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ABSTRACT
    The high degree of purity required for the fissile and fertile elements used as fuels in nuclear reactors has made solvent extraction the choice as the purification method in the different steps of the fuel cycle. This technique, owing to its specificity, and its adaptability both to continuous multistage processes and to remote control, has served to achieve the requisite purities with safe, reliable operation. A review of the different steps of the cycle, including uranium and thorium production, uranium enrichment, reprocessing, and the recovery of transuranics, highlights the diversity of the solvents used and the improvements made to the processes and the equipment. According to the different authors, this technique is capable of meeting future needs, aimed to reduce the harmful effects associated with the nuclear fuel cycle to the lowest possible levels.

FOREWORD

Solvent extraction in the nuclear fuel cycle! Not a new subject. Spence [14] at the 1971 ISEC and, more recently, Naylor [27] at the 1986 ISEC have discussed it brilliantly.

Today, I should like to review the general features of the method, its application in the different steps of the cycle, including the elements of nuclear importance such as thorium and transuranic by-products of reprocessing.

INTRODUCTION

The first question that comes to mind is: why solvent extraction? A historical review of the first nuclear applications of this technique has been compiled by Spence. He showed that the purity required for the uranium feeding the first atomic reactors was far above the usual standards for industrial metals. The need accordingly arose for a separation method involving the specific properties of uranium, particularly the property of uranyl nitrate of being soluble in ethyl ether. A first industrial installation was built in the United States, in which countercurrent extraction in a cascade succession of stages achieved good recovery of the uranium, and thorough purification by means of effective washing. A few years later, the reprocessing of fuels from natural uranium reactors drew on the same technique to recover and purify the unconsumed uranium and the plutonium formed, with comparable properties at the same degree of oxidation. For reprocessing, the objective of recovering fissile species was compounded by extremely high decontamination standards concerning the ß/γ emitter fission products. To minimize personnel irradiation, the process was implemented in remote-controlled and maintained installations. The extraction technique proved to be ideal for these constraints.

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As to the process, the refining of uranium and the reprocessing of natural uranium fuels underwent similar developments in the first few years, with respect to the choice of solvents and their application in a continuous, high-performance process.

Ethyl ether being highly flammable, it was supplanted by less flammable ethers and ketones, which were applied in industrial installations. Very soon tributylphosphate replaced the ethers and ketones which demanded a high concentration of nitrate ions in the aqueous phase, playing the rôle of salting out agents.

The first extraction processes already set the structure of the now classic flow charts: extraction/scrubbing/stripping cycle, applied to the purification of an element, extraction/ washing/partition/stripping cycle for the combined purification of two elements and their separation.

Extraction units are divided into three classes: mixers/settlers, columns, and centrifugal extractors. The selection criteria are based on transfer kinetics in two-phase systems, speed of resolution of emulsions, capacity, and extractor size, factors influencing the investment costs, and, in some cases, criticality constraints. Over the years, constant improvements were made in each class of equipment, tending to boost efficiency, capacity and reliability in a hostile environment.

URANIUM PRODUCTION

Uranium is produced in two steps: (1) extraction from ores with a usual assay of 10^{-3} or sometimes less, yielding a solid compound containing more than 70% uranium (normally uranates), and (2) refining of this compound to obtain uranium of nuclear purity.

In the hydrometallurgy of uranium, solvent extraction emerged as an effective means of concentrating and purifying the element conveniently. From 1956, researchers at the ORNL [9] investigated amino compounds for the extraction of uranium and thorium from the aqueous solutions produced by the sulphuric leaching of uranium ores. This oxidized aqueous solution contains hexavalent uranium in the form of anionic uranyl sulphate complexes, which can be fixed on anion exchange resins or be extracted by amino solvents. The solvent extraction process developed (Amex process), over fixation on a fixed resin bed, offers the advantage of continuous operation with higher capacity. Tertiary amines are generally employed, diluted in aliphatic diluents containing a small amount of heavy alcohol (preventing the appearance of insolubles) or in aromatic diluents. This process is in widespread use today (United States, Canada, South Africa, France etc). Note that in South Africa [8,15] and France, some installations have used a mixed process (Eluex process) in which extraction by amines was performed on eluates of ion exchange resins. Due to the slow kinetics of the transfer reaction, the industrial installations use mixers/settlers of various types, and the current trend favours models in which circulation of the phases and agitation are performed by the same turbine.

Another important source of uranium is the recovery of this element as a by-product of the manufacture of phosphoric acid from phosphates. In the early 1970s, the following three processes were developed [29], given here by order of importance.

(1) The TOPO/D2EHPA process (trioctyl phosphine oxide/di-2 ethyl hexyl phosphoric acid) which uses two purification cycles, and in which the extracted species is hexavalent uranium.

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Uranium is stripped in the first cycle by reduction to U (IV) by the Fe (II) ion in phosphoric medium. Oxidation is then necessary to extract the hexavalent uranium in the second cycle, and stripping is carried out with ammonium carbonate. Improvements to this process have been proposed [1], aimed to reduce it to one cycle (URPHOS process) or to replace the two solvents by more efficient compounds of the same class, di-n-hexyl methoxy phosphine oxide for TOPO, and bis-dibutoxy 1-3 propyl phosphoric acid for D2EHPA, but these modifications did not lead to industrial applications.

(2)   The OPPA process, which was used in the production of super phosphates. The solvent, octylpyrophosphoric acid, is employed diluted to 3% in kerosene. It extracts the tetravalent uranium, which is stripped by hydrofluoric acid in the form of the tetrafluoride UF_4. This process was used by Gardinier Inc.

(3)   The MOPPA/DOPPA process, in which the solvent consists of an equimolecular mixture of mono- and di-octylphenyl phosphoric acids, extracting tetravalent uranium. Stripping takes place in 10 M phosphoric acid medium in the first cycle. In the second cycle, stripping is carried out with ammonium carbonate. The process has been used in Canada.

Many solvents were considered, but developments in the uranium market in the 1980s led to the closure of many production units, and the TOPO D2EHPA process is the only one used today in the area of phosphoric acid. R and D projects were simultaneously curtailed.

Mixers/settlers are generally used today. Pilot experiments in pulsed columns have been described on the TOPO/D2EHPA process [7] and in centrifugal extractors [18] (ISEC 1986) on the process using mono- and di-alkyl phosphoric acids.

After dissolution in nitric acid and, if required, clarification, the concentrates are ., ned by extracting the uranyl nitrate with tributylphosphate. The uranium solution (about 400 g•t^{-1}) is sent to the extractor against a countercurrent stream of organic solution, consisting of TBP diluted to 20 to 40% in a paraffinic hydrocarbon. The desired purity is obtained by washing the solvent with nitric acid or purified uranyl nitrate. The nitrate is then stripped in deionized water. These liquid/liquid extractions take place in mixers/settlers or, more generally, in pulsed or mechanically-agitated columns.

THORIUM PRODUCTION

Unlike uranium, thorium does not have a fissile isotope, but like ^{238}U, ^{232}Th can lead to a fissile isotope by the capture of a neutron. The uranium 233 formed can hence allow a chain reaction. The thorium thus represents a potential reserve that is interesting for the supply of nuclear power. The possibility of regeneration has been inventoried, leading to programs for the purification of thorium and the production of uranium 233. While this alternative has not to any degree enjoyed the development comparable to that of uranium, work has been carried out on it in many countries.

Monazite is one of the most important of natural thorium resources. Concentrates are obtained after sulphuric or sodium leaching by precipitation methods. However, several solvent extraction processes have been employed on solutions from sulphuric leaching [17]. They are based on the

ORNL work already mentioned, thorium being extracted preferentially by primary or secondary amines. The uranium present is removed by extraction in a tertiary amine. The thorium is then extracted in a primary amine.

Also noteworthy is the use of di-alkyl phosphoric acids to perform extraction, with the thorium then recovered in sulphate form after stripping with 10 M sulphuric acid.

For uranothorianite ores, the presence of thorium and uranium leads to the simultaneous purification of both elements by the extraction of their nitrates with tributylphosphate. Since thorium is less extractable, the aqueous phase must contain large amounts of nitrates. For example, the Bouchet plant (France) used 33% TBP in kerosene to extract an aqueous solution of U and Th nitrates containing 1 M HNO_3 and 4 M $NaNO_3$. The U and Th nitrates were recovered by stripping with water from TBP, and the thorium was precipitated from this solution by oxalic acid [12].

Thorium is refined from impure concentrates in a tributylphosphate extraction cycle [6]. The concentration used varies from one country to another. The diluent may be paraffinic (kerosene) or aromatic (Solvesso-150, xylene). Weldon Spring (USA) extracted thorium from a nitric solution in a concentration of 0·5 M in acid, 1·25 M in magnesium nitrate. The 45% solvent in hexane was treated with water, thus achieving incomplete partition of the thorium and small amounts of uranium present. The aqueous solution obtained was purified by extracting the uranium entrained with the thorium, by 10% TBP.

These nitrate extractions with TBP were performed in mixers/settlers or in columns.

ENRICHMENT

Enrichment is the step of the fuel cycle that involves the physical separation of the two uranium isotopes 235 and 238, by gaseous diffusion and by centrifugation in present industrial processes, and possibly by laser extraction in the future. It is interesting to note that the separation technique by chemical exchange, investigated since the 1960s, has led in France to a process which, although lacking industrial implementation, reached the pilot stage before closing process development in 1988. This is the Chemex process, a term which incorporates the two components, chemistry and extraction. The main features of this process were reported recently [20].

The exchange reaction occurs between the species U^{3+} and U^{4+}, with the isotope 238 being concentrated in the trivalent species. Separation is based on liquid/liquid extraction exploiting the different behaviours of the two species in hydrochloric medium. Tetravalent uranium is extracted in tributylphosphate, whereas U^{3+} remains in the aqueous phase. The TBP is used at about 40% in a commercial mixture of alkyl benzenes (Solvesso 150). The U concentration is 0·5 to 0·6 mol·l^{-1}. The aqueous phase contains 4·6 to 5·2 mol·l^{-1} of hydrochloric acid, and 1·5 to 1·8 mol·l^{-1} of uranium consisting of 94% trivalent uranium.

Pulsed columns are used for this exchange reaction, operating in a continuous organic phase. Given the large number of stages necessary to achieve significant enrichment, the columns are mounted in series. The cascade has a reflux recycling the uranium at its two ends: in the aqueous phase after reduction, and in the organic phase after oxidation and extraction.

In the pilot plant experiment conducted in Grenoble, 16 columns were used in series, each of them 150 mm in diameter and 50 m high.

REPROCESSING

The goal of this operation is to recover the non-transmuted uranium and the plutonium formed for subsequent uses: recycling after enrichment for U, fabrication of weapons or mixed fuels for Pu. These elements are purified in a liquid/liquid extraction step after dissolution of the fuels in nitric medium.

Due to the high radioactivity of the irradiated fuels, considerable R and D work and constant improvements in industrial operation have been carried out to guarantee (1) quantitative recovery of perfectly decontaminated species (decontamination factor 10^6 to 10^8), (2) safe conditions for operating personnel, (3) maximum reduction of wastes, and (4) packaging of the wastes.

Historically, after the implementation of the Redox process using methylisobutylketone as solvent in the United States [11], and the Butex process using dibutoxy di-ethyl ether in the United Kingdom [16], tributylphosphate became the sole choice in the 1950s. Today, as observed by Naylor [22] at ISEC 1988, it still represents the universal solvent for the nuclear fuel cycle, because of its many favourable properties: satisfactory extraction power eliminating the need for salting out agents, good chemical stability, good physical properties although its density and viscosity require its dilution in heavier solvents than water, carbon tetrachloride CCl4, for example, or lighter solvents such as paraffinic hydrocarbons. Some installations have operated with CCl4, while most of the others use either n-dodecane, mixtures of isomers of hydrogenated tetrapropylene, or saturated hydrocarbons containing naphthenes.

No single extraction flow sheet with TBP exists, but many flow sheets adapted to the problem at hand [28]. For natural uranium or slightly enriched fuels, the TBP concentration normally used is 30%. The uranium and plutonium are co-extracted and then separated by reducing partition, in which the plutonium reduced to the trivalent species is returned to the aqueous phase. The uranium is then stripped with very dilute acid. This partition can be carried out either in the first cycle or in the second. In every case, it is followed by one or more purification cycles for each of the elements.

In the processing of highly-enriched fuels (often based on U/Al alloy), the plutonium in very small quantities is not recovered. In reduced form (Pu III), it follows the fission products. The uranium purification cycles use dilute TBP (less than 10% as a rule).

The reprocessing of mixed fuels from fast breeder reactors (UO_2/PuO_2 mixture), already carried out in pilot installations, is characterized by an increase in the Pu/U mass ratio.

Irrespective of the type of fuel reprocessed, the U/Pu separation operation is essential, and the decontamination factor of U in Pu is close to 10^6. The reducing agents used to perform this separation are ferrous sulphamate, a rapid reducing agent but presenting the drawback of introducing foreign salts into the system, uranous nitrate stabilized with hydrazine, also rapid, whose ions increase the uranium inventory, and hydroxylamine nitrate stabilized with hydrazine, whose action is slower than the other two, but without increasing the salt content. The use of electrolysis in

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stabilized medium help to avoid the introduction of a reducing chemical reagent [25]. It has not yet been applied to large industrial units.

Among the specific features of nuclear fuel reprocessing, the effect of $\alpha/\beta/\gamma$ radiation on the solvent causes a change in its properties. The appearance of di- and mono-butyl phosphoric acids has many consequences. On the one hand, these compounds are strong chelatants to the ions and species in solution such as uranyl ions, tetravalent plutonium and zirconium, and their extraction is increased, while their stripping becomes more difficult.

Losses of fissile material in the effluents, and a concomitant increase in their activity are observed. As to zirconium, this chelating action is reflected by an increase in the γ activity of the solvent and possibly the appearance of precipitates at the interface of the two aqueous and organic liquids. These solids accumulate, causing increasing solvent degradation and decreasing performance.

Some of these compounds also display surfactant properties. If their content is too high, the operation of the extractors is disturbed, particularly by the physicochemical change in the materials, such as wettability.

Prevention of the formation of these acidic compounds relies in particular on the maximum possible reduction of contact time between the aqueous phase containing the fission products and the organic phase. Short contact time extractors have been employed, including columns and centrifugal extractors. The latter have been used since 1966 at the American Savannah River plant in the first extraction cycle, with highly satisfactory results [23]. At the Marcoule plant where mixers/settlers are employed, the process has been altered, since prevention by reducing contact time was unfeasible. The introduction of hydrofluoric acid into the aqueous solution in strictly calculated quantities has led, through selective chelating of zirconium, to a significant improvement in performance [5]. This process has been in operation for 20 years.

Very close attention has been paid to these processes and to their consequences in the design and construction of the large facilities in service and being built in France. Bernard and Chenevier [3] have described the improvements made to the process and to the equipment of the UP3 plant. They include the following.

(1)   Special treatment of the solvent discharged from the plutonium purification cycles before its regeneration and recycle. This consists of stripping the tetravalent uranium in mixers/settlers, traces of plutonium subsisting in the TBP after stripping with hydroxylamine nitrate.

(2)   Vacuum distillation of the solvent, regenerated in the standard manner by carbonate and caustic washing. This operation, performed on a part of the stream, achieves additional decontamination and serves to remove the heavy products resulting from the degradation of TBP.

(3)   Diluent washing of all the aqueous streams leaving the extractors to remove the soluble or entrained TBP. The subsequent degradation of the TBP tends to disturb the operation of the evaporators. This organic washing stream has a low throughput and is added to the rest of the solvent at the regenerator inlet.

(4)   New extraction units are planned in the first cycle. These are annular columns designed to solve criticality problems. They are fitted with baffle plates. It has been shown that this type of

plate is far less sensitive to a variation in wettability of the material than sieve trays. If the acidic alkyl phosphorus compounds are deposited on the surfaces, they become hydrophobic and considerable disturbances are observed in the hydrodynamic conditions and hence in performance. These consequences are absent with baffle plates.

It is interesting to note that, in addition to TBP, tertiary amines have been used in some installations [30]: La Hague, Eurochemic in the plutonium purification cycle, Eurex in the reprocessing of irradiated U/Al fuel. At the La Hague plant, extraction by trilaurylamine was performed in nitric medium of moderate acidity, the extracted species being $Pu(NO_3)_6(R_3HN)_2$. The plutonium was stripped without changing the oxidation state, by placing the solvent in contact with a sulphuric aqueous solution. The low capacity of the solvent, and the presence of sulphate ions, led to the replacement of this purification cycle by a tributylphosphate cycle after seven years of operation.

After nitric dissolution of metallic thorium, or of the oxide ThO_2 or the mixed oxide ThO_2/UO_2, irradiated thorium was reprocessed from the 1950s in the United States, and also, on a smaller scale, in the United Kingdom and France. The process used is similar to the Purex process (Thorex process). It employs TBP [4]. the main differences are as follows: (1) the low extraction coefficient of thorium compared with uranium, hence the need to salt out by aluminium nitrate in weak acid medium, or by strong nitric acid, (2) thorium/uranium partition is performed without a valency change, exploiting the difference in extractibility of the two elements, and (3) the limited solubility of thorium nitrate in the TBP/paraffinic diluent mixture leading to low saturation and to decontamination of fission products lower than that obtained in the Purex process.

One of the planned uses was the reprocessing of ThO_2/UO_2 fuels from high-temperature reactors. The limited development of these reactors and of the uranium 233/Th reactor led to the abandonment of these projects.

RECOVERY OF TRANSURANIUM ELEMENTS

Among the by-products of the reprocessing of irradiated fuels, the transuranium elements Np, Am and Cm have given rise to recovery for subsequent use in various applications, chiefly to supply the programme of isotopic power generators. The irradiation of these elements in high-flux reactors has led to the production of plutonium 238 and curium 244, as well as transcurium elements. Although these activities appear as auxiliary to the fuel cycle, they are associated with it by their general characteristics: very high radioactivity of the isotopes, high purity required. Thus the methods of approach to the treatment of targets benefited from the experience gained in reprocessing and, in exchange, provided information about the extraction of trivalent actinide species, and the degradation of solvents containing short-lived emitters, two problems that reprocessing may have to contend with in the future.

In the extraction processes, neptunium 237 has properties similar to those of uranium and plutonium in the same valency state. The species NpO_2^+ is relatively unextractible and stable. By slight changes in the conditions of the Purex process [13], neptunium can, in the first cycle, either accompany the fission products, or accompany the U and Pu, most of it following one or the other in

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partition. It is then separated from them in their respective purification cycles. Since it is in very dilute solution, it can be recycled to the process for concentration. Final purification is carried out on anion exchange resin or by liquid/liquid extraction using a tertiary amine, the extracted species being the hexanitrate $Np(NO_3)_6(R_3NH)_2$. In the treatment of irradiated targets for the production of plutonium 238, the same separation methods are found, namely ion exchange or liquid/liquid extraction, as indicated above for the purification of neptunium. In the latter case, the first cycle is designed to extract the tetravalent species of neptunium and plutonium, with the separation of plutonium being performed by reduction to the trivalent state, followed by a purification cycle for each element [2].

The elements americium and curium have properties very similar to those of rare earths, particularly in oxidation state +3 of the ions in solution. Their extraction from high-level waste solutions was described by Orth [24] at the 1971 ISEC. Batch processing by 50% TBP of these extremely radioactive solutions, whose acidity has been reduced and the nitrate concentration raised to 6 M, leads to the recovery of the mixture of trivalent actinides and lanthanides. The separation of these two families of compounds represents the delicate part of the purification step. It has been the subject of many liquid/liquid extraction investigations: (1) extraction cycles in concentrated chloride medium, the solvent being a tertiary amine: the species $M\,Cl_5(R_3NH)_2$ are more stable in the case of actinides, which allows their separation (Tramex process), (2) extraction by TBP in nitric medium followed by separation by chromatographic development with diethylene triamine pentacetic acid (DTPA) on ion exchange resin, and (3) the Talspeak process using extraction in nitric medium by di-2-ethylhexyl phosphoric acid (D2EHPA) in the presence of DTPA: a similar process was developed with trilaurylamine and then TBP as solvents, and implemented in the extraction chromatography technique [21].

In recent years, research has been directed towards the extraction of the actinide elements from aqueous reprocessing effluents. The goal is to minimize the presence of long-lived emitters in the wastes to be stored, to limit their long-term detriment. The search for solvents capable of extracting the trivalent elements in highly acidic medium, without the addition of nitrates, has been guided towards bidentate compounds. Carbamoyl methylene phosphonates and phosphine oxides have been suggested by American researchers, and were reviewed by Schulz [26] at ISEC 88. They allow extraction in up to 7 M nitric or hydrochloric acid medium. The Truex process has thus been tried out in American production sites to treat high- and medium-level liquid residues [19]. The solvent is octyl phenyl N-N-di-isobutyl carbamoyl methyl phosphine oxide (CMPC), which can be used in a mixture with TBP. The trivalent elements are stripped by dilute acid, and the tetravalent elements by the HNO_3/HF mixture.

Another class of solvents, currently under development in France in particular [10], is represented by the diamides of carboxylic acid, which offer the advantage over organophosphorous compounds of being completely incinerable. Here also, extraction can be achieved in highly acidic medium, with stripping by dilute acid.

CONCLUSIONS

As we have seen, the solvent extraction process has been applied for over 40 years to a wide variety of purification problems in the different steps of the fuel cycle, and often in extremely severe irradiation conditions. The experience gained concerns many organic compounds involving the main mechanisms of extraction: solvation, cation exchange and anion exchange.

This experience has furnished an invaluable body of data to pursue the essential objectives: enhanced recovery performance of valuable elements, and reduction of the activity of wastes to be packaged.

Intensive fuel reprocessing may prove advisable in the long term. One could then consider not only the separation of uranium and plutonium, but also that of all the elements with long-lived isotopes, whose detriment would be unacceptable for future generations. Should such a programme become necessary, solvent extraction will occupy an important place in the processes, given the qualities hitherto exploited in the fuel cycle.

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