

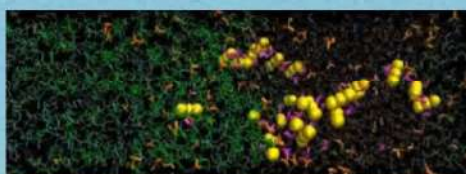
Special ASSET Bulletin on Separation Science and Technology

On the occasion of

SESTEC-2024

HSNC University, Mumbai

July 10-14, 2024



**Association of Separation Scientists and
Technologists (ASSET)**

**Editor
A. Bhattacharyya**

Main Products (M.O.C. in M.S. or S.S. Construction)	
Item Name	Description
1. Fume Hood (LCV, CV, VAV & FAC)	Bench Type , Walk in, Low Bench & Super Structure
2. Wall Bench	Plinth Mounted, C-Frame & Sliding Module Designed
3. Island Bench or Center Table	With Reagent rack, Sink Module, Service Pendant
4. Chemical Storage Cabinet	Inside P.P or FRP Lining
5. Slotted Angle Rack	
6. Anti-Vibration Table	
7. Column Storage Cabinet	
8. Storage Cabinet	With Glass Door & Metal Door
9. Wall Mounted Cabinet	With Glass Door & Metal Door
10. Locker Cabinet	
11. Cross Over Bench	
12. Apron Cabinet	
Item Name	Description
1. Spool Extractor	Indian Make or Imported Make
2. Eye Wash	Single Cup or Double Cup
3. Safety Shower with Eye -Wash	M.S or S.S Construction
4. P.P or S.S Sink	Oval, Rectangle Shape
5. Exhaust Blower	P.P Construction
6. Laboratory Stood & Chair	
7. Water Faucets	One Way, Two Way & Three Way
8. Canopy Hood	
9. Peg - Board	
10. Fire Safety Cabinet	P.P Material With Drain Arrangement
Item Name	Description
1. Granite,	
2. Epoxy,	
3. Phenolic Resin,	
4. Ceramic,	
5. Stainless Steel	
6. Back Painted Glass,	
7. Melamine/ Laminated ply etc.	
Office Furniture	Work -Top Material
File Storage Cabinet	
Computer Tables	

Special ASSET Bulletin on

Separation Science and Technology

On the occasion of

SESTEC-2024

HSNC University, Mumbai

July 10-14, 2024



**Association of Separation Scientists and
Technologists (ASSET)**

**Editor
A. Bhattacharyya**

डॉ. अजित कुमार मोहान्ती
Dr. Ajit Kumar Mohanty



अध्यक्ष, परमाणु ऊर्जा आयोग
व
सचिव, परमाणु ऊर्जा विभाग
Chairman, Atomic Energy Commission
&
Secretary, Department of Atomic Energy



MESSAGE

I am pleased to learn that the XIth DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024) is being organized at HSNC University, Mumbai, India during 10 -13 July 2024.

Separation science and technology plays a pivotal role in various stages of the nuclear fuel cycle, from recovering uranium and thorium from ores in the front end to efficiently retrieving fissile materials from the spent fuels in the back end. Depending on the natural resource availability, different countries opt for either open (without recycling) or closed (with recycling) nuclear fuel cycles. The Indian nuclear power program is committed to the closed fuel cycle approach and has developed schemes for the recovery of valuable radionuclides from the spent fuel thereby maximizing the use of natural uranium and thorium resources.

Innovative, efficient, selective, cost-effective, environmentally benign, and commercially viable separation schemes and related technologies are crucial for reprocessing spent nuclear fuels and extracting fissile materials from natural resources. Separation science and technology also plays a key role in producing highly pure radioisotopes for medical and other societal applications. The scalability of laboratory-scale R&D to commercial implementation is heavily influenced by chemical engineering considerations.

I understand that a good number of participants from overseas countries will be presenting their research work at the symposium. SESTEC-2024 will provide a vital platform for researchers and engineers in the field of Separation Science and Technology to interact, share their insights, and address real-world challenges related to separation processes.

I am confident that SESTEC-2024 will comprehensively cover robust and efficient separations in the nuclear fuel cycle, as well as novel separations in diverse fields such as energy, bio refinery, water purification, wastewater treatment, solvent synthesis, and purification.

I extend my best wishes to all participants of SESTEC-2024.

Ajit Kumar Mohanty
(Ajit Kumar Mohanty)



विवेक भसीन
Vivek Bhasin



निदेशक, भामा परमाणु अनुसंधान केंद्र
Director, Bhabha Atomic Research Centre
सदस्य, परमाणु ऊर्जा आयोग
Member, Atomic Energy Commission



MESSAGE

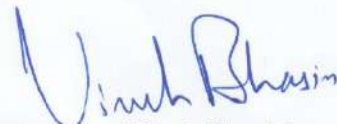
I am glad to know that the XIth DAE-BRNS Biennial Symposium on "Emerging Trends in Separation Science and Technology" (SESTEC-2024) will be held at HSNL University, Mumbai, India, from July 10th to 13th, 2024.

Separation science plays a pivotal part in many areas of science and technology including nuclear science. India's nuclear power program is based on a three-stage closed nuclear fuel cycle, where reprocessing of the spent nuclear fuel poses significant challenges due to the complex nature of the dissolver solution and the associated radio-toxicity. Presently, the PUREX process is the primary process for separating Uranium and Plutonium from the dissolver solution. Management of the high level waste is another challenging step in the back end of the nuclear fuel cycle. In recent years, non-aqueous reprocessing involving dissolution of spent fuel in molten salt/ionic liquids followed by preferential electrochemical separation has emerged as a novel and viable approach and poised to play a significant role in ambitious Indian nuclear energy program. Solid adsorbent based treatment of large-volume low-radioactivity waste solution is cost effective procedure. Environmental remediation of contaminated sites requires robust understanding of environmental chemical behaviour of long lived actinides and fission products. Research and development of efficient and selective adsorbents for various radionuclides will thus be crucial for a safe nuclear energy program.

Outside the nuclear industry, separation science and technology also plays an important role in waste water treatment where membrane based separation methods are routinely employed. Other sorbents like activated carbons, composite nanomaterials with specific functionalities are being increasingly employed by researchers worldwide. Apart from these, 'green' separation methods using deep eutectic solvents and other methods like electro coagulation find applications for the separation of heavy metals from industrial effluents.

SESTEC-2024 technical program covers a wide range of presentations on various aspects of separation science and technology. I am delighted to note the overwhelming participation from various DAE units, CSIR labs, IITs and universities. A good number of distinguished overseas speakers, renowned pioneers in their fields, will deliver presentations. I am confident that the deliberations at this symposium will inspire young researchers and will provide excellent opportunities for networking, sharing ideas, and fostering innovation which can positively impact India's efforts in achieving Amritkaal goals.

I wish SESTEC-2024 a grand success.


(Vivek Bhasin)

01.07.2024



From the President's desk



Prof. P.K. Mohapatra

Director, Radiochemistry & Isotope Group

& Head, Radiochemistry Division

Bhabha Atomic Research Centre, Mumbai-400085, India

Senior Professor, HBNI

Tel: +91-22-2559 5498(O); Fax: +91-22-2550 5151

Dear ASSET Members,

Time has come for the most awaited event co-organized by the Association of Separation Scientists and Technologists (ASSET), i.e., the SESTEC 2024 symposium. As you are aware, ASSET was conceived during the closing ceremony of the first edition of SESTEC held at BARC in 2004. Subsequently, ASSET was formed and registered in the year 2008 to provide a common platform to the separation scientists and engineers to have joint meetings and discuss at various platforms including theme meetings, seminars, and regular symposia like SESTEC. It has since made rapid progress as the separation scientist and technologist community got bigger and stronger.

Though objective of ASSET was to target research areas related to the nuclear fuel cycle by DAE as well as non-DAE researchers, it has been actively supporting other relevant areas such as waste water remediation, bioseparations, sludge hygienization, radiopharmaceuticals, etc. In the last few months, ASSET has been conducting several theme meetings on these interesting areas of research having immense societal relevance.

Coming to the SESTEC series of symposia, the last two editions were conducted in the virtual mode due COVID pandemic related restrictions. With the SESTEC 2024, we are limping back to normalcy and there has been an overwhelming response by the participants. I welcome the overseas participants who are joining after a gap of 6 years. ASSET continuously motivates the young researchers in the field of separation science and technology by giving various awards, viz. Dr. P.N. Pathak Memorial Award, THERMAX-ASSET Awards for the best Ph.D/M.Tech thesis in the field of separation science and technology and best oral/poster paper awards during the SESTEC symposium.

ASSET has been publishing series of thematic bulletins covering various topics in the area of separation science and technology and its applications in diverse fields. In this special issue being brought out on the occasion of the eleventh edition of SESTEC at HSNC University, Mumbai, the topics covered include Separation Science of critical elements, Back End Nuclear Fuel Cycle and Theoretical Studies.

A handwritten signature in black ink, appearing to read 'P.K. Mohapatra'.

(P.K. Mohapatra)

July 10, 2024

Editor's Note

Dear ASSET Members,

Separation science and technology has immense applications in various fields for the benefit of the society viz. nuclear industries, pharmaceutical industries, water treatment, bio-remediation etc. One of the important objectives of ASSET is to bring out bulletins on various topics related to separation science and technology.

In the recent past, ASSET has brought out a number of bulletins covering the topics in separation science and technology, like "Uranium Harvesting for Energy Applications", "Waste water Remediation Strategies: Current Status and Future Perspective", "Separation Technology in Radiopharmaceutical Science", "Radiation Processing of Sewage Sludge" etc.

This bulletin is a special issue to be released on the occasion of SESTEC-2024. There are four articles in this issue covering different aspects of separation science and technology in the field of back end of the nuclear fuel cycle, computational modeling and simulation of the separation processes, separation of chemically similar rare earth elements. All the topics covered in this bulletin has crucial role in the program of the Department of Atomic Energy (DAE).

I wish to record my heartfelt thanks to all the contributing authors, Shri. K.T. Shenoy, Director, Chemical Engineering Group, Dr. S. Manohar, Director, Nuclear Recycle Group, Dr. A. Sharma, Director, Beam Technology Development Group, Dr. R. Tewari, Director, Materials Group, Dr. D.K. Singh, Dr. Kartikey Kumar Yadav, Dr. (Smt.) M. Anitha, Dr. Alok Awasthi, MP&CED and B.R.Mishra, General Manager(R&D,I), IREL, D. Singh, CMD, IREL for accepting our invitation for and their efforts in submitting the articles in a short span of time.

I am thankful to Dr. P.K. Mohapatra, Presisent ASSET and Dr. S. Jeyakumar, Vice-President, ASSET for their support in bringing out this bulletin.

Arunasis Bhattacharyya

Contents

Sr. No.	Title	Page No.
1	Interfacing the Atomistic and Continuum modelling for Process intensification in Separation Science and Technology: Initiatives in Chemical Engineering Group <i>K.T. Shenoy</i>	1
2	Advances in Separation Science and Technology in the Back-end of Nuclear Fuel Cycle <i>Smitha Manohar</i>	20
3	Development of Scalable Solvent Extraction Technologies for Separation and Purification of High Purity Individual Rare Earths from Primary Resources and Secondary resources <i>D. K. Singh, K. K.Yadav, M. Anitha, A. Awasthi, R. Tewari, B.R.Mishra, D. Singh</i>	34
4	Separation Science and Technology: Process development strategies and perspectives on work at BTDG, BARC <i>Archana Sharma</i>	49

**Interfacing the Atomistic and Continuum modelling for Process intensification in
Separation Science and Technology:
Initiatives in Chemical Engineering Group**

K.T. Shenoy

Director, Chemical Engineering Group, BARC, Trombay, Mumbai-400085, India

Email: shenoykt@barc.gov.in

Abstract

Separation Science has played stellar role in nuclear material processing since inception. Even though, the separation of nuclear materials in fuel cycle is well established, separation science still plays dominant role in making the separation process greener and more intensified. Also, there is ever growing need for separation of value material from dilute and/ or harsh chemical streams. Chemical Engineering Group (ChEG) in Bhabha Atomic Research Centre continues its pioneering role in application of separation science. While the expertise in atomistic modelling enables in design of new and efficient extractants for separation, the specialisation in Computational Fluid Dynamics enables efficient contactor design. This holistic approach has enabled implementation of new ligands with better selectivity & stability; and better industrial contactors with higher specific throughput in the nuclear fuel cycle. The article highlights the significance of the modelling in separation science and also some glimpses of more challenging separations being pursued in ChEG.

Introduction

Atomistic modelling comprising of Quantum Mechanics, Molecular Dynamics (MD) and Ab initio Simulations, is a prospective tool for the calculation of various molecular properties & events by capturing the complex molecular interactions. The strategy for computation of a molecular system is commonly started based on its state i.e. whether gas, liquid, solid phase or mixture of states. Accordingly, the computational techniques are chosen. Initially, a trial molecular system is designed using a graphical user interface software to generate the atomic coordinates as the input for next level of calculations depending on the molecular parameters to be evaluated. Mostly, structure and energetic of isolated molecules and periodic solids are evaluated using Quantum electronic structure calculations (QESC), where density functional theory (DFT) is the work horse. Whereas for condensed phase and amorphous state, MD simulations are extensively used for predicting the thermo-physical and dynamical properties of the molecular system. In the case of QESC, Schrodinger Equation is solved, whereas for MD simulation, Newton's Equation of Motion is used. Atomistic modelling provides useful estimates of the properties and behaviour of materials needed to do traditional chemical engineering process development and design.

Solvent extraction is the pivotal separation process in the nuclear fuel cycle. Specific types of equipment are essential for different solvent extraction processes practiced in the front-end and the back-end of the nuclear fuel cycle. The intricacy of the underlying processes, which involve turbulent flow, two-phase or multiphase flow dynamics, and the phenomena of droplet breakage and coalescence, makes it impractical to design solvent extraction equipment solely from fundamental principles. Consequently, the design process relies heavily on empirical correlations found in literature, experimentation across different scales, and practical operational insights. However, recent advancements such as Computational Fluid Dynamics (CFD) and

improvements in computational hardware are facilitating a deeper understanding of how solvent extraction equipment operate. These tools are driving efforts towards achieving optimal designs, efficient operation, and effective scale-up of solvent extraction systems.

First-principlesbased Understanding of Solvent Extraction

The preferential transfer of metal ion from aqueous to organic phase underlies the process of solvent extraction. Continuing developments of this process are intended at optimizing the efficiency and kinetics of the separation and recovery of rare earth, precious metals, as well as the reprocessing of spent nuclear fuel. Although the interaction of metal ions with various chemical species at the organic-aqueous-interface is likely to determine the efficiency and kinetics of extraction, little is known about the mechanism of metal ion transport across the interface. A detailed first-principles investigation of solvent extraction on the atomic scale which includes screening of extractants, solvents (diluent) and effect of physiochemical parameters on the metal ion transfer to compliment the experimental solvent extraction mechanism is very much needed.

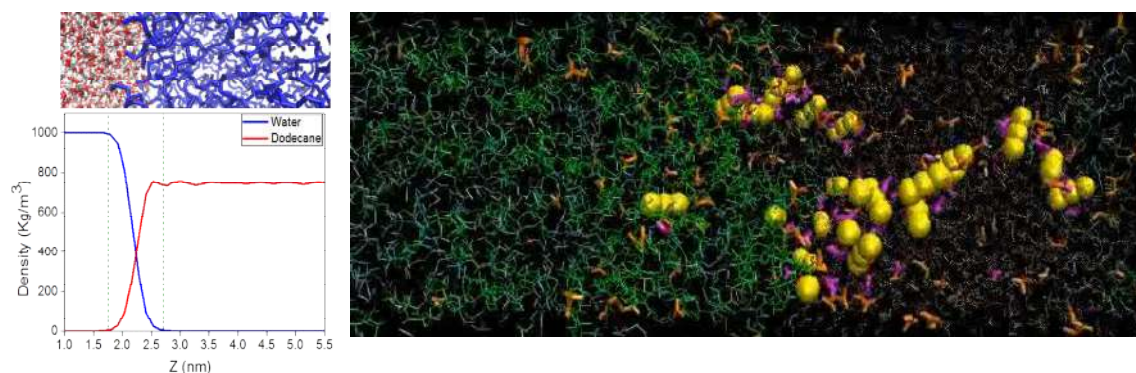


Figure 1: (Left) Calculated interface of water and dodecane bi-phasic system; (Right) MD snap shot of uranyl ion (yellow) extraction in the organic phase.

In solvent extraction, the selection of solvent and molecular extractant is arrived by innumerable trial experiments. Furthermore, thermophysical and dynamical properties of solute-solvent systems are also experimentally determined for interpretation of the experimental results. Overall, selection of solvent-ligand system for preferential complexation and selective extraction for a specific metal ion by performing experiments is a tiresome and expensive issue. Due to inherent difficulty, the understanding of molecular details at liquid-liquid interface using only experimental technique is inadequate to establish the interfacial behaviour. This is mostly due to the fluidity of the interface and its concealed environment, which restricts the experimental facts. First-principles atomistic modelling with the aid of supercomputational facility and machine learning can capture the complex molecular phenomena in solvent extraction process at different spatial and time scales. Therefore, atomistic modelling has been used extensively to expedite and to reach a reasonable conclusion in minimum no of trials of experiments and thus reduce the cost as well as time for conducting solvent extraction.

CFD Modeling of Fundamental Phenomena Relevant to Solvent Extraction

As previously discussed, computational fluid dynamics (CFD) modelling is increasingly utilized for analysing solvent extraction equipment to provide detailed insights into the dynamics of

liquid-liquid two-phase flow and mass transfer phenomena. In CFD modelling at the equipment level, solving the governing equations necessitates appropriate closure equations. These closure equations, which estimate parameters like drag coefficient or mass transfer coefficient, are primarily empirical in nature. Therefore, the accuracy of equipment-level CFD models hinges on the precision of the accuracy of such empirical closures. To mitigate the empirical nature of equipment-level CFD models, closure equations can be derived more fundamentally by conducting CFD modelling at the droplet level, which involves simulations at the scale of individual droplets. Such CFD studies are valuable because experimental investigations at the droplet level are typically challenging to conduct.

CFD simulations have been conducted to understand the drag phenomenon in liquid-liquid systems, focusing on internal circulation within droplets and turbulence effects in the continuous phase on drag coefficients. A CFD-based drag model has been developed and integrated into equipment-level CFD models. Similarly, CFD studies have been used to examine drop formation at nozzles and holes in plates submerged in a quiescent continuous phase. However, further research is needed to understand drop formation and droplet breakage under complex flow conditions of the continuous phase. Detailed studies on mass transfer from individual droplets have been conducted using CFD models that account for internal circulation effects on mass transfer. A CFD-based correlation has been derived to estimate the Sherwood number for mass transfer from spherical droplets under steady and pulsatile flows of the continuous phase. This correlation has been successfully implemented in equipment-level mass transfer models. The influence of droplet shape on mass transfer has also been investigated using CFD. However, additional research is required to comprehend mass transfer in the presence of Marangoni convection and from deformable droplets. Extensive efforts have been dedicated to understanding liquid-liquid two-phase flow and mass transfer in microchannels, which are being explored for enhancing solvent extraction processes. CFD simulations have been employed to fundamentally understand the hydrodynamics of liquid-liquid two-phase flow and mass transfer in various flow regimes (slug flow, droplet flow, core-annular flow) in microchannels. These fundamental studies are gradually advancing towards the development of empirical-free CFD models for solvent extraction equipment.

Modelling of Solvent Extraction Equipment

Extensive research employing Computational Fluid Dynamics (CFD) modelling has been conducted to gain a fundamental understanding of the underlying transport phenomena in solvent extraction equipment. This understanding is crucial for designing, optimizing, and scaling-up such equipment. While the flow in solvent extraction systems typically involves two-phase or multiphase dynamics, there are instances where single-phase CFD modelling proves beneficial. A notable example is the design of pump-mix mixers, where single-phase CFD simulations have been utilized to develop impellers and also for sizing high-capacity pump-mix mixers essential for recovering valuable materials from low-concentration streams.

Two-phase CFD modelling of dispersed liquid-liquid flow, assuming mono-dispersed droplets, represents a more advanced stage in the modelling of solvent extraction equipment. The Euler-Euler method is widely utilized for such simulations, while the mixture k - ϵ model is the predominant turbulence model employed. Extensive CFD investigations with assumption of mono-dispersed droplets have focused on simulating liquid-liquid two-phase flow within air pulsed columns (pulsed sieve plate and pulsed disc and doughnut columns) which due to being maintenance-free are integral to solvent extraction processes in the nuclear fuel cycle. These

studies have yielded fundamental insights into the hydrodynamics of liquid-liquid two-phase flow, including spatial and temporal variations of dispersed phase hold-up and specific interfacial area under varying operational parameters (such as continuous phase velocity, dispersed phase velocity, pulsing frequency, pulsing amplitude) and geometric parameters (such as plate spacing, fraction open area, column diameter).

Coupling two-phase CFD with population balance (PB) to create a CFD-PB model is necessary to move away from the assumption of constant diameter mono-dispersed droplets. This approach realistically captures the continuous processes of drop breakage and coalescence. The predictions of flow patterns and droplet sizes in the CFD-PB model depend on the chosen models for breakage rate, coalescence rate, and distribution of daughter droplets, as well as the values assigned to constants in these models. Therefore, careful selection and validation of these models against experimental data are crucial steps in developing an accurate CFD-PB model. CFD-PB modelling has been applied to air pulsed columns. In columnar contactors like air pulsed columns, axial mixing or back-mixing poses a significant challenge that can impair mass transfer efficiency. This issue becomes more critical during scale-up, where an increase in column diameter typically leads to greater axial dispersion. Hence, accurately predicting the axial dispersion coefficient or Peclet number through CFD modelling is essential for effective scale-up. Studies employing CFD modeling for predicting axial dispersion coefficients in air pulsed columns have been extensively conducted and validated.

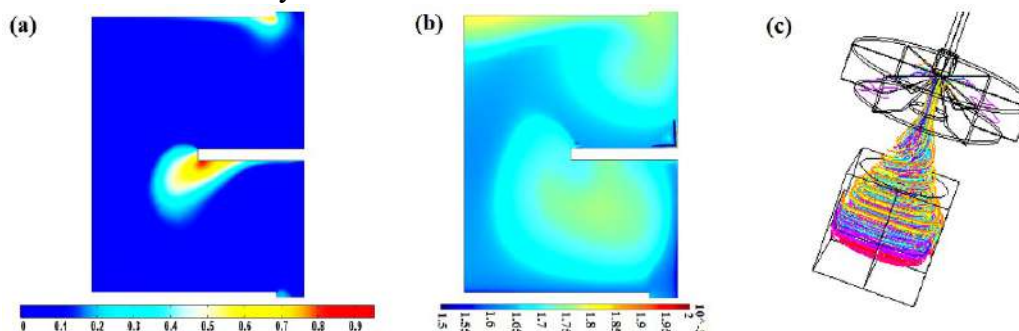


Figure 2: Variation of (a) dispersed phase holdup and (b) Sauter mean drop diameter in an interdisc space of a pulsed disc and doughnut column and (c) path lines followed by the liquid from the inlet to the impeller eye in a pump-mix mixer.

Though the ultimate objective of using a solvent extraction equipment is to achieve mass transfer, CFD modelling of mass transfer in solvent extraction equipment are scarce. This scarcity is mainly due to the complexities involved in solving additional equations necessary for modelling mass transfer, as well as the challenges in conducting mass transfer experiments for validation, which typically require a once-through flow unlike closed-loop flow experiments. Moreover, the considerable height of contactors restricts the feasibility of using CFD for simulating mass transfer, given the extensive computational time required to simulate the entire column height. To address these challenges, a novel approach has been developed that integrates CFD-PB modelling with a classical axial dispersion model to predict mass transfer in columnar contactors. In this approach, hydrodynamic parameters crucial for mass transfer, such as dispersed phase hold-up, droplet diameter, axial dispersion coefficients of both dispersed and continuous phases, are obtained from CFD-PB simulations. Subsequently, mass transfer is estimated using a customized classical axial dispersion model (ADM) tailored for two-phase flow with interphase mass transfer. Simulators based on this innovative approach have been

developed and rigorously validated. A specific example of this is Pulsed Disc and Doughnut Column (PDCC), development work on which included setting-up a 3" inch diameter column testing facility, conducting uranium extraction and stripping experiment, development, and validation of CFD-PB and AD models. This work on PDCC has led to setting up of a bench-scale plant which will be used to demonstrate complete solvent extraction cycle (extraction, scrubbing and stripping) and a pilot-scale facility to decipher the scale-up methodology.

The above-mentioned studies highlight the advancement and validation of robust computational tools capable of simulating flow and mass transfer in solvent extraction equipment. This paves the way for methodologies ensuring sound and optimal design practices, as well as confident scale-up.

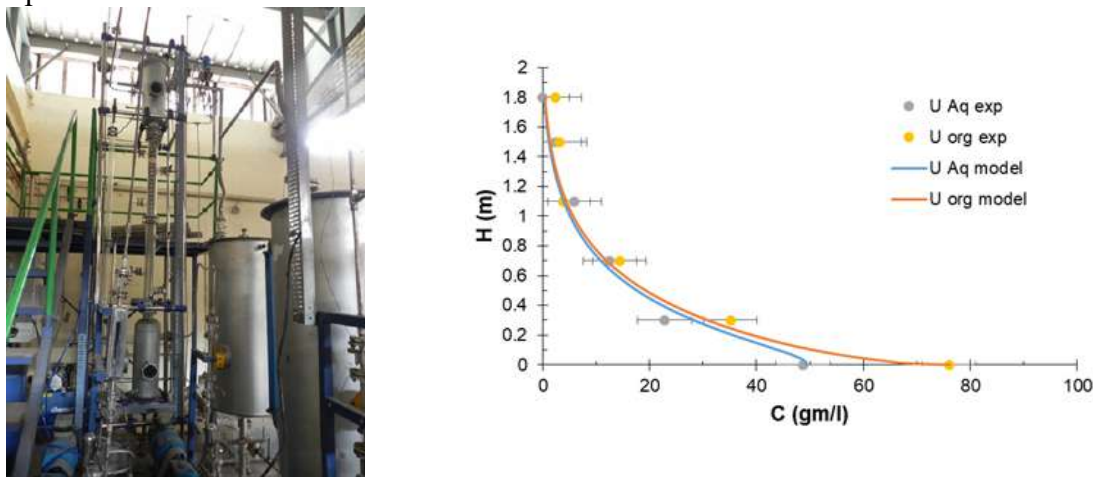


Figure 3: Facility for testing 3 inch diameter PDCC for uranium extraction and stripping; and comparison of experimentally obtained uranium concentration profiles in aqueous and organic phases during uranium stripping in PDCC with the concentration profiles obtained by CFD-PB and AD model.

Separation of metal ions and isotopes using column chromatography

Selective separation of metal ions and isotopes play a crucial role in the nuclear energy programme. Removal of radioactive fission product, ^{90}Sr from liquid nuclear waste is very crucial as it has high radioactivity (β ray emission with $t_{1/2}$ of 28.8 years) and heat generation capacity (energy of β emission 0.55 MeV) with appreciable amount available in high level liquid waste (HLLW). Despite its extreme toxicity, mercury is used in various industrial processes, leading to contamination of wastewater and leaching from disposal sites. The tolerance limit for mercury in drinking water is 0.001 mg/L, and the CPCB in India sets the discharge limit in industrial wastewater at 0.01 mg/L. Therefore, wastewater containing mercury must be treated before discharge to minimize its severe impacts. The isotopes of zinc (Zn) and gadolinium (Gd) are crucial in various applications due to their unique properties. Zinc isotopes are essential in biological and environmental studies as tracers and play a significant role in nuclear power reactors by reducing the presence of Co-60. Gadolinium isotopes, especially Gd-155 and Gd-157, are important as burnable poison in nuclear reactors to control reactivity. These isotopes are indispensable for advancing nuclear technology.

Chromatographic methods for separation of metal ions and isotopes offer numerous advantages over alternative techniques. These methods are highly scalable, suitable for both laboratory and industrial-scale operations. Isotope separations using chromatography typically consume less

energy compared to methods like centrifugation, electromagnetic, and laser-based isotope separation, making them more cost-effective and environmentally friendly. Chromatography provides flexibility by allowing modifications to the stationary and mobile phases to adapt to different isotopes and elements.

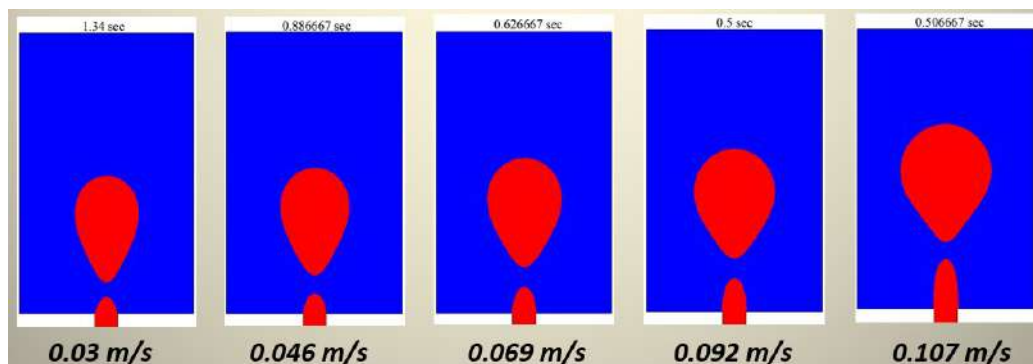


Figure 4: CFD modeling of phenomenon of drop formation at a hole in a plate immersed in a quiescent continuous phase for different velocities of the dispersed phase

Molecular modeling and experimental chromatographic studies were conducted to evaluate the feasibility of Zn and Gd isotope separation using cation exchange and crown ether-grafted resins. In addition, Amidoamine functionalized multi-walled carbon nanotubes (MWCNT-AA) have been prepared and characterized. Separation of mercury (II) ions from aqueous solution by solid-liquid extraction has been investigated using the synthesized material as an adsorbent (MWCNT-AA). Dibenzo-18-crown-6 functionalized chloromethyl- polystyrene (CMPS-DB18C6) resin which displays an excellent affinity toward Sr^{2+} ion adsorption from aqueous solution was used for separation of Sr^{2+} ions using column chromatography. Batch equilibrium studies were carried out for optimizing parameters such as concentration, pH, kinetics, and temperature.

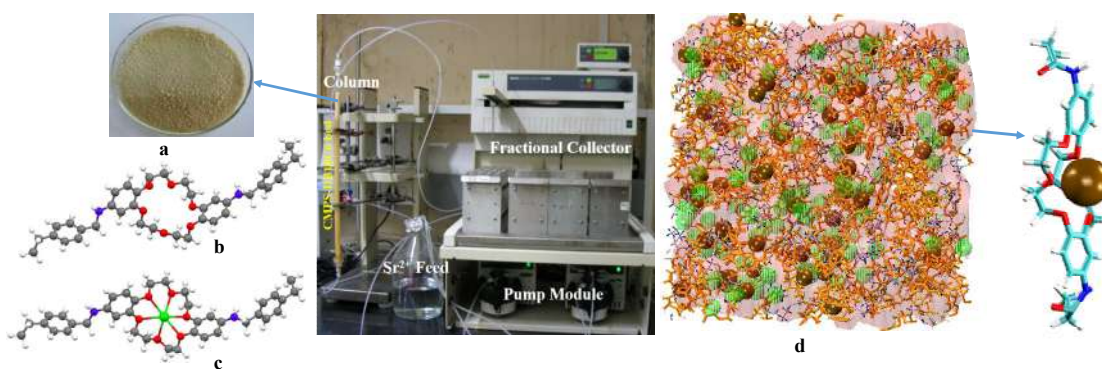


Figure 5: Fixed bed column set up with fractional collector for the separation of Sr^{2+} ion with CMPS-DB18C6 resin. (a) Prepared CMPS-DB18C6 resin; DFT optimized structure of (b) CMPS-DB18C6 and (c) CMPS-DB18C6- Sr^{2+} complex and (d) MD snapshot of Sr ion encapsulated resin.

Column chromatographic separation of Li, Zn, and Gd isotopes was performed using DOWEX50X8, PMAB15C5, CMPSDB18C6, and PMADB18C6 resins. The isotope separation factors for Zn and Gd were found to be one order lower with cation exchange resin compared to crown ether-grafted resins. The heavier isotopes of Zn and Gd were enriched at the front of the

adsorption band, while lighter isotopes were enriched at the rear. Crown ether grafted PMAB15C5 and PMADB18C6 resins were suitable for Zn and Gd isotopes, respectively. These findings will aid in the design and development of future isotopic enrichment technologies using chemical exchange methods.

Process development for separation & purification very high purity gases by De-Oxo catalysis

In chemical/ nuclear process industries, many processes and applications require feed gases, completely free from H₂/O₂ impurities. Commonly purification methods are selected based on the type of gas to be purified and the impurities to be removed, such as: inert, reactive, flammable and so on. In applications where removal of oxygen, carbon monoxide, hydrogen, and hydrocarbons is required, metal catalysts are typically used. Metal catalysts such as nickel, copper, platinum and palladium etc. are commonly used based on the process conditions. These catalysts are normally supported on high surface area supports such as Y-alumina, silica, activated carbon, zeolite etc. to have better dispersion and activity of the catalyst material.

BARC has developed De-Oxo catalyst for removal of impurities, either oxygen or hydrogen by recombination reaction. Advantage of such process is, they are operated at ambient condition with very high activity. Such catalysts are used extensively at DAE for Helium cover gas purification, nuclear reactor containment building, hydrogen mitigation and purification of electrolytic hydrogen/ oxygen streamsetc. The novel De-oxo catalyst is developed in-house as per the following reaction:



In industries, hydrogen is also produced on large scale by naphtha-steam reforming and this may contain hydrocarbon as impurity. To remove traces of hydrocarbons from hydrogen stream de-oxo catalyst can also be employed, if the feed gas carry traces of oxygen:

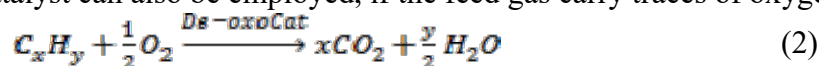


Figure 6: Palladium (0.5% & 1.0%) on Alumina Catalyst developed by BARC

The type of de-oxocatalyst to be employed depends on the feed conditions. A variety of de-oxo catalysts such as mixture of Pt/Pd supported on Y-alumina and other support materials have been developed and tested for process gas purification applications.

Separation of Noble gases from Air using adsorption-based processes

Separation of Noble gases from ambient air is extremely difficult and very important for the safety of nuclear reactor operation. Major radioactive noble gases produced during nuclear

reactor operation are activation product Ar^{41} and fission products like Kr^{85} , Kr^{87} , Kr^{88} , Xe^{133} , Xe^{135} , Xe^{138} etc. During severe accident scenario like core meltdown in a nuclear reactor, there's a risk of air borne activity release through the Noble gas fission products, which cannot be trapped with the typical filtration system. Activated Charcoal has been identified as one of the promising adsorbents for the separation of krypton from ambient Air.

BARC is working on physical adsorption-based separation technique for separation of noble gases from air, as it is the only industrially feasible technique for such separations. Challenges are selective adsorption of noble gases, which are very lean in concentration from the other constituents of air. The isotherm data available in the literature mostly consider single component adsorption on the micro- or meso- porous adsorbent material, whereas the equilibrium adsorption capacity of the gases, in presence of air is observed to be very low. For designing a filtration system that can trap Noble gases from the air, adsorption studies have been carried out with Activated Charcoal of different sizes and specifications, such as 4-8mesh, 1.2mm pellets, 3.2mm pellets etc. Breakthrough studies have been carried out at ambient conditions with 1% Inert gases in air mixture and screening of the adsorbent materials has been carried out, based on the adsorption capacities obtained. It was found that, 4-8mesh Activated Charcoal has got the highest adsorption capacity among these. Analytical model also has been developed and validated using the experimental data.



Figure7: Experimental setup for breakthrough studies with packing material

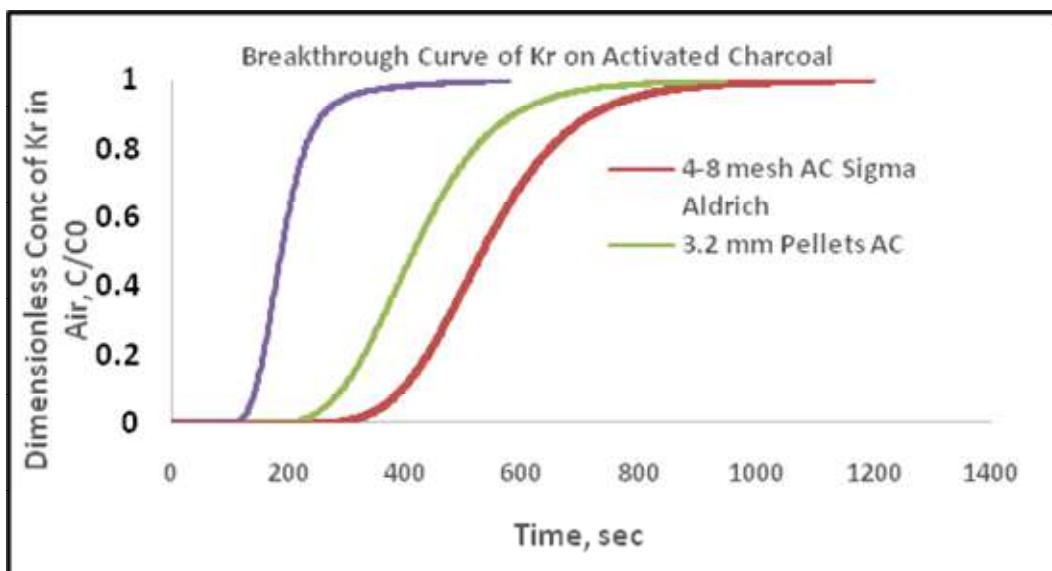


Figure 8: Breakthrough curve of Krypton in Air on different Activated Charcoal adsorbents at RT.

Development of absorption-based CO₂ separation from air for Blue H₂

Among the greenhouse gases, CO₂ produced during fossil fuel burning, has the major contribution for the global warming and removal of CO₂ from the atmosphere is mandatory for meeting GoI's net zero target by 2070 and Blue Hydrogen production. There are different technologies reported for separation of CO₂ from air such as membrane, absorption, adsorption and cryogenic distillation. However, membranes are less effective at low concentration range and Cryogenic processes are energy intensive, so, Adsorption & Absorption based processes are only economically viable.

Due to the relatively low specific energy consumption and associated low operating costs compared with the other processes, BARC is working on the system development for adsorptive separation of CO₂ from air.

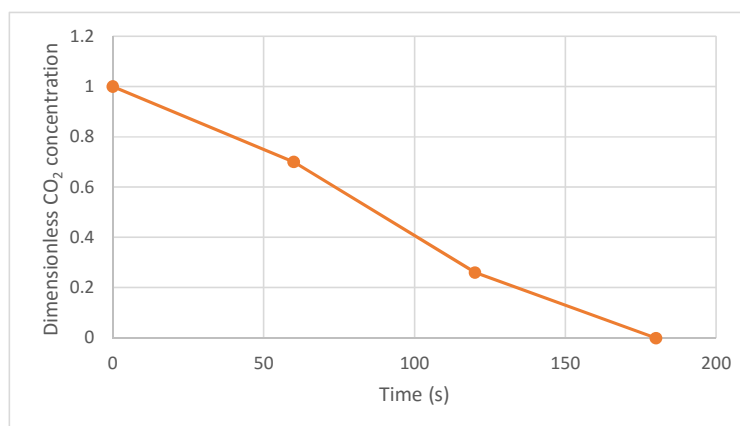


Figure 9: Novel chemical adsorbent for CO₂ adsorption (left). Dimensionless CO₂ concentration versus time at 30°C (right)

In adsorption, both physical and chemical adsorption is reported for the above application. In physical adsorption, the adsorbents such as zeolites and activated carbons are generally used and the separation is based on the pore size of the adsorbent. The adsorbents with large interfacial area with pore diameter less than 0.7 nm is generally favoured for CO₂ adsorption. MSA 13X is having the highest equilibrium capacity for CO₂ among zeolites. The physical adsorption and desorption are generally carried out at relatively mild operating conditions. However, the adsorption capacity of physical adsorbents is limited. The chemical adsorbents are generally, alkali metal compounds, calcium oxides and magnesia. Due to the formation of chemical bonds, the heat of adsorption and desorption are generally high. The chemical adsorbents also require high operating temperatures (>200 deg. C) for desorption. The adsorption kinetics of a novel chemical adsorbent with adsorption of CO₂ at ambient conditions and regeneration at a relatively lower temperature (<100 deg. C) with reasonable adsorption capacity is studied. The material has been tested in a recirculating packed bed batch reactor for estimating the adsorption kinetics. A typical result on the reduction in CO₂ concentration with time at ambient conditions is shown in Figure 9.

Separation of impurities from Chlorosilane mixture using fractional distillation

Semiconductor silicon has become the most important and characteristic material of our silicon age, due to its application from Photovoltaic (PV) to consumer electronics till Quantum computing. High purity mono-crystalline silicon is used for fabrication of semiconductors, integrated circuits, high power device and radiation detectors. The silicon semiconductor industry is closely guarded and material supply is also restricted in the open international market. Hence, to achieve Atmanirbharta for high purity silicon technology, developmental work for demonstration of technology has been carried out at BARC. Worldwide many processes have been tried for production of high purity silicon. This includes both chemical as well as metallurgical processes. Out of these Siemens process is the most popular and widely accepted process for production of semiconductor or PV grade silicon. Quartzite sand is major source of silica which is economical to be used as raw material for production of silicon. Metallurgical grade silicon is produced by carbothermic reduction of high purity silica (SiO₂). For obtaining ultra-high purity silicon, metallurgical grade silicon is converted to a volatile precursor Trichlorosilane (TCS) and purified to $\geq 10N$ purity using distillation cascade (Fig. 10). Polysilicon is produced back by reducing high purity precursor on silicon slim rod in a chemical vapor deposition (CVD) reactor.



Figure10: TCS Distillation facility at BARC

For production of High Purity Trichlorosilane, BARC has developed fractional Distillation cascade comprising series of distillation units to achieve the required purity. The total impurities are divided into two groups major impurities (Fe, Ca, Al) and minor impurities (P, B, As). Out of these the impurities only BCl_3 has low boiling point in comparison to TCS, rest all have higher boiling point. Although the separation factor for individual impurity with TCS is sufficiently large but in-order to achieve such extremely high purity level, large number of separation stages are required. Distillation cascade has been optimized using Marginal Vapor Flow Rate in order to optimize operating cost for the process. A typical simulation of distillation cascade is shown below (Fig. 11):

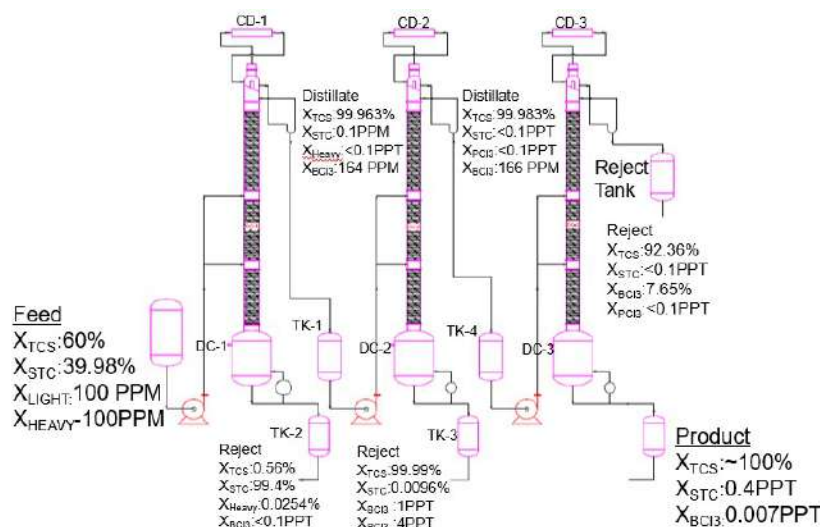


Figure 11: Schematic of TCS Distillation Cascade

Electrochemical separation of hydrogen and helium

Demand of helium is continuously increasing across the globe due to its important applications in scientific, industrial and medical fields. Recovery of non-synthesizable helium gas is very crucial due to limited reserve, limited production and constrained supply of helium gas. Major sources of Helium are natural gas, synthesis gas or terrestrial gas. However, independent of the source, all the other impurities can be separated from helium with relatively ease, except hydrogen due to their very similar physical properties. Currently, several conventional technologies are available for separation of hydrogen and helium from its gas mixture such as pressure swing adsorption, cryogenic distillation, and membrane-based separation. All these separation methods have different throughput, holdup time, efficiency, scalability and technical maturity. Preference and choice of technology is dependent upon source, capacity of production, time of separation, purity of product, life of equipment required, requirement of man-power, maintenance etc.

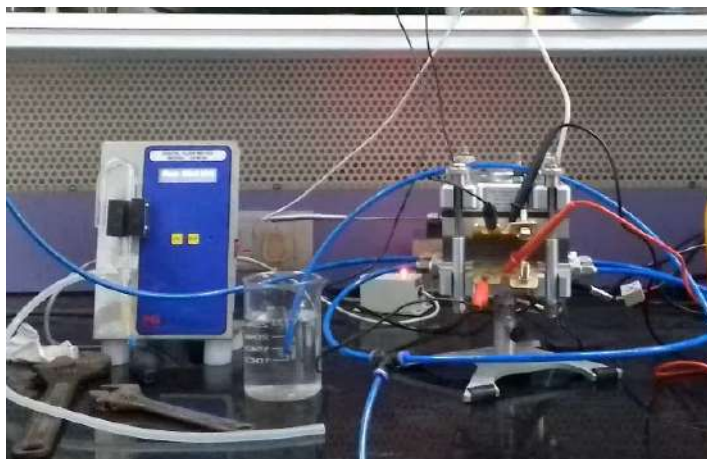
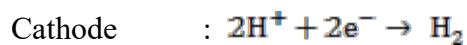


Figure 12: Lab scale proton exchange membrane electrolyser setup

ChEG is working on novel electrochemical separation technique for hydrogen-helium gas mixture. This method has several advantages over conventional methods such as high degree of separation, low energy consumption, high efficiency, single step operation, small footprint and less manpower for operation. Electrochemical cell contains Proton Exchange Membrane (PEM) based diaphragm, which conducts proton (hydrogen ion). The working principle of electrochemical separation of hydrogen is given elsewhere. The following are the anodic and cathodic reactions



In this process, hydrogen-helium gas mixture is fed at anode compartment of the electrochemical cell. At anode, hydrogen is converted into proton and electron. Proton migrates through PEM whereas electrons are transported through external electrical circuit. At cathode catalyst layer, proton recombines with electron and produce pure hydrogen. Remaining Helium gas leaves the anode compartment, which is quite pure. A typical electrochemical polarization (V-I characteristic) curve from the present study is shown in Figure 13.

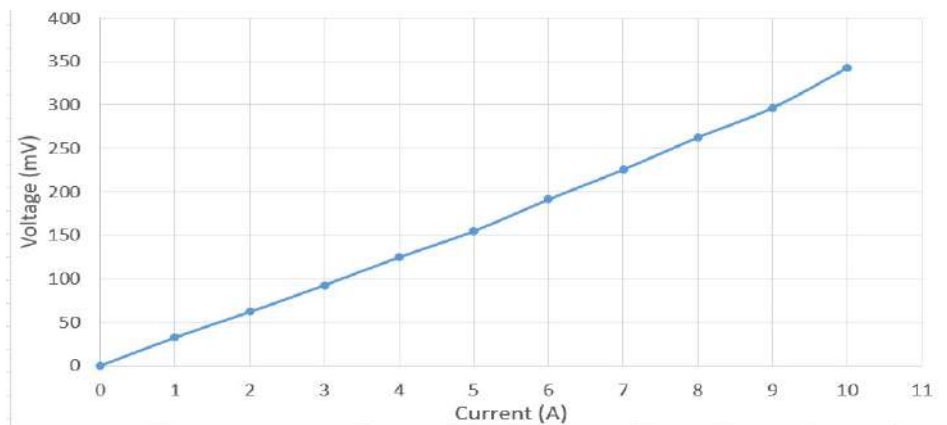


Figure 13: Polarization curve for Hydrogen-Helium separation at 30 °C and 1 atm.

Catalytic Exchange based Isotope Separation processes (LPCE and VPCE)

Liquid Phase Catalytic Exchange (LPCE) and Vapour Phase Catalytic Exchange (VPCE) are two different types of catalytic hydrogen isotope exchange processed between water and hydrogen streams having potential application in the front end of deuterium isotope enrichment cascade for reactor grade heavy water production starting from light water of natural abundance. The heart of both the processes is the deuterium isotope exchange reversible reaction between vapour form of water and gaseous hydrogen.

In LPCE process, the water vapour required for reaction is generated in situ from the feed liquid water inside the packed bed reactor assisted by subsequent step of catalytic exchange reaction with hydrogen gas flowing in counter-current fashion. Whereas in VPCE process, the catalytic exchange reactor is fed directly with water vapour that is generated externally and then made to react with hydrogen gas flowing in concurrent fashion through the column. Platinum supported on porous carbon is found to yield excellent catalytic activities at moderate operating conditions. However, the presence of liquid water results in severe deactivation of the catalyst. Hence, in VPCE process, platinum supported on activated carbon in suitable form could be used whereas in LPCE process, where direct contact of liquid water is present, a suitable hydrophobic binder like PTFE, SDBC, etc. shall be mixed which reduce active metal loading and thereby reduced specific catalytic activity. The isotope exchange reaction taking place between semi heavy water vapour and hydrogen gas is depicted as follows:

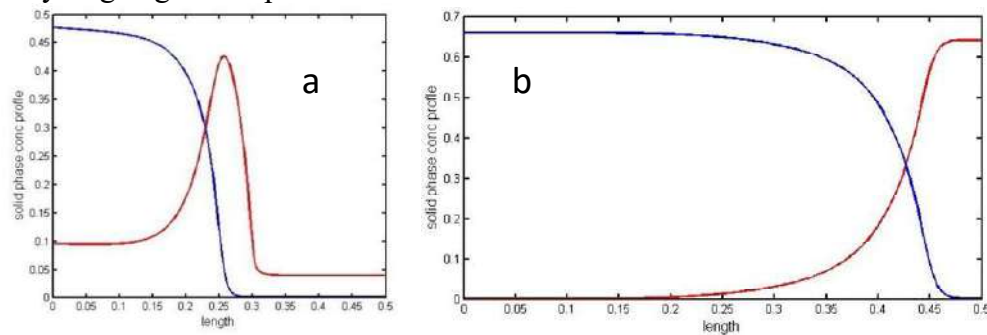
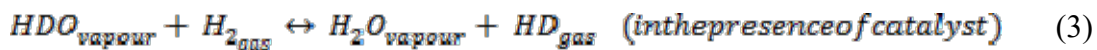


Figure 15: Solid phase conc. profile (H/Pd (blue) or D/Pd(red) at the end of (a) Pressurization step (b) Displacement step



ChEG is actively pursuing the research and development of novel design configurations of multifunctional packed bed reactors and development of high activity hydrophobic catalysts for LPCE and VPCE processes for technologies like in the production of heavy water or deuterium depleted water, normalisation of O-18 enriched heavy water, etc. Novel designs of catalysts based on platinum with different supports like activated carbon and carbon aerogel were considered and extensively studied for coating as bulk catalysts in the form of raschig rings, film coated catalysts on stainless steel Dixon rings and as film coated catalysts on specialized modules of structured packing.



Figure 16: Test facility for LPCE and VPCE experiments

Based on batch and flow reactor experiments, the catalytic activity of each catalyst was evaluated and the reactor bed optimisation was carried out for various operating parameters, with the objective of maximising the key performance indicator of these exchange processes and overall volumetric mass transfer coefficient. A typical variation of individual mass transfer/reaction steps involved in LPCE reactor for a dixon ring catalyst of specific composition is shown in Figure17.

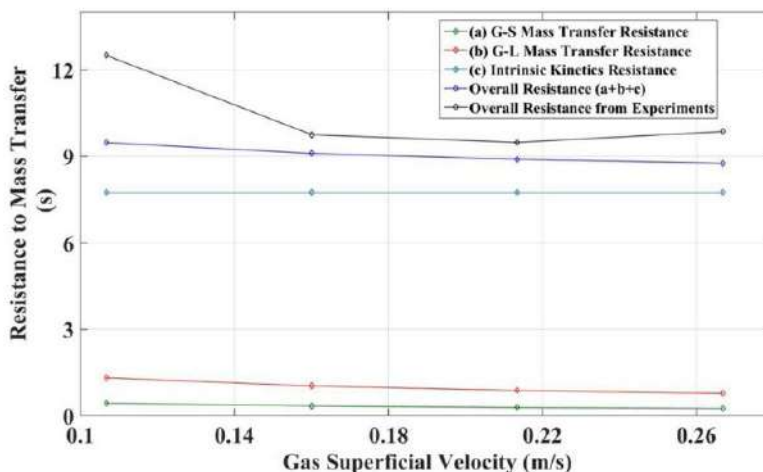


Figure 17: Contribution of resistances of various steps in LPCE Process for a specified catalyst

Metal membranes and membrane reactors for hydrogen production

In thermochemical process or cycle, water is dissociated into hydrogen and oxygen through a series of chemical reactions at comparatively lower temperatures and all the reactants are recycled within the process. Iodine-sulphur (IS) thermochemical process is a promising route of green hydrogen production amongst the various alternatives due to its high thermochemical efficiency and its ability to couple it to high temperature nuclear reactor. Ammonia is primarily used as a hydrogen carrier because it has a high hydrogen content by weight (approximately 17.6%). It can be used to store hydrogen and decomposed at point-of-use to generate hydrogen. Membrane reactor (MR) is a device in which reaction and membrane-based separation takes

place in the same unit. At the reactor level, the membrane can improve the efficiency of the process by selectively transporting one or more of the components from the reaction mixture, thereby enhancing the reaction conversion as well as removing any unwanted by products. Their role is critical in achieving sustainable and economically viable hydrogen production for various industrial and energy applications.

IS thermochemical process for hydrogen production

In the IS thermochemical cycle, HI decomposition is the hydrogen producing step. The equilibrium conversion of HI decomposition reaction is only ~22% at 723 which reduces the thermochemical efficiency. A packed bed single-tube MR assembly was fabricated with integration of the in-house synthesized Ta membrane (Figure 18(b)). The membrane was fabricated by depositing Ta on porous alumina support using DC magnetron sputtering setup (Figure 18 (a)). An enhanced HI to hydrogen single-pass conversion of ~94 % was obtained against the usual equilibrium conversion value of ~ 22 %, with hydrogen production of ~ 8 LPH. Figure 18(d) shows the decomposition setup. Ta-based 4-tube MR (Figure 18(c)) was also developed for HI decomposition studies. A single-pass conversion of ~82% has been obtained at 2 bar of trans membrane pressure. This is the first time a multi-tube MR has been reported for HI_x processing section of IS process.

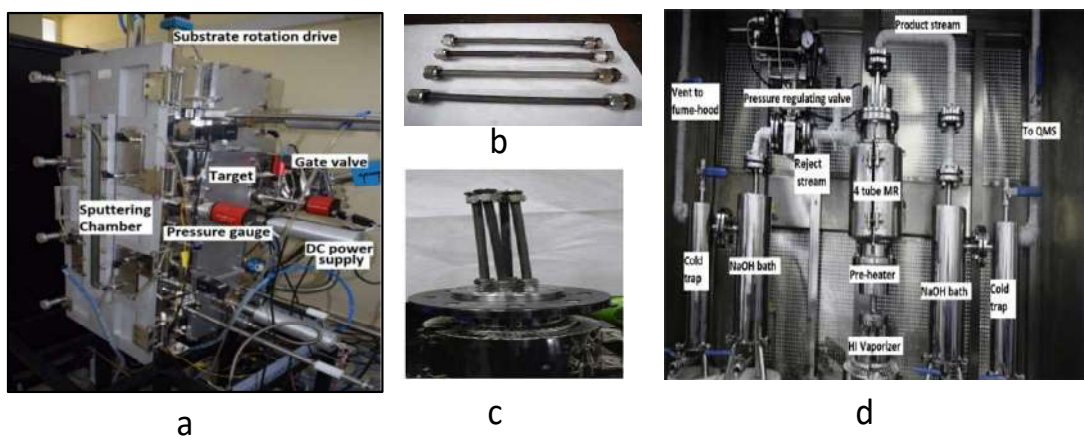


Figure 18: (a) DC magnetron sputtering assembly, (b) Ta membranes, (c) multi-tube MR assembly and (d) HI decomposition setup.

Ammonia cracking for hydrogen production

A ceramic-supported Pd-Ag alloy membrane was fabricated and used for decomposition of ammonia in a membrane reactor. Ammonia decomposition was carried out in packed bed MR (PBMR) at different operating parameters and the experimental results were used for validation of CFD simulations. Experiments were also carried out for a packed bed reactor without membrane. A conversion of ~93% was achieved in PBMR at a temperature of 773 K and 1 bar, as against a conversion of ~80% in conventional reactor. The CFD model was further extrapolated to simulate 3D geometry of multi-tube membrane reactor and effect of various parameters on performance of multi-tube MR were studied.

Development of hollow fibre ultrafiltration membranes

Hollow fibre module configuration appears promising in ultrafiltration membrane applications due to its relatively higher packing density, ease of backwashing, ease of cleaning and lower

pressure-drop, since it can be operated at laminar flow regime with higher cross-flow velocity. Efforts are therefore made to develop hollow fibre membranes suitable for various applications. Hollow fibre ultrafiltration membrane spinning machine (Figure 21) was designed, installed and commissioned for pilot scale production of hollow fibre membrane (Figure 22) with batch capacity of 10 km length. Polyethersulfone based hollow fibre ultrafiltration membrane were developed with ID: 200 μm - 700 μm & OD: 270 μm - 1120 μm . A prototype of hollow-fibre membrane-based water purifying bottle (Figure 23) was designed and fabricated for on-site purification of water. The full unit contains bottle housing, cap, cartridge potted with hollow fibre membrane (id: 200 μm , OD: 330 μm), pressurizing bulb with one way air valve and pressure regulator. The bottle is provided with provision to clean and replace membrane cartridge. In-house developed hollow fibre membranes were potted to make the cartridges and fit into the bottle of capacity 750 ml with pressurising arrangement (upto 1 kg/cm^2). The bottle has been tested to remove turbidity of seawater from > 100 NTU to less than 1 NTU. Microbial load removal with respect to E. coli is 4 log reduction. The bottle can purify with water output of 200 ml in 5 minutes. It's being now commercialised through know-how transfer.



Figure 21: Hollow fibre membrane spinning machine

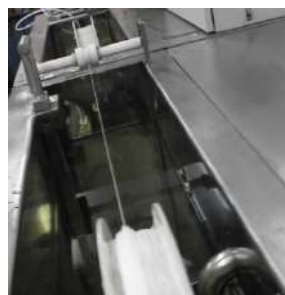


Figure 22: Hollow fibre membrane being spun



Figure 23: Hollow-fibre membrane-based water purifying bottle

Development of ZLD desalination system for recovery of valuable minerals

Currently, recovery of water from conventional desalination process is limited to 30-50%. Remaining 70-50% of the feed water is lost as concentrate, also known as 'brine'. Discharge of brine impact the aquatic environment. Management of brine in a sustainable and environment friendly way is a challenge, particularly in land locked areas. The solution lies in Zero Liquid Discharge (ZLD) desalination. A pilot plant for ZLD desalination system consisting of 10 cu.m/d brine purification unit (Figure 24) is setup followed with 5 cu.m/d brine concentrator unit (Figure 25). Flowsheet has been envisaged for an integrated ZLD desalination system, a multi-step process, consisting of brine purification process to remove scale forming components to avoid scaling threat, followed with concentration of brine to its saturation limit and finally crystallization of saturated brine to recover high purity salt.



Figure 24: 10 cu.m/d Brine Purification System.



Figure 25: 5 cu.m/d Brine Concentrator Unit.

In brine purification process (BPP), calcium and magnesium and sulphate ions are removed from the brine through reactive precipitation process. In the next step, brine concentrator (BC) unit, an indigenously developed falling film evaporator, is used to concentrate the brine up to 22% which is closed to its saturation level thereby minimizes the brine volume and recovers low conductivity distilled water (< 5 micro-Siemens/cm). Production of high purity sodium chloride salts (purity $> 99.9\%$) from the concentrated and purified brine has been demonstrated in lab scale and setting up a forced circulation crystallizer (FCC) unit for demonstration in pilot scale.

Conclusion

Chemical Engineering Group has the unique combination of expertise in separation science which can give holistic solution from concept to commissioning. This is evident from the many difficult separation problems briefly described in the article.

References:

1. Sk. M. Ali, A.Boda, A.K. Singha Deb, P.Sahu, K.T. Shenoy, Computational Chemistry Assisted Design and Screening of Ligand-Solvent Systems for Metal Ion Separation, *Frontiers in Computational Chemistry*, **2017**, Volume: 3 3, 75, Bentham Science.
2. P.Sahu, Sk. M. Ali, K.T. Shenoy, *Physical Chemistry Chemical Physics*, **2016**, 18, 23769-23784.
3. P. Sahu, Sk. M. Ali, K.T. Shenoy, *Computational product and process modelling*, **2017**, 12, 20160024.
4. P. Sahu, A.K. Singha Deb, Sk. M. Ali, K.T. Shenoy, *J. Mol. Liquids*, **2021**, 330, 115621.
5. A. Das, Sk. M. Ali, *Phys. Chem. Chem. Phys.*, **2024**, 26, 6916-6938.
6. R. Natarajan, *Progress in Nuclear Energy*, 2017, 101 Part A, 118-132.
7. K.K. Singh, S.M. Mahajani, K.T. Shenoy, S.K. Ghosh, *AIChE Journal*, **2008**, 54, 42-55.
8. K.K. Singh, S.M. Mahajani, K.T. Shenoy, S.K. Ghosh, *Industrial & Engineering Chemistry Research*, **2007**, 46, 2180–2190.
9. S. Sarkar, K.K. Singh, K.T. Shenoy, *Separation & Purification Technology*, **2019**, 209, 608-622.
10. N. Sen, K.K. Singh, A.W. Patwardhan, S. Mukhopadhyay, K.T. Shenoy, *Separation Science & Technology*, **2018**, 53, 2587-2600.
11. S. Sarkar, K.K. Singh, S.M. Mahajani, K.T. Shenoy, *Solvent Extraction and Ion Exchange*, **2020**, 38, 536-554.

12. N. Sen, K.K. Singh, A.W. Patwardhan, K.T. Shenoy, Solvent Extraction and Ion Exchange, **2021**, 39, 328-352.
 13. N. Sen, K.K. Singh, S. Mukhopadhyay, K.T. Shenoy, Chemical Engineering Communications, **2019**, 206, 1317-1336.
 14. A. Roy, N. Sen, K.K. Singh, K.T. Shenoy, R.B. Grover, Solvent Extraction & Ion Exchange, **2019**, 37, 191-210.
 15. S. Sarkar, K.K. Singh, K.T. Shenoy, Chemical Engineering Science, **2023**, 267, 118240.
 16. R.K. Chaurasiya, K.K. Singh, Chemical Engineering Science, **2022**, 249, 117295.
 17. A. Boda, P. Sahu, AK Singha Deb, and Sk. M. Ali. Separation and Purification Technology, **2022**, 289, 120709.
 18. A.K. Singha Deb, P. Sahu, A. Boda, Sk. M. Ali, K. T. Shenoy, D. Upadhyay. Physical Chemistry Chemical Physics, **2020**, 22, 14682-14693.
 19. A. Boda, A.K. Singha Deb, Sk. M. Ali, K. T. Shenoy, S. Mohan. Molecular Systems Design & Engineering, **2017**, 2, 640-652.
 20. A.K. Singha Deb, M. Manju, A. Sengupta, Sk. M. Ali. Chemical Engineering Journal Advances, **2022**, 11, 100308.
 21. A.K. Singha Deb, V. Dwivedi, K. Dasgupta, Sk. M. Ali, K.T. Shenoy. Chemical Engineering Journal, **2017**, 313, 899-911.
 22. K. C. Sandeep et.al., International Journal of Hydrogen Energy, **2014**, 39, 17906-17912.
 23. A.Monpezat, S.Topin, L.Deliere, D.Farrusseng, B.Coasne, Ind. Eng. Chem. Res,**2019**, 58, 4560-4571.
 24. V. Presser, J. McDonough, S.H. Yeon,Y.Gogotsi, Energy Environ Sci, **2011**, 4, 3059–3066.
 25. W.O. Mara, R.B. Herring, L.P. Hunt, Handbook of Semiconductor Silicon Technology, **1990**.
 26. B. M. Oliver, J.G. Bradley,Harry,Geochim. Cosmochim. Acta, **1984**, 44, 1769–1767, 1984.
 27. M. Rhandi,M.Trégaro, F.Druart, J.Deseure, M.Chatenet, Chin. J. Catal., **2020**, 41, 756–769, 2020.
 28. B.M. Andreev, E.P. Magomedbekov, Sep. Sci. Technol., **2001**, 36, 2027-2086.
 29. B. Reddy, K. Mistry, R. Kumar, S. Mohan, S. Mahajani, Sep. Sci& Tech., **2016**, 51, 784-796.
 30. K. A. Mistry, N. S. Shenoy, K. Bhanja, D. K. Kohli, K. T. Shenoy, Chemical Engineering Research and Design, **2023**, 192, 487-499.
 31. R. Kumar, S. Mohan, S. Mahajani, Industrial & Engineering Chemistry Research, **2013**.
-



Shri K. T. Shenoy joined Chemical Engineering Division of Bhabha Atomic Research Centre in 1988 after completing one-year Orientation Course (31st 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. Currently, he is leading the team in scaling up and technology deployment of green hydrogen production and desalination technologies. He is involved in many safety committees of BARC and AERB. He was designated as Head, Chemical Engineering Division, BARC in Jan. 2013. He took over as Associate Director, Chemical Engineering Group in October, 2020. Currently, he is Director, Chemical Engineering Group since August, 2022.

Advances in Separation Science and Technology in the Back-end of Nuclear Fuel Cycle

Smitha Manohar

Nuclear Recycle Group

Bhabha Atomic Research Centre, Mumbai-400085, India

Abstract

Back end of the nuclear fuel cycle plays a significant role in ensuring sustainability of our Nuclear Power Programme. In this regard, separation science and technology has and will continue to be the mainstay, to achieve the end objectives of the back end. With the induction of varied reactor systems including thermal and fast spectrum, the back end stands poised to evolve strategies that are commensurate with the fuel used. While the near term is dominated by hydroprocessing, induction of pyroprocessing of fuel seems inevitable as we look at Molten Salt reactors and metal fuelled fast reactors. Conversion of process development activities into a deployable technology for the back-end of the fuel cycle calls for multi-disciplinary set of activities culminating in demonstration of the process using actual waste before it is adopted for regular processing. This paper aims to highlight key developmental areas which have not only transformed radioactive waste management today but also holds potential for addressing waste management needs of the future.

Introduction

With more than 5 decades of operating experience, back end of the fuel cycle in the Indian context has matured and well evolved to address the challenges of now and the future of nuclear energy [1].

The application of separation science and technology in the back end started with the basic PUREX process but has evolved over a period of time to address near total separation and higher throughputs of our recycling facilities. India has three such facilities at Trombay, Tarapur and Kalpakkam, respectively (Fig.1) The global challenge of management of high level waste has been addressed in the past decade by the development of partitioning technology that has the potential not only to reduce the waste volumes for disposal but also to yield radioisotopes for societal applications. Demonstration of such technologies are changing the perception of waste to that of wealth. As we deploy this technology on large scale and induct them in our forthcoming back end facilities, we will have the opportunity to accrue the benefits of partitioning strategy and minimize the waste for disposal to a very large extent. Development and plant scale deployment of selective ion exchange resins and other separation modalities are aiding processing of all types of non HLW waste streams ensuring that the overall discharges to the environment has witnessed a steep downward trend over the last few decades. Such indigenous, industrially matured technology is being now extended to set up an integrated nuclear recycle project (INRP) and a Fast Reactor Fuel Recycle Facility (FRFCF) being set up at Kalpakkam (Fig.2) While INRP, Tarapur with a nameplate capacity of 600 Te/year will demonstrate such large scale back end operations in an integrated way, the FRFCF will address the back end needs of prototype fast breeder reactor of our country. This paper will highlight a few key developmental areas which has largely impacted back end of the fuel cycle and are being deployed in the back end facilities of the future.



Fig.1: Indian Reprocessing facilities at Trombay, Tarapur and Kalpakkam



Fig. 2: Upcomming Integrated nuclear recycle project with a name plate capacity of 600 T/year at Tarapur and Fast Reactor Fuel Recycle Facility (FRFCF) at Kalpakkam

Recycling of spent fuel

The well entrenched PUREX process forms the basis of all our recycle facilities. Adopting good practices and incorporation of improved technologies have resulted in sustained higher through puts, increased separation efficiencies and higher decontamination factors resulting in acceptable product quality. The challenging activities with regard to spent fuel handling, head-end operations, dissolution, solvent extraction cycles and final conversions are all carried out in conformity with internationally laid out safety regulations. A few key developmental areas with regard to separation science are listed below.

Although 30% TBP in n-dodecane has been the work horse for such applications, many of the related issues posed problems in regular operation viz, limited extent of evaporation due to presence of organics in aqueous phase and solvent management. Such issues have been addressed appropriately by the use of diluent washes and the alkaline hydrolysis process for the treatment of spent solvent. The diluent thus separated from the alkaline hydrolysis process is recycled back into the facilities leading to resource utilization. In line with the requirement of recycling of other types of fuels in the future, developmental efforts have also been carried out with regard to U/Pu partitioning processes. The conventional U^{+4} process has been upgraded and HAN based processes have also been developed and kept ready for deployment as required in the future.

With superior neutronic and material properties along with advantage of lower production of long-lived actinides, Th -U fuel has attracted the world towards its utilization for nuclear energy. The Indian three-stage nuclear power programme envisages a largescale utilization of thorium due to its abundant availability, while uranium resources in India are limited. For a complete understanding of the Thorium cycle, laboratory studies were carried out to establish processing of irradiated thorium to recover ^{233}U and ^{232}Th and recycle these to the reactor. Thorium rods irradiated in a research reactor were successfully processed at the Uranium Thorium Separation Facility (UTSF). With know-how gained from the UTSF operating experience, processing of Thorium bundles irradiated in power reactors (PHWRs) was successfully demonstrated at Power Reactor Thorium Reprocessing Facility (PRTRF) (Fig.3). The challenges like inertness of sintered Thorium for chemical dissolution, radiological hazards due to presence of ^{232}U contamination in ^{233}U , safe handling of highly dispersive gaseous decay product Radon-220 (Rn) during processing and increasing dose of ^{228}Th containing raffinate during its interim storage were successfully addressed at PRTRF.



Fig. 3: Power Reactor Thorium Reprocessing Facility, (PRTRF), Trombay

Generation of radioactive waste and their characteristics

During the initial stages of our programme, various wastes emanating from reprocessing operations were classified based on their activities as low level, intermediate level and high level waste. While a few separation techniques like co-precipitation and adsorption were envisaged for low level waste, by and large it was decided to immobilise intermediate level waste in cement matrix and high level waste in glass matrix. Immobilisation of waste in cement matrices is known to increase the waste volumes for disposal. In this regard developmental efforts were focused to the identification of selective ion-exchange resins. As a culmination of such efforts, resins like resorcinol formaldehyde and IDA were formulated and synthesised indigenously. The various challenges with regard to industrial manufacturing of such resins on large scale were

successfully addressed, resulting in deployment of such ion-exchange treatment processes for Intermediate level waste. The present status of such plants are that they treat about 1000 m³/year and are found very robust with regard to plant applications. The result of such a treatment process is the multifold reduction in waste volumes for disposal in Near Surface Disposal Facilities. With regard to low level treatment, it has been observed that a combination of separation steps including Chemical Treatment, IX and membrane based processes can lead to a substantial reduction in discharges in line with ALARA. With the development and deployment of partitioning strategy, we are close to realising our goals with regard to a substantial reduction in waste volumes for final disposal.

Management of low-level liquid waste

The low-level liquid waste generated in nuclear facilities is relatively clean having a very low concentration of radionuclides but their volumes are significantly large. The complexity of the LLW stream is highlighted by the fact that it is received from multiple facilities. Even within a facility, widely differing streams ranging from process condensates, decontamination effluents, potentially active effluents, chemical wastes etc are generated. Hence, a process which is rugged in nature needs to be employed for this stream. The broad characteristics of the LLW are given in Table 1.

Table 1: Typical LLW Characteristics

Parameter	Value
Generation rate	50 to 1500 m ³ /day
pH	8-10
Gross β	10^{-5} to 2×10^{-2} mCi/L
Total Solids	Upto 1000 mg/lit

The gross beta activity contributors are predominantly due to ¹³⁷Cs and ⁹⁰Sr. In some cases, particularly, the effluent generated from the treatment of ILW, has contamination of other radionuclides such as ¹⁰⁶Ru, ¹²⁵Sb and ⁹⁹Tc. Therefore, treatment of the LLW demands highly efficient processes for separation of the radionuclides to the extent of meeting stringent regulatory limits for environmental discharge. Indeed, initial R&D activities had resulted in selection of a robust treatment process viz., chemical co-precipitation for achieving initial aim of meeting discharge limits. This process has been observed to be quite successful for LLW upto 15 Bq/mL. It has the advantage of customizing the process based on the feed composition and thus can cater to varied feed composition. Recent R&D focused on near-zero discharges is quite successful by invoking a combination separation technique such as ion exchange in conjunction with chemical precipitation. Particularly, an ion exchange system comprised of 500 L columns filled with synthetic zeolites 4A has been made operational at ETP, Trombay for the separation of ¹³⁷Cs and ⁹⁰Sr respectively (Fig.4).

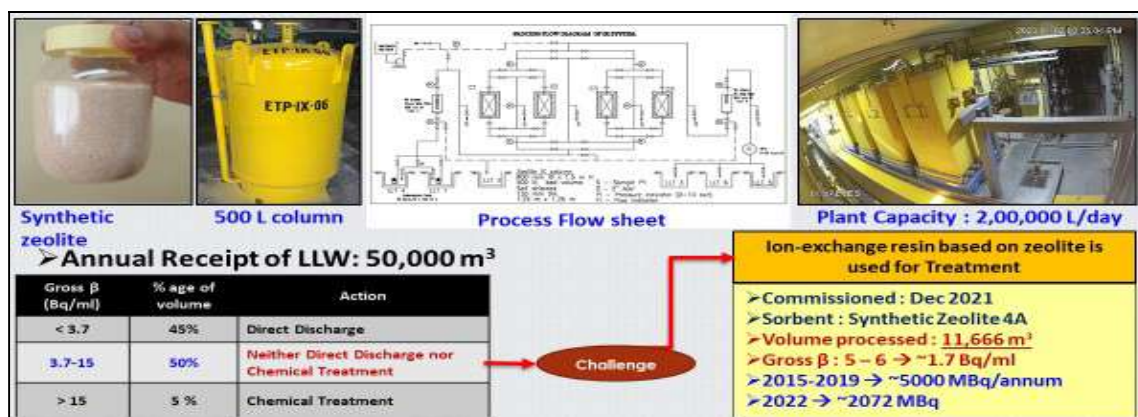


Fig.4: Zeolite based ion exchange system operational at Effluent Treatment Plant, Trombay

Adaptation of the polishing scheme helped to reduce discharges significantly. R&D is underway to develop more efficient sorbents for separation of Cs and Sr. Membrane-based processes have been tested on pilot-scale and found to be suitable for relatively “clean” waste streams i.e. streams devoid of salts of Ca, Si and organics. Further R&D is required to be pursued to develop “rugged” membranes to cater to LLW streams to achieve “Near-Zero Discharges”

Management of intermediate-level liquid waste

The intermediate-level liquid waste (ILW) which is generated during volume reduction of HLW by evaporation is mildly acidic and contains only a fraction of the radionuclides. Historically, it was neutralized by addition of NaOH and Na₂CO₃ for economic storage in carbon steel tanks. In recent times, the ILW as generated is stored in SS tank.

Separation of ¹³⁷Cs & ⁹⁰Sr

Alkaline Intermediate waste (ILW) typically has an activity ranging from 5 – 20 mCi/L, mostly contributed by ¹³⁷Cs and traces of ⁹⁰Sr, ¹⁰⁶Ru and ⁹⁹Tc and it contains as high as 200 g/L of inactive salts. In comparison to HLW, the volumes of ILW are significantly higher and the radioactivity contents are about 3 orders of magnitude lower. Towards efficient management of the waste streams, it is desirable to separate the radionuclides into a small volume and the large volumes of decontaminated effluent should be amenable for discharge to the environment. Generally, for the treatment of ILW, selective separation of radionuclides by ion exchange-based processes is found to be more suitable due to a combination of factors like high decontamination performance, high (DF), generation of low volumes of secondary waste leading to appreciable volume reduction factor (VRF), operational simplicity, and ruggedness.

In India, the selective separation of ¹³⁷Cs and ⁹⁰Sr is accomplished by an ion exchange process utilizing Resorcinol Formaldehyde, resin and commercially available Imminodiacetic acid resin, respectively. The Resorcinol Formaldehyde (RF) resin developed indigenously is known to have very high selectivity for Cs under these conditions. This distribution coefficient for Cs is as high as 10, 000 mL/g in presence of 4 M Na ions, which indicates a large volumes of waste can be treated with a small amount of the resin. Further, loaded Cs can easily be eluted in dilute HNO₃ and the resin is amenable for use in loading–elution mode. The process was deployed at plant scale initially at WIP, Tarapur and thereafter implemented at Trombay and Kalpakkam for the management of ILW (Fig.5). The Imminodiacetic acid resin (IDAR) also possesses weakly

acidic groups that ionise and participate in ion exchange reactions. The selectivity of the resin for Sr is also quite high owing to the formation of a chelate complex. In this case, also, the Sr can very easily be eluted using dilute acid. Owing to the similar loading-elution condition, the separation of Sr is being carried out using a column in series along with Cs.

Decad waste solution generated from chemical dissolution of Aluminium clad fuel also falls under the category and is being successfully treated using the system. The noteworthy observation is that the presence of substantial amount of aluminium in solution has no effect on ion exchange performance, indicating the experience gain from here will be used for the management of Aluminium bearing waste streams arising from dissolution of futuristic Aluminide fuels.

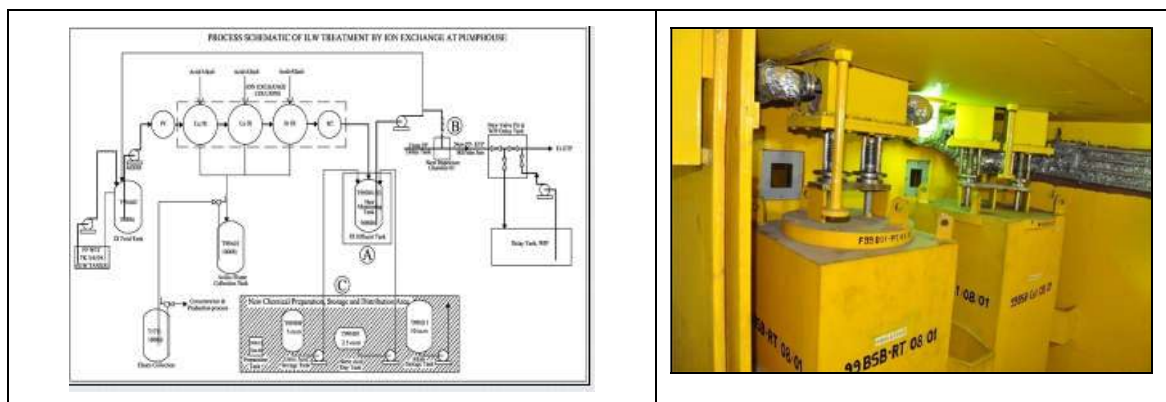


Fig. 5: Process flowsheet and actual in cell view of Pump House Ion Exchange (PHIX) system

Separation of ^{99}Tc

^{99}Tc is a rare element, produced only in nuclear fission reactions and it is present in the nuclear waste as TcO_4^- ion. It is a low-energy beta emitter (290 KeV) but a long-term contributor to environmental hazards owing to its very long half-life (2.13×10^5 years). It is the primary activity contributor in the ILW effluent obtained after ion exchange separation of ^{137}Cs and ^{90}Sr . Extant processes for ^{99}Tc sequestration include ion exchange, precipitation and solvent extraction-based processes. However, the volume of sludge generation and secondary waste management becomes challenging in such cases. Recently, a novel reduction and mineralization process utilizing the corrosion products of mild steel (MS) wool has been developed and patented [2]. In brief, MS wool is taken in a reactor and waste after adjustment to pH 2 fed to the reactor. The system is kept under continuous air sparging conditions for about 8 hours and then allowed to settle. During the process, Tc(VII) is reduced to Tc(IV) and incorporated into the crystal lattice of iron oxides or oxy-hydroxides such as goethite or magnetite. The in-situ mineralization of the radioelement helped complete the decontamination of the waste and generated a very low volume of the sludge. As an added advantage, co-decontamination of ^{106}Ru and ^{125}Sb also occurs during the process. A pilot-scale facility at NRB, Tarapur is set up and made operational for the routine sequestration of the radioelement. Notwithstanding, separation of ^{106}Ru and ^{125}Sb from low and intermediate-level waste remains a challenging task and is attributed to the complex aqueous chemistry of these radioelements.

Management of high-level waste

Conventionally, HLW is immobilized in a vitreous matrix, and stored in an air-cooled vault for an interim period to remove the decay heat before its final disposal in a geological repository [3]. However, the Partitioning & Transmutation (P&T) strategy is perceived as a step in the direction of reducing the waste for final disposal. In this regard, the partitioning step is well recognized as the first approach towards the goal of reduction in radio-toxicity. The first industrial experience in setting up and operation of a completely indigenous Actinide Partitioning Demonstration Facility (ASDF) at Tarapur in the year 2013 has paved the way for this strategy to be inducted into our back-end plants[4-5]. The second such facility was set up and commissioned in 2015 at Trombay, which has not only led to separation of radionuclides from the inactive content of HLLW but has also made it possible for the use of few of the radionuclides for societal applications. Important among them are ^{137}Cs , which is separated and converted to glass pencils for its use as blood irradiators and ^{90}Sr , which is purified further and milked for ^{90}Y , which is being used for therapeutic application as ^{90}Y -acetate. Very recently, ^{106}Ru separated from waste has also been used for preparation of eye plaques for treatment of eye-cancer with very positive feedback. The ^{241}Am separated from the ASDF demonstration trials, is presently being envisaged to be used for the transmutation experiments using fast neutron spectrum. The smooth and uninterrupted operation of both these facilities have strengthened our knowledge base for extending such technologies to more of our plants including that at Kalpakkam in the near future.

HLLW Partitioning program in India

A three-cycle, solvent extraction-based Actinides separation demonstration facility (ASDF) was set up at SSSF, Tarapur [Fig.6a]. The plant demonstrated bulk separation of actinides along with rare earth followed by separation of trivalent actinides from the lanthanides. **Table 2** gives the details of solvents deployed for three different cycles of ASDF.

Table 2: Solvent systems deployed at ASDF, Tarapur

Solvent Extraction	Objective	Solvent deployed
Cycle 1	U separation	30% TBP in n-Dodecane
Cycle 2	Actinide + Rare Earth bulk separation	0.2 M TEHDGA in 30% IDA in n-dodecane/ DTPA+ lactic acid as strippant
Cycle 3	Actinide – Lanthanide separation	0.4 M D2EHPA in n-dodecane

In the first cycle, residual Uranium and Plutonium are recovered from HLLW. The second cycle is aimed at bulk separation of Actinide-Lanthanides. This has been accomplished by employing N,N,N',N'-tetra-2-ethylhexyl diglycolamide (TEHDGA) in isodecyl alcohol-n dodecane. TEHDGA exhibits very high distribution values for Am(III) under HLW acidity conditions ($D_{\text{Am}} > 100$). The high extraction of Am(III) at 3-4 M acidity and gradual decrease in the D_{Am} values at lower acidity (between 2M HNO_3 to pH 2) makes it very promising for the partitioning of actinides from HLW solution. It may be noted that TEHDGA extracts lanthanides and actinides together, owing to their similar valence and chemical properties and therefore it

necessitates separation of minor actinides and lanthanides. Among the minor actinides, ^{241}Am is considered a prime candidate for partitioning and transmutation because it is present in relatively large amounts and is a major contributor to radiotoxicity.

In the Third Cycle at ASDF, ^{241}Am was separated by deploying a modified TALPEAK process. This process involves using 0.2 M D2EHPA (Di-2-ethylhexyl-phosphoric acid) in n-dodecane to selectively extract the lanthanides from an aqueous phase comprising of 0.05 M DTPA – 1 M Lactic Acid adjusted to pH ~ 2.6 which retains the Am(III). Further by adopting an appropriate polishing process followed by a reconversion step leading to obtaining AmO_2 having an acceptable level of β - γ contamination (of < 3 mCi/g of product) is obtained. The ^{241}Am separated from the ASDF demonstration trials, is presently being envisaged to be used for the transmutation experiments in a fast neutron spectrum and alternatively, as a heat source /RTGs.

In view of first time demonstration of partitioning technology, various features have been provided right from design stage to overcome unexpected challenges. Design provisions were made to address the uncertainties with regard to separation process. Recycle provisions were inbuilt in the system to ensure product purity with high decontamination factors. An elaborate solvent management provisions was worked out and incorporated leading to handling of multiple organic systems in the same cell. Focused attention was also given to secondary stream management including spent solvent streams.

Air lift-based mixer settler units were selected as extraction equipment (Fig.6b) for the partitioning facilities as it imparts many benefits and better suits to desired applications. Air lift-based mixer settler unit gives flexibility in terms of number of stages for extraction, large range of organic to aqueous (O/A) ratios and flow rates, and also enable handling of varying densities of streams etc. Besides this, mixer settler unit does not require hot-cells having higher head room, as in case of air pulsed column, and helps in designing compact hot-cells. This further strengthens the selection of air lift-based mixer settler unit for said applications of extraction process. With the aim of eliminating all moving/maintainable parts of the mixer-settler, the agitator of conventional mixer-settler unit is replaced by an innovatively designed static mixing element CALMIX (Combined AirLifting and MIXing), which uses air to create high turbulence effecting the intimate contact of the two phases i.e., aqueous and organic. The CALMIX has three identical square cross-section flow channel. One of them is the organic downcomer, which facilitates taking organic from top from previous settler irrespective of interface position. The other two flow channels are two identical annular flow path airlift created by locating airline at the center of flow channel. Both flow-channels get combined in the upper part of the mixing element which is similar to a vent pot with two inputs. This part is called mixing zone, where intense mixing takes place and the mixed phase along with air, are discharged through suitably sized holes provided in this region. As the energy for dispersion is supplied in the form of air, the liquid droplets do not experience shear and hence are easy to coalesce, resulting in a more compact settler design. The required contact time and the physical characteristics of the two phases form the design basis for the mixing element. The corresponding settlers are designed in a conventional manner. These units are provided with end-settlers to take care of any entrained phases in the terminal streams.



Fig.6 : (a) Actinide separation demonstration facility, Tarapur (b) Air lift-based mixer settler unit utilized for the partitioning of HLW

After the successful demonstration of partitioning facility at ASDF, Tarapur, another such facility has been set up and operated successfully at Trombay. In Trombay also, a three-cycle based solvent extraction processflowsheet has been implemented with the major thrust to address separation of inactive components of waste from the radioactive elements, thereby precluding unwanted loading of vitrified glass with inactive components of waste. In contrast to Tarapurflowsheet, the 2nd cycle of Trombayflowsheet is aimed at a new solvent extraction-based separation process for the recovery of ¹³⁷Cs. **Table 3** gives the details of solvents deployed for three different cycles of the solvent extraction system, Trombay.

Table 3: Solvent Systems Deployed at Solvent Extraction System, Trombay

Solvent Extraction	Objective	Solvent deployed
Cycle 1	Uranium separation	30% TBP in n-Dodecane
Cycle 2	Cesium separation	0.03 M Calyx Crown 6 (CC6) in 50% IDA in n-dodecane
Cycle 3	Strontium, Actinide & Lanthanide separation	0.4 M TEHDGA in 15% IDA in n-dodecane

Recovery and utilization of ¹³⁷Cs

In 2nd cycle of Trombayflowsheet, an indigenously developed novel solvent, 1,3-dioctyloxycalix[4]arene-18-crown-6, abbreviated as Calix Crown 6 has been employed for the recovery of ¹³⁷Cs. The solvent in *n*-dodecane modified with isodecyl alcohol exhibits an exceptional selectivity for Cs over other alkali metal ions, thereby very effective in producing purified ¹³⁷Cs from high-level waste. The effectiveness of the process is well demonstrated with actual HLW of reprocessing origin having an acidity of 3.5 M nitric acid and 1.8 Ci/l of ¹³⁷Cs. Almost 99.97 % of Cs were extracted and quantitatively stripped using 0.01 M nitric acid. More than 5 lakh Ci of ¹³⁷Cs have been separated from the high-level waste.

In the third cycle, a combined separation of Strontium-Actinide-Lanthanide is accomplished by employing 0.4 M TEHDGA in 15% IDA-dodacane solvent system. The separated Sr-An-Ln

stream from HLW has paved the way for the recovery of Sr in pure form and is being used in radiopharmaceutical applications as discussed below.

In summary, both the partitioning facilities have been operated successfully with actual HLLW demonstrating the partitioning technology at an engineering scale. ASDF, Tarapur demonstrated the partitioning of minor actinides from HLLW by treating few tens of m³ of HLLW for recovery of minor actinides of desired purity. The solvent extraction-based pre-treatment system at WIP, Trombay enabled effective treatment of more than 100 m³ of HLLW with recovery of ~ 0.5 million Ci of Cs-137 and multifold reduction of vitrified waste volume to save precious repository space (Fig.7 and 8) Success of partitioning technology paves the way for their deployment as a pre-treatment step for facilities managing HLLW generated from the reprocessing of power reactor spent nuclear fuel leading to a significant reduction of radiotoxicity. Further focused efforts are also being directed towards secondary waste stream management including solvent management. Alternate and improved solvent systems are also being researched, especially for addressing the challenging task of An/Ln separation.

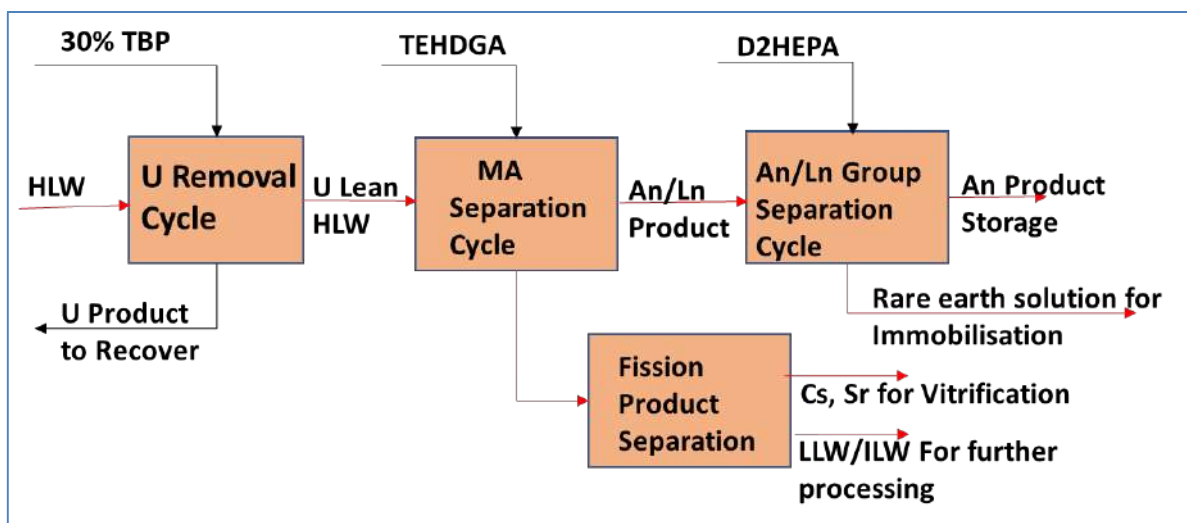


Fig 7 Proposed Partitioning Flowsheet for HLLW from power reactor fuel reprocessing

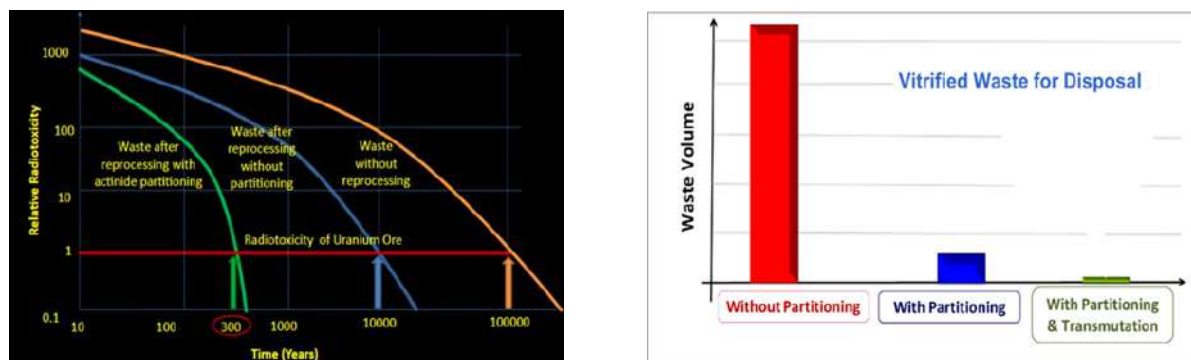


Fig.8: Benefits of Partitioning system deployment (a) Reduction in radiotoxicity (b) Waste volume minimisation for final disposal of vitrified waste

In addition, it paved the way for utilization of the radionuclides in various societal applications. For example, ^{137}Cs is useful as an irradiation source in place of ^{60}Co in many applications. In fact, the recovered ^{137}Cs have been used for the fabrication of sources for blood irradiators after incorporating it in non-leachable glass form. About 30 blood irradiators have been fabricated and are being used in various hospitals. Similarly, ^{90}Y , the daughter product of ^{90}Sr , and ^{106}Ru are being used in medical applications as discussed below.

Recovery and utilization of ^{90}Y

The separation of ^{90}Sr is another important milestone achieved recently. From the TEHDGA strip product as discussed above, ^{90}Sr was further separated in radiochemically pure form and used for milking its daughter, ^{90}Y , for use as a radiopharmaceutical in treating liver cancer and neuroendocrine tumours. The most important challenge in this separation is to achieve desired radiochemical purity as it is intended to be used in in-vitro therapeutic applications. The process adopted for separating ultrapure ^{90}Sr envisages a multistep separation technique using solvent extraction, extraction chromatography, radiochemical precipitation and membrane separation. ^{90}Y is regularly milked from purified solution of ^{90}Sr solution using two stage Supported Liquid Membran (SLM). The separated clinical-grade carrier-free ^{90}Y is being supplied to the Radiation Medicine Centre (RMC), Parel, for cancer therapy.

Recovery and utilization of ^{106}Ru

^{106}Ru (half-life of 368 days) present in the HLW is a beneficial fission product for brachytherapy applications, particularly eye cancer treatment. The high energy beta radiation emitted from its daughter ^{106}Rh is used for this purpose. In India, recovery of ^{106}Ru is carried out from raffinate obtained after the three-cycle solvent extraction process, as discussed above. The process utilizes the oxidation of Runitrosyl nitrate to RuO_4 by adding KIO_4 followed by its extraction in chlorinated CCl_4 (Fig. 9). The extracted RuO_4 then recovered back by reductive stripping using Hydrazine solution. The separated ^{106}Ru is then used to prepare the brachytherapy sources. Technology for manufacturing of brachytherapy sources has been established and about 30 plaques have been supplied to various hospitals. These plaques have been used successfully to treat more than 150 treatments.

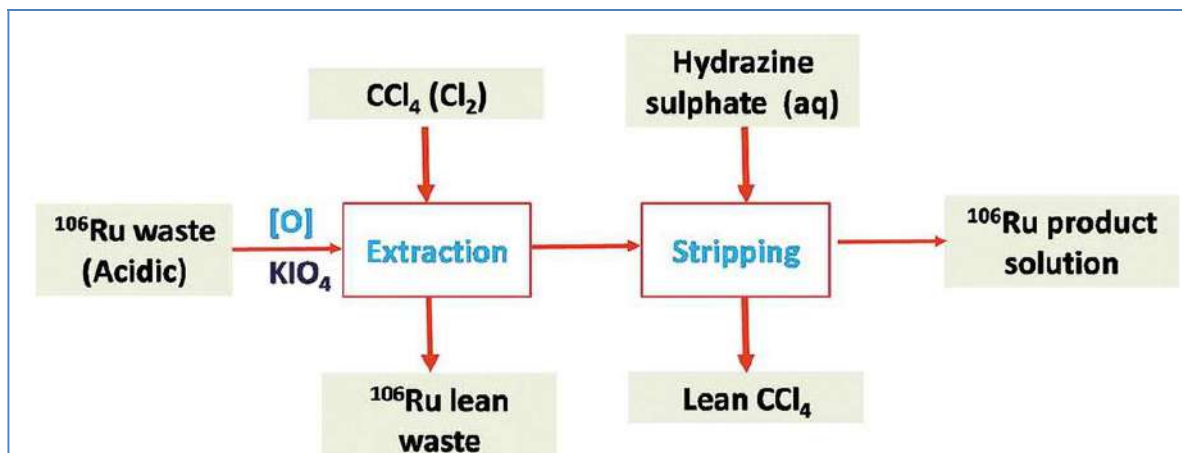


Fig.9: Separation of Purified ^{106}Ru from acidic solution

R&D activities at the laboratory

Process development for the separation of actinides from lanthanides

Though both partitioning facilities are being successfully operated and meet the design objectives, sufficient scope exists to improvise processes and in particular, for the separation of actinides from lanthanides. For example, the separation factor achieved for Am(III)-Ln(III) separation by the TALSPEAK process is 10-15 and the process requires rigid pH control within a narrow pH range. Also, the dissolution of DTPA and subsequent pH adjustment results in a high salt-loaded aqueous stream, complicating secondary waste management.

Further R&D works are being directed to produce high-purity actinides products. Towards this, a novel solvent, Camphor-bistriazinyl pyridine has been developed. The laboratory-scale evaluation of the solvent shows good promise for the separation of the chemically pure ^{241}Am . The high efficacy of the solvent has been experimentally verified with the achieving of a separation factor ($^{241}\text{Am}/^{155}\text{Eu}$) of about 100. In addition, the feasibility of using the solvent in chromatography column mode and direct separation of ^{241}Am from HLW is being explored.

Recovery of ^{90}Sr for utilization as heat source

Development of a novel solvent, 4,4', (5')-di-(t-butylcyclohexano)-18-crown-6, is being pursued with the emphasis on bulk scale separation of ^{90}Sr from HLW. The solvent has a significantly higher Sr extraction ability which can be attributed to the combined effect of better size matching and higher charge density to the crown oxygen due to the presence of cyclohexano moieties. Further, stripping of Sr from the organic phase can easily be carried out using dilute HNO_3 . Successful development of the process meets requirement of ^{90}Sr for utilization as a heat source for RHU and RTG and also for fabrication of beta battery.

Decontamination Reagents and specific extractants

Development of specific reagent/processes for the decontamination of metallic surfaces is gaining renewed interests in view of the overgrowing applications of radioactive processes and also for the management of ageing process equipments/plants. It can be noted that decontamination of metallic surfaces which has been used over the years need strong reagents to remove adsorb/absorb radionuclides from the surfaces. Most of the occasions, the radionuclides have been found to be migrated to few microns through grain boundaries and therefore calls for removal of the surface layer to dislodge the radionuclides. Keeping these in mind, $\text{Ag}^{++}/\text{Ag}^+$ and $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox based processes are being evaluated for the said applications. Both the redox coupled system have very high oxidation potential and also have high capability for removal of surface layers with high corrosion rates.

Recently, Cerium(IV) based metal decontamination process was demonstrated at engineering scale using the GB-representative SS304L components. A reactor involving the in-situ regeneration of Ce(IV) by ozone was employed for treating about 3 kg of SS304L components using ~ 0.4 M Ce(IV) solution in 4 M HNO_3 for 3 hours. During the test, Ce(IV) concentration profile was kept constant by employing suitable ozone inputs to keep effectiveness of the system unchanged. Despite of the irregular shape of the components, uniform the corrosion attack corresponding to about 15 micron removal of the top surfaces was observed (**Fig.10**), indicating high potential of the process for the decontamination of metallic surfaces.



Fig. 10 :Decontamination of metallic surfaces using $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox system

Conclusions

The initiation of Research & Development activities at the inception of the atomic energy program helped India to be self-reliant. Successful development of back-end fuel cycle activities both from separation science and technologies came up simultaneously and contributed immensely towards achieving sustainable development of nuclear energy program. Sufficient scope exists to improvise processes and technologies with innovative approaches for significant reduction of the radiotoxicity and hazard posed by radioactive substances to humans and the environment. Indeed, ongoing R&D activities in laboratories will bring many innovations and provide uninterrupted support towards fulfilling the ambitious nuclear energy program that has been laid down to meet energy demand for new India.

Acknowledgements

This article is the result of intensive and dedicated efforts of a large number of scientists and engineers working over six decades in the Nuclear Recycle Group. I would like to thank each of them for their contribution to the department.

References

1. A.N. Prasad, S.V. Kumar, Fuel Reprocessing experience in India, Int. Conf on Nuclear Power Experience, Vienna, 1982), Vienna (1983), 831
2. Process for the removal of ^{99}Tc from liquid intermediate level waste of spent fuel reprocessing J G Shah, S Pahan, A Ananthanarayanan, US Patent 10553324, 16076523 (2020).
3. C.P. Kaushik, Indian Program for Vitrification of High Level Radioactive Liquid Waste, Procedia Materials Science, Volume 7, 2014, Pages 16-22.

4. Smitha Manohar, J.N. Sharma, B.V. Shah & P.K. Wattal, Process Development for Bulk Separation of Trivalent Actinides and Lanthanides from Radioactive High-Level Liquid Waste. Nuclear Science and Engineering, 156(1), 96–102.
<https://doi.org/10.13182/NSE07-A2688>
5. Smitha Manohar and U. Dani, Partitioning Of High Level Liquid Waste : Operational Experience and the Way Forward, BARC Newsletter, Jan-Feb 2022.



Smt. Smitha Manohar, Director Nuclear Recycle Group, BARC, is a Chemical Engineer from the 30th batch of BARC Training School. She joined the Bhabha Atomic Research Centre in the year 1987 and has more than 35 years of experience in the field of Back End of the Nuclear Fuel Cycle. She has a wide experience in developing and deploying innovative processes in the back end leading to both waste minimization and value recovery. As a lead person in shaping of the partitioning programme of our country, her contributions have resulted in demonstration of partitioning processes which is resulting in separation of valuable radionuclides for societal benefits and also in waste volume reduction. Among other award, she is the recipient of the prestigious Homi Bhabha Science and Technology Award for the year 2018.

Development of Scalable Solvent Extraction Technologies for Separation and Purification of High Purity Individual Rare Earths from Primary Resources and Secondary resources

D. K. Singh, K. K.Yadav, M. Anitha, A. Awasthi, R. Tewari

Materials group,
Bhabha Atomic Research Centre, Mumbai – 400085

B.R.Mishra, D. Singh
IREL (India) Limited

Abstract

The increasing demand for rare earth elements (REEs) in high-tech applications, particularly in green technologies, necessitates advanced separation and purification methods. This paper describes the development and optimization of scalable solvent extraction (SX) technologies for the separation of high-purity individual rare earth oxides from both primary (monazite) and secondary (e-waste) sources. The Materials Group at BARC, in collaboration with IREL (India) Limited, has pioneered processes employing organophosphorus extractants like DEHPA and EHEHPA to achieve the desired purity levels. Key innovations include development of dual cycle SX process comprising multi stage counter current mixer settler assemblies for effective separation and recovery of high purity rare earths such as yttrium, neodymium, gadolinium, terbium and dysprosium from mineral /concentrates. Overall recovery of rare earths in each case was always >97%. Additionally, a hydrometallurgical process for recovering REEs from Nd-Fe-B magnet scrap is discussed, emphasizing its efficiency and environmental benefits. These technological advancements not only ensure a sustainable supply of critical materials but also address the environmental challenges posed by e-waste.

Introduction

Rare earth elements are increasingly in demand globally for critical and strategic uses in most high-tech gadgets, from advanced military technology to mobile phones. Ever increasing demand of rare earths utilization in green technologies such as electronic car batteries, solar panels, wind turbines made the prospect of rare earths pivotal as there is no substitute. The development of rare earths industry has special significance to India both for strategic and commercial interest, because of availability of rich resource of monazite mineral which is estimated to be about 13 million tons. IREL (India) Limited processes monazite (a source of rare earths, thorium and uranium) to separate rare earths from thorium and uranium. The rare earths are fractionated into three groups namely light rare earths (LRE), middle rare earths (MRE) and heavy rare earths (HRE) by solvent extraction employing organophosphorous based extractants DEHPA(di-2-ethyl hexyl phosphoric acid) or EHEHPA (2- ethyl hexyl phosphonic acid mono 2-ethyl hexyl ester). The core program on rare earths of Materials Group, BARC in hydrometallurgy is the development of process flow-sheet for the separation of high purity individual rare earth oxides from primary and secondary sources. Innovative approach of solvent extraction based process flow-sheets (technical know-how) for the production of high purity

oxides of yttrium, dysprosium, gadolinium, terbium, neodymium and praseodymium from crude LRE/MRE/HRE concentrates is described in section 1 of this paper.

This paper also throws light (section 2) on recent progress in the field of end of life e-waste recycling, particularly rare earth elements. Recycling provides a sustainable alternative by conserving these valuable elements, reducing reliance on primary mining operations. In addition, electronic waste, including products containing rare earth elements, represents a significant environmental challenge. Once oxides are produced, they are used either as such or converting them to metals, alloys, permanent magnet depending upon the requirement in various sectors.

1. Methodology of REE separation and brief description:

Separation of rare earth elements with similar chemical properties and having low separation factor is a challenging and a vexed problem. Further producing high purity (4N) of heavy rare earths present in ppm level in Monazite requires careful optimization and development of scalable technologies. Solvent extraction (SX) technology is work horse in separation of rare earths. Basic approach is adopted to selectivity separate one rare earth after another by SX using organophosphorus extractant (D2EHPA or EHEHPA) while producing by product which forms feed stock for further separation. The approach to produce the individual high purity rare earths employing in multi stage mixer settlers assemblies are identical, but optimization of process variables differ considerably with feed source, product specification, chemistry of leach solution, presence of anions in feed, its acidity, concentration of metal ion etc. The sequence of extraction of rare earths with D2EHPA/EHEHPA is: La < Ce < Pr < Nd < Sm < Eu < Gd < Tb < Dy < Ho < Y < Er < Tm < Yb < Lu. The general separation scheme to produce individual high purity rare earth oxide which are developed at BARC and practiced at IREL is shown in Fig.1. Yttrium oxide (99.99%) is separated from HRE concentrate in a two cycle SX process. This generates a by-product of Dy concentrate (~70%), which is purified to ~99% dysprosium oxide in another SX process flowsheet. Dy purification circuit generates a Tb rich by-product and Tb purity is enhanced >99% in another SX circuit

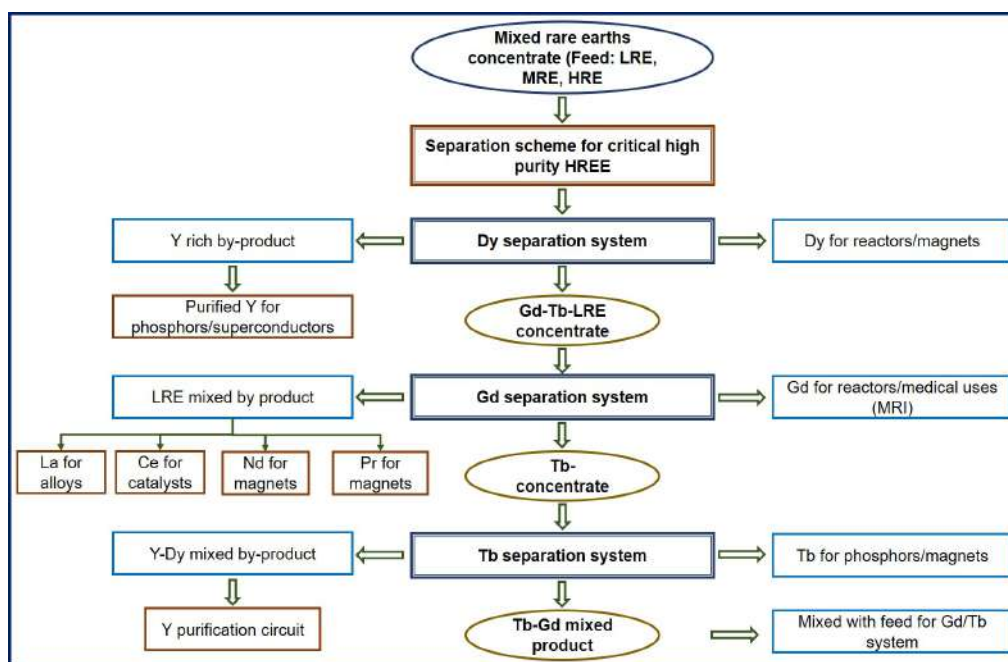


Fig.1: Paradigm of rare earth separation

Solvent Extraction Process flow-sheets development for the production of high purity critical heavy rare earths at IREL Plant

a) Dual cycle SX process for Yttrium purification:

HRE concentrate of monazite processing is feed for yttrium purification by SX employing two cycles using EHEHPA and Aliquat336 (quaternary ammonium salt). Under optimized conditions in first SX cycle EHEHPA extracts most of the heavy rare earth excluding Dy. Loaded organic is back extracted and strip solution is fed to second cycle SX circuit with Aliquat336 as extractant. Aliquat336 as extractant, when operated in thiocyanate medium gives preferential separation of other HRE over Yttrium. The purity of yttrium oxide obtained in second cycle is >99.9%. The optimized conditions for both the cycles are shown in yttrium purification flow-sheet (Fig.2) and product samples are shown in Fig.3. The careful optimization of process variables allows the flexibility to operate the second cycle counter current SX process with 60% to 80% Y feed solution to produce 99.99% pure Y_2O_3 without any process related with over all yield or recovery of yttrium to >98%. The second cycle operation rendered a by-product rich HRE concentrate having ~40% erbium along with critical HRE such as Yb, Tm, Ho etc. This 40% by product rich in Er forms feed for its purification and generation of Yb/Ho rich fraction for further processing. The attractive feature of the developed process was to take care variation of yttrium content in HRE fraction in the range of 60-80% and even was found to be amenable for the mixture of monazite and xenotime fractions at certain proportion.

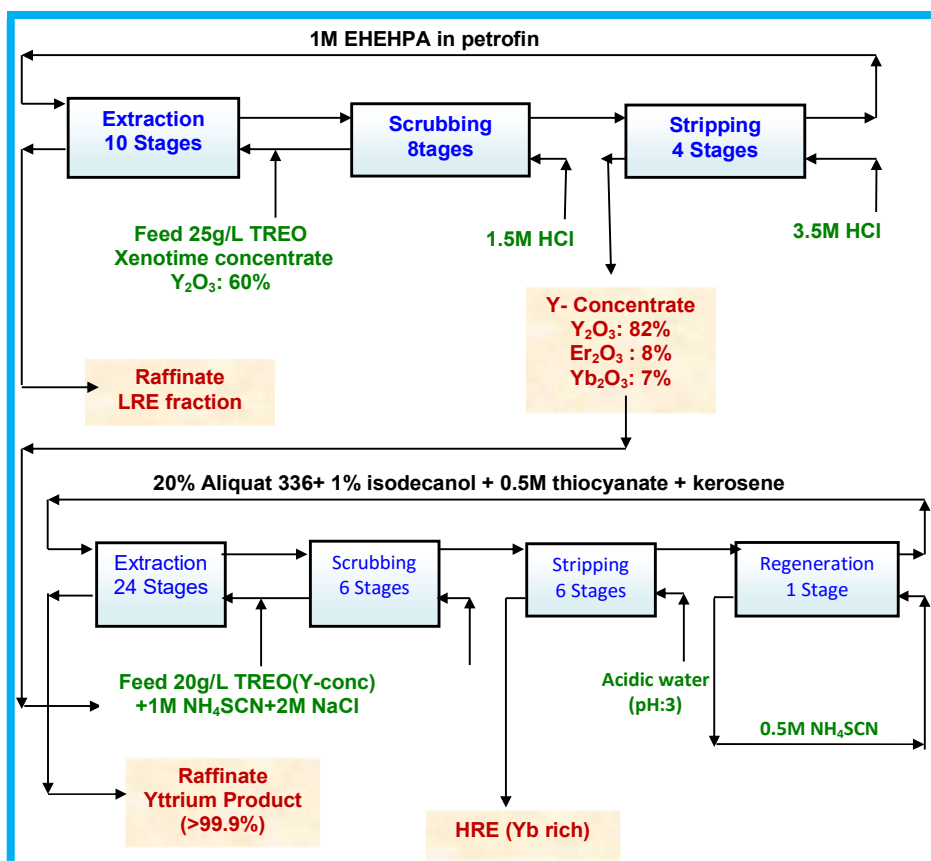


Fig. 2: Process flow sheet for yttrium purification

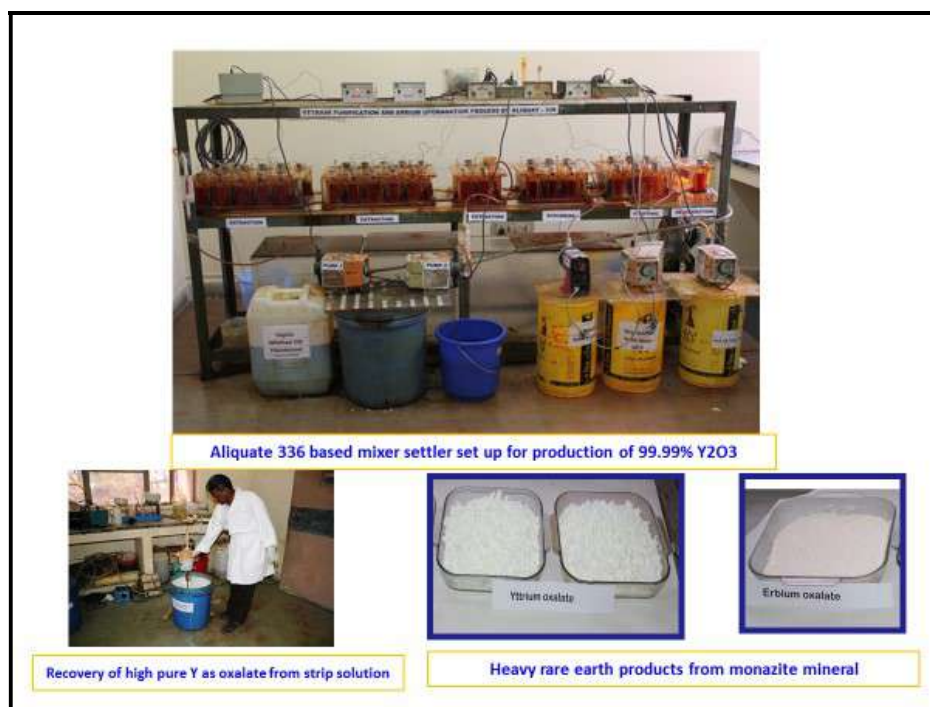


Fig. 3: Second cycle SX set up for producing 99.99% Y₂O₃ from monazite HRE fraction along with Y product and Er rich HREE by-product



Fig. 4: Xenotime feed source, 1st & 2nd cycle SX set up, mixed product obtained in 1st cycle, high pure Y product from complex HRE mineral Xenotime: process demonstration to IREL personnel

b) Separation of neodymium:

The counter current solvent extraction process for separation of neodymium is carried out in mixer settler units comprising 18 stages of extraction, 60 stages of scrubbing, 6 stages of stripping for Nd and 6-stages of stripping for samarium. The aqueous feed solution for this process is the raffinate obtained after the recovery of samarium and heavier rare earths and containing Nd, Pr, Ce and La. Saponified PC88A (EHEHPA) is used as extractant and the solvent preferentially extract Nd and part of Pr leaving La and Ce in the raffinate. The loaded solvent after 18 stages of extraction flows into a series of 60 stages of mixer settlers and scrubbed with a dilute solution of neodymium chloride which is mildly acidic. The scrub solution thus obtained is re-circulated to the extraction section by mixing with the aqueous feed solution. Most of the Pr, Ce and La co-extracted are scrubbed out in this step thereby purifying Nd. The scrubbed extract flows into another six stage mixer settler unit and Nd is recovered from the extract by stripping with dilute HCl. The extract after removal of Nd flows into another six stage mixer settler unit and is stripped with strong HCl. The solvent PC88A regenerated in this step is recycled back to the process. Nd is precipitated by the addition of oxalic acid as Nd-oxalate, filtered and calcined to oxide at 1000°C. This process yielded Nd₂O₃ with >99%. 1T/Y Pilot plants of capacity 1T/Y are setup by IREL based on BARC technology and Nd₂O₃ and Pr₆O₁₁ produced at RED, Alwaye, IREL are shown below.



Fig. 5: Product images Nd₂O₃ and Pr₆O₁₁ produced from IREL plants

c) Purification of gadolinium:

Gadolinium concentrate (~70%) obtained during samarium purification process was taken for the separation purposes. The separation factor between Tb and Gd is 5.8. Taking advantage of the higher separation factor, the feed elements are grouped into Gd and lighter rare earths and Tb and heavier rare earths necessitating a two cycle separation scheme. In the first step, Gd, Sm, Nd and Pr are separated out in the raffinate phase while Tb, Dy and Y are extractant into the organic phase. A two cycle process yielded the required purity of gadolinium (99.9%) in the raffinate with 97% recovery employing EHEHPA as an extractant in both cycles. Following precipitation with oxalic acid and its conversion to oxide after ignition, gadolinium oxide was obtained. This high purity gadolinium oxide is converted to nitrate form (Gd(NO₃)₃.6H₂O) under optimized conditions (Fig. 6). The analysed impurity elements (µg/g) in gadolinium nitrate are: Na <1, Mg <1, Cl < 6.5, Cu <1, Y - 4, Nd <1, Sm <1, Eu - 7, Dy <1, Tb <1. The product gadolinium nitrate produced meet the specifications for PHWR applications. 150 Kg of gadolinium nitrate was supplied to TAPS, Tarapur and 250 Kg to KAPP-3 for its application in PHWR (Fig.4). Based on BARC developed technology, Pilot scale facility for Gd₂O₃ production at 1T/Y has been

setup by IREL at Alwaye (Fig. 7) and also for conversion to nuclear grade gadolinium nitrate to meet the demand of NPCIL for reactivity control, through moderator liquid poison system as well as for reactor shut down system.



Fig.6: Nuclear grade gadolinium nitrate hexa hydrate supplied to NPCIL for its use in KAPP-3

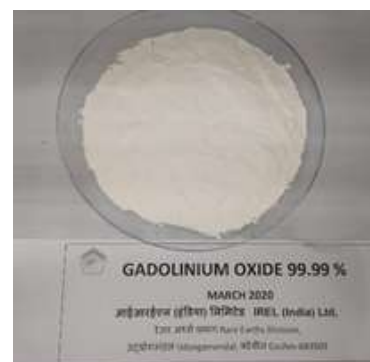


Fig. 7: Pilot scale facility for Gd oxide production at IREL

d) Dysprosium purification process:

Dysprosium of ~95% purity finds application in nuclear reactor as control material. A program was under taken for the separation and purification of dysprosium from HRE fraction ($Y_2O_3 \sim 60-67\%$, $Dy_2O_3 \sim 20-25\%$, $Gd_2O_3 \sim 4\%$, $Tb_4O_7 \sim 4.0\%$, $Ho_2O_3 \sim 3\%$, $Er_2O_3 \sim 3.0\%$, $Sm_2O_3 \sim 1.06\%$). The challenging task of separating Dy_2O_3 from host of other rare earths has been successfully accomplished by adopting a dual cycle of solvent extraction using EHEHPA. Yttrium including heavy rare earth fractions are separated in the product strip solution, while dysprosium is concentrated in the raffinate solution in the first cycle and purified further in the second cycle. Under optimized conditions of process parameters continuous operations of mixer settler yielded kilogram quantity of Dy_2O_3 with ~99% purity and recovery 98%. The overall process also produces two concentrates namely yttrium (>93%, 1st cycle) and terbium (>54%, 2nd cycle) as source materials for further up-gradation of these elements. Performance evaluation test of continuous counter-current set-up was also done. The running samples data were observed to

be consistent in terms of recovery and purity for both the cycles. This indicated the excellent performance of the mixer settler assemblies. Process details were shared with IREL for commercial production and based on the technology developed IREL has set up a plant of 1T/Y capacity for production of Dy_2O_3 from monazite concentrates to meet strategic requirement of the country (Fig.8).

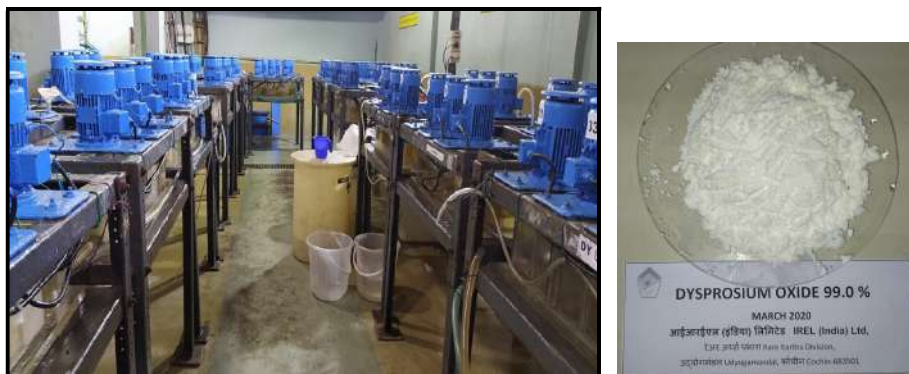


Fig.8: Pilot plant at IREL for producing high purity Dy_2O_3

e) Purification of terbium:

During the processing of yttrium (60–93%), a dysprosium fraction analyzing 50% Dy_2O_3 containing 14% Tb_2O_3 is obtained. Dysprosium is purified in another circuit to 97 % where by terbium concentrate assaying Tb_4O_7 - 70%, Dy_2O_3 - 28%, Gd_2O_3 - 1.3% and Y_2O_3 - 0.3% is obtained. A process has been developed to obtain high grade Tb_4O_7 by solvent extraction using 1M EHEHPA. The distribution ratio (D) of terbium as a function of acidity and metal concentration has been evaluated. Effects of phase ratio (O/A), feed metal concentration, acidities of feed and scrub solutions on D have been studied. It was found that when feed acidity increased from 0.12 – 0.33 M HCl, the % extraction decreased from 45.2 – 31.5 % at 1:1 phase ratio. When O/A was varied from 0.5 to 2 from a feed of 50 g/l, the % extraction increased from 14.3 – 39 %. These results were verified with the calculated values using mathematical models developed earlier. The experimental parameters have been optimized based on the simulated data. A counter-current set-up comprising of 8 stages of extraction, 8 stages of scrubbing and 4 stages of stripping was operated. The recovery and purity of terbium oxide obtained was found to be 97% and >99% respectively (Fig 9).



Fig. 9: Counter current SX process for Tb purification and Tb_4O_7 (>99%) product

2. Process development for recovery of Rare Earths Elements from secondary source: Nd-Fe-B Magnetic Scrap

Rare earth elements (REE) and compounds have become indispensable in recent technological advancements, playing a crucial role in modern electronics and high-tech products. One notable application of REE is in Nd-Fe-B permanent magnets, which are a staggering 2000 times stronger than ferrite magnets. Nd-Fe-B permanent magnets are integral components in computer hard drives, electric car motors, wind turbines and smartphone technologies. Given the essential role of these magnets in various critical technologies, abundance of discarded computer hard disk drives presents a valuable resource of the vital neodymium metal. In an Nd-Fe-B magnet, approximately 30% neodymium is present, along with smaller fractions of praseodymium, terbium, and dysprosium. Consequently, developing technologies for the efficient recovery of rare earth elements from magnetic scrap is imperative to alleviate the scarcity in their supply. The need for developing new processes for recycling rare earth elements is underscored by several critical factors that impact both environmental sustainability and availability of these essential materials for technological applications. Developing efficient recycling processes helps in managing and reducing the growing e-waste problems, turning it into a valuable resource rather than a burden on the environment. In response to these challenges, an energy-efficient, cost-effective, and environmentally friendly hydrometallurgy-based process has been developed. This innovative approach aims to recover high-value critical rare earths from end of life hard disk drive magnets.

A hydrometallurgical process has been developed to recover valuable REEs (Nd, Pr, Dy) from the discarded computer hard disk drive magnets. The procedure entails the following separate processes, each of which is explained in detail in terms of optimising the leaching process's efficiency through optimisation studies. This involves determining the ideal temperature, duration, and particle size, as well as the acid concentration.

Approximately 500 discarded hard disk drives, obtained from the Computer Division of BARC, are manually dismantled (Fig. 10). The goal was to separate the Nd-Fe-B magnet along with its casing. The Nd-Fe-B magnets were then subjected to thermal demagnetization. This involves heating magnets to 350 °C for over 1 hour in a muffle furnace. This step ensures removal of magnetic properties from the material and ease in subsequent physical and chemical treatment of NdFeB alloy powder. The demagnetized Nd-Fe-B material was crushed using a jaw

crusher to achieve a particle size of up to 0.5 mm.(Fig. 11). This increases the surface area of the powder and enables complete leaching of the scrap in the mineral acid. The crushed and ball-milled material was subsequently subjected to leaching in different mineral acids such as sulfuric acid, hydrochloric acid, nitric acid. The leached scrap powder solution is subjected to selective precipitation of RE by addition of stoichiometric amount of sodium sulfate resulting in precipitation of RE double sulphates. This step is crucial for the removal of iron present in the filtrate. Depending on the required product specifications, the double sulphate is further converted to either rare earth hydroxide or rare earth oxalate (Fig. 12). This conversion process ensures the production of high-purity rare earth as oxalate precipitate with rejected iron in filtrate phase only. The recovery and purity of the rare earth products were also evaluated and results indicated that the recovery exceeded 85%, and the purity greater than 98%. Detailed process flow sheet is shown in Fig. 13.



Fig. 10: NdFeB magnets recovered from EOL computer hard disk drives



Fig. 11 NdFeB magnet powder after jaw crushing magnet (100 pieces)



Fig. 12: Rare earth oxide separated from NdFeB magnet scrap

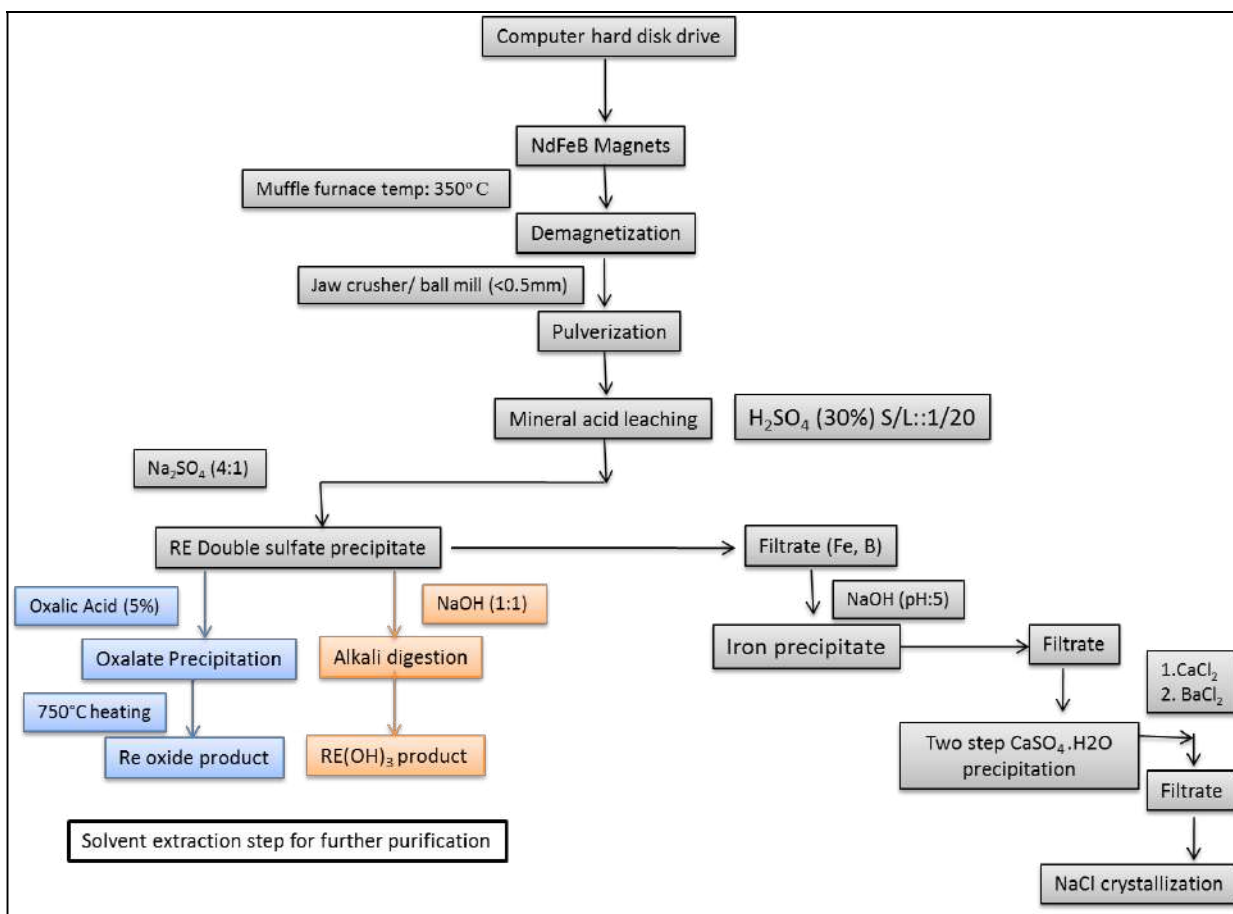


Fig. 13: Process flow sheet for NdFeB recycling

Novel separation methods like hollow fibre membrane or polymeric beads are employed to further separate individual REEs (Nd and Dy) from the mixed rare earths obtained above. The mixed rare earth concentrate was re-dissolved in acid to separate Dy from other rare earths by using Hollow Fibre Membrane (HFM) in a non-dispersive mode and EHEHPA as an extractant. Effect of various hydrodynamic parameters including aqueous phase acidity, extractant

concentration, REE concentration in feed, phase ratio and flow rates of aqueous and extractant were optimized to separate Dy from the mixed rare earth leach liquor. Taking the advantage of fast extraction kinetics of dysprosium, two cycle HFM-NDSX approach was adopted to concentrate Dy from 20 to 83% in first cycle while raising its purity >97% in the second cycle (Fig. 14). The overall process also yielded neodymium-praseodymium (>99% purity) rich by-product.

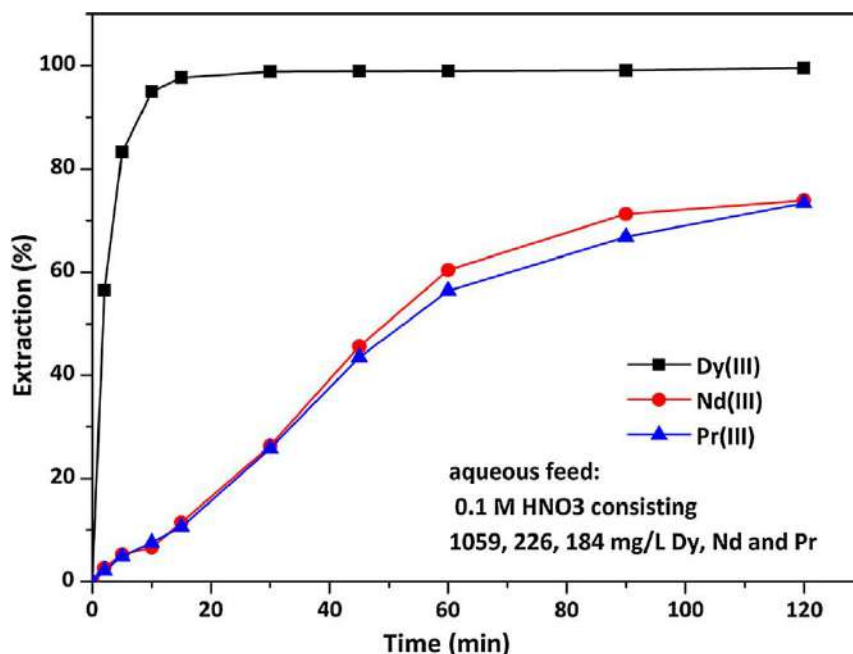


Fig. 14: Purification of Dy(III) from mixed rare earths feed; organic phase: 0.5 M EHEHPA; aqueous phase: 1059, 226, 184 mg/L of Dy(III), Nd(III) and Pr(III) respectively in 0.1 M HNO₃; flow rate: 100 mL/min.

Conclusion

The development of advanced solvent extraction technologies at BARC and their successful implementation by IREL (India) Limited represents a significant milestone in the field of rare earth element separation and purification. The optimized processes for yttrium, neodymium, gadolinium, dysprosium, and terbium ensure production of high purity rare earth oxide with good yield. The innovative approach to recycling rare earths from e-waste further underscores the commitment to sustainability and resource conservation. The developed hydrometallurgical process to recycle end of life hard disk drive based NdFeb magnetic scrap is transferred to IREL for pilot plant scale operation at its Rare Earth and Titanium Theme park at Bhopal. The continuous improvement and scaling of these processes will play a crucial role in securing a reliable supply of rare earth elements essential for future technological developments.

References:

1. T.K.S.Murthy, T.K.Mukherjee, Rare Earths, Occurance, Production and Applications, First Edition 2002, Publisher Indian Institute of Metals & Technolgy Information, Forecasting and Assessment Council (TIFAC).
2. T.K.S.Murthy, T.K.Mukherjee, Non-ferrous Metals Strategy cum Source Book (Book No.6), Rare Earth Metals, Firsrt Edition 2001, Publisher Indian Institute of Metals & Technolgy Information, Forecasting and Assessment Council (TIFAC).
3. D.K.Singh, M.Anitha, V.Kain, Development of solvent extraction process for erbium purification, Separation Science and Technology, 52, (2017) 2284-2290.
4. Kartikey K. Yadav, D.K.Singh, V Kain, Separation of Terbium from aqueous phase employing hollow fibre supported liquid membrane with PC88A as carrier, Separation Science and Technology, 10.1080/01496395.2018.1541471 (2018).
5. Kartikey K. Yadav, M. Anitha, D. K. Singh, V. Kain, NdFeB magnet recycling: Dysprosium recovery by non-dispersive solvent extraction employing hollow fibre membrane contactor, Separation and Purification Technology, 194, 265-271, (2018).
6. D.K. Singh, M.K. Kotekar, H. Singh, Development of a solvent extraction process for production of nuclear grade dysprosium oxide from a crude concentrate, Desalination 232 (2008) 49–58.



Dr. Dhruva Kumar Singh, a gold medalist in M.Sc (Chemistry) from Magadh University Bodhgaya, joined Bhabha Atomic Research Centre (BARC), Mumbai in 1991 after completing the training school's 34th batch. He earned his Ph.D. from Mumbai University in 2001 and conducted post-doctoral research (2002-2004) at The Florida State University, USA under renowned nuclear scientist Prof. G.R. Choppin. Dr. Singh is a recognized expert in rare earth resource processing, contributing over three decades at BARC to developing process flow-sheets for uranium, rare earths, and base metals from primary and secondary sources. Currently, he heads BARC's Hydrometallurgy & Rare Earths Development Section in the Materials Processing & Corrosion Engineering Division, Materials Group, and serves as a faculty member at Homi Bhabha National Institute, DAE. Dr. Singh holds memberships in several professional bodies, including Secretary of the Indian Institute of Metals (IIM, Mumbai Chapter) and Joint Secretary of the Rare Earths Association of India (REAI). With over 300 publications in International Journal & conference and numerous invited lectures, he contributes to various scientific committees in the area of critical minerals and rare earths. Recognized with the INS Medal in 2006, Hindustan Zinc Gold Medal by Indian Institute of Metal in 2018 and the Ministry of Steel's "Metallurgist of the Year" award in 2015, Dr. Singh continues to receive accolades, including the "VASVIK Award 2022" for his pivotal role in commercializing rare earth products nationally.



Dr. Kartikey Kumar Yadav joined Rare Earths Development Section of Materials Group, BARC through 50th batch of training school in 2007 after completing his M.Sc. from Lucknow University. Dr. Kartikey K Yadav did his Ph.D from on 'Studies on the separation of rare earths using solid phase extraction and liquid membrane techniques' from HBNI, Mumbai India Year 2016. Dr. Kartikey Kumar Yadav is an expert in the field of separation and purification of critically important elements. These include Rare Earth Elements (REE: Nd, Pr, Dy, Y & Sm), base metals (Co, Ni) from different sources i.e., primary ores e.g. Monazite & Xenotime, secondary sources e.g. e-waste, steel alloy scrap and lean sources e.g. liquid effluent streams from IREL plants. Dr. Yadav has developed and illustrated hydrometallurgical processes to recover high pure Rare Earth elements & base metals indigenously at kg scale from their respective sources. He has received DAE's Young Applied Scientist Award in 2014.



Dr. (Smt.) M. Anitha has joined Uranium & Rare Earths Extraction Division of Materials Group, BARC in 1995 after graduating from 38th OCES batch of BARC Training School in Chemistry stream. Dr. Anitha did her M.Sc (Chemistry) from University of Hyderabad in 1994. She was awarded PhD in Chemistry from University of Mumbai in the year 2007 on research work in the field of rare phosphors. Dr. M. Anitha has expertise in the field of separation and purification of rare earths and uranium. She had developed and demonstrated solvent extraction process flowsheets for high purity dysprosium oxide, neodymium oxide, yttrium oxide, gadolinium oxide, terbium oxide from primary resources for large scale production at IREL. Dr. Anitha has also worked exhaustively in the separation of uranium from industrial grade phosphoric acid by various extractants and she has one patent titled "A process for recovery of high purity uranium from fertiliser grade weak phosphoric acid" to her credit. She has expertise in the field of development of rare earth based phosphors for lamp, upconversion, X-ray intensifying screen and radioluminescent applications. She has published over 150 publications in International Journals and Conferences. She has been conferred with a DAE Group award in 2018 and 2020.



Dr. Alok Awasthi did his B.E. (Metallurgical) degree from University of Roorkee in 1988, and doctoral degree from Kyoto University in 2001. He joined BARC in 1990 after graduating from 33rd batch of BARC Training School. His research interest include extraction and refining of rare metals, metallurgical thermochemistry and thermal analysis. He is currently the Head of Materials Processing & Corrosion Engineering Division of Bhabha Atomic Research Centre.



Dr. Raghvendra Tewari, presently is outstanding scientist and Head, Materials science division of Bhabha atomic research centre. He is also a senior professor at Homi Bhabha National Institute. Currently he is involved in development of structural materials for molten salt and fusions reactors. Dr. R. Tewari joined BARC after graduating from BARC training school in the year 1989. He did his Ph.D from IIT-Bombay in the year 2000. He served BARC under various capacities in the field of Physical Metallurgy. He is specialized in the fields of refractory metal alloys, transmission electron microscopy, materials for nuclear reactors, alloy designing. He extensively worked

and guided young scientists, researchers in the development of alloys, composites and intermetallics based on Zr, Ni, Nb, Ti, Pb-Li. He is recipient of prestigious *Rolls Royce Research fellowship (2003-2004)* from University of Cincinnati, US and *Fellowship of Electron Microscope Society (2014)* from EMSI. He was also Visiting Fellow at Ohio State University, USA & University of North Texas, USA during the period 01.06.2014 to 01.09.2014. He published more than 210 research articles in international journals. Dr. R. Tewari received several national/international awards in his career. Some of them include: *Young Metallurgist Award (2000)* From Ministry of Iron and Steel, *Scientific & Technical Excellence Award (2010)* From DAE, *SRC Fellowship (2011)* From DAE, *Homi Bhabha Science & Technology Award (2013)* From DAE, *Metallurgist of the Year (2016)* From Ministry of Iron and Steel.



Dr. B.R. Mishra presently working in M/s IREL(India) Limited as Deputy General Manager(R&D,I) at Orissa Sands Complex, Chatrapur. He is also coordinating Corporate Research programme as Member Secretary to IREL Technology Development Council (IRELTDC). Currently, he is involved in solving complex process problems of Monazite processing plant for improving efficiency, productivity and value addition to Thorium & Rare earths required for the strategic sector. Dr Mishra did his Ph.D from Berhampur University, Berhampur, Year 2001. His research project was on ‘Stabilisation and Properties of Some Mixed Oxide Ceramics’. He has

served IREL at various capacities in the field of Process and Quality Control, Research & Development on ‘Beach sand heavy minerals’. He has experience in setting up and operation of pilot plants for validation of home grown technologies for production of value added products like high purity zirconium oxide and stabilised zirconium oxides having high tech ceramic engineering application, high purity titanium dioxide, Thermal Barrier coating materials and Yttrium oxide from the Pilot plants. A patent application was also filed at DAE-IPR cell for production of high purity zirconium compounds from zircon in 2015.



Dr. Deependra Singh serves as the Chairman and Managing Director of IREL (India) Limited, a Central Public Sector Undertaking under the Department of Atomic Energy, Government of India. With over 35 years of diverse experience in mining, mineral processing, and the rare earth sector, Dr. Singh has held several key positions, including Director (Marketing) at IREL and Director (Corporate Planning & Business Development) at EDCIL (India) Ltd. He holds a degree in Engineering, an M. Tech in Industrial Design, an MBA in Marketing, and a PhD in Mineral Technology. Dr. Singh has contributed to numerous international projects under organizations like the World Bank, OPEC, and the Asian Development Bank, and has been a UNIDO fellow in Germany. He has delivered over 75 presentations on international mineral and rare earth topics. His accolades include the Best CEO Corporate Management Innovative Excellence Award (2021 & 2022), Outstanding Business Leadership Award (2022), and the Lifetime Achievement Award for his contributions to the rare earth field in India (2023). He has also been recognized as an Eminent Engineering Personality and received the Atma Nirbaratha Award (2023) and the CEO of the Year Award (2024), among others. Dr. Singh is actively involved in various professional bodies, including serving as President of the Rare Earth Association of India, Chairman of the Western Region CAPEXIL, and Chairman of the Indian Institute of Metals (Mumbai Chapter). He is a member of several research and governing boards, contributing to the development of the mining and minerals sector in India.

Separation Science and Technology: Process development strategies and perspectives on work at BTDG, BARC

Archana Sharma^{1,2}

¹Homi Bhabha National Institute, Mumbai, ²Beam Technology Development Group, BARC, Mumbai

Email: arsharma@barc.gov.in

Abstract

This chapter presents a brief account of the work on the development of processes in the field of separation science and technology at Beam Technology Development Group, BARC. The activities outlined in this chapter are (a) Studies for dissolution of lanthanides from metallic substrates and (b) Separation of impurities like sodium and iron from lanthanides by solvent extraction and ion extraction chromatography.

1. Introduction

With the alarming rate of rise of cancer cases in India, the demand for radionuclides are at an all-time high for diagnosis and therapeutics. Lanthanides are finding widespread applications in cancer treatment and medical imaging. Generally, gamma or positron emitting radionuclides are used in imaging while particulate (α , β) emitting radionuclides find application in therapy. A special class of radionuclide that emits particulates along with a low energy (~ 50 - 300 keV) gamma is most suited for the combined action of therapy and diagnostics. Lutetium-177 is one of the widely used theragnostic radionuclide that fits the bill. It has β energies (497 keV and 379 keV) and γ (208 keV and 112 keV) for targeted beta therapy applications. Elementally pure targets of ^{176}Lu are neutron activated in a research reactor (Dhruva, India) for production of the required isotope; ^{177}Lu [1,2]. Targets of ^{176}Lu are prepared by dissolution of Lu in mineral acid. The present study discusses the dissolution kinetics of the target in nitric acid. The dissolution in acid was further intensified by the application of ultrasound to achieve a doubling of the dissolution rate, based on recent reports on the work carried out with heavy metal compounds [3].

The impurity limits for metallic impurities iron, sodium, copper and zinc in the target should be minimal to avoid competition during chelation and generation of unnecessary activation products [4]. To achieve this specification, the common impurities need to be removed/ reduced in the target. Solvent extraction and extraction chromatography-based separation processes are some of the suitable methods for carrying out this separation [5]. These two methods have been investigated for the above application. Extraction chromatography technique offers unique advantages, (1) the high selectivity of the solvent in combination with (2) a separation methodology in a single unit operation on a packed bed akin to other to conventional chromatographic methods implemented with multiple wash and eluant cycles.

In the solvent extraction process, two solvents, CMPO and TEHDGA have been screened for the separation [6].

Similarly, feasibility studies were carried out using ion extraction chromatography method to purify and concentrate ytterbium with respect to the above impurities. DGA resin commercially available from EICHROM and TRISKEM(TODGA, diglycolamide N, N,N',N'-tetraoctyldiglycolamideadsorbed on an inert resin) was used for the separation studies. The distribution coefficient data experimentally observed in different concentrations of nitric acid / hydrochloric acid into n-dodecane organic phase; formed the basis for selecting the wash and elution conditions [7] [8].

1.1. Relevant Rare-earth Chemistry

The rare-earths of interest in the current study, Ytterbium(Yb) and Lutetium (Lu) are part of the f-block elements (lanthanides) with the outer electrons added in the 4f level. The rare earth elements are chemically similar, due to the similarity of their outer electronic configuration and also because of lanthanide contraction. The contraction is significant and leads to a steady decrease in the atomic and ionic size with increasing atomic number from Lanthanum (La) to Lutetium (Lu). This is due to the inefficient shielding of outer e^- by one another in the same 'f' sub-shell. From La to Lu, nuclear charge increases and the number of 4f electrons increase by one at each step. However, the shielding of these 4f electrons from one another is inefficient due to orbital shape. This leads to an increase in the effectiveness of the nuclear charge causing a decrease in size, causing lanthanide contraction, with La being the most tightly bound and Lu the least tightly bound. The complete f^{14} configuration confers a tri-positive state to Lu (Lu^{3+}). while Yb displays both a 2+ and 3+ state due to the tendency to achieve a f^{14} configuration [9].

The relevant physical properties of the above two elements viz., Yb, Lu is presented in Table 1 [10].

TABLE 1: Important Physical properties of Yb, Lu

Property	Yb	Lu
Atomic number	70	71
Atomic Weight	173.04	174.97
Density (g/cc) at 25 ⁰ C	6.972	9.84
Melting Point (⁰ C)	816	1675
Vapour Pressure [9] Log P/P _a = A-(B/T)-C Log (T) T in Kelvin		
A	14.117	13.799
B	8111	22423
C	1.0849	0.6200
Heat Capacity at 0 ⁰ C (C _p) (cal/g atom ⁰ C)	6.14	6.37
Ionization energy (eV)	6.3	5.4

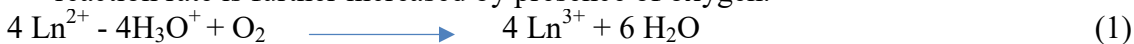
Elemental lanthanides are highly electropositive and easily oxidized, primarily to the +3 state. Dilute aqueous mineral acids rapidly convert the metals to solutions of the tri-positive ions.

1.2 Chemical reactions of elemental lanthanides (Ln)

- (1) With oxygen: Ln_2O_3 is formed slowly at room temperature, ignites above 150 to 180 ⁰C[10].
- (2) With oxygen in presence of moisture: $Ln_2O_3.xH_2O$; rapid with lighter Ln at room temperature, heavier Ln gives Ln_2O_3 .
- (3) H^+ (any mineral acid): gives $Ln^{3+} + H_2$. The reaction is rapid at room temperature also.

(4) H_2O : Ln_2O_3 or $\text{Ln}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ (+ H_2). Slow at room temperature, rapid at higher temperatures.

(5) Yb^{2+} ions are rapidly oxidized to the tri-positive species by the hydronium ion. This reaction rate is further increased by presence of oxygen.



2. Kinetics of Lu dissolution

2.1 Choice of acid

Some of the mineral acids considered are HF, HCl, H_2SO_4 , HNO_3 . The rare-earth fluoride salts are insoluble and HF handling is difficult. Hence, it is not considered. The chloride salts are soluble, but the chloride medium generally corrodes a lot of substrate metals. Lanthanides tend to form double salts with sulphates some of which are not soluble. Lanthanide nitrates are highly soluble and suitable for leaching. Hence, nitric acid is chosen as the acid for dissolution studies with the lanthanides.

2.2. Kinetic studies of Lu dissolution

The dissolution of lutetium in nitric acid can be summarized by the following reaction.



The kinetic data of Lu dissolution was generated by dissolving a 30mg Lu metallic bead in different concentrations of nitric acid. The aliquots were withdrawn for 60 minutes at different time steps and the quantitative measurement of Lu concentration was done in ICPOES. Since Lu is a pure solid, the rate of reaction will be proportional only to the concentration of nitric acid used.

For first order reaction, $-\text{d}C_A/\text{d}t = kC_A$ (3)

On integrating (3), $-\ln(1-x) = kt$ (4)

Where, C_A is the concentration of the reactant, x is the fractional conversion, k is the reaction rate constant and t is the time.

Assuming first order dependence of Lu dissolution on the concentration of acid, a plot of $-\ln(1-x)$ as a function of time t , was made. It showed linear dependence thereby confirming the assumption that the reaction is first order w.r.t. nitric acid.

However, dissolution in acid at room temperature without any intensification can lead to pitting and stagnant film formation. Stirring was avoided to minimize contamination from the stirrer. Ultrasound/ sonication is a non-contact type of intensification technique in which sound waves are used to generate microstreaming and increased dissolution [3]. Therefore, sonication was explored for Lu dissolution.

2.3. Kinetics of Lu dissolution with ultrasound

The most pertinent effects of ultrasound, in the order of 20 to 100kHz, on liquid-solid systems are mechanical, and are attributed to symmetric and asymmetric cavitation. The bubbles act as microscopic reactors causing sonolysis of the vapours trapped inside them just before collapse. In addition, shock waves are produced which have the potential of creating microscopic turbulence within interfacial films surrounding nearby solid particles, also referred to as microstreaming [3]. This phenomenon increases the mass transfer across the film, thereby increasing the intrinsic mass transfer coefficient, as well as possibly reducing the film thickness.

A similar exercise was carried out in a 1.5 litre ultrasonic bath to evaluate the intensification in dissolution brought about by ultrasound. The frequency of the bath used was 20 kHz and the intensity of the sound was 10 W/ cm² based on previous studies [3].

The variation of the Lu concentration with time was plotted in Figure 1. The study further showed linear dependence of dissolution reaction on the acid concentration. It was found that there is a doubling of the rate by using ultrasound, evident from the k values calculated. The activation energy of the sonicated dissolution was 15.18kJ/mol.

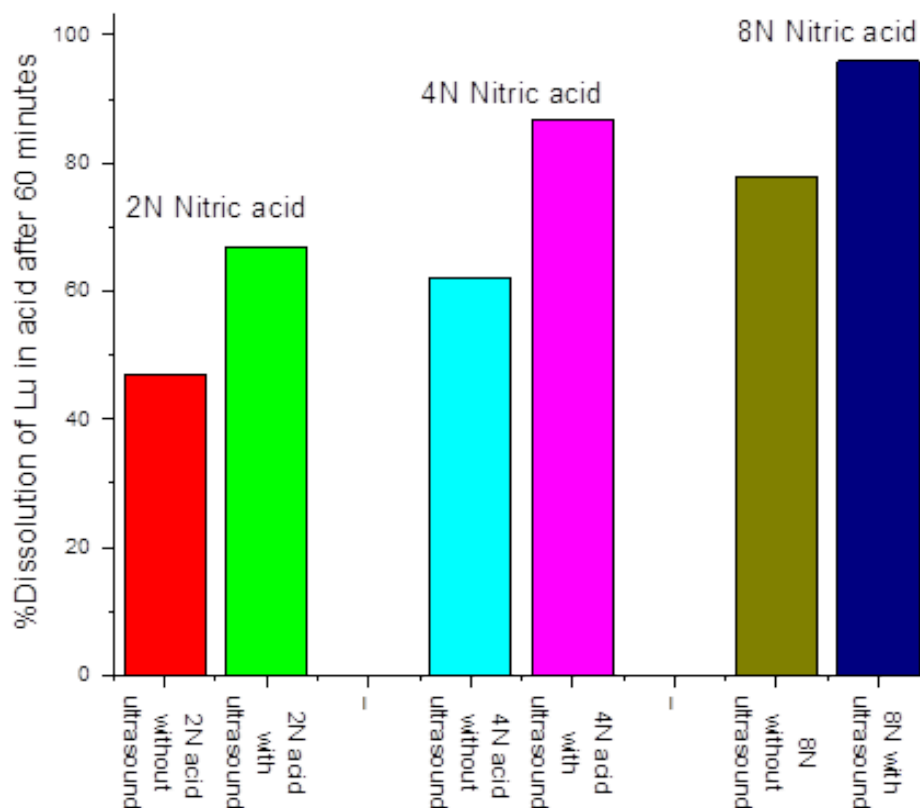


Figure 1: % Recovery of Lu with/without ultrasound at various acid concentration (1 h)

2.4 Conclusion of dissolution studies

The introduction of sonication for the dissolution of Lu resulted in the near doubling of the rate. Further, if the same process is carried out for dissolution from a metallic substrate, it is important to check for the possible erosion of the parent material from the substrate along with the Lu. In the next section, the purification work is detailed.

3. Purification of Simulated Yb solution using Solvent extraction and Extraction Chromatography

3.1 Solvent extraction

Using a simulated solution of Yb, Na and Fe extraction in the CMPO – nitric acid and TEHDGA-nitric acid system was tried. While CMPO was found to be ineffective, TEHDGA was found to be more efficient in the impurity separation (Table 2).

Table 2: Solvent extraction for purification of Yb in CMPO and TEHDGA

Solvent	Feed	Yb (ppm)	Na (ppm)	Fe (ppm)
2 M CMPO - 2M nitric acid	Feed	103.6	106	10
	Raffinate	30	106	8
TEHDGA - 2M nitric acid	Feed	103.6	106	10
	Raffinate	BDL	104	9.8
TEHDGA - 4M nitric acid	Feed	103.6	106	10
	Raffinate	BDL	101.4	7.6

3.2 Ion extraction chromatography

The simulated solution was used as feed in the ion extraction chromatography experiment. The simulated solution prepared in 4 M nitric acid was loaded onto a 3 g DGA resin column [11]. The resin was then washed successively with 4M, 1.5 M, 0.1 M nitric acid and with one bed volume of DM water [7]. The elution of Yb was done by using 0.05 M HCl. The distribution/fractionation of the individual impurity metals and ytterbium in the wash/ eluent solution cuts was quantified by ICPOES technique [12].

Figure 2 shows the experimental purification profile obtained in the recovery of the Yb target solution free of other metal ion impurities. DGA resin is reported to have a high selectivity for the lanthanides (Yb) with +3 oxidation state [7]. This is confirmed in the results, as Yb is seen to be loaded on the resin. The other impurities, viz., sodium, copper, zinc with an oxidation state of +1 and +2 predictably have low affinity for the resin [7]. Iron which exists in +3 oxidation state in nitric acid medium, with a very low distribution coefficient in the resin under the loading conditions (4 M nitric acid) also does not get significantly loaded on the resin. The final elution of the purified Yb from the resin bed is carried out with low molarity HCl (0.05 M HCl). As can be seen in Figure 2, except sodium, rest of the impurities have been separated from Yb product by the extraction chromatography method on DGA resin. The sodium ingress in the eluant stream is most likely from a cross-contamination in the experiment as Na with +1 oxidation state is not expected to get loaded on to the resin. This cross-contamination is planned to be tackled by a more rigorous experimental procedure.

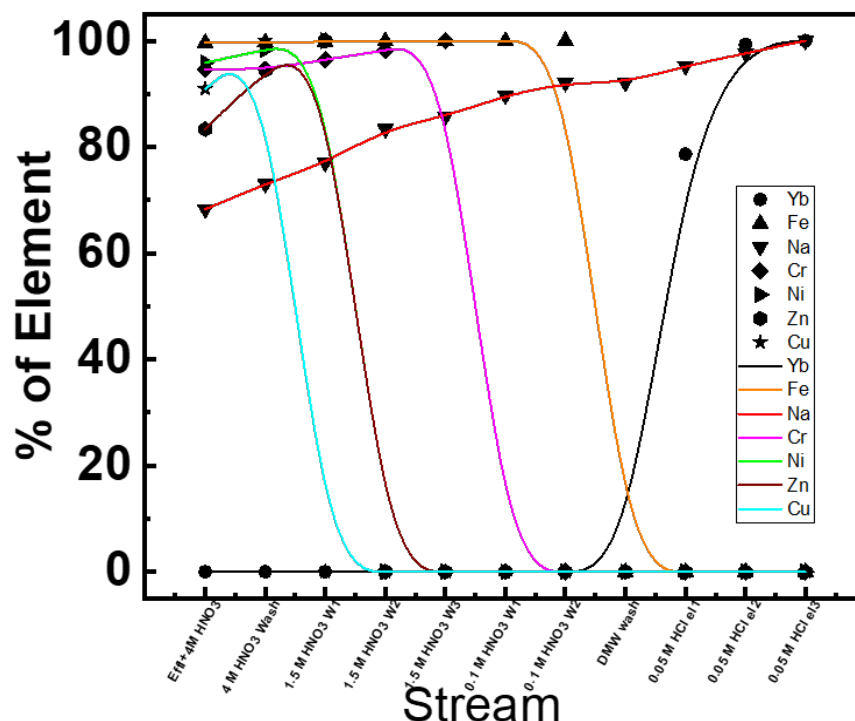


Figure 2: Ion extraction chromatography profile of Yb separation from metallic impurities

3.3 Conclusion

The two separation methods of solvent extraction (TEHDGA) and ion extraction chromatography (DGA) have been found to be effective for the separation of common metallic impurities from Yb. Detailed studies are required to optimize the process parameters.

Acknowledgement

Shri Soumitra Kundu, Head, ATLAD, Shri Sanjay Sethi, Smt. Anupama Prabhala and Ms. Sutanwi Lahiri, ATLAD are acknowledged for planning, conducting the experiments and interpretation of the results. Dr. Anupam Mathur, Shri Dheeraj Kumar and Dr. Usha Pandey, BRIT are acknowledged for their inputs to the development of the ion extraction chromatography process. Smt. Manisha Venkatesh, ACD and Smt. Vidya Chandorkar, Nuclear recycle group is acknowledged for ICPOES analysis of the lanthanide samples.

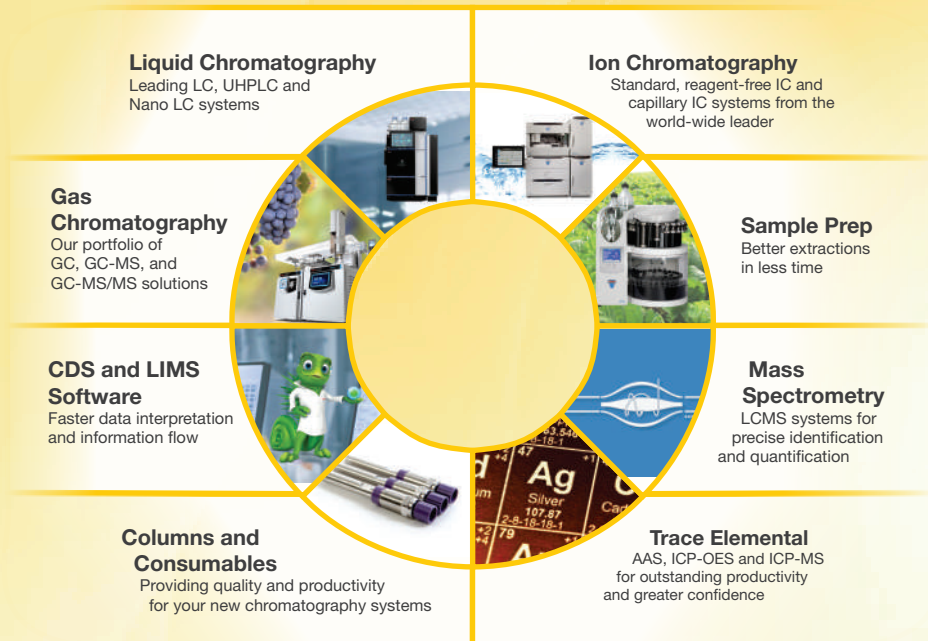
References

1. Sandip Basu et al., "One decade of 'Bench to Bedside peptide receptor radionuclide therapy with indigenous [¹⁷⁷Lu] Lu-DOTATATE obtained through 'Direct' neutron activation route: lessons learnt including practice evolution in an Indian setting", Am J Nucl Med Mol Imaging, 10(4), pp. 178-211, 2020. www.ajnmml.us/ISSN:2160-8407.
2. C. S. Cutler, C.J. Smith, G. J. Ehrhardt, T. T. Tyler, S. S. Jurisson, "Current and potential therapeutic uses of lanthanide radioisotopes", Cancer Biotherapy Radiopharmaceuticals, 15, pp. 531-545, 2000.

3. S. Lahiri, D. Mandal, A. Ghosh, P. R. Gogate, R. L. Bhardwaj, Cavitation-assisted decontamination of yttria from graphite of different densities, *Ultrason. Sonochem.*, 73 105520, 2021.
4. International Atomic Energy Agency, "Quality control in the production of radiopharmaceuticals," IAEA TECDOC-1856, pp. 63, 2018.
5. R. A. Kuznetsov, K. S. Bobrovskayaa, V. V. Svetukhina, A. N. Fomina, and A. V. Zhukova, "Production of Lutetium-177 – Process Aspects", *Radiochemistry*, Vol. 61, No. 4, pp. 381–395, 2019.
6. E. P Horwitz, D R Mc Alister, A. H Bond, R E Barrans Jr, "Novel Extraction chromatographic resins based on Tetraalkyldiglycolamides: Characterization and Potential applications", *Solvent Ext Ion Exc*, 23 (3) p. 319-344, 2005.
7. Zhi-Xuan Zhu, Yuji Sasaki, Hideya Suzuki, Shinichi Suzuki, Takaumi Kimura, "Cumulative study on solvent extraction of elements by TODGA from nitric acid into n-dodecane", *Analytica Chimica Acta*, 527, pp., 163–168, 2004.
8. A. Pourmand and N. Dauphas, "Distribution coefficients of 60 elements on TODGA resin: Application to Ca, Lu, Hf, U and Th isotope geochemistry," *Talanta*, vol. 81, no. 3, pp. 741–753, 2010, doi: 10.1016/j.talanta.2010.01.008.
9. F. Albert Cotton, Geoffery Wilkinson, "Advanced Inorganic Chemistry, A comprehensive Text", 3rd edition, Interscience Publishers, John Wiley & Sons.
10. Therald Moeller, "The Chemistry of Lanthanides", Chapter 44 of *Comprehensive Inorganic Chemistry*, edited by J.C. Bailar Jr., H.J. Emeleus, Sir Ronald Nyholm, A.F. Trotman-Dickenson, Pergamon Press.
11. Anupama P., Dheeraj Kumar, Arpit Mitra, Anupam Mathur, Manisha V., Usha Pandey, and Sanjay Sethi, "Elemental purification of indigenously produced isotopically enriched ytterbium precursor for radiopharmaceuticals" in 16th DAE-BRNS Symposium on Nuclear & Radiochemistry (NUCAR-2023), Mumbai; May 1-5, 2023.
12. Beata Zawisa et al., "Determination of rare-earth elements by spectroscopic technique: a review," *Journal Anal. At. Spectrom.*, 26, pp. 2373, 2011, doi: 10.1039/c1ja10140d.



Dr. Archana Sharma received the B.E degree in electrical engineering from Regional Engineering College, Bhopal, India, in 1987. M.Sc. (Engg.) and then Ph.D. degrees from the Indian Institute of Science (IISc), Bangalore, India, in 1994 and 2002, respectively. She joined as a Scientific Officer with BARC, Mumbai in 1988 after completing OCES program in electrical engineering with 31st batch of BARC Training School. Currently, she is Director, Beam Technology Development Group (BTDG) in BARC. Her field of specialization is multi-gigawatt pulsed electron beam generators based on Marx generators and linear induction accelerators. Her research interests include high-power microwave (HPM), Flash X-ray (FXR) and industrial electron beam accelerators. Dr. Sharma is a fellow of Indian National Academy for Engineering (INAE), Institute of Engineering and Technology (IET), and Institute of Engineers (IE). She is recipient of Homi Bhabha Science and Technology Award. She has over 100 scientific publications/presentations in international/national journals/conferences. She is a senior professor of Homi Bhabha National Institute (HBNI) and a recognized guide for both HBNI and Mumbai University.



World-class solutions

Transform your science

Thermo Scientific™ products help pharma, biopharma, research, academia, environmental, testing labs, proteomics and food safety customers around the world to meet the challenges they face every day.

From routine analysis to pioneering discoveries, our innovations help scientists solve complex analytical challenges, empowering them to conduct the work they need to do, the way they want to do it.



SPITZEN ANALYTIC INSTRUMENTS PVT. LTD.

We provide quality and cost effective answers to analytical challenges!!!

SPECTRAL SYSTEMS

ADVANCED TECHNOLOGIES

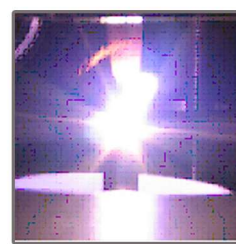
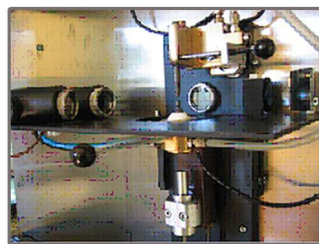
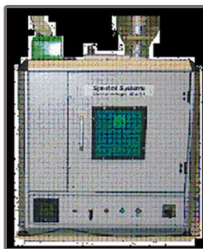


Spectral Systems

Augsburger Straße 37

D-82256 Fürstenfeldbruck

www.spectral-systems.de



DC-Arc model DCA-302, basic unit:

The system DCA-302 is an autarkical excitation unit for the adaption to different emission spectrometers by a flexible UV-quartz-fiber-optic.

The DC-Arc system features

- The Arc stand with the dimensions of 50x50x55 cm contains the quick-change electrode-holders (distances adjustable from the outside),
- Special optic in 90° double-version,
- Electronic gas-control by mass-flow-controllers,
- Power supply in modern and fast switched-mode technique (1.5 – 30A)
- HV- ignition-unit.

Office: Brahmand Complex, Phase-5, Bldg No.- 4, G-2, GB Road, Thane (W), Maharashtra Pin – 400 607

Tel: +91 22 62231412, 8655774574 Email: sales@spitzenanalytical.com

Works: Bldg. No. D-7, Gala No. 128, First Floor, Bhumi World Industrial Park, Pimpas Village, Kalyan Nasik Highway, Bhiwandi, Maharashtra Pin: 421301

HITACHI

Inspire the Next

A Powerful innovative XRF analytical Solution Combining performance with flexibility from Hitachi High Tech

Lab-X5000 benchtop XRF Elemental Analyser

The LAB-X5000 features streamlined software inspired by the point-and-shoot simplicity of our handheld analysers that combines with true one-touch measurement capabilities to offer the shortest measurement start sequence in the industry. The routine analysis screen is designed for easy reading of results, with large font, pass/fail indicators and SmartCheck messages to provide instructions to operators about how to handle out-of-specification results; all presented cleanly without clutter from icons and menus.

LAB-X5000 highlights:

- Element range Na (11) – U (92)
- 7" industrial grade touch screen
- Entirely new user interface
- One-touch measurement start
- Data handling capabilities including USB and LiveConnect
- High resolution SDD
- Smaller footprint compared to Lab-X3500
- Audible alert after measurement
- Atmospheric compensation for Air path
- Helium option for lighter elements (Na, Mg)



X-Supreme 8000

The X-Supreme8000 is a Bench Top Energy Disperse XRF which performs with the latest Hitachi High-Tech powerful Silicon Drift Detector (SDD) and high reliability X-ray tube. These technologies guarantee precise multi-element analysis at concentrations ranging from high percentage down to ppm levels of detection, covering elements from Na11 to U92 in the periodic table. It also got a 10-position sample carousel for unattended operation, and an integrated industrial grade embedded PC for storage of results. Simultaneous single or multi-element analysis with 'Live Updates' – results obtained 5 seconds after measurement starts, allowing a rapid assessment to be made. Results obtained using empirical calibrations for highest accuracy and traceability

Customized application include

- Minerals and mining
- Petrochemicals – fuels, lubrication Oils
- Wood pressure treatments
- Cement & Ceramics
- Food and Cosmetics
- Plastic and Polymers
- Education



VOLGA INSTRUMENTS PVT. LTD.

Office: G-1, Bldg. No.4, Phase-5, Brahmand Complex, Azad Nagar, G.B. Road, Thane (W), Maharashtra – 400607

Tel :022-62231413/8655774573 Email : sales@volga-inst.com Web : www.volga-inst.com

MEME
संरक्षित, लघु एवं मध्यम उद्यम
MEMO, SMALL & MEDIUM ENTERPRISES

Storage & Fume Extractor for Reagents (SAFER)



Manufactured By



In Technology Transfer
with BARC



Address : 38, Electronic Complex,
Opp. ITI, Pardeshipura, INDORE 452010 (M.P.)
MOB : +91-98269 69100

PANDEY ENTERPRISES

09869 042738 / 09969 111452

www.pandeyenterprises.com

Authorized Dealer for

- ◆ Rectiphase Capacitor
- ◆ Almonard
- ◆ Surya
- ◆ Usha International
- ◆ Deepti Air System



E-Mail: pandeyenterprises@yahoo.co.in



ALMONARD

USHA



भारी पानी बोर्ड, मुंबई परमाणु ऊर्जा विभाग

Heavy Water Board, Mumbai
Department of Atomic Energy

प्रौद्योगिकीय संपदा के माध्यम से राष्ट्र का गौरवान्वयन
Creating Pride for the Nation through Technological Wealth

नाभिकीय एवं विशेष ग्रेड का भारी पानी
Nuclear & Special Grade
Heavy Water
पोटेशियम धातु Potassium Metal



ड्यूटेरियम गैस Deuterium Gas
एनएमआर विलायक NMR Solvents
(CDCl_3 ; Acetone- d_6 ; DMSO- d_6 ;
Acetonitrile- d_3 etc.)



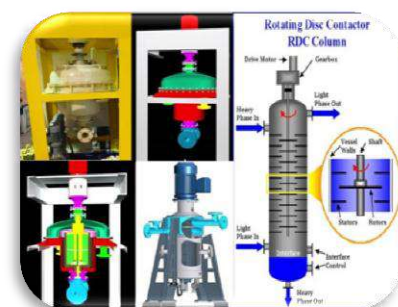
बोरॉन-10&11 Boron-10&11
नाभिकीय ग्रेड सोडियम
Nuclear Grade Sodium



स्वास्थ्य सेवा हेतु सामग्री
Materials for Healthcare
(पीईटी स्कॅनिंग हेतु ऑक्सीजन-18 जल
 ^{18}O Water for PET Scanning;
कैंसर के उपचार हेतु ड्यूटेरियम क्षीण जल
Deuterium Depleted Water for
Cancer Care)



निष्कर्षण धातुकर्म हेतु
विलायक
Solvents for Extractive
Metallurgy



नए उपकरण, पदार्थों और प्रक्रियाओं का
विकास तथा अभियांत्रिकी सेवाएं
Development of Novel Equipment,
Materials & Processes and
Engineering Services



सौर ऊर्जा का उपयोग Harnessing Solar Power
फ्लू गैस कंडीशनिंग Flue Gas Conditioning
वर्षा जल संचयन Rain Water Harvesting

www.hwb.gov.in

RARE EARTH ELEMENTS

CATALYSING ENERGY TRANSITION



IREL (India) Limited
(Formerly Indian Rare Earths Ltd)
A Govt. of India Undertaking
A Miniratna-I Company

200K+
Employment generation

10K+
CSR beneficiaries

1.5K+
Industries supported
in the value chain

1K+
Families rehabilitated

1.5K+
Acres of Green belt
developed

INDUSTRIES CATERED

AEROSPACE | CONSTRUCTION | COSMETICS & SKIN-CARE | CHEMICALS | DEFENCE | ELECTRIC VEHICLES | ELECTRONICS
GLASS & CERAMICS | GREEN ENERGY | GUIDANCE & CONTROL SYSTEM | HEALTH CARE | LASER | METAL & ALLOYS | NUCLEAR POWER
PAINTS & COATING | PETRO CHEMICALS | PRECISION CASTING | PROSTHETICS | REFRACTORIES & FOUNDRIES | TELECOMMUNICATION



CORPORATE OFFICE:

PLOT NO. 1207, ECIL BLDG., VEER SAVARKAR MARG, OPP. SIDDHIVINAYAK TEMPLE, PRABHADEVI, MUMBAI-400 028
PHONE: 022-24211630, 24382042, 24220230 | FAX: 022-24220236 | EMAIL: CONTACTUS@IREL.CO.IN

DEEP FREEZER



SOLVENT



BOD INCUBATOR



CIRCULATOR



FUME HOOD



With best compliments from



BATHULA INC is young marketing/distribution and service support company in the field of LABORATORY INSTRUMENTS, CHEMICALS & CONSUMABLES.

We offer solvents for LC-MS, HPLC, GC-MS, GC HEADSPACE, HIGH PURITY ACIDS for Trace Analysis, PHARMACEUTICAL EXCIPIENTS, Certified Standards for ICP/ICP-MS & AAS, BUFFER & CONDUCTIVITY SOLUTIONS, KARL FISCHER REAGENTS, SYRINGE FILTERS & FILTER PAPERS, HPLC & GC VIALS, STORAGE VIALS, CAPS & SEPTAS from the world's re-owned manufacturer such as CARLO ERBA-FRANCE, CPA CHEM-BULGARIA, CHEMLAB-BELGIUM, REAGECON-IRELAND, NU CHEK PREP-USA, QUVEON-USA, MEMBRANE SOLUTIONS-USA.

Supplier of Autoclave Steam Sterilizer, Bio Freezer, BOD Incubator, Hot air Oven, Deep Freezer Circulating Bath Chiller, Humidity Test Chamber, Magnetic Stirrer, Orbital Shaker, Shaking Incubator, Ultrasonic bath, Ultrasonic chiller bath, probe sonicator, Vacuum Leak Detection System, etc.

Supplier and manufacturer of Laboratory furniture, Fume Hoods, Specialised in customized Modular Lab Workstation/Furniture

Sales

Technical
Support

Repair of
HV Power Supply

98672-28029



ram@bathulainc.com

rambathula29@googlemail.com

Metrohm India Private Limited

A comprehensive range of analytical solutions



Handheld Raman



Ion Chromatography



Omnis - Titrator



VIONIC powered
by INTELLO



Elga - Lab Water



Near-infrared
spectroscopy



pH Meter - 913

Now every
CHEMIST
can afford
Metrohm pH Meter.

Metrohm is one of the world's most trusted manufacturers of high precision instruments for laboratory and process analysis. The company was founded in 1943 by engineer Bertold Suhner in Herisau, Switzerland, where it is headquartered to this day.

In India Metrohm India Pvt. Ltd. is serving Indian market for more than 2 decades. At Metrohm, we offer a comprehensive portfolio of analytical technologies ranging from titration and ion chromatography to near-infrared and Raman spectroscopy, as well as several other techniques.

