

## Reprocessing of spent nuclear waste using ionic liquids

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**Abstract**—Nuclear power has once again attracted from all over the world due to many factors including the rise in oil process and environmental concerns on greenhouse gas emission resulting in global warming. However, spent fuel from nuclear power reactors is an enormous problem both from radiation hazard and economical point of view. Therefore, this review presents an overview of application of ionic liquids (ILs) in spent fuel reprocessing, particularly in the extraction of high-level radioactive aqueous waste from the processing of nuclear fuel.

Key words: Ionic Liquid, Spent Nuclear Waste, Extraction, Radioactive, Reprocessing

### INTRODUCTION

Due to the depletion of fossil fuels and environmental issues with the use of fossil fuels, nuclear power has attracted a renewed interest from all over the world. Nuclear energy is a cheap, environmental friendly and non-polluting energy source. Although energy from nuclear resources can be obtained through fission or fusion reactions, most power generators in use employ fission reaction. Fission involves the breaking of heavy nucleus after capture of neutron into fragments of smaller nuclei and neutrons with generation of a vast amount of energy. The heat generated from the fission reaction is used to heat water and generate steam for turbine operation and electrical power generation.

Commercial nuclear fuel is usually made up of Uranium (U). It is mined as an ore containing less than 0.5% of uranium oxide ( $U_3O_8$ ). Uranium from ores contains mainly 2 isotopes about 0.7%  $U^{235}$  and the remaining  $U^{238}$ . Most nuclear reactors cannot operate with the low concentration of  $U^{235}$  which is responsible for most of the fission reaction. Uranium oxide in the ore is extracted, purified and then converted to uranium hexafluoride ( $UF_6$ ). After conversion, a physical process such as diffusion or centrifugation is performed for enrichment of  $U^{235}$  to about 3.5% to 5%. The enriched  $UF_6$  is converted to  $UO_2$  and formed into small cylindrical pellets. The pellets are heated at high temperatures to form hard ceramic pellets, and then loaded to zirconium alloy or stainless steel to form fuel rods [1]. The fuel rods are fed to the reactors and bombarded with slow neutrons to start fission reactions. This then starts nuclear chain reaction wherein  $U^{235}$ , the readily fissionable material, releases more neutrons upon contact with free neutron. The other uranium isotope  $U^{238}$  is also able to capture neutrons but does not readily undergo fission upon contact with neutrons but instead is transformed into  $Pu^{239}$  after a neutron capture and 2 electron emissions.  $Pu^{239}$  on the other hand undergoes fission reaction upon capture of neutron and splits into fragments of lighter atoms and neutrons with generation of energy. The chain reaction continues for some time and stops

until nuclear fuel composition is unable to sustain further fission reactions. At the end of the cycle unreacted uranium (about 99% of the initial amount), fission products, and actinide elements are left in the reactor and collectively called as Spent Nuclear Fuel (SNF) [2].

The exact composition of SNF varies with the reactor used. Most nuclear reactors being used at present are light water reactors wherein unreacted uranium consisting of  $U^{235}$  and  $U^{238}$  accounts for about 95.6% of SNF with  $U^{235}$  approximately 1%. Fission products is divided into 3 subgroups, namely, the stable short lived fission products, major fission products composed of Cesium (Cs) and Strontium (Sr), and long-lived fission products primarily Iodine (I) and Technetium (Tc), constituting 3%, 0.3%, and 0.1% of SNF, respectively. Actinides, on the other hand, constitute about 1% of SNF having about 0.9% plutonium (Pu) and 0.1% Long-lived minor actinides primarily composed of Neptunium (Np), Americium (Am), and Curium (Cm) [3]. The products contained in SNF are radioactive with half-lives from days to millions of years which give a lot of threat to human health and environment. Therefore it is necessary to process SNF and keep it away from human and environment contact. Processing of SNF depends on the type of nuclear cycle being used for electrical energy generation. Nuclear fuel cycles available are the once through fuel option, reprocessing fuel cycle (RFC), and the advanced fuel cycle (AFC) [6]. In the once through fuel option, the short lived fission products in SNF is allowed to decay and cooled in ponds containing water where it stays for about 7-10 years to about 20 years. After such period of time the remaining radioactive materials are confined into smaller volume through immobilization of SNF into a vitrified glass. The vitrified glass form of SNF is then deposited into a geological repository and stored for a long time. Countries like US, Sweden, Spain, Canada, and Korea employ the once through fuel cycle [3]. RFC process option is essentially the same as the once throughput option but with the additional process for recovery of uranium and plutonium before making it into vitrified glass form and deposition into geological repository. AFC process option is an extension of RFC wherein not only uranium and plutonium are recovered but the other radioactive fission products as well. In AFC, long-term radio toxicity is reduced through

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partitioning and transmutation [3]. In the once through cycle, expensive handling and reprocessing of highly radioactive SNF is avoided but long term storage in large geologic repositories is necessary. Employing the RFC option allows recycle of recovered uranium and plutonium which in turn reduces use of fresh Uranium by about 30%.

Uranium and Plutonium are conventionally recovered through PUREX process. PUREX, an abbreviation for Plutonium (P) Uranium (UR) Extraction (EX), makes use of about 30% tri-*n*-butyl phosphate (TBP) with kerosene or pure *n*-dodecane as diluent [4]. In this process, uranium and plutonium are extracted as  $\text{UO}_2^{2+}$  and  $\text{Pu}^{4+}$  and then converted to  $\text{UO}_2$  and  $\text{PuO}_2$ . Aside from uranium and plutonium, various fission products can be recovered from SNF. Thus some extraction processes have been developed using different extracting agents to recover fission products from PUREX raffinate.  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  having half-lives of 30 and 29 years, respectively, account for significant radiation and heat load from SNF [5]. Strontium extraction (SREX) is achieved by using various extracting agents usually crown ethers which could either be dicyclohexyl-18-crown-6 (DCH18C6) or 4',4'(5')-di-(*t*-butyldicyclo-hexano)-18-crown-6 in 1-octanol [6,7]. Cesium extraction (CSEX) on the other hand is usually done with the use of Calix-arenes [8]. Calix[4]arene-bis-(*tert*-octylbenzo-crown-6) is the extracting agent usually being used with an iso-paraffinic solvent as a diluent [9,10]. TRUEX process, on the other hand, which makes use of octyl(phenyl)-N,N-dibutylcarbamoyl-methylphosphine oxide (CMPO) as extractant and alkanes as solvents or diluents, is the extraction of trans uranium elements (TRU's) especially the actinides and the rare earth elements along with the residual plutonium and uranium in the PUREX raffinate [3].

The extraction processes developed for SNF treatment and recovery utilize organic solvents that are volatile, hazardous, toxic, flammable, and unstable towards the radiation and heat generated by SNF [11,12]. Since the undesirable properties of these conventional solvents may pose several threats and problems both to plant operation and to environment, ionic liquids (ILs) are gaining recognition in nuclear reprocessing industry as possible candidates to replace conventional solvents. ILs are basically liquids composed entirely of ions. The interest for ILs stems from their potential as 'green solvents' because of their negligible vapor pressure, non-flammability and thermal stability which makes them attractive alternatives for volatile organic solvents [13]. In chemical processes, ILs exhibit excellent physical characteristics including the ability to dissolve polar and nonpolar organic, inorganic, and polymeric compounds. Moreover, the number of combinations of anions and cations encompassed by ILs is vast, and their associated synthetic flexibility has lead to ILs being referred to as 'designer solvents' [14]. In the past few years, ILs are being extensively explored for various (bio)catalytic reactions and separation processes [15-18]. Recently, ILs are receiving increasing attention for possible application in nuclear fuel cycle. This review, therefore, provides an overview of application of ILs in spent fuel reprocessing, particularly in the extraction of high-level radioactive aqueous waste from the processing of nuclear fuel.

## RECOVERY OF URANIUM

The PUREX process is the major method used for recovery of

uranium and plutonium from high-level waste (HLW) using TBP in kerosene or dodecane. The possibility of using ILs instead of kerosene for extraction of uranium has been investigated. A series of studies were conducted by Giridhar et al. for the extraction of uranium (U(VI)) from nitric acid ( $\text{HNO}_3$ ) solution using TBP and ILs as diluents with direct electrodeposition of uranium from ILs phase [19-25]. Using 1.1 M TBP in 1-butyl-3-methyl imidazolium hexafluorophosphate ( $[\text{Bmim}]\text{[PF}_6]$ ), distribution ratio for U(VI) ( $D_{\text{U(VI)}}$ ) increases with increase in  $\text{HNO}_3$  concentration having a range of 0.05-33.2 for  $\text{HNO}_3$  concentrations of 0.01 to 8 M.  $D_{\text{U(VI)}}$  values are comparable with those obtained with the use of dodecane as diluents from 0.01 to 4 M  $\text{HNO}_3$  but greater  $D_{\text{U(VI)}}$  with increase in  $\text{HNO}_3$  from 4 to 8 M, since  $D_{\text{U(VI)}}$  values for TBP-dodecane system decrease with increase in  $\text{HNO}_3$  concentration from 4 M to 8 M [19]. The use of 1.1 M TBP in 1-octyl-3-methyl imidazolium hexafluorophosphate ( $[\text{Omim}]\text{[PF}_6]$ ) yields a lower  $D_{\text{U(VI)}}$  having a range of 0 to 12 for 0 to 8 M  $\text{HNO}_3$  [20]. Having 1.1 M TBP in 1-butyl-3-methyl-imidazolium bis(trifluoromethanesulphonyl) imide ( $[\text{Bmim}]\text{[Tf}_2\text{N]}$ ) gives a lower  $D_{\text{U(VI)}}$  compared to those obtained with dodecane and  $[\text{Bmim}]\text{[PF}_6]$  as diluents. The highest value of  $D_{\text{U(VI)}}$  with use of 1.1 M TBP in  $[\text{Bmim}]\text{[Tf}_2\text{N]}$  is 19.7 at 0.01 M  $\text{HNO}_3$ .  $D_{\text{U(VI)}}$  values as a function of  $\text{HNO}_3$  concentration for TBP in  $[\text{Bmim}]\text{[Tf}_2\text{N]}$  does not follow the trend observed with dodecane,  $[\text{Bmim}]\text{[PF}_6]$ , and  $[\text{Omim}]\text{[PF}_6]$  as diluents. In the TBP- $[\text{Bmim}]\text{[Tf}_2\text{N}]$  system,  $D_{\text{U(VI)}}$  decreases from 0.01 to 1 M  $\text{HNO}_3$  and then increases from 1 to 8 M  $\text{HNO}_3$ . Reduction of U(VI) in  $[\text{Bmim}]\text{[Tf}_2\text{N}]$  at -2.1 V (vs. Pd) under controlled potential electrolysis undergoes a single step two electron transfer at the working electrode producing an amorphous uranium oxide (O/M ratio=2.3) [21]. Electrochemical reduction of U(VI) in 1-butyl-3-methylimidazolium chloride ( $[\text{Bmim}]\text{[Cl]}$ ) to U(IV) at a glassy carbon working electrode forms  $\text{UO}_2$  deposit through an irreversible single step two electron transfer with nearly 5%  $[\text{Bmim}]\text{[Cl]}$  entrapped. Diffusion coefficient and activation energy of U(IV) in  $[\text{Bmim}]\text{[Cl]}$  are  $\sim 10^{-8}$   $\text{cm}^2/\text{s}$  and 54 kJ/mol respectively, in the temperature range of 343-373 K [22]. Ouadi et al., on the other hand, synthesized a class of functional hydrophobic ILs based on quaternary ammonium cation bearing phosphoryl moieties [23]. By using synthesized IL (1.1 M) in tri-*n*-butylmethyl ammonium bis(trifluoromethanesulphonyl) ( $[\text{Me}_3\text{NBu}]\text{[Tf}_2\text{N}]$ ), a remarkable distribution ratio for U(VI) ( $D_{\text{U(VI)}}$  value of 170) was obtained. The mode of partitioning of uranyl ion between various TBP-containing *N,N*-dialkyl-imidazolium-based ILs and nitrate-containing aqueous phase was shown to change from an ion exchange process to extraction of neutral uranyl-TBP-nitrate complex as the aqueous nitrate concentration or hydrophobicity of IL cation is increased [24].

## RECOVERY OF CESIUM AND STRONTIUM

Fission products,  $^{90}\text{Sr}$  ( $t_{1/2}$ =30.1 years) and  $^{137}\text{Cs}$  ( $t_{1/2}$ =28.5 years), are the major sources of radioactivity and heat in nuclear wastes. Their removal prior to further separation greatly simplifies subsequent waste handling and storage [3]. The liquid-liquid extraction of  $^{137}\text{Cs}^{+}$  and  $^{90}\text{Sr}^{2+}$  from aqueous tank waste into hydrophobic organic solvents like 1,2-dichloroethane, dichloromethane, toluene, xylene, with various ionophores such as macrocyclic ligands have been studied extensively. However, the high vapor pressure, flammable, and toxic nature of such solvents pose some problems. As a result, hy-

drophobic ILs have been investigated as substitutes for the organic solvents normally used in this application [25].

Recovery of  $\text{Sr}(\text{NO}_3)_2$  from aqueous phase at initial pH of 4.10 using 0.15 M dicyclohexyl-18-crown-6 (DCH18C6) yields  $D_{\text{Sr}}$  of values greater than 1 for DCH18C6 in ILs and less than 1 for DCH18C6 in conventional organic solvents [26]. The  $D_{\text{Sr}}$  values range from 4.2 to  $5.4 \times 10^3$  for DCH18C6 in 1-butyl-2,3-dimethylimidazolium hexafluorophosphate ( $[\text{BuMe}_2\text{Im}][\text{PF}_6]$ ) and 1-propyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ( $[\text{PrMeIm}][\text{Tf}_2\text{N}]$ ), respectively. Aside from DCH18C6, crown ethers like 18-crown-6 (18C6) and 4,4'-(5')-di-(*tert*-butylcyclohexano)-18-crown-6 (Dtb18C6) in 1-alkyl-3-methylimidazolium hexafluorophosphate ( $[\text{C}_n\text{mim}][\text{PF}_6]$ ,  $n=4, 6, 8$ ) were also used to extract not only  $\text{Sr}^{2+}$  but also  $\text{Na}^+$  and  $\text{Cs}^+$  ions [27]. Highest distribution ratios for the metal ions were attained with use of Dtb18C6 in  $[\text{C}_4\text{mim}][\text{PF}_6]$  with  $\text{Sr}^{2+}$  having highest distribution while  $\text{Na}^+$  the lowest. Distribution ratios of the metal ions decreased with increase in  $\text{HNO}_3$  concentration from 0.001 M to 1 M, but increased from 1 M onwards. It is to be taken note that IL anion  $\text{PF}_6^-$  decomposes and IL solubility in water increases at high  $\text{HNO}_3$  concentration. The mechanism of facilitated  $\text{Sr}^{2+}$  ion transfer from the aqueous phase into ILs phase varies which depends on ILs used. The predominant mode of  $\text{Sr}^{2+}$  transfer from  $\text{HNO}_3$  media shifts from cation exchange to strontium nitrate ether complex partitioning as the hydrophobicity of IL cation is increased [28]. It has been demonstrated with the use of DCH18C6 in 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]-imides with the alkyl group being *n*-pentyl, *n*-hexyl, *n*-octyl, or *n*-decane. After extraction the concentration of  $\text{Sr}^{2+}$  is much greater compared to that of the  $\text{NO}_3^-$  in IL phase when the alkyl group of IL cation is *n*-pentyl. The difference in concentrations of  $\text{Sr}^{2+}$  and  $\text{NO}_3^-$  in ILs decrease as the IL cation alkyl group increases, with it being equal when the alkyl group is *n*-decyl. This result is also supported by the findings based on the effect of  $\text{HNO}_3$  concentration on  $D_{\text{Sr}}$  value. The  $D_{\text{Sr}}$  value is relatively large at low  $\text{HNO}_3$  when the alkyl group is *n*-pentyl but decrease as  $\text{HNO}_3$  concentration increase. It increases with increase in  $\text{HNO}_3$  concentration for *n*-decyl as alkyl group.

The extraction of  $\text{Cs}^+$  from aqueous solutions using Calix[4]arene-bis(*tert*-octylbenzo-crown-6) (BOBCalixC6) in 1-alkyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ( $[\text{C}_n\text{mim}][\text{Tf}_2\text{N}]$ ,  $n=2, 3, 4, 6$  or 8) has been investigated by Luo et al. [29-31]. Distribution ratio of  $\text{Cs}^+$  ( $D_{\text{Cs}}$ ) increases with increase in BOBCalixC6 concentration but decrease with the increase of alkyl chain length. Using different counter anions has no significant effect on  $D_{\text{Cs}}$ . The selectivity of BOBCalixC6 in ILs is for  $\text{Cs}^+$  far greater compared to  $\text{Sr}^{2+}$  and higher compared to  $\text{K}^+$ . Presence of a sacrificial cationic exchanger sodium tetraphenylborate ( $\text{NaBPh}_4$ ) reduces IL cation exchange with aqueous media by 24% [29]. A number of monoaza substituted crown ethers and task specific ionic liquids (TSILs) bearing an aza-crown ether fragment were synthesized for the extraction of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  [30,31]. Among the monoaza substituted crown ethers the highest  $D_{\text{Sr}}^{2+}$  was obtained with the use of *N*-octylaza-18-crown-6 (0.1 M) in  $[\text{C}_2\text{mim}][\text{Tf}_2\text{N}]$  but slightly lower when compared with use of 0.1 M DCH18C6 in the same IL. The TSILs yield lesser  $D_{\text{Sr}}$  and  $D_{\text{Cs}}$  compared to those obtained with the use of DCH18C6 and *N*-octylaza-18-crown-6. Extraction of  $\text{Sr}^{2+}$  using the synthesized crown ethers shows a great preference in ILs containing a cation with a less hydrophobic alkyl group. Reuse of monoaza substituted

crown ethers in ILs has no significant change in extraction efficiencies. More than 90% recovery of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  can be achieved by stripping. Crown ethers DCH18C6 and BOBCalixC6 were also used in tri-*n*-butylmethylammonium bis[(trifluoromethyl)sulfonyl]imide ( $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ ) for extraction and direct electro-deposition of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$ , respectively [25,32]. The crown ethers in  $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$  showed a great ability in extracting  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  from aqueous phase with or without a small amount of toluene in IL phase. Electrochemical reduction of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  from crown ethers in  $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$  into a mercury pool electrode is achieved with columbic efficiency of 70 and 90% for the respective ions. Pretreatment of aqueous phase by anion exchange of  $\text{NO}_3^-$  to  $\text{Cl}^-$  was done before extraction of  $\text{Cs}^+$  and  $\text{Sr}^{2+}$  into crown ether in  $[\text{Bu}_3\text{MeN}][\text{Tf}_2\text{N}]$ . Pretreatment of aqueous phase along with removal of oxygen and water were done to eliminate interference of those species in the electrochemical reduction of  $\text{Sr}^{2+}$  and  $\text{Cs}^+$  directly from IL.

## RECOVERY OF ACTINIDES AND LANTHANIDES

Lanthanides are being used as catalysts, phosphors, coloring for glass and ceramics and many more. Due to their radioactive nature, actinides on the other hand have found their place in nuclear fuel generation and cancer treatment. SNF contains small amounts of actinides and lanthanides with actinides posing much of long term problem since it takes about  $10^5$  years to reduce about 99.99% of them. Transmutation, on the other hand, is projected to cause the same reduction for only about 500 to 700 years [3]. Before attaining that, however, separation of actinides from SNF especially from lanthanides has to be achieved. Liquid-liquid extraction of actinides have been tested with use of extracting agents like 2, 6-di(5,6-dipropyl-1,2,4-triazine-3-yl)pyridine (*n*-Pr-BTP) and aromatic dithiophosphonic acids contained in organic solvents like toluene, xylene, and butanol [33,34]. Since most of the diluents used are volatile and flammable, the use of ILs as diluents or as the extracting agent itself have been investigated and presented below.

The IL  $[\text{Bmim}][\text{PF}_6]$  has been used to contain 1 M TBP and 0.1 M octyl(phenyl)-*N,N*-diisobutylcarbamoylmethyl phosphine oxide (CMPO) for extraction of Plutonium ( $\text{Pu}^{4+}$ ), Thorium ( $\text{Th}^{4+}$ ), Americium ( $\text{Am}^{3+}$ ), and Uranium ( $\text{UO}_2^{2+}$ ) ions giving a higher distribution ratio compared to dodecane containing TBP and CMPO [35]. An identical extraction behavior in partitioning and coordination complexes of metal ions  $\text{UO}_2^{2+}$ ,  $\text{Am}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Eu}^{3+}$  is observed using extractant Cyanex-272 in dodecane and 1-decyl-3-methylimidazolium bis(trifluoromethyl sulfonyl) imide ( $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$ ). Having Cyanex-272 in  $[\text{C}_{10}\text{mim}][\text{Tf}_2\text{N}]$  generally gives a larger distribution ratio.

Pure  $[\text{Omim}][\text{PF}_6]$  has been successfully employed for separation of cerium (IV) from  $\text{HNO}_3$  solutions containing  $\text{Th}^{4+}$ , and lanthanides (III) with a D value of greater than 80 at 4 M  $\text{HNO}_3$ . More than 98% of extracted cerium (IV) can be recovered by stripping with use of 1 mL of  $\text{H}_2\text{O}$ , 0.02 M aqueous  $\text{K}_2\text{PF}_6$ , or 1%  $\text{H}_2\text{O}_2$ -0.1 M  $\text{HNO}_3$  in  $\text{H}_2\text{O}$  per 5 mL of  $[\text{Omim}][\text{PF}_6]$  [36]. Extraction of lanthanide ions ( $\text{Y}^{3+}$ ,  $\text{Eu}^{3+}$ ,  $\text{Ce}^{3+}$  and  $\text{La}^{3+}$ ) from acid solutions is not enhanced by organophosphorous PC-88A in  $[\text{Omim}][\text{Tf}_2\text{N}]$  and  $[\text{C}_{12}\text{mim}][\text{Tf}_2\text{N}]$  compared to PC-88A in dodecane. However the extraction mechanisms are the same for the two classes of solvents. Selectivity of extraction of the lanthanide ions by PC-88A in ILs are compara-

ble to those obtained with the use of PC-88A in dodecane wherein the order is  $\text{La}^{3+} > \text{Ce}^{3+} > \text{Eu}^{3+} > \text{Y}^{3+}$ . Quantitative stripping of the lanthanide cation using 0.5 M  $\text{HNO}_3$  is achieved in  $[\text{C}_{12}\text{mim}][\text{Tf}_2\text{N}]$ , but not in  $[\text{Omim}][\text{Tf}_2\text{N}]$  [37]. Extraction behavior of lanthanides using *N,N,N,N*-tetra(*n*-octyl)diglycolamide (TOGDA) in  $[\text{Bmim}][\text{Tf}_2\text{N}]$  is different compared to using TOGDA in iso-octane. At low  $\text{HNO}_3$  concentrations, extractability of lanthanides is high for TOGDA in ILs but for the iso-octane system higher extractability is achieved at high  $\text{HNO}_3$  concentrations. The IL system requires lesser amount of TOGDA to achieve the same extractability for lanthanides in the iso-octane system. The transfer of lanthanides with TOGDA into ILs proceeds via a cation-exchange mechanism, in contrast to ion pair extraction in the iso-octane system. TOGDA provides selectivity for the middle lanthanides in ILs systems, but heavier lanthanides in the iso-octane system [38].

Electrochemical studies for lanthanides (Sm, Yb, Tm, and Eu) and actinides (Np and U) in  $\text{AlCl}_3$ -*1-n*-butylpyridinium chloride melts have been reported. Reversible reduction of trivalent Yb, Sm, Eu, and Tm to divalent states was observed in very acidic melts and precipitation of the lanthanide cations at basic melts [39,40]. The  $E_{1/2}$  potentials of these lanthanide cations were reported to be +1.230, +0.660, +0.020, and +1.855 V for Yb, Sm, Tm, and Eu, respectively (at Al electrode in a melt containing 57% mol  $\text{AlCl}_3$ ). Electrochemical study of uranium in acidic  $\text{AlCl}_3$ -*N*-(*n*-butyl)pyridinium chloride reveals an irreversible reduction of U(IV) to U(III) on a glassy carbon electrode in a 2 : 1 melt. An irreversible oxidation of U(IV) to U(V) is observed to be strongly dependent on the melt acidity. Trivalent uranium (U(III)) existed as  $\text{U}^{3+}$  while U(IV) as chloro-complexes [41]. Electrochemical study of Neptunium in  $\text{AlCl}_3$ -*1-n*-butylpyridinium chloride melts reported a quasi-reversible reduction of Np(IV) to Np(III) at glassy carbon electrode both in acidic and basic melts with the acidic melt being a very weak solvating medium [42]. The electrochemical behavior of Sm, Eu, and Yb in  $[\text{Tf}_2\text{N}]$  based ILs combined in either 1-ethyl-3-methylimidazolium or 1-*n*-butyl-1-methylpyrrolidinium shows a quasi-irreversible or irreversible reduction of Sm(III), Eu(III), and Yb(III) to Sm(II), Eu(II), and Yb(II) at -1.6, -0.3, and -1.0 V, respectively. The diffusion coefficients for these lanthanides were estimated to be  $10^{-8} \text{ cm}^2/\text{s}$  [43].

## STABILITY OF IONIC LIQUIDS

The ability of a liquid to contain radioactive materials and to take radiation from the nuclear waste materials has to be taken into account when dealing with nuclear wastes. These concerns on ILs have been considered and studied by various research groups [44-52]. The ability to contain a radioactive material especially plutonium has been measured through calculation of the critical mass of plutonium in two ILs,  $[\text{Emim}][\text{AlCl}_3]$  and  $[\text{Emim}][\text{BF}_4]$ . The critical concentrations calculated for Pu in  $[\text{Emim}][\text{AlCl}_3]$  and  $[\text{Emim}][\text{BF}_4]$  are 150 and 1,000 g/L respectively which are an order higher compared to those obtained with an aqueous system [44]. Some 1,3-dialkylimidazolium based ILs containing nitrate and chloride anion, were subjected to 400 kGy dose of gamma radiation. Radiolysis of ILs were less than 1% which is relatively stable compared to the TBP-kerosene mixture which undergoes up to 15% radiolysis under the same conditions. Although darkening of ILs

occurred, no insoluble product was observed [45]. Two 1-butyl-3-methyl imidazolium based ILs namely  $[\text{Bmim}][\text{PF}_6]$  and  $[\text{Bmim}][\text{Tf}_2\text{N}]$  were studied with gamma radiolysis under argon or air atmosphere. At 600 kGy of gamma radiation dose, darkening was observed in ILs but there was no change in its physical properties except for the increase in viscosity. At a gamma radiation dose exceeding 1,200 kGy, IL radiolysis was below 1 mol% yielding the radicals  $\text{Bu}^\cdot$ ,  $\text{H}^\cdot$ ,  $\text{F}^\cdot$ , and  $\text{CF}_3^\cdot$  [46]. IL  $[\text{MeBu}_3\text{N}][\text{Tf}_2\text{N}]$  has been subjected to a  $^{137}\text{Cs}$  gamma irradiation dose of 2 MGy dry or after contact with water under argon or air atmosphere. ILs was highly stable regardless of the conditions having a radiolytic disappearance of 0.38 and 0.25  $\mu\text{mol}/\text{J}$  for the cation and anion respectively, producing radicals mainly composed of  $\text{Bu}^\cdot$ ,  $\text{Me}^\cdot$ ,  $\text{H}^\cdot$ ,  $\text{F}^\cdot$ , and  $\text{CF}_3^\cdot$  [47]. In a series of studies,  $[\text{Bmim}][\text{BF}_4]$  and  $[\text{Bmim}][\text{PF}_6]$  were placed under gamma radiation upto 100 kGy [48,49]. Darkening of  $[\text{Bmim}][\text{BF}_4]$  was observed while the viscosity of  $[\text{Bmim}][\text{PF}_6]$  decreased by up to 10%. Exposure to 550 kGy dose of radiation causes the darkening of  $[\text{Bmim}][\text{PF}_6]$  and  $[\text{Bmim}][\text{Tf}_2\text{N}]$  [50,51]. Darkening of ILs could be suppressed by incorporation of a small amount of either  $\text{KMnO}_4$  or  $\text{HNO}_3$ . The presence of  $\text{HNO}_3$  in  $[\text{Bmim}][\text{PF}_6]$  slightly accelerates radiolysis of ILs. The amount of non-volatile radiolysis products for both ILs does not exceed 1%. Another way to test stability of ILs with radiation is by the amount of  $\text{H}_2$  that is produced. Electron beam irradiation at 2.8 MeV was given to 1-hexyl-3-methylimidazolium, 1-hexyl-4-(dimethyl-amino)pyridinium, 1-butyl-1-methylpyrrolidinium, triethylammonium, or trioctyl(tetradecyl) phosphonium cations associated with bis(trifluoromethylsulfonyl)imide anion. The generated  $\text{H}_2$  range from  $2.6 \times 10^{-8} \text{ mol}/\text{J}$  for the imidazolium based ILs to  $2.5 \times 10^{-7} \text{ mol}/\text{J}$  for the phosphonium base ILs. These results are comparable to those obtained with studies of non-ionic aliphatic and aromatic organic compounds [52].

## CONCLUSIONS AND OUTLOOK

The treatment of nuclear waste is an interesting field of application for ILs. The use of their wide electrochemical window by extraction and direct electrodeposition is a very promising process and could potentially reduce the number of steps of the nuclear waste treatment. However, there are some issues that should be taken note of like the extraction efficiency, mode of extraction, stability, actual performance, and cost of ILs. The efficiency of extraction with the use of ILs as solvents is comparable and at times greater than with the use of organic solvents. This makes ILs more advantageous to use due to its non-flammable and non-volatile nature. Since the extracted metal ion can be electrochemically deposited directly from the IL, the stripping process is eliminated. TSILs could also play an important role in extraction efficiency wherein, new ILs can be synthesized with high efficiency and selectivity for a specific nuclear waste component. Some studies revealed that the mode of extraction using ILs involves cation exchange between IL cation and the metal ion which could mean loss of ILs. Though this phenomenon is not observed in more hydrophobic type of ILs, it somehow limits the choice of ILs. Interplay with the electrochemical window, hydrophobicity, and extraction efficiency of an IL would be crucial for the selection of proper IL. Stability of ILs seems not to be much of a problem, since it has been shown that ILs are relatively stable under radioactive environment. Actual performance with spent nu-

clear fuel is very important. Most of the studies regarding use of ILs in nuclear waste treatment deal with single component extraction and direct electro-deposition. It would be interesting to test the performance of ILs in the separation of a certain component from the actual nuclear waste or a solution made up with a similar characteristics and composition of actual waste and use ILs for extraction of all the valuables in an integrated process. One of the major hindrances of applying ILs in nuclear waste treatment would be its cost and impact on the overall economics of the recovery processes. However, since ILs are not volatile and do not undergo much radiolysis, ILs could negate the effect of the cost of ILs in the overall economics. High viscosities of ILs could also contribute to increase the cost of integrating ILs in nuclear waste treatment. However, there are  $10^{18}$  possible combinations to circumvent this problem. Even with the advantages provided by ILs, further studies are still needed to realize the role of ILs in nuclear waste treatment like in the recovery of PGMs where in only a few reports have been cited.

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