffusivity of TiAP for solvent extraction purposes. The polarity of the solvent plays an important role during ion transport. Dodecane as a nonpolar solvent does not have any influence on interfacial properties except changing the physical properties of ligand–solvent system. Therefore, it is of fundamental interest to study the effect of polar solvent as octanol in place of dodecane during the interphase mass transfer. How the molecular level structure and interactions due to the polar and non-polar nature of solvent dictates the mass transfer at the interface. Hence, the objective of the study is not only to explore a potential replacement of dodecane but also to develop an understanding on the effect of polar solvent in liquid–liquid extraction (LLE).

The extensive MD simulations studies have been performed with octanol as a polar solvent to find out the advantages and disadvantages of such solvent in the field of spent fuel reprocessing. The octanol is normally used as phase modifier to reduce the aggregation of ligand in organic phase. Though the density of pure octanol is comparatively higher than dodecane but the diffusivity of pure octanol is quite high around 2.5 times of dodecane which is advantageous for any ligand–solvent system. Further, the diffusivity of TiAP in octanol medium has been improved compared to dodecane medium which is favorable for LLE. Further, the simulation studies of simple biphasic system predict that the water–octanol system offers better mass transfer ability over water–dodecane[3] system because of high total interface thickness (w_t) which is always favored for designing any solvent extraction system. Furthermore, the studies were extended to complex biphasic system where the w_t was found to be decreased with mole fraction of TiAP and increased with nitric acid molarity.[4] It can be noted that the polar solvent created a reverse trend of interfacial properties from nonpolar solvent due to the presence of Hbonding between water and polar solvent.

System	w_t (nm)	γ (mN/m)	w_c (nm)	w_i (nm)
Water - Solvent				
Dodecane	0.767	49.3	0.202	0.740
Octanol	1.14	21.6	0.175	1.127
30% TiAP composition with pure water				
Dodecane	1.12	23.2	0.169	1.107
Octanol	1.04	25.6	0.160	0.997
30% TiAP composition with 3M nitric acid				
Dodecane	1.05	26.1	0.274	1.014
Octanol	1.13	21.1	0.177	1.116

The extraction of uranyl ion using 30% TiAP/octanol[4] from aqueous phase was found to be smaller than 30% TiAP/dodecane whereas the back extraction of uranyl ion from organic phase was highly efficient for 30% TiAP/octanol system. The recovery of uranyl ions from organic phase to aqueous phase is improved from 87.1% (TiAP/dodecane)[5] to 94.3% for TiAP/octanol[4] system. The interaction energy computed using DFT for water–octanol interaction (-11.99 kcal/mol) was significantly higher than that of water–water interaction (4.63kcal/mol). The simulation studies suggest that the extraction system can be designed in such a way that the dodecane and octanol both can be used as a solvent with an appropriate ratio which can improve both the extraction and back extraction of uranyl ion in the PUREX process.

Key words: *PUREX, TiAP, Polar solvent, Uranyl ion, interfacial tension and interface thickness.*

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Density Functional Theoretical Studies on Complexation of U(VI) with Glyphosate

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Glyphosate (N-(phosphonomethyl)glycine) is a widely used, broad-spectrum commercial herbicide, which exists in the zwitterionic form. From a coordination chemistry point of view, glyphosate could be very effective ligand towards certain metal ions owing to the presence of strong binding sites such as phosphate, amine and carboxylate [1]. This complexation is significant for environmental studies because it can affect the mobility of metal ions such as migration of uranium in soil and water. The complexation studies of uranium with glyphosate is important not only in order to understand the migration of U(VI) in soil through complexation with glyphosate but also to obtain the interesting fundamental information owing to unique coordination chemistry of the linear UO_2.

To get insight into coordination mode of U(VI)-glyphosate complexes density functional theoretical calculations were carried out. The geometries of ligand, and predicted complexes (ML and ML_2) were optimized at the DFT level of calculations using the TURBOMOLE program package. The geometry optimization for all the structures was performed without any symmetry restriction using the B3LYP functional with the triple-ζ valence plus polarization (TZVP) basis set, as implemented in the TURBOMOLE package [2]. The aqueous-phase energetics was calculated using a conductor-like screening model (COSMO) approach. The following equation representing the complexation of U(VI) with glyphosate was used to estimate the overall energetics of the complexation process.

$$[UO_2(H_2O)_5]^{2+} + m\mathrm{Gly}^{3-} \rightleftharpoons [UO_2(\mathrm{Gly})_m(H_2O)_n] + (5\text{-}n)\ H_2O \qquad (1)$$

Based on different possible coordination modes of the ligand, the various initial guess geometries were used for structure optimization of the ML and ML_2 complexes of U(VI)-glyphosate. The binding energies were calculated for all of the possible geometries of U(VI)-glyphosate complexes in both gas and aqueous phases. The binding energies are becoming less negative with successive complexations; *i.e.,* the affinity of glyphosate is reducing upon successive complexations with U(VI).

In ML_1 glyphosate binds to U(VI) with amine N, COO^- and one of the phosphonate oxygen. In ML_2 one of the glyphosate binds with amine N, COO^- and phosphonate oxygen and another glyphosate unit binds with COOand phosphonate oxygen along with the amine hydrogen H-bonded to uranyl ayl oxygen (fig. 1). Experimental (IR) studies also confirmed the binding of COO^- and phosphonate oxygen to U(VI). Using the cyclic voltammetry, the redox speciation of uranyl was performed in presence of glyphosate and the diffusion coefficent value for the complex was determined.

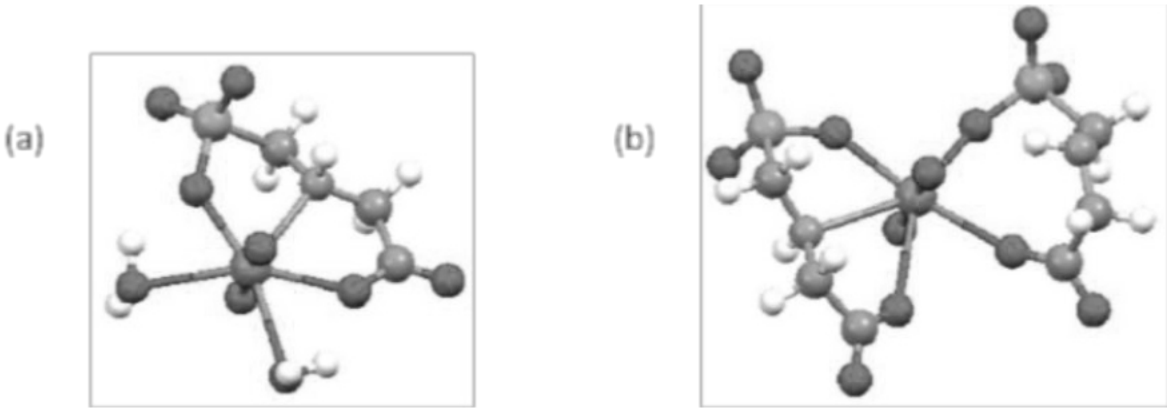

***Fig**: DFT Optimised structure of (a) UO_2-glyphosate and (b) UO_2-(glyphosate)$_2$*

***Key words:** Uranium, Glyphosate, Complexation, DFT*

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Determination of Composition of Alpha Emitting Radio-nuclides in HLW in Reprocessing Facility

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The aim of reprocessing facility is to separate Pu and depleted uranium by Purex process from spent fuel. In this process, the waste generated through operation contains high radio-activity, and is designated as HLLW[1]. It is getting vitrified in glass matrix and stored under long term surveillance. The knowledge of radionuclides of HLW is required for safe handling, providing adequate shielding and containment, effective cooling design. This also ensure compliance with regulatory requirements and waste treatment. The knowledge of alpha emitting radionuclides in HLW is required as they contribute significantly in long term radiotoxicity resulting in disposal challenge and environmental risk to the biota. In thisregard, it was planned to determine the composition of alpha emitting radionuclides in HLW using the tools of alpha spectrometer (PAS-01) and thermal ionisation mass spectrometry (TIMS-3090), and explained in this paper.

It is well known that major contributors to the alpha dose in HLW are Am and Cm, to some extent Pu, Np and U. Extraction and stripping methodologies were adopted for isotopic analysis, and fresh samples were used for each element during separation. After the separation of U and Pu using TBP, Am and Cm were extracted from HLW sample using TEHDGA and DTPA [2] for isotopic analysis. Due to poor resolution (~30 KeV) of alpha spectrometry different peaks of Am isotopes were not clearly separated. Hence, Am isotopes were analysed by TIMS, and Cm isotopes were measured by alpha spectrometry as shown in fig.1. For analysis of Pu, it was extracted in 0.5 M TTA in xylene and followed by stripping in 8 M nitric acid. It was then analysed in TIMS and alpha spectrometry. U was analysed in TIMS, after it's separation by 30% TBP with ferrous sulphamate (to avoid Pu extraction). Np was extracted using ferrous sulphamate, hydroxylamine hydrochloride and TTA mixture followed by analysis in alpha spectrometry. Alpha activities of different radionuclides as shown in table 1 were measured by alpha spectrometry. Very diluted sample was used for the alpha activity measurement of Am and Cm, and interferring Pu activity was deducted from Pu+Am total activity to get Am activity. During Am analysis in TIMS, Cm-242 may have interference with Am- 242, but alpha spectrometry data indicated that Cm-242 activity was very low, and it has short half-life (163 days). Therefore, it has negligible interference (in the order of 10^{-5}) in Am-242 measurement. Low activity of Np was found in alpha spectrometry, similar result was mentioned in BARC report [3]. The methodologies adopted—combining chemical separation, alpha spectroscopy, and mass spectrometric analysis—proved effective for reliable composition determination even in complex waste matrices. In conclusion, the determination of alpha- emitting radionuclide composition in HLW not only supports safe nuclear waste management but also strengthens the scientific basis for advanced reprocessing and disposal technologies in the nuclear fuel cycle.

Table-1

Radio-Nuclides	Alpha Activity (%)	Isotopes and Composition (%)	
U	< 0.001	$^{234}_{92}$	<0.01
		$^{235}_{92}$	0.27
		$^{236}_{92}$	0.07
		$^{238}_{92}$	99.65
Np	0.003	$^{237}_{93}$	----
Pu	0.078	$^{238}_{94}$	0.15
		$^{239}_{94}$	69.01
		$^{240}_{94}$	26.00
		$^{241}_{94}$	2.86
		$^{242}_{94}$	1.98
Am	95.419	$^{241}_{95}$	96.82
		$^{242}_{95}$	0.12
		$^{243}_{95}$	3.06
Cm	4.500	$^{242}_{96}$	0.10
		$^{244}_{96}$	99.90

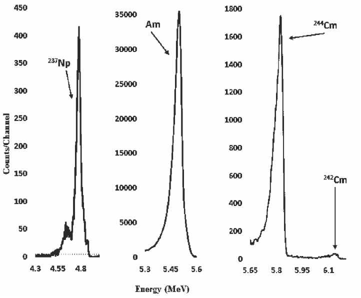

Fig. 1: *Alpha spectrometry data*

Key words: *Chemical Separation, Alpha emitting radionuclides, HLW, Alpha spectrometry, Mass Spectrometry*

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Estimation of U/Pu of Mixed Carbide Fuel Irradiated in FBTR, by Direct Loading Method using TIMSR

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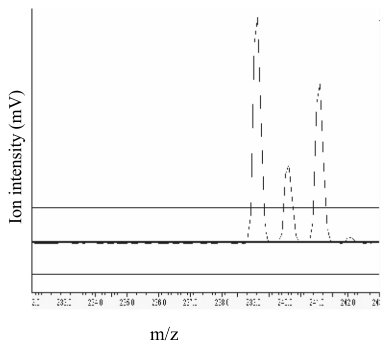
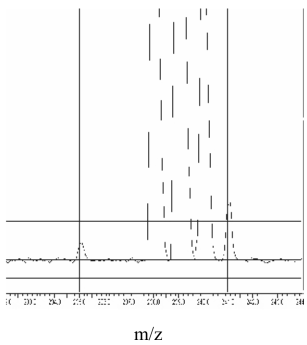
The isobaric interference of ^{238}U with ^{238}Pu and that of ^{241}Am with ^{241}Pu necessitates ion exchange separation of the constituent elements (in addition to Sm-Nd isobaric interference) for fast reactor fuel for its U,Pu estimation or burn up evaluation by TIMS. An extended heating program for the sample inside TIMS was developed for the removal of Am utilizing the fact that heat of vaporization of Am is 1.49 times lower than that of Pu and vapor pressure is two orders higher than that of Pu. Interference from ^{238}U makes it necessary to correct the ratio ^{238}Pu/^{239}Pu by alpha spectroscopy [1] in conventional method. Whereas, in direct loading method, by making one set of isotopic ratio (^{238}Pu/^{239}Pu) measurements before building up of uranium signals, the ^{238}Pu/^{239}Pu ratio can be determined almost free from uranium interference. Concentrations of individual elements were determined by IDMS by the addition of known quantities of proper spikes for each element of interest. The present study deals with analysis of irradiated Mark I (30%U-70%Pu) mixed carbide fuel of FBTR for U and Pu concentrations by direct loading method, employing the large differences in vapor pressures of U, Pu and the interfering element Am, without any chemical separation as in conventional method. The method found its applicability for PHWR spent fuel (10000 MWd/t) [2] as well as for (U, Pu) mixed oxide fuel of 100 GWd/t, with less than 4 % uncertainty in burn-up. Applicability of the technique with advanced fuel like carbide fuel is discussed in this study and compared with reported value [3]. About 40 µl of dissolver solution of mixed carbide fuel, without subjecting to any chemical separation was loaded on Re filament for isotopic composition measurements. Another aliquot of 0.0409g (~40 µl) sample was mixed with 0.5833g of ^{240}Pu spike and 0.9978 g of ^{233}U spike, mixed well to attain homogeneity and the residues were dissolved in ~10 µl of 0.75 M nitric acid and loaded on to Re filaments (in duplicate) for Isotopic dilution mass spectrometric analysis.

The triple filament assembly containing dissolver solution was heated slowly to 5.5/1.5A with constant heating rates. At 1.55 A, ^{241}Am signal started to appear as its vapor pressure is remarkably higher than that of other actinides present on the filament (vapor pressures of Am, Pu, U are 5.52, 1.34e-2 and 4.2e-5 Torr respectively at 1800 K). The intensity of Am increases with filament temperature and at 1.78 A, signal corresponding to Pu isotopes started to appear, but with no U signal. The ratio ^{238}Pu/^{239}Pu was measured at this scenario; subsequently the filament current was increased to 2.2A, to measure ^{240}Pu/^{239}Pu , ^{242}Pu/^{239}Pu and all the isotopic ratios of U. Am intensity was falling continuously throughout this period, waited for about another 55 minutes to reduce the ^{241}Am intensity to a minimum steady level, then measured ^{241}Pu/^{239}Pu. The spiked mixture was analyzed for ^{233}U/^{238}U and ^{240}Pu/^{239}Pu directly as they are unaffected with any interfering isotopes. From the above values, concentration of U and Pu were evaluated by IDMS equation. The method is advantageous in view of lesser analysis time, lack of chemical separations, no liquid waste generation, less exposure and very less sample requirement compared to conventional method.



Mass spectrum of dissolver solution at filament current of 5.5/1.78 A



Mass spectrum of dissolver solution at filament current of 5.5/2.2 A

Relative abundances of U and Pu isotopes measured by direct loading method and by conventional method

Element	Mass No.	Atom fraction observed (by direct loading method)	Atom fraction reported (by conventional method)
U	233	0.0001±0.0001	0.0001±0.0001
	234	0.0002±0.0001	0.0002±0.0001
	235	0.0076±0.0002	0.0075±0.0001
	236	0.0006±0.0002	0.0007±0.0001
	238	0.9917±0.0008	0.9914±0.0006
Pu	238	0.0006±0.0001	0.0004±0.0001
	239	0.9020±0.0006	0.9041±0.0003
	240	0.0901±0.0004	0.091±0.0003
	241	0.0045±0.0008	0.0027±0.0003
	242	0.0005±0.0003	0.0004±0.0002
Concentration ratio; U/Pu		**0.64**	**0.67**

Key words: *Americium, Isobaric interference, preferential evaporation, Thermodynamics*

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Bench-Scale Separation of Zirconium from Americium by Solvent Extraction using Hydroxyacetamide Extractant

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A future fast reactor fuel based on U-19Pu-10Zr is being researched in IGCAR. The possibility of an aqueous PUREX based separation was adopted for the reprocessing of the fuel as an interim option, as the suggested pyrochemical reprocessing for metal fuel is yet to be fully demonstrated. Zirconium separation from the above nuclear wastes draws attention due to its complicated aqueous chemistry which could pose serious challenges to the subsequent processing of the nuclear waste. In this context, Zr recovery from a feed solution containing approximately 2.8 g of Zr and 135 mg of Am was attempted.

The feasibility of dissolution of unirradiated U-19Pu-10Zr fuel pellets in nitric acid medium and subsequent aqueous reprocessing steps using different tri-alkyl phosphate based solvents was earlier demonstrated at our lab in IGCAR, Kalpakkam [1]. After quantitative extraction of U and Pu, the raffinate solution (3 Liters) which remained after the reprocessing steps was found to contain 970 ppm of Zr along with 45 ppm of Am in ~ 2 M nitric acid. This raffinate solution was subjected to batch mode solvent extraction steps for the separation of Am. A solvent phase consisting of 0.1 M DOHyA (*N,N*-di-octyl-2-hydroxyacetamide) in *n*- dodecane was chosen for this purpose based on a comparison of preliminary studies using different glycolamide and alkyl phosphate based extractants. This monoglycolamide solvent showed high selectivity for extraction of Zr especially at low acidities of aqueous feeds (< 2M), where the extraction of Am by DOHyA was very low[2]. The separation was achieved by ten solvent extraction batches in an aspirator bottle set-up (Fig.1a) carried out in a radioactive fume-hood. 300 mL of the Am-Zr solution was mixed with 300 mL of DOHyA solvent in each batch, by magnetic stirring (600 rpm) for 30 minutes. The results of ICP-OES analysis revealed that the concentration of Zr in the feed was reduced from 970 ppm to 27 ppm after the extraction. Approximately 7%- 10%of Am in the feed was transferred to the organic phase and 35-40 ppm of Am remained in the solution during this step. This co- extracted Am was selectively scrubbed using 150 mL of 0.3 M nitric acid solution. The Zr extracted to the DOHyA phase was then stripped using 300 mL of 0.2 M oxalic acid solution in 0.1 M nitric acid. The recovered solvent was subsequently used for the next extraction batch. The total feed solution (3 liters) was treated with one liter of DOHyA solvent by the above procedure. The feed and scrub solutions were evaporated to ~ 50 mL and further treated with DOHyA solvent for final purification yielding ~ 120 mg of pure Am in concentrated nitric acid.

Fig 1a. *The aspirator bottle set-up used for batch solvent extraction steps*

Fig.1b. *Dilute nitric acid solutions with separated americium showing the characteristic pink glow*

Key words: *Americium, Zirconium, Hydroxyacetamide, Solvent extraction, Mutual separation*

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Experimental Study on Retention of Iodine in Liquid Sodium Pool Under Reactor Accident Conditions

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In Sodium-cooled Fast Reactors, clad breach event can lead to the release of fission gases such as xenon and krypton into the primary sodium coolant. These gases rise as buoyant bubbles to cover gas through the sodium pool and may carry with them volatile fission products, including radioactive iodine isotope ^{131}I. Iodine (^{131}I, half-life: ~ 8 days) released from failed fuel pins pose a significant radiological risk to the exposed population in the short term. The experiment was conducted to study the percentage of iodine retention in the liquid sodium pool. This study is important for sodium cooled fast reactors source term analysis due to the radiological consequences associated with Iodine.

The set up (shown in Figure 1) consists of the iodine vessel, the interaction vessel with sodium and the charcoal-based iodine trap system. The 1.8-meter height interaction vessel consists of 8.2 kg of sodium. 30 grams of iodine was taken in a crucible and placed in 0.5-liter vessel. The Iodine vessel was initially pressurized to 4 bar and heated to 190 °C. Argon as an inert carrier gas was used to transport iodine vapor into the sodium pool. The iodine was injected into the sodium pool through nozzle, submerged at 28 cm below the sodium surface. As the Iodine–Argon bubbles rose through the sodium column in the interaction vessel, the reaction of iodine with sodium occurred primarily at the bubble – sodium interface. To monitor iodine and aerosol formation in the cover gas, the gas mixture was passed through Andersen sampler for collecting aerosols and an activated charcoal trap for capturing residual iodine vapor. Simultaneously, a sodium sampling cup was placed within the interaction vessel to analyze iodine retained in the sodium.

After completion of the experiment, all iodine-bearing components were rinsed with a sodium thiosulphate solution. The Iodine present in solutions was estimated using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). A total of 97.6% of injected iodine was found to be retained in the sodium pool with iodine-laden argon bubbles injected at a depth of 28 cm in a 200 °C sodium pool. This high efficiency is due to the chemical reaction between iodine and sodium, resulting in the formation of non-volatile sodium iodide in sodium pool.

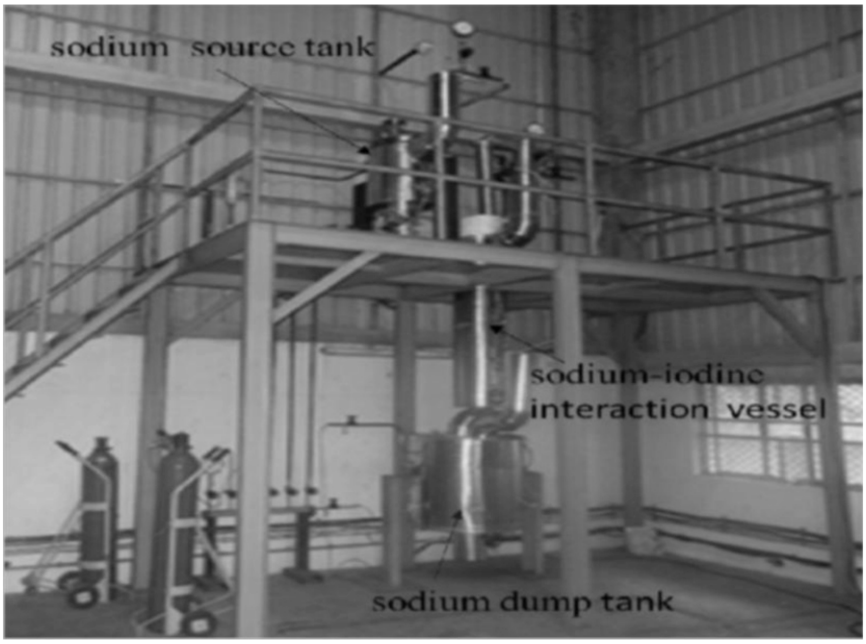

Figure1. *Experimental Setup*

Key words: *Sodium cooled Fast Reactor, Sodium, Iodine, Sodium Iodide*

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Quality Control Assessment of Carrier-Free ^{32}P Orthophosphate Produced via the ^{32}S(n,p)^{32}P Reaction in FBTR

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Carrier-free ^{32}P (β^-_{max} = 1.71 MeV and $t_{1/2}$ = 14.28 d) with ultra-high chemical and radiochemical purity is essential for its application in radio-labelled nucleotide synthesis [1,2]. Trace metal and anionic impurities can act as potent inhibitors of enzymatic phosphorylation reactions involved in the preparation of γ-ATP and other ^{32}P-labelled nucleotides. These impurities can interfere with enzyme–substrate binding, alter reaction kinetics, and reduce product yields. Therefore, stringent radiochemical and chemical purification of ^{32}P is mandatory to ensure compatibility with downstream biochemical reactions and to achieve high specific-activity products suitable for molecular-biology and genetic-engineering applications. Carrier-free ^{32}P is being produced in Fast Breeder Test Reactor (FBTR) through ^{32}S(n,p)^{32}P reaction using strontium sulphate as target and radiochemical purification of ^{32}P was carried out in Hotcells [2].

The purity of the ^{32}P product was confirmed by subjecting representative samples to a series of standard quality control evaluations. Radionuclidic purity was assessed by alpha and gamma spectrometric analyses, which confirmed the absence of any alpha- or gamma-emitting impurities. The HPGe gamma spectrum (Fig. 1) exhibited only bremsstrahlung radiation arising from the high-energy beta emissions of ^{32}P, indicating radionuclidic purity of the product. Cerenkov and liquid scintillation counting (LSC) measurements were recorded periodically to monitor decay kinetics, as shown in Fig. 2. The half-lives determined from Cerenkov and LSC data were 14.2 and$_3$14.3 days, respectively, which are in excellent agreement with the literature value. This concordance confirms the absence of additional β-emitting impurities in the ^{32}P product. The radiochemical purity (RCP) was tested using Thin Layer Chromatography (TLC) method in which samples (1-2 µL) were spotted on PEI-cellulose TLC plates and developed using 0.2 M KH_2PO_4 (pH 3.5) as the mobile phase. After development, plates were counted using Cerenkov counting and found to have more than 99% RCP (Fig.3). The ^{32}P concentration was quantified spectrophotometrically using a working dye containing malachite green, ammonium molybdate and Tween-20. Each reaction received 100 µL of dye and phosphate standards (0.5–5 nmol) to generate a calibration curve by measuring absorbance at 620 nm. The unknown H ^{32}P O$_4$ sample was analyzed, and its ^{32}P concentration was obtained from the curve and the specific activity of ^{32}P was calculated to > 6000 Ci/mmol. Trace metal ion contamination in the ^{32}P sample was assessed by ICP-AES. All metallic impurities (Al, Ti, Ca, Mg, Fe, Sr, P and Pb) in ^{32}P product were below the detection limits (0.1 mg/L or 0.1 ppm), confirming their absence. Anionic impurities in the ^{32}P sample were analyzed by ion chromatography (IC). Sulphate and nitrate were detected only at trace (ppb) levels, confirming the chemical purity of the ^{32}P product with respect to anionic contaminants. The ^{32}P product is currently being evaluated at BRIT-RC, Hyderabad for its suitability in bio-tagging applications.

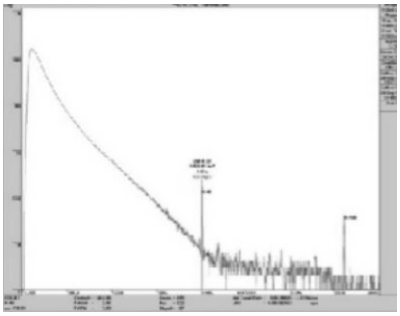

Fig.1 *Gamma spectrum of ^{32}P.*

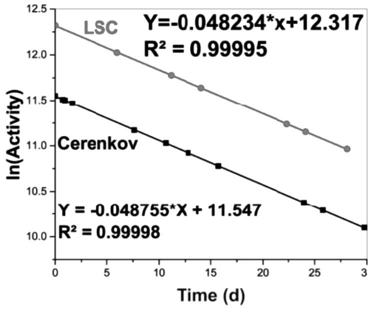

Fig.2 *Decay profile of ^{32}P*

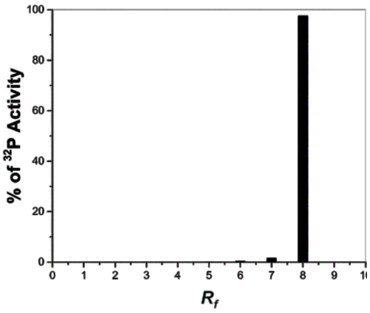

Fig.3 *TLC pattern of ^{32}P product*

Key words: *^{32}P, FBTR, Half-life, Specific Activity, Quality Control*

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Safety Assessment of $SrSO_4$ for ^{32}P Production in FBTR: Chemical, Thermal and Radiation Compatibility Studies

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Fast reactors provide high-energy neutron fluxes (~10^{15} ncm^2s^{-1}), enabling the efficient production of carrier- free radioisotopes through threshold reactions such as (n,p) and (n,α). Isotopes including ^{89}Sr and ^{32}P produced in these systems have widespread applications in medicine, biology, and industry. Carrier-free ^{32}P ($t_{1/2}$ =14.28 d, β^{-}_{max}=1.71 MeV;) with ultra-high purity is particularly important for radio-labelled nucleotide synthesis [1]. Fast reactors operate at elevated temperatures; hence, the target material must withstand prolonged irradiation without structural or phase degradation. Strontium Sulphate ($SrSO_4$) was selected for ^{32}P production due to its high thermal stability under FBTR conditions. Additionally, the target must remain chemically compatible with liquid sodium coolant and stainless-steel cladding to prevent corrosion, dissolution or secondary phase formation that could adversely impact reactor safety. In addition, degradation response of $SrSO_4$ under gamma irradiation was also evaluated across multiple dose levels to determine its chemical stability and suitability for use as a target material. Compatibility of sintered $SrSO_4$ pellets with sodium was investigated to simulate a hypothetical capsule breach during irradiation in FBTR. $SrSO_4$ pellets were placed in alumina crucibles and immersed in sodium, followed by encapsulation in stainless steel capsules. The capsules were exposed at 550°C for 30, 60 and 100 days. After cooling, sodium was distilled off and the resulting powders analyzed by X-ray diffraction (XRD) to identify reaction products. Pellets retrieved after sodium exposure showed significant discoloration, loss of mechanical integrity and measurable weight gain, indicating pronounced chemical interaction. After 30 days, sodium was completely consumed, confirming its participation in reaction with $SrSO_4$. XRD patterns of the reacted powders differed from unreacted $SrSO_4$ and matched the signatures of SrO, Na_2S and Na_2O, establishing the formation of these products via a thermodynamically favorable reaction (Fig.1). The brittle nature and fragmentation of the pellets indicate that $SrSO_4$ undergoes extensive decomposition in molten sodium, underscoring the need for double stainless-steel encapsulation to eliminate the risk of sodium ingress during irradiation. Interaction of $SrSO_4$ with SS316L cladding material was evaluated under simulated irradiation conditions. $SrSO_4$ pellets were placed between SS316L top and bottom discs inside alumina crucibles and sealed in stainless-steel vessels, followed by annealing at 550°C for 10 to 100 days. Post-exposure visual inspection showed no structural degradation of either the pellet or SS316L, except minor discoloration of the clad due to annealing. SEM–EDS analyses of the clad surfaces indicated only superficial adherence of $SrSO_4$ without elemental diffusion into SS316L. Subsequent EDXRF and Spark-OES measurements confirmed nearly identical bulk composition before and after exposure, demonstrating that $SrSO_4$ interaction with SS316L is negligible. Gamma irradiation stability of $SrSO_4$ pellets was assessed using a GC-5000 ^{60}Co source at 530 Gy/h. Pellets exposed to 127.2 to 5400 kGy showed IR spectra identical to the un-irradiated sample, indicating no structural degradation (Fig.2). The present study demonstrated that $SrSO_4$ is chemically compatible with SS and stable under gamma-radiation exposure; however, it reacts with liquid sodium. Therefore, irradiation of $SrSO_4$ in the FBTR was performed under a double-encapsulation configuration to ensure safe containment and prevent sodium interaction.

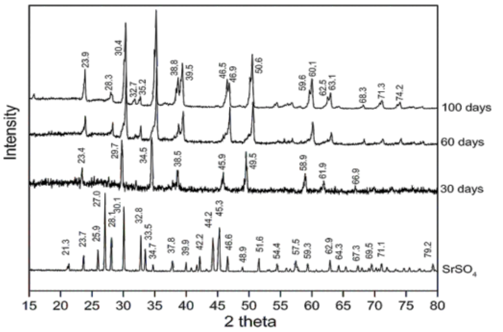

***Fig.1** XRD pattern of $SrSO_4$ before and after interaction with **Na** at 550°C.*

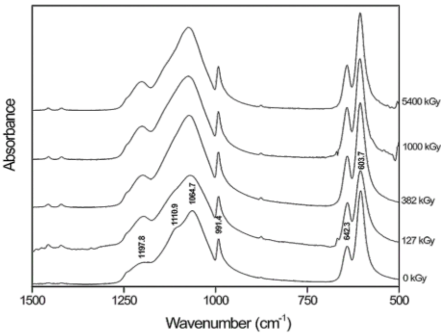

***Fig.2** FTIR spectra of $SrSO_4$ exposed to radiation dose at 127, 382, 1000 & 5400 kGy.*

***Key words:** ^{32}P, FBTR, Sodium, Compatibility, Radiation degradation*

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Design & Fabrication of a Multi-task Table for the Radiochemical Separation of ^{32}P from FBTR Irradiated $SrSO_4$ Pellets in Hot Cells

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This technical report documents the design, development and intended application of a multi-task modular laboratory table engineered for deployment in hot-cell facilities supporting remote radiochemical operations. The system has been specifically configured to meet the stringent requirements of radiochemical separation of phosphorus-32 (^{32}P), where safe remote handling, mechanical robustness and precise alignment of process components are critical. Approximately 110 pellets of strontium sulfate ($SrSO_4$) were irradiated in the Fast Breeder Test Reactor (FBTR) for duration of 33 days, corresponding to nearly two half-lives of ^{32}P. Though ^{32}P is a pure beta emitter that can be handled with minimal shielding, however, the irradiated batch exhibited a dose rate of ~100 R/h, necessitating radiochemical processing within shielded hot-cell environments. The external transfer port (ExTP) of the hot cells has a diameter of 280 mm, imposing dimensional constraints on the introduction of equipment. To address this limitation, a dismountable, multi-task modular table was designed to pass through the ExTP and subsequently be assembled inside the cell. The multi-task table made of SS304L integrates four core functional modules: (i) a tilting-vessel mechanism for controlled rotation and decanting operations, (ii) a vessel-holding vice for secure clamping and remote removal of lids, (iii) a dedicated mounting provision for ion-exchange resin columns used during ^{32}P separation and purification steps and (iv) an air ejector equipment for filtration. The tilting mechanism is based on a rigid pivot assembly with defined angular locking positions, enabling precise mechanical control through master–slave manipulators while minimizing risks of spillage or vessel instability. The vice assembly features adjustable, chemical-resistant clamping jaws that can accommodate vessels of varying diameters under hot-cell conditions without deformation or slippage. The ion-exchange column fixture is designed as a modular support unit, compatible with standard column geometries, ensuring stable elution, washing and resin conditioning by remote operations required for efficient ^{32}P processing. Remote processing of ^{32}P was carried out inside hot cells by dissolving the irradiated pellets in a Titanium dissolver vessel, where the vessel lid was tightened with manipulator while the vice held the vessel in place. The dissolver vessel was heated on a hot plate under controlled heating at 120 °C for 24 hours. Once the dissolution was complete, the lid was opened and the vessel was transferred to the tilting mechanism to transfer the reaction mixture into a beaker. The reaction mixture was filtered off using a funnel with filter paper with air ejector suction. The residue part was dissolved with 4M HCl and then the resultant solution was precipitated with $FeCl_3$ and NH_3. The precipitate was dissolved in 1 M HCl and loaded into a pre-loaded ion-exchange column, mounted on the multi-tasking table. Elution was carried out with 0.1 M HCl using a weighing burette and the ^{32}P fraction was collected in a bottle. The integrated platform improves workflow efficiency in the hot cell by consolidating multiple process steps into a single, compact and structurally rigid system. This reduces the number of standalone fixtures, enhances reproducibility of operations and supports safer remote manipulation. Overall, the multi-task table provides a robust and ergonomically optimized solution for radiochemical laboratories engaged in ^{32}P production and similar isotope-handling processes.

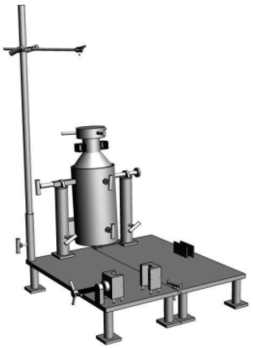

Fig. 1: *Multi-task Table*

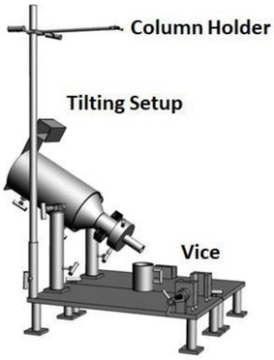

Fig. 2: *Tilting-vessel mechanism*

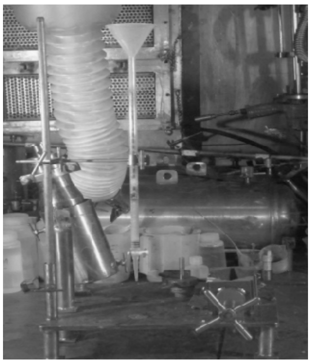

Fig. 3: *Ion-exchange column*

Key words: *Multi-task table, Radiochemical separation, ^{32}P, tilting-vessel mechanism, vice*

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1. G.V.S. Ashok Kumar, *J. Radioanal. Nucl. Chem.* 302 (2014), 939

Measurements of Radiocarbon Concentrations in Plant Leaves Using Carbon Dioxide Absorption Method

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Radiocarbon (^{14}C) is a pure beta emitter with endpoint energy of 156 keV. The half-life of ^{14}C is 5700±30 years. The ^{14}C produced in the reactors due to neutron activation of target elements like ^{13}C, ^{14}N and ^{17}O present in the coolant, moderator, fuel and other structural materials. The ^{14}C also produced due to natural cosmogenic production, atmospheric nuclear weapon testing. The released carbon-14 from the nuclear power plants is integrated into the natural carbon cycle in the environment and then enters into the food chain. Hence, monitoring carbon-14 in the vicinity of nuclear power plants is essential to observe any increase in natural background levels [1]. Quantification of radiocarbon levels in the environmental samples are carried out either using Accelerator mass spectrometry method (AMS) or by liquid scintillation spectrometry. The carbon dioxide absorption method is a pre treatment technique used for quantification of ^{14}C activity levels in the environmental samples using liquid scintillation counter (LSC). In the Carbon dioxide absorption method, the carbon dioxide (CO_2) is produced from the carbon present in the sample either by acidification or by combustion techniques [2]. The produced CO_2 is absorbed in the Carbo-Sorb E and Permaflour absorption mixture and measured in LSC for ^{14}C activity levels.

The present study focuses on the measurements of specific activity levels of ^{14}C in the plant leave samples using the carbon dioxide absorption method. Five different plant leaf samples with total of 25 No's were collected within the IGCAR campus. The samples were dried at room temperature and grounded to homogenous powder form using mixer and grinder. In this study, the total carbon present in the leave samples were measured using TOC analyzer. The average total carbon is found to be 39.2±4.0 in 25 plant leaf samples. Parr Oxygen bomb (USA, 1121) was used in this study for combustion of plant leaf samples. The carbon dioxide released in combustion is absorbed in two bubblers containing 2N sodium hydroxide solutions. It is observed that an average of 83 % of carbon is trapped in bubbler 1 and 17% of carbon is trapped in bubbler 2. The carbonate formed is precipitated as barium carbonate using barium chloride. The barium carbonate formed is used in carbon dioxide absorption method for measurement of radiocarbon levels using liquid scintillation system. The liquid scintillation counting system was calibrated using NIST Oxalic standard. The method was validated using IAEA certified reference material and the relative bias in measured and actual values was found to be 2.1%. The measured ^{14}C activity concentration levels in the plant leaf samples ranged between the 70.7 and 110.3 Bq/kg an average activity concentration of 93.9±10.5 Bq/kg.

Figure1: *Experimental set up for combustion and*

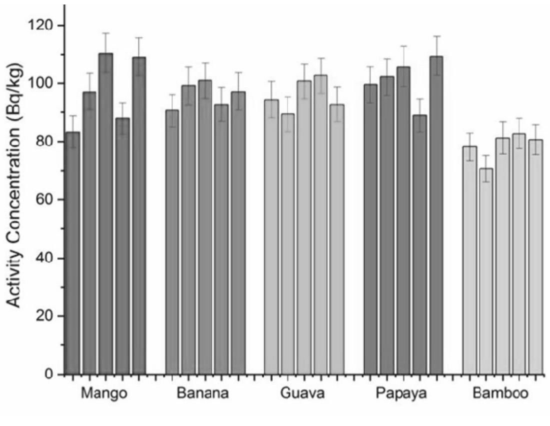

Figure2: *Variation of specific activity levels in different*

Keywords: *Radiocarbon; liquid scintillation counter; Carbon dioxide absorption method.*

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G-9

Polyoxometalate (POM) Based Polymeric Beads for Extraction of Americium

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The complexation of actinide cations by polyoxometalates (POMs) has been a vibrant area of research over the past five decades. A highly effective way to obtain POMs with specific properties is to form hybrid composite materials by loading POMs onto various supports. In our previous studies, we synthesized a composite material that effectively extracted americium [1]. Building on this success, we attempted to develop a more stable and efficient composite material for the extraction of actinides. Composite polysulfone (PS) beads containing phosphotugstate ($Na_7[PW_{11}O_{39}]\cdot xH_2O$) ($PW_{11}$) were prepared by phase inversion using tri-capryl methyl ammonium chloride (Aliquat-336) in chloroform. The lacunary POM (PW_{11}) was synthesized according to a literature method [2]; 7.25 g of sodium tungstate dihydrate and 0.28 g of sodium hydrogen phosphate were dissolved in 15 mL of DI water, and then the mixed solution was heated to 80−90°C and pH adjusted to 4.8 with nitric acid under vigorous stirring. The reaction solution was concentrated to 7.5 mL using rotatory evaporation and followed with extraction by acetone (8mL × 3). The final product was obtained by evaporating the collected aqueous phase.$_2$The POM and the composite POM bead were characterized using different techniques such as SEM, FTIR, TGA etc. Different type of beads with varying PW_{11} loading (12.5% and 25%) were prepared and tested. The synthesized POM beads were evaluated for solid-phase extraction of Am^{3+}, Eu^{3+}, and UO_2^{2+} from from buffer solutions. They exhibited promising distribution coefficients (Kd ≈ 10^3 mL/g) with equilibrium reached in 4–5 h for Am^{3+} and Eu^{3+} (Fig.1a), but negligible uptake for UO^{2+} at pH 5.7, demonstrating selectivity for Am(III) and Eu(III) over U(VI). Desorption of Am^{3+} was slow, with only 68% recovery using 0.5 M HEDTA over 6 hours, indicating strong absorption. The beads showed high Am(III) extraction efficiency across a wide pH range (Fig.1b), with particularly significant extraction efficiencies at pH 5–6, suggesting their potential for radionuclide extraction from biological and environmental samples.

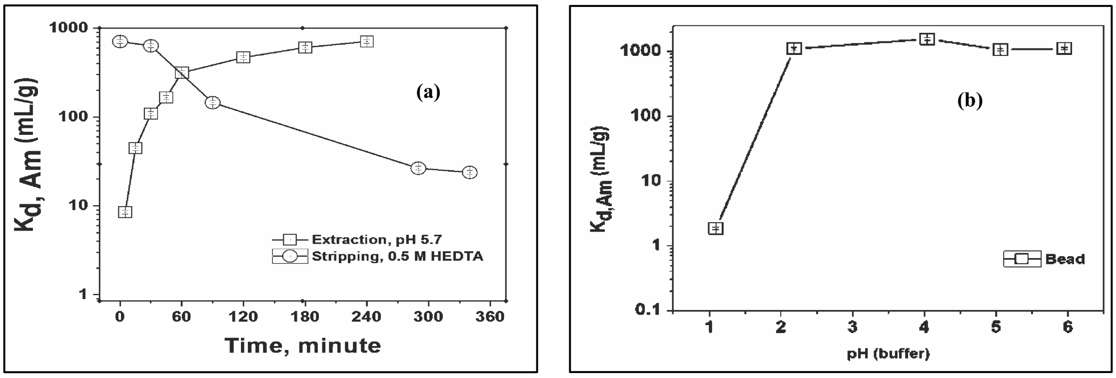

Fig. 1: *(a) Sorption and desorption for synthesized composite bead for Am(III) (b) K_d of Am(III) with the composite bead at pH 1 to 6*

Key words: *Polymeric Bead, Lacunary POM, Extraction*

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Development of Polystyrene based scintillation sensor for Americium

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Sensitive and selective detection of americium (Am) is crucial in nuclear safeguards, radioactive waste management, and environmental monitoring, due to its radiotoxicity and long-term persistence. Conventional analytical techniques such as α-spectrometry and ICP-MS, although highly accurate, require extensive radiochemical separations, long analysis times, and specialized laboratory infrastructure. Scintillation-based sensors, particularly those incorporating functionalized polymer matrices, offer a promising alternative due to their ability to combine pre-concentration and radiometric detection within a single platform. In our earlier studies, a polystyrene (PS)-based scintillation sensor was developed for the selective extraction and ultratrace assay of plutonium [1]. The sensor demonstrated excellent sensitivity, selectivity, reusability, and a linear response across a wide range of Pu concentrations. Building on this approach, the present work focuses on developing a scintillation sensor tailored for the selective extraction and detection of Am. In this context, two well-established actinide extractants - N,N,N',N'-tetraoctyldiglycolamide (TODGA) and di-(2-ethylhexyl)phosphoric acid (DEHPA) [2]- were used to prepare PS-based scintillation sensors. The two extractants were selected based on their complementary acidity dependent binding characteristics for Am^{3+}, with TODGA retaining the high extraction efficiency in molar range of acidity while DEHPA performing under mildly acidic conditions. Therefore, Am^{3+} uptake and detection in these two substrates was studied at two acidic conditions, 2 $molL^{-1}$ and pH1 HNO_3. The polystyrene polymer inclusion films (PIFs) were prepared by a solvent casting method using PPO as the scintillator, MSB as the wavelength shifter, and varying amounts (12 to 41%) of the Am-selective ligands, TODGA or DEHPA. Figs. 1 and 2 show the PMT-based pulse-height spectra for the PS–TODGA and PS–DEHPA substrates, respectively. A systematic shift of the pulse-height spectra toward lower channels is observed as the extractant loading increases from 12 to 41%, with significantly lower overall pulse height at the highest extractant loading. Additionally, an increase in lower-energy contributions is evident, likely arising from conversion electrons, γ-rays, or other lower-energy radiations. This broadening can lead to inaccurate peak area estimation. To address this, Am activity was calculated using only the right half of the pulse-height peak. Table 1 summarizes the expected and measured Am uptake activities for both substrate systems. As seen from the table, the relative deviation between expected and measured activity decreases with increasing extractant loading, reaching within 14% for the highest TODGA loading and within 7% for the highest DEHPA loading. These results demonstrate the feasibility of using PS-based scintillation substrates for the simultaneous pre-concentration and radiometric detection of americium.

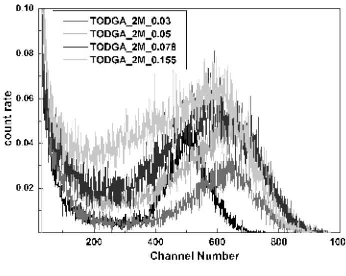


Fig1.*Pulse Height spectra of Am^{3+} loaded PS-TODGA*

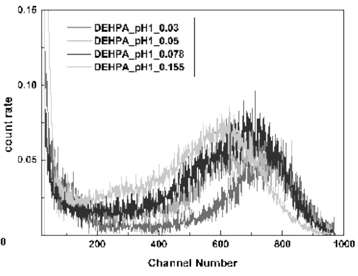
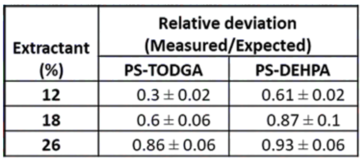


Fig2.*Pulse Height spectra spectra of Am^{3+} loaded PS-DEHPA*

Table.*Relative Deviation of Measured and Expected Am3+ activity in PS substrated*



Extractant (%)	Relative deviation (Measured/Expected)	
	PS-TODGA	PS-DEHPA
12	0.3 ± 0.02	0.61 ± 0.02
18	0.6 ± 0.06	0.87 ± 0.1
26	0.86 ± 0.06	0.93 ± 0.06

Key words: *Polymer inclusion film, Americium, TODGA, DEHPA, scintillation*

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Studies on Suitable Stripping Agent for The Quantitative Recovery of ^{237}Np From Organic Effluent

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The ^{23} Np is one of the key transuranic nuclides formed during the irradiation of nuclear fuel in nuclear reactors and it is formed through a series of neutron-capture and radioactive-decay processes involving uranium isotopes present in the fuel. The ^{23} Np concentration in a fast reactor is expected to be higher than in a thermal reactor because the n,2n reaction cross section of ^{23} U which is greater in the fast spectrum. In nuclear fuel reprocessing, the unutilized uranium (U) and plutonium (Pu) from spent nuclear fuel is being recovered leaving gamma emitting fission products and minor actinides in high level wastes.

Generally, PUREX process being followed for quantitative recovery of U & Pu from spent fuel dissolver solution. Since, Np exists in multiple oxidation states in feed solution of solvent extraction, it distributes into different process streams. Therefore, determining its concentration in each stream is essential in view of its recovery for potential applications and to minimize the radiotoxicity in waste streams. Determining its concentration is challenging due to its complex chemistry, low alpha specific activity, very low concentration and interference from other actinides.

The present work involves identifying a suitable stripping reagent for the quantitative recovery of Np from organic liquid waste (OLW) into the aqueous phase, followed by the separation of Np from Pu prior to the determination of ^{23} Np by alpha spectrometry. Feasibility studies were carried out using reagents such as sodium carbonate, hydrazine carbonate, and oxalic acid. The selection of the Np stripping reagent was guided by the criteria like, minimizing interference from TBP degradation products present in the spent solvent and ensuring quantitative recovery. Among the reagents tested, 0.5 N oxalic acid was found to be the most promising for stripping Np from OLW. The D value for the distribution of Np among lean organic and 0.5 M oxalic acid was measured with ^{239}Np tracer and found to be 0.05. Hence three sequential contacts were optimized in order to have quantitative recovery of Np from the organic sample. The oxalic acid present in the strip solution was subsequently decomposed by heating with 10 M nitric acid. The oxidation state of Pu and Np were conditioned to +3 and +4 respectively using ferrous sulphamate and acidity adjusted to 1.0 M. The Np (IV) in conditioned feed solution was selectively extracted into organic phase consisting 0.5 M TTA/xylene maintaining O/A ratio = 0.5. The D for Np(IV)for this condition was determined with the help of ^{239}Np tracer and found to be 9.4 and for Pu(III) by alpha radiometry is ~ 0.01. The quantitative extraction of Np is achieved by three sequential contacts. A known volume of loaded organic phase consisting Np is transferred on to SS planchet, deposited and Np concentration was obtained from its characteristic alpha energy at 4.78 MeV using silicon surface barrier semiconductor detector. The typical alpha spectrum obtained was shown in Fig 1. The concentration of ^{237}Np in the OLW sample was determined as 0.05 ± 0.005 mg/L. The obtained results were validated by gamma spectrometry after the ^{23}Np in the organic effluent had reached secular equilibrium with its daughter nuclide, ^{233}Pa. This measurement was carried out after a period corresponding to ten half-lives of the daughter isotope to ensure complete decay of any ^{233}Pa co-extracted during the solvent-extraction cycle and establish the required equilibrium. The recovery and separation method for ^{237}Np described in the present study overcomes this difficulty and is adaptable for the determination of ^{237}Np in spent solvent

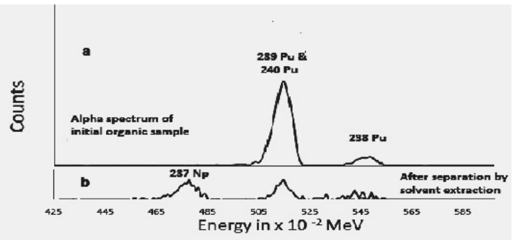

***Fig 1** : a) α spectrum of initial OLW b) α spectrum of the ^{237}Np & Pu in the HTTA phase (3 Hrs counting)*

Key words: *Neptunium, Plutonium, OLW, oxalic acid etc*

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Radiochemical Separation of Carrier-Free ^{32}P Produced in FBTR via the $^{32}S(n,p)^{32}P$ Reaction

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^{32}P is a pure beta emitter with β^{-}_{max} energy of 1.71 MeV & decays with a half-life of 14.28 d. ^{32}P is extensively used for tagging biomolecules, labeled nucleotides and in molecular biology kits and is supplied nationwide for advanced research in biology, agriculture, healthcare and genetic engineering [1,2]. High specific active and carrier-free ^{32}P can be produced in FBTR through $^{32}S(n,p)^{32}P$ reaction. A total of 110 strontium sulphate ($SrSO_4$) pellets, each weighing ~1 g, were encapsulated in double-walled SS-316 cladding and locked in a steel carrier sub-assembly. The pellets were irradiated in the 5th ring of FBTR at a reactor power of 40 MWt for 33 days. Post-irradiation, the sub-assembly was transferred to RML hotcells for mechanical cutting and subsequently to RCL hot-cells for radiochemical processing. 25 irradiated $SrSO_4$ pellets were dissolved in titanium vessel (Fig.1a) inside the hot-cells using boiling sodium carbonate solution for 24 h in the stiochiometric ratio of 1:3, resulting in the conversion of $SrSO_4$ to $SrCO_3$ as a solid residue and Na_2SO_4 in the solution [1].

$$SrSO_4+Na_2CO_3 \rightarrow SrCO_3{-}+Na_2SO_4$$

The ^{32}Phosphate is distributed between both the $SrCO_3$ residue and the Na_2SO_4 filtrate. After filtration, the $SrCO_3$ residue was dissolved in hydrochloric acid, followed by the addition of $FeCl_3$ and ammonia solution, resulting co-precipitation of phosphate along with $Fe(OH)_3$ (Fig.1b). Likewise, the ^{32}Phosphate present in the Na_2SO_4 filtrate independently recovered by co-precipitation with $Fe(OH)_3$ under similar conditions. The precipitates obtained in both cases were dissolved separately in 1M HCl, and the solutions were subsequently conditioned to 0.1M HCl. Each solution was then passed through a cation-exchange chromatography column to retain the Fe(III) & trace Sr(II) ions. The ^{32}P was eluted in the form of phosphate using 0.1 M HCl. The eluates were further subjected to anion-exchange chromatography to remove anionic impurities, particularly sulphate (Fig.1c). The ^{32}P was eluted with 0.01M HCl in a total volume of approximately 50 mL, while the sulphate remained bound to the resin. Aliquots from both the residue and filtrate-driven fractions after purification were analyzed by liquid scintillation counting (LSC) for activity quantification of ^{32}P. The activity assay indicated that more than 90% of the total ^{32}P produced in the $SrSO_4$ target was associated with the $SrCO_3$ residue fraction. LSC measurements confirmed a total yield of approximately 1.2 Ci of ^{32}P per 25 g pellet batch at the time of separation. The final purified ^{32}P solution was repeatedly evaporated with the addition of Millipore (Bio-Pak) water under an IR lamp to reduce the volume and then adjusted to a small volume at pH 6. The purified ^{32}P underwent a complete quality control evaluation, including chemical purity, radiochemical purity (>99%), radionuclidic purity (>99.9%) and specific activity (>6000 Ci/mmol) determined by ICP-OES, TLC, beta- gamma counting and spectrophotometry respectively. Three ^{32}P batches containing 140 mCi each were dispatched to BRIT-RC, Hyderabad for quality-assurance studies.

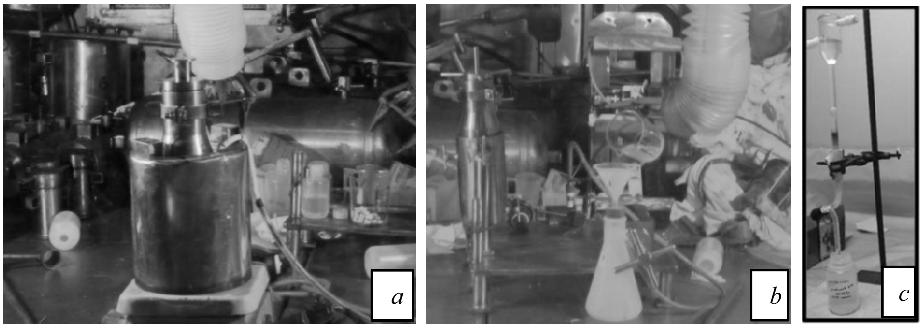

Fig.1 *Radiochemical processing of ^{32}P inside Hotcells depicting (a) Dissolution (b) Precipitation (c) Ion-exchange chromatography.*

Key words: *^{32}P, Radioisotope, FBTR, Radiochemical Separations, ion-exchange chromatography*

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Applicability of Encapsulated Porous Polymeric Beads for Extraction Of Plutonium From Urine Samples

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Assessment of internal contamination due to plutonium (Pu) by in-vitro bioassay is primarily carried out through the analysis of urine samples, due to ease of sample collection, analysis and interpretation. The most common techniques for Pu separation from urine samples are ion-exchange and extraction chromatography[1]. In the current study, porous polymeric beads with encapsulated liquid extractants were synthesized[2] using the phase inversion technique, and utilized for extraction of Pu from urine samples. The encapsulated beads were synthesized using three different liquid extractants: TBP, Aliquat 336, and PC-88A. Initial experiments were performed to determine whether these synthesized beads could extract Pu from an aqueous medium prior applying them for urine samples. For this study 40 mg of the synthesized beads were equilibrated with aqueous solution (1 mL) spiked with 5.0 Bq Pu(α) for a time of 240 mins. The oxidation state of Pu was adjusted to +4 using a pinch of $NaNO_2$ salt. Following equilibration, the Pu(α) activity in aqueous solution was measured using Packard Tricarb 4910 TR liquid scintillation counter to determine the extraction efficiency. The PC-88A encapsulated porous (PEP) beads showed promising results (~80% extraction) and hence, was selected for extracting Pu from urine samples.

To determine the optimal acidic condition for Pu extraction from urine samples, experiments were carried out by varying acidity of urine sample (0.05 to 8.0M). For these experiments, 1 mL of acidified urine sample spiked with known concentration (5 Bq) of Pu(α) was equilibrated with 40 mg of synthesized PEP beads for 240 mins. Fig. 1 shows the effect of urine acidity on Pu extraction (%) by PEP beads. It was observed that maximum extraction of Pu was observed (~90%) for urine sample with 0.2M acid concentration. The effect of contact time on adsorption of Pu by PEP beads from urine sample matrix was also investigated and results obtained are shown in Fig. 2. It was observed that Pu gets rapidly extracted in first 30 mins and after 60 mins, no significant increase in extraction of Pu from urine matrix was observed (~90%), indicating PEP beads can be utilized for extraction of Pu from urine sample matrix.

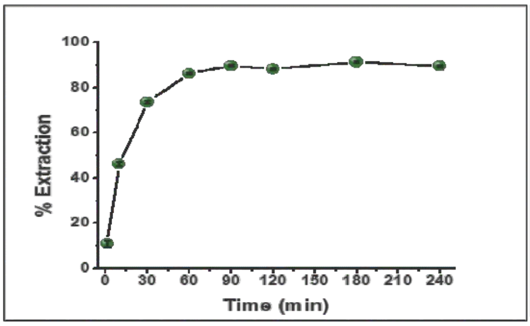

Fig. 1: *% Extraction of Pu by the PEP beads as a function of urine acidity.*

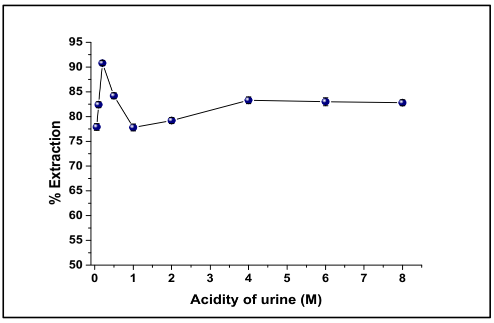

Fig. 2: *% Extraction of Pu by the PEP beads as a function of time.*

Key words: *Urine, PC-88A, Plutonium*

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G-14

Application of EGMP-Based Polymer Inclusion Films for Ultra-Trace Plutonium Pre-Concentration and Detection from Complex Environmental Matrices

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Ultra-trace quantification of plutonium (Pu) demands highly selective and efficient pre-concentration techniques that remain efficient even for large-volume and compositionally diverse environmental samples. In our earlier work, we developed scintillating ethyl glycol methacrylate phosphate (EGMP)-based polystyrene polymer inclusion films (PIFs) for the ultra-trace detection of Pu [1]. Building upon this foundation, the present study evaluates the performance of an EGMP-based substrate for Pu uptake from varied aqueous systems and examines its suitability for pre-concentration applications relevant to environmental radiochemical analysis. The synthesized substrates were characterized for their surface features using scanning electron microscopy (SEM) and contact-angle measurements, while their chemical and luminescent properties were examined using Fourier transform infrared (FT-IR) spectroscopy and fluorescence spectroscopy, respectively. Along with this, the substrate was further characterized for its Pu uptake and deloading kinetics. Uptake kinetics were determined by equilibrating the substrate in 2 mL of 2 mol L^{-1} HNO_3 spiked with known Pu activity, and 20 µL aliquots were periodically withdrawn for counting using a low-background PMT setup. The substrate exhibited markedly improved sorption behavior relative to previously reported PS-based systems [2], achieving adsorption equilibrium in ~2 h (Fig. 1). Deloading studies were performed by equilibrating the Pu-loaded substrate with hydrogen peroxide in 2 mol L^{-1} HNO_3. The percentage of Pu deloaded from the substrate, determined by pre- and post-equilibration counts of the substrate, reached (93 ± 2)% after approximately 50 h (Fig. 2), indicating efficient reductive stripping of Pu. The maximum loading capacity of the developed substrate was also measured by equilibrating a known weight of the substrate with 2 molL^{-1} HNO_3 spiked with excess known Pu tracer ions. The substrate capacity was found to be 226 ± 9 µgg^{-1} of Pu in 2 molL^{-1} HNO_3 (which corresponds to $(92.2 \pm 3.7)\text{x}10^5$ Bq g^{-1} of Pu). The applicability of the developed substrates for the pre-concentration and detection of Pu from varied matrices was assessed by studying the Pu uptake from the representative aqueous samples with different origins such as sea, pond and tap water at two sample volumes (2 and 5 mL). As summarized in Table 1, the measured Pu uptake values were within 15% of the expected values across all the three sample types and both volumes, demonstrating the robustness of the methodology and confirming that the developed analytical methodology is applicable to variable matrices.

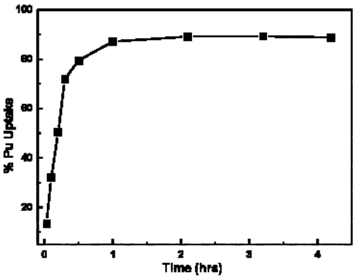


Fig. 1 The kinetics of Pu uptake by PIFs in 2 molL^{-1} $HNO^{3.}$

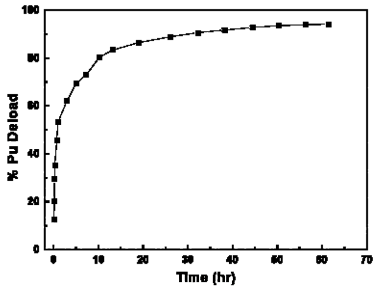
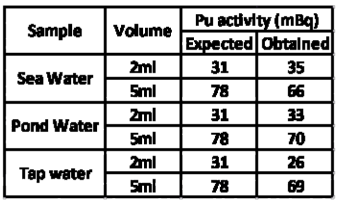


Fig. 2 Deloading Kinetic of PIFS by hydrogen peroxide in 2 molL^{-1} $HNO_{3.}$



Sample	Volume	Pu activity (mBq)	
		Expected	Obtained
Sea Water	2ml	31	35
	5ml	78	66
Pond Water	2ml	31	33
	5ml	78	70
Tap water	2ml	31	26
	5ml	78	69

***Table 1.** Expected and measured Pu Activity by PIFs from varied Matrices.*

***Keywords:** Polymer Inclusion film, ethyl glycol methacrylate phosphate, scintillation*

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Extraction Paper Chromatography for Radionuclide Quality Control in $^{89}SrCl_2$ Radiopharmaceutical

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$^{89}SrCl_2$ is an important radiopharmaceutical used for bone-pain palliation. ^{89}Sr is being produced in FBTR through the ^{89}Y(n,p)^{89}Sr reaction using Y_2O_3 as the target material. During irradiation, ^{89}Sr can further undergo the (n,γ) reaction to form ^{89}Sr, which subsequently remains in secular equilibrium with its daughter ^{89}Y. As a pure β^- emitter (E_{max} = 1.46 MeV, $t_{½}$ = 50.53 d), radionuclidic purity (RNP) of ^{89}Sr must be stringently controlled, particularly with respect to long-lived β-emitting impurity such as ^{90}Sr/^{90}Y [1]. The presence of ^{89}Sr was quantified indirectly through the activity of its daughter ^{90}Y under conditions of secular equilibrium. After complete ingrowth of ^{89}Y, the mixture was subjected to ion-exchange separation on a Nucleosil cation- exchange column using 10 mM HIBA +2 mM EDA eluent at a flow rate of 1.0 mL·min^{-1}. The ^{90}Y fraction eluting at a retention time of 11 min, following passage through the conductivity detector, was collected and subsequently measured by Cerenkov counting. Although this technique has been routinely employed in earlier studies, it is highly pH-dependent and requires a sufficiently high activity of the ^{89}Sr for accurate analysis. Therefore, in the present work, an alternative and simpler extraction paper chromatographic (EPC) methodology has been explored to achieve reliable determination of ^{89}Sr [2]. In this method, Whatman filter paper strips (18×1 cm) were impregnated with HDEHP to serve as the stationary phase and subsequently dried to ensure uniform coating. Method optimization was performed using the γ- emitting tracers, viz. $^{85+89}$Sr and ^{88}Y, to mimic the chromatographic behavior of Sr and Y, respectively. Due to low affinity of Sr and the high distribution coefficient of Y in 0.1 M HCl, the same was used as the mobile phase. The chromatogram was developed for 2 hours, after which the strip was sectioned into 1-cm segments and analyzed by gamma spectrometry using 50 % HPGe detector. The chromatographic behavior of ^{85}Sr was monitored using its 514 keV γ-emission, while the characteristics of ^{88}Y were followed using its 898 and 1836 keV γ-lines. Under these conditions, Sr and Y exhibited distinct and well-resolved RF values of 1.0 (Sr) and 0.0 (Y), enabling efficient separation and identification of potential ^{90}Sr/^{90}Y impurities.

The methodology was adopted to the ^{89}Sr samples, each containing an activity of 370 kBq, were subjected to the same chromatographic procedure and analyzed by Cerenkov counting for quality control assessment. The activity corresponding to RF = 0 (Y fraction) was found to be at background levels, while the entire measurable activity appeared at RF = 1, confirming the absence of both ^{90}Y and ^{90}Sr in the product. Overall, the radionuclidic purity of the $^{89}SrCl_2$ samples met pharmacopeial specifications for β-emitting activity. Rigorous quality control of the ^{89}Sr radiopharmaceutical remains essential, as even trace levels of ^{90}Sr or its daughter ^{90}Y can significantly influence patient dosimetry and safety. Thus, the present EPC method provided a simple, rapid, and highly effective separation between Sr and Y, making it particularly suitable for detecting ^{90}Sr in ultra trace levels.

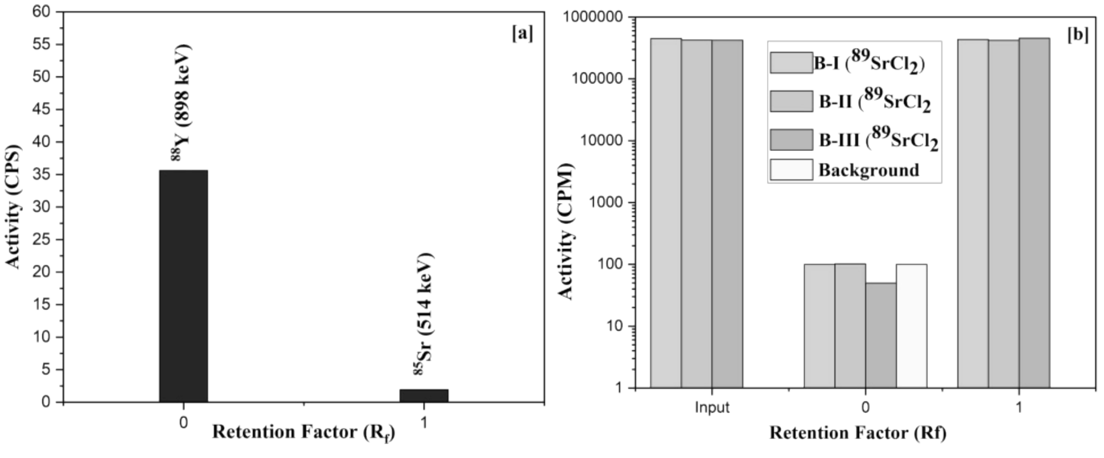

Fig.1. *EPC patterns of (a)* $^{85+89}$*Sr and* ^{88}*Y tracers (b)* $^{89}SrCl_2$ *samples*

Key words: Radiopharmaceutical, Radionuclidic Quality Control, Secular Equilibrium, Paper Chromatography

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Exploring the Use of Metal Phosphonate Based MOF: Zirconium Amino tris (methylene phosphonic acid) (Zr-ATMP) for Removal of Trivalent Lanthanides Metal Ions

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Aminotris(methylenephosphonic acid) (ATMP), a claw-type chelating molecule (Figure-1), contains six structural hydroxyl groups and multiple Lewis-basic donor sites capable of coordinating with metal ions. When ATMP is integrated with tetravalent metal ions through a sol–gel synthesis route, the resulting hybrid materials exhibit tunable porosity, enhanced ion-exchange capacity (IEC), and strong affinity and selectivity toward diverse metal ions. In our earlier work **[1]**, we reported the synthesis, characterization, and ion-exchange properties of zirconium aminotris(methylenephosphonic acid) (Zr-ATMP). The authors have demonstrated the use of Zr-ATMP **[1]** as ion exchangers for the separations of transition metal and heavy metal ions. Good ion exchange properties of Zr-ATMP motivate us to explore its applicability in separation of trivalent lanthanides metal ions (La^{3+}, Pr^{3+}, Nd^{3+} and Sm^{3+}). In the present work, an attempt has been to investigate the sorption behavior of these metal ions towards Zr-ATMP exchanger in various electrolytes / acidic media with different concentrations. Further, various parameters, like effect of pH, metal ion concentration, contact time and temperature, have been investigated in order to have an idea about possible separation of metal ion pairs. In order to understand uptake behavior of Zr-ATMP, studies of kinetics, thermodynamics and adsorption isotherms are also investigated.

To demonstrate the practical applicability of the synthesized material for ion-exchange applications, its performance was evaluated in different electrolyte media to assess stability and effectiveness under realistic effluent conditions. The effects of metal-ion on the distribution coefficient (K_d) for lanthanides metal ions were determined by the batch method using Zr-ATMP. Based on K_d (mL.g^{-1}) selectivity order for metal ions towards Zr-ATMP is Nd^{3+}(15000)> Sm^{3+}(8320) > Pr^{3+}(632) > La^{3+}(552) Further, K_d values of Zr-ATMP was compared with previously reported metal(IV) phosphonates to show the superiority of presently synthesized materials. Separation factor (α) values have been calculated based on K_d values and the results reveal feasibility of binary lanthanide separations using Zr-ATMP.

Single elution study reveals the % metal eluted in all cases is in the range 55 to 99 %. Good elution is observed for single metal ions due to non-interference of elements. Higher concentration of eluant and acids in general, are better eluants.

Binary separations for following metal ion pairs Nd^{3+}-La^{3+}, Nd^{3+}-Pr^{3+} and Nd^{3+}-Sm^{3+} have been performed using concept of high separation factor in a particular medium. In binary separations, separation efficiency is in the range from 64–93 %. In all cases of binary separation, irrespective of metal ion pair, maximum % metal eluted is Nd^{3+}(67.0%), Sm^{3+}(73.0%), Pr^{3+}(87.6%) and La^{3+}(89.7%). This observation is in keeping with separation factor (α) and K_d values of metal ions.

Overall separation studies of this material show possibility of its promising use as an efficient ion exchanger in the treatment of water containing radioactive metal waste. Generally, the decay storage or ion exchange treatment is used for the aqueous waste generated from the low nuclear power research reactor, depending upon the chemical processes used, mainly acidic nature was found due to acidic chemicals utilized during the process as per the report of IAEA-TECDOC-654, 1992. To utilize the Zr-ATMP as a potential ion exchange materials for the treatment of such waste. The exchanger used could be effectively regenerated by desorbing metal ions with concentrated acid. K_d retention remained nearly constant for up to five regeneration cycles, confirming the material's reusability without significant loss of performance. Overall, the efficient binary and ternary metal separations, combined with excellent stability and regenerability, underscore the strong potential of Zr-ATMP as an effective and durable cation-exchange material.

Key words: *Zirconium amino tris(methylenephosphonic acid), Hybrid ion exchanger, Zirconium phosphonate, Cation exchanger, Separation of lanthanides, Metal-Organic framework*

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Extraction Studies of Strontium-90 from HLLW from Fast Reactor Fuel using BARC developed Crown Ether.

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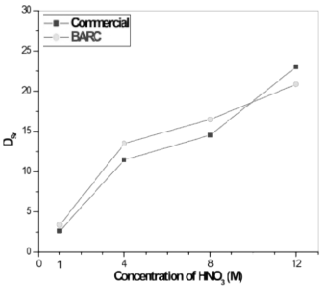
The safe management of high-level liquid waste (HLLW) arising from aqueous reprocessing of spent nuclear fuel represents a critical step in closing the nuclear fuel cycle. HLLW from reprocessed Fast Reactor mixed carbide fuel (FBTR) is far more radioactive ((5-10)x10^4 Ci/L) with very high concentration of fission product and more alpha-rich compared to HLLW generated from PHWR fuel [1]. Among the fission products present in HLLW, strontium-90 (^{90}Sr) is of particular concern owing to its high fission yield, significant heat generation and long radiological half-life. The selective extraction and separation of ^{90}Sr from complex acidic waste matrices, offers strategic benefits, including a reduction in waste volume, minimization of decay heat load and potential resource recovery [2]. In this context, the present work investigates the solvent extraction behavior of strontium from HLLW generated from PUREX reprocessing of FBTR mixed carbide fuel using a Crown Ether synthesized by Bhabha Atomic Research Centre (BARC), India [3]. Batch studies were conducted using both commercial and BARC-synthesized crown ethers with inactive strontium solutions. The aqueous solution containing a known concentration of Sr was equilibrated with 0.1 M DTBDCH18C6 in n-Octanol for 10 min. The aqueous phase was collected after phase separation and analyzed for Sr. Both commercial and BARC- synthesized crown ethers showed similar distribution ratio values over a wide range of nitric acid concentrations varying from 1M to 12M. Figure 1 compares the distribution ratio of Sr in commercial as well as BARC- synthesized crown ethers. Similarly, batch studies were conducted using HLLW solution arising from the reprocessing of FBTR fuel with both crown ethers to investigate the extraction behavior of other fission products. No extraction was observed for the fission products, such as ^{125}Sb, ^{144}Ce-^{144}Pr and $^{154+155}$Eu, whereas trace amounts of ^{137}Cs and ^{106}Ru are found to be extracted into the crown ether, along with ^{90}Sr (Fig. 2a). To minimize these radionuclidic impurities, scrubbing with 12 M nitric acid was performed, and the reduction in their activities was observed. After completing five stages of scrubbing, the impurities were reduced to the lowest possible levels and shown in the Figure 2 (b). Back extraction was carried out to strip the ^{90}Sr into an aqueous medium. The back-extracted aqueous phase showed no ^{137}Cs in both cases. With respect to initial extraction, approximately 0.07 and 0.15% of ^{106}Ru remained in the aqueous phase after back extraction in commercial and BARC-produced crown ethers, respectively. Commercial crown ether achieved an extraction of~93% of Sr from HLLW using ICP-OES estimation of aqueous phase before and after extraction and the LSC counting indicated that the BARC-synthesized crown ether achieved a relative extraction of about 90% of ^{90}Sr compared to the commercial crown ether. Alpha counting of the undiluted aqueous phase planchettes showed residual alpha activities of 0.0155 and 0.0099 % relative to the initial feed activity, after back-extraction from the commercial and BARC-synthesized crown ethers, respectively. Overall, the BARC-developed crown ether exhibited high distribution ratios, showing similar extraction behavior to that of the commercial crown ether, making it a promising candidate for Sr extraction developed in-house from HLLW of Fast Reactor Fuel.



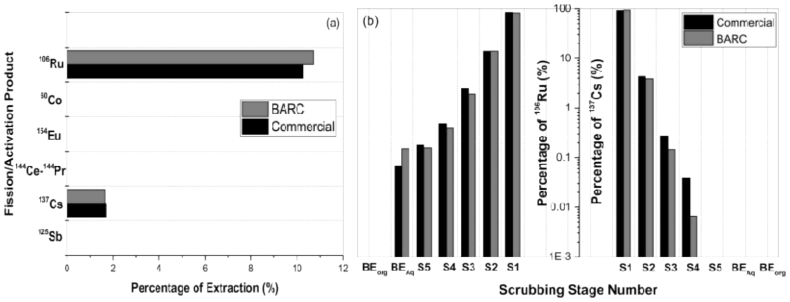


Fig. 1: *D_M values of Sr w.r.t. HNO_3* ***Fig. 2:*** *(a) Extraction & (b) Scrubbing behaviour of ^{137}Cs & ^{106}Ru.*

Key words: *HLLW, ^{90}Sr, BARC produced Crown Ether, Extraction behavior*

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Separation and Purification of Radiochemical-Grade ^{90}Sr from high level wastes of FBTR spent fuels reprocessing

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Spent fuel discharged from the Fast Breeder Test Reactor (FBTR) is reprocessed at the Demonstration of Fast Reactor Fuel Reprocessing Plant, Reprocessing Group. Analysis has shown that the high-level wastes (HLW) generated from FBTR spent fuel reprocessing are a rich source of ^{90}Sr, with an estimated concentration of 20-25 Ci of ^{90}Sr per kg of spent fuel. Since ^{90}Sr decays to ^{90}Y a pure beta emitter (β_{max}= 2.28 MeV, $T_{1/2}$= 64.1 h) widely used in cancer therapy as a nuclear medicine, its recovery from HLW presents significant potential for medical applications. To selectively separate ^{90}Sr from HLW, a solvent extraction experiment was conducted in a hot cell. The extractant used was 0.1 M 4,4',5-di-(t-butylcyclohexano)-18-crown-6 in a 1:1 mixture of n- octanol and n-dodecane. The required volume of HLW was collected using a modified sample vial and transferred to the extraction setup inside the hot cell. The acidity of the aqueous phase was adjusted to 8 M HNO **,** followed by solvent extraction with the pre-equilibrated organic phase. After extraction, the Sr-loaded organic phase was scrubbed three times with 10 M HNO_3 to remove co-extracted impurities, followed by stripping with 0.01 M nitric acid. Any residual dissolved organic material present in strip product was removed by washing with n-dodecane. The stripped solution was concentrated and purified by radiochemical precipitation**.** The concentrated stripped solution was mixed with inactive strontium nitrate and ferric nitrate, and the mixture was precipitated with ammonium hydroxide and filtered. The resulting filtrate was treated with sodium carbonate at pH ~ 1 to precipitate strontium as $SrCO_3$. The final $SrCO_3$ precipitate was washed and dissolved in a minimal volume of 1 M HNO_3 for further use. The gross beta activity of purified ^{90}Sr was analyzed by GM and LSC counter and gamma impurity present in solution was analyzed by gamma spectroscopy using HPGe detector. Gross Alpha activity and alpha emitting isotopes present in Sr solution was assayed by ZnS (Ag) scintillator and PIPS detector respectively. The analytical results show that the alpha and gamma contamination in the purified strontium were found to be < 10^{-9} Ci per 1.0 Ci of ^{90}Sr and less than the background activity, respectively.

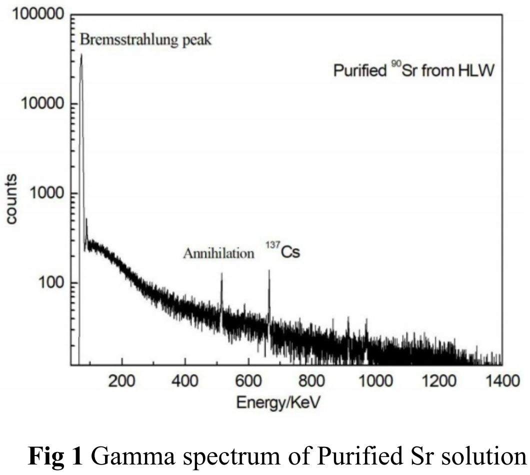

Fig 1 Gamma spectrum of Purified Sr solution

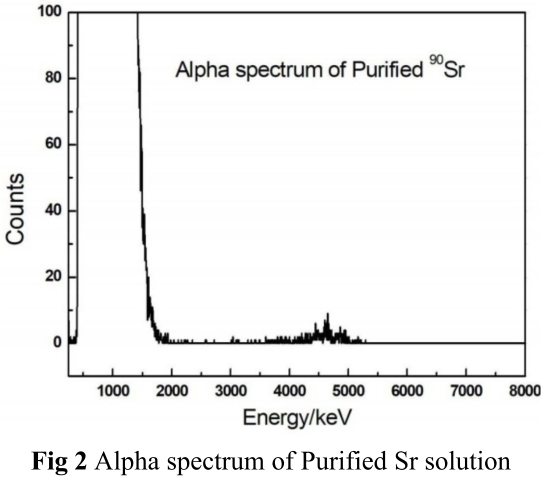

Fig 2 Alpha spectrum of Purified Sr solution

Key words: *Fast reactor, HLW, Strontium*

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Radiolytic Degradation of Sr-specific Crown Ether and Its Impact on the Extraction of Strontium

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Strontium-90 (^{90}Sr, $t_{1/2}$ = 28.5 y), a high-yield fission product and prominent contributor to long-term radiotoxicity and decay heat in high-level radioactive liquid waste (HLLW), necessitates its selective separation as part of nuclear waste management and isotope recovery strategies [1]. Given the elevated radiation fields inherent to HLLW matrices, any solvent system employed for Sr extraction from such highly radioactive environments must exhibit robust radiolytic stability to preserve its extraction efficiency and ionic selectivity under sustained gamma irradiation. Radiolytic degradation can compromise solvent performance by altering ligand structure, reducing complexation capacity, or generating interfering byproducts [2]. To evaluate the radiation tolerance of the Sr-selective DtDCH18C6 crown ether, the solvent was subjected to cumulative gamma doses up to 1000 kGy. Post-irradiation, the distribution ratio (D_M) for Sr was determined under standardized conditions to assess the retention of extraction efficacy.

0.1 M DtDCH18C6 ether was dissolved in n-octanol and sealed in 2 mL plastic vials for gamma irradiation. Samples were irradiated in a 90 Ci Co-60 gamma chamber (GammaCell 220, BRIT, India) with a dose rate of approximately 3.5 kGy/h. Samples were exposed to cumulative gamma doses of 100, 200, 300, 400, 500 and 1000 kGy at ambient temperature. Irradiated samples were stored in the dark at 4 °C until use to prevent secondary photolytic reactions. Visual inspection revealed no phase separation or discoloration up to 500 kGy; however, slight yellowing was observed at 1000 kGy as seen in Fig. 1, indicating the formation of minor radiolytic byproducts. IR spectra (Fig.2) also reveal that there is no significant degradation as there are new peaks when compared with the pristine system. Equal volumes (2 mL each) of irradiated DtDCH18C6/n-octanol and simulated HLLW were mixed in plastic vials. The biphasic system was equilibrated for 10 minutes and a 10-minute settling period, the aqueous phase was carefully collected without any organic phase. Concentrations of all elements in the aqueous phase were measured using ICP-OES. Distribution ratio (D_M) values were plotted against absorbed dose in Fig. 3 to evaluate degradation-induced loss in extraction efficiency. A gradual decline in D_M was observed with increasing dose, attributed to partial scission of the crown ether ring and formation of less selective degradation products. The DtDCH18C6/ n-octanol solvent system exhibited notable resistance to gamma-induced degradation up to 500 kGy. The solvent remained monophasic and extractable throughout the dose range. Despite a 50% drop in extraction efficiency at 1000 kGy, the system retained functional selectivity for Sr as can be seen from the insignificant variation in the distribution ratios of other elements, indicating its suitability for short-term deployment with HLLW. Stripping efficiency of strontium from loaded organic phase was > 95% in all the cases. The DtDCH18C6/n-octanol system demonstrates promising radiolytic tolerance up to 500 kGy, with acceptable performance up to 1000 kGy.

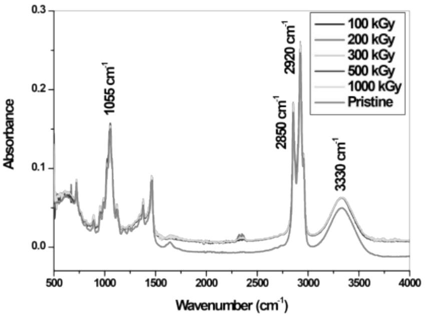

Fig. 1: *IR spectra of degraded & pristine DTDCH18C6/n-octanol system*

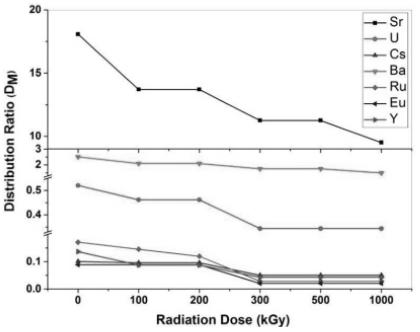

Fig. 2: *D_M values of Sr as a function of radiation dose*

Key words: *HLLW, ^{90}Sr, BARC produced Crown Ether, Extraction behavior*

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Sorption Study of U(VI) by Mesoporous Magnetic Nanoparticles (MMNPs) in Three Different State of Urine Matrix

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Presence of natural uranium in human body is usually quantified by analyzing biological excreta sample mainly urine sample. Urine being a complex biological matrix it requires a lengthy laborious radiochemical separation for estimation of U(VI) present in urine sample[1]. Now-a-days various extractants are studied mostly in aqueous medium for selective extraction of actinides[2]. Here an attempt has been made to extract U(VI) by mesoporous magnetic nanoparticles (MMNPs) from the spiked urine sample in three different state: -a) fresh urine, b) digested urine and c) pre-filter passed urine. Pre-filter resin was purchased from Triskem International; it can specifically remove organic impurities from sample matrix. Silica coated Mn doped Fe_3O_4 nanoparticles labelled as MNP-100 were dispersed in mesoporous KIT-6 (KIT-6 is labelled as MNP-0) by 3 wt% and the dispersed sample is labelled as MNP-1. Synthesis and characterization of these magnetic nanoparticles (MNPs) are given in our earlier literature, where MNP-1 exhibited inspiring U(VI) extraction property from aqueous medium[3].

In this study a uranium [U(nat.) in U(VI) form] standard solution (204.8 ± 12.6 mBq/mL) was spiked into 50 mL urine samples in three different sets. In the first set, an unprocessed urine sample (fresh urine) was used. In the second set, the urine sample was digested by heating it in the presence of a strong oxidizing medium and in the third set, the urine sample was passed through a pre-filter resin. A 50 mg portion of magnetic nanoparticles (MNPs: MNP-0, MNP-1, and MNP-100) was added to each type of urine sample (fresh urine, digested urine, and pre-filtered passed urine) at pH 6.0 ± 0.5. The samples were thoroughly mixed for 5–6 hours using an orbital shaker. Subsequently, a 5 mL aliquot was taken from each equilibrium mixture for centrifugation and the resulting supernatant was wet-digested. The digested solutions were then analyzed by LED fluorimetry to determine the residual U(nat.) activity.

Fig. 1 shows U(VI) sorption percentage as a function of MNP dispersion in different state of urine matrix. It is observed that U(VI) sorption is negligible in fresh urine sample due to presence of enormous organic and inorganic impurities as compared to digested urine sample. U(VI) sorption was further enhanced in PF-treated urine sample for all the MMNPs. It suggests that removal efficiency of organic interferences is better in PF-urine than digested urine. The superior uranium sorption exhibited by MNP-1 in digested and PF-treated urine mainly arises from the synergistic combination of high surface area KIT-6 and Mn-doped Fe_3O_4 active sites. However, in real urine samples, the presence of competing inorganic ions, organic constituents, and strong complexing ligands may alter uranium speciation and significantly suppresses its interaction with the limited number of active sites in MNP-1. These materials are found to be recyclable and useful for U(VI) extraction in urine sample.

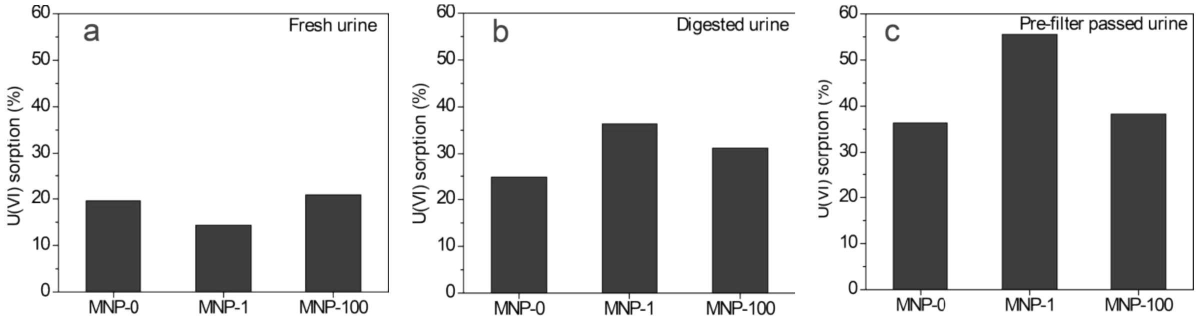

Fig. 1: *U(VI) sorption study by MNPs in (a) fresh urine, (b) digested urine and (c) pre-filter passed urine samples.*

Key words: *Uranium, sorption, urine, LED-fluorimetry*

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G-21

Simultaneous Determination of U & Pu in Dissolver Solution by Isotope Dilution Thermal Ionization Mass Spectrometry Using Solvent Extraction

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Accurate determination of elements like U and Pu in spent fuel dissolver tank solution is an integral part of nuclear material accounting in reprocessing plants. Potentiometric method is widely used for estimation of U. Isotope Dilution Mass Spectrometry (IDMS) combined with an ion exchange purification is commonly used for Pu estimation. The ion exchange process for purification requires an extended period and generates significant secondary waste. It is possible to estimate both U & Pu simultaneously by IDMS method using suitable spikes. Here a simple and fast method of extraction and purification has been studied.$_3$For demonstration of the uniqueness of the methodology based on solvent extraction, initially a suitable aliquot of simulated dissolver tank solution containing U and Pu is diluted suitably with 2 M of HNO_3. Simulated dissolver solution contained Pu and depleted U from PHWR origin. Certain portion of the dilution is spiked with ^{233}U and Pu of Research Reactor and the remaining dilution is kept for determination of isotopic composition of U & Pu in sample. It is then treated with 3 M of $NH_2OH.HNO_3$ and dried completely with heating to convert all Pu to Pu(III). Subsequently 1 M of HNO_3 and 5 M of $NaNO_2$ solutions are added in the mixture to convert all Pu to Pu(IV). These two steps ensure complete chemical exchange and isotopic homogenization. Pu purification is carried out using a solvent extraction process with 0.25 M of HTTA (2- Thenoyltrifluoroacetone) in 1 M HNO_3 medium followed by washing of organic layer with 1 M HNO_3 and back-extraction by 8 M HNO_3. Back-extracted Pu is treated with conc. HNO_3 and 30% H_2O_2 and dried using IR lamp to remove traces of organic. The purified Pu is redissolved in 0.5 M HNO_3 and the alpha activity ratio is determined by preparing a planchet source for recording the alpha spectrum. Pu isotopic composition is determined for purified sample and mixtures using Thermal Ionization Mass Spectrometer (TIMS) developed by TPD, BARC. Aqueous portion of HTTA procedure contains U which is extracted by hexone (MIBK) from a medium containing 1 M HNO_3 and 6 M NO^{-}. Washing is done by same medium and back extraction of U is carried out using 0.05 M HNO_3. Back-extracted U is treated with conc. HNO_3 and 30% H_2O_2 and dried using IR lamp. The Isotopic composition of U is measured by TIMS.

In order to determine U & Pu concentrations in the dissolver solution, the concentration and isotopic compositions of spikes should be known accurately. Individual concentrations can then be determined using the following equations with terms bearing their usual meanings:

$$C_{Sa,\ U} = \frac{C_{Sp} \times W_{Sp}}{W_{Sa}} \times \frac{R_{Sp(3/8)} - R_{m(3/8)}}{R_{m(3/8)} - R_{Sa(3/8)}} \times \frac{U\ At.\ Wt._{Sa}}{U\ At.\ Wt._{Sp}} \times \frac{A.F.\ of\ 238U\ in\ Spike}{A.F.\ of\ 238U\ in\ Sample}$$

$$C_{Sa,\ Pu} = \frac{C_{Sp} \times W_{Sp}}{W_{Sa}} \times \frac{R_{Sp(0/9)} - R_{m(0/9)}}{R_{m(0/9)} - R_{Sa(0/9)}} \times \frac{Pu\ At.\ Wt._{Sa}}{Pu\ At.\ Wt._{Sp}} \times \frac{A.F.\ of\ 239Pu\ in\ Spike}{A.F.\ of\ 239Pu\ in\ Sample}$$

Table: Concentrations of U & Pu in Simulated Solution

Sample	Sample ratio $U^{233}/U^{238}[R_{Sa}]$	Mixture ratio $U^{233}/U^{238}[R_m]$	U conc. (g/kg) by IDMS	% RSD for U conc.
Simulated	0.000176	0.239561, 0.247116	159.98	0.02
Sample	**Sample ratio $Pu^{240}/Pu^{239}[R_{Sa}]$**	**Mixture ratio Pu^{240}/Pu^{239} $[R_m]$**	**Pu conc. (mg/kg) by IDMS**	**% RSD for Pu conc.**
Simulated	0.450861	0.206121, 0.205805	654.45	2.4

The results indicate that the proposed method has potential for routine uses for simultaneous measurement of U & Pu in dissolver solution with minimal time. The method benefits from the low exposure for the analyst with minimum generation of secondary waste.

Key words: *Uranium, Plutonium, Solvent extraction, HTTA, MIBK, IDMS, TIMS, Alpha Spectrometry*

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Analysis of Phosphorous in Uranium Product Streams of PUREX Process by ICP-OESG

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The PUREX (Plutonium–Uranium Extraction) process is a widely used solvent-extraction method for the reprocessing of spent nuclear fuel. It involves dissolving irradiated fuel in nitric acid and selectively extracting uranium (U) and plutonium (Pu) using tributyl phosphate (TBP) diluted in n-Dodecane solvent. The PUREX process generally operates in multiple extraction cycles to achieve efficient separation and purification of U and Pu from dissolved spent fuel. During each of these cycles, TBP comes into repeated contact with the aqueous phase under strong acidic and radiolytic conditions. Such exposure promotes the chemical and radiolytic degradation of TBP, leading to the formation of by-products such as dibutyl phosphate (DBP), monobutyl phosphate (MBP) as well as a certain amount of dissolved TBP. These degradation products can significantly affect overall solvent extraction performance by altering phase behavior, modifying distribution ratios, and contributing to the accumulation of muck in process equipment [1]. In addition, these degradation products can adversely affect the quality of aqueous samples. Dissolved TBP can also lead to red-oil formation in evaporator systems. Therefore, the analysis of phosphorus-containing species in aqueous process streams is essential for ensuring stable operation and achieving the desired process performance.

Uranium product stream samples are checked for phosphorous content before they are taken for evaporation and also prior to being transferred to the Uranium Purification cycle. Monitoring the phosphorous content is required to understand the TBP degradation. In addition, the dissolved TBP content in these samples is routinely analysed by Gas Chromatography. The total phosphorus content is also determined whenever required, and ICP-OES is used for this estimation. In such analyses, phosphorous must be measured in the presence of high uranium matrix, which can introduce significant spectral and matrix interferences. To minimize these effects a TEHDGA impregnated resin is used to selectively retain uranium, thereby generating uranium free solution that enables accurate quantification of phosphorous. The impregnated resins preparation and its extraction behavior is given in our previous studies [2]. In the present study, simulated uranium and phosphorous spiked samples are prepared in 1M nitric acid. Phosphorous also spiked in real samples and checked the extraction. Extraction experiments were carried out in duplicate with two different concentrations of phosphorous by equilibrating 100 mg of adsorbent with 5 mL of simulated and phosphorous spiked process samples. After the stipulated equilibration time, the concentrations of U and P present in the aqueous phase before and after equilibration were determined by ICP-OES and the results are presented in the table1. Analysis of the simulated and process samples showed that the uranium concentration, which ranged from approximately 103–130 ppm before extraction, was reduced to < 5 ppm in all cases, confirming the near-quantitative removal of uranium by the extraction procedure. In contrast, the phosphorus concentration remained unchanged after extraction. These results demonstrate that uranium is selectively extracted with negligible loss of phosphorus, thereby validating the suitability of this method for the accurate determination of total phosphorus content in aqueous streams of the PUREX process.

Table 1. *ICP-OES analysis results of U and P in simulated and process samples*

Element	Concentration (ppm)			
	Before Extraction	After Extraction	Before Extraction	After Extraction
	Simulated Sample -1		Simulated Sample -2	
Uranium	104.7	< 5	103.4	< 5
Phosphorous	10.98	10.27	1.15	1.05
	Simulated Process Sample-1		Simulated Process Sample-2	
Uranium	105.9	< 5	129.8	< 5
Phosphorous	10.86	10.69	1.36	1.31

Keywords: *PUREX process, Tributyl Phosphate, Degradation, ICP-OES, Impregnated resins*

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Overview of Transfer Factors of Radionuclides and Nutrients from Soil to Tobacco Plants and The Influence Physicochemical Parameters in Tobacco-Growing Areas of Karnataka, India

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The transfer of natural radionuclides from soil to plants is a crucial factor in assessing environmental radiation exposure and associated health risks. The activity concentrations of primordial radionuclides Radium-226 (226Ra), Thorium-232 (232Th), and Potassium-40 (40K) in soil and tobacco plant samples from tobacco- growing areas in Karnataka state were determined by Gamma-ray spectrometry using an HPGe detector. The average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the soil samples were found to be 25.1 ± 2.05, 116.9 ± 4.35 and 403.8 ± 7.9 Bq.kg^{-1} respectively. And the average activity concentrations of ^{226}Ra, ^{232}Th and ^{40}K in the tobacco plant samples were found to be 0.44 ± 3.63, 22.72 ± 2.95 and 5013.1 ± 42.3 Bq.kg^{-1} respectively. The physicochemical parameters of the soil samples were estimated by standard methods and analyzed systematically in this paper. Transfer factors (TFs) were calculated to assess the mobility of radionuclides from soil to plants. The results showed considerable variation in radionuclide activity and TF values across different locations, with ^{40}K exhibiting the highest transfer factors. The correlation between these parameters and natural radionuclides was examined using Pearson's correlation coefficient. Notably, some parameters showed positive correlation coefficients with radionuclides, while others showed negative correlations. This phenomenon is discussed in detail within the paper. The results showed that low soil pH, higher organic carbon content, and sandy texture enhance radionuclide mobility and uptake by plants, whereas clay-rich soils tend to immobilize radionuclides, thereby reducing transfer factors. Furthermore, the calculated radiological hazard indices for natural radioactivity were assessed against internationally accepted values.

Keywords: *Primordial radionuclides (^{226}Ra, ^{232}Th, ^{40}K), Gamma-ray spectrometry HPGe detector, Transfer factor, Hazard indices, physicochemical parameters, Local geology*

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Preliminary Studies on Sequential Estimation of Uranium and Plutonium in Urine Matrix for Triage

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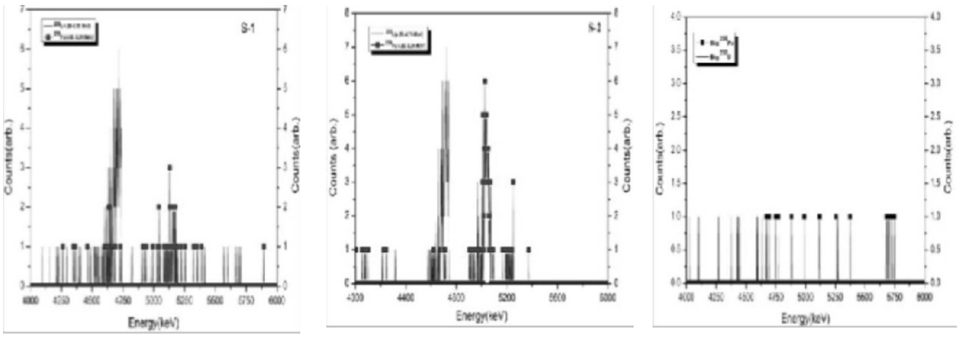
Occupational radiation workers of fuel reprocessing and fuel fabrication facilities are monitored for internal exposure due to actinides by uranalysis. Intake and committed effective dose are estimated from the results of urine analysis using bio-kinetic and dosimetric models given by International Commission on Radiological Protection (ICRP). High sample throughput is critical in an emergency situation, which necessitates the development of simple, reliable and rapid methods for radionuclide analysis. In this study, attempts were made for the sequential estimation of uranium (U) and plutonium (Pu) using Dowex resin as an anion exchanger by spiking known activity of ^{233}U (8.4-11.2 mBq) and ^{239}Pu (5.36-9.94 mBq) in urine samples. These urine samples were initially wet oxidized with conc. HNO_3 and H_2O_2, co-precipitated with $Ca_3(PO_4)_2$ and loaded on Dowex resin preconditioned with 8M HCl. Uranium was selectively eluted with 5MHCl-3M $HClO_4$ [1] followed by plutonium with1.5M $NH_2OH.HCl$ [1,2]. The eluted uranium and plutonium were electrodeposited on stainless steel planchette and counted in alpha spectrometer. It was observed that the radiochemical recovery of uranium and plutonium was in the range of 79.93 - 83.33% and 42.66 - 49.35% (Table 1) with an average recovery percentage of 81.56 ± 2.55% and 46.00 ± 4.73% respectively. The alpha spectra of the two samples along with the background spectrum are given in Fig. 1 a, b & c respectively. Uranium and plutonium estimated in this method was rapid (5 days) than the conventional method (7 days). The Minimum Detectable Activity (MDA) of this method is 1.0 mBq/d for ^{239}Pu and 0.6 mBq/d for ^{233}U. In case of ^{239}Pu, it is well below the derived investigation levels for nitrate compounds for post intake period of 15 days while for Nat.U, it is more than 1 year for F class. Further studies are in progress towards improving recovery of uranium and plutonium as well as to reduce MDA and analysis time for triage in the event of radiological emergency.



(a) **(b)** **(c)**

Fig. 1 *Alpha Spectrum of S-1, S-2 (a, b) and Background Spectrum (c)*

Table 1: *Recovery Percentage of ^{233}U and ^{239}Pu in Urine Samples*

Sample Code	^{233}U spiked (mBq)	^{233}U Recovered (mBq)	^{233}U Recovery (%)	^{239}Pu spiked (mBq)	^{239}Pu Recovered (mBq)	^{239}Pu Recovery (%)
S-1	11.2	8.93	79.73	9.94	4.24	42.66
S-2	8.4	7.00	83.33	9.30	4.59	49.35

Key words: *Ion-Exchange, Uranium, Plutonium, Dowex Resin, Alpha Spectrometer*

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A Double Column Approach for Preparation of ^{188}W/^{188}Re Generator using Indigenously Produced Low Specific Activity ^{188}W

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Rhenium-188 ($T_{½}$ = 16.9 h, E_{bmax} = 2.12 MeV, 155 keV ray) is an important no-carrier added (NCA) grade radiometal obtained from ^{188}W/^{188}Re generator, which facilitates its widespread use in nuclear medicine practices for radionuclide therapy (1). The ^{188}W radioisotope was produced indigenously by irradiation of ^{186}W (98.6% enriched) target via successive (n, γ) steps using a neutron flux 1 x 10^{14} n cm^{-2} s^{-1} in the Dhruva reactor by long time irradiation of 6 months which was selected based on the half-life of ^{188}W ($T_{1/2}$ = 63d). ^{188}W was produced of low specific activity due to the successive (n, γ) reaction. A facile radiochemical separation procedure based on double column chromatography using mesoporous alumina sorbent has been developed to repeatedly retrieve ^{188}Re in a form suitable for preparation of radiopharmaceuticals. Compared to a larger single column generator, the overall radioactive concentration of ^{188}Re eluted from the double column generator is much higher and hence suitable for radiopharmaceuticals preparation. ^{188}W in form of sodium Tungstate (3.7 GBq) at pH~3 was passed through the columns for loading of ^{188}W. Tungsten-188 was selectively trapped in the chromatographic columns and after allowing for growth of ^{188}Re, it was eluted in 10 mL of 0.9 % NaCl (w/v) solution. The schematic diagram of the radiochemical separation process is shown in Fig. A.

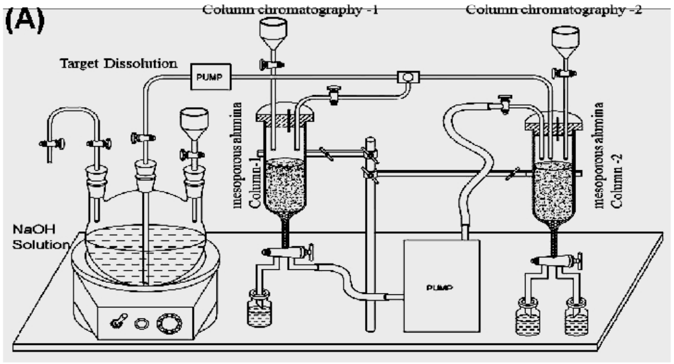

Fig. (A) *Schematic diagram of the set up for radiochemical processing and separation.*

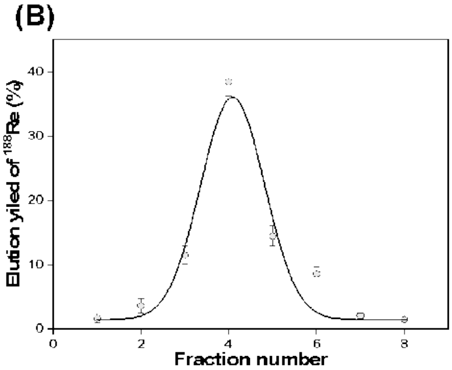

Fig. (B) *Double column elution profile of ^{188}Re.*

After the radiochemical separation, the g-ray spectrum of ^{188}Re was recorded in a high purity germanium (HPGe) detector coupled with multichannel analyzer. The presence of W radioisotopes could not be detected in the ^{188}Re solution. The overall yield of ^{188}Re was > 85 % (Fig. B) and it was obtained with > 98 % radiochemical purity (in the form of ReO $^{-}$), which was suitable for preparation of radiopharmaceuticals. The radiochemical impurities were ReO_2 and Al^{3+} which are present within the permissible limit. The generator was continuously eluted twice a week for a period of 3 months. The overall performance of the generator remained consistent over this period of time. This facile radiochemical separation strategy would aid towards obtaining clinical grade ^{188}Re form using low specific activity ^{188}W for formulation of radiopharmaceuticals.

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G-26

Study of Tc Uptake from Low Level Radioactive liquid Waste by TPAC and Its Extent of Utilization

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Low level radioactive liquid waste (LLW) generated in the treatment of Intermediate level radioactive liquid waste (ILW) using Resorcinol Formaldehyde resin in Ion-exchange method. The LLW generated here is alkaline with high salt content. It contains different radioisotopes namely ^{106}Ru, ^{125}Sb, ^{99}Tc, ^{137}Cs, ^{90}Sr and traces of Pu^{239}. Here ^{99}Tc is present as the pertechnetate ion. It is considered as a long-term hazard in nuclear waste disposal due to its long half-life, around 2.13 × 10^5 yrs and high mobility. Hence it needs to be separated from LLW to maximum possible extent prior to discharge in environment [1]. To achieve this separation of ^{99}Tc from LLW, it needs to analyse the ^{99}Tc content in feed LLW and treated LLW. Different methods are available for Tc determination based on gravimetric, titrimetric, crown ether based and other analytical methods [2,3]. Out of these methods, we utilse the method based on the Extraction of ^{99}Tc from LLW waste by Tetraphenyl-Arsonium-Chloride (TPAC) in Nitrobenzene (NB) then radiometric determination of ^{99}Tc content in the organic part by activity counting in GM counter, then confirming the beta cut-off in GM counter using Al-absorber and confirming the gamma isotopes [4,5]. After our ^{99}Tc estimation analysis, we send the secondary waste liquids generated during analysis, aqueous as well as organic in the respective radioactive waste tanks. Then for next estimation, TPAC in nitrobenzene taken freshly. Thus we utilise this TPAC only for one equilibration, then we discard this TPAC solution. But to know this extraction in detail and to find the usability of the used organic part, this study initiated.

The present paper deals with the study of ^{99}Tc uptake from LLW by TPAC in Nitrobenzene using different concentrations of ^{99}Tc. The present paper also deals with the usability of this used TPAC solution for further Tc-estimation.The different concentration of ^{99}Tc is taken and the respective distribution co-efficient (D- value) determined. The graph of D-Value Vs ^{99}Tc-Concentration is shown in Graph-1.

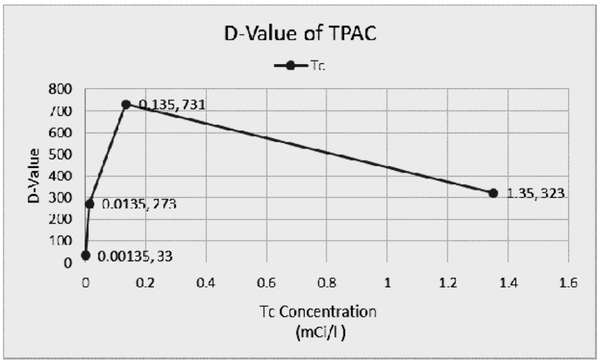

Fig.1 *–1. D-Value for different concentration*

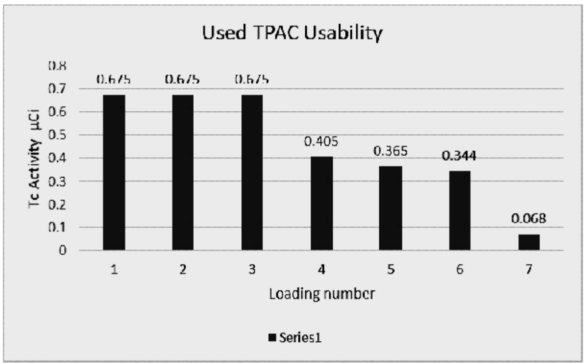

Fig.2*. Multiple loading of TPAC in NB*

The usability of the used organic part of TPAC in nitrobenzene solution was checked for further uptake of ^{99}Tc. The used TPAC was equilibrated with fresh ^{99}Tc-solution, this step was repeated till the Tc- uptake capacity of TPAC in nitrobenzene gets saturated. Here up to 3 loading, the used TPAC was taking all the Tc content in the aqueous ^{99}Tc-soln. But further, the leakage of activity started. Thereafter up to 6 loading, the used TPAC showed the partial uptake of Tc from aqueous Tc-solution, with reducing trend of Tc uptake seen here. But further after 7th loading onwards, there was very less or negligible uptake. During this study, it comes to know that TPAC in NB has specific D-value in different ^{99}Tc concentrations and also came to know that the one time equilibrated TPAC can be used for atleast 3 times for further ^{99}Tc estimation in LLW sample of the plant.

Key words: pertechnetate, Tetraphenyl-Arsonium-Chloride, distribution co-efficient.

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Thermodynamic Stability and Aqueous Speciation of Uranyl and Neodymium Complexes with Quinic Acid

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Separation of actinides and lanthanides is the central step for successful nuclear fuel reprocessing. Further, the intra and inter separation of trivalent actinides and lanthanides is difficult due to the similarities in the physiochemical properties. Hydroxycarboxylic acids, such as α-hydroxyisobutyric acid and mandelic acid have been well-known eluting reagents for the liquid chromatographic separation of actinides and lanthanides [1-2]. Recently, an ion interaction chromatography method was developed using quinic acid for quick separation of U and Th with the aim of their quantification at trace-level concentrations [3]. Aqueous speciation and structural elucidation in terms of coordination modes and stoichiometry of Th(IV) complexes have proven to be beneficial in understanding the mechanism behind the differential complexing pattern. Present studies focused on determining the stability and speciation of uranyl and neodymium ion on complexing with quinic acid in nitrate medium. Spectrophotometry titrations were carried out in the wavelength range of 375-525 nm for UO_2^{2+} and 450-770 nm for Nd^{3+} with incremental additions of quinic acid solution. Nonlinear least square analysis employed to determine stability (log K) and speciation of the complexes.

Increase in intensity with peak shift was observed (Fig. 1) on addition of quinic acid to UO_2^{2+}/ Nd^{3+} indicating a stronger complexation tendency. Nonlinear least square analysis showed formation of three successive complexes ML_i (i=1-3) for UO_2^{2+}/ Nd^{3+}; and the corresponding log K_i (i=1-3) values were found to be 3.60 ± 0.06, 1.75 ± 0.18, 1.00 ± 0.25 for UO_2^{2+}-QA complexes, and 2.94 ± 0.06, 2.49 ± 0.08, 1.27 ± 0.14 for Nd^{3+}-QA complexes respectively. QA from stronger ML complexes with UO_2^{2+} compared to Nd^{3+}; while the Nd^{3+} forms stronger ML_2 and ML_3 complexes compared to UO_2^{2+}. Quinic acid acts as hard acid and interactions are primarily dominated by ionic potential of cation. UO_2^{2+} having higher effective charge (~3.3) can strongly bind with QA than Nd^{3+}, which reflected in determined log K_{ML} values. For successive complexation, steric hindrance, availability of coordination space around cation for further ligand attachment also plays crucial role in defining the stability. Nd^{3+} has spherical coordination, while UO_2^{2+} has restricted coordination (equatorial space) only, because of which the successive ligand attachment is relatively more favorable in later cation than former. Thus, at lower L/M ratios, UO_2^{2+} has preference for QA, and at higher L/M ratios, Nd^{3+} complexes with QA, which could help to separate lanthanide from uranyl.

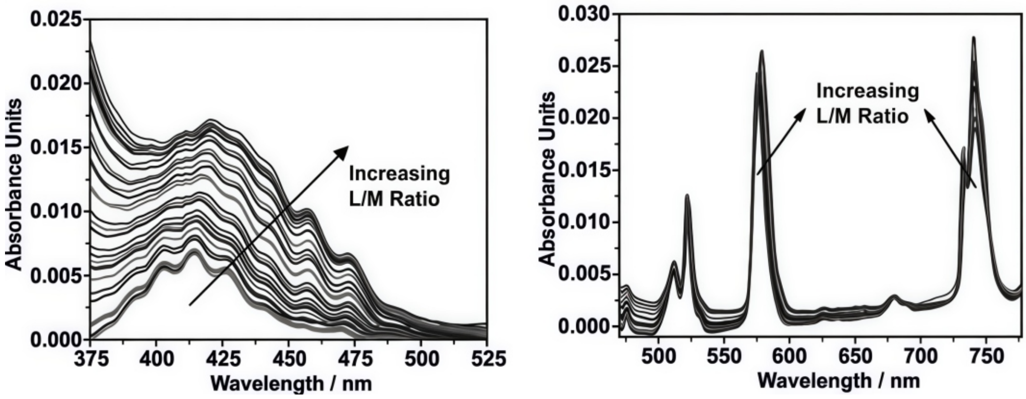

Figure 1: *Absorption spectra of* UO_2^{2+} *(left) and* Nd^{3+} *with incremental additions of Quinic acid (QA) solution.* $[UO_2^{2+}/Nd^{3+}]=0.003$ *M; and* $[QA]=0.4$ *M.*

Key words: *Uranium, Neodymium, Stability, Spectrophotometry, Thermodynamics*

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Soil-to-Wheat Transfer of ^{137}Cs and ^{40}K in Agricultural Fields around GHAVP, Haryana, India

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The long-term migration of radionuclides such as ^{137}Cs in the environment often occurs through dispersion of contaminated soil particles. However, the transfer of ^{137}Cs from soil to plants, particularly wheat (*Triticum aestivum*), remains insufficiently understood. In radio ecological studies, the soil-to-plant transfer factor (TF or F_v) [1] is commonly used to estimate radionuclide movement through the food chain, serving as a key parameter for assessing ingestion doses to humans. Given that India is one of the largest producers and consumers of wheat globally, understanding radionuclide uptake by wheat is of significant importance. This study aims to determine the activity concentrations of ^{137}Cs and ^{40}K in soil and wheat grain samples, and to evaluate their corresponding transfer factors (F_v) and discrimination factors (DF), for agricultural fields surrounding the under-construction Gorakhpur Haryana Anu Vidyut Pariyojana (GHAVP) site in Haryana, India.

Eighteen paired soil and wheat samples were collected from different locations. Samples were oven-dried at 100 °C for 24 h, ground, and sieved to 250 µm. Approximately 1 kg of each sample was sealed in airtight containers and analyzed using a 3″ × 3″ NaI (Tl) scintillation detector based gamma spectrometry system. The activity concentrations of ^{137}Cs and ^{40}K were determined from their respective γ-ray energies at 661.62 keV and 1460.7 keV.

Activity concentration **A (Bq/kg DW)** of each radionuclide was determined using:

$$A = \frac{C}{\varepsilon \times I \times W},$$

Where: C= Net count rate (cps), ε=detector efficiency, I= Gamma Intensity, W=sample weight (kg) he **soil-to-plant transfer factor (F_v)** was calculated as:

$$F\nu = \frac{A_{wheat}}{A_{soil}},$$

Where A_{wheat} and A_{soil} are the activity concentrations (Bq/kg DW) of the radionuclide in the wheat and corresponding soil, respectively.

To evaluate the relative absorption efficiency of cesium and potassium, the **discrimination factor (DF)** as:

$$\frac{F\nu(\mathrm{Cs})}{F\nu(\mathrm{K})},$$

DF value less than unity indicates a preferential absorption of potassium (K^+) over cesium (Cs^+) by the plant. **Table 1** shows that ^{40}K exhibits higher mobility and uptake efficiency due to its essential biological role and greater bioavailability in soil. The activity concentration of ^{137}Cs was found to be two orders of magnitude lower than that of ^{40}K in both soil and grain, indicating minimal contamination by anthropogenic radionuclides. The measured radionuclide levels were below global average values and do not pose any significant radiological risk.

Table 1. *^{137}Cs and ^{40}K activity in soil and wheat grain with transfer and discrimination factors*

Location/ Matrix	**^{137}Cs(Bq/kg DW)**	**^{40}K(Bq/kg DW)**	**^{137}Cs F_v**	**^{40}K F_v**	**DF**
	Range (Mean)				
GHAVP Site – Soil	0.890–2.180(1.38)	481–658 (536)	–	–	–
GHAVP Site – Wheat	0.012–0.074(0.03)	108–288 (188)	0.013–0.034 (0.022)	0.22–0.48 (0.35)	0.063
Ajay K et al. [2]	–	–	0.080–0.090 (0.070)	1.3–1.5 (1.1)	0.064
Deepak et al. [3]	–	–	0.004–0.024 (0.020)	0.21–0.34 (0.26)	0.077

The study indicates that the transfer of ^{137}Cs from soil to wheat grain is significantly lower than that of ^{40}K. The preferential uptake of potassium reflects its essential role in plant physiology, while cesium shows limited mobility in soil. The low activity levels of both radionuclides, particularly ^{137}Cs, suggest that the soils around the GHAVP site are radiologically safe and within global average limits.

Keywords: *Soil-to-plant transfer, ^{137}Cs, ^{40}K, transfer factor, discrimination factor*

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Processes Governing Groundwater Salinization in the Bhuj Sandstone Aquifer: Insights from Hydrochemical Speciation and Inverse Geochemical Modelling Study

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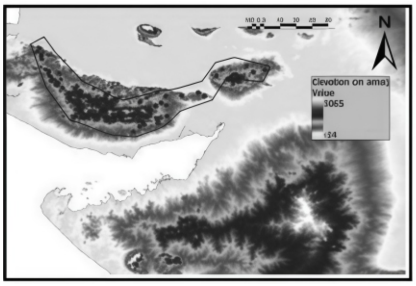
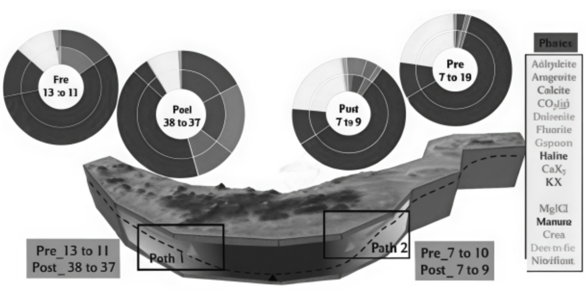
Groundwater salinization in the Bhuj Sandstone aquifer of Kutch, western Gujarat, has emerged as a major constraint on regional water security, affecting drinking-water supply, agriculture, and livelihoods of nearly two million residents. Although seawater intrusion is often presumed to drive salinity in coastal aquifers, the increasing salinity reported across this arid–semi-arid terrain required a detailed assessment of alternative salinisation pathways, including evaporite dissolution, deep brines, irrigation return flows, and inputs from domestic or industrial wastewater.

Hydrogeochemical speciation analysis was performed based on groundwater samples collected from Bhuj Sandstone aquifer system, during the pre- and post-monsoon periods of 2019–2020. The speciation study helped in evaluating the saturation state of key mineral phases responsible for regulating groundwater chemistry [1]. Major aqueous species of Ca–CO_3, Mg–CO_3, Na–Cl, Ca–SO_4, Mg–SO_4, and F^- complexes were examined, along with associated mineral phases including calcite, aragonite, dolomite, halite, gypsum/anhydrite, and fluorite. Comparison of physico-chemical data with Bureau of Indian Standards (BIS) and World Health Organization (WHO) guidelines showed that although post-monsoon recharge improved certain water-quality parameters, Total Dissolved Solids (TDS), hardness, and major ions continued to exceed permissible limits in many samples. Nitrate displayed minimal seasonal change, reflecting persistent anthropogenic inputs. Hydrochemical facies interpreted from Piper diagrams indicated that most samples belonged to the Na–Cl type, confirming a dominant evaporite signature. A subset of post-monsoon samples shifted toward mixed Ca–Na–HCO_3 facies, suggesting dilution by recent recharge. Results from the Hydrochemical Facies Evolution Diagram (HFE-D) further placed most samples within the freshening domain rather than along seawater-intrusion trajectories, reinforcing the conclusion that marine mixing is not a primary driver of salinity in this aquifer system.

Saturation index–based speciation revealed consistent undersaturation for halite, gypsum/anhydrite, and fluorite, indicating their tendency to dissolve, whereas calcite, aragonite, and dolomite remained near equilibrium to oversaturated, favouring precipitation under certain conditions. These thermodynamic constraints were incorporated into inverse geochemical modelling using PHREEQC along four representative groundwater flow paths. From 136 minimal-phase models, eight statistically robust models were retained. Model outputs identified halite dissolution as the principal geochemical process governing salinity, followed by cation-exchange reactions involving CaX_2, NaX, and KX. Gypsum dissolution and carbonate precipitation/dissolution showed seasonal variability, while evaporation had limited influence. Anthropogenic processes—particularly urea and manure contributions followed by nitrification—were reflected in the nitrogen-speciation terms of the models.

The integrated speciation, facies interpretation, and inverse-modelling results establish that salinity evolution in the Bhuj Sandstone aquifer is driven mainly by evaporite dissolution and ion-exchange reactions rather than seawater intrusion, offering key insights for sustainable groundwater-management planning.





Key words: *Groundwater Salinisation, Hydrogeochemical Speciation, Inverse Geochemical Modeling, Phase mole transfer; Facies Evaluation*

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Design and Synthesis of Small Organic Molecular Heterocyclic Scaffolds for Selective Recognition and Separation of Actinides

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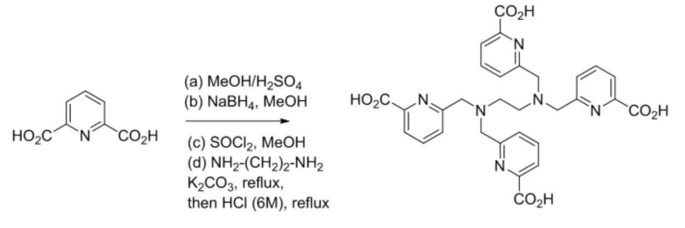
Selective recognition and subsequent separation of the individual actinides such as americium (Am) and europium (Eu) remains an unsolved problem and regarded as a prominent field of research across the globe. Through this coordinated research project, new organic scaffolds having heterocyclic framework will be designed, synthesized and evaluated for the selective recognition and separation of trivalent Am and Eu from nuclear waste. As a proof of concept a known ligand having multiple binding sites were synthesized (Scheme 1).



Scheme 1. *Synthesis* of *ligand*

To evaluate the potential of the ligand for Am/Eu separation, we measured the distribution ratio (D) of Am and Eu at different nitric acid concentration in the presence of 10 mM H4TPAEN (please note: H4TPAEN is water soluble). For organic phase, we used 0.1M TODGA+5% v/v *iso*-decanol/dodecane solution as it is well known solvent for actinide portioning

As evident from Figure 1, best results were noted at 0.2 M HNO_3 where no appreciable Am was extracted, but more than 75% Eu could be extracted in single contact with SF values of 45. With these encouraging results further studies are in progress to test the feasibility of application of this ligand for 1-cycle actinide partitioning.

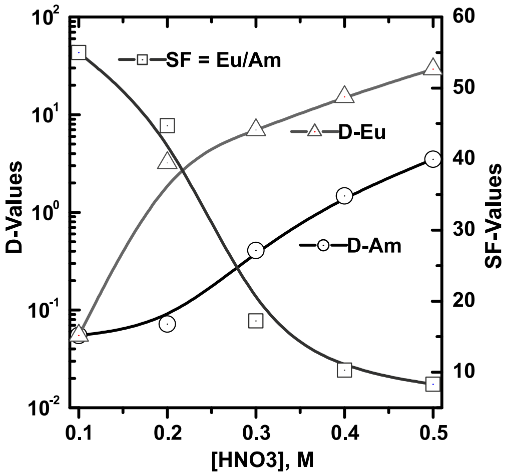


Fig. 1. *Effect of HNO_3 concentration on separation of Am over Eu. Org. Phase: 0.1M TODGA, Aq. Phase: 10 mM H4TPAEN at different HNO_3 concentration.*

Key words: Selective extraction of Am and Cm, Heterocyclic based small organic molecules, Novel methods for ligand synthesis

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Investigation of Interfacial Species Formed on Sorption of Selenite Oxyanion on Iron Oxyhydroxide Polymorphs

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Iron oxyhydroxide polymorphs, such as goethite (α-FeOOH) and lepidocrocite (γ-FeOOH), widely exist in terrestrial environments, and play important roles in mediating heavy metal mobility [1]. They further act as template for secondary mineral formation, e.g., during Fe(II)-induced ferrihydrite transformation their participation modifies the speciation of the contaminants thereby impacting their retention characteristics over the migration path. Structurally, both the polymorph stabilizes in orthorhombic lattice structure with distinct electronic structure difference. Band gap attributed to lepidocrocite (1.8 - 2.0 eV) is in general lower compared to goethite's 2.1 - 2.5 eV. In the present study, Selenite interfacial species on laboratory-synthesized iron oxyhydroxide (goethite and lepidocrocite) nanoparticles were investigated at near neutral pH value using the X-ray Absorption Fine Structure (XAFS) Spectroscopy.

In a hydrothermal synthesis procedure, Goethite (α- FeOOH) was synthesized by hydrolysis of ferric nitrate solution at pH > 12 and 70 ^{0}C for 60 hours. Lepidocrocite was achieved in similar procedure using tetra-hydrated ferrous chloride as starting material and air was pumped at the rate of ~ 500 mL/min during the hydrolysis of Fe(III) ions. XRD pattern of the synthesized nanoparticles are shown in Fig. 1. Selenite ion (1 mM) was contacted with nanoparticles in 0.01 M $NaNO_3$medium at pH ~ 6 and after the equilibration period of 24 hours, particles were separated using centrifugation (14 000 rpm), air-dried and mixed with cellulose to make a pellet for XAFS measurement at Se K-edge. Fig. 2 presents the R-space data for the Se(IV)-interfacial species formed at Goethite and Lepidocrocite nanoparticles. The values indicated in Fig. 2 present the phase corrected distance and coordination number for Se-O and Se-Fe coordination shells for the interfacial species forming on the Lp and Gt nanoparticles.

The EXAFS data corresponds to bidentate binuclear binding of Selenite ion on the Fe(III)-O octahedra corners on both the nanoparticles. However, the biding is stronger on the lepidocrocite nanoparticles with smaller Se-O distance. The basis of this stronger binding lies in the electronic structure difference of the two solids and will be discussed during the presentation in the symposium.

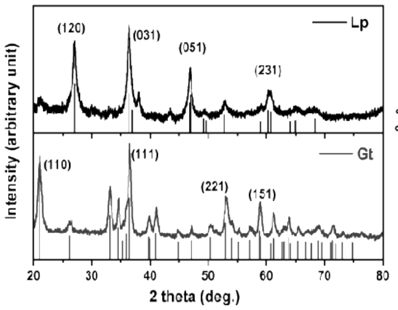

***Fig. 1** XRD profile of the solids*

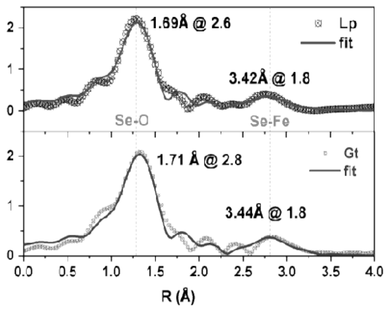

***Fig. 2** EXAFS data for the interfacial species*

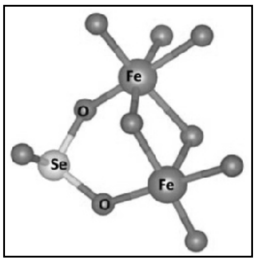

***Fig. 3** Coordination details of the interfacial species*

***Key words:** Goethite, Lepidocrocite, Selenite, EXAFS*

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Speciation of Neptunium in Non-aqueous Methane Sulphonic Acid (MSA) medium

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Non-aqueous methane sulphonic acid (MSA) has emerged as an interesting type of novel solvent in the 21st century that is garnering attention in the metal recovery through electrowinning process [1-2]. This solvent employed as the promising alternatives to the conventional organic solvents and ionic liquids and has solved the issues surrounding the conventional recovery processes. MSA has many positive features for use as solvent in metal recovery processes, such as low volatility, a wide liquid range, a large electrochemical window, low toxicity and interesting feature of stabilization of different oxidation states of metal ions vis-a-vis aqueous medium. Careful control of redox speciation of Np plays a vital role in its separation from nuclear waste streams. In the present study, the chemical speciation of Np such as coordination mode, stable oxidation state, redox potential, diffusion coefficient etc. was probed in MSA media. UV-Vis absorption spectra were recorded for fresh Np solution in MSA media after IR heating and after every 7 days [Fig.1a]. Initially absorption peaks were depicted at 725 nm and 967 nm, which suggested the existence of a single oxidation state i.e., Np(IV). After a month, the spectra showed absorption peaks at 725 nm, and 981 nm 967 nm, indicating mixture of Np(V) and Np(IV). Cyclic voltammetry was used to understand the stable oxidation state of Np species in MSA media for the initial solution using glassy carbon as working electrode [Fig. 1b]. The two reduction peaks were found to be associated with the Np(IV)/Np(V) and Np(V)/Np(VI) couples. The diffusion coefficient (D_0) and electron transfer rate constant (k^0) values of Np in MSA medium were obtained to be 3.2×10^{-7} cm^2/sec and 1.5×10^{-4} cm/sec. This finding was further confirmed by in situ spectro electrochemistry (SEC) which indicated enhancement in the absorption intensity corresponding to Np(V) during oxidative electrolysis at 981 nm. The effect of U and Pu addition on speciation of Np in MSA media was also examined. U(VI0 and Pu(IV) in MSA were added to fresh Np solution and vice versa, but no major changes were found for Np CV and DPV. The findings of the present study have potential application in nuclear waste management and reprocessing of spent nuclear fuel.

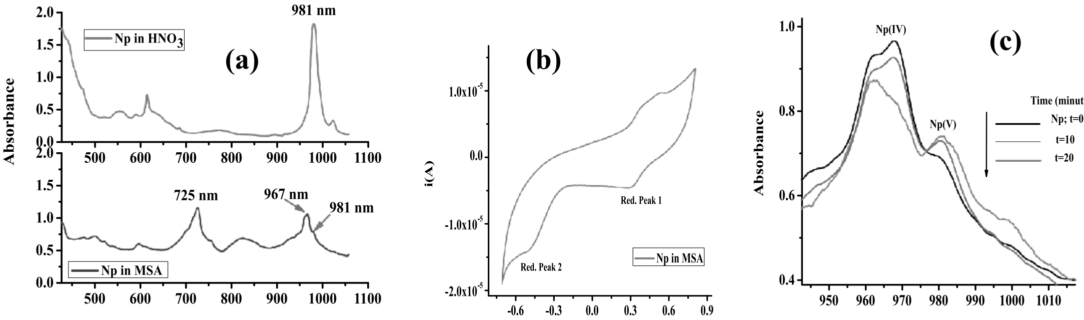

Figure 1. *(a) UV-Visible (b) CV plots of Np in MSA (c) SEC spectra obtained during oxidative electrolysis*

Key words: *Neptunium, Methane sulphonic acid, Speciation*

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Redox Speciation of Uranyl Ion in Eutectic Solvent Electrolytes for Advancement of Uranium Redox Flow Battery (URFB)

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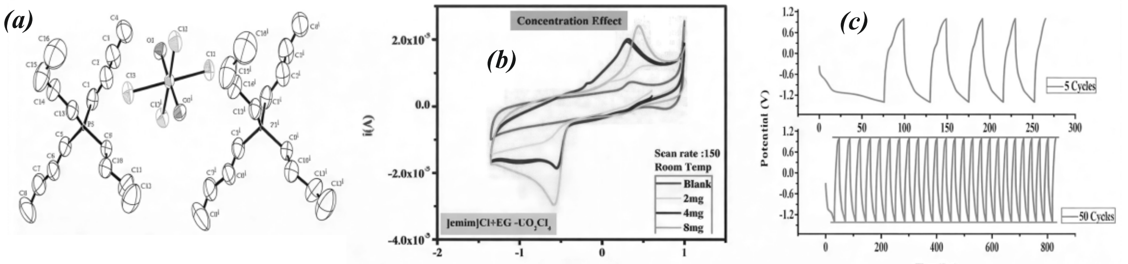
Uranium enrichment is an important step for nuclear fuel generation which results into formation of Depleted Uranium (DU) as process residue. DU has no significant utility, as a result DU (almost 10^6 tons) accumulated as nuclear waste across the globe [1]. International energy agency (IEA) has set the target to achieve the net-zero carbon till 2050. To achieve this, the development of renewable energy source is highly required. The energy storage devices mostly based on Li-ion, however, its power density is low and mining process of Li from its ores has harmful effects on ecosystem. Compared to Li-ion, the RFB is suitable alternate due to its compact infrastructure, high power, and energy density. Electrolyte is a key component of RFB. Deep eutectic solvent (DES) is obtained by mixing metal salt or Hydrogen Bond Donor (HBD) with Hydrogen Bond Acceptor (HBA), can be considered as smart electrolyte due to its exceptional features such as broad electrochemical window, easy synthesis, low vapor pressure, environment friendly and economically viable compared to conventional ionic, organic, and aqueous etc. electrolyte system. In this study three conducting eutectic electrolytes were synthesized by taking combinations of 1-ethyl-3-methylimidazolium chloride and ethylene glycol. In addition, the Uranyl tetrachloride crystal was synthesized and characterized by IR, and Single Crystal XRD [Fig. 1a]. 8 mg of Uranyl tetrachloride crystal was directly dissolved in 1 ml of above eutectic electrolytes with increasing concentration [Fig. 1b]. The redox speciation of dissolved uranium species in above electrolytes was monitored by cyclic voltammetry to understand the stable oxidation state, diffusion coefficient (D_0) and electron transfer kinetic parameters. The electron transfer process was found to be U(VI)-U(V) conversion which is quasi-reversible in nature and show no change in redox behaviour with varying temperature. The D_0 and k^0 values for UO_2^{2+}/UO_2^+ couple were evaluated to be $4.02x10^{-8}$ cm^2/sec, and $1.5x10^{-4}$ cm/sec, respectively. The uranium as cathode active material exhibited stable charge/discharge characteristics with a good coulombic efficiency upto 50 cycles [Fig. 1c]. This work demonstrates the utilization of DU as a redox active material in RFB as a renewable energy source.



plots with

- *Figure 1.* *(a) Crystal Structure of Uranyl tetrachloride, (b) CV With increasing concentration of Uranyl tetrachloride in electrolyte (c) Battery testing performance charge/discharge process of U*

Key words: *Depleted Uranium, Redox flow Battery, Deep eutectic solvent, Netzero emission, electrolyte*

Reference

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H-8

Trend Analysis of Short-lived Progeny Concentration with the Variation of Temperature and Humidity for Waste Management Facility, Tarapur

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In nuclear facility, the major sources of airborne radioactivity during different operations are β and α emitting radionuclides [1]. The regulatory body stipulates that along with the long-term trends for external radiation levels and airborne contamination, it is required to account the contribution from the short lived progenies. It is a control measure to maintain occupational health and safety for the workers. It is well known that there is a seasonal variation in short lived radon progenies concentration (like ^{218}Po, ^{214}Pb, ^{214}Bi) and also with ventilation pattern. With lowering ventilation, short lived progeny build up is more feasible and vice versa. Yearly trend analysis of the short lived progeny is required to set proper alarm progeny concentration [2] due to limit for continuous air monitors (CAM monitors), as sometimes due to build-up of short lived activity faulty alarms are received. This trend of any radiation facility should be well identified and documented. It will help to identify the change in operating conditions and remedial actions could be started immediately. This paper makes an attempt to study the trend of short lived airborne activity in the waste management facility and in turn will help to check the integrity of the facility along with the safety measures to control the airborne contamination.

It was planned to assess the short lived airborne contamination data over a two-year period in the study, viz., 1st jan-2023 to 31st dec-2024. In this regard, 4-day delay counting activity measurements of CAM filter papers for 9 installed CAM monitors in 9 distinct locations were assessed. With the flow rate of CAMs (70 lpm), the sampling time (24 h) and efficiency of α (25%), the Airborne Particulate Radioactivity (APR) concentration (Bq/m^3) of various locations of the facility have been estimated with the variation of month.

For two year trend analysis of short lived progeny for all the CAMs were carried out also. The airborne short lived α activity concentrations in different locations were plotted, which showed variation due to ventilation pattern, combined effect of temperature and humidity. Effect of humidity variation on APR was also carried out. With the increase in humidity, short lived activity decreases and vice versa. Similar type trend was achieved for temperature variation also. Variation of APR with temperature was also carried out.

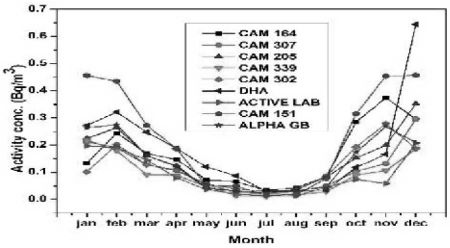

***Figure1.** Variation of short lived concentration during a period of two-year in various locations*

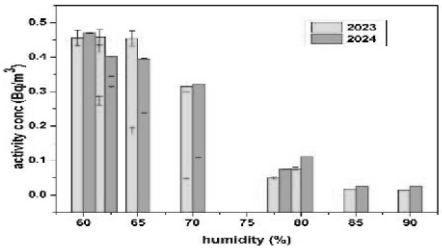

***Figure2.** Activity concentration with humidity*

The outlier observations (3σ away from the mean) have not been considered for trend analysis. The normalized observations w.r.t. variation of concentrations throughout the year (2-year trend) for individual CAM were assessed. Statistical tests were performed to check whether the concentration is stationary or not. This trend analysis of activity also will help to set instrumental alarm limit with confidence using computation.

Key words: *Radon progeny, waste management facility, airborne activity, humidity*

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Influence of Salinity on Major-Ion Speciation in Geothermal Waters Under Identical Reservoir Temperatures

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Electrical Conductivity (EC) serves as a robust field proxy for a fluid's ionic strength (μ) and is an important indicator of water–rock interaction in geothermal systems [1]. Although higher EC generally reflects higher dissolved solute concentrations, the resulting activity (log a_i) values, which control chemical reactivity, mineral solubility, are further influenced by temperature and μ-dependent activity coefficients (γ).

In this study, the GeoT computer code was used to carry out speciation analysis of major ions (Na, K, Ca, and Mg) for two thermal waters at 160 °C. These thermal waters are collected from the Tuwa (TA-1) and Maktupur (MK-1) region in the Gujarat geothermal area. These fluids exhibit wide contrast in salinity, with EC values of ~6898 μS/cm for TA-1 and ~1248 μS/cm for MK-1. For most of free cations, the high-EC fluid (TA-1) shows uniformly higher log a_i values which are quite expected (Fig. 1). The NaCl complex activity was higher in TA-1 compared to MK-1 as was the $CaSO_4$complex. Two crucial species, i.e. $Mg^{2+}$and $NaCO_3^-$ exhibited an inverse trend, highlighting the power of coupled reactions in controlling speciation:

- **Magnesium Anomaly (Mg^{2+})**: Mg^{2+} activity is lower in the high-EC fluid (TA-1) than in the low-EC fluid (MK-1), contrary to the expected EC–activity relationship. This suggests that Mg^{2+} may be limited by mineral solubility (e.g., precipitation of Mg-silicate or Mg-hydroxide phases), which is more effective in the chemically evolved, high-EC water.
- **Carbonate Complex Inversion ($NaCO_3^-$)**: This inversion points to a significant difference in the activity of the CO_3^{2-} ligand, suggesting that the TA-1 fluid has a much lower total Dissolved Inorganic Carbon (DIC), forcing the carbonate system equilibrium away from the CO_3^{2-} species and thus suppressing the activity of its complexed forms.

This comparative study thus reveals that EC is the primary control on the activity of major dissolved species, with the higher EC fluid (TA-1) having high concentration of free cations. However, the anomalous activity of Mg^{2+} and $NaCO_3^-$demonstrates that along with EC, ionic strength and mineral solubility also control the final speciation of the hydrothermal fluid (Fig. 2).

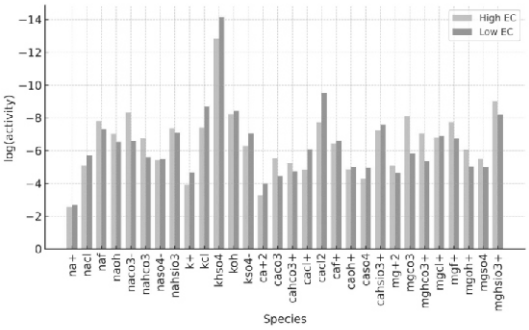

Fig 1: *Distribution of species at 160 °C*

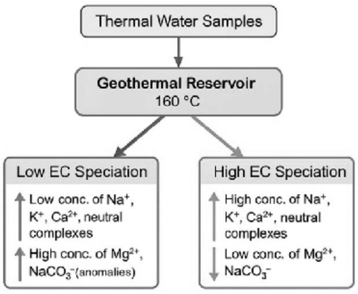

Fig 2: *Flowchart of the process*

Key words: *Thermal waters, speciation, salinity, reservoir fluid composition*

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Redox Speciation of Uranium at ATMP Functionalized Magnetic Nanoparticle Modified Electrode

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To understand the mobility and reactivity of Uranium (U) under environmental conditions, the studies on its speciation in aqueous phase is essential [1-2]. Contamination caused by U in the aquatic environments primarily arises from anthropogenic activities such as milling and mining operations resulting in harmful impacts on living organisms. Specifically, the hexavalent state of Uranium, U(VI), is very toxic, highly soluble making its accurate speciation and detection critically important. The redox behavior of Uranium is complex as it exist in several oxidation states from +III to +VI, having strong tendency to form stable complexes with ligands containing functional groups such as phosphate, carboxylate, hydroxyl further complicates its speciation at trace level. Uranium undergoes hydrolysis in aqueous solution which leads to formation of hydroxo complexes which influences speciation. Electrochemical techniques have emerged as promising platforms for speciation and detection of U due to their selectivity, sensitivity, and reproducibility. Therefore, electrochemical method provides effective and practical approach for detection and speciation of uranium in aqueous media, which significantly contributes to environmental and radiological safety as well. Magnetic nano particles (MNPs) are nanometer sized materials having high surface area-to-volume ratio, surface modifiability and have high chemical and thermal stability. Electrochemical sensors utilizing advanced nanomaterials, especially magnetic nano particles are increasingly employed in electrochemical sensors owing to their excellent sensitivity and selectivity, broad dynamic range, extremely low detection and quantification limits, low operational cost and rapid response times. Magnetic nanoparticles (MNPs), when functionalized with actinide-specific chelating ligands, form a MNP–chelator complex capable of selectively coordinating actinide ions from complex matrices. Phosphonates, due to their dibasic groups, are well known actinide specific chelators. Their ability to bind metals enables applications in catalyst and sensor applications. Using conventional electrode, the redox speciation of uranium (U) is challenging at its low level concentration because of slow redox kinetics. Herein, we synthesized Aminotrismethylenephosphonic acid (ATMP) modified MNPs to modify electrode for examining the redox speciation of uranium in aqueous phase. The XPS spectra [Fig. 1a] confirm the binding of ATMP on the MNP surface. The cyclic voltammetry (CV) and differential pulse voltammetry (DPV) [Fig. 1(b-c)] were performed with varying pH at both bare GC and ATMP-MNP@GC to determine the redox energetic and kinetic parameters of uranium. The modified electrode shows enhancement in peak current and shift in peak potential of uranium, confirming the interaction of ATMP with U. The diffusion coefficient of U at ATMP-MNP@GC electrode (6.1×10^{-6} cm^2/sec) is found to be higher than the bare GC (1.2×10^{-6} cm^2/sec). The detection limit for the present electrode for understanding speciation of uranium is $(5.1 \pm 0.07) \times 10^{-9}$ M. The appreciable response of ATMP-MNP@GC electrode towards the U aqueous solutions makes it potential candidate for understanding the speciation and detection of uranium at trace level.

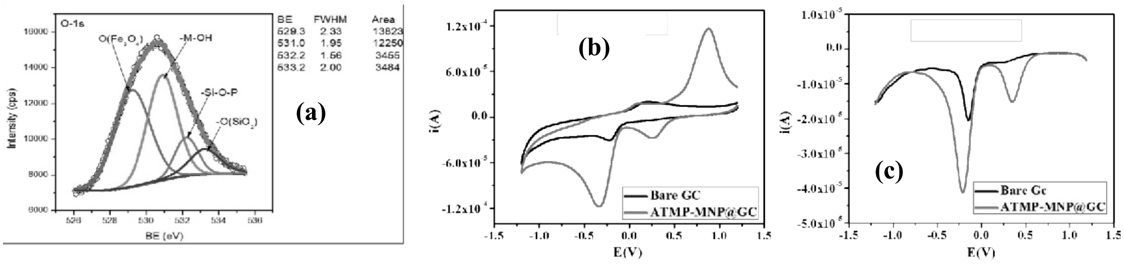

Figure 1. *(a) XPS spectra of ATMP-MNP (b) Cyclic voltammetry and (c) Differential pulse voltammetry plot of Uranyl [10^{-4} M, pH 4, 0.1 M NaClO$_4$] at bare GC and ATMP-MNP@GC electrode*

Key words: *Redox speciation, Magnetic nanoparticle, ATMP, Cyclic voltammetry*

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Complexation of U(VI) with Deep Eutectic Solvent Based on 2-Methylimidazole and Diglycolic acid

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Uranium is one of the most important actinide as it is used as a fuel in nuclear industry. It is also used as an analogue of +VI actinides to understand the fundamental chemistry of +VI actinides. In nuclear industry dissolution of fuel is a crucial step whether it is fabrication, purification or refining process. Conventionally, dissolution of uranium is carried out in nitric acid medium however there are several issues are associated with usage of nitric acid medium such as requirement of high volume, associated safety concern with handling, corrosion, toxicity due to evolution of gaseous product NOX etc. In the recent years green solvents like deep eutectic solvents (DES) are being explored for dissolution of uranium because of several suitable properties such as higher viscosity, surface tension, high chemical and electrochemical stability, ionic conductivity, ability to solubilize both inorganic and organic compounds, easy synthesis and low cost [1]. We synthesized a new DES based on 2-Methylimidazole (2-MIM) and diglycolic acid (DGA) and carried out the dissolution studies for U(VI). It is crucial to understand the complexation between uranyl and DES in order to understand the dissolution process. In the current paper Uv-Visible spectrophotometric studies and density functional theoretical calculations were carried out to understand the complexation of U(VI) with 2MIM-DGA.

In order to understand the speciation and stability of U(VI) complexes with 2MIM-DGA (proportion ratio of 2-MIM and DGA is 2:1) the UV-Visible absorption studies were performed. U(VI) forms ML_1 (U(VI)-(2MIM-DGA)) and ML_2 (U(VI)-$(2MIM\text{-}DGA)_2$) type of complexes with 2MIM-DGA (Fig. 1(a)). The obtained stability constant values (log K) for complexes are 5.89 (U(VI)-(2MIM-DGA)) and 3.56 (U(VI)-$(2MIM\text{-}DGA)_2$) respectively. To get insight into the coordination mode of U(VI)-2MIM-DGA complexes density functional theoretical calculations were carried out. The geometries of ligand, and predicted complexes (U(VI)-$(2MIM\text{-}DGA)_2$; proportion ratio of 2-MIM and DGA is 1:1 and 2:1) were optimized at the DFT level of calculations using the TURBOMOLE program package. The geometry optimization for all the structures was performed without any symmetry restriction using the B3LYP functional with the triple-ζ valence plus polarization (TZVP) basis set, as implemented in the TURBOMOLE package [2]. The aqueous-phase energetics was calculated using a conductor-like screening model (COSMO) approach. Minimum energy structure of U(VI)-$(2MIM\text{-}DGA)_2$ (2MIM:DGA- 1:1) revealed that two DGA units of DES binds tridentically to U(VI) with one C=O oxygen, one C-O^- oxygen and one ether oxygen. The one 2MIM unit is placed in between two DGA units forming H bond with both of them (Fig. 1(b)). While in case of U(VI)-$(2MIM\text{-}DGA)_2$ (2MIM:DGA- 2:1), two DGA binds tridentically to U(VI) with two C-O^- oxygens and one ether oxygen. In this case, the 2MIM unit is H-bonded to only one DGA.

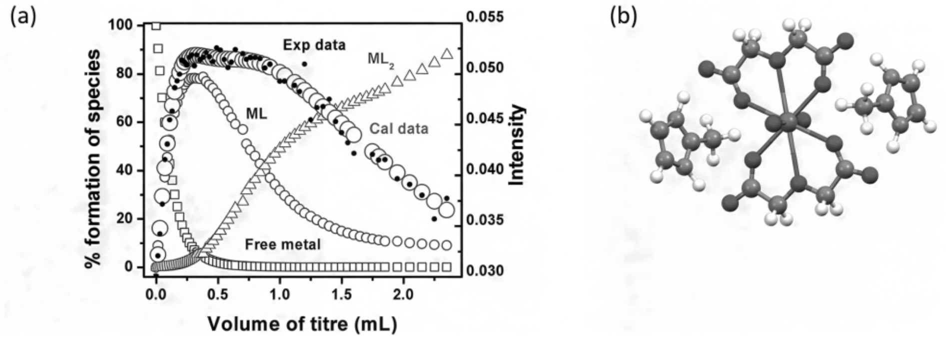

***Fig. (a)** Speciation diagram for complexation of U(VI) with 2MIM-DGA; (b) DFT optimized structure of U(VI)-$(2MIM\text{-}DGA)_2$(the ratio of 2MIM:DGA is 1:1).*

***Key words:** Uranium, DES, Stability constant, Spectrophotometry, DFT*

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Formation of Tetrafluoroborate Anion from Mixture of Hydrofluoric Acid and Boric acid: Speciation Analysis

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Boron is a neutron poison and its presence in nuclear fuel material has to be restricted within specification limits. Boron, in presence of high fluoride concentrations, as in molten salt fuel condition, exist in boron-fluoride complexes. Preparation of standard tetrafluoroborate anion (BF_4^-) ion aliquots as well as assurance of BF_4^- ion formation in the sample aliquot are mandatory prior to quantification of boron as BF_4^- ion by any analytical procedure. No defined speciation for Boron-Fluoride system available in literature. From the available thermodynamic data from the literature [1-2], using PhreeqC geochemical code [3], speciation plots for boron complexes with fluoride ion were constructed for various B:F ratios starting from 1:1 to 1:1000. Speciation showed that, at B:F = 1:10 ratio, both $BF_3(OH)$ and BF_4^- are at equal proportions (Figure 1 C), and at 1:100 ratio, BF_4^- accounts to 96 % (Figure 1 F). at B:F = 1:1000 ratio, > 99.5 % BF_4^- formation (Figure 1 H)was achieved. Kinetics plays a crucial role on formation of BF_4^-. Stepwise formation of $BF(OH)_3$, $BF_2(OH)_2$, $BF_3(OH)$ species from $B(OH)_3$ are very rapid reactions, while formation of BF_4^- from $BF_3(OH)$ is a slow reaction and requires higher temperatures (> 60 ^{0}C) to fasten the formation. Further, the formed BF_4^- has the tendency to undergo hydrolysis to form $BF_3(OH)$ back. The extent of hydrolysis depends on the amount of BF_4^- formed and can be controlled by adding HF to the solution [4]. From the available kinetics data for hydrolysis of BF_4^- in aqueous solution, degree of hydrolysis with amount of BF_4^- formed was constructed. Extent of hydrolysis of BF_4^- is around 77 %, 35 %, 14 %, and 5 %, when starting concentration of BF_4^- is 0.001, 0.01, 0.1, and 5 M respectively (Figure 1 J). The detailed speciation analysis showed that the formation of BF_4^- favoured when fluoride is 200 times higher than boron and in high acidic conditions (pH ≤ ~1). BF_4^- formation also favoured at slightly higher pH (~ 4) subjected to very high fluoride concentration (B:F ratio ≥ 1000). Very high content of fluoride ion (Figure 1 I), leading to formation of BF_4^-at higher concentrations, which could prevent back hydrolysis to of $BF_4^-BF_3(OH)$ (Figure 1 I).

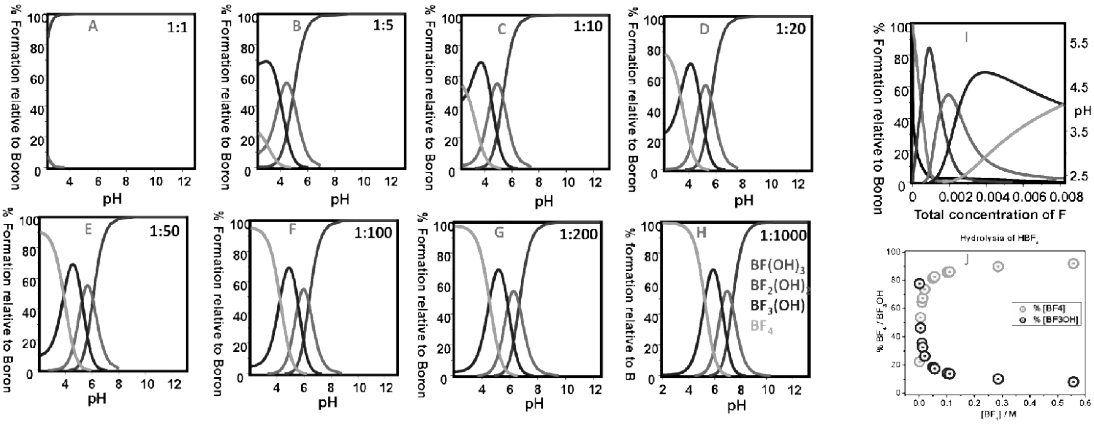

Figure 1: (A-H). Speciation plots for boric acid ($B(OH)_3$ = 10 ppm) and HF interaction with varying B:F ratio and pH of the solution.

Key words: *Boron, Speciation, Stability, Fluoroborate, Boric acid*

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Ion Chromatographic Separation of Uranium and Thorium in Coal Fly Ash

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India releases a huge amount of coal fly ash, a byproduct of coal combustion, through thermal power generation. Coal contains uranium and thorium, the naturally occurring radioactive materials (NORM). During the combustion of coal, both U and Th get more concentrated and present in the solid coal fly ash. This poses environmental concern. Therefore, the concentration of uranium and thorium present in the coal fly ash needs to be determined and this necessitates the need for separating uranium and thorium from the coal fly ash samples for their accurate determination at low level concentration.

A complete dissolution of a coal fly ash (CFA) sample is a difficult task as it contains the oxides of silicon and aluminium. Therefore, a bifluoride fusion method is followed for obtaining a clear solution of CFA. Ammonium bifluoride (ABF) is used as the fusion agent. Appropriate amount of the CFA sample is taken in a Teflon container and mixed with ABF by maintaining the ABF to sample ratio around 30. The fusion of the materials was carried out in a furnace in the temperature range of 220-230ºC for half an hour. The fused mass is treated with nitric acid and finally it is taken in 1% HNO_3 for subsequent separation and analysis.

Although many methods are reported for the separation of U and Th from different matrices, HPLC and IC chromatography methods are the preferred analytical separation methods for determining U and Th. For this purpose, most of the studies utilized α-HIBA as a complexing agent and the separation is realized as the α-HIBA complexes of U and Th [1]. Since the separation of U and Th using α-HIBA gives the peaks of U and Th in between the lanthanides, a complexing agent that would separate U and Th from the lanthanide fraction is desirable. In view of this, the present study explored the separation of U and Th using malonic acid, a simple dicarboxylic acid. A reversed phase column was dynamically modified into anion exchange column by using tetrabutylammonium hydroxide (TBA-OH). Effect of TBA-OH and the complexing agent, malonic acid in separating U and Th was extensively investigated. Based on the results, the separation conditions were optimized wherein a concentration gradient elution profile was followed by varying the concentration of malonic acid from 25mM to 600 mM. Fig. 1 shows a typical chromatogram obtained for a standard. Subsequently, interference from lanthanides and other transition metal ions at U and Th peaks was studied and it was observed that there was no interference from these metal ions.

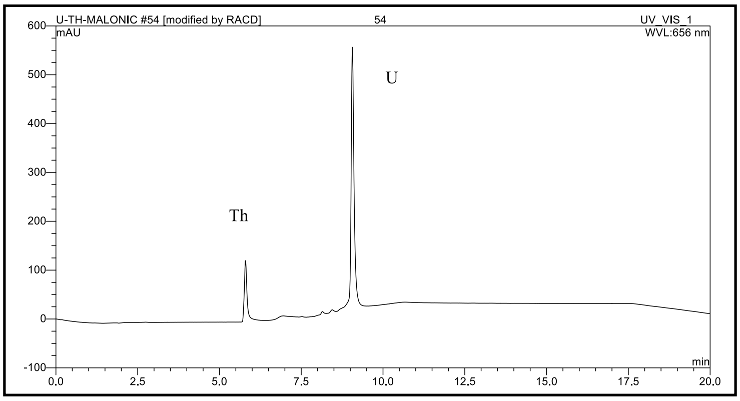

Figure 1. *Typical Chromatogram obtained for a standard solution of U and Th (each 2 ppm). Column: Hypercil C-18 Column (4x250mm); Eluent: 3 mM TBA-OH + 25 to 600 mM Malonic acid (Concentration gradient) @ pH 4. Flow rate: 1 mL/min. Post Column detection with Arsenazo-III at 656 nm.*

Key words: *ion chromatography, reversed phase, coal fly ash, uranium and thorium.*

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