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CHEMISTRY OF NUCLEAR FUEL REPROCESSING: CURRENT STATUS

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Current status on the chemical aspects of nuclear fuel reprocessing is presented with special emphasis on the Purex process which continues to be the process of choice for the last four decades. Better decontamination from fission products, new methods for uranium-plutonium partitioning and removal of actinides from high active waste are challenging areas in process chemistry. The development work on TRUEX and DIAMEX processes for treating high active waste is briefly described. An overview of pyrochemical processes, which are important for Integral Fast Reactor Concept, is presented.

In all nuclear reactors plutonium is produced due to neutron capture by fertile ^{238}U. About 30 kg of fissile plutonium is produced in a Pressurised Water Reactor (PWR) while it generates 1 TWh of electricity. In the initial phases of power generation ^{239}Pu is the main isotope of plutonium but the isotopic composition changes as a function of burn up of the fuel and the spent fuel after a burn up of about 33,000 MWD/te has ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu isotopes (1.8, 57.8, 22.6, 12.2, 5.6%). Long term usage of nuclear energy implies recycling of this plutonium, preferably in fast reactors, so that the energy potential of uranium, which is almost 40 times the energy potential of oil reserves, is fully exploited. The spent fuel contains 2–6 kg of plutonium per tonne of the fuel. Spent fuel reprocessing helps in the isolation of plutonium and unused uranium, from highly radioactive fission products, and their recycle for nuclear power production. Fuel reprocessing also enables proper management of the radioactive waste. During 1993, 430 reactors, with an installed capacity of 337,800 MWe, supplied 2090 TWh of electricity.[1] About 60 te of plutonium was produced concurrently with power generation in 1993. Bulk of this plutonium is not isolated because a number of countries are exploring the possibility of direct disposal of spent fuel as a waste,

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though it has significant energy potential in the form of plutonium and uranium. Nevertheless, many countries are reprocessing the spent fuel and the inventory of plutonium separated from power reactor spent fuel is estimated to be about 100 te in 1994.[2] In addition, a large tonnage of spent fuel, from weapon grade plutonium producing reactors, has been reprocessed to isolate more than 200 te of plutonium for weapons programmes.[3] It is thus seen that several thousand tonnes of spent fuel have been reprocessed to isolate plutonium and more would be treated in future. The science and technology of spent fuel reprocessing started way back in 1944 and has been continuously evolving in the last 50 years. A major credit for the success of reprocessing must go to the Oak Ridge National Laboratory and the Knolls Atomic Power Laboratory who pioneered the development of Purex process, the workhorse of the reprocessing industry today. Before delving into the recent developments in spent fuel reprocessing it may be useful to briefly recapitulate the historical developments. The article also carries a brief account of the pyrochemical reprocessing which has assumed importance in the context of conceptual metallic fuelled fast reactors. The chemistry of fuel reprocessing is covered in a vast literature including books, journal publications and proceedings of several conferences devoted to this subject. In view of the limitation on the size of the article, the references cited mainly include some review articles and recently published literature.

Historical aspects

Separation of uranium and plutonium, from a large number of fission product elements, is primarily based on complexing and redox properties of these actinides. Distribution methods based on precipitation, solvent extraction and ion exchange have been explored and successfully exploited for fuel reprocessing.

Bismuth Phosphate Process was the first to enable large scale separation of plutonium and a plant at Hanford, USA used this process during 1945 to 1951. The process, designed for the recovery of plutonium only, was based on the fact that $BiPO_4$ precipitate selectively carries Pu(IV) and not Pu(VI) or U(VI). Repeated precipitation and dissolution were used to obtain the desired purity of plutonium product.[4]

Based on the known use of diethyl ether for the purification of uranium, processes based on ethers and ketones were investigated for fuel reprocessing. Dibutyl ether of diethylene glycol (Butex, $C_4H_9\text{-}O\text{-}C_2H_4\text{-}OC_2H_4\text{-}OC_4H_9$) was selected as the solvent by the British and the process was called Butex process.[5,6] It is based on selective extraction of U(VI) and Pu(IV) from 3 M nitric acid solution.

Ferrous sulphamate was used to partition uranium and plutonium. The process was used at Windscale, UK from 1952 to 1970.

Hanford switched over to a solvent extraction process in 1951. Methyl isobutylketone (Hexone, $CH_3COCH_2CH(CH_3)_2$) was the reagent used for the Redox process employed at this site. The process is based on the selective extraction of U(VI) and Pu(VI) from a feed solution having 0.3 M HNO_3+0.1 M $Na_2Cr_2O_7$ into Hexone with 1.3 M $Al(NO_3)_3$ scrub.[7,8] Uranium-plutonium were partitioned by using ferrous sulphamate and purified further by Hexone extraction.

The performance and limitations of these processes, which were subsequently replaced by the Purex process, have been reviewed by many authors.[9-11] The Purex process opened its innings at Savannah River, USA in 1954 and has been in continuous use ever since.[12,13] A large R&D effort is devoted to improvements in the Purex process and to develop alternate extractants.

Purex process

The acronym PUREX was given by Lanham and Runion for Plutonium, Uranium, Reduction Extraction.[14] The process aims at nearly complete recovery of uranium and plutonium with fission product decontamination factors in the range of 10^6–10^8. All countries which have produced significant quantities of plutonium have used the Purex process.[15-19] The process has some similarity to Butex and Redox processes. Tri-n-butyl phosphate (TBP) dissolved in a hydrocarbon diluent is used as the extraction medium in place of Hexone or Butex. In view of the large scale application of the process in nuclear industry a multi-volume monograph entitled "The Science and Technology of Tributyl Phosphate" has been published by CRC press. Volume III is devoted to nuclear fuel reprocessing.[20] The process generally has two product streams and three waste streams: Product streams are uranium nitrate solution and plutonium nitrate solution and the waste streams are classified as high active, intermediate active and low active according to the levels of radioactivity. Basic features of the reprocessing of spent oxide fuels are similar. The process steps include:

(I) Head end treatment involving chopping of fuel pins, dissolution of fuel pellets in nitric acid, feed clarification and adjustment of chemical conditions of the solution for solvent extraction.

(ii) Codecontamination involving extraction of U(VI) and of Pu(IV) in 20–30% TBP leaving bulk of the fission products in aqueous phase which goes as high active waste.

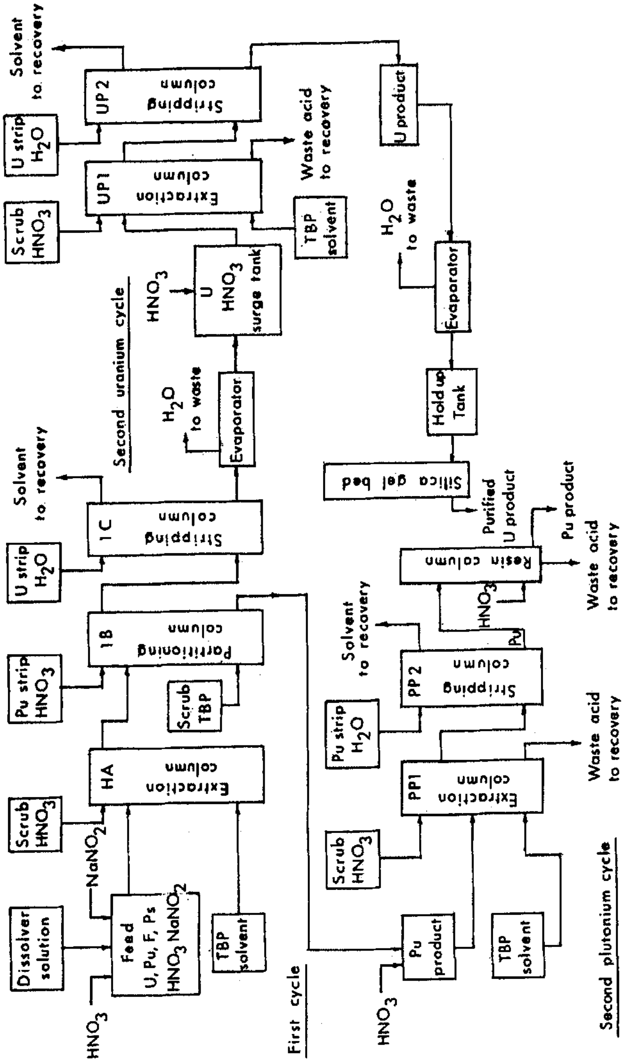

Fig. 1. Purex Process Flowsheet[10]

(iii) Washing/scrubbing of the organic stream with nitric acid, sometimes using two nitric acid scrubs of different HNO_3 concentration, to backwash some fission products co-extracted with uranium and plutonium.

(iv) Partitioning of uranium and plutonium by selective reduction of Pu(IV) in the organic phase to Pu(III) which reports to the aqueous phase, and back extraction of U(VI) with dilute nitric acid.

(v) Further treatment of uranium and plutonium in the aqueous streams to obtain U and Pu products of desired purity.

(vi) Treating the used solvent for its recycle.

The evolution of the Purex process flowsheet is described by COLEMAN and LEUZE.[21] Flowsheets of a number of reprocessing plants have been reviewed by SWANSON.[22] A typical flowsheet is given in Fig. 1.[10] The flowsheet shows an ion-exchange purification step for plutonium which is not present in many plants. Chemical aspects of various process steps are continuously under development to:

(I) improve recoveries of uranium and plutonium and the decontamination factors.

(ii) reduce waste generated.

(iii) simplify process e.g. reduce number of cycles

(iv) remove long-lived actinides and fission products from high level waste to minimize hazards of its long term storage.

(v) develop alternate processes.

Laboratory basic chemistry studies and development work using active facilities are very important in this technology. This aspect is highlighted by the recent work, reported by DENNIS and PHILLIPS, carried out for THORP which has allowed a flowsheet to be adopted using only three instead of usual five, solvent extraction cycles.[23] This has considerably reduced the size, complexity and cost of the plant as well as the number of waste streams requiring treatment. THORP has started treating spent fuel from January, 1995.[24] Some recent developments in various process steps are discussed below.

Fuel dissolution and feed adjustment

Fuel rods/bundles are mechanically chopped into small pieces and taken to a dissolver (continous or batch type) for treatment with hot 8–10 M HNO_3. Air is sparged to reduce the evolution of NO/NO_2 gas and have fumeless dissolution.[25] Essentially all fuel constituents, U, Pu, other actinides and fission products are dissolved leaving behind the zircaloy/stainless steel clad which is disposed off as high active solid waste. A small amount of fine residue is always left behind and it mainly consists of small particles of noble metal (Ru, Rh, Pd, Tc, Mo) alloy containing small amounts of plutonium, complex fission product oxide particles and

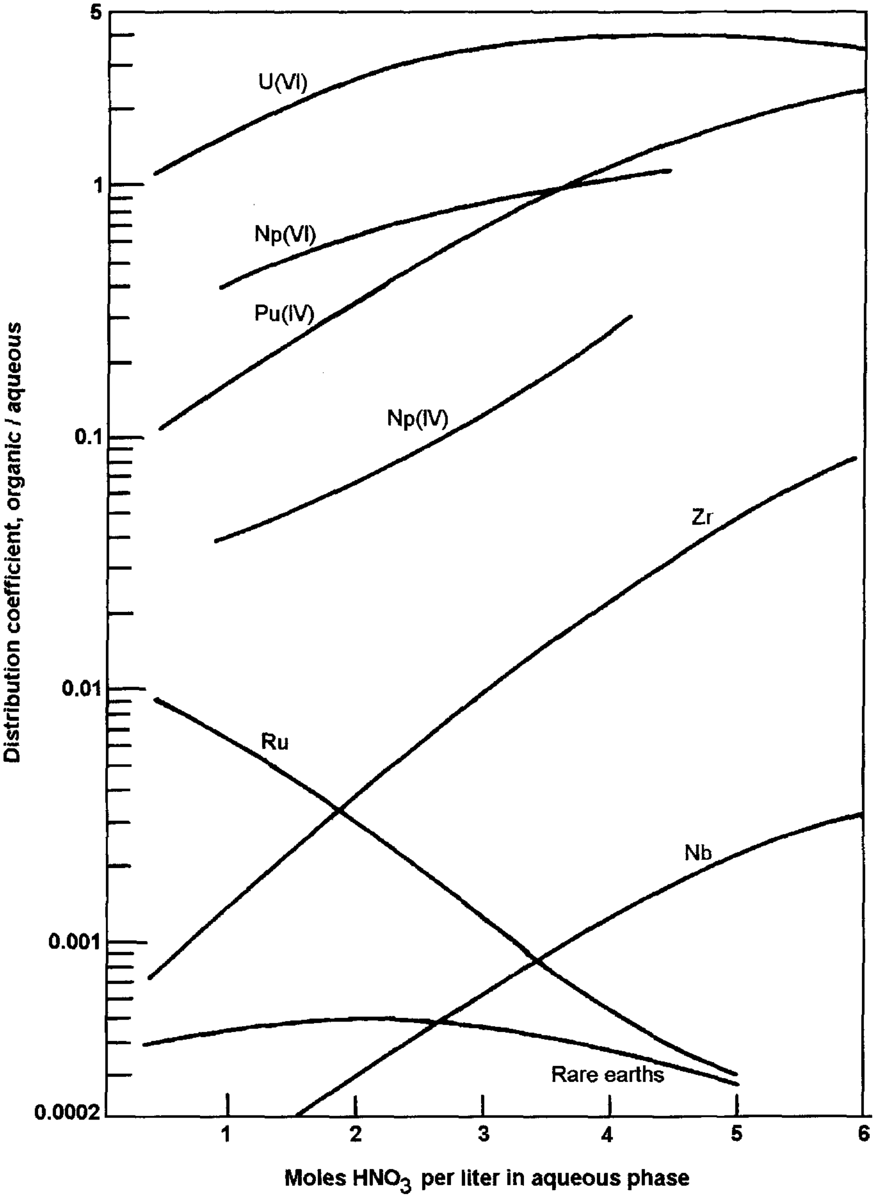

Fig. 2. Effect of nitric acid concentration on distribution ratio in 30 v/o TBP 80 percent saturated with uranium (~100g/l) at 25 °C.[25] *Unpublished data from authors' laboratory

impurities.[26,27] In the reprocessing of FBR fuels, the fine residue contained upto 0.74% of the total plutonium.[19] This residue is separated from the solution by using a high speed centrifuge.

The dissolver solution is adjusted to have HNO_3 concentration of 2-3 M and plutonium as Pu(IV). Bulk of the plutonium in the dissolver solution is present as Pu(IV), but a small amount present as Pu(VI) or Pu(III) is adjusted to Pu(IV). Earlier, most plants have used $NaNO_2$ for this purpose but of late many plants use N_2O_4 or hydroxyl amine as these reagents do not add to the solids in high level waste.[25] Recent studies have shown that the conversion of all plutonium to Pu(IV) can be achieved electrolytically.[28] Reduction of plutonium to Pu(III) by ferrous sulphamate followed by oxidation to Pu(IV) by NO_2 gas has also been used.[29]

The distribution ratios of U, Np and Pu, along with some fission products, under typical Purex process conditions are shown in Fig. 2.[25] Unpublished distribution ratio data for Pu(III), from the authors' laboratory, is included in the figure.

Codecontamination

Counter-current contact of dissolver solution with 20-30% TBP in a centrifugal contactor/pulsed column/mixer settler is used to extract uranium and plutonium into the organic phase. At room temperature the distribution ratio (D) of U(VI) is higher than that of Pu(IV). This can result in accumulation of plutonium in some stages of extraction section, especially for FBR fuels, and lead to losses of plutonium to the raffinate.[27] The D value for U(VI) decreases and that for Pu(IV) increases with temperature particularly at higher nitric acid concentration.[27,30] Based on this approach, and results obtained with active laboratory counter current extraction experiments, an improved Purex process, Impurex, has been suggested. In this the extraction of U(VI) and Pu(IV) is carried out from 5 M nitric acid at 50 °C.[28]

In the case of TBP, when the concentration of tetravalent ions like Zr(IV), Th(IV) or Pu(IV) exceeds a certain limit, the organic phase splits into two phases (third phase formation), a lighter phase rich in diluent and a heavier phase containing the metal. Several studies on the formation of third phase due to saturation by plutonium species have been reported in the literature.[27,31-35] The limiting organic concentration (LOC) for Pu(IV) depends upon the temperature, diluent, HNO_3 and U(VI) concentrations. For Pu(IV), LOC increases with (i) increasing temperature, (ii) increased branching of alkyl group of diluent, (iii) addition of aromatic or polar solvents to the diluent and (iv) decreasing chain length for n-paraffinic diluents. With 30% TBP, third phase formation can be avoided by limiting the Pu loading of the solvent to <30 g/l.[27]

Partitioning of uranium and plutonium

In the first cycle, the extraction of U and Pu into TBP and scrubbing of the TBP phase with nitric acid is followed by partitioning of uranium and plutonium. This is based on the selective reduction of Pu(IV) to practically inextractable Pu(III) by contact with an aqueous stream having a suitable reducing agent. Many reagents have been tried for partitioning of plutonium, the most prominent being (i) ferrous sulphamate (ii) a mixture of U(IV) and hydrazine (N_2H_4) (iii) a mixture of hydroxyl amine nitrate (HAN) with N_2H_4.[11,36-40] In each case the primary reducing agent is supported by a scavenger for HNO_2 which would reoxidise Pu(III) to Pu(IV) and inhibit partitioning.

Negative role of nitric/nitrous acid in partitioning: In the conditions prevalent in a partitioning contactor, the aqueous phase HNO_3 concentration can increase from about 0.1 M to >2 M by the back extraction of HNO_3 from the organic phase. Under these conditions nitric acid tends to oxidise Pu(III) to Pu(IV) with nitrous acid playing an autocatalytic role. DUKES has suggested one of the possible mechanisms as:[36]

$$HNO_3 + HNO_2 \rightarrow N_2O_4 + H_2O \qquad (1)$$

$$N_2O_4 + Pu^{3+} + H^+ \rightarrow Pu^{4+} + HNO_2 + NO_2 \qquad (2)$$

It is thus essential to scavenge HNO_2 during partitioning. Also nitrous acid is favourably extracted into the organic phase and its autocatalytic reoxidation of Pu(III) to Pu(IV) appears to be much more in the organic phase. None of the scavengers, normally used for HNO_2, is extracted in the organic phase. In the mixed systems existing in the partitioning contactor, SZE et. al have proposed the following mechanism:[40]

$$Pu(NO_3)_3 \cdot 3TBP + NO_2 \rightarrow Pu(NO_3)_3NO_2 2TBP + TBP \qquad (3)$$

$$Pu(NO_3)_3 \cdot NO_2 2TBP + HNO_3 \rightarrow Pu(NO_3)_4 2TBP + HNO_2 \qquad (4)$$

Partitioning with ferrous sulphamate: Ferrous is a good reducing agent for conversion of Pu(IV) to Pu(III). Sulphamic acid is an excellent scavenger for HNO_2.

$$NH_2SO_3H + HNO_2 \rightarrow N_2 + H_2SO_4 + H_2O \qquad (5)$$

Ferrous sulphamate has therefore found extensive application for partitioning for more than two decades and it is not sensitive to operational changes in acidity and temperature.[11] Typical solution used for partitioning is

0.03 M Fe $(NH_2SO_3)_2$+0.1 M HNO_3 and this is introduced at the end of the contactor from where organic phase exits. At low nitiric acid concentration HNO_2 behaves as a reducing agent and helps U-Pu partitioning.[41] Because Fe(II)/Fe(III) couple is close to that of Pu(III)/Pu(IV), and even in the presence of $NH_2SO_3^-$ ion there is an appreciable oxidation of Fe (II) and Pu(III) by HNO_2, a fairly large excess (20–40 times the stoichiometric requirement) has to be added to achieve good separation of uranium from plutonium.[39] This adds about 45 kg of ferric sulphate to the high active waste per tonne of the spent fuel reprocessed.[42] Besides, the sulphate ion leads to enhanced corrosion of the stainless steel compnents. The reagent has therefore been partly or totally replaced by other reagents.

Partitioning with U(IV) – hydrazine: Theremodynamically U(IV) is a stronger reducing agent than Fe(II) and it does not introduce any additional metal into the system. Hydrazine helps in (I) stabilising U(IV), in nitric acid medium, during its preparation from U(IV) by HNO_2. Relevant reactions are as follows:[42]

$$2Pu^{4+} + U^{4+} + 2H_2O \rightarrow 2Pu^{3+} + UO_2^{2+} + 4H^+ \qquad (6)$$

$$U^{4+} + NO_3^- + H_2O \rightarrow UO_2^{2+} + NO_2^- + 2H^+ \qquad (7)$$

$$U^{4+} + 2NO_2^- \rightarrow UO_2^{2+} + 2NO \qquad (8)$$

$$2NO + NO_3^- + H_2O \rightarrow 2H^+ + 3NO_2^- \qquad (9)$$

Hydrazine destroys NO_2^- as per the following reactions:

$$N_2H_5^+ + NO_2^- \rightarrow HN_3 + 2H_2O \qquad (10)$$

$$HN_3 + H^+ + NO_2^- \rightarrow N_2O + N_2 + H_2O \qquad (11)$$

Since U(IV) is extractable by TBP, atleast two U(IV) containing aqueous streams, one of high acidity and another of low acidity, are used for partitioning of U–Pu. In a typical flowsheet one stream containing 1.0 M U(IV) in 2.0 M HNO_3 + 0.16 M N_2H_4 is fed to the contactor at the centre at a location just near the organic feed entry.[39] High acidity in this stream is useful in pushing U(IV) into the organic phase, thereby facilitating the reduction of Pu(IV) present in the organic phase. The second partitioning stream containing 0.05 M U(IV) in 0.2 M HNO_3 + 0.16 M N_2H_4 is fed at the end delivering uranium product in the organic phase. An organic scrub with 20–30% TBP from the opposite end is used to remove residual uranium from the plutonium product. Low acidity is used in the second partitioning stream as it facilitates reduction of Pu (IV) to Pu(III) by U(IV). Recent studies have shown that technetium catalyses the destruction of hydrazine, thereby increasing its consumption. Normally U(IV) used is 4 to 6 times the stoichiometric requirement.[39]

Partitioning with hydroxylamine nitrate and hydrazine: Hydroxylamine nitrate (HAN) can readily reduce Pu(IV) to Pu(III) as follows:

$$4Pu^{4+} + 2NH_3OH^+ \rightarrow 4Pu^{3+} + N_2O + H_2O + 6H^+ \qquad (12)$$

HAN can itself scavenge HNO_2 as follows:[43]

$$NH_3OHNO_3 + HNO_2 \rightarrow N_2O + HNO_3 + 2H_2O \qquad (13)$$

However, this reaction does not destroy HNO_2 at a sufficient rate to prevent reoxidation of Pu(III) to Pu(IV). Hydrazine is therefore added as an HNO_2 scavenger. Typical solution used for partitioning is 0.05 M HNO_3, +0.4 M NH_3OHNO_3+0.02 M N_2H_4.[39] Availability of NO_3^- from HAN partly compensates for low NO_3^- concentration at low acidity and helps in keeping uranium in the organic phase. HAN is not required in large excess and it can be readily destroyed by heating the solution to >60 °C before sending the solution to the plutonium purification cycle.[37,38] Recently DENNIS et al. have carried out laboratory investigations on the use of 0.19 M HAN in 0.1 M HNO_3 as a partitioning agent and have reported encouraging results.[44]

Partitioning with hydroxylamine nitrate + ferrous sulphamate: A mixture of HAN + Fe $(NH_2SO_3)_2$ has been successfully used as a partitioning reagent at Savannah River plant. This combination has reduced the ferrous sulphamate requirement by 70%. HAN reduces both Pu(IV) as well as Fe(III) and enhances process efficiency. Typical composition of the partitioning reagent is 0.11 M HNO_3 + 0.04 $Fe(NH_2SO_3)_2$ + 0.056 M NH_3OHNO_3.[13]

Partitioning by electrolytic reduction: In situ electro-reduction would permit partitioning of U-Pu without the addition of an external partitioning agent. The chemistry as well as the equipment (mixer settler as well as electropulse column) have been developed for use in the Purex process.[45,46] Typical aqueous phase suggested for partitioning by electro-reduction is 0.1 M HNO_3 + 0.2 M N_2H_4.

The use of hydrazine as a nitrite scavenger leads to the production of HN_3 and NH_4NO_3 which present safety problems. Reaction of N_2H_4 with Tc leads to gas formation and hydraulic disturbances.[43] Electroreduction partitioning has been tried without adding N_2H_4 by keeping the nitric acid concentration below 0.7 M.[28] Similarly partitioning using a mixture of U(IV) + HAN has been explored and appears feasible.[43]

Partitioning with a complexing agent: Pu^{4+} ion has higher ionic potential as compared to UO_2^{2+} ion and therefore forms stronger complexes with various ligands. A number of complexing agents have been investigated for U–Pu partitioning but of these only sulphate (in the form of sulphuric acid) has found industrial application. In the organic phase containing U and Pu, uranium concentration is substantially higher than that of plutonium and any partitioning scheme using H_2SO_4 can be effective only if the distribution ratio of U and Pu differ by a factor of >50.[38]

It is observed that in the extraction of U(VI) and Pu(IV) from 1 M HNO_3, addition of H_2SO_4 decreases the extraction gradually for U(VI) and sharply for Pu(IV).[47,48] At 1 M HNO_3 + 1 M H_2SO_4 the distribution ratios differ by a factor of 90 and this medium can, therefore, be used for partitioning. This has been successfully employed in FBR fuel reprocessing plant at Dounreay, UK. where a mixture of $HNO_3+H_2SO_4$, with a small addition of ferrous sulphamate, is routinely used.[19] The plant has processed about 23 te of fuel containing 3.5 te of plutonium.

Fission products decontamination

In the Purex process the desired decontamination of the product U and Pu from most of the fission products is easily attained. However, there are a some fission products (FP) which are known as problematic or troublesome as their removal to the desired degree has been found difficult. These are ^{95}Zr–^{95}Nb and ^{103,106}Ru, and their chemistry is comprehensively reviewed in many articles.[13,25,49-52]

The behaviour of long-lived fission products ^{129}I and ^{99}Tc in the Purex process has become a matter of some concern as both of them may enter the environment via waste streams.[51-56] Also Tc decreases ^{95}Zr decontamination factors and the stability of hydrazine containing partitioning reagents.[57,58]

^{95}Zirconium–^{95}Niobium: In nitric acid solutions, Zr exists only in tetravalent oxidation state, Zr(IV), but in many chemical forms depending primarily on acidity, Zr concentration and temperature.[13,51,52] Hydrolysis and polymerisation, both of which increase with increasing temperature and decreasing acidity, change the Zr(IV) species in solution. Several species of the type $Zr(OH)_x(NO_3)_{4-x}$ have been reported in the aqueous phase. McKibben[13] reported that there are at least two Zr(IV) species in the solvent and their exchange rate is slow, the primary species being $Zr(NO_3)_4.2TBP$ while other species in equilibrium with it has higher TBP/Zr ratio. Increasing temperature and nitric acid concentration increase the extraction of Zr.

Though ^{95}Nb is practically inextractable into TBP, the presence of silica in the solution results in ^{95}Nb extraction.[13] The removal of silica from the dissolver solution by gelatin treatment prevents the extraction of ^{95}Nb.[59]

The principal reason for the extraction of ^{95}Zr–^{95}Nb is the presence of radiolytic and hydrolytic degradation products of TBP and the diluent, in the solvent.[50]

Though these degradation products cannot be eliminated, their concentration can be minimised by using short residence time contactors which reduce the radiation exposure to the solvent and consequently the radiolytic degradation products.

Zr(IV) with high ionic potential forms very strong complexes with fluoride and this has been successfully exploited, for about 20 years, to improve ^{95}Zr DF in the French Purex process plants.[60,61]

^{103,106}Ruthenium: Several investigations have been carried out with a view to understanding the chemical behaviour of Ru in the Purex process.[49–52] About 30–50% of Ru remains with the insoluble residue during fuel dissolution.[26,52] The chemistry of Ru is complicated due to a variety of ruthenium species that may be present in the solution and the relatively slow rate of their interconversion. In the fuel solution ruthenium is present as complexes of $RuNO^{3+}$, where the ligands may be NO_3^-, NO_2^-, OH^- and H_2O. The mechanism of extraction of $Ru(NO)(NO_3)_3.(H_2O)_2.2TBP$, the species most extracted, has been suggested.[50,51] Fast extraction and slow scrubbing improve decontamination both for Zr–Nb and Ru. Usually split scrub, one with high acidity and high temperature which favours decontamination from Ru and the other with low acidity at approximately 30 °C for Zr–Nb decontamination is used.

^{129}Iodine: The potential radiological hazard of the fission product iodine was recognised from the beginning of fuel reprocessing. Of the fission produced iodine isotopes, the hazard of ^{131}I having 8 days half-life was considered to be serious and this became a major factor in deciding the cooling period for spent fuel before it is reprocessed. Cooling of spent fuel for about 6 months or more results in almost complete decay of ^{131}I and its potential hazard is almost eliminated. The concern for fission produced long-lived (1.6×10^7 yrs) ^{129}I is relatively of recent origin.[54]

The fuel dissolution, in hot 8–10 M nitric acid, results in rapid oxidation of ^{129}I to elemental iodine which volatilizes to accompany the dissolver off gases (DOG). It is reported that >99% of ^{129}I escapes to DOG while about 1% remains in the dissolver solution, where it is suggested to be present as iodate.[54]

Iodine-129 present in the dissolver solution would be distributed among various streams during solvent extraction process. A major fraction of it is extracted by the solvent, from which it is removed only partially in the solvent washing and hence ^{129}I may accumulate in the recycled solvent.[54] If ^{129}I can be removed from the dissolver solution prior to the solvent extraction, it would facilitate greatly its trapping. Sparging nitric oxide gas through the dissolver solution, after adding some inactive IO_3^-, has been proposed to remove iodine from this solution.[62] SAKURAI et al. in a recent study on the dissolution of specimens of spent PWR fuels have shown that iodine in the solution is present in the form of colloids of AgI and

PdI_2.[63] Heating of the fuel solution for a few hours, in the absence of NO_x, followed by NO_x sparging has been suggested for the expulsion of ^{129}I.[63]

^{99}Technetium: The chemical behaviour of ^{99}Tc, in the Purex process was not of much concern probably due its low specific activity and the low energy beta emission.[55] Recently, however, it is recognized that it may enter the environment as a result of nuclear fuel cycle activities especially of fuel reprocessing.[56] The fission yield of ^{99}Tc is high ($\sim 6\%$) and it is estimated that about 1 kg of ^{99}Tc is present in one ton of spent fuel (3.5% ^{235}U) with 35–40 GWd/te burn up.[55,56]

During fuel dissolution bulk ($>95\%$) of the ^{99}Tc gets dissolved and is present in its highest oxidation state as pertechnetate anion TcO_4^-. Numerous investigations on the extraction of Tc into TBP have been reported.[51,56] The extraction of TcO_4^- follows the equilibrium.

$$H^+ + TcO_4^- + 3TBP \rightarrow HTcO_4.3TBP \qquad (14)$$

The extraction increases with HNO_3 concentration upto ~ 0.7 M but further increase in HNO_3 concentration decreases the extraction of Tc.[64] Extraction also decreases with increasing temperature. The presence of some cations such as U(VI), Pu(IV), Zr(IV), Ce(IV) etc., usually present in the dissolver solution, enhances the extraction of Tc.[65] The coextraction of Tc occurs by replacement of NO_3^- by TcO_4^- in the extracted complexes of U(VI), Pu(IV) and Zr(IV) as is shown below:

$$UO_2(NO_3)_2.2TBP + TcO_4^- \rightarrow UO_2(NO_3)(TcO_4).2TBP + NO_3^- \qquad (15)$$

$$M(NO_3)_4.2TBP + TcO_4^- \rightarrow M(NO_3)_3.(TcO_4).2TBP + NO_3^- \ (M = Zr \text{ or } Pu) \qquad (16)$$

The coextraction of Tc with Zr(IV) is most important.[57] Recent laboratory studies in UK aimed at developing chemical flowsheet conditions to be used in THORP plant have revealed that the Zr(IV) present in the fuel solution causes 100% extraction of Tc from the fuel solution.[57]

The coextracted Tc complicates the partitioning of U and Pu when N_2H_4 is also present in the reductant used. The presence of Tc during partitioning, catalyses the oxidation of hydrazine by nitric acid.[11] The chemical reactions involve initial slow reduction of Tc(VII) to Tc(IV) followed by Tc(IV) catalysed reduction of Tc(VII) by hydrazine.[58] It is now well recognised that to avoid the excessive consumption of N_2H_4 leading to hazardous products viz. HN_3 and NH_4NO_3, it is necessary to remove coextracted Tc from U and Pu in the solvent prior to U–Pu partitioning. The removal of Tc has been demonstrated in UK[66] and actually incorporated in the UP3 plant in France.[18] This involves a separate scrub with 5–6 M HNO_3, which besides removing Tc would also improve DF from Ru.

Neptunium

Neptunium-237 is formed in small but significant quantities in uranium fueled nuclear reactors. In early stages of fuel reprocessing, the study of chemical behaviour of ^{237}Np or its recovery during fuel reprocessing was practically of no interest due probably to very small quantities of ^{237}Np involved or a lack of any application of ^{237}Np. The use of ^{238}Pu as the heat source for radioisotopic power batteries, especially in the USA, demanded ^{237}Np from which ^{238}Pu could be produced by neutron irradiation. The chemical behaviour of ^{237}Np in the Purex process was investigated to enable the recovery of ^{237}Np. Large quantities of ^{237}Np were successfully recovered by suitable modifications to permit the ^{237}Np recovery. By 1976, 320 kg of ^{238}Pu was produced in Savannah River by irradiating ^{237}Np.[16] SCHULZ and BENEDICT have comprehensively reviewed the processes used for the recovery of ^{237}Np.[67]

With much larger quantities of ^{237}Np formed in high burn up LWR fuels and the low specification limit of 1500 alpha dpm/g U for transuranics in the recovered uranium, it becomes necessary to achieve a DF of about 1000 for recovered uranium from ^{237}Np.[53] Several laboratory investigations, with simulated or spent fuel solutions, have been carried out to devise methods for the desired decontamination of recovered uranium from Np. In the dissolver solution Np exists mainly as Np(V) which is virtually inextractable into TBP. Neptunium as Np(VI) is highly extractable while Np(IV) is moderately extractable into TBP. The extraction behaviour of neptunium, is decided by the role of nitrous acid in the nitric acid oxidation of Np(V) as shown below:

$$2\mathrm{NpO_2}^+ + \mathrm{HNO_3} + 2\mathrm{H}^+ \rightarrow 2\mathrm{NpO_2}^{2+} + \mathrm{HNO_2} + \mathrm{H_2O} \qquad (17)$$

With 10^{-3}–10^{-4} M HNO_2, most of the Np is coextracted as Np(VI) alongwith U and Pu. With higher concentration of HNO_2 ($>$10–2 M) Np follows the aqueous raffinate alongwith the FPs.[67]

It has been reported[68] by KOLARIK and SCHULER, that Np could not be diverted to aqueous raffinate by using high concentration of HNO_2 and even in the presence of 0.05 M HNO_2, 95% of Np was coextracted alongwith U and Pu. They have explored the use of various reducing agents to selectively reduce Np(VI) to Np(V) and observed that butyraldehyde reduces Np(VI) to Np(V) but not Pu(IV) to Pu(III). They established flowsheet conditions for >99% Np removal using butyraldehyde. UCHIYAMA et al. have observed that while n-butyraldehyde: reduces Np(VI) to Np(V) but not Pu(IV) to Pu(III), isobutyraldehyde reduces both Np(VI) and Pu(IV).[69] Based on these results they have proposed flowsheet conditions using n- and iso-butyraldehydes for the separation of Np, Pu and U by the Purex process.

In the Purex process the U–Pu partitioning is usually achieved by using ferrous sulphamate, U(IV)-N_2H_4 or HAN- N_2H_4 as the reductants. The path of Np coextracted as Np(VI) during partitioning is decided by the reductant used, the acidity, temperature, uranium loading of the solvent and the contact time. Ferrous sulphamate reduces Np(VI) to Np(IV) which is moderately extracted and the Np(IV) may mainly accompany U if the acidity is high and U loading is moderate or it may be distributed between U and Pu streams resulting from partitioning. U(IV) reduces Np(VI) to Np(V) rapidly but further reduction to Np(IV) is slow. Thus with U(IV) as the reductant, Np coextracted as Np(VI) may be distributed between U and Pu streams, the actual fraction accompanying either stream is decided by the prevailing conditions. HAN reduces Np(VI) to Np(V) quite fast but further reduction to Np(IV) is extremely slow and hence with HAN as the reductant, for U–Pu separation, most of the Np may end up with the aqueous Pu stream.

Neptunium accompanying U during partitioning will exist as Np(IV) and its removal during the final purification of U requires its conversion to inextractable Np(V). It was reported that heating Np(IV) in low acid quantitatively converts Np(IV) to Np(V).[70] This method has been used to convert Np(IV) to Np(V) and its subsequent removal in the final uranium purification cycle.[23] Any Pu present is removed by HAN scrubbing of uranium loaded solvent. During scrubbing Np removal is not affected as HAN reduces Np(V) to the Np(IV) very slowly. The presence of Fe(III), however, catalyses the reduction thereby decreasing the DF of U from Np.[23]

Solvent degradation and treatment

Solvent degradation: It is known from the inception of the Purex process that the solvent undergoes hydrolytic and radiolytic degradation and the products of the degradation have adverse effect on the performance of the process. Extensive investigations have been carried on solvent degradation and a number of excellent reviews have been published.[71-74] The presence of degradation products in the solvent causes various problems such as decrease in DFs as a consequence of the retention of fission products (Ru, Zr, Nb) in the solvent, loss of U and Pu to the waste streams, formation of emulsion and formation of interfacial cruds and precipitates.[75]

The degradation products of TBP viz. dibutyl and monobutyl phosphoric acids, H_3PO_4 and butanol are well recognised and the strong affinity for Zr–Nb, Ru and for Pu leading to the decrease in DFs and in Pu and U recovery is known.[71-74]

Different degradation products formed in the Purex process solvent are reported by STIEGLITZ and BAKER[75] and also by MARKOV et al.[76] The diluent degradation process and the effects of its products are relatively less clearly understood. Recently, however, the use of sophisticated analytical techniques such as, IR spectroscopy, paper chromatography, gas chromatography, mass spectrometry and ion chromatography have helped in the identification of a number degradation products.[75–79] These include alkyl nitrates, nitroalkanes, aldehydes, ketones, esters, alcohols and carboxylic acids and through secondary reactions they generate various surfactants, complexants, emulsifier and crud formers which tend to interfere in the process.[78] Neace has reported that diluent degradation products are not removable from the solvent by common washing solutions. Surfactants cause interfacial crud formation, react with TBP to form strong complexants for Zr–Nb which unlike DBP are not removable by common solvent wash solutions.[78] The surfactants also lead to the formation of non-strippable Ru species in the solvent. He concluded that the presence or absence of surfactants in the solvents is an index of their suitability for the Purex process.[78]

TALLENT et al. have proposed that HNO_2 and free radicals $\bullet NO_2$ and $RCH_2\bullet$ play an important role in the degradation of n-paraffinic hydrocarbons (NPH)) diluent in 30% TBP - 70% NPH.[77] Changing the diluents from kerosene to linear hydrocarbons has substantially decreased retention of ruthenium by the solvent and its radiolytic degradation.[74] The primary degradation products of TBP and the diluent interact to form secondary products including long chain organic compounds not removable by common washing methods. An example is the formation of long chain acidic organophosphates which retain Zr(IV) or Pu(IV).

Solvent treatment: Several methods have been investigated for the removal of degradation products from the solvent before it is reused. These are (a) Washing with Na_2CO_3 (b) Washing with hydrazine and hydroxylamine salts (c) Using solid sorbents and (d) Vacuum distillation.

All Purex process plants at present use scrubbing with Na_2CO_3 solution and details of the procedures used in different plants are tabulated by NAYLOR.[71] Neither complexants nor long chain degradation products are removed by Na_2CO_3 washing. Its main limitation, however, is that it produces a large quantity of medium active solid waste, mostly $NaNO_3$, approximately 100 kg per ton of the fuel reprocessed.[74] This has led to an exploration for alternate reagents, which can be destroyed by decomposition to gaseous products, thereby not adding to the solid waste. Hydrazine carbonate and hydrazine oxalate have been investigated for this purpose.[74]

A large number of solid sorbents have been explored for primary or secondary cleanup of the solvent.[73,74] Of these hydrous titanium oxide (HTO), NaOH treated silica gel, PbO_2 on silica gel, macroreticular resins and activated alumina have shown promising laboratory results for the solvent cleanup. The macroreticular strong base resin Amberlyst A-26 was tested at Savannah River Plant using approximately 200 litre resin bed column for the solvent cleanup with some success but with eventual conclusion that this method would not be cost effective.

Vacuum distillation of the Purex solvent for its regeneration has been developed and will be implemented for the first time in a French Purex plant.[80] The method consists of (a) washing the spent solvent by Na_2CO_3 solution followed by water to remove sodium salts in the solvents (b) vacuum dehydration (c) vacuum distillation, (d) rectification of the distillate to yield the diluent and concentrated TBP (60–80%) fractions. Bulk of the solvent (95%) vaporises leaving about 5% active residue mainly consisting of TBP enriched in degradation products. The concentrated TBP is washed with NaOH solution prior to its recycling. The diluent and the TBP thus regenerated meet solvent quality requirements for their reuse in the plant.

New processes

Crystallisation of nitrates for refining U and Pu

Crystallisation is one of the oldest methods of purification and this has recently been studied to explore its applicability for refining uranium and plutonium streams after the first cycle.[17,81-83] R&D work in this field is concentrated on the crystallisation of $UO_2(NO_3)_2.6H_2O$(UNH) in which impurity atoms do not get incorporated due to its rigid lattice. The crystallisation of UNH was carried out using the first cycle uranium product resulting from reprocessing of LWR fuel, with about 3% burn up and cooled for 2 1/2 years.[82] The decontamination factors obtained for most impurities were >100. Addition of small amounts of U(IV) (1-2 g U(IV)/l) to UNH solution prior to crystallisation resulted in excellent separation from Pu and Tc. Over 90% U recovery with removal of $>99\%$ impurities can be accomplished by UNH crystallisation.

Preliminary work on plutonyl nitrate crystallisation has shown that similar separation factors for residual fission products are obtained.[82]

The crystallisation process produces no additional waste streams as the resulting mother liquors and the wash liquors can be recycled to the aqueous feed of the first Purex process cycle.

Amides as extractants

If the extractants used for nuclear fuel reprocessing or actinide separations from high active waste were completely incinerable, the radioactive wastes generated can be significantly reduced. MUSIKAS and coworkers have explored the prospects of using N, N-dialkylamides as alternatives to TBP for fuel reprocessing.[84-86] Several amides R_2NCOR', where R and R' are alkyl groups, have been studied. Based on the extraction data for U(VI), Pu(IV) and fission products and the solubility of U(VI) amide complex in hydrocarbon diluents, amides with R=di 2- ethylhexyl and $R'=-C_3H_7$, $-C_5H_{11}$ $-CH(CH_3)_2$ or $-CH_2C(CH_3)_3$, are found potentially useful for fuel reprocessing. A flowsheet alternate to Purex, based on the results of laboratory counter current studies using 1 M DOiBA, $(CH_3)_2CHCO-N(CH_2-CH-C_2H_5-C_4H_9)_2$ and 0.5 M DOBA, C_3H_7 $CON(CH_2-CH-C_2H_5-C_4H_9)_2$ in hydrocarbons, has been proposed.[84-86]

Removal of actinides from high active waste (HAW)

Organophosphorous reagents

Liquid high active waste generated from nuclear fuel reprocessing contains long-lived alpha emitting actinides namely Np, Pu, Am and Cm. If these actinides are isolated from the rest of HAW, long term radiological risks of the HAW will be reduced very effectively. The techniques explored or under development for the same have been recently reviewed by THOMPSON.[87] Several studies have been devoted to develop solvent extraction methods for the removal/recovery of the actinides from HAW with or without reducing the acidity. Main extractants investigated have been summarised recently by MUSIKAS.[88] Laboratory studies have established that actinides can be successfully removed using common extractants such as di-2-ethylhexylphosphoric acid (HDEHP) if the acidity is very low. Use of TBP for extraction by reducing HAW acidity and addition of $Al(NO_3)_3$ has also been explored. TACHIMORI et al. have shown, di-isodecylphosphoric acid (HDIDP) to be somewhat superior to HDEHP for the same purpose.[89] ZHU and JIAO have explored the use of mixed trialkylphosphine oxide (TRPO) as an extractant for the removal of U, Np, Pu and Am from HAW.[90]

Several bifunctional organophosphorus extractants have been intensively studied to explore their potential for removing actinides from acidic HAW. Of these, carbamoylmethylphosphonates (CMP) and carbamoylmethylphosphine oxides (CMPO) have proved to be superior to others as they are able to extract tri-, tetra- and hexavalent actinides from strong nitric acid solutions.[91] HORWITZ and SCHULZ have extensively investigated the use of octyl(phenyl)-N,N diisobutylcarbamoyl methylphosphineoxide [OϕD(iB)CMPO].[92] Its favourable properties viz. low aqueous phase solubility, high resistance to both chemical and radiolytic degradation, compatibility with various organic diluents, high affinity and capacity for all the actinide (III), (IV) and (VI) ions from both aqueous HNO_3 and HCl solutions and ease of stripping has made this as a reagent of choice for the TRUEX process developed for the removal of actinides from HAW. In the TRUEX process, Np in HAW feed is first reduced to Np(IV) with ferrous sulphamate. All the actinides from 1–3 M HNO_3 waste solutions are extracted by 0.2–0.25 M CMPO - 1–1.2 M TBP - hydrocarbon extractant. Besides, the lanthanides and Tc in HAW are also extracted. From the actinide loaded organic phase trivalent actinides (Am and Cm) are selectively stripped with 0.04 HNO_3 followed by stripping of tetravalent actinides (Pu and Np) using 0.05 M HNO_3 + 0.05 M HF. U(VI) and pertechnetate are finaly removed with Na_2CO_3 during solvent washing step.

Batch and counter-current tests of the TRUEX process with various actual waste solutions have been very successful. After pilot plant tests, full plant scale TRUEX process is to be operated at HANFORD.[92]

Diamides

MUSIKAS and coworkers have explored the prospects of using N,N-tetraalkyl 2-alkylpropane diamides for actinides removal from HAW.[84–86,88] Among the diamides studied N, N tetraalkyl, 2-alkylmalonamides are promising. The malonamides explored include $(C_8H_{17}CH_3NCO)_2CH_2$, and $(C_4H_9CH_3NCO)_2CHR$ with R=$-C_6H_{13}$, - $C_2H_4OC_2H_5$ and $C_2H_4OC_2H_4$-O-C_6H_{13} and all these are able to extract trivalent actinides from 3–6 M HNO_3. In a recent work, N,N'-dimethyl-dibutyl 1,2-tetradecylmalonamide, DMDBTMA ($(C_4H_9CH_3NCO)_2CHC_{14}H_{29}$) has been selected to develop DIAMEX process.[93] Recent counter-current experiments with DIAMEX process using HAW have shown encouraging results. Main features of diamides are compared with CMPO by MUSIKAS in a recent publication.[88] Diamides are easy to synthesize and purify, are about 10 times cheaper than CMPO and can be destroyed by humid thermolysis. Aliphatic hydrocarbons can be used as diluent for diamides while CMPO requires 1.2 M TBP for using aliphatic hydrocarbons.

Non-aqueous techniques for reprocessing of nuclear fuels

Processing of spent nuclear fuels by non-aqueous techniques has been a fascinating idea from the early stages of reprocessing technology. Extensive research has been carried out at various laboratories to develop a variety of non-aqueous processes, but three which reached a reasonable level of engineering scale development are: (i) Fluoride volatility[94] (ii) Pyrochemical reprocessing[95] and (iii) Salt cycle process.[96] Each of these, while addressing some problems related to aqueous processing, had their own drawbacks. Fluoride volalitity process could readily remove uranium from the spent fuel as UF_6 but recovery of plutonium was fraught with problems due to the instability of PuF_6 at process temperatures and radiation fields. Pyrochemical processes relied on reactions in molten salt-liquid metal media and are best suited when the fuel is either a salt or a metal. Further, the liquid metal media like Mg–Zn, Mg–Cu alloys are highly corrosive and require refractory metal process equipment such as mixer settlers, process vessels and piping. The salt cycle process is based on the selective dissolution of $UO_2/(U,Pu)O_2$ in molten chloride (NaCl–KCl) media and electrolytic reduction of UO_2^{++} and PuO_2^{++} ions from the salt on to a cathode. As specification limit for chloride in power reactor fuels is <10 ppm, the use of chloride medium for reprocessing would not be very desirable. There has been a revival of interest in pyrochemical processes due to the development of Integral Fast Reactor (IFR) concept. The following section briefly discusses the prominent pyrochemical processes with a major emphasis on recent work related to IFR fuel reprocessing.

Pyrochemical reprocessing of molten salt fuels

Molten fluoride salt was used as fuel for Molten Salt Reactor Experiment (MSRE) and formed the basis for the Molten Salt Breeder Reactor (MSBR) concept having fuel with a nominal composition of 71.7 mol% ^7LiF, 16 mol% BeF_2, 12 mol% ThF_4 and 0.3 mol% $^{233}UF_4$.[97,98] The fuel would be continuously reprocessed for the isolation of ^{233}Pa (for its decay to ^{233}U) and to remove neutron absorbing fission products such as rare earths. A salt stream from the reactor would first be fluorinated to remove upto 99% of uranium as UF_6 which would be recycled back to the reactor after reduction to UF_4. The fuel salt would then be processed by reaction with lithium reductant dissolved in liquid bismuth. The reduction reaction for a salt constituent MF_n can be written as:

$$MF_n(\text{salt}) + nLi(Bi) \rightarrow M(Bi) + n\,LiF\,(\text{salt}) \qquad (18)$$

$$-\Delta G_r^o/RT = \ln K = \ln[X(M).\,\gamma(M).a(LiF)^n/(X(MF_n).\,\gamma(MF_n).a(Li)^n] \qquad (19)$$

where $\Delta G_r^o = [n\Delta G_f^o(LiF) - \Delta G_f^o(MF_n)]$, K is the equilibrium constant for the reaction and a, X and γ are the activity, concentration and activity coefficient of each constituent. If we define the distribution ratio D as $X(M)/X(MF_n)$ then we can write:

$$\ln D=[\Delta G_f^o(MF_n)-n\Delta G_f^o(LiF)]/RT-\ln\gamma(M)-n\ln a(LiF)+ +\ln\gamma(MF_n)+n\ln a(Li) \qquad (20)$$

So in addition to the differences in the free energies of formation of LiF and MF_n, the activity coefficients of metal M and salt MF_n in the respective phases have important bearing on the selective separation of various constituents. Experiment have shown that U, Pa and Zr can be extracted from the salt phase into the metal phase with a low (0.2 at%) concentration of lithium in bismuth. By increasing lithium concentration to 5 and 50 at% it is possible to respectively separate the rare earths and divalent fission products. Engineering scale developments have also been carried out on various process steps.[97-99]

Pyrochemical reprocessing of oxide fuels

Oxides of uranium, plutonium, zirconium etc., can be readily reduced with Mg–Zn alloys in molten flux media.[100-102] After reduction, equilibria similar to those described in equation (18) dictate the distribution of various metals between the salt and the alloy phases.[95,103] In the flowsheet proposed for reprocessing of plutonium based oxide fuels, it is possible to obtain purified (DF 10^3–10^4) uranium and plutonium in Zn–Mg alloy streams, leaving fission products in different salt streams. Zinc and magnesium are subsequently removed from uranium and plutonium alloy streams by vacuum distillation and the metals oxidised to UO_2 and PuO_2 for use in fuel refabrication.

Pyrochemical reprocessing of metallic fuels for fast reactor

Enriched uranium metal alloy was used as fuel for the entire life span of Experimental Breeder Reactor II (EBR II) and the fuel was reprocessed by a simple and elegant pyrometallurgical method.[103,104] Metallic fuels were not preferred for use in fast reactors earlier because they could barely achieve a burn up of 2 at% against the requirement of about 10 at%. But the development of U–Zr and U–Pu–Zr alloy fuels, which could withstand high burn up, has led to the development of Integral Fast Reactor (IFR) concept in which pyrochemical reprocessing of the fuel is an integral part of the reactor complex.[105] Nominal fuel and blanket compositions for an IFR are proposed as U–Pu–Zr(75–15–10 at%) and U–Zr(90–10 at%). Electrochemically driven redox reactions in molten chloride (LiCl–KCl eutectic) and molten cadmium media form the basis for the separation of U and Pu from fission products.[103,106,107] Reactions similar to that described by equation (18) determine the chemical equilibria, LiCl replacing LiF and Cd replacing the bismuth phase. The first step in the process is the dissolution of the chopped fuel in molten cadmium bath which subsequently acts as an anode. The rate of dissolution of the spent fuel can be enhanced by making the cadmium pool as a cathode and the spent fuel as an anode. Whereas U and Pu have adequate solubility in Cd, some of the noble metals (Mo,Tc,Ru,Rh, Pd), zirconium and stainless steel clad are insoluble and are discarded as waste. Oxidising or reducing conditions can be established in the cell either chemically or electrochemically. By a proper selection of the redox conditions, it is possible to selectively transfer U and Pu from the cadmium anode to a suitable cathode leaving fission product elements more noble than U/Pu in the cadmium anode and fission products with more stable chlorides (rare earths, alkaline earths) in the salt phase. In IFR fuel reprocessing the reactions are electrochemically driven and there is no need for mixer-settlers or packed columns. Also cadmium is chemically compatible with iron and refractory metals are not required for process equipment.

A schematic of the electrochemical cell is shown in Fig. 3. The recommended temperature of operation is 775 K. For simplicity, it is assumed that the cell contains only uranium and plutonium in the molten cadmium pool and the molten salt.

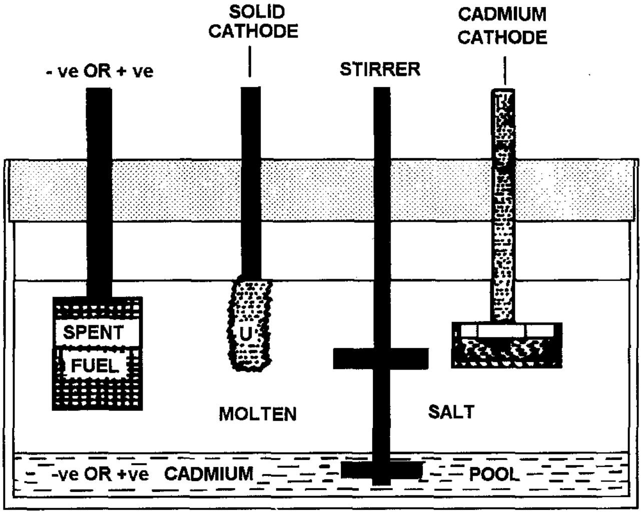

Fig. 3. Conceptual electrorefiner for IFR fuel

By making the cadmium metal pool as anode and having a solid iron/molybdenum as cathode electrochemical transfer of U/Pu from the anode to cathode can take place. As $PuCl_3$ is considerably more stable with respect to UCl_3, plutonium reduced at the cathode immediately reacts with UCl_3 in salt solution to give U metal. So by using a solid cathode for electrorefining it is possible to selectively remove uranium from the cadmium metal anode pool. To facilitate the deposition of uranium along with plutonium, it is necessary to decrease the activity of plutonium in the cathode so that it cannot react with UCl_3 in the salt phase and give uranium. This can be achieved by using a molten cadmium as a cathode in which the activity of plutonium is very low (4×10^{-6} at low Pu concentration). In a dynamic system, such as an electrochemical cell, complete chemical equilibrium cannot be established in a few hours. For example, the cadmium anode and the cadmium cathode would have different compositions but are in contact with same salt. In the absence of electrochemical transport it would take extremely long time for the two cadmium phases to have a composition which is in equilibrium with the salt. For estimating the relative transport of U or Pu from the anode to the cathode the concept of limited equilibrium has been suggested which would prevail for all constituents having significant concentration of their chlorides in the salt phase.[106,107] Under this assumption, which is valid for each time slot in which the composition changes are marginal, cadmium at the cathode as well as the anode are in equilibrium with the salt which has a uniform composition throughout the cell. If we assume equilibrium at the cathode as well as the anode equation (21) can be derived

$$a_u(\text{anode})/a_u(\text{cathode}) = a_{Pu}(\text{anode})/a_{Pu}(\text{cathode}) \qquad (21)$$

This ratio would tend towards unity as equilibrium is approached. Equation (21) forms the basis of a computational code for evaluating the transport of U, Pu, or other constituent metals, from the anode to the cathode.[107] Calculations can be refined by using a model based on diffusion layer theory as suggested by Kobayashi and Tokiwai and good agreement has been observed with the available experimental data.[108] The U/Pu products obtained by deposition on solid or liquid cathode are postulated to have adequate decontamination from fission products (DF ~ 10^3) for their direct use for remote fabrication into fuel pin by injection moulding. Experimental studies on these aspects are in progress. Techniques have also been proposed to define metal based waste form for pyroprocessing wastes.[109] The problem of transuranics in the waste is almost eliminated as they accompany the U/Pu streams and are recycled back into the reactor.

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