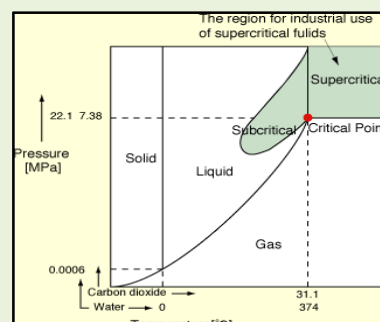
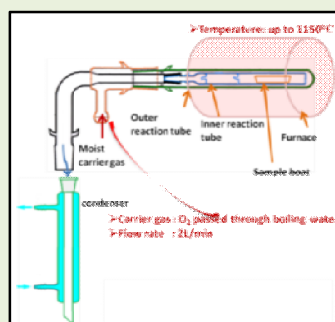
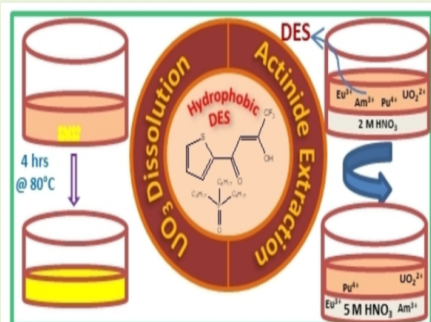
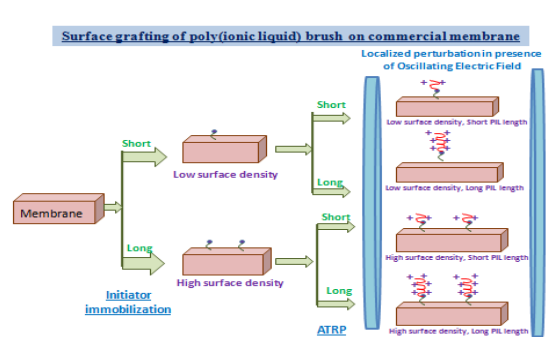
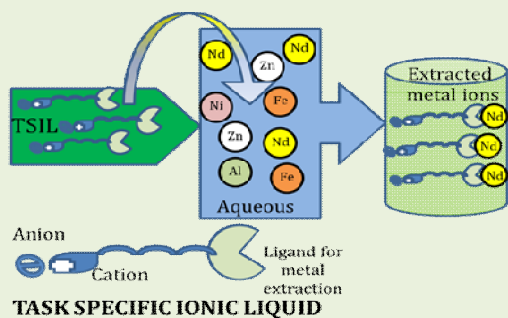




Advancement in Green Separations



Guest Editor: Brahmmananda Rao

Message

Guest Editor, ASSET Bulletin on "Advancement in Green Separation"



Greetings to all the members of ASSET.

Green chemistry has emerged as an important approach in addressing the environmental challenges arising from rapid industrial growth and the resulting increase in pollution. Among the twelve principles of green chemistry, the minimization or elimination of volatile and toxic solvents plays a pivotal role in designing sustainable chemical processes. This can be effectively achieved through different approaches such as solvent-free synthesis, the use of water as a reaction medium, ionic liquids, deep eutectic solvents and supercritical fluids. Deep eutectic solvents are a versatile class of environmentally friendly liquids formed by mixing two or more components are finding various applications including its potential application in separations invarious aspects of nuclear fuel cycle. Ionic Liquids which are in vogue for quite some time are salts in a liquid state, typically have melting points below 100 °C, and often composed of large, asymmetrical organic cations and inorganic anions which find various application in Green separations, catalysis, electrochemistry, pharmaceuticals and in various separations including nuclear industry. Some of the ionic liquids are also potential replacement of n-Dodecane as diluent in solvent extraction. Supercritical fluids (SCFs) have gained significant attention as environmentally benign alternatives to conventional organic solvents. Industrially, SCFs have been successfully employed in the extraction of natural products, including the decaffeination of coffee and the recovery of bioactive compounds from herbs and pharmaceutical materials. Furthermore, recent advancements highlight their role in environmental remediation, where SCFs, in combination with suitable ligands, are utilized for the selective recovery of metal ions from soil and water samples. In addition to extraction and separation processes, SCFs are increasingly being utilized in nanoparticle synthesis, dry cleaning, and as reaction media for a variety of chemical transformations. Collectively, their wide-ranging applications and inherent versatility highlight their role as effective and environmentally benign tools, establishing them as a promising avenue for the future of green chemistry.

We thank all the authors for their valuable contribution to this bulletin and express our gratitude to Dr. Arijit Sengupta, Editor, ASSET for bringing out an important topic in ASSET thematic bulletin covering all aspects of green separations with emphasis in nuclear, geological, and environmental analysis.

Dr. C.V.S. Brahmmananda Rao

Message

President, ASSET



Dear Members,

Greetings from ASSET!

I am delighted to learn that the second ASSET bulletin of this year is on the topic "Advancements in Green Separation", the most essential and environmentally friendly separation methods. Green separations replace the traditional use of toxic solvents with safer alternatives that have very few environmental impacts. In addition to the solvent reduction or replacement of volatile organic compounds, green separations focus on energy efficiency, miniaturisation, and renewability.

I am happy to see five articles on some of the important areas of green separation, including Deep Eutectic Solvents (DES), Supercritical Fluid Extraction (SFE), Ionic Liquids, poly- and ionic liquid membranes and pyrohydrolysis. These separations play a pivotal role in separation science, right from the lab to industries, and have wide applications in various industries. I am sure these articles will help all members learn more about green separations.

I thank Dr. Arijit Sengupta, Editor, ASSET, for his sincere efforts in bringing out this bulletin. My special thanks are due to Dr. Brahmananda Rao, Head, FChD, IGCAR, for being the guest editor of this bulletin and also for shouldering the editorial responsibility in bringing the bulletin into shape. I record my heartfelt thanks to all the authors. I am highly indebted to Prof. P.K. Mohapatra and Prof. V.K. Manchanda for their wholehearted support.

My special thanks to the vice presidents, the secretary, and all the executive committee members of ASSET.

Dr. Jeyakumar Subbiah

Contents

Sl. No.	Title	Authors	Page no.
1	Deep Eutectic Solvents in Radiochemical Separations: A Sustainable Route for Lanthanide and Actinide Extraction	Arkaprava Layek and Ruma Gupta	4 - 18
2	Role of Supercritical Fluid Extraction for Green Separation	Ankita Rao	19 - 27
3	Application of Ionic Liquids in Hydrometallurgical Recovery of Rare Earths and Precious Metals from Electronic Waste	N. Nav Vigyan, and R. Ruhela	28 - 34
4	Poly(ionic liquids) and Ionic Liquid Membranes in Separation Science	Arijit Sengupta	35 - 48
5	Pyrohydrolysis as a Green Separation Approach for Halogens and Non-Metals: Advances and Applications in Nuclear, Geological, and Environmental Analysis	V. G. Mishra, and S. Jeyakumar	49 - 64

Deep Eutectic Solvents in Radiochemical Separations: A Sustainable Route for Lanthanide and Actinide Extraction

Arkaprava Layek^{1,2} and Ruma Gupta^{*1,2}

¹Fuel Chemistry Division

Bhabha Atomic Research Centre, Mumbai 400085, India

²Homi Bhabha National Institute, Trombay, Mumbai 400094, India

(Corresponding Author: Email: rumac@barc.gov.in)

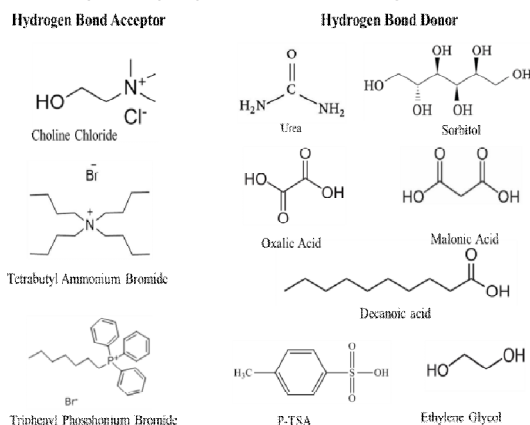
1. Introduction

The global pursuit of sustainable and clean energy sources has placed nuclear power at the forefront of long-term energy strategies [1, 2]. As a low-carbon, high-capacity, and continuous power source, nuclear energy plays a pivotal role in mitigating the adverse effects of fossil fuel dependence [3, 4]. At present, nuclear power contributes approximately 11% of global electricity production and is recognized as a reliable and scalable alternative to conventional energy sources. Its negligible greenhouse gas emissions during operation make it a critical component of global climate change mitigation efforts [1-4].

Despite these advantages, the large-scale deployment of nuclear power faces significant challenges, foremost among them being the safe management of radioactive waste and the efficient reprocessing of spent nuclear fuel [5-8]. Conventional reprocessing technologies—most notably the PUREX (Plutonium Uranium Extraction) process and pyrochemical methods—are well established and have been deployed for decades [5-7]. However, both approaches involve highly complex, resource-intensive operations, often requiring the handling of corrosive, high-temperature media. Furthermore, they generate substantial volumes of secondary waste, posing additional environmental and safety concerns [8]. These limitations have intensified the search for next-generation reprocessing strategies that are efficient, environmentally sustainable, and compatible with stringent nuclear safety standards [8].

In this quest for innovation, green solvent systems have emerged as promising candidates. Among them, Deep Eutectic Solvents (DESs) are attracting increasing interest for radiochemical separations [9-

12]. DESs are formed by combining a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), yielding a eutectic mixture whose melting point is significantly lower than that of either constituent [9-14]. The components are often inexpensive, biodegradable, and readily available—for example, choline chloride paired with urea [11, 12]. This combination of low cost, ease of synthesis, and inherent environmental compatibility positions DESs as a sustainable alternative to traditional organic solvents and even to ionic liquids (ILs), which, although effective,



suffer from high cost and poor biodegradability [11, 12, 15-17].

Figure 1: Commonly reported HBAs and HBDs for preparation of the DESs.

DESs share many of the advantageous physicochemical properties of ILs, including negligible vapor pressure, high chemical and thermal stability, and wide electrochemical windows. They can dissolve a broad spectrum of metal salts and support diverse redox chemistries [11, 12, 18, 19]. Critically, the hydrogen-bonding network intrinsic to DESs produces unique solvation environments capable of stabilizing unusual or transient oxidation states of metal ions. This is particularly relevant for the processing of redox-active f-

block elements—lanthanides and actinides—where control over oxidation state is essential for selective separation [20].

The development of DESs for nuclear applications builds upon prior work with ILs in actinide and lanthanide separations, where low volatility and radiation stability have been proven advantageous [15, 17, 20]. However, DESs offer additional benefits in terms of sustainability, cost-effectiveness, and adaptability [9, 11, 12, 16]. In the nuclear sector, DESs are being actively investigated for (i) selective lanthanide–actinide separation, (ii) electrodeposition of actinide metals, and (iii) stabilization of radionuclides in analytical workflows. Fine-tuning the HBA–HBD combination allows for precise control over solvation and redox properties, enabling highly efficient separations and electrochemical transformations [9, 12, 16, 18, 19]. Common HBAs used in DES formulation include quaternary ammonium salts such as choline chloride, though phosphonium- and sulfonium-based salts have also been employed in high-temperature nuclear separations. Abbott et al. classified DESs into four main types [12]:

Type I: Quaternary salt + metal halide (e.g., $\text{ChCl} + \text{ZnCl}_2$)

Type II: Quaternary salt + hydrated metal halide (e.g., $\text{ChCl} + \text{FeCl}_3 \cdot 6\text{H}_2\text{O}$)

Type III: Quaternary salt + HBD (e.g., $\text{ChCl} + \text{urea}$)

Type IV: Metal halide + HBD (e.g., $\text{FeCl}_3 + \text{urea}$)

In radiochemistry, Type III and Type IV DESs are most widely studied due to their lower corrosivity and tunable solvation environments, which are compatible with both aqueous and molten salt nuclear workflows.

The physicochemical origin of the lowered melting point in DESs lies in strong hydrogen bonding between the HBA and HBD, which disrupts the individual crystalline lattices and promotes charge delocalization. This, in turn, reduces lattice energy and, together with entropy effects from mixing components of different molecular geometries, shifts the eutectic point to a lower temperature. The eutectic composition corresponds to the minimum

Gibbs free energy for the mixture at a given temperature. Such characteristics not only enable operation at lower temperatures than conventional molten salts but also allow DES properties to be fine-tuned for specific nuclear processes [9, 11, 12, 18, 20].

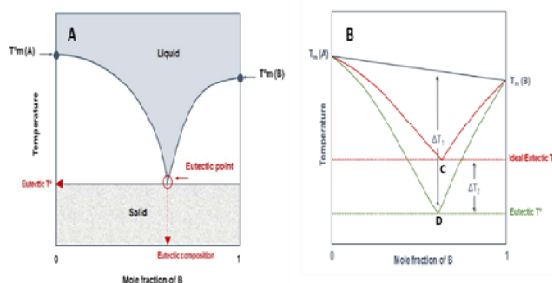


Figure 2: A) General solid-liquid phase diagram of a binary mixture. $T_m(A)$ and $T_m(B)$ represent the melting point of components A and B, respectively and the eutectic point gives the composition and the minimum melting temperature of the eutectic mixture B) Solid-liquid phase diagram representing a simple ideal eutectic mixture (red line) and a deep eutectic mixture (green line). ΔT is the corresponding depression in the freezing point [11, 12].

These unique solvent properties have direct implications for nuclear reprocessing. The negligible vapor pressure of DESs minimizes the volatilization of radiolytic products, reducing both operational losses and radiological hazards. Their wide electrochemical window facilitates the electrodeposition of highly reactive actinide metals, including uranium, thorium, and plutonium. Moreover, the polarity of DESs can be systematically adjusted via changes to the HBD structure, enabling selective complexation of target species. Many DESs also exhibit thermal stability up to 150–200 °C, sufficient for a range of nuclear separation processes.

Nevertheless, DESs are not without limitations. Their typically high viscosities—often exceeding 100 cP at room temperature—can hinder mass transport and slow down extraction kinetics [21, 22]. Approaches to mitigate this include the use of hydrated DESs or blending with low-viscosity co-solvents [21, 23]. While DESs have been studied extensively in catalysis, materials synthesis, and metal recovery, their application to f-block chemistry—especially actinide systems—remains comparatively underexplored. This scarcity of research stems largely from the radiological hazards inherent to actinide handling and the vulnerability of some DESs to radiolytic degradation [20, 24–26].

The overarching objective of this chapter is to address this knowledge gap by highlighting recent advances in the design of DESs with enhanced radiation resistance, improved thermal and electrochemical stability, and tailored solvation properties for f-block element chemistry. By focusing on their role in enabling efficient, selective, and sustainable separations, this work aims to establish DESs as a viable platform for the next generation of nuclear fuel cycle technologies [20, 26].

2. Deep Eutectic Solvents (DESs) in Lanthanide and Actinide Separations

Deep eutectic solvents (DESs) present several unique advantages for the selective extraction and separation of lanthanides and actinides, owing to their tunable physicochemical properties, strong hydrogen-bond networks, and capacity to dissolve a wide range of inorganic salts [12]. Functionalized DESs containing acidic ligands—such as phosphinic acids, β -diketones, and carboxylic acids—have demonstrated remarkable selectivity in coordinating either lighter or heavier lanthanides, driven by subtle but significant differences in ionic radii, hydration energies, and coordination preferences [27–29]. For instance, choline chloride–oxalic acid DESs enable pH-tunable solubility control, facilitating the selective precipitation of certain rare earth elements (REEs) by adjusting proton activity within the solvent matrix [30, 31]. Moreover, DESs can be integrated with ion exchange workflows, where they serve as a pre-concentration medium for lanthanides, enhancing the throughput and efficiency of subsequent column chromatography [32]. A notable example is the choline chloride–2-ethylhexanoic acid DES, which achieved separation factors exceeding 50 for Nd(III) and Dy(III) under optimized extraction conditions, while completely avoiding volatile organic compounds (VOCs), making it an environmentally safer alternative to conventional organic diluents [10].

In the case of actinide separation, DESs offer distinct mechanistic advantages critical for nuclear fuel cycle operations, waste treatment, and environmental remediation [20]. One of the key mechanisms is oxidation state stabilization, wherein DESs, through ligand coordination

and hydrogen-bond-mediated solvation, maintain specific oxidation states such as U(VI) in the uranyl form or Pu(IV), thereby facilitating targeted extraction [19]. Ligand functionalization of DESs with diglycolamides, phosphine oxides, or carbamoylmethylphosphine oxides has been shown to significantly enhance actinide binding affinity, even in the presence of competing metal ions [33]. Additionally, DESs enable electrochemical deposition of actinides at lower overpotentials than aqueous electrolytes, a feature that allows both selective separation and recovery in a single step. For example, a betaine–malonic acid DES extracted U(VI) from nitrate media with distribution ratios above 100, maintained stability under α -radiolysis conditions, and permitted efficient back-extraction into dilute mineral acids for product recovery[34].

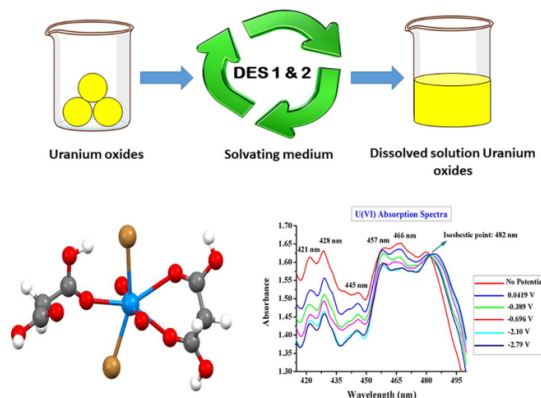


Figure 3: Dissolution of Uranium oxides and their redox speciation in two imidazolium-based DES[34].

Perhaps the most technically challenging separation in nuclear reprocessing is the partitioning of trivalent actinides from lanthanides, given their almost identical ionic radii and +3 oxidation state [35]. DESs contribute to overcoming this barrier through "soft donor selectivity," wherein sulfur-containing ligands such as thioamides preferentially coordinate actinides due to their greater covalency relative to lanthanides [36]. Synergistic and eutectic-phase strategies that pair DES/HES media with high-performance extractants (e.g., TODGA) have delivered very high distribution ratios and excellent impurity rejection—for example, a TODGA/decanoic-acid hydrophobic eutectic solvent achieved lanthanide D values up to $\sim 2 \times 10^2$ and Separation Factor (SF) of $(\text{Dy/Fe}) > 10^4$ —while DES co-solvents have been shown to accelerate SANEX-type

minor-actinide separations[37]. A striking example is the use of a choline chloride–urea DES modified with bis-2-ethylhexyl phosphoric acid, which produced Am(III)/Eu(III) separation factors above 150 under mild conditions [38]. Recent studies have further demonstrated that tailoring the hydrogen bond donor/acceptor ratio in DESs and incorporating task-specific ligands can fine-tune the competitive binding equilibria, offering scalable and more sustainable pathways for high-purity recovery of both strategic lanthanides and radiotoxic actinides [11, 12, 33].

3. Mechanisms of Lanthanide and Actinide Extraction in DESs

The extraction of lanthanides and actinides in deep eutectic solvents (DESs) is fundamentally dictated by ligand–metal coordination chemistry, which is uniquely tuned by the hydrogen-bond network of the DES matrix. The cooperative interplay between the hydrogen bond acceptor (HBA), hydrogen bond donor (HBD), and any additional co-solvents or dopants defines the solvation shell structure, redox stability, and selectivity profile for target actinide/lanthanide ions.

3.1 Solvation and Complexation

In DESs, the HBD and HBA components often provide functional groups capable of direct coordination to the metal center. For example, in ChCl–urea systems, urea contributes carbonyl O atoms, while ethylene glycol-based DESs provide hydroxyl O atoms, enabling robust inner-sphere coordination[39]. This principle extends to hydrophobic DESs containing alkyl triphenylphosphonium bromide, as demonstrated in uranyl ion interaction studies, where the bulky phosphonium cation modulates solvation sphere polarity and steric accessibility, enhancing the stability of U(VI) complexes[40]. Further, studies on Eu(III)–DES complexes revealed that DES ligands can modulate excited-state lifetimes and redox potentials, indicating strong electronic coupling between the DES coordination environment and the lanthanide center[41]. Similar effects were observed in hydrophobic DESs for plutonium sequestration, where inner-sphere coordination with DES-derived functional groups was central to both

extraction efficiency and redox stability of Pu(III)[42]. DES matrices also influence hydration number and ligand exchange rates, altering extraction thermodynamics. Highly viscous DESs can slow ligand exchange, favoring kinetically stable complexes, while lower viscosity DESs or hydrated variants promote faster equilibration [11]. Stabilization of charged complexes is further aided by the low dielectric constants of DESs, as observed in blue-light-emitting hydrophobic DESs that also function as liquid scintillators for radiometric detection [43].

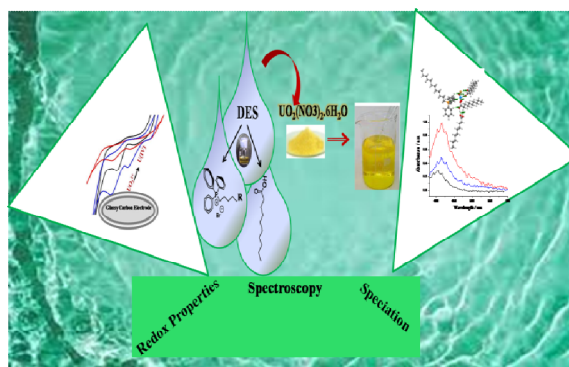


Figure 4: Mechanistic Approach to Reveal Interaction of Uranyl Ions in Alkyltriphenylphosphonium Bromide-Based Deep Eutectic Solvent [40].

3.2 Role of Water Content

Although DESs are often referred to as “anhydrous,” most contain residual water (~1–3 wt%) from hygroscopic precursors[11]. Controlled hydration has been shown to be beneficial, reducing viscosity and facilitating faster diffusion of metal species[44]. For example, in hydrophobic DESs used for Pu extraction, trace hydration improved mass transfer rates without significantly disrupting complexation equilibria[42]. Hydration also modifies selectivity. In uranyl–phosphonium bromide DES systems, water competes with DES ligands in the first solvation shell, thereby altering coordination geometry and extraction efficiency. In Eu(III)–DES photophysical studies, hydration influenced both fluorescence quantum yield and redox activity by modifying solvation polarity[41]. However, excessive water (>10 wt%) can disrupt the hydrogen-bonded eutectic network, shifting the medium toward aqueous-like behavior, which diminishes the selectivity advantages of DES-based extraction systems[11].

3.3 Anion Effects

The anion present in either the DES HBA or the metal salt feed plays a decisive role in extraction efficiency and speciation. For example: Nitrate and perchlorate anions typically favor outer-sphere complexation, leading to enhanced solubility of metal salts without strongly perturbing inner-sphere coordination geometry[45]. Chloride-rich DESs facilitate inner-sphere halide coordination, stabilizing lower oxidation states of actinides (e.g., U(III), Pu(III)) — a mechanism critical in both plutonium separation and in selective Pu recovery in the presence of Th(IV)[42].

The combination of controlled ligand–metal coordination, water-mediated solvation tuning, and targeted anion selection thus provides a versatile framework for designing DESs for selective and efficient lanthanide/actinide extraction, separation, and sensing. Spectroscopic and computational studies on uranyl and related species show that DES environments alter coordination numbers and bond distances relative to water, producing distinctive solvation structures that influence extractability [46]. Indirectly, the hydrogen-bond network and the lower dielectric environment of many DESs tune the stability and dynamics of charged complexes by changing the balance between electrostatic and covalent interactions; lower dielectric screening tends to favor neutral or less highly charged complexes, while the relatively high viscosity of many DESs reduces ligand-exchange rates and can kinetically trap specific coordination motifs[11, 39]. These combined thermodynamic and kinetic effects explain why certain extractants (for example, oxygen-donor DGAs or phosphorus-based ligands) show enhanced selectivity in DES media compared with conventional organic diluents[33]. Controlled hydration therefore often increases apparent extraction kinetics and can shift selectivity by changing the competitive solvation between DES ligands and water molecules[40, 41, 47, 48].

By contrast, excessive hydration collapses the eutectic structure and drives the medium toward aqueous behavior, eroding DES-specific selectivity advantages. Anion identity—whether present in the HBA (e.g., Cl^- , Br^-) or in the metal feed (e.g., NO_3^- , Cl^- , F^-)—further modulates extraction

chemistry [45]. Nitrate- and perchlorate-rich environments typically favour outer-sphere complexation and high metal salt solubility, whereas chloride-rich DESs can enable inner-sphere halide coordination that stabilizes lower oxidation states (important for U(III)/Pu(III) chemistry)[42]. It is conceivable that fluoride-bearing DESs could enable mixed-ligand complexation of actinide fluorides, potentially mirroring behaviors seen in molten-salt systems; however, experimental validation is still pending [46]. Notably, recent work has shown that embedding redox-active components in HDES formulations permits in-situ control of actinide valence (e.g., reducing Np(V) to Np(IV)), thereby opening new selectivity windows unattainable with inert diluents[50]. Taken together, these observations emphasize that extraction in DESs is not simply “the same chemistry in a different solvent” but rather a re-balancing of solvation thermodynamics and kinetics by hydrogen-bond networks, anion coordination, viscosity, and water activity — all of which can be rationally tuned to favour selective Ln/An partitioning[51].

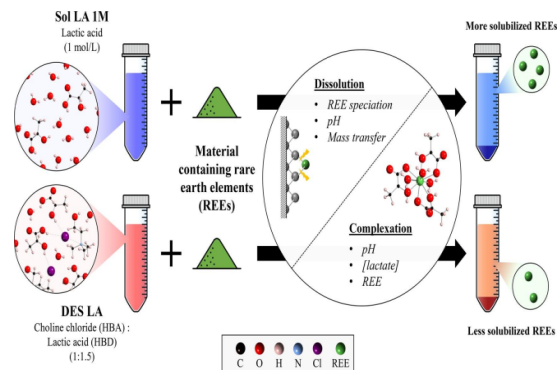


Figure 5: Schematic showing dissolution of rare-earth elements[49]

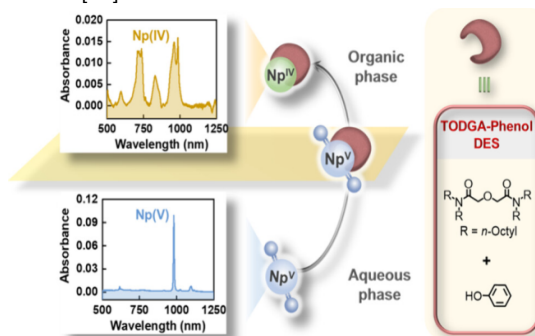


Figure 6: Schematic of recovery of Neptunium using Redoxable Deep Eutectic Solvent [50].

4. Process Optimization Strategies in DES - Mediated Radiochemical Separations

Process optimization is a crucial step in transitioning deep eutectic solvent (DES)-based separation strategies from proof-of-concept laboratory demonstrations to reliable, scalable, and economically viable industrial processes. Achieving this requires the systematic fine-tuning of several interdependent parameters, including DES composition, operating temperature, proton activity (pH), ligand loading, and key extraction conditions such as phase ratio and contact time. Temperature exerts a pronounced influence on DES performance because viscosity, mass transfer, and diffusivity are strongly temperature dependent. For instance, a choline chloride–urea DES (1:2 molar ratio) exhibits a viscosity of approximately 750 mPa·s at 25 °C, which drops to ~200 mPa·s at 60 °C, significantly enhancing mass transfer and, consequently, separation efficiency[52]. However, prolonged exposure to elevated temperatures can degrade thermolabile hydrogen bond donors (HBDs), such as sugars or amino acids, or promote water uptake from the atmosphere, thereby altering the solvent composition and reducing performance stability[11, 52]. Water content plays a similarly dual role: while small, controlled additions of water (typically 5–15 wt %) can lower viscosity and facilitate phase disengagement without markedly affecting solvation power, excessive hydration disrupts the hydrogen-bond network, dilutes complexation efficiency, and may even cause phase instability[12].

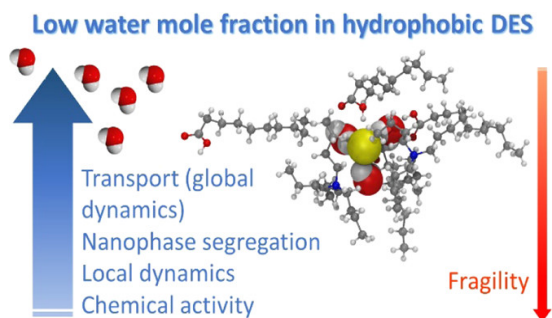


Figure 7: Schematic representation of Effect of Water on a Hydrophobic Deep Eutectic Solvent[53].

Ligand functionalization within DESs has emerged as an important optimization pathway. Embedding extractants such as phosphine oxides, diglycolamides (DGAs),

or calixarene derivatives directly into eutectic matrices can yield synergistic advantages, including mitigation of third-phase formation, improvement in selectivity for trivalent actinides over lanthanides, and enhanced stability under challenging conditions[54]. For instance, multi-armed or dendrimeric DGA architectures, as well as TODGA derivatives incorporated into structured platforms, have been reported to substantially improve americium(III) extraction efficiencies relative to unmodified TODGA systems [55]. Fundamental studies of TODGA in conventional solvents also highlight that its extraction performance is strongly enthalpy-driven and metal-dependent, providing a rationale for tuning its behavior in alternative media [56]. In parallel, calixarene-based ligands functionalized with phosphine oxide or diamide groups have demonstrated strong complexation toward rare-earth ions, illustrating the broader utility of such functionalized platforms[57, 58].

Recent studies have also explored the direct use of TODGA as a hydrogen-bond acceptor in DES formulation. For example, a hydrophobic tridentate ligand, TODGA (N, N, N', N'-tetraoctyldiglycolamide), has been combined with phenol as a hydrogen-bond donor to construct a novel DES, where TODGA provides strong affinity toward trivalent and tetravalent actinides and phenol offers a low-cost aromatic component with reducing capabilities. This DES was characterized using complementary techniques (NMR, FT-IR, TGA, DSC) and evaluated for its potential in neptunium recovery through solvent extraction, with mechanistic insights obtained via spectroscopic and solvent extraction analysis [50].

From a process perspective, DESs provide high density and immiscibility with aqueous nitrate solutions, which allows flexibility in phase ratios and supports efficient contact even at shorter timescales when agitation or ultrasound is applied. Moreover, stripping can often be accomplished with relatively mild reagents such as dilute HCl, oxalic acid, or carbonate solutions, approaches that are compatible with closed-loop recycling and consistent with green chemistry principles [12].

Despite significant advances, DES-based separations face persistent challenges. High viscosity remains a fundamental limitation; many DESs exhibit viscosities exceeding 100 cP at room temperature, which hinders mass transfer and often requires a delicate balance between dilution or heating (to lower viscosity) and maintaining extraction efficiency.

Another concern is radiolytic stability. Although data on DESs under high-dose radiation is limited, studies on similar systems such as ionic liquids (ILs) reveal that irradiation can generate radicals that disrupt solvent structure—suggesting that DES HBD components may similarly degrade under harsh radiation environments. Computational work has also screened candidate DES components for enhanced radiation tolerance, highlighting the need for informed selection for nuclear applications [59].

From an engineering standpoint, scaling up DES-based operations raises practical issues. The high viscosity of DESs complicates pumping and flow in conventional contactors, potentially necessitating temperature control or custom designs to maintain optimal processing conditions. Moisture ingress in humid environments can disrupt the eutectic network, and there is a general lack of published data on full-scale deployment.

Finally, regulatory acceptance depends on comprehensive safety and environmental evaluation—including compatibility with materials, waste management, and understanding of long-term degradation pathways under processing conditions. However, such lifecycle and regulatory assessments for DESs in nuclear separations remain largely unexplored in peer-reviewed literature[60].

From a sustainability and circular economy perspective, DESs are inherently aligned with several principles of green chemistry: they are frequently biodegradable, exhibit low volatility, and can be synthesized from renewable feedstocks[11]. Their negligible vapor pressure minimizes fugitive emissions, while their recyclability significantly reduces secondary waste generation[61]. Moreover, replacing volatile organic solvents with DESs lowers the

volume of hazardous waste and enables multiple reuse cycles without substantial performance loss. Importantly, DESs can be tailored to selectively recover critical metals such as lanthanides and actinides from spent nuclear fuel and process waste streams, supporting a closed-loop resource recovery strategy[62]. For instance, neodymium and dysprosium recovered from spent magnets using DESs can be reintegrated into advanced manufacturing processes, thereby reducing dependence on primary mining and contributing to a more sustainable nuclear and high-tech materials supply chain[38].

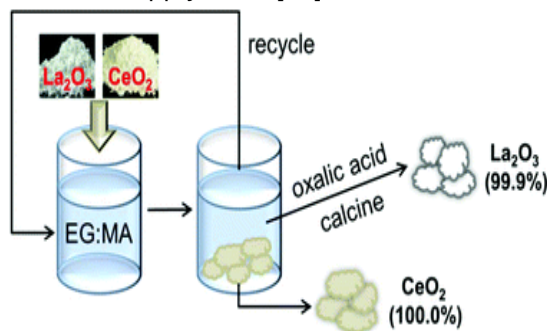


Figure 8: A strategy for the dissolution and separation of rare earth oxides by novel Brønsted acidic deep eutectic solvents [31].

5. Case Studies: DES in Lanthanide and Actinide Extraction

5.1 Extraction of Light Lanthanides

The light lanthanides—particularly lanthanum through neodymium—play pivotal roles in advanced technologies such as high-performance magnets, lasers, and catalytic systems. Traditional extraction methods often use organophosphorus reagents dissolved in hydrocarbon diluents, which can suffer from limited selectivity and create environmentally hazardous organic waste[63]. Deep eutectic solvents (DESs), by contrast, enable greener, more selective separations. In a representative study by Abbott et al., a choline chloride–urea DES functionalized with a diglycolamide (DGA) ligand achieved distribution ratios of approximately 150 for both La(III) and Nd(III) under mild acidic conditions, with stripping efficiencies exceeding 95%. Mechanistic insights attribute this performance to the strong hydrogen-bonding interactions of urea, which not only assist solvation of the metal–DGA complex but also promote faster mass transport within the viscous DES

medium — a combination that enhances both extraction efficiency and process speed[64].

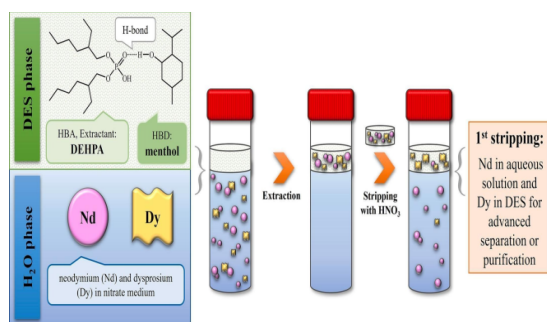


Figure9: Selective separation of neodymium(III) using dual function DEHPA-menthol deep eutectic solvent[64].

5.2 Extraction of Heavy Lanthanides

Separating heavy lanthanides (terbium through lutetium) remains particularly challenging because of their almost identical ionic radii and chemistry. HDEHP is a well-established extractant for lanthanide separations. Advanced spectral studies have characterized its coordination with lanthanide ions in organic phases, informing its selectivity mechanisms [65]. Additionally, HDEHP-based extraction chromatography materials have been successfully used to separate heavy lanthanides such as Tb and Gd from HCl solutions [66]. These studies support the potential of optimized DES systems enriched with acidic extractants to achieve enhanced separation factors in heavy lanthanide pairs[66].

5.3 Synergistic DES–Ligand Systems

An emerging strategy in lanthanide extraction is to exploit synergism between the DES matrix and embedded ligands. Crown ethers are known for their f-block selectivity in conventional solvents. For instance, a review of crown ether applications highlights their high extraction efficiency of lanthanides. Structural studies further show that crown ethers form stable complexes with Eu(III) owing to configurational fit and donor-atom arrangement. Though direct evidence of a DES–crown ether system enhancing Eu(III) uptake remains to be published, these findings suggest that embedding crown ethers into a DES matrix could potentially yield synergistic improvements in uptake efficiency[67].

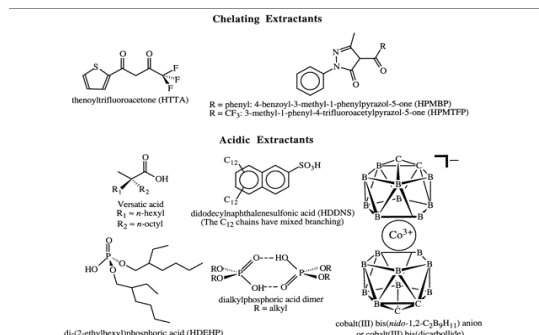


Figure 10: Two-dimensional structures of some extractants used in synergistic solvent extraction [68].

5.4 Uranium(VI) Extraction

Efficient extraction of uranium(VI) (uranyl) remains paramount in nuclear reprocessing. In traditional PUREX systems, TBP in nitrate media forms neutral uranyl complexes (e.g., $\text{UO}_2(\text{TBP})_2(\text{NO}_3)_2$), allowing for solvation-type extraction and subsequent back-extraction via nitrate concentration changes or acid stripping. Inspired by ionic-liquid extraction platforms, DGAs have been used to extract uranyl ions into ionic media with notable efficiency.

Although analogous implementations within DES formulations—especially those mimicking ionic-liquid behavior with high nitrate solubility—have yet to appear in peer-reviewed literature, these cases strongly support the conceptual viability of DESs for selective U(VI) extraction with milder back-extraction strategies[69].

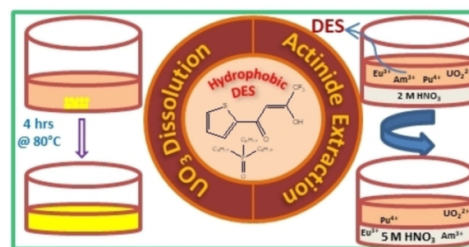


Figure11 :Extraction and partitioning ofactinides and lanthanides using a hydrophobic DES having low density and viscosity based on Thenoyltrifluoroacetone (HTTA) and Trioctyl phosphine oxide (TOPO) and dissolution of uranium oxide using this DES medium[70].

5.5 Plutonium and Minor Actinides

CMPO has demonstrated significant resistance to gamma-ray-induced degradation—distribution ratios of Am(III) remain stable up to ~100 kGy, and can even increase at higher doses due to formation of extractively active degradation

products. While similar data for DES-based systems (e.g., betaine–ethylene glycol functionalized with CMPO) is yet unavailable in the literature, these results suggest potential for high radiolytic resilience in such formulations[71].

5.6. Partitioning from Lanthanides

Separation of Am(III) from Eu(III) remains challenging due to near-identical chemistry. However, when DESs are used as co-solvents—such as in systems employing choline-based DES with CyMe₄-BTBP—Separation Factors (SF) of up to ≈ 25 have been demonstrated, highlighting the potential of DES environments to enhance Am/Eu selectivity. This improved performance coincides with studies showing that extractant efficiency (e.g., TODGA) can vary considerably with solvent medium, including eutectic systems which modulate solvation landscapes[33].

6. Future Outlook and Challenges

Laboratory-scale investigations have unequivocally demonstrated the promise of deep eutectic solvents (DESs) for selective actinide and lanthanide separations. However, their successful transition to industrial-scale nuclear operations necessitates addressing several critical challenges.

A primary concern is radiolytic stability, as DES components are likely to encounter sustained exposure to intense α , β , and γ radiation in real nuclear waste streams. Such exposure can induce bond scission in hydrogen bond donors (HBDs) and acceptors (HBAs), generating radicals and degradation products that could alter solvent properties, disrupt complexation equilibria, or impair extraction efficiency. Future efforts must focus on designing radiation-hard DES formulations, possibly incorporating aromatic HBAs, sterically hindered HBDs, or stabilizing radical scavengers to mitigate decomposition.

The inherently high viscosity of many DESs poses another bottleneck, as it slows mass transfer and can limit phase disengagement rates. Mitigation strategies—such as dilution with low-viscosity co-solvents (e.g., short-chain alcohols or water) or operation at elevated temperatures—can enhance diffusivity, but they risk altering solvation structures and reducing extraction selectivity. This trade-off highlights the

need for rational viscosity control without compromising molecular recognition.

Metal recovery and solvent recyclability are equally important from both sustainability and cost-effectiveness perspectives. While recent studies have demonstrated that DESs can be regenerated and reused for over ten operational cycles with negligible extraction loss, the gradual build-up of radiolysis products, hydrolysis residues, or trace fission products may affect long-term performance. Comprehensive investigations into purification protocols—such as in-line adsorption or distillation—are essential to enable closed-loop recycling under nuclear plant conditions.

An emerging frontier lies in integrating DESs with electrochemical technologies. The intrinsic ionic conductivity of DESs makes them attractive electrolytes for processes that directly couple liquid–liquid extraction with electrodeposition, potentially bypassing intermediate stripping stages and enabling direct recovery of high-purity metallic actinides or lanthanides. Such hybrid electrochemical–solvent extraction systems could revolutionize resource recovery from complex nuclear matrices.

Finally, regulatory acceptance remains a decisive factor for deployment in nuclear facilities. Large-scale adoption will require comprehensive safety assessments, demonstration of long-term chemical stability under operational conditions, and compatibility with existing process equipment. Furthermore, compliance with IAEA guidelines on waste minimization and secondary waste generation must be rigorously demonstrated to ensure environmental and operational viability.

In summary, DESs combine molecular tunability, environmentally benign composition, and functional versatility—making them prime candidates for the next generation of radiochemical separation media. Addressing the challenges of radiolytic robustness, viscosity control, solvent recycling, electrochemical integration, and regulatory compliance will be pivotal to translating their laboratory success into industrial reality.

7. Conclusions

Deep eutectic solvents (DESs) represent a transformative advancement in the design of alternative media for nuclear separations, offering a unique convergence of molecular tunability, green chemistry

principles, and process adaptability. By judicious selection and structural modification of hydrogen bond acceptors (HBAs) and hydrogen bond donors (HBDs), DESs can be tailored to achieve exceptional selectivity for target actinides and lanthanides while simultaneously imparting radiolytic stability and chemical compatibility with aqueous, organic, and molten salt matrices. Their intrinsic low volatility, low toxicity, and potential for bio-derived components position them as safer and more sustainable alternatives to traditional organic extractants.

Recent developments underscore the feasibility of DESs not merely as extraction media but as multifunctional platforms—capable of integrating solvent extraction, ion exchange, and electrochemical recovery within a single operational framework. This multifunctionality is particularly attractive for next-generation nuclear fuel cycle strategies, where process intensification and minimization of secondary waste are critical objectives. Furthermore, the ability to incorporate luminescent or redox-active components into the DES matrix opens avenues for in-situ process monitoring and real-time solvent health diagnostics, bridging separation chemistry with smart process control.

Nevertheless, significant engineering and scientific challenges remain. High viscosities can impede mass transfer, particularly in large-scale counter-current contactors, necessitating innovations in formulation chemistry and equipment design. Radiolytic degradation, though mitigated by recent advances in radiation-resistant DES formulations, requires systematic evaluation under realistic operational doses and dose rates. Thermal and oxidative stability must also be ensured for applications in high-temperature or molten salt environments. Moreover, large-scale implementation demands robust solvent regeneration and recycling protocols, ensuring both economic viability and environmental stewardship. Looking forward, synergistic integration of DES-based separations with advanced reprocessing flowsheets—such as those incorporating pyrochemical processing, hybrid aqueous–molten salt operations, or electrorefining—could redefine the technological landscape of actinide partitioning. Key priorities for future research include: (i) the rational design of

DESs with intrinsic radiolysis resistance; (ii) development of low-viscosity, task-specific formulations; (iii) establishment of closed-loop solvent management systems; and (iv) comprehensive techno-economic and lifecycle analyses to guide industrial adoption. In conclusion, DESs have matured from laboratory curiosities into strategically relevant, next-generation separation media with the capacity to address long-standing challenges in nuclear fuel reprocessing. If ongoing innovations in chemistry, engineering, and process integration continue to converge, DES-based systems could evolve from promising alternatives to core enabling technologies in the sustainable nuclear fuel cycle of the future.

8. References

1. M. Khaleel, Z. Yusupov, S. Rekik, H. Kılıç, Y.F. Nassar, H.J. El-Khozondar, A.A. Ahmed, *Energy Exploration & Exploitation* 43 (2025) 1126.
2. A. Verbruggen, B. Wealer, *The Palgrave Handbook of Global Sustainability*, Springer, 2021, p. 1-25.
3. F. Böse, A. Wimmers, C. von Hirschhausen, AT-OM & RS-EC Research Groups, Workgroup for Infrastructure Policy (WIP), TU Berlin (2023).
4. A. Froggatt, M. Schneider, *The International Spectator* 46 (2011) 41.
5. G. Choppin, J.-O. Liljenzin, J. Rydberg, C. Ekberg, *Radiochemistry and nuclear chemistry*. Academic Press, 2013.
6. S. Tachimori, Y. Morita, *Overview of solvent extraction chemistry for reprocessing*. CRC Press: Boca Raton, FL, 2010.
7. K. Van Hecke, P. Goethals, (2006).
8. A. Paulillo, J.M. Dodds, A. Milliken, S.J. Palethorpe, P. Lettieri, *Sustainable Materials and Technologies* 25 (2020) e00186.
9. A.P. Abbott, G. Capper, D.L. Davies, R.K. Rasheed, V. Tambyrajah, *Chemical communications* (2003) 70.
10. D.J. Van Osch, L.F. Zubeir, A. Van Den Bruinhorst, M.A. Rocha, M.C.

- Kroon, *Green Chemistry*17 (2015) 4518.
11. Q. Zhang, K.D.O. Vigier, S. Royer, F. Jérôme, *Chemical Society Reviews*41 (2012) 7108.
12. E.L. Smith, A.P. Abbott, K.S. Ryder, *Chemical reviews*114 (2014) 11060.
13. M. Francisco, A. van den Bruinhorst, M.C. Kroon, *Angewandte Chemie international edition*52 (2013) 3074.
14. F. Yang, Q. Zheng, H. Tan, X. Wang, *Journal of Molecular Liquids*399 (2024) 124332.
15. M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, *Nature materials*8 (2009) 621.
16. Y. Dai, J. Van Spronsen, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, *Analytica chimica acta*766 (2013) 61.
17. M.L. Dietz, *Separation Science and Technology*41 (2006) 2047.
18. A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, *Journal of the American Chemical Society*126 (2004) 9142.
19. R. Bernasconi, G. Panzeri, A. Accogli, F. Liberale, L. Nobili, L. Magagnin, *Intech. Prog. Dev. Lon. Liq*(2017) 235.
20. M.L. Dietz, D.C. Stepinski, *Talanta*75 (2008) 598.
21. L.K. Savi, D. Carpiné, N. Waszczynskyj, R.H. Ribani, C.W.I. Haminiuk, *Fluid Phase Equilibria*488 (2019) 40.
22. R. Stefanovic, M. Ludwig, G.B. Webber, R. Atkin, A.J. Page, *Physical Chemistry Chemical Physics*19 (2017) 3297.
23. H. Kivela, M. Salomaki, P. Vainikka, E. Makila, F. Poletti, S. Ruggeri, F. Terzi, J. Lukkari, *The Journal of Physical Chemistry B*126 (2022) 513.
24. G. Arrachart, J. Couturier, S. Dourdain, C. Levard, S. Pellet-Rostaing, *Processes*9 (2021) 1202.
25. B. Liang, J. Gu, X. Zeng, W. Yuan, M. Rao, B. Xiao, H. Hu, *Molecules*29 (2024) 4624.
26. X. Sun, H. Luo, S. Dai, *Chemical reviews*112 (2012) 2100.
27. S. Riaño, M. Petranikova, B. Onghena, T. Vander Hoogerstraete, D. Banerjee, M.R.S. Foreman, C. Ekberg, K. Binnemans, *RSC Advances*7 (2017) 32100.
28. J. Almeida, R. Craveiro, P. Faria, A.S. Silva, E. Mateus, S. Barreiros, A. Paiva, A.B. Ribeiro, *Science of the Total Environment*710 (2020) 136364.
29. N. Peeters, K. Janssens, D. de Vos, K. Binnemans, S. Riaño, *Green Chemistry*24 (2022) 6685.
30. E. Habibi, K. Ghanemi, M. Fallah-Mehrjardi, A. Dadolahi-Sohrab, *Analytica chimica acta*762 (2013) 61.
31. W. Chen, J. Jiang, X. Lan, X. Zhao, H. Mou, T. Mu, *Green chemistry*21 (2019) 4748.
32. A. Berthod, M. Ruiz-Angel, S. Carda-Broch, *Journal of Chromatography A*1184 (2008) 6.
33. G. Colombo Dugoni, E. Mossini, E. Macerata, A. Sacchetti, A. Mele, M. Mariani, *ACS Omega*6 (2021) 3602.
34. A. Srivastava, P. Sahu, M.S. Murali, S. Musharaf Ali, M. Sahu, J.S. Pillai, N. Rawat, *Journal of Electroanalytical Chemistry*901 (2021) 115752.
35. G. Inman, I.C. Nlebedim, D. Prodius, *Energies*15 (2022) 628.
36. X. Yang, L. Xu, D. Fang, A. Zhang, C. Xiao, *Chemical Communications*60 (2024) 11415.
37. B. Bernicot, G. Arrachart, S. Dourdain, N. Schaeffer, A. Dias, S. Pellet-Rostaing, *Green Chemistry*(2025)
38. F.J. Alguacil, *Molecules*29 (2024) 1356.
39. A. Layek, S. Patil, R. Gupta, R.R. Dumpala, A. Balhara, A. Ghosh, *Journal of Molecular Liquids*414 (2024) 126159.
40. S.M. Patil, R.M. Rao Dumpala, D. Goswami, R. Dawar, R. Gupta, *Inorganic Chemistry*61 (2022) 12599.
41. S.M. Patil, R. Agrawal, R. Gupta, S.K. Gupta, A. Ghosh, S. Kumar, K. Jayachandran, T.K. Ghanty, *Dalton Transactions*52 (2023) 17349.

42. S.M. Patil, K. Jayachandran, M. Sahu, R. Gupta, Journal of The Electrochemical Society170 (2023) 113503.
43. S.M. Patil, S.K. Gupta, D. Goswami, A. Ghosh, M. Tyagi, B.B. Dhotare, T.K. Ghanty, R. Gupta, ACS Applied Electronic Materials4 (2022) 2175.
44. R. Gupta, B. Vats, A.K. Pandey, M.K. Sharma, P. Sahu, A.K. Yadav, S.M. Ali, S. Kannan, The Journal of Physical Chemistry B124 (2019) 181.
45. V. Babain, M. Alyapyshev, C. Ekberg, T. Todd, Solvent Extraction and Ion Exchange41 (2023) 253.
46. H. Yamamoto, M. Hattori, K. Ito, M. Shikano, K. Yoshii, The Journal of Physical Chemistry Letters15 (2024) 6249.
47. J.T. Amphlett, Y. Lee, W. Yang, D. Kang, N.-E. Sung, J. Park, E.C. Jung, S. Choi, ACS omega7 (2021) 921.
48. O.S. Hammond, E.K. Bathke, D.T. Bowron, K.J. Edler, Inorganic Chemistry62 (2023) 18069.
49. J. Couturier, C. Levard, B. Collin, P. Chaurand, V. Vidal, O. Mathon, A. Duvivier, B. Angeletti, D. Borschneck, J. Rose, S. Pellet-Rostaing, G. Arrachart, Separation and Purification Technology366 (2025) 132740.
50. Q. Tang, S. Liu, H. Hao, X. Dong, Y. Guo, Y. Lu, Z. Wang, C. Xu, Chem & Bio Engineering(2025).
51. N. Kumar, B. Sadhu, A.E. Clark, Rare Earth Elements and Actinides: Progress in Computational Science Applications(2021) 249.
52. A. Yadav, S. Pandey, Journal of Chemical & Engineering Data59 (2014) 2221.
53. H. Kivelä, M. Salomäki, P. Vainikka, E. Mäkilä, F. Poletti, S. Ruggeri, F. Terzi, J. Lukkari, The Journal of Physical Chemistry B126 (2022) 513.
54. B. Bernicot, G. Arrachart, S. Dourdain, N. Schaeffer, G. Teixeira, S. Pellet-Rostaing, Journal of Molecular Liquids427 (2025) 127332.
55. M.S. Khan, K.B. Ansari, A. Fatima, M.K.A. Mesfer, M. Danish, A. Tawfik, U. Maheshwari, AQUA—Water Infrastructure, Ecosystems and Society73 (2024) 73.
56. I. Kajan, M. Florianová, C. Ekberg, A.V. Matyskin, RSC advances11 (2021) 36707.
57. J.F. Dozol, R. Ludwig, Ion Exchange and Solvent Extraction19 (2010) 195.
58. D. Ternova, Université de Strasbourg; Kiïvs'kij nacional'nij unïversitet imeni Tarasa ..., 2014.
59. Y. Chen, D. Yu, Z. Liu, Z. Xue, T. Mu, New Journal of Chemistry46 (2022) 17640.
60. D. Lakshmi, R. Padmashini, G. Ezhilarasi, P. Sivaraman, R. Zahira, S. Chenniappan, Distributed Energy Storage Systems for Digital Power Systems, Elsevier, 2025, p. 35-51.
61. Z. Maugeri, P.D. de María, Rsc Advances2 (2012) 421.
62. Z. Yuan, H. Liu, W.F. Yong, Q. She, J. Esteban, Green Chemistry24 (2022) 1895.
63. V.S. Kislik, Solvent extraction: classical and novel approaches. Elsevier, 2011.
64. A. Anupan, A. Imyim, S. Fuangswasdi, Journal of Molecular Liquids432 (2025) 127760.
65. I. Yildiz, (2023).
66. F. Monroy-Guzman, C.d.C. De la Cruz Barba, E. Jaime Salinas, V. Garibay-Feblés, T.N. Nava Entzana, Metals10 (2020) 1390.
67. V. Lakshmanan, S. Vijayan, Extraction 2018: Proceedings of the First Global Conference on Extractive Metallurgy, Springer, 2018, p. 1913-1930.
68. A.H. Bond, M.L. Dietz, R. Chiarizia, Industrial & Engineering Chemistry Research39 (2000) 3442.
69. Y. Shen, X. Tan, L. Wang, W. Wu, Separation and purification technology78 (2011) 298.
70. J. Gamare, B.G. Vats, European Journal of Inorganic Chemistry26 (2023) e202300441.
71. B.J. Mincher, S.P. Mezyk, G. Elias, G.S. Groenewold, C.L. Riddle, L.G.

ASSET Bulletin on "Advancement in Green Separation"

Olson, Solvent Extraction and Ion
Exchange³¹ (2013) 715.



Dr. Ruma Gupta is a Scientific Officer (F) at the Fuel Chemistry Division, Bhabha Atomic Research Centre (BARC), and Assistant Professor at the HomiBhabha National Institute, Mumbai. She is from 52nd batch of the BARC Training School in 2008 and subsequently joined BARC in 2009. Dr. Gupta obtained her B.Sc. (Hons.) and M.Sc. in Chemistry from Hindu College, University of Delhi, followed by a Ph.D. in Chemistry from HBNI, Mumbai. Her research interests span actinide and lanthanide electrochemistry, synthesis of modified electrodes, development of electrochemical sensors for actinide detection, design of task-specific ionic liquids and deep eutectic solvents, solvometallurgical approaches, solvent extraction processes, and the application of actinide and rare-earth chemistry in nuclear fuel cycle back-end operations and decontamination. Dr. Gupta has published over 80 research papers in reputed international journals and conference proceedings. Her scientific contributions have been recognized through several awards, including the Department of Atomic Energy Young Scientist Award (2018), INSA-PAS Bilateral Exchange Fellowship (2016), DST Travel Fellowship (2014), and election as a Young Associate of the Maharashtra Academy of Sciences (2022). Most recently, she was elected as a Member of the National Academy of Sciences, India (NASI) in 2025.



Mr. Arkaprava Layek joined Fuel Chemistry Division, Bhabha Atomic Research Centre in 2022 after graduating from 16th batch (65th batch) of BARC Training School, IGCAR. He completed his B.Sc from Banaras Hindu University (BHU), Varanasi and M.Sc from University of Hyderabad (UoH), Telangana. After clearing M.Sc., his area of interest includes Deep Eutectic Solvents for extraction and separation of actinides and lanthanides, electrochemistry of lanthanides and actinides, design of sensors for precise actinide detection, electrocatalysis etc. He has total 7 publications in various peer-reviewed journals and conferences till now. He was awarded with the **"Best Poster Award"** in NUCAR-2025 conference.

Role of Supercritical Fluid Extraction for Green Separation

Ankita Rao^{1,2}

¹Radiochemistry Division,

Bhabha Atomic Research Centre, Mumbai 400085, India

²Homi Bhabha National Institute, Trombay, Mumbai 400094, India

(Corresponding Author: Email: ankita@barc.gov.in)

Introduction

Albeit separation of component of interest from varied matrices has been carried out since the inception of human civilization, development of innovative and environmentally benign schemes for separation and purification is endeavored. Over past few decades, enhanced global demand for safety and quality in edible and medicinal products have led to quest for alternative methods. Separation of metal ions of interest from various matrices is of profound importance in chemical analysis, industrial chemistry and is practically indispensable in the various stages of nuclear fuel cycle. Though conventional separation techniques like solvent extraction, ion exchange, distillation and precipitation are extensively employed; there is strong impetus to search for alternative techniques. Supercritical fluid extraction (SFE) is an area of active research being pursued fervently owing to its simplicity, ease of operation and most importantly minimization of the generation of secondary waste. CO₂ is a popular choice for the Supercritical Fluid (SCF) due to its attractive properties [1, 2].

The objective of green chemistry is to reduce the usage and production of hazardous substances for chemical processes, while reducing energy consumption and moving toward renewable sources [3]. Also, green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal. Green chemistry aims to reduce pollution at its source by minimizing or eliminating the hazards of chemical feedstocks, reagents, solvents, and products. The principles of Green Chemistry are given in Fig.1. The present article describes the fundamentals aspects of SC CO₂ extraction, its inherent advantages and enumerates few key applications of this green separation technique for organic compounds as well as

metal ions, with special emphasis to the nuclear industry. Between 2000 and 2024, there have been over 7800 research studies related to "supercritical CO₂ fluid extraction" in the SCOPUS database (2024). Therefore, the details of this promising technology should be well understood and further developed.

Historical Perspective

Supercritical fluid behaviour of a substance was first observed in 1822 by Baron Cagniard de la Tour. He noted that when the temperature of certain sum was increased by heating each of them in a closed glass container, then the gas-liquid boundary disappeared. Hannay and Hogarth in 1879 found that solid compounds could be dissolved in supercritical fluid when the fluid possessed densities close to liquid densities. In 1898 Villard carried out the reaction of supercritical ethane with iodine to form 1, 2-iodoethane. The first work on metal ion extraction was first reported by Laintz et al. only in 1990 when SFE of Cu²⁺ ion was carried out using fluorinated complexing agent.



Fig.1. Principles of Green Chemistry

Basic Aspects

As shown in the pressure-temperature phase diagram of a pure component (Fig.2), for a substance to exist in a particular phase there are well defined values of temperature and pressure that must be attained. Along the liquid-gas phase boundary, there exists a critical point represented by its critical temperature (T_c) and critical pressure (P_c). Keeping the pressure constant, at temperatures just below the critical point a substance will exist in its liquid state and similarly keeping the temperature constant, at pressures just below the critical point a substance will exist in its gaseous state. Upon attaining temperatures and pressures beyond critical point, the distinction between liquid and gaseous phases disappears and it forms a homogenous fluid known as supercritical fluid (SCF).

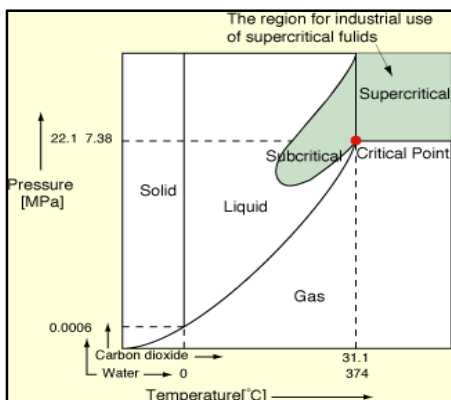


Fig.2. P-T Phase diagram for CO₂

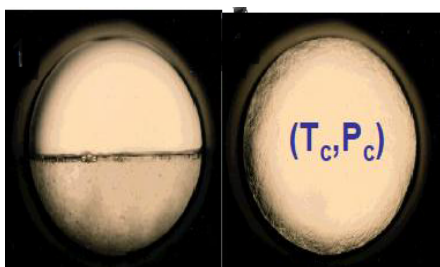


Fig.3. Visualization of transition from liquid-vapour equilibria to supercritical state for CO₂

At critical point distinction between the liquid and vapour phases disappears, as can be seen in Fig.3. The properties of supercritical fluid compare with that gas and liquid substance as can be seen from the Table 1. Supercritical fluids have unique physical properties intermediate between those of liquids and gases. They

have viscosities and diffusivities similar to those of gases, making it easier for the fluid to permeate into the given matrix, while also having their densities similar to those of liquids, making it possible to extract the desired compound from the matrix. The order of magnitude of physical properties of solvents in different states of matter is given in Table 1.

The density can be changed by tuning pressure and temperature near the critical point. A small increase in pressure causes a large increase in the density of the the supercritical phase. Many other physical properties also show large gradients with pressure near the critical point, e.g. viscosity, relative permittivity and solvent strength, which are all closely related to the density.

Table1. Order of magnitude of physical properties of solvents in different states

Property	State		
	Gas	SCF	Liquid
Density (g/ cm ³)	10 ⁻³	0.3	1
Diffusivity (cm ² / s)	10 ⁻¹	10 ⁻³	5x10 ⁻³
Viscosity (g/ cm.s)	10 ⁻⁴	10 ⁻³	10 ⁻²

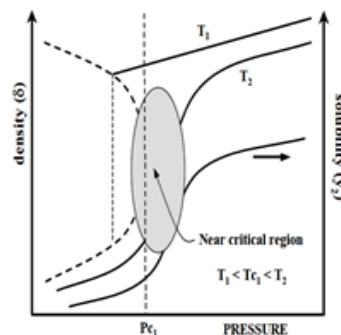


Fig.4. Density and solid solubility in fluid phase as a function of pressure

Carbon dioxide as Supercritical Fluid

The choice of a supercritical fluid depends mainly on the temperature and pressure conditions required to get the fluid into its supercritical state. A list of various fluids with their supercritical temperatures and pressures is given in Table 2.

Among all the possible fluids, over the years carbon dioxide (CO₂) has gained particular interest to be used as a supercritical fluid for SFE. This is mainly due to its low critical temperature (304 K) and low critical pressure (73 bar/ 72.8

atm). It has several other advantages such as being non-toxic, non-flammable, environmentally compatible solvent that can be recovered post-processing and is miscible with many organic solvents. The TLV (threshold limit value for airborne concentration at 298 K for which nearly all workers may be daily exposed without any adverse effect) is quite high, 5000 ppm, rendering it less toxic than most of the organic solvents like acetone (TLV = 750 ppm) and chloroform (TLV= 10 ppm). It is benign and cross contamination of other phase or residual CO₂ in the material processed is not a matter of concern. CO₂ being non-polar, cannot dissolve polar and high molecular weight compounds. To extract such compounds, 0-20 mol. % of polar or non-polar co-solvents known as modifiers are incorporated with CO₂ to increase their solubility in the SCF.

Table 2. Various Supercritical Solvents with their critical parameters²⁶

Solvent	Critical Temperature (K)	Critical Pressure In MPa; (In atm)
Carbon dioxide (CO ₂)	304.1	7.38 (72.8)
Water (H ₂ O)	647.096	22.064 (217.755)
Methanol (CH ₃ OH)	512.6	8.09 (79.8)
Ethanol (C ₂ H ₅ OH)	513.9	6.14 (60.6)
Acetone (C ₃ H ₆ O)	508.1	4.70 (46.4)
Methane (CH ₄)	190.4	4.60 (45.4)
Ethane (C ₂ H ₆)	305.3	4.87 (48.1)
Ethylene (C ₂ H ₄)	282.4	5.04 (49.7)
Propane (C ₃ H ₈)	369.8	4.25 (41.9)
Propylene (C ₃ H ₆)	364.9	4.60 (45.4)
Nitrous oxide (N ₂ O)	306.57	7.35 (72.5)

The behavior of density of SCF as a function of temperature and pressure can be understood using Peng-Robinson Equation of State (PREOS) [1] that is derived from the Van der Waals equation for one component fluid which can be considered as an improvement and/or modification of the ideal gas equation. The ideal gas equation is given as:

$$P=(RT)/V_m \quad (1)$$

And the Van der Waals equation is given as:

$$P=[RT/(V_m-b)]-[a/V_m^2] \quad (2)$$

Where P is the pressure, R is the universal gas constant, T is the absolute temperature, V_m is the molar volume, and

constants a and b are known as Van der Waals parameters.

Where P is the pressure, R is the universal gas constant, T is the absolute temperature, V_m is the molar volume, and constants a and b are known as Van der Waals parameters.

Herein the ideal values of volume are obtained by correcting the measured values of volume by introducing the term (V_m-b) which accounts for 'effective' molar volume in consideration of a finite volume occupied by a particle as opposed to ideal gas considerations of it being negligible. Similarly, the second term [a/V_m²] accounts for corrections applied to measured values of pressure since unlike ideal gas considerations of molecules showing no interactions with each other, they display van der Waals forces in close proximity to each other.

To obtain the Peng-Robinson Equation, the second term of the above equation is modified as follows:

$$P=RT/(V_m-b)-a(T)/(V_m^2+2V_m b-b^2) \quad (3)$$

Further from the PREOS the values of molar volume (V_c) and compressibility factor (Z_c) can be calculated as follows:

$$V_c=3.9514b \quad (4)$$

$$Z_c=P_c V_c / RT_c = 0.3074 \quad (5)$$

For example, the densities of pure CO₂ calculated using the Peng-Robinson Equation of State in the temperature and pressure range relevant to the current study is shown in Table.3 given below: ¹⁸

From the data it is clearly evident that at a constant temperature, increasing the pressure of CO₂ increases its density and similarly, at a constant pressure, increasing the temperature of the system decreases the density of CO₂. Thus, by fluctuating the temperature and pressure parameters can drastically vary the density, thus the solvating power of the fluid under supercritical conditions.

Table3. Densities (g/cm³) of pure CO₂ calculated using PREOS

[Parameters]	Pressure (bar)			
Temperature (°C)	150	200	240	260
50	0.655	0.762	0.818	0.840
60	0.559	0.692	0.758	0.785
70	0.473	0.623	0.700	0.730
80	0.408	0.560	0.643	0.676

Quantitative estimation of solubility of a given solute in a supercritical fluid can be understood by Chrastil [4] empirical correlation that can be given as follows:

$$\log S = k \log \rho + C \quad (6)$$

Where S is the solubility of an organic compound (in g/L), and ρ is the density of supercritical fluid, k is the number of CO_2 molecules that solvate the given solute and C is a constant that involves various thermal properties such as heat of vaporization, heat of solvation and/or volatility of the solute. This equation that was originally proposed for organic compounds, was found to be effective for metal ion complexes as well.

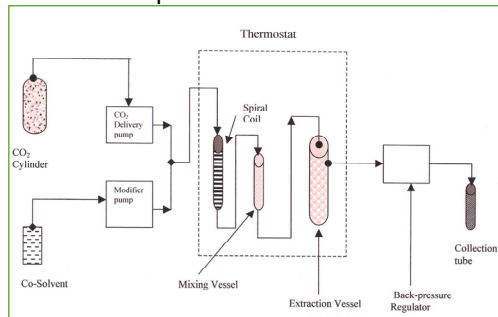


Fig. 5. Schematic of laboratory experimental set-up

While organic compounds can be extracted by SC CO_2 directly or by using modifiers like methanol, to carry out supercritical fluid extraction of metal ions using apolar solvents like CO_2 , suitable complexation agents are employed to first allow the complexation of metal ions, followed by which the soluble metal ion complex is extracted by SC CO_2 .

Complexation can be carried out in SFE in two ways:

i. Online complexation-Complexing agent is solubilised in SC CO_2 stream and then subjected for matrix containing target metal ion.

ii. In Situ Complexation- Complexing agent can be directly added to matrix of interest.

After complexation, the extraction can be carried out essentially in two modes:

i. Static Mode of Extraction - In this mode of extraction, the system is allowed to attain and remain at particular temperature and pressure for certain period of time followed by collection.

ii. Dynamic mode of Extraction In this mode of extraction, at particular temperature and pressure the collection of complexes is carried out.

Parameters controlling SFE

- Solubility & stability of complexing agents

- Complexing ability
- Solubility of metal complex
- Water & pH
- Temperature & pressure
- Chemical form of metal species
- Matrix

The instrumental set-up (Fig.5) consists of CO_2 cylinder, CO_2 delivery pump, co-solvent pump, thermostat, back-pressure regulator and collection vessel. Operation and functioning of each of the components is described elsewhere [5].

Comparison of Conventional solvent extraction with SC CO_2 extraction: Green quotient

In liquid waste generation takes place. In extraction process desired material must be accumulated in the organic phase during loading; the ratio of the aqueous phase to organic phase the volume should not more than ~ 10 . This leads to the use of large volumes of solvent, particularly when the feed is lean. This adverse effect can possibly be eliminated by the usage of non-toxic SC CO_2 for SFE.

Due to low viscosity and high diffusivities of SC CO_2 , the mass transfer characteristics of SCFs are excellent as compared to that of liquid solvents. In solvent extraction of metals, the chemical reactions occurring at the interface may be faster as compared to mass transfer processes, making the mass transfer step the kinetically rate determining step.

SC CO_2 helps to eliminate the residual contamination which takes place in liquid-liquid extraction.

Lower surface tension of SC CO_2 over traditional organic solvents, resulting to increased dispersed phase surface area, which may reduce the required equipment size for a particular solvent-to-feed ratio.

The tunability of the density of SC CO_2 by varying temperature and pressure conditions leads to the accessibility towards a spectrum of solvent properties for a single SCF facilitating processing of multiple products in a single plant.

SFE is generally thought to be energy intensive. However, the energy needed to attain the SCF state for CO_2 is compensated by the negligible energy required for solvent recovery from the extract by simple depressurization as well as low cost of CO_2 , higher concentration of a desirable component in extracts and no effluent pollution related cost.

Solid matrices loaded with metal compounds may be directly subjected to SFE due to the high penetration ability of SCFs leading to extraction of the component of interest. Thus, SFE may lead to minimization in the usage of acid required for pre-treatment of matrices before conventional solvent extraction. Minimization of acid usage and organic volume is a very important advantage with respect to the nuclear industry where management of secondary nuclear waste poses a great problem. In certain nuclear applications like the reprocessing of irradiated fuel, the problems associated with radiolytic degradation of organic solvent are a matter of concern. CO_2 is radio chemically stable and leads to no third phase formation. Therefore, SC CO_2 provides faster, cleaner and efficient extractions, as they generally become gas after the extraction and escape leaving the dissolved solute.

Application of SC CO_2 Extraction for Organic compounds[1]

The technologies like supercritical fluid extraction over traditional high temperature and solvent intensive methods like Soxhlet extraction etc. has gained popularity for rapid, contamination-free extraction for many food and pharmaceutical products. The SFE method has been reported to display some noteworthy advantages over traditional techniques, such as shorter extraction times, low environmental impact, and yields clean, non-thermally-degraded final product of interest.

Large scale plants have been in commercial operation since the late 1970s for decaffeination of coffee and tea, refining of cooking oils, recovering flavors from spices and other plant materials (Fig.6). A commercial plant was built in the 1980s for the separation of ethanol from water in combination with distillation. The processing of heavy hydrocarbons employing SCF has been commercialized already. Other applications of SFE include chemical separations and purification, polymer processing, regeneration of activated carbon and other adsorbents, deposition of materials in micro porous substrates etc. In addition to environmentally driven replacement of organic solvents, SCF have direct environmental application in the remediation of soil, water and waste matrices. The oxidation of organic

contaminants in supercritical water has been studied extensively as an alternative to incineration. SCF has been investigated as solvent medium for several important chemical reactions.



Fig.6. SC CO_2 extraction of organic compounds

Application of SC CO_2 Extraction for Metal Ion Separation

There are extensive reports based on supercritical fluid extraction of metal ions using various complexing agents, some of their structures are given in Fig.7 [6, 7]. The first report of supercritical fluid CO_2 extraction of metal ion viz. Cu^{2+} by fluorinated complexing agent was by Lin et al. In the recent past, supercritical fluid CO_2 extraction has been explored extensively for toxic metal removal from various waste streams and recovery of valuable metal ions from secondary sources viz. electronic waste, fly ash, spent catalyst etc. [8-12]. Fig. 8 provides a pictorial overview of our recent work on direct, acid-free Mo recovery from solid matrices.

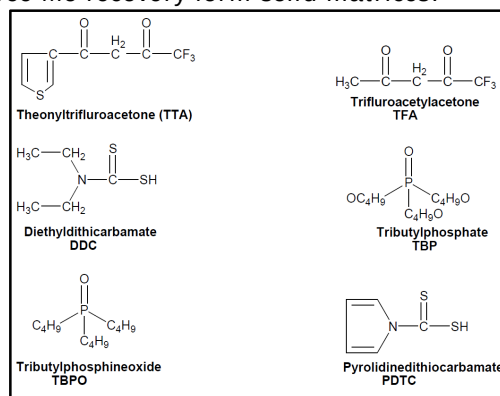


Fig.7. Some complexing agents used for SC CO_2 extraction

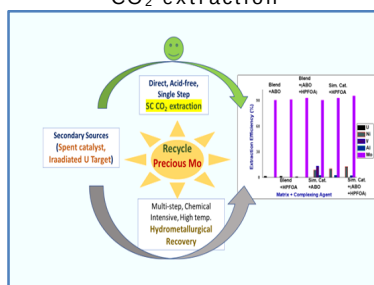


Fig.8. Pictorial overview of Mo recovery study from solid matrices [11]

Application of SC CO₂ Extraction for Nuclear Industry

There exists literature on the solvent extraction of actinides (viz. U, Th, Pu, Np) from nitric acid medium with organophosphorus extractants viz. TBP, TOPO, DEHPA, as the complexing agents as these systems are very commonly encountered in various stages of nuclear fuel cycle. However, SC CO₂ extraction of lanthanides and actinides from solids with β -diketone was first reported by C.M. Wai et al. [13]. Several studies have been carried out on SFE of uranium, thorium and plutonium from nitric acid medium employing different sets of ligands (organophosphorus, diketones, amides) [14-16]. In order to get an insight into the SFE process vis-à-vis solvent extraction, we have carried out thorough parametric study for the U-TBP-HNO₃ system. Density of supercritical fluid plays a vital role as solvent strength is directly related to density and density is markedly affected by pressure and temperature conditions. Also, under extraction conditions, the supercritical phase is continuously renewed by flowing SCF. The SFE process is, therefore, considered to be combined effect of equilibrium process and extraction kinetics [17]. Fig. 9 depicts a scheme for SC CO₂ extraction of U with TBP.

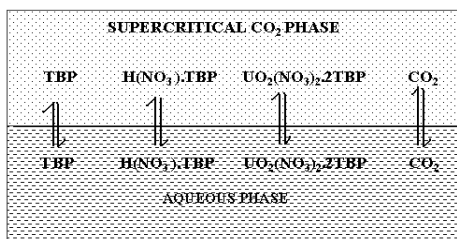


Fig.9. Scheme for SC CO₂ extraction of U from nitric acid medium with TBP as complexing agent

Also, attractive is the possibility of direct dissolution and extraction of actinides employing complexing agent-acid adducts (like TBP.HNO₃ adduct) from solid matrices. The adduct can be considered as a reverse micelle, where the actinide dissolution takes place in the aqueous core and the corresponding metal-complex becomes soluble and is extracted in the SC CO₂ medium (Fig.10).

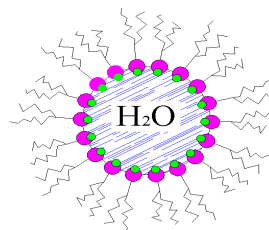


Fig.10. Reverse micelle structure of complexing agent adducts

The various applications of SFE for the nuclear industry for different stages of nuclear fuel cycle viz. ores, spent nuclear fuels and radioactive wastes are depicted in Fig.11.

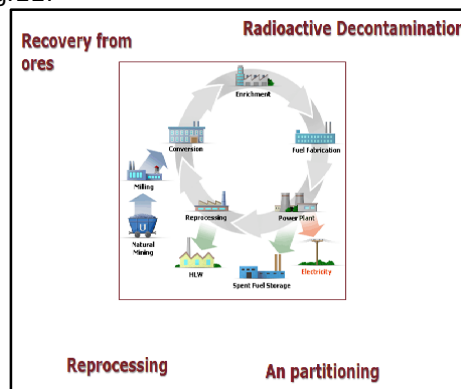


Fig.11. Application of SC CO₂ extraction for nuclear industry

SC CO₂ extraction of uranium from various ores, yellow cake matrices and secondary sources (fly ash, scraps) have been extensively reported [18-21].

Uranium SFE from crude matrices viz. SDU, MDU, HTUP, rock phosphate ores have been studied by our group using alkyl phosphate adducts and incinerable amide adducts [22-24]. Single medium of TRP/amide-HNO₃ adduct was used for dissolution as well as complexation and usage of free acid was avoided. The resultant $UO_2(NO_3)_2$ complex with amide/TRP was highly soluble in supercritical CO₂.

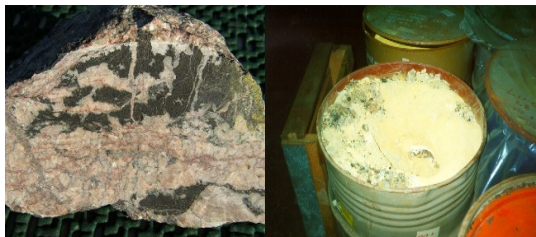


Fig.12. Ore and yellow cake matrices investigated for SC CO₂ extraction of uranium

The hydrometallurgical routes of spent nuclear fuel reprocessing viz. PUREX process, with modifications according to nature of fuel and burn-up has been the workhorse for nuclear industry since decades. This process, based on TBP as extractant suffers from several limitations. Hence, non-aqueous routes are being explored fervently. Towards that direction, Russia developed The RELICT process (REprocessing by Liquid Carbon dioxide Treatment) based on the dissolution of spent nuclear fuel oxides employing TBP-nitric acid adduct in liquid CO₂ at ambient temperature and pressure condition of 25 °C and 6-7 MPa [25, 26]. This process was demonstrated using actual RBMK and VVER spent fuels. experiments. Japan put forth the Supercritical fluid Direct eXtraction (SUPERDIREX) process where spent nuclear fuel dissolution, feed clarification and U, Pu extraction were combined in a single step with TBP-HNO₃ adduct in terms of 'direct extraction column' [27].

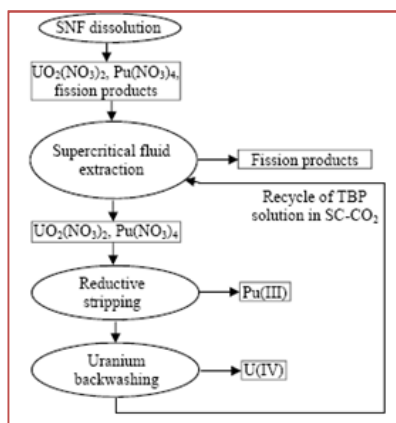


Fig.13. SUPER-DIREX process for nuclear fuel reprocessing

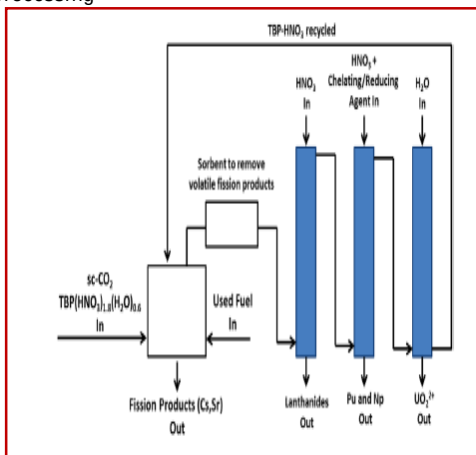


Fig.14. Actinide partitioning scheme using SC CO₂ extraction

Partitioning of actinides from fission products was also explored in spent nuclear fuel [28], as described schematically in Fig.14. The process was based on three extractor systems, where lanthanides, Pu-Np and U were segregated in subsequent stages and the adduct was regenerated. AREVA NP and University of Idaho co-developed and patented process for recovery of enriched uranium from Incinerator Ash of LEU fabrication plant by using TBP-HNO₃ adduct [29]. The process scheme is depicted in Fig.15.

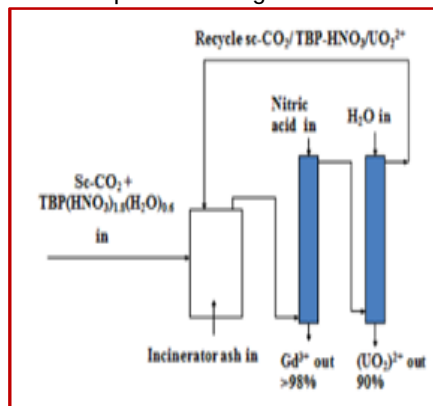


Fig. 15. SC CO₂ dissolution of U and Gd oxides in incinerator ash followed by selective stripping

Decontamination of polymeric wastes from Pu and Am was demonstrated [30]. Recovery of U and Pu from pyrochemical salt matrix using SFE was also reported [31]. Surface decontamination of radioactive metal wastes was demonstrated using acid in SC CO₂ emulsions [32]. Few studies of SC CO₂ extraction in conjunction with eutectic solvents have been reported for uranium matrix dissolution-extraction and decontamination applications [33, 34].

Conclusions

SC CO₂ extraction finds widespread application for residue-free, ambient temperature separation of natural products and organic compounds and has been a popular industrial technology. The aspect of waste minimization, chemical inventory reduction and process simplification also assumes considerable significance for metal ion separations relevant to various industrial applications, which may override the energy intensive SCF production step. Also, the techno economic studies on supercritical fluid extraction of actinides have indicated a more efficient and environmentally sustainable technology

with respect to reduction in process steps and radioactive waste reduction.

References

1. M. A. Mchugh, V.J. Kruckonis, *Supercritical Fluid Extraction Principles and Practice*, Butterworth-Heinemann (1994).
2. M. Mukhopadhyay, *Natural Extracts using Supercritical Carbon Dioxide*, CRC press (2000).
3. P. T. Anastas, J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press (2000).
4. J. Chrastil, *J. Phys. Chem.*, 86, 3016 (1982).
5. A. Rao, *Supercritical Fluid extraction of Metal ions from various matrices*, Ph.D. Dissertation, CHEM01200604021, HBNI.
6. C. Erkey, *J. of Supercritical Fluids*, 17, 259 (2000).
7. N. G. Smart, T. Carleson, T. Kast, A. A. Clifford, M. D. Burford, C. M. Wai, *Talanta*, 44, 137 (1997).
8. S.M. Ghoreishi, K. Ansari, H.S. Ghaziaskar, *J. Supercrit. Fluids*, 72 (2012), pp. 288-297.
9. F. Wu, X. Liu, G. Qu, P. Ning, *Sep. Purif. Technol.*, 301 (2022), 122043.
10. J. Fazari, Md Z. Hossain, P. Charpentier, *J. materials Science*, 59, 12257 (2024).
11. A. Rao, A. S. Kanekar, A. Sengupta, R. Gupta, *New J. Chem.*, 49 (2024), 1400-1409.
12. J. Zhang, J. Anawati, G. Azimi, *Waste Management*, 139 (2022), 168.
13. C. M. Wai and S. Wang, *Journal of Chromatography*, 785, 369 (1997).
14. Y. Meguro, S. Iso, H. Takeishi, Z. Yoshida, *Radiochimic. Acta*, 75, 185 (1996).
15. Kumar, R., Sivaraman, N., Srinivasan, T. G., Rao, P. R. V.: *Radiochim. Acta* 90, 141, (2002).
16. Kumar, R., Sivaraman, N., Vaidivu, E. S., Srinivasan, T. G., Rao, P. R. V.: *Radiochim. Acta* 91, 197 (2003).
17. A. Rao, P. Kumar and K.L. Ramakumar, *Radiochimica Acta*, 96 (2008) 787-798.
18. L. T. K. Dung, T. Imai, O. Tomioka, M. Nakashima, K. Takahashi, Y. Meguro, *Anal. Sci.*, 22, 2006.
19. 24. Wang W., Tan K., Xie E., Liu J., Cai G., *Adv. Mater. Res.* 2013, 634, 3517-3521.25.
20. Leybros A., Hertz H. A., Hartmann D., Grandjean A., Boutin O., *Chem. Eng. J.* 2017, 316, 196-203.
21. A. S. Kanekar, P. Pathak, P. K. Mohapatra, R. Acharya, V.K. Manchanda, *Desalination and Water Treatment* 38 (2012) 190-194.
22. Prabhat P., Rao A., Kumar P., Tomar B. S., *Hydrometallurgy*, 2016, 164, 177-183.
23. P. Prabhat, A. Rao, V.G. Mishra, D.J. Shah, P. Kumar, B.S. Tomar, *Radiochim. Acta* (2020), <https://doi.org/10.1515/ract-2020-0009>
24. A. S. Kanekar, S. S. Kumar, A. Rao, S. Dhara, *Industrial and Engineering Chemistry Research* (2024) <https://doi.org/10.1021/acs.iecr.4c03075>.
25. B. F. Myasoedov, Yu. M. Kulyako, T. I. Trofimov, M. D. Samsonov, D. A. Malikov, T. Mariutina and B. Ya. Spivakov, *Radiochim. Acta* 97 (2009) 473- 477.
26. M. D. Samsonov, A. Yu. Shadrin, D. N. Shafikov, Yu. M. Kulyako, B. F. Myasoedov, *Radiochemistry*, 2011, Vol. 53, No. 2, 111-122.
27. T. Shimada, S. Ogumo, N. Ishihara, Y. Kosaka, Y. Mori, *J. Nucl. Sci. Technol.*, Suppl 3, (2002), 757-760.
28. B.J. Mincher, C. M. Wai, R.V. Fox, D.L. Baek, C. Yen, M. E. Case, *J. Radioanal. Nucl. Chem.* (2016) 307, 2543-2547.
29. *Radioactive decontamination*, September/October 2008, *Radwaste Solutions*.
30. K. Sujatha, K.C. Pitchaiah, N. Sivaraman, K. Nagarajan, T.G. Srinivasan, P.R. Vasudeva Rao, *Desalination and Water Treatment* 52 (2014) 470- 475.
31. K.C.Pitchaiah, K.Sujatha,,J.Deepitha,S. Ghosh, N.Sivaraman, *J. Supercrit. Fluids* 147 (2019) 194-204.
32. M. Koh, J. Yoo, M. Ju, B. Joo, K. Park, H. Kim, H. Kim, *Ind. Eng. Chem. Res.*, 47, (2008), 278-283.
33. A. Rao, A. Srivastava, A., 2021. *Sep. Purif. Technol.* 257, 117950-117958.
34. H. Lv, J.Gao, J. Chen, T. Li, Y. Liang, B. Hu, F. Ma, Y. Xue, Y. Yan, E. O. Tutu, *Chemical Engineering Journal*, 490, 15 June 2024, 151793.



Dr. Ankita Rao obtained her M.Sc. From Calcutta University in 2004 and joined Radiochemistry and isotope Group in 2005, after successful completion of one-year orientation course, OCES (48th. Batch). She has worked on Supercritical Fluid Extraction (SFE) of actinides and obtained her Ph.D. from HBNI in 2011 on the topic "Supercritical fluid extraction of metal ions from various matrices". She has been involved in studies for probing redox speciation of actinides in solutions, separation of actinides involving sustainable methodologies, purification of fission molybdenum and recovery of plutonium from analytical solutions as well as refractory matrices. She has more than 50 publications in the form of peer reviewed journals and technical reports. As part of NUMAC CELL, she is also responsible for Nuclear Material Accounting Database Management for all DAE facilities

Application of Ionic Liquids in Hydrometallurgical Recovery of Rare Earths and Precious Metals from Electronic Waste

N. Nav Vigyan, R. Ruhela*

Materials Processing Division, Bhabha Atomic Research Centre

*Dr. Ritesh Ruhela, riteshr@barc.gov.in; 022-69293031

Introduction

Ionic liquids refer to a class of materials comprising of cations and anions in liquid form, however, the term is now more commonly used to specify "Room Temperature Ionic Liquids", i.e., ionic compounds with melting points well below 100 °C. The contradictory properties of being an ionic compound but also having lower melting point is due to presence of at least one of the ions having bulky asymmetrical organic structure, thereby sterically hindering the formation of long range ordered lattice found in ionic salts. Ionic liquids as such can be formed from millions of combinations of cations and anions and therefore the ideal ionic liquid for an application can be designed specifically to perform the desired 'task', and in context of hydrometallurgy being selective metal extraction. Some common cations and anions found in the ionic liquids are given below in Figure 1[1].

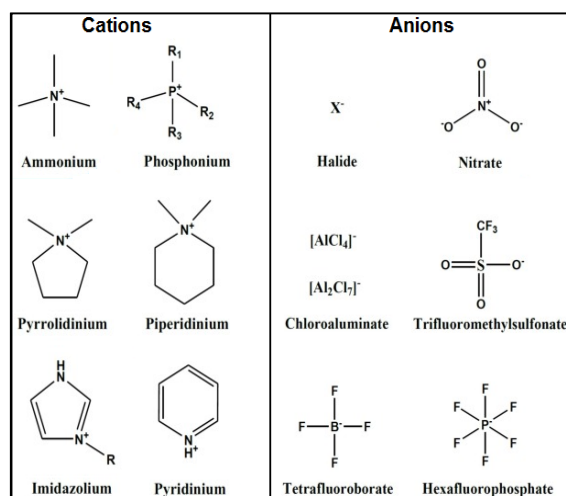


Figure 1. Some common cations and anions combined to form ionic liquids

The tunability of the properties of ionic liquid especially about its application in selective metal extraction needs further deliberation. The first parameter to be

optimized is the hardness-softness of the desired ion pair taken for metal extraction. Strength of the metal-ligand interactions could be evaluated using the qualitative Pearson's Hard-Soft Acid-Base (HSAB) theory which establishes, akin to "like dissolves like", the preference for hard acid to pair with hard base and that of soft acid to pair with soft base[2]. HSAB principle is used to categorize Lewis's acid/base as hard, soft, or borderline based on their charge density, polarizability, and oxidation state. Accordingly, cations of high charge (e.g., lanthanides) act as hard acids whilst many oxygen bearing functional groups (e.g., phosphates, carbonates, nitrates, or carboxylates) act as hard bases.

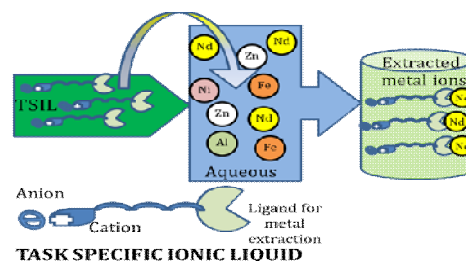


Figure 2. Selective metal extraction with task specific ionic liquids (TSILs)

When it comes to precious metals like cations of gold and silver, they act as soft acids, hence prefers interactions with soft bases like sulphur or nitrogen-based ligands. Transition metals like Cu and Ni come in borderline category that shows preference for ternary amines and amidic groups. In this way, choosing the right IL depends primarily on the nature of the metal to be extracted, to thermodynamically favour the desired equilibrium governed by the HSAB principle.

Apart from the thermodynamic factor, the kinetics of extraction is also an important

parameter to be optimized, which is influenced by density and viscosity of the ionic liquid medium[3]. Viscosity also depends upon the chemical structure of ILs and can also be affected by hydrogen bonding and van der Waals interactions therein, hence affected also by the acidity of the aqueous phase in contact with respect to the degree of protonation[4]. Longer alkyl chain leads to less density and high viscosity, but also significantly enhances the hydrophobicity [5]. Fluorinated anions like (hexafluorophosphate $[PF_6]^-$ or bis(trifluoro- methyl)sulfonyl imide $[NTf_2]^-$) also improves hydrophobicity, whereas ionic liquids with smaller anions like halides and nitrates tend to have some degree of aqueous solubility especially upon metal uptake. The lyotropic series anions with an ascending order of hydrophobicity is as given; $[SO_4]^{2-} \leq Cl^- \leq Br^- \leq [NO_3]^- \leq I^- \leq [ClO_4]^- \leq [SCN]^- \leq [NTf_2]^-$ [6].

When it comes to hydrometallurgical applications, it can be broadly classified in three categories; first as leachant to substitute mineral acids for selective dissolution of metals from solid feed, secondly as metal selective extractant/ion exchanger instead of molecular solvent for selective solvent extraction of metal of interest from impure leach liquor into the organic phase, and third as a medium for electrodeposition from purified metal bearing solution instead of aqueous medium and direct recovery of metal value. The possibility of using ionic liquids to be able to selectively leach targeted metals from the solid waste, and later selectively electrodeposit them onto a desired substrate holds potential for almost eliminating "water" from hydrometallurgy and in fact transform the field into iono-metallurgy or solvo-metallurgy [7]. This property is especially useful when the feed material is complex and contains not just metals but also plastics and fibres, the most suitable candidate being the electronic waste. E-waste production has been growing at an

exponential rate owing to growth in population, economy, and burgeoning demand for newer electronic equipments [8]. Since high temperature process is inherently unsuitable for e-waste due to generation of toxic volatile fumes, the most suitable route is hydrometallurgy. However, since the feed is multi-metal and complex, there is dire need for designer solvents to address the major bottleneck, that is to obtain high selectivity and consequently higher purity from e-waste streams to make the process economical and profitable.

In e-waste processing, ionic liquids, are at certain junctures, have started to replace and sometimes even outperform classical organic solvents as green solvents or extractants for the recovery of metals [9]. The added economic impetus of selectively recovering metals of high value like gold and rare earths acts as a driving force for tapping into the vast resource of electronic wastes, which are now aptly termed as urban mines. Herein, some of the recent progresses have been summarised and highlighted the potential for application of ionic liquids for recovery of precious metal gold and rare earth elements from electronic waste.

Ionic Liquids		
Unique applications in separation and recovery of valuable metals from e-waste		
Selective solvent extraction using task specific ionic liquids <u>Rare Earths Elements</u> - Y, Eu & Tb from fluorescent Lamp Phosphors - Nd, Dy, Pr & Sm from RE permanent magnets		Selective leaching followed by direct electrodeposition <u>Platinum Group Metals</u> - Au from RAM finger chips & Integrated Circuits - Pd from monolithic ceramic capacitors

Figure 3. Application of ionic liquids in rare earth and precious metal recovery from e-waste

Ionic liquids for recovery of precious metal gold from e-waste

Ionic liquids have been seen as a boon to the gold extraction industry as it is seen as the potential replacement of toxic and environmentally harsh cyanide-based

process. In case of recovery of gold from e-waste which is found in RAM and IC finger chips, hydrochloric acid and nitric acid combinations are typically used for leaching, wherein gold primarily forms anionic halide complexes. To promote soft-soft interactions, pyrrolidinium based ILs have been evaluated with different N-substituents directly for solvent free extraction of Au. It has been found that the ester group ($-\text{COOR}$) proved beneficial to the extraction process and provided enhanced hydrophobicity. $[\text{Pyr-EA}][\text{NTf}_2]$ was also found to be selective for Au over other common metals found in CPU [10]. Another common approach is the use of phosphonium based cationic species, known for being softer than ammonium analogues. Nguyen et al. [11] utilized a Cyphos IL 109 as the extractant with xylene as diluent to extract gold as AuCl_4^- . The anion exchange extraction mechanism was confirmed the occurrence of $[\text{P66614}][\text{AuCl}_4]$ as the extracted complex. Using the same ionic liquid, anionic exchange of gold was also observed when the ionic liquid was immobilized onto a biopolymer substrate [12]. In a novel approach, Aliquat 336 was combined with tri-iodide anions to formulate an ionic liquid that showed selective leaching of Au from e-waste over Cu owing to enhanced soft-soft interactions between the Au and iodide. Stripping was carried out using ethylene diamine solution, and the used ionic liquid was also regenerated via reaction with iodine [13]. In the e-waste PCB matrix, gold is commonly associated with the most abundant metal in e-waste, that is copper. An interesting approach of recovering both the metals simultaneously using an imidazolium based ionic liquid grafted with carboxylic acid group as cation and bromide as anion. In this case, anion exchange of gold, co-ordinate complexation of Cu by N lone pair donors of imidazole, and leaching of Cu selectively by acidic carboxyl group, all three mechanisms were identified and elucidated. [14]

Ionic liquids in recovery of rare earth metals from e-waste

Among the valuable metals, rare earth elements are primarily found in three sources among e-waste, i.e. in NdFeB magnets, Sm-Co magnets and fluorescent lamp phosphor powder.

NdFeB and SmCo magnets

Aliquat 336 has been extensively used as the cationic component of ionic liquid due to low cost, availability and chemical stability. Tricaprylmethylammonium nitrate ($[\text{A336}][\text{NO}_3]$) has been tested as synergistic diluent along with TBP as an extractant for the recovery of Pr in which the addition of sodium nitrate (NaNO_3) significantly enhanced REs extraction [15]. In another study, phosphonium based ionic liquid was used to separate Co, Nd and Dy from iron free leachate at pH 2 wherein Co was extracted as it is and Nd-Dy extraction was carried out using IL with ethylene diamine tetraacetic acid (EDTA) as a selective complexing agent $[\text{P66614}]$ [16]. Comparative studies have also been conducted for the recovery of Nd and Pr from NdFeB magnets using different bifunctional ILs [17], e.g. trioctylmethylammonium bis-(2,4,4-trimethylpentyl) phosphate (R4NCy) and trioctylmethylammonium di-(2-ethylhexyl) phosphate (R4ND), which were found to perform better than conventional solvents like Aliquat 336, Cyanex 272 and D2EHPA, under similar experimental conditions. Combinations of amine and organophosphorus solvents, like that of Primene 81R and Cyanex 572, have also been tested for Nd, Tb and Dy recovery from Nd-Fe-B magnets in HCl medium. [18] When REs were extracted, there was no change in pH due to absence of exchangeable proton. Another important magnet other than NdFeB is the SmCo magnet, wherein both Sm and Co are targeted for recovery. The common extractants include Cyanex 272 and Aliquat 336, wherein the former is used to target Sm and latter to recover other base metals like Co, Fe and Cu [19]. There

have also been studies on variation of counter ions to Aliquat 336 in undiluted form, for example chloride, nitrate or thiocyanate wherein co-extraction of Sm is also reported [20]. One of most successful attempts to recycle end-of-life magnets has been application of multifunctional amide ionic liquids (MAIL) which has gone from laboratory to 10 tonnes per annum scale, with final commercialisation reaching to 400 tonnes per annum. [21]

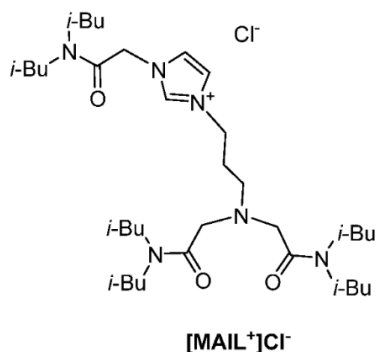


Figure 4. Multifunctional amide ionic liquid (MAIL)

Waste phosphor lamp powder

REs bearing phosphor are widely used in CFLs and LFLs along with its use in phosphors of picture tubes and other equipment involving contrast agents. REs present in phosphor is different from that of magnet chemically, wherein Y, Eu, Gd, Ce and Tb have been found in different color fractions. Although there are many reported work with recovery of REs from phosphor, most have not included the presence of toxic heavy metal impurity, mercury, which is always going to be present in the real-world phosphor fractions. Leaching of phosphor is carried generally in HCl medium and for Tb, alkali fusion has also been tested. One of the most common ionic liquid combinations used for RE recovery from phosphors is imidazolium based ionic liquid with hydrophobic anions like [Tf₂N]. One example is the use of [C₄mim][NTf₂] as diluent and *N,N*-dioctyldiglycolamic acid (DODGAA) as extractant, which is known for high solubility and selectivity for rare earths in

the ionic liquid medium [22]. Another approach is the use of bifunctional ionic liquid with amine cation and organophosphorus anion like [A336][P204] & [A336][P507] as synergistic combination for REs recovery from phosphor leachate generated in nitric acid medium [23]. Yet, another combination of an amine with higher basicity, Primene, along with D2EHPA, or combination of Primene and Cyanex 572 were also reported specifically for Y-Eu recovery from red phosphor [24]. In one study, an IL mixture of [P66614][NO₃] and DEHEHP was used for the selective separation of REEs (Ce, Y, Eu, and Tb) from waste fluorescent lamp phosphor leachate [25]. It was found that within four stages, all the REs could be completely extracted into the IL phase, leaving aside non-REs in the aqueous phase. The combination of Cyphos IL 104 along with TOPO has also been reported for Y and Eu recovery from phosphor powder leachate of HCl wherein recovery was carried out by solvent extraction followed by chemical reduction of Eu from +3 to +2 state using Zn followed by precipitation in sulphuric acid medium as Eu(II) Sulfate [26].

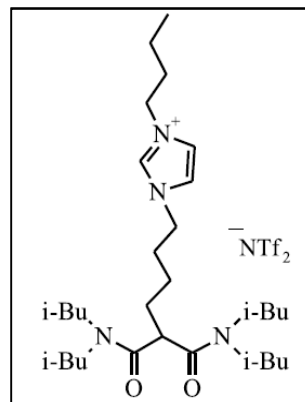


Figure 5. Malonamide functionalized task specific ionic liquid for rare earth recovery from e-waste

It is to be considered that most experiments using ionic liquids have been carried out in synthetic feeds or in small fractions without considering the aspects of further scale up, or serving the curiosity of the research community, but hardly gone to solve real world problems

at industrial scale. An exception to this trend is seen in the case of Malonamide functionalized ionic liquids which was designed to show very high selectivity for REMs over transition and base metals due to di-amidic donor site, as given in figure 3 [27]. Quantitative stripping in acidic media and good recyclability reported as one of promising candidate for implementation at industrial scale.

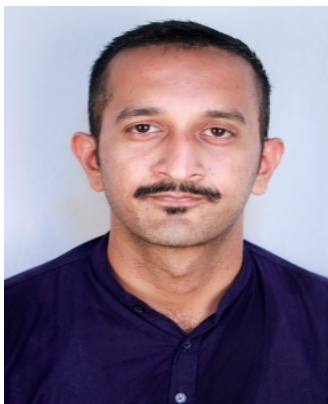
Conclusions

Ionic liquids, although well studied for more than two decades now, are still yet to be fully exploited at industrial scale for e-waste recycling owing to high cost and other technological challenges. However, there is an increasing interest and some breakthroughs wherein their application especially in REE recycling and Au direct dissolution and electrodeposition are being proven at pilot scale level. Instead of fixating to available combinations, design of ionic liquids with task specific side chains for metal uptake seems to be the way ahead for exploiting them at industrial level for recovery of rare earths and precious metals from e-waste.

References

1. Vishakha Kaim, Jukka Rintala, Chao He; Selective recovery of rare earth elements from e-waste via ionic liquid extraction: A review; *Separation and Purification Technology* 306 (2023) 122699
2. Ralph G. Pearson; *Hard and Soft Acids and Bases*; Physical and inorganic chemistry; Vol 85, No 22 (1963)
3. C. Micheau, G. Arrachart, R. Turgis, M. Lejeune, M. Draye, S. Michel, S. Legeai, S. Pellet-Rostaing, Ionic liquids as extraction media in a two-step eco-friendly process for selective tantalum recovery, *ACS Sustain. Chem. Eng.* 8 (2020) 1954–1963
4. P. Bonhôte, A.-P. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Grätzel, Hydrophobic, highly conductive ambient-temperature molten salts, *Inorg. Chem.* 35 (1996) 1168–1178
5. J. Jacquemin, P. Husson, A.A.H. Padua, V. Majer, Density and viscosity of several pure and water-saturated ionic liquids, *Green Chem.* 8 (2006) 172–180
6. W. Kunz, J. Henle, B.W. Ninham, 'Zur Lehre von der Wirkung der Salze' (about the science of the effect of salts): Franz Hofmeister's historical papers, *Curr. Opin. Colloid Interface Sci.* 9 (2004) 19–37
7. A. P. Abbott, G. Frisch, S. J. Gurman, A. R. Hillman, J. Hartley, F. Holyoak and K. S. Ryder; Ionometallurgy: designer redox properties for metal processing; *Chem. Commun.*, 2011, 47, 10031–10033
8. R Ruhela, N Iyer, C Limje, A K Yadav, M Yadav, M Vartak, D Bhattacharyya & D K Singh; Sustainable Recycling of Copper from Printed Circuit Boards with Imino diacetamide Resin - Transformation from Electronic Scrap to Copper Oxide Nanoparticles; *ACS Sustainable Chem. Eng.* 2024, 12, 687–694
9. N. Schaeffer, H. Passos, I. Billard, N. Papaiconomou, J.A.P. Coutinho, Recovery of metals from waste electrical and electronic equipment (WEEE) using unconventional solvents based on ionic liquids, *Crit. Rev. Environ. Sci. Technology*, 48 (2018) 859–922
10. Xiaoxia Liu, Yangyang Wang, Ronghao Liu, Ping Lv, Wenfeng Xue, Jinxin Guo, Huiying Wei, and Yanzhao Yang; Selective and Efficient Gold Extraction from E-Waste by Pyrrolidinium-Based Ionic Liquids with Various N-Substituents [*ACS Sustainable Chem. Eng.* 2023, 11, 638–648]
11. Nguyen, V. T.; Lee, J.-c.; Jeong, J.; Kim, B. S.; Cote, G., and Chagnes, A. Extraction of Gold (III) from Acidic Chloride Media Using Phosphonium-based Ionic Liquid as an Anion Exchanger. *Ind. Eng. Chem. Res.*

- 2015, 54(4), 1350–1358. DOI: 10.1021/ie5045742.
12. Campos, K.; Vincent, T.; Bunio, P.; Trochimczuk, A.; Guibal, E. Gold Recovery from HCl Solutions Using Cyphos IL-101 (A Quaternary Phosphonium Ionic Liquid) Immobilized in Biopolymer Capsules. *Solv. Extract. Ion Exch.* 2008, 26(5), 570–601.
13. Xiaolu Yin, Ronghao Liu, Ying Yue, Jun Li & Yanzhao Yang; Ultra-fast and selective recycling of gold from electronic waste based on triiodide ionic liquids *AIChE J.* 2025;71; e18773.
14. Sajith Babu M K, Madhumitha M, and Srinivasarao K; A Dual-Function Insoluble Ionic Liquid for the Selective Recovery of Gold and Copper from E-Waste; *ChemSusChem* 2025, 18, e202402419
15. Y. Kikuchi, M. Matsumiya, S. Kawakami, Extraction of rare earth ions from Nd-Fe- B magnet wastes with TBP in tricaprylmethylammonium nitrate, *Solvent Extr. Res. Dev. Japan.* 21 (2014) 137–145
16. S. Riano, K. Binnemans, Extraction and separation of neodymium and dysprosium from used NdFeB magnets: an application of ionic liquids in solvent extraction towards the recycling of magnets, *Green Chem.* 17 (2015) 2931–2942
17. E. Padhan, K. Sarangi, Recovery of Nd and Pr from NdFeB magnet leachates with bi-functional ionic liquids based on Aliquat 336 and Cyanex 272, *Hydrometallurgy.* 167 (2017) 134–140
18. S. Pavón, A. Fortuny, M.T. Coll, A.M. Sastre, Neodymium recovery from NdFeB magnet wastes using Primene 81R-Cyanex 572 IL by solvent extraction, *J. Environ. Manage.* 222 (2018) 359–367
19. M. Orefice, H. Audoor, Z. Li, K. Binnemans, Solvometallurgical route for the recovery of Sm Co, Cu and Fe from SmCo permanent magnets, *Sep. Purif. Technol.* 219 (2019) 281–289
20. S. Sobekova Foltova, T. Vander Hoogerstraete, D. Banerjee, K. Binnemans, Samarium/cobalt separation by solvent extraction with undiluted quaternary ammonium ionic liquids, *Sep. Purif. Technol.* 210 (2019) 209–218.
21. P. Nockemann, R. Ruhela, Separation of rare earth metals, 2020, GB2560871A.
22. F. Yang, F. Kubota, Y. Baba, N. Kamiya, M. Goto, Selective extraction and recovery of rare earth metals from phosphor powders in waste fluorescent lamps using an ionic liquid system, *J. Hazard. Mater.* 254–255 (2013) 79–88
23. H. Yang, W. Wang, H. Cui, D. Zhang, Y. Liu, J. Chen, Recovery of rare earth elements from simulated fluorescent powder using bifunctional ionic liquid extractants (Bif-ILEs), *J. Chem. Technol. Biotechnol.* 87 (2012) 198–205
24. C. Tunsu, J.B. Lapp, C. Ekberg, T. Retegan, Selective separation of yttrium and europium using Cyanex 572 for applications in fluorescent lamp waste processing, *Hydrometallurgy.* 166 (2016) 98–106
25. J. Zhao, Z. Yu, H. Liu, Extraction of rare earths by undiluted [P666,14] [NO₃] and DEHEHP, and the recovery of rare earths from lamp phosphors, *J. Mater. Cycles Waste Manag.* 21 (2019) 1518–1525
26. B.B. Mishra, N. Devi, K. Sarangi, Yttrium and europium recycling from phosphor powder of waste tube light by combined route of hydrometallurgy and chemical reduction, *Miner. Eng.* 136 (2019) 43–49
27. R. Boyd, C. Carroll, S. Dandil, C. Acikgoz, R. Ruhela, and P. Nockemann; Malonamide-Functionalized Ionic Liquid for Recovery of Rare-Earth Metals from End-Of-Life Products (Lamp Phosphors); *ACS Sustainable Chem. Eng.* 2020, 8, 18706–18711.



Shri Nikhilesh Nav Vigyan joined Hydrometallurgy Section, Materials Processing Division in 2013 after completing his graduation from IDD Metallurgical Engineering, IIT-BHU, Varanasi. He has since been working on separation sciences with focus on metal-ligand interactions in novel functionalized polymeric resins specifically for nuclear and critical metals. He is also pursuing PhD on novel metal selective polymeric resins for recovery of precious and hazardous metals from secondary sources and has been co-developer of in-house resin-based technology for recovery of copper oxide nanoparticles from end-of-life printed circuit boards. He has published more than 10 international journal publications till now



Dr. Ritesh Ruhela joined Bhabha Atomic Research Centre in 2005 after graduating from the OCES - 48th batch of BARC Training School. He completed his M.Sc. (Chemistry) from CCS University and worked as Junior Research Fellow in IIP, CSIR for one year after qualifying for CSIR-NET fellowship. He obtained Ph.D. (Chemical Science) from Homi Bhabha National Institute in the year 2013. He was awarded Marie Curie International Incoming Fellowship and worked as postdoctoral researcher at Queens University Ionic Liquid Laboratories (QUILL), Belfast, UK. His expertise includes design of ligands and task specific ionic liquids for selective metal extraction, rare earth metal intra group separation, radioactive waste management and ligand grafted polymer resin for industrial effluent management and e-waste recycling. He has obtained 2 international patents and published more than 50 international journal publications till now. He has transferred technologies for production of copper selective polymeric resin and copper oxide nanoparticles from depopulated PCBs (e-waste) to 7 private industries.

Poly(ionic liquids) and Ionic Liquid Membranes in Separation Science

Arijit Sengupta^{1,2}

¹Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400085, India; ²Homi Bhabha National Institute, Mumbai 400094, India

(Corresponding Author: Email: arijita@barc.gov.in)

Introduction

Poly(ionic liquid)s (PILs) refer to polymers that have ionic liquid (IL) units integrated into their polymer backbone. They exhibit the properties of both ionic liquids and polymers. Essentially, PILs are polymers in which every repeating unit has an ionic liquid architecture [1-2]. They can be created by polymerizing ionic liquid monomers or by functionalizing already existing polymers with IL side groups. The fusion of ionic liquid and polymer properties results in materials that possess tunable characteristics. PILs are essentially a category of ionic polymers that include ionic units in their structure. The ionic species are located either in the side chain or in the backbone of the PILs. Due to the strong intermolecular interactions among the macromolecular chains, PILs are solid in nature. Based on their structure, PILs are generally classified into three sub-classes.

- I. Polycation type [Figure 1]
- II. Polyanion type [Figure 2]
- III. Amphoter type [Figure 3]

PILs possess several advantageous characteristics, such as a designable structure, strong processing ability, high stability, tunable solubility, and a rich diversity of structures. They also provide unique functions, including the transport of target ions, a polar environment, and mechanical strength. Moreover, PILs exhibit superior ionic conductivity, chemical stability, and non-flammability when compared to nonionic polymers. Their role in functional polymer materials is underscored by their flexible hydrophilic/hydrophobic nature. The conducting mechanism in PILs is distinct from that of conducting polymers, with either the anions or cations functioning as mobile ionic conductors. PILs find extensive applications in polymer science, materials science, catalysis, and separations. A wide

array of cations, such as imidazolium, pyrrolidinium, pyridinium, ammonium, or phosphonium, along with anions like Cl^- , Br^- , I^- , PF_6^- , BF_4^- , or NTf_2^- , can be included in PILs.

Characteristics of PILs

Structural diversity

The attributes of PILs can be modified by adjusting the structure of the ion-pair composition and/or the polymer backbone. PILs obtained from the same IL monomer can demonstrate different characteristics when they adopt a variety of polymer architectures, such as linear, star-shaped, branched, and cyclic forms. Furthermore, an IL monomer can be linked to neutral monomers, resulting in copolymers. IL monomers can randomly copolymerize with nonionic monomers, leading to copolymers with adjustable charge density. PILs created through free radical polymerization, step-growth polymerization, and ring-opening polymerization can also result in PILs with various structural orientations [3-4].

Polycation type

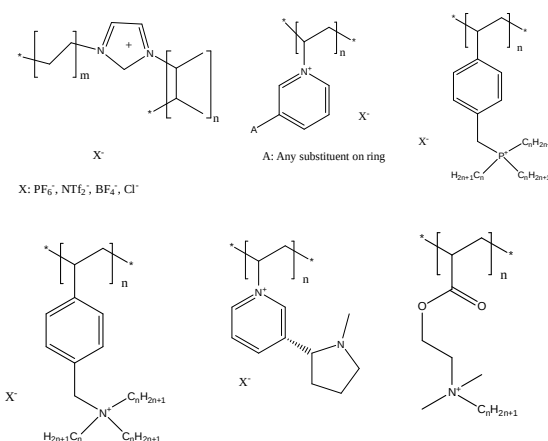


Figure 1: Chemical structures for PILs having polymerized cations with mobile anions

Polyanion type

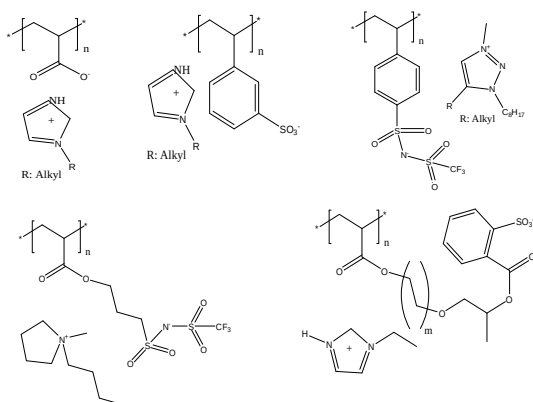


Figure 2: Chemical structures for PILs having polymerized anions with mobile cations

Amphoter type

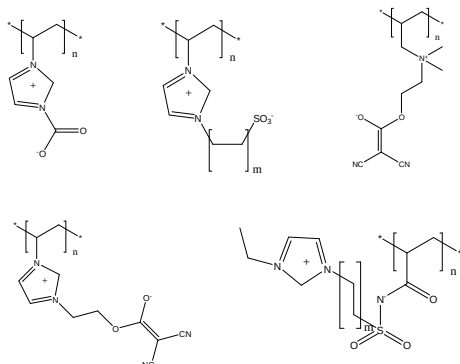


Figure 3: Chemical structures for PILs having polymerized cations as well as anions

Wide range of solubilizing nature

Counter ion metathesis is a widely used and simple approach for modifying the structures and properties of PILs, especially in contrast to altering the backbone. Counter ion exchange reactions can be utilized to switch between the hydrophilic and hydrophobic properties of PILs. The anion metathesis reactions permit PILs to carry hydrophobic counter anions (like PF_6^- and NTf_2^-), facilitating their separation from aqueous solutions. Hydrophobic PILs can dissolve in compatible organic solvents. The tunable solubility of PILs allows for a diverse range of processing conditions. A PIL that is either soluble or dispersible in a liquid can engage in electrostatic interactions with charged species, thus binding the PIL and paving the way for the

creation of PIL-composites with favorable properties [5-6]. These solution mixture systems are conducive to various polymer casting methods, such as spin coating, drop casting, electrospinning, and extrusion.

Stability towards drastic chemical environment

Owing to the exceptional stability of ionic liquids (IL), polymeric ionic liquids (PILs) are asserted to exhibit significant resistance to extreme chemical environments when compared to the most neutral polymers. Nevertheless, structural rearrangements and crosslinking may take place in specific chemical conditions. The highly nucleophilic characteristic of the hydroxide (OH^-) anion contributes to the chemical instability observed in PILs. Furthermore, PILs that incorporate imidazolium cations may undergo a ring-opening reaction in highly alkaline environments, leading to the formation of active (poly)-carbene intermediates [7-10]. Poly(ionic liquids) (PILs) based on styrene and containing saturated N-heterocyclic cations of varying ring sizes (including methylpyrrolidinium, methylpiperidinium, methylazepanium, methylazocanium, and methylazonanium) showed remarkable alkaline chemical stability, as confirmed through ^1H NMR spectroscopy [11]. Following 4 weeks in 40 mol equivalents of KOH at 80 °C, the PILs revealed an improvement in ion conductivity as the water content increased.

Thermal stability

Thermal stability is not solely determined by the repeating units; the backbone of the polymer also plays a crucial role. In the case of PILs, the ion pair associated with the IL unit is particularly influential in establishing their thermal stability. The thermal stability of PILs, which depend on the chemical structures of both ion pairs and backbones, shows a wide range of decomposition onset temperatures (150 - 400 °C) [12-15]. In neutral polymers, the inclusion of aromatic rings in PILs (instead of aliphatic groups) leads to improved thermal stability. Furthermore, an increased length of the alkyl spacer that connects the polymer backbone to the ion pair enhances the thermal stability of the

PILs. The trend observed in the thermal stability of PILs is as follows: imidazolium > pyridinium > pyrrolidinium > ammonium, and $\text{Br}^- > \text{PF}_6^- > \text{BF}_4^- > \text{CF}_3\text{SO}_3^-$ for the ions involved.

Ion Conductivity

The inherent property of ion conductivity in PILs leads to their widespread use in battery and fuel cell research. Blending PILs with other conductive elements enhances their performance in electrochemical applications [16-19]. The ion conductivity is attributed to the movement of counter ions that are associated with the polymer backbone, driven by an external electric field. Since the majority of reported PILs exist as solids at room temperature, the counter ions function as charge carriers. Consequently, PILs are classified as quasi-single-ion conductors. This classification results in PILs exhibiting lower conductivity when compared to their monomeric ionic liquids. The diverse structures of PILs facilitate tunable ion conductivity. Factors such as chemical structures, the backbone, combinations of ion pairs, and the spacers between the backbone and ion pairs significantly influence the ion conductivity of PILs. The density of ionic liquids within copolymers is offset by a decrease in the glass transition temperature (T_g), which in turn increases ion mobility. A minimal amount of water that is readily absorbed by PILs aids in ion transport, contributing to the high ion conductivity in environments with high moisture content.

Broad Electrochemical Stability Window

PILs reveal an extensive electrochemical window that can extend up to 5.0 V, making them suitable as unique electrolytes for electrochemical processes that are otherwise difficult for standard systems [20-22]. In the context of pyrrolidinium PILs with TFSI as the counter anion, the electrochemical window is 5.0 V but reduces at higher temperatures. The electrochemical windows of PILs can be fine-tuned based on the polymerized ions and semi-free counter ions. PILs featuring pyrrolidinium as the constituent cations demonstrate the widest electrochemical window. The basic characteristic of ionic liquids is their relatively low charge density;

that is, a small charge is present on large cations or anions. Due to this low charge density, the chemical reactivity, whether in oxidation or reduction, is lower. Neither the cations have a strong attraction for electrons, nor do the anions have a strong tendency to lose electrons. As a result, they are stable across a broad range of applied potentials. *Compatibility with*

Organic-Inorganic-Polymeric Composite materials

PILs are classified as surface-active agents and are compatible with a wide array of materials, including inorganics, organics, inorganic-organic hybrids, and biomaterials. The broad compatibility of PILs with various substances is attributed to both non-covalent and covalent bonding mechanisms [23-25]. Significant interactions that influence different PILs include electrostatic interactions, cation- π interactions, hydrogen bonding, and van der Waals forces. The Poly-(1-vinyl-3-ethylimidazolium bromide) PIL can facilitate the transfer of CNTs from an aqueous phase to an organic phase through an anion exchange reaction, which is driven by the 'cation- π ' interactive force. When PILs are immobilized on graphene, the surface properties of the graphene sheets transition from hydrophilic to hydrophobic. PILs that are attached to the surface of graphene oxide (GO) enhance the compatibility of GO with the IL electrolyte, thereby increasing the effective surface area of the electrode [26-29]. Functional counterions can be incorporated into PILs through the process of ion metathesis. Additionally, PILs exhibit hydrogen bonding with proton donors such as amino acids. PILs that possess coordination sites (N, O, and P) within their heterocyclic rings can form covalent bonds with metal materials through coordination bonds, resulting in stable composites. Atom transfer radical polymerization (ATRP) has enabled the growth of PIL on a silicon wafer for applications in smart textiles and intelligent microfluidic switching. Noncovalent PIL composites provide a foundation for the creation of fascinating supramolecular assemblies.

Synthesis of PILs

Polymerization of monomers

Similar to conventional polymers, PILs can be produced through the direct polymerization of counter monomers via either addition polymerization or condensation polymerization [Figure 4]. PILs synthesized through direct polymerization exhibit high purity and incorporate ionic liquids throughout the main chain. N-(4-tert-butylbenzyl)-4-chloropyridinium (BPymCl) serves as an initiator, while various ion exchange reagents such as NaBPh₄, NaBF₄, and TBABF₄ have been employed in the synthesis of PILs [30]. The synthesis process consists of three steps. Initially, the initiator reacts with the monomer. In the subsequent step, chain growth occurs as additional monomers are introduced to the newly formed chains. The final step involves the termination of these chains. It is crucial to prevent unnecessary chain growth to regulate the length of the chains. To achieve this, a terminator can be added to the reaction mixture. The resulting PILs consist of repetitive units of the IL cations forming the backbone; an anion exchange can be performed either prior to or following the termination reaction to immobilize the corresponding anions. Hirai et al. reported a one-pot synthesis of PILs featuring 1,2,3-triazolium-based backbones through click chemistry. This method is particularly appealing due to its efficiency and orthogonality, resulting in the desired polymers. Steinkoenig et al. described a reversible addition fragmentation chain transfer (RAFT) polymerization technique for the synthesis of PILs with a polystyrene backbone [31]. The ILs, which do not possess groups susceptible to polymerization, must be modified using reactive heteroatoms such as nitrogen atoms found in ILs. An atomic transformation radical polymerization (ATRP) utilizing CuBr/CuBr₂ as the initiator can be employed for the synthesis and controlled growth of polymeric brushes of PILs.

Research has demonstrated that PILs are viewed as smart materials with multi-responsive attributes in response to external stimuli, including temperature, pH, oxidative doping, and anion presence. Wang et al. added -COOH to the ionic liquid monomer before engaging in copolymerization with divinylbenzene (DVB) [32]. The initial addition of -COOH is intended to enhance the acidity of the final

PILs. In addition, the -COOH can react with NaOH to modify the conductivity of the final PILs. The same research group also examined the epoxide group for the synthesis of epoxide-functionalized PILs, which can be further transformed into other groups through ring-opening reactions.

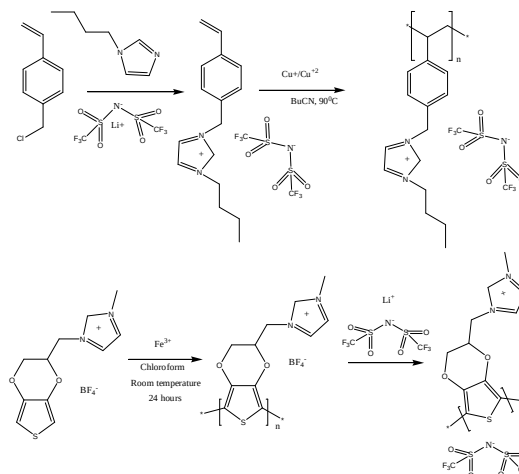


Figure 4: PILs synthesized by polymerization of the monomers

Polymer modification

Unlike the monomers-polymerization-PIL pathway, the post-polymerization modification of pre-synthesized polymers mitigates the drawbacks of direct polymerization. The chemical modification route is more straightforward to manage and can be executed under mild chemical conditions. The relative molecular weight and distribution of synthesized PILs can be tailored according to various structures and functions, resulting in improved physicochemical properties. Yang et al. synthesized poly[(alkyl-biphenyl pyridinium) bromide] using superacid-catalyzed polymerization followed by quaternization [33]. A step-growth polymerization was performed between biphenyl and 4-acetylpyridine under superacid conditions. This approach is free from contamination by any base-sensitive diaryl ether bridges and benzylic C-H. Due to the acidic nature of the medium, the nitrogen atom in the pyridine ring was also protonated. The length of the alkyl chain could be adjusted by utilizing different alkylation agents. Reiter et al. created siloxane-based PIL through post-

polymerization modification of commercially available polysiloxane derivatives [34]. Stumphauser et al. synthesized a poly(ionic liquid) co-network (PIL-CN), poly(1-vinylimidazole)-L-poly(tetrahydrofuran) (PVIm-L-PTHF) [35]. Based on the same groups (vinyl polymerization), free radical copolymerization of the N-vinylimidazole monomer (VIm) and the methacrylate-telechelic poly(tetrahydrofuran) (MA-PTHF-MA) macro-crosslinker was conducted in the presence of an initiator. Subsequently, alkylation of the poly(1-vinylimidazole) with methyl iodide was performed to yield the PVIm-L-PTHF co-network. Carrasco et al. produced a series of PIL block copolymers from the styrene-co-2-vinylpyridine copolymer [36]. Free radical copolymerization was executed to form (a) PIL-COOH-Br, PIL-COOH-S, PIL-COONa-OH and (b) PIL-E and PIL-2OH, along with the quaternization of nitrogen atoms. Direct quaternization resulted in a polymeric ionic liquid block polymer with Br⁻ as the counter anion. In addition to the integration of IL units into pre-synthesized polymers, certain polymers that are composed of units from PIL precursor molecules can also be transformed into PILs. An imidazolium-based PIL was fabricated by modifying poly(vinylimidazole). The first phase involved the synthesis of the reactive modifier molecule. The second phase was the preparation of poly(vinylimidazole) through the direct polymerization of vinylimidazole, facilitated by the AIBN initiator. The third phase involved the grafting of the molecule onto poly(vinylimidazole). Despite the significant progress made, each method has its own strengths and weaknesses. Polymerization is restricted to monomers that contain polymerizable functional groups. In some cases, it is necessary to modify the functional groups of monomers, such as azide and vinyl, to enable subsequent polymerization. Additionally, quaternization of the pyridine or imidazole ring can introduce considerable steric hindrance, which may be unfavorable for polymerization. Similar to conventional polymer synthesis, it is challenging to control the molecular weight within a narrow range during the direct polymerization of ionic liquid monomers. For the modification of pre-synthesized polymers, a critical issue is how to accurately manage the ratio of ionic species

in the final PIL structures. Moreover, only polymers that contain functional groups are appropriate for conversion into PILs. When compared to the direct polymerization of monomers that can occur in a solution state, executing this method in solution is difficult, as most common polymers are insoluble in typical solvents. Figure 5 illustrates examples of post-polymerization modifications to achieve PILs.

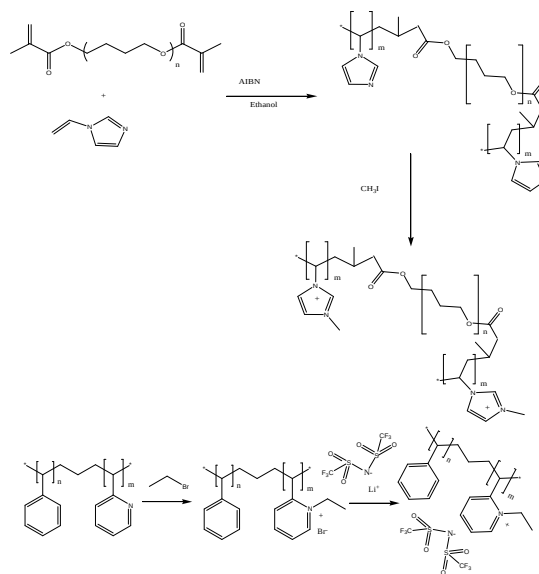


Figure 5: PILs synthesized by polymer modifications

Mesoporous PIL microspheres in adsorption

PIL microspheres are recognized for their effectiveness in the removal of anionic pollutants through inter-column ion exchange. Among the various separation methods, adsorption is the most preferred due to its high efficiency, exceptional sensitivity, and affordability. Cationic monomers, namely N, N'-methylene-bis (1-(3-vinyl imidazole)) chloride and N, N'-methylene-bis (1-(3-vinyl imidazole)) bromine, are utilized in the process of radical polymerization [37]. The results indicate that the dried microspheres have a high capacity for adsorbing Cr (VI). The PIL microsphere, poly(1-vinyl-3-(2-methoxy-2-oxyl ethyl)imidazolium) hexafluorophosphate, exhibited rapid ion-exchange between the anionic moieties and DNA fragments, achieving a capacity of 190.7 $\mu\text{g mg}^{-1}$. It has been demonstrated that rapid DNA isolation and detachment from the microspheres can be accomplished using a higher concentration of salt. The

PIL microspheres are employed for the adsorption and isolation of plasmid DNA from *E. coli* cell cultures [38]. Furthermore, porous microspheres derived from pyridine were used for the adsorption of organic dyes such as Congo Red (CR), Bromo Phenol Blue (BPB), Sunset Yellow (SY), Allizarine Yellow R (AR), Safranin T (ST), and Methylene Blue (MB) [39-41]. The microspheres showed excellent adsorption performance for CR, SY, and BPB, partial adsorption for AR, and minimal adsorption for ST and MB due to their polycationic nature. The microspheres are capable of absorbing anionic organic dyes but show limited adsorption for cationic dyes, demonstrating a superior selective adsorption ability for SY in a mixed solution of SY and MB.

PIL membranes in unconventional separations

PILs are distinguished by their unique combination of ionic liquid properties, which include a high degree of tunability, along with the advantageous characteristics of polymers, such as substantial chemical and mechanical stability. The antimicrobial properties of PILs provide an added layer of protection against biofouling in wastewater treatment applications. Modifications to PILs have been implemented to create selective layers on porous supports, enabling non-conventional separation through π cloud interactions between the PILs and the aromatic compounds found in the feed [42-44]. The separation of aromatics from their aliphatic homologues, such as the heptane-toluene separation, poses significant challenges. Various membrane-based technologies, including cross-linking, pervaporation, and the introduction of metal-organic frameworks into membranes, have been investigated. While some results have been relatively successful, there is still a persistent demand for effective separation methods. The π electron cloud density of the compounds in the feed is the key driving force for these PIL-based separations. Therefore, conjugate systems are likely to exhibit a greater affinity for the PIL active layer, resulting in the fractionation of compounds such as benzene, naphthalene, anthracene, and phenanthrene. The substituents on the aromatic ring that possess electron-donating or withdrawing

properties demonstrate varying affinities for PIL membranes. Moreover, PIL membranes show a preferential affinity for stereochemical isomers, including cis/trans stilbene, with the cis isomer characterized by having two phenyl groups on the same side. The steric hindrance between the two ortho hydrogen atoms causes both phenyl rings to lose their planarity in relation to the alkene moiety, which disrupts the extended conjugation. In contrast, such stereochemical constraints were not present in the trans isomers. As a result, the PILs demonstrate a preferential affinity for the trans isomer over the cis isomer, leading to a fractionation between these two isomers. The positive surface charge on PIL membranes, coupled with their excellent hydrophilicity, was also leveraged in dye separation induced by π electrons. The extended conjugation of the dye molecules facilitates interactions with the π electron clouds of the PILs. The $-NH_2$ or $-NO_2$ groups attached to the dye molecules possess different π electron densities due to the resonance effect of the former and the -inductive effect of the latter. These electronic factors were found to influence the differential interactions with PILs and their distinct separation capabilities. Additionally, PILs were utilized in the fractionation of sugars. The trend in the affinity of these sugars towards PIL membranes was observed as follows: Galactose > Mannose > Fructose > Glucose > Xylose. It was noted that hexoses exhibit superior permeation compared to pentoses, while aldoses provide better permeation than ketoses.

PIL Membrane in CO₂/Light Gas Separations

PIL and PIL/IL ionogel were observed to have a significant affinity for CO₂ gas and a selectivity for CO₂ over a CO₂-N₂ mixture [45-47]. The mechanical properties of the PIL ion-gel materials were found to be adequate, resembling solid characteristics. An increase in the loading of ionic liquid on the PIL-IL active layer resulted in a more gel-like mechanical behavior. The structural integrity between the PIL iongel and ionic liquid was primarily due to the electrostatic interactions between the ionic liquid moieties and PIL. This PIL-IL gel facilitated the transport of gas molecules, as indicated by the enhancement in CO₂

permeability within the composite materials. The choice of thickness for the active layer also plays a significant role in boosting gas permeability through PIL-IL iongel materials. To tackle the issue of surface tension, a two-step synthetic process based on membrane casting was utilized. Initially, a thin film of pre-polymerized PIL was cast onto a support layer using its methanolic solution. Subsequently, a free ionic liquid isopropanolic solution was allowed to soak into the PIL layer to create the PIL-IL active layer, aimed at achieving the desired CO₂ permeability. Furthermore, to increase the loading of free ionic liquid while ensuring the necessary mechanical strength without compromising CO₂ permeability, various cross-linking strategies have been reviewed in the literature. The optimal crosslinked PIL-IL materials achieved a separation factor of CO₂ over N₂ of 35 or more. The low partial pressure of CO₂ in flue gas enabled the transport of gas molecules through the membranes via a 'hopping' mechanism. The active sites within the membrane contributed to the reversible chemical conversion of the target gas molecules while they hopped across the membrane surface. Therefore, the partial pressure of gas molecules and the surface density of the active open sites on the membrane are essential factors in improving the permeability and selectivity of the desired gas molecules. The molecular sieving and preferential adsorption properties of zeolite meso-porous materials have been further enhanced by the creation of a Zeolite-PIL-IL mixed matrix membrane, which improves CO₂ permeability and selectivity. However, the particle size, geometry, and orientation of the zeolite particles within the blended matrix PIL-IL membrane significantly influenced overall performance. The incorporation of porous materials into neutral polymers to enhance gas permeation led to high-permeance, non-selective free volume defects that adversely affected the membrane's selectivity. The combination of charged PILs and free-standing IL as a nonvolatile interfacial lubricant allows the PIL/IL matrix to adhere effectively to the zeolite, with the IL filling the resulting interfacial defects, resulting in the PIL/IL ion-gel being an outstanding platform for the synthesis of membranes optimized for selectivity and permeability.

Supported ionic liquid membranes

The rheological properties of ionic liquids are essential in influencing the total mass transport through supported ionic liquid membranes [48-51]. Given that the viscosity of all ionic liquids does not depend on shear rate, they are likely to exhibit characteristics of a Newtonian fluid. Consequently, it can be assumed that ionic liquids represent a three-dimensional network of linked cations and anions through weak hydrogen bonding and Van der Waals forces. They should not be interpreted as a statistical collection of anions and cations. The decline in viscosity coefficient values with an increase in temperature for ionic liquids follows the Arrhenius equation. However, across a wide temperature range (10 °C - 90 °C), the viscosity changes adhere to the Vogel-Fulcher-Tammann equation. Alkyl methylimidazolium ionic liquids with PF₆⁻ anions were found to be more viscous than those with BF₄⁻ as the constituent anions. Additionally, an increase in the alkyl group chain length at the C₃ position resulted in higher viscosity. The total viscosity coefficient values of ionic liquids are greater than those of conventional molecular diluents, which have slower mass transfer in biphasic mass transfer systems. However, the increase in mass transfer resistance is partially alleviated when ionic liquid is used as a pore-filling solvent in conventional porous membrane materials or as supported liquid membranes (SLM). The mass transfer resistance of a membrane is proportional to its thickness. Due to the thin thickness used in SLMs (> 20 m), the reduction in mass transfer coefficient is less pronounced compared to that seen in conventional extraction processes. Different strategies were employed to evaluate the effect of the supporting material on the stability of SLMs.

- I. In the course of membrane operation, one must evaluate if there is any displacement of ionic liquid from the membrane pores into the surrounding environment.
- II. Following contact with the aqueous phases, it is crucial to verify whether the SLM still preserves its hydrophobic properties.

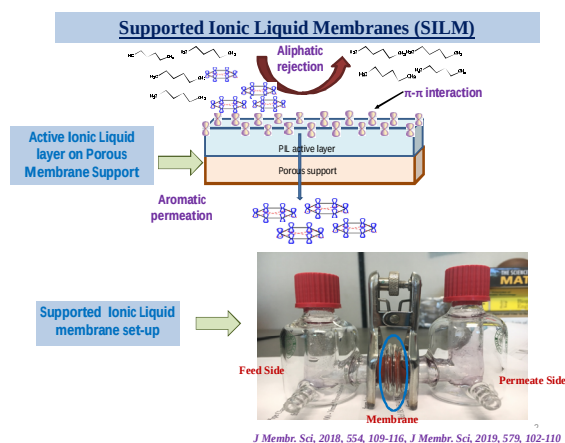


Figure 6: Supported Ionic Liquid Membrane for the separation of *n*-Hexane-Benzene

In the scenario where Nylaflon acts as the supporting membrane, a slight increase in the concentration of ionic liquid in the aqueous phase was recorded; however, for the majority of other materials, the ionic liquid concentration in the aqueous phase remained stable throughout the entire experiment, indicating that there was no displacement of ionic liquid from the membrane's pores. This is further evidenced by the fact that a larger quantity of ionic liquid was retained on the membrane's surface after blotting, which strongly implies that the ionic liquid detected in the aqueous phase cannot be attributed to pore-displaced ionic liquids, but rather to the excess that remained on the membrane's surface. The concentration of ionic liquid in the aqueous phase was lower than its aqueous solubility, which is attributed to the stronger affinity through Van der Waals interactions with the membrane materials. The excess ionic liquid present on the membrane surface can be removed through vigorous stirring. The immobilized ionic liquid within the pore is situated there due to favorable partitioning, leading to a stable supported liquid membrane (SLM). To evaluate the hydrophilicity of the membrane surface before and after pore filling with ionic liquid, a water droplet is placed on the membrane surface. The duration for the water droplets to permeate through the membrane and the water contact angle are taken into account in assessing hydrophilicity. The introduction of ionic liquid into the hydrophobic membrane pores resulted in a decrease in hydrophobic characteristics, as the ionic liquids possess ionic properties.

The high surface tension exhibited by ionic liquids offers improved tolerance to mechanical forces, pressure, and temperature. A thin active layer with a brief diffusion length enables the transport of targeted species, which offsets the slow mass transfer linked to the high viscosity of ionic liquids. Supported ionic liquid membranes (SILM) containing 1,3-dialkylimidazolium ionic liquids have shown selectivity for organic compounds in aqueous feeds. The water microenvironment generated through reverse micellar aggregation is essential to the transport process, resulting in a non-selective predominating mechanism. Figure 6 provides a schematic representation of the mutual separation of aromatic and aliphatic compounds through the SILM / Active PIL layer on a porous membrane support layer. SILM that contains 1-butyl-3-methylimidazolium hexafluorophosphate (C_4mimPF_6) has been noted for its strong performance stability and selectivity in the separation of toluene and cyclohexane. This SILM was also used for the dehydration of water-alcohol mixtures, utilizing its affinity for water molecules. Moreover, SILMs with 1-n-octyl-3-methylimidazolium hexafluorophosphate (C_8mimPF_6) were applied to extract amino acids from aqueous solutions, capitalizing on the acidic, basic, and zwitterionic features of the amino acids and their preferential interactions with the SILM. The effects of various ionic liquids (1-butyl-3-methylimidazolium hexafluorophosphate: C_4mimPF_6 , 1-octyl-3-methylimidazolium hexafluorophosphate: C_8mimPF_6 , and 1-decyl-3-methylimidazolium hexafluorophosphate: $C_{10}mimPF_6$) on the selective transport of organic alcohols, ketones, and amines have been illustrated. The SILM with C_4mimPF_6 facilitated preferential separation between secondary and tertiary amines through hydrogen bonding interactions on a polyvinylidene fluoride (PVDF) membrane support. Based on the hydrophobic nature of the feed molecules, selective transport of benzene, toluene, and p-xylene can also be achieved. The increased solubility of gas molecules in ionic liquids, combined with the high membrane integrity due to low volatilization or reduced thermal loss of the ionic liquid, makes the SILM an appealing option for gas separation, especially for CO_2 .

Ionic liquids that are phosphonium-based show a preference for extracting lactic and butyric acids over conventional extraction methods. The pertraction of lactic acid through a supported ionic liquid membrane (SILM) in a spiral channel flat sheet module using tetradecyl(trihexyl)phosphonium bis(2,4,4-trimethylpentyl)phosphinate was determined to be effective. The loading of the ionic liquid had little effect on the mass transfer process. However, using a feed with concentrated lactic acid resulted in a lower mass-transfer coefficient, while temperature had an inverse effect on this coefficient. The overall transport process was divided into the elementary steps described below:

- I. At the Feed-SILM interface: The splitting of reverse micelles
- II. Formation of lactic acid-ionic liquid aqueous species
- III. The SILM facilitates the transport of lactic acid-ionic liquid aqueous species.
- IV. At the SILM-Product interface: The splitting of the transported lactic acid-ionic liquid aqueous complex
- V. The formation of reverse micellar aggregation by ionic liquid at the SILM-Product interface.
- VI. The transportation of reverse micellar aggregates through SILM.

Electric-Responsive membrane

Concentration polarization is a prominent fouling problem that membrane technologists encounter. The application of various membrane modules, including cross flow, has been leveraged to create local disturbances near the membrane feed interface through external stimuli to mitigate this issue. The fabrication of magnetic responsive membranes, either by incorporating a magnetically activated active membrane layer or by grafting a polymer brush with a magnetically active endpoint onto commercially available membranes, can be effective. Depending on the characteristics of the membrane pores, such as microfiltration, ultrafiltration, or nanofiltration, various strategies can be adopted to control the location, length, and surface density of the magnetically activated polymer brush. In a similar manner, PIL brushes can also be grafted onto commercially available membranes like regenerated cellulose. Since the

counter anions are mobile, these brushes act like electrically charged tails in the presence of appropriate feed solutions. Therefore, under an oscillating electric field, these PIL brushes are expected to generate local disturbances [52-53]. The local perturbations can be externally tuned according to the frequency of the oscillating electric field. With an increase in the frequency of the external oscillating electric field, the movement of these PIL brushes is enhanced. This stimulus response can be controlled remotely. At very high frequencies, the interaction is so intense that the PIL brushes do not have sufficient time for their orientation or reorientation movements. Thus, this ultimately resulted in heat energy or localized heating on these PIL brushes.

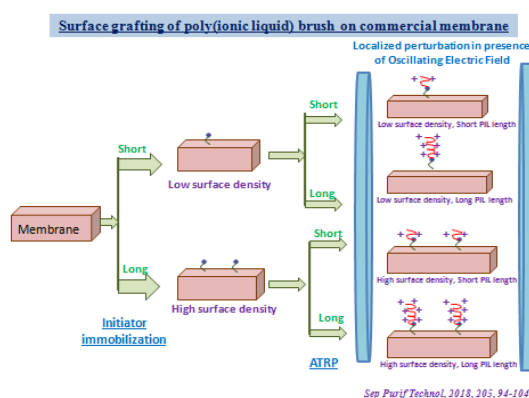


Figure 7: Schematic for the fabrication of Electric-Responsive membrane through control grafting of PIL brush

The remotely controlled local perturbations near the interface disrupt concentration polarization, leading to a significant reduction in membrane fouling. However, the additional PIL layer and its movement created an extra transport barrier for the targeted molecules to pass through the membrane. Consequently, a compromise in feed permeability may be encountered. The local heating at higher applied oscillating frequencies exhibited a reverse effect on permeability aspects, thereby improving membrane performance. This discussion has revealed that the choice of a suitable external oscillating frequency can enhance membrane fouling by reducing concentration polarization without much compromise on membrane permeability. Clearly, the characteristics of the feed solutions, the type of membrane materials, pore size, porosity, and the nature of the PIL brush greatly influence the optimization

of such stimuli responses. Electric responsive membranes have been developed through the controlled surface grafting of PILs onto commercially available regenerated cellulose ultrafiltration membranes. The grafting of PIL led to a rougher surface texture, a decrease in pore size, and an increase in hydrophilicity. The stimuli response induces micromixing, alleviating concentration polarization and improving the antifouling properties of the responsive membranes. Local perturbation was found to reduce water flux while enhancing protein rejection. At an oscillating electric field of 1 kHz, localized heating was more dominant than micromixing. Conversely, at lower frequencies (in Hz), greater perturbation resulted in decreased permeability. The membrane's response to the electric field was found to be reversible, indicating no memory effect.

Anti microbial activity

The antimicrobial characteristics of ionic liquids, including PILs and SILMs, significantly improve the membrane's resistance to bio-fouling, which is crucial when treating municipal waste or other streams that can foster microorganism growth over time. The PILs, which undergo polymerization at the cationic site, engage in electrostatic interactions with the phosphate groups present on microbial cell membranes, which are inherently anionic. This interaction leads to the insertion of hydrophobic groups into the cell membranes, disrupting their integrity [54-57]. Consequently, this disruption causes the leakage of cytoplasmic contents, resulting in cell lysis. Similarly, the antimicrobial properties of the less studied PILs with a repetitive anionic backbone may follow the same mechanism for damaging bacterial cell membranes. The loosely bound counter cations of these PILs interact electrostatically with the negatively charged cell membranes. Subsequently, the hydrophobic segments of the PILs infiltrate the hydrophobic regions of the microbial lipid membranes, ultimately causing cytoplasmic leakage and cell death. In addition to electrostatic interactions, the hydrophobic-hydrophobic interactions between the PILs and the phospholipid bilayer of cellular membranes are significant contributors to cell destruction.

Given this context, PILs with a higher organophilic nature, characterized by increased hydrophobic substituents, exhibit enhanced antimicrobial activity. Thus, the anticipated trend is: methyl < butyl < benzyl. The addition of hydrophilic hydroxyl groups to the PIL backbone reduces its antimicrobial efficacy. Our results align with several previous studies. The PIL Trp anion demonstrated effective antimicrobial activity against both *E. coli* and *S. aureus*, while the PIL with Pro anion failed to inhibit the growth of the bacterial strain.

PILs characterized by a repeated cationic backbone and featuring leucine and phenylalanine pendants demonstrated superior antimicrobial activity against *E. coli* in comparison to PILs with alanine pendants. The antimicrobial performance against *S. aureus* was greater than that against *E. coli* and *C. albicans*, as indicated by the inhibition zone diameters ($a_{S. aureus} \sim 33 \pm 1.2$ mm, $a_{E. coli} \sim 28 \pm 0.8$ mm, $a_{C. albicans} \sim 19 \pm 0.4$ mm). Variations in cell wall composition and thickness among pathogens result in a species-dependent antimicrobial activity of PIL membranes against different microorganisms. Gram-negative bacteria have a multilayer cell wall that is protected by an outer lipopolysaccharide membrane layer, while Gram-positive bacteria are encased only by a peptidoglycan cell wall. The incorporation of antimicrobial polymers into the loosely packed porous layer is relatively easy, facilitating interference with cell membrane integrity. For Gram-negative bacteria, the outer layer provides resistance to biocides. The double membrane structure of Gram-negative bacteria makes them more resilient than the single membrane structure of Gram-positive bacteria. The cell wall of Gram-positive bacteria is more cationic and hydrophobic than that of Gram-negative bacteria, leading to enhanced electrostatic and hydrophobic interactions. In fungi, the multilayer cell wall is considerably thicker than that of bacteria, resulting in challenging penetration.

The antifouling properties of PIL membranes were demonstrated through SEM images. Significant membrane fouling occurred while processing actual produced water samples with conventional membranes. Conversely, the hydrophilic modification of hydrophobic membranes, such as polyvinylidene fluoride and

polypropylene, using substances like hexaethylene methacrylate and ethylene diamine, resulted in less fouling. The IL-based membrane also exhibited antibacterial activity against both gram-positive and gram-negative bacteria. A notable reduction in the live/dead bacterial cell ratio was recorded in the presence of the IL-based membrane, along with a decrease in the bacterial colonies formed during incubation.

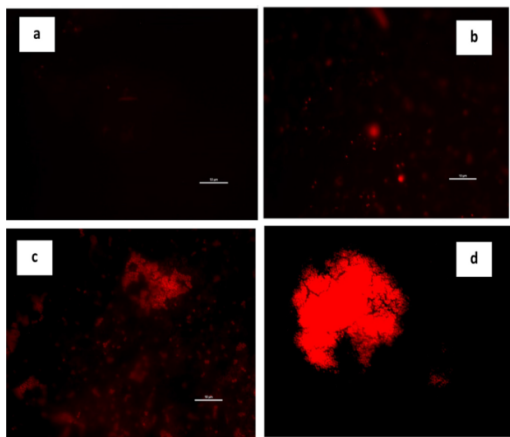


Figure 8. Microscopic images for antibacterial activity of SIL membranes using *Staphylococcus aureus*, (a) PTFE base membranes; (b) 1 allyl 3 vinyl imidazolium bromide; (c) 1 butyl 3 vinyl imidazolium bromide; (d) 1 hexyl 3 vinyl imidazolium chloride [Journal of Membrane Science, 556, 2018, 1-11]

Conclusions

By implementing minor structural modifications, IL-based separation heralds a new era of characteristic adjustments. It broadens the scope of application within modern technology, energy utilization, and even fuel cell technologies. To showcase fascinating chemistry, there is a need to explore innovative ionic liquids. To reduce overall expenses, large-scale production of IL must commence. Identifying IL with low viscosity is essential to improve mass transfer kinetics. New structure-activity relationships in ionic liquids necessitate further exploration. To tackle the limitations of ionic liquids, research has also begun to identify Deep Eutectic Solvents as viable alternatives to conventional IL. Polymeric materials have undergone a transformation in the past century. The PILs combine the beneficial properties of both ionic liquids and polymers. Although the mechanical strength, electrical, and ionic conductivity of PILs are lower compared to many

inorganic ionic materials, their affordability, extensive processability, tunability, flexibility, and affinity for both hydrophilic and hydrophobic groups position PILs as promising alternative candidates in the realms of separation science, polymer chemistry, wearable technology, personal medicine, and bioelectronics. For the synthesis of PILs, more environmentally friendly approaches are of utmost importance. Traditionally, two methods are employed: either the direct polymerization of ionic liquid monomers or the modification of existing polymers to produce PILs. Both methods involve multiple steps and consume significant amounts of solvents and energy. For the first method, it is crucial to incorporate groups into ionic liquid molecules, enabling them to participate in polymerization reactions. For the second method, the introduction of reactive groups into polymer chains is often necessary to attach the ionic liquid unit. Furthermore, most PILs cannot be utilized directly, making it essential to investigate advanced processes for integrating functionalization. In the latter strategy, it is frequently necessary to incorporate reactive groups into polymer chains to enable the grafting of the ionic liquid unit. Moreover, most PILs cannot be applied directly, thus necessitating the exploration of advanced processes to incorporate functionalization into the formation of PILs to meet application needs. Beyond synthesis procedures, the stability of PILs directly affects their applications. To achieve a better understanding of the ionic bonds in PILs, there is an urgent requirement for more fundamental experimental studies and theoretical insights. Similar to ionic bonded inorganic substances, PILs have specific solubility products in water, and exceeding these thresholds may lead to the dissociation of the PILs. The biocompatibility and toxicity of PILs are still not fully understood in relation to their structure-activity relationship. The development of PIL-based sensors is one of the most promising areas to investigate. As functional materials or components of advanced devices, PILs will inevitably enter the environment during their application or at the end of their lifecycle. For sustainable development, it is critical to assess the environmental risks associated with PILs. A better understanding of the degradation mechanisms of PILs is always desired for

industrial applications. PIL-based electrolytes are considered to be safe. An increasing number of PIL electrolytes have been developed, although their cytotoxicity can sometimes be greater than that of liquid inorganic alternatives

References

1. C. J. Clarke, W. C. Tu, O. Levers, A.Bröhl, J. P. Hallett, *Chem. Rev.* **118** (2018) 747.
2. V. Hessel, N. N. Tran, M. R. Asrami, Q. D. Tran, N. Van Duc Long, M. Escribà-Gelonch, J. O. Tejada, S. Linke, K. Sundmacher, *Green Chem.* 2022, Advance Article, DOI: 10.1039/D1GC03662A
3. T.Welton, *Biophys Rev.***10**(2018) 691.
4. Y. L. Wang, B. Li, S.Sarman, F. Mocci, Z. Y. Lu, J. Yuan, A. Laaksonen, M. D. Fayer, *Chem. Rev.***120** (2020) 5798.
5. M. Watanabe, M. L. Thomas, S. Zhang, K. Ueno, T. Yasuda, K.Dokko, *Chem. Rev.***117** (2017) 7190.
6. R. Hayes, G. G. Warr, R. Atkin, *Chem. Rev.***115** (2015)6357.
7. P.Hapiot, C. Lagrost, *Chem. Rev.***108** (2008) 2238.
8. S. Zhang, J. Zhang, Y. Zhang, Y. Deng, *Chem.Rev.***117** (2017) 6755.
9. C. Agatemor, K.N. Ibsen, E.E.L. Tanner, S. Mitragotri, *Bioeng. Transl. Med.* **3** (2018) 7.
10. K. S. Egorova, E. G. Gordeev, V. P. Ananikov, *Chem. Rev.* **117** (2017) 7132.
11. M.Amde, Jing-Fu Liu, and L. Pang, *Environ. Sci. Technol.* **49** (2015)12611.
12. M.Khraisheh, F. AlMomani, M. Inamdar, M. K. Hassan, and M. A. Al-Ghouti, *J. Mol. Liq.* **337** (2021)116421.
13. J.F. Wishart, *Radiation and Radical Chemistry of Ionic Liquids for Energy Applications in Ionic Liquids: Current State and Future Directions.* (2017) 251. DOI:10.1021/bk-2017-1250.ch011.
14. X.Sun, H. Luo, S. Dai, *Chem. Rev.* **112** (2012) 2100.
15. B. J. Mincher, and J. F. Wishart, *Solvent Extr. Ion Exch.* **32** (2014) 563.
16. N. V. Ilawe, J. Fu, S. Ramanathan, B. M. Wong, J. Wu, *J. Phys. Chem. C* **120** (2016) 27757.
17. M.Straka, *Phys. Sci. Rev.* **1** (2016) 20160074.
18. S.H. Ha, R. N. Menchavez, and Y. M. Koo, *Korean J. Chem. Eng.* **27** (2010)1360.
19. B.J. Mincher, G. Modolo, and S. P. Mezyk, *Solvent Extr. Ion Exch.* **27** (2009) 1.
20. J. F. Wishart, *J. Phys. Chem. Lett.* **1** (2010) 3225.
21. J. F. Wishart, I. A. Shkrob, *Ionic Liquids: From Knowledge to Application.* (2010) 119. DOI:10.1021/bk-2009-1030.ch008
22. Z. Xue, L. Qin, J. Jiang, T. Mu, G. Gao, *Phys. Chem. Chem. Phys.* **20** (2018) 8382.
23. L. Berthon, S. I. Nikitenko, I. Bisel, C. Berthon, M. Faucon, B. Saucerotte, N. Zorz, Ph. Moisy, *Dalton Trans.* (2006) 2526.
24. I.A. Shkrob, T. W. Marin, S. D. Chemerisov, J. L. Hatcher, J. F. Wishart, *J. Phys. Chem. B* **115**(2011) 3889.
25. I. A. Shkrob, S. D. Chemerisov, J. F. Wishart, *J. Phys. Chem. B* **111** (2007)11786.
26. I.A. Shkrob, T. W. Marin, S. D. Chemerisov, J. F. Wishart, *J. Phys. Chem. B* **115** (2011) 3872.
27. I.A. Shkrob, S. D. Chemerisov, J. F. Wishart, *arXiv: Chemical Physics*, (2007)arXiv:physics/0703027.
28. P.Tarábek, S. Liu, K. Haygarth, and D. M. Bartels, *Radiat. Phys. Chem.* **78** (2009)168.
29. A. Guleria, A. K. Singh, S. Adhikari, S. K. Sarkar, *Dalton Trans.* **43**(2014) 609.
30. A. Guleria, A. K. Singh, S. Adhikari, *Phys. Chem. Chem. Phys.* **17** (2015)11053.
31. S. Wang, J. Liu, L. Yuan, Z. Cui, J. Peng, J. Li, M. Zhai, W. Liu, *Phys. Chem. Chem. Phys.* **16**(2014)18729.
32. R. P. Morco, J. M. Joseph, J. C. Wren, *RSC Adv.* **5** (2015) 28570.
33. T.ElAchkar, H. Greige-Gerges, S. Fourmentin, *Environ Chem Lett.* **19**(2021)3397.
34. Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, *Chem. Soc. Rev.* **41** (2012) 7108.
35. Emma L. Smith, Andrew P. Abbott, Karl S. Ryder, *Chem. Rev.* **114** (2014) 11060.
36. B. B. Hansen, S. Spittle, B. Chen, D. Poe, Y. Zhang, J. M. Klein, A. Horton, L.Adhikari, T.Zelovich, B. W. Doherty, B.Gurkan, E. J. Maginn, A.Ragauskas, M.Dadmun, T. A. Zawodzinski, G. A.

- Baker, M. E. Tuckerman, R. F. Savinell, J. R. Sangoro, Chem. Rev. **121** (2021)1232.
37. A. P. Abbott, G. Capper, D. L. Davies, H. L. Munro, R. K. Rasheed, V. Tambyrajah, Chem. Commun. (2001) 2010.
38. G.C.Dugoni, E.Mossini, E. Macerata, A.Sacchetti, A. Mele, M.Mariani, ACS Omega **6**(2021) 3602.
39. R. Gupta, B. G. Vats, A. K. Pandey, M. K. Sharma, P.Sahu, A. K. Yadav, S. K. Musharaf Ali, S. Kannan, J. Phys. Chem. B **124** (2020)181.
40. M. Gilmore, É. N. McCourt, F. Connolly, P.Nockemann, M.Swadźba-Kwaśny, J. D. Holbrey, ACS Sustainable Chem. Eng. **6** (2018) 17323.
41. L. Das, S. Adhikari, J. Phys. Chem. B **122** (2018)8900.
42. O. S. Hammond, A. Mudring, Chem. Commun. (2022) Advance Article, DOI: 10.1039/D1CC06543B
43. D. V. Wagle, H. Zhao, G. A. Baker, Acc. Chem. Res. **47** (2014) 2299.
44. J.Łuczak, M.Paszkiewicz, A.Krukowska, A.Malankowska, A.Zaleska-Medynska, Adv. Colloid Interface Sci. **230** (2016)13.
45. Z. He, P.Alexandridis, Phys. Chem. Chem. Phys. **17** (2015)18238.
46. X. Duan, J. Ma, J. Lian, W. Zheng, CrystEngComm. **16** (2014) 2550.
47. A.Guleria, A. K. Singh, M. C. Rath, S. Adhikari S. K. Sarkar, Dalton Trans. **42** (2013)15159.
48. L. Das, A.Guleria, S. Neogy, S. Adhikari, RSC Adv. **6** (2016) 92934.
49. A.Guleria, A. K. Singh, M. C. Rath, Sisir K. Sarkar, S. Adhikari, Dalton Trans.**43** (2014) 11843.
50. A.Guleria, S. Neogy, S. Adhikari, Mat. Lett. **217** (2018)198.
51. A.Guleria, S. Chakraborty, S. Neogy, D. K. Maurya, S. Adhikari, Chem Comm. **54** (2018) 8753.
52. A.Guleria, D. K. Maurya, S. Neogy, B. S. Raorane, S. Adhikari, New J. Chem.**44** (2020) 4578.
53. A.Guleria, A. K. Singh, S. Neogy, S. Adhikari, Mat. Chem. Phys. **202** (2017)204.
54. ApuravGuleria, S. Neogy, B. S. Raorane, S. Adhikari, Mat. Chem. Phys. **253** (2020) 123369.
55. A.Guleria, C. M. Baby, A. Tomy, D. K. Maurya, S. Neogy, A. K. Debnath, S. Adhikari, J. Phys. Chem. C **125** (2021) 13933.
56. Lee, Jae-Seung, Nanotech. Rev.**6** (2017) 271.
57. L. Das, L. D. Koonathan, A. Kunwar, S. Neogy, A. K. Debnath, S. Adhikari, Mater. Adv. **2** (2021) 4303.



Arijit Sengupta is a Scientific Officer (G) at the RC & I Group, Bhabha Atomic Research Centre, Mumbai. He joined after graduating from 51st batch of BARC Training School. He has worked on application of multi-functional materials (ionic liquids; carbon nanotubes; grapheneoxides, Metal-organic frameworks, magnetic nanoparticles and other novel functionalized materials) for the extraction and complexation of lanthanides/actinides. He has also worked on responsive membranes through surface modifications. He did his Post-doc during 2016-2018 from University of Arkansas, USA. He is having journal publications (citation ~6900, h index ~46), 1 Patent, 4 Book Chapters, 2 BARC reports and 1 BARC News Letter to his credit. He is a recognized Ph.D guide from HBNI. He is recipient of Young Scientist Award, Indian Science Congress Association (ISCA), 2016; Young Scientist Award, Department of Atomic Energy (DAE), Government of India, 2019, Tarun Datta Memorial Award, Indian Association of Nuclear Chemists and Allied Scientists (IANCAS), 2020; Prof. H.J. Arniker Best Ph.D. Thesis Award, IANCAS, 2015; Best M.Phil Thesis Award, THERMAX/ Association of Separation Scientists and Technologists (ASSET), 2012; Department of Atomic Energy (DAE) Group Achievement Award, 2012; Young Scientist Award from Indian Society of Analytical Scientists, 2024; and Society of Material Chemistry (SMC), Bronze Medal in 2021. He is in the Editorial Board of Radiochimica Acta.

Pyrohydrolysis as a Green Separation Approach for Halogens and Non-Metals: Advances and Applications in Nuclear, Geological, and Environmental Analysis

V. G. Mishra^{*1}, S. Jeyakumar²

¹Radioanalytical Chemistry Division,
Bhabha Atomic Research Centre, Mumbai 400085, India

²Radiochemistry Division,
Bhabha Atomic Research Centre, Mumbai 400085, India
(Corresponding Author: Email: vgmishra@barc.gov.in)

Introduction

The reliable determination of halogens in complex solid matrices has long remained a critical challenge in analytical chemistry. These elements are typically present at ultra-trace levels, ranging from parts per billion (ppb) to parts per million (ppm), and often occur in chemically inert or volatile forms. Their accurate quantification is further complicated by the heterogeneous nature of matrices such as silicate rocks, nuclear fuels, contaminated soils, industrial slags, and biological materials. In particular, fluorine, chlorine, bromine, and iodine demand careful analytical attention due to their high reactivity, volatility, and tendency to form complex compounds.

The importance of halogen and other non-metal analyses extends across multiple scientific and technological domains. In the nuclear industry, the non metals including halogens have direct influence on the fuel integrity, fuel performance, corrosion behavior, and long-term radioactive waste management. In environmental monitoring, the assessment of fluorine and iodine in soils and groundwater is essential, particularly for contamination or pollution tracking, evaluating human exposure, and ensuring regulatory compliance [1–6]. Similarly, in geochemical exploration and industrial quality control, halogens and non-metals such as boron serve both as geochemical tracers and as functional additives in manufacturing.

Classical wet chemistry techniques, including alkali fusion followed by either titrimetric or spectrophotometric methods have been followed for the determination of halogens. However, these approaches suffer from inherent limitations such as- excess reagent consumption, significant matrix interferences, analyte loss through volatilization, and limited sensitivity. The digestion of silicate and oxide rich matrices,

in particular, demands aggressive reagents and extended heating, which not only pose safety hazards but also increase the risk of contamination and analyte loss. In the nuclear context, where radiological safety and small sample size are paramount, such drawbacks severely restrict the applicability of conventional methods.

To address these challenges, pyrohydrolysis has emerged as a potential alternative. Pyrohydrolysis, a high-temperature process enables the selective release of halogens and volatile non-metals. The volatile products are subsequently trapped in an absorption medium prior to their quantification. Pyrohydrolysis offers distinct advantages over digestion or dissolution based methods: (i) it eliminates the need for matrix dissolution, (ii) reduces contamination and interference risks, and (iii) minimizes reagent use, thereby providing a safer and more environmentally sustainable approach [7].

The integration of pyrohydrolysis with advanced detection systems has further enhanced its utility. Combination with ion chromatography (IC) enables high-resolution, multi-analyte detection with excellent sensitivity and selectivity, while techniques such as inductively coupled plasma mass spectrometry (ICP-MS) extend the detection limits into the sub-ppb range. This synergy has significantly expanded the scope of pyrohydrolysis, making it indispensable for trace or ultra-trace level analysis of halogens in nuclear, geological, and environmental applications.

The present article reveals key findings from diverse studies on pyrohydrolysis, spanning fundamental principles, technological innovations, and practical applications. Specifically, it aims to (i) discuss the mechanisms underlying pyrohydrolysis, (ii) trace the evolution of experimental setups, and (c) evaluate its

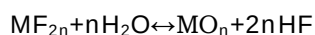
applications across a variety of sample types.

Principle and Evolution of Pyrohydrolysis

Pyrohydrolysis represents a high-temperature separation technique mainly used as a sample preparation technique that exploits gas-solid interactions for the separation of volatile analytes, particularly halogens and other nonmetals such as boron and sulfur.

The underlying principle of pyrohydrolysis is based on the thermal decomposition in the presence of a moist carrier gas. At elevated temperatures, typically in the range of 900–1100°C, sample matrices undergo reaction with steam (water) that release volatile hydrogen halides (HF, HCl, HBr, HI) or other gaseous oxides (fig.1). These reaction products are swept away by carrier gas and subsequently trapped in absorbing medium, most commonly alkaline solutions such as sodium hydroxide. Once trapped, the analytes can be quantitatively determined by sensitive instrumental methods such as ion chromatography (IC) or Ion Selective Electrode (ISE).

The general reaction for halide-bearing compounds can be summarized as:



Where M = metal or matrix element, X = F, Cl, Br, I

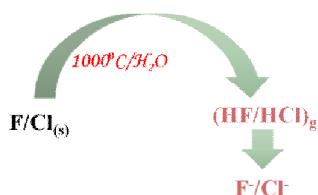


Fig. 1. Pictorial representation of the pyrohydrolysis mechanism.

The efficiency of the separation depends on several factors, including the chemical bonding environment of the halogen, the oxidation state of the matrix, and the thermodynamic stability of the compound.

Refractory materials such as silicates, titanates, and certain oxides pose specific challenges due to their strong metal-halogen bonds and thermal stability. In these materials, to achieve complete

volatilization, accelerators such as U_3O_8 , V_2O_5 , WO_3 , or SiO_2 are often introduced. This addition not only facilitates breakdown of the matrix but also enhances the release kinetics of halogens. Other parameters influencing separation efficiency include carrier gas choice and composition, its flow rate, reaction temperature, and duration of pyrohydrolysis. Therefore, optimizing the above conditions is crucial for obtaining reproducible and quantitative recovery, especially in complex matrices.

The evolution of pyrohydrolysis as an analytical separation tool has been closely linked with advances in detection technology. Initially, the method relied on colorimetric or titrimetric determinations of separated analytes, which were limited in sensitivity and specificity. The use of ion chromatography for analyzing the pyrohydrolysed distillate made a remarkable and major turning point, enabling simultaneous multi-analyte separation with high resolution and precision. More recently, use of ICP-MS for the analysis of pyrohydrolysis distillate has extended the detection limits to the ppb to sub-ppb level, greatly expanding its applicability for ultra-trace analyses. These developments have placed pyrohydrolysis as a green method of sample preparation that continues to evolve in line with modern analytical requirements.

Typical Instrumentation Setup

During the initial phase platinum based pyrohydrolysis apparatuses were used, however there were some associated limitations. To overcome the equipment limitations, Susano and et. al. [8] proposed nickel tubes instead of platinum, while Gillies and colleagues [9] introduced a silica-based apparatus for the process. In a similar effort to optimize materials, Adams and Williams [10] employed high-silica Corning Code 7900 glass (96% silica) for their pyrohydrolysis setup. These contributions collectively demonstrate the evolution of pyrohydrolysis techniques, highlighting advancements in apparatus design. In recent applications in general quartz based pyrohydrolysis apparatuses are being employed [11].

A standard pyrohydrolysis apparatus as shown in Fig.2, consists of components:

Furnace Unit: Electrically heated furnace capable of maintaining temperatures up to 1100°C with programmable control. Tube furnaces are common.

Reaction Zone: Often a quartz reaction tube where the sample (typical sample size 50–1000 mg) is placed in a boat or crucible. The tube is flushed with moist carrier gas.

Moist carrier gas: A controlled moist carrier gas (argon, oxygen or air) connected to the reaction tube.

Trapping solution: Absorbers filled with dilute alkali (e.g., Na_2CO_3 , NaOH , or water) are used for quantitative capture of HX gases. Sometimes multiple traps can be used to ensure complete absorption.

Pyrohydrolysis apparatuses have also been designed and fabricated specially and specifically for glove-box compatibility to analyze radioactive samples [11]. A Pyrohydrolysis apparatus design used in our laboratories is depicted in fig. 3.

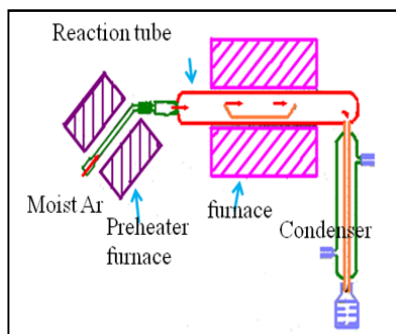


Fig.2. Pictorial representation of a typical pyrohydrolysis set up.

Halogen Separation and Post-Pyrohydrolysis Analytical Determination:

After pyrohydrolysis, the pyrohydrolysis distillate containing halides is a simple aqueous medium and their analysis is a simplified step due to the generation of clean and matrix free distillates, which minimize interference. This allows compatibility with several techniques. Ion chromatography is the most used, followed by ISE.

Ion-Selective Electrode (ISE): ISE based measurements are known for many anions (NO_3^- , F^- , Cl^- , S^{2-} , I^- , Br^- , ClO_4^- , CN^-) and cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , Li^+ , Ag^+ , Cd^{2+} , NH_4^+ , Pb^{2+}). However, for the determination of fluorine in several matrices the

combination of pyrohydrolysis separation followed by ISE is one of the widely employed methods due to its high reliability. The ISE method measures potential developed between an ion selective and reference electrode in a buffered pyrohydrolysis distillate. In ISE method, F concentrations above 0.15 mg/L and a stable pH of solution is prerequisite. Ammonium acetate buffers are used to keep pH near 5.5, as extreme pH affects accuracy. Though limited by sensitivity and selectivity, ISE is still suitable for high fluoride matrices like fossil fuels, coal, and supplements [12].

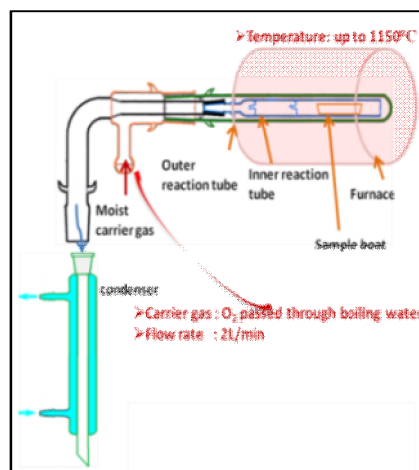


Fig.3. Pictorial representation of a pyrohydrolysis set up designed for Glove Box operations.

Inductively Coupled Plasma Mass Spectrometer (ICP-MS):

ICP-MS is highly sensitive, fast and ideal for Br and I, but less suitable for F due to high ionization energy and interference from polyatomic species. It supports a wide dynamic range and low detection limits but may suffer from carbon based interferences and memory effects from volatile halogen compounds [13]. To avoid this, basic solutions like NH_4OH are used in trapping. Pyrohydrolysis offers a clean distillate, making the sample solution more amenable to the ICP-MS. It has been used for several samples like geological materials, coal, and fuels, providing accurate results and low RSDs.

Ion Chromatography (IC): Combination of ion chromatography and pyrohydrolysis is a powerful technique for the determination of fluorine, chlorine and boron especially in the presence of other ions of both cations

and anions. IC utilizes ion-exchange resins to separate ionic species followed by conductometric detection. It is particularly well suited for the analysis of halides, oxyanions (e.g., sulfate), and small organic acids. It uses polymer based columns of both strong and weak ion exchangers and carbonate/NaOH based mobile phases. Detection is typically via conductivity, enhanced by suppressors [14].

The main advantage of IC is that it provides separation and determination simultaneously. When paired with pyrohydrolysis, IC allows the quantitative determination of multiple analytes (anions or cations) from a single sample. Therefore, it has capability to analyse a selected number of ions in presence of other ions of the similar charges and thereby eliminates or minimizes the interferences. The pyrohydrolysis-IC combined approach thus represents an efficient solution for a variety of application areas [15]. IC is widely applied for the separation and determination of fluorine and chlorine as fluoride and chloride ions respectively. Determination of F and Cl in complex matrices like soil, coal, rocks and nuclear materials is turned to be simple and reliable due to application of pyrohydrolysis

although certain associated challenges like separation of organic anions that are formed during pyrohydrolysis. In such cases, the desired separation is realized by varying eluent concentration or by using concentration gradient elution or by choosing the column with required efficiency. IC offers low detection limits, good multi-element capability, and better performance than ISE and plasma methods, especially for fluorine and chlorine, which plasma techniques struggle to detect.

Advantages of Pyrohydrolysis over Conventional Techniques

Compared to fusion (e.g., alkali carbonate/sulfate melts) and acid digestion pyrohydrolysis offers several analytical and operational advantages as mentioned in table 1. These advantages make pyrohydrolysis particularly suitable for trace level analysis in variety of scientific domains such as:

- Geochemistry and mineral exploration
- Nuclear fuel fabrication and reprocessing
- Environmental
- Cement and construction material
- Glass and ceramic industries

Table 1: Comparison of pyrohydrolysis with wet analytical Methods

Aspect	Pyrohydrolysis	Wet Digestion / Fusion
Sample matrix tolerance	High (can handle silicates, ores, etc.)	Moderate to low (matrix-dependent)
Reagent contamination	Minimal (moist carrier gas + trapping solution)	High
Halogen loss risk	Low (closed system for gas-phase collection)	High (volatilization in open digests)
Selectivity for halides	Excellent (Separation of volatile HX)	Poor to moderate (matrix interference)
Compatibility with IC	High (clean aqueous extracts)	Moderate (acidic or salted matrix)
Safety and handling	Safer and green method	Requires high-risk chemicals

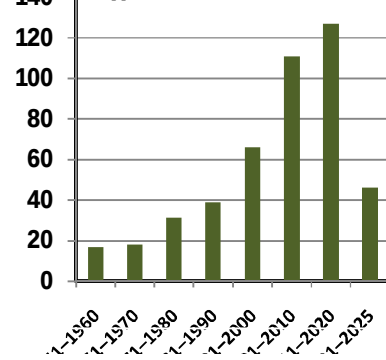
Historical Development and Analytical Applications

Historically, pyrohydrolysis has been widely investigated for the separation of halides, with its first applications dating back to the 1950s in a variety of complex matrices such as halocarbons, uranium oxide, radioactive wastes, glasses, silicates, and rare Earths, particularly for the determination of fluorine and chlorine [16-21]. One of the earliest references to this technique was a paper published by Warf [17], whose work was later expanded upon by other researchers. A key advancement in the methodology was the introduction of additives, or "accelerators," such as uranium oxide (U_3O_8), which significantly improved separation efficiency. These accelerators react with the matrix when mixed with the sample, aiding in the release of halides. Powell and Menis [22] further refined the method through both micro and macro scale fluoride separations from inorganic materials, systematically evaluating the effect of various accelerator. They also highlighted the benefits of using moist oxygen instead of steam to enhance reaction kinetics. These developments are especially useful for (i) Silicate-rich rocks (e.g., granites, basalts, feldspars) [21, 22] where F is bound as CaF_2 or MgF_2 in a tight lattice; (ii) High-temperature minerals (e.g., phosphates, titanates) where halogen mobility is low; (iii) Determination of fluoride in slag, fly ash, and cementitious materials, where binding to iron, aluminum, and calcium is common. The overall simplicity of pyrohydrolysis, requiring no aggressive digestion reagents made it especially suitable for refractory samples. These developments have shaped pyrohydrolysis into a reliable and adaptable technique for halide analysis across diverse sample types.

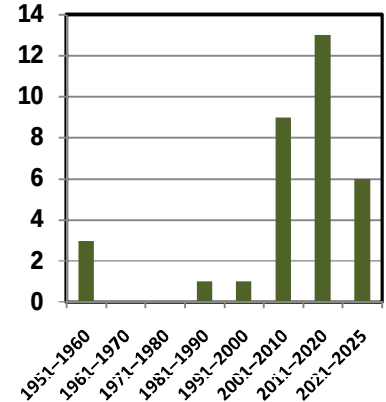
The details plotted in the figure 4 suggest that, from 1951 to 2025, the number of publications on pyrohydrolysis has shown a consistent upward trend, reflecting growing scientific interest and advancements in pyrohydrolysis. The most productive decade was 2011-2020, with 127 articles, followed by 111 during 2001-2010. Notably, nuclear related studies increased significantly after 1990, reaching a peak of 18 articles in the 2011–2020 decade and continuing with 14 more between 2021 and 2025. A significant rise in the number of publications using accelerators is observed after 2000, with a

peak of 13 in 2011–2020 and 6 more from 2021 to 2025. This increased use of accelerators likely indicates a shift toward analyzing more complex or challenging matrices. Overall, the data suggests not only a rising interest in pyrohydrolysis but also its expanding application in nuclear science and advanced materials analysis.

(i) Total Research Articles



(ii) Pyrohydrolysis using Accelerators



(iii) Application to Nuclear materials

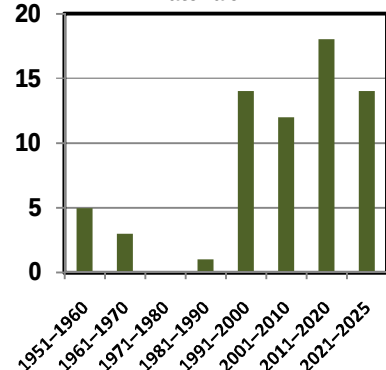


Fig.4. (i) Overall number of publications using pyrohydrolysis (ii) publications using accelerators and (iii) number of articles discussing application to nuclear materials

Geological and Environmental Applications of Pyrohydrolysis

In geological materials, halogens are important tracers of magmatic processes, metamorphic evolution, and ore genesis. Fluorine and chlorine are often incorporated in minerals like fluorite, apatite, mica, and amphiboles. They play a key role in volcanic degassing, hydrothermal fluid transport, and mantle melting dynamics. Chlorine isotopes are also used to trace the origin of fluids in geochemical reservoirs, while fluorine content in igneous rocks is used to interpret volatile budgets and magma crystallization histories [23-26].

Halide ions, especially chloride and bromide, are major constituents in environmental matrices and play key roles in acid-base equilibria, ozone depletion, and redox reactions. Iodine speciation in sediments and groundwater is used to assess nutrient cycling, radioactive contamination, and marine-terrestrial exchange [27-30].

Pyrohydrolysis offers a unique advantage for separating halides in complex environmental matrices where organic and inorganic species coexist. Samples like sewage sludge, fly ash, contaminated soils, and lake sediments are decomposed thermally, and halides are extracted into an aqueous medium for subsequent quantification [31,32]. Importantly, the method ensures destruction of organic interferences, a common problem in other extraction methods. Its ability to cleanly and specifically volatilize target analytes without introducing matrix interferences makes it valuable for complex geological materials like rocks, sediments, coal, and crude oil.

Geochemical and Mineral Matrices: In geochemistry, pyrohydrolysis has been applied extensively to extract halogens from silicate rocks and mineral matrices [33-35]. Kenji S. and co-workers [36] successfully quantified fluorine, chlorine, and sulfur from volcanic silicate glasses by conducting pyrohydrolysis at 1250 °C using V₂O₅ as an accelerator, followed by ion chromatography detection. Similarly, Bonifacie et al. [33] optimized Cl extraction for isotopic studies from silicate rocks prior to isotope ratio mass spectrometry (IRMS), achieving nearly quantitative yields

(100 ± 8%). This methodology was extended to scapolite minerals to measure Cl isotopes, emphasizing the ability of pyrohydrolysis separation for clean isotope ratio determinations in complex matrices.

Thakur et al. [37] developed a methodology using pyrohydrolysis coupled with ion chromatography for the quantification of chlorine in high-silica environmental matrices such as soil and rock phosphate. The method employed a U₃O₈ accelerator to facilitate the complete release of chloride species during pyrohydrolysis. This approach proved effective for trace chloride analysis in materials with complex silicate structures, which are otherwise resistant to conventional digestion techniques. The chlorine content in the analyzed samples, including bentonite and phosphate rock references, ranged from 70 to 200 mg/kg. The method achieved a detection limit of 12 mg/kg for chloride and was validated against Instrumental Neutron Activation Analysis (INAA), a standard reference technique. Figure 5 represents the flow chart for the pyrohydrolysis-IC method followed. The comparison of the data with INAA along with the p-value is represented in table 2.

Table 2: Comparison of total chloride contents, determined in real samples and reference materials using INAA and pyrohydrolysis-IC

Samples	INAA Cl ($mg\ kg^{-1}$)	Pyrohydrolysis-IC Cl ($mg\ kg^{-1}$)	p value
RP-1	113±9	120±8	0.3710
RP-2	204±11	196±6	0.3308
BNT-1	150± 10	137±12	0.2229
BNT-2	111±9	118±14	0.5067
BCR-032	141±8	146±10	0.5360
USGS CRM G-2 (70 $mg\ kg^{-1}$ Cl, information value)	77±4	79±9	0.7428

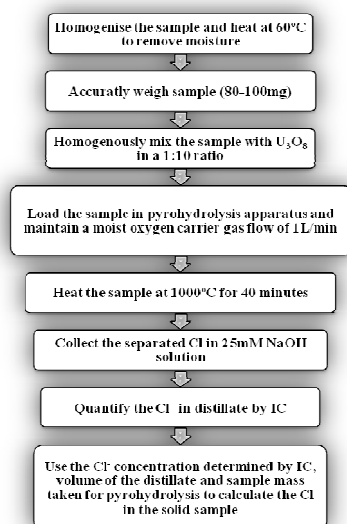


Fig.5. Flow chart showing the step wise complete procedure used in pyrohydrolysis-IC method

Coal, Oil, and Sedimentary Rocks: Coal and other fossil-fuels have also been studied extensively [38,39]. Because of coal's high organic and sulfur content, pyrohydrolysis conditions must be carefully optimized to prevent deflagration. Wua et al. conducted an in-depth optimization study for iodine recovery from coal, identifying conditions that maximize recovery while minimizing interferences [40].

B. Peng et al. [41] developed a comprehensive protocol for determining F, Cl, Br, and I in coal using pyrohydrolysis-IC, achieving improved detection limits through parameter optimization. In lignite coal, Sredović and colleagues [42] used statistical optimization tools to fine-tune pyrohydrolysis conditions for fluorine extraction, correlating the findings with corrosion risks in thermal power plants. Further bromide and iodide were determined in bottom ash and fly ash from multiple thermal power plants using pyrohydrolysis followed by ICP-MS. The matrix elimination capacity of the technique allowed reliable detection of halogens at trace levels, aiding environmental monitoring and regulatory compliance [43].

Geological Reference Materials and Sediments: Several studies have used pyrohydrolysis to certify geological reference materials. Sekimoto and Ebihara applied both pyrohydrolysis and radiochemical neutron activation analysis (RNAA) to determine halogen content in bauxite, granite, and feldspar standards [34]. They reported improved iodine recoveries when using V_2O_5 as a flux, especially at 1060°C for 15 minutes, supporting its suitability for routine geochemical applications.

Pagea et al. used pyrohydrolysis to explore halogen behavior in subducting slabs, extracting F, Cl, Br, and I to study their mobility during subduction [44]. S. Dai et al. employed pyrohydrolysis-FISE (fluoride ion-selective electrode) coupling to trace fluorine in environmental matrices, contributing insights into fluorosis pathways [45].

Other notable contributions include halide analysis in magmatic apatites, sediments, cement, and clay [46-48]. Pyrohydrolysis has consistently proven superior to conventional acid digestion or alkaline fusion in these matrices, especially in reducing contamination and improving detection limits.

Food, Pharmaceuticals, and Biological Samples

Need for Halide Control: In pharmaceuticals and food-grade materials, halide content must be strictly regulated due to their potential toxicity, interactions with active pharmaceutical ingredients (APIs), and degradation of excipients [49-51]. Fluoride, while beneficial in trace amounts (e.g., in toothpaste), is toxic at elevated levels and must be carefully monitored in food, water, and supplements [52, 53]. Chloride levels also impact osmotic balance, ionic strength, and bioavailability in biological matrices [54].

Application of Pyrohydrolysis: Owing to its robustness, pyrohydrolysis is now being adapted for biological and pharmaceutical samples, particularly in regulatory contexts [55-57]. With modified setups and low-temperature decomposition (for thermolabile samples), fluoride and chloride can be reliably extracted and quantified.

Nuclear material Analysis

Maintaining chemical purity in nuclear fuels is essential, as trace levels of halides like fluoride and chloride can corrode cladding materials. Specification limits are stringent in the case of nuclear fuels and reactor materials: for instance, the UO_2 and $(\text{U,Pu})\text{O}_2$ mixed oxide fuels, F and Cl must not exceed 10 and 15 ppm (thermal reactors) whereas for the mixed carbide fuels, limits are 10 ppm (F) and 20 ppm (Cl). In cladding materials, Cl must be <25 ppm for Zr-Nb alloys and <30 ppm for Zircaloy.

Several authors have reported effective strategies for the determination of fluorine and chlorine, in complex nuclear fuel matrices using pyrohydrolysis coupled with IC.

A study carried out by Mahajan et.al. [11] outlines a pyrohydrolysis based method to determine halides in UO_2 and $(\text{U,Pu})\text{C}$ fuels. Using moist oxygen and heating at 900–950 °C, the halides were separated efficiently. spectrophotometric method and ion selective potentiometric method were standardized for the determination of chloride and fluoride, respectively. Precision tests on a sintered uranium oxide sample showed consistent results, with fluoride averaging 10.5 ± 0.6 ppm and chloride 6.5 ± 1.6 ppm, each with a 6% RSD over 15 trials.

In a similar study [58], authors investigated the pyrohydrolysis method for the separation of F and Cl from U-Zr and U-Pu-Zr alloy nuclear fuels. The work emphasized the significance of the carrier gas environment in achieving complete decomposition of the fuel matrix. While pyrohydrolysis using moist argon required 60–90 minutes to ensure complete halide removal, moist oxygen as a carrier gas facilitated complete pyrohydrolysis at 900°C within just 30 minutes (figure 6 and 7). This improvement was attributed to the formation of $\alpha\text{-U}_3\text{O}_8$ in an oxidizing environment, which enhanced matrix breakdown. The study demonstrated halide recoveries exceeding 90% under optimized conditions and further showed that the method could be extended to U-Pu-Zr alloys, thus highlighting its applicability across metallic fuel systems. The Data

%S.D. for Cl was 3.04% and for F was 3.97% (n=5) for a U-Zr alloy sample subjected to the developed method. Table 3 represents F and Cl values determined in some real samples.

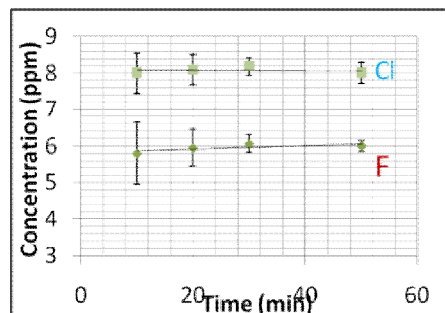


Fig.6. Recovery of F and Cl from a U-Zr alloy sample as a function of pyrohydrolysis time period.

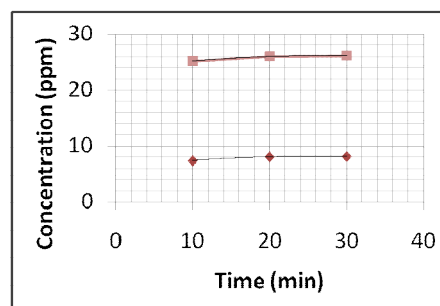


Fig.7. Recovery of F and Cl from a U-Pu-Zr alloy sample as a function of pyrohydrolysis time period.

Table 3: Total fluorine and chloride contents, determined in real U-Zr and U-Pu-Zr alloy samples using pyrohydrolysis-IC.

Pyrohydrolysis followed by IC		
samples	F content (ppm)	Cl content (ppm)
UZr alloy-1	4.1 ± 0.4	4.8 ± 0.3
UZr alloy-2	3.6 ± 0.4	9.2 ± 0.4
UZr alloy-3	5.0 ± 0.3	8.3 ± 0.5
UPuZr alloy-1	8.1 ± 0.6	25.8 ± 0.13
UPuZr alloy-2	2.9 ± 0.2	6.4 ± 0.4
UPuZr alloy-3	1.0 ± 0.2	4.3 ± 0.4
UPuZr alloy-4	1.6 ± 0.3	3.8 ± 0.5

The upgraded research reactor APSARA-U uses LEU as the fuel which requires the use of high-density U_3Si_2 fuel to maintain reactivity. A robust analytical method was developed for the simultaneous trace-level determination of, chlorine and fluorine in uranium silicide fuel [59]. The method combines pyrohydrolysis for separation with ion chromatography for quantification. An isocratic ion chromatography procedure

with optimized pyrohydrolysis conditions enabled sensitive detection of these impurities. Studies showed that moist oxygen was a more effective carrier gas than argon during pyrohydrolysis, promoting the formation of low-density U_3O_8 , which expands the matrix and enhances exposure to water vapor. Recovery studies demonstrated that Cl and F could be effectively recovered within 20 minutes of pyrohydrolysis at 1150 °C. The recovery of F and Cl as a function of pyrohydrolysis time period is represented in figure 8.

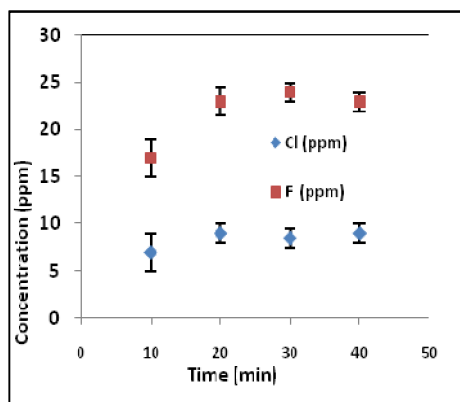


Fig.8. Recovery of F and Cl from an U_3Si_2 sample as a function of pyrohydrolysis time period.

In addition to U and Pu containing matrices, separation of F and Cl has been also carried out from Th matrix using pyrohydrolysis. The study by Pandey et al. [60] presents a rapid and efficient method for quantitative extraction of fluoride and chloride from thorium based nuclear fuels using WO_3 as an accelerator in pyrohydrolysis. The method operates at 950 °C with moist oxygen, significantly lowering the usual temperature requirements. Ion chromatography was used for simultaneous determination, achieving over 92% recovery for both halides with good reproducibility. As per the study, compared to V_2O_5 , WO_3 showed superior performance as an accelerator without forming volatile or glassy residues.

These studies collectively demonstrate the adaptability and reliability of pyrohydrolysis for halide determination in challenging nuclear matrices. This is also evident from the ASTM C1502-09 standard test method [61] which covers the determination of chlorine and fluorine in nuclear-grade uranium dioxide powder and pellets, nuclear grade gadolinium oxide powder and gadolinium oxide-uranium oxide (Gd_2O_3 -

UO_2) powder and pellets. With a 2 gram UO_2 sample size the detection limit of the method was reported to be 4 $\mu g/g$ for chlorine and 2 $\mu g/g$ for fluorine.

Separation and Determination of Boron

Since 1959, [62] pyrohydrolysis has been effectively employed for the separation and determination of boron in various complex matrices. One early method involved pyrohydrolysis of a mixture of glass sample, uranium oxide, and sodium metasilicate nonahydrate in a platinum tube, with boron quantified via mannitol-sodium hydroxide titration. The same year, researchers demonstrated the separation of boron from metals and alloys like zirconium, Zircaloy, stainless steel, and boron carbide using a nickel apparatus [62-64]. By 1964, pyrohydrolysis was successfully applied to boron steel, where the sample was pyrohydrolysed and boron was collected in sodium hydroxide and measured using mannitol-based coulometry [65].

The potential of pyrohydrolysis for the separation of boron from borosilicate glasses was recognized based on two key observations. First, boric oxide exhibits significant volatility at the high temperatures. Second, boric acid (H_3BO_3) is known to readily undergo volatilization due to its relatively low boiling point of approximately 300°C (H_3BO_3 is formed during pyrohydrolysis of B in presence of water vapor). These characteristics suggested that pyrohydrolysis, which had already proven effective for separating volatile halides from various inorganic matrices, could also be adapted for the efficient separation and quantification of boron from complex matrices. The pictorial representation of B separation using pyrohydrolysis is presented in figure 9. Volatilized boric acid can be easily captured in an alkaline solution, which is then suitable for quantitative analysis.

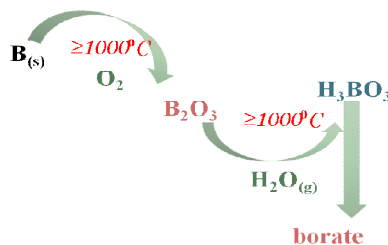


Fig.9. Pictorial representation of the pyrohydrolytic separation of B.

Accurate determination of boron in nuclear fuels is very important due to its strong neutron absorption properties, which can adversely affect reactor performance and safety if present beyond permissible limits. For instance, the specification limits for boron in UO_2 thermal reactor fuel is 0.3ppm whereas the Fast Breeder Test Reactor (FBTR) fuels is $4\text{ }\mu\text{g/g}$, highlighting the need for highly sensitive and precise analytical techniques.

A reliable and sensitive analytical method based on pyrohydrolysis and ion chromatography has been developed for the simultaneous separation and quantification of boron, fluorine and chlorine in nuclear fuel matrices such as U_3O_8 , (U,Pu)C, and Pu-alloys. The method involves initial pyrohydrolytic extraction of B and determination using ion chromatography [66].

In this line an important application to nuclear material is determination of percent level B in B doped Zr-Nb alloy which is used as neutron control rods in advance nuclear reactors [67]. During the fabrication of the material it is important to determine the final B content specially its distribution across the control rod. The initial studies with pyrohydrolysis showed that the matrix did not open at 1000°C temperature (usually used for pyrohydrolysis). The observed behavior was due to the formation of ZrO_2 protective layer. This may cause trapping of B present in the interior of the matrix. Therefore pyrohydrolysis was carried out at different temperatures and it was found that the opening of matrix requires a higher temperature of 1200°C (for 1h) for complete oxidation in presence of moist oxygen carrier gas. The separated B was trapped in a dilute NaOH solution as borate ion and was analyzed using ion chromatography. For IC analysis B was separated on an anion exchange column using combination of NaOH and d-mannitol as the eluent.

Similarly, Raut and et.al. [68] presented an important application of pyrohydrolysis in B determination in paraffin wax. Boron compounds are effective in shielding against high-energy neutrons, with borated paraffin wax widely used in radiotherapy and nuclear applications. To ensure uniform boron distribution in waxes containing boric acid or boron carbide, a

pyrohydrolysis-ion chromatography method was developed. Wax samples, mixed with U_3O_8 , were pyrohydrolyzed in moist O_2 at 950°C for 60–90 min. Additionally the method was compared with an alkali-based separation method. The Determination of B in the pyrohydrolysis distillate was carried out with IC as the boron–mannitol complex.

Separation of Molybdenum using pyrohydrolysis

Pyrohydrolysis is now evident that it is a well-established, greener alternative for separating non-metal analytes (e.g. halogens and boron) from sample matrices. However, its application to metal separations had not been previously demonstrated. In a study, Mishra et al. demonstrated a novel and environmental friendly method for the selective separation and determination of molybdenum from solid uranium matrices using pyrohydrolysis [69]. The technique relies on the mechanism wherein molybdenum, present in the uranium matrix, is converted into $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ at high temperatures (around 1000°C) in the presence of moist oxygen. The $\text{MoO}_3 \cdot n\text{H}_2\text{O}$ thus formed has high vapour pressure and can be volatilized (figure 10).

The volatilized MoO_3 is then efficiently trapped in a dilute alkali medium and quantified using ion chromatography, which allows for detection at ppm levels. The process achieved more than 95% recovery of Mo across different uranium-based samples such as UO_2 , and uranium alloys. This was confirmed using a TGA, XRD (figure 11) and by processing standards with known Mo content.

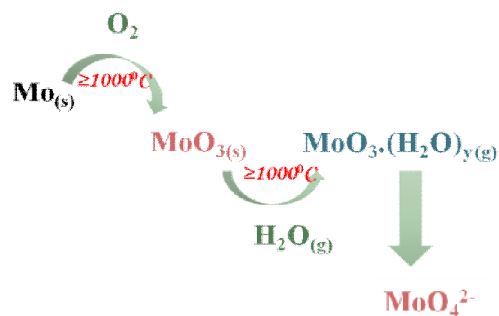


Fig.10. Pictorial representation of the pyrohydrolytic separation of Mo.

Accuracy of the developed method was evaluated by analyzing a certified reference material of U_3O_8 (ILCE-4, Department of Atomic Energy (DAE), Mumbai, India). Finally the method was utilized in determination of Mo in ADU samples. This work not only extends the scope of pyrohydrolysis from traditional halide and non-metal analysis to transition metal separation but also aligns with green chemistry principles by avoiding the use of concentrated acids or organic solvents.

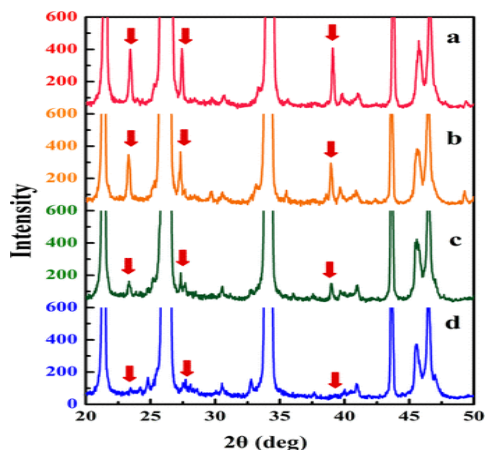


Fig.11: XRD patterns of UO_2 and MoO_3 mixture recorded after (a) 1/2, (b) 1, (c) 1 1/2, and (d) 2 h of pyrohydrolysis. The downward arrow symbol indicates a few major peaks for MoO_3 .

In this line it is also important to mention that the capability of the pyrohydrolysis separation method can be utilized for the simultaneous separation of analytes

important in nuclear material analysis i.e. F, Cl, B and Mo. Along with F and Cl the quantification of B and Mo in uranium based fuels is essential due to their critical roles in neutron economy and fuel performance. Based on the simultaneous separation of these analytes using pyrohydrolysis, Mishra et al. [70] reported a method for the simultaneous separation and determination of B, Cl, F, and Mo in uranium silicide fuel using pyrohydrolysis followed by ion chromatography determination. The pyrohydrolysis conditions were optimized to ensure effective separation of all target analytes from the fuel matrix and a two-step isocratic IC method was proposed for their separation and determination. The method allowed for trace-level quantification of B, Cl, F (with detection limits of 0.5–0.6 $\mu\text{g/g}$), and Mo (detection limit of 2.5 $\mu\text{g/g}$). Importantly, boron was cross-verified via spectrophotometry, and molybdenum by ICP-AES. To support such analysis using IC a gradient elution method was also proposed [71]. Where, all the four analytes i.e. B, F, Cl and Mo in the pyrohydrolysis distillate were separated and detected simultaneously in a single IC run. By enabling multi-element detection in a single workflow, this approach reduces analytical time (fig.13).

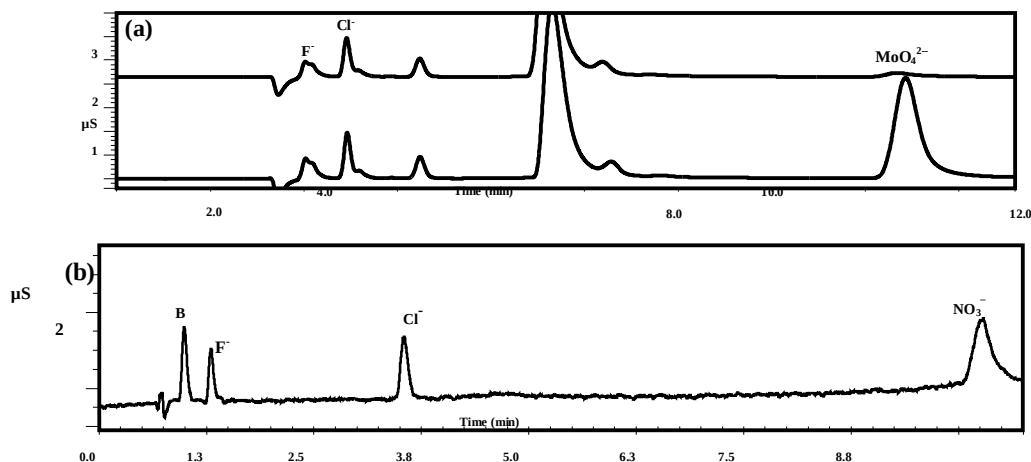


Fig.12: (a) chromatogram of pyrohydrolysis distillate of a real sample (2) Chromatogram of a standard anion mixture containing, fluoride (0.5ppm), chloride (1ppm) nitrate (1ppm) and molybdate (5 ppm). Eluent: 15mM NaOH, Flow Rate: 1ml/min. (b) Chromatogram of a standard anion mixture containing boron (1ppm), fluoride (0.5ppm), chloride (1ppm) and nitrate (5ppm), Eluent: 5mM NaOH + 0.56M d-mannitol, Flow Rate: 1ml/min.

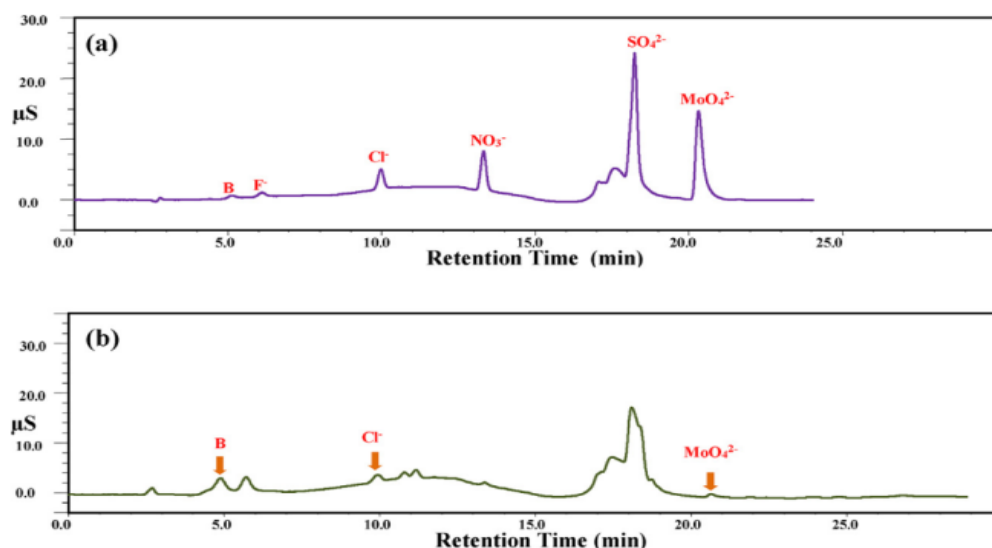


Fig.13. Chromatograms with the optimized gradient elution program for (a) a mixed anion standard containing B(1 g/mL), F⁻(0.5 g/mL), Cl⁻(1 g/mL), NO₃⁻ (4 g/mL), SO₄²⁻(10 g/mL) and MoO₄²⁻(30 g/mL) (b) pyrohydrolysis distillate of a root sample of rice plant.

Limitations and Challenges

Despite its numerous benefits, pyrohydrolysis is not without limitations:

- I. Sample throughput is relatively low (1-2 samples/hour)
- II. Temperature control is crucial - underdone samples yield low recovery
- III. Incomplete recovery of analyte in highly refractory matrices without proper accelerants
- IV. Condensation or backflow of gases if the gas path is not well-designed
- V. Operator training is needed for precise handling

However, many of these issues are being progressively addressed through proper modifications in design and methodologies.

Instrumental Constraints and Scalability

Traditional pyrohydrolysis setups rely on open furnace systems or quartz combustion tubes, requiring manual sample loading, precise temperature regulation, and controlled moisture flow. These setups are often labor-intensive and prone to operator-induced variability. Additionally, in nuclear installations, manual handling of high radioactive samples is impractical and unsafe. In addition depending upon the apparatus design there can be a restriction to the maximum amount of sample that can be analysed. To enhance the applicability of pyrohydrolysis, research

should focus on the following future directions:

• **Automation and Miniaturization:** Advancement in robotics and engineering to produce compact/scaled up, pyrohydrolysis units suitable for glovebox or field deployment.

• **Hybrid Analytical Coupling:** Integration of pyrohydrolysis with detection systems such as IC-MS (Ion Chromatography–Mass Spectrometry), ICP-MS, or fluorometric sensors to improve selectivity and sensitivity.

• **Computational Modeling:** Use of thermodynamic and kinetic simulation software to predict halide behavior, optimize reaction pathways, and design experiments more efficiently.

Conclusions

The analysis of halogens and other volatile non-metals in complex materials such as nuclear fuels, geological samples, and environmental samples is very important in analytical chemistry. These elements affect reactor safety, material performance, and our understanding of natural processes. Pyrohydrolysis is a useful and reliable method for the separation and determination of halogens, boron, and other volatile elements in different types of samples. Its main advantage is that it can

release these elements directly from solid samples using controlled heating, without using hazardous chemicals. This reduces the need to handle dangerous reagents and lowers waste generation. This is especially important in the nuclear field, where even trace levels of halogen impurities can compromise fuel integrity, accelerate cladding corrosion, and ultimately affect reactor safety. In environmental and geological studies, pyrohydrolysis combined with suitable detection methods helps in accurate measurement of halogens and boron in soils, sediments, and minerals. This supports studies on pollution, groundwater quality, and geochemical processes. Recent developments, such as the use of accelerator based methods, have improved the technique further. These advances allow better recovery of analytes from complex matrices that are otherwise difficult to analyze. Innovations in apparatus design and process optimization are expected to broaden its applicability to increasingly complex matrices. Thus, pyrohydrolysis remains an indispensable green separation method at the intersection of nuclear science, environmental studies, and analytical chemistry.

References

1. B. Joachim-Mrosko, T. Kawamoto, H. Bureau, *Elements* 18 (2022) 35–40.
2. WHO, Chloride in Drinking Water: Background Document for Development of WHO Guidelines for Drinking-Water Quality, World Health Organization, Geneva, 2003.
3. WHO, Inadequate or Excess Fluoride: A Major Public Health Concern, World Health Organization, Geneva, 2019.
4. F. M. Fordyce, Fluorine: human health risks, in: J. Nriagu (Ed.), *Encyclopedia of Environmental Health*, second ed., Elsevier, Oxford, 2019, pp. 41–50.
5. J. Feiteiro, M. Mariana, E. Cairr~ao, *Environ. Pollut.* 285 (2021) 117475–85.
6. F. G. Antes, F. A. Duarte, E. L. M. Flores, J. N. G. Paniz, E. M. M. Flores, V. L. Dressler, *Quim. Nova* 33 (2010) 1130–1134.
7. V. G. Mishra, S. Jeyakumar, *Open Access J Sci.* 2(6) (2018) 389–393.
8. RFP-601 C. IJ. Susano, J. C. White, and J. E. Lee, *Anal. Chem.*, 27 (1955) 453–454.
9. Gillies, G M, Report No. AERE-C/M-225, Oct. 1954.
10. Adams PB, Williams JP. *J Am Ceram Soc.* 41(9) (1958) 377–380.
11. M. A. Mahajan, M. V. R. Prasad, H. R. Mhatre, R. M. Sawant, R. K. Rastogi, G. H. Rizvi, N. K. Chaudhuri, *J. Radioanal. Nucl. Chem.* 148 (1991) 93–100.
12. Daiana Kaminski Oliveira, Cristian Rafael Andriolli, Thamires Rafaelle Silva, Vitoria Hagemann Cauduro, Eder Lisandro Moraes Flores, Rochele Sogari Picoloto, Erico Marlon Moraes Flores, *Talanta* 293 (2025) 128080–89.
13. Renan G. Marim, Diego Galvan, Daniel L.G. Borges, Eduardo S. Chaves, *Microchem. J.* 214 (2025) 114077–86.
14. B. Lopez-Ruiz, *J. Chromatogr. A.* 881 (2000) 607–627.
15. Mishra, V.G., Thakur, U.K., Shah, D.J. et al. *J Radioanal Nucl Chem.* 332 (2023) 15–22.
16. R Rickard, Francis Ball, W Harris, *Anal. Chem.* 23 (1951) 919–921.
17. J. C. Warf, W. D. Cline, R. D. Tevebaugh, *Anal. Chem.* 26 (1954) 342–346.
18. L. Morgan, *Analyst* 89 (1964) 621–623.
19. J. E. Lee, J. H. Edgerton, M. T. Kelley, *Anal. Chem.* 28 (1956) 1441–1443.
20. J. O. Hibbits, *Anal. Chem.*, 29 (1957) 1760–1762.
21. P. B. Adams, J. P. Williams, *J Am Ceram Soc.* 41(9) (1958) 377–380.
22. R. H. Powell, O. Menis, *Anal. Chem.* 30(9) (1958) 1546–1549.
23. A. R. Gahler, G. Porter, *Anal. Chem.*, 29 (1957) 296–298.
24. Budisa N., Kubyshkin V., Schulze-Makuch D. *Life (Basel).* 4(3) (2014) 374–385.
25. Kenneth T. K., Estelle F. R. C.R. *Chim.* 21(8) (2018) 749–756.
26. Carroll M. R., Webster J. D. *Rev. Mineral. Geochem.* 30 (1994) 231–279.
27. B. W. Yardley, *Econ. Geol.* 100 (2005) 613–632.
28. A. Aiuppa, D. R. Baker, J. D. Webster, *Chem. Geol.* 263 (2009) 1–18.
29. D. R. Baker, *Chem. Geol.* 263 (2009) 82–88.

30. J. D. Webster, C. M. Tappen, C. W. Mandeville, *Geochim. Cosmochim. Acta* 73 (2009) 559-581.
31. Keenan L. Evans, James G. Tarter, Carleton B. Moore, *Anal. Chem.* 53(6) (1981) 925-928.
32. N. F. Bernal, S. A. Gleeson, M. P. Chem. *Geol.* 451(20) (2017) 90-103.
33. M. Bonifacie, N. Jendrzewski, P. Agrinier, *Chem. Geol.* 24 (2007) 187-201.
34. S. Sekimoto, M. Ebihara, *Geostand Geoanal Res.* 41(2) (2017) 213-219.
35. S. Sekimoto, M. Ebihara, *Geostand Geoanal Res.*, 41(2) (2017) 213-219.
36. Kenji Shimizu, Takayuki Ushikubo, Morihisa Hamada, Shoichi Itoh, Yoshinori Higashi, Eiichi Takahashi, Motoo Ito, *Geochem. J.* 51 (2017) 299-313.
37. Uday Kumar Thakur, Vivekchandra Guruprasad Mishra, Raghunath Acharya, Subbiah Jeyakumar, *Sep. Sci. Technol.* (2025) 1-7.
38. F. G. Antes, F. A. Duarte, E. L. M. Flores, *Quimica Nova.* 33(5) (2010) 1130.
39. F. G. Antes, M.D.F.P. Dos Santos, R. C. Loureno Guimarães, *Anal Methods.* 3(2) (2011) 288-293.
40. D. Wua, H. Deng, W. Wang, *Anal Chim Act.* 601 (2003) 183-188.
41. B. Peng, D. Wu, J. Lai, *Fuel.* 94 (2002) 629-631.
42. I. Sredović, Lj. Rajaković, *J. Hazard Mater.* 177 (2009) 445-451.
43. T. Tanaka, S. Inoba, S. Kawada, *Bunseki Kagaku.* 59(2) (2010) 137-150.
44. L. Pagé, K. Hattori, J. C. M. Hoog, *Earth Planet Sci Lett.* 442 (2016) 133-142.
45. S. Dai, W. Li, Y. Tang, *Appl Geochem.* 22(5) (2007) 1017-1024.
46. F. A. Duarte, E. R. Pereira, E. L. M. Flores, *Quimica Nova.* 36(5) (2001) 716-719.
47. P. Bing-Xian, W. Dai-She, *J Anal Chem.* 41(10) (2013) 1499-1504.
48. M. A. W. Marks, T. Wenzel, M. J. Whitehouse, *Chem Geology.* 291 (2013) 241-255.
49. Yue Pan, *ACS Med. Chem. Lett.* 10 (2019) 1016-1019.
50. Kenneth L. Kirk, *J. Fluor. Chem.* 127 (2006) 1013-1029.
51. Bingxian Peng, Bingxian Peng, Xinrui Li, Jing Luo, Xing Yu, *Energ. Fuel.* 33 (2019) 9272-9279.
52. Eleonor Velez-León, Sebastián Machuca-Ordóñez, Emilia Guerrero-Coello, María Centeno-Dávila, Magaly Jiménez-Romero, Daniela Tobar-Almache, *J. Food Compos. Anal.* 145 (2025) 107753-67.
53. Eduardo da Silva Macedo, Bruno Luís Ferreira, Renan Guilherme Marim, Diego Galvan, Eduardo Sidinei Chaves, *Food Anal. Methods.* 18 (2025) 27-38.
54. Yoshinori Marunaka, *J Physiol Sci.* 73(1) (2023) 31-49.
55. Daiana Kaminski Oliveira, Cristian Rafael Andriolli, Thamires Rafaelle Silva, Vitoria Hagemann Cauduro, Eder Lisandro Moraes Flores, Rochele Sogari Picoloto, Erico Marlon Moraes Flores, *Talanta* 293 (2025) 128080-128089.
56. Gabriel Toneto Druzian, Mariele S. Nascimento, Rafael F. Santos, Erico M. M. Flores, *Talanta* 199 (2019) 124-130.
57. C. Fu, N. J. Shi, L. X. Feng, Y. Q. Cai, H. F. Wang, *Jiliang Xuebao Acta Metrologica Sinica*, 40(6) (2019) 1129-1134.
58. V. G. Mishra, S. K. Sali, D. J. Shah, U. K. Thakur, R. M. Sawant, B. S. Tomar, *Radiochim. Acta.* 102(10) (2014) 895-901.
59. V. G. Mishra, U. K. Thakur, D.J. Shah, A. Sengupta, S. Jeyakumar, M. K. Saxena, *J. Radioanal. Nucl. Chem.* 332(1) (2023) 15-22.
60. Ashish Pandey, Anoop Kelkar, R. K. Singhal, Chetan Baghra, Amrit Prakash, Mohd. Afzal, J. P. Panakkal, *J Radioanal Nucl Chem.* 293 (2012) 743-749.
61. ASTM C1502-09, Standard Test Method for Determination of Total Chlorine and Fluorine in Uranium Dioxide and Gadolinium Oxide.
62. V. R. Wiederkehr, G. W. Goward, *Anal. Chem.* 31 (1959) 2102-2103.
63. G. J. McKinley, H. F. Wendt, *Anal. Chem.* 37 (1965) 947-950.
64. L. Morgan, *Analyst* 89 (1964) 621-623.
65. Takayoshi Yoshimori, Tomoo Miwa, Tsugio Takeuchi, *Talanta* 11(7) (1964) 993-1001.

66. S. Jeyakumar, Vaibhavi V. Raut, K. L. Ramakumar, Talanta 76 (2008) 1246–1251.
67. Vivekchandra Guruprasad Mishra, Uday Kumar Thakur, Dipti Jayesh Shah, Mrinal Kanti Das, Subbiah Jeyakumar, Pentapati Sitaramanjaneyulu, Sep. Sci. Technol. 54(10) (2018) 1681–1686.
68. Raut, V.V., Jeyakumar, S., Shah, D.J. Shah, U. K. Thakur, B. S. Tomar, K. L. Ramakumar, Anal. Sci. 31 (2015) 219–223.
69. Vivekchandra G. Mishra, Uday K. Thakur, Dipti J. Shah, Neeraj K. Gupta, Subbiah Jeyakumar, Bhupendra S. Tomar, Karanam L. Ramakumar, Anal. Chem. 87 (2015) 10728–10733.
70. V. G. Mishra, U. K. Thakur, D. J. Shah, et al. J Radioanal Nucl Chem. 332 (2023) 15–22.
71. Vivekchandra Guruprasad Mishra, Mrinal Kanti Das, Dipti Jayesh Shah, Subbiah Jeyakumar, Bhupendra Singh Tomar, Karanam Lakshminarayana Ramakumar, J. Chromatogr. A. 1532 (2018) 144–149.

. ASSET Bulletin on "Advancement in Green Separation"



Dr. V. G. Mishra joined Radioanalytical Chemistry Division, Bhabha Atomic Research Centre in 2008 after graduating from 51st batch of BARC Training School. He is involved in development of CQC methods for various kinds of nuclear materials using pyrohydrolysis and ion chromatography. His research interest includes studies on separation of various species using ion chromatography and separation using pyrohydrolysis with a view to explore the mechanism involved during separation.



Dr. Subbiah Jeyakumar obtained his M.Sc. in Chemistry from Madurai Kamaraj University, Madurai. He obtained his PhD in analytical chemistry from the University of Mumbai. He joined the Fuel Chemistry Division of Bhabha Atomic Research Centre, Mumbai, in 1988. He started his career in the field of inorganic mass spectrometry and chemical quality control of nuclear fuels, particularly plutonium fuels for the Fast Reactor Program. He has more than 60 journal papers and more than 150 papers in several international/national conference and reports. He headed the Complex Chemistry Section of the Radioanalytical Chemistry Division from 2014 to 2024. Currently Dr. Jeyakumar is Heading the Radiochemistry Division of BARC. His field of research interest includes chemical characterization of nuclear fuels and reactor materials, HPLC, ion chromatography, pyrohydrolytic separations, capillary electrophoresis, radioanalytical techniques and inorganic mass spectrometry for geological investigations. Dr. Jeyakumar is a Professor of Homi Bhabha National Institute (HBNI). He is a peer reviewer of many international journals. Dr. Jeyakumar authored 3 book chapters. He is a member of several scientific bodies, viz., IANCAS, INS, and ISMAS, etc. He is the President of the Association of Separation Scientists and Technologists (ASSET). He was awarded Department of Atomic Energy Group Achievement Award in 2010 for his contribution to the FBTR program and in 2018 for the characterisation of high purity Gd-nitrate to be used in the Power reactors