CHEMICAL REVIEWS

Review

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Recovery of Uranium from Wet Phosphoric Acid by Solvent Extraction Processes

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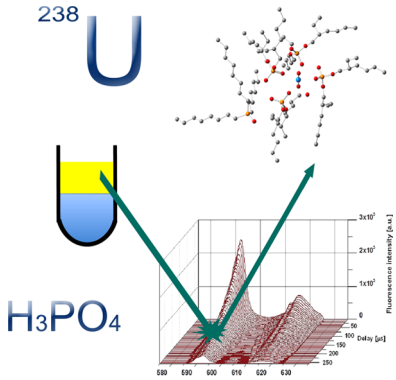

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1. INTRODUCTION

Uranium is mainly used as fuel for the production of nuclear energy as harnessed in generating electricity in many countries such as the United States, France, UK, Japan, India, China, and others. To a lesser extent, uranium is also used in reactors for propulsion of naval vessels, for basic and applied research, and for production of radioisotopes for multiple applications such as the treatment of cancer or for medical imaging. Uranium is recovered from ores by hydrometallurgical processes including ore dressing (physical separation and grinding), ore leaching, and purification by solvent extraction or, less commonly, resin-ion exchange. Leaching extracts the metal from ores, producing leachate solutions that then feed the liquid–liquid extraction processes where the metal is selectively extracted into a water-immiscible organic phase (Figure 1). The loaded extraction solvent is fed into the stripping step where the metal is back-extracted into an appropriate aqueous solution, thereby achieving concentration of the uranium and purification from other metals in the initial leachate. In certain cases, other valuable metals such as molybdenum and vanadium can be coextracted and recovered as valuable byproducts. In all cases, uranium is precipitated from the resulting strip solutions as convenient salts such as ammonium diuranate, collectively called yellow cake.

Today, the world produces 64 000 tons of uranium per year, whereas current reactors require approximately 78 000 tons of uranium each year.[4] The difference comes from drawdown of nuclear stockpiles, especially conversion of weapons materials to fuels. Nevertheless, current mining will not meet demand in the next decades, thereby incentivizing additional production from a number of mines and permitted projects on standby.

Since the 1950s, much research has focused on the recovery of uranium from wet phosphoric acid (WPA) because of the potential for this resource to supply a significant part of the world uranium production.[1−3] For instance, 11 000 tons of uranium could have been produced from WPA toward the total of 57 000 tons of uranium produced in the world in 2011.[4] Furthermore, the exploitation of this unconventional resource is economically

Received: March 17, 2014
Published: November 17, 2014

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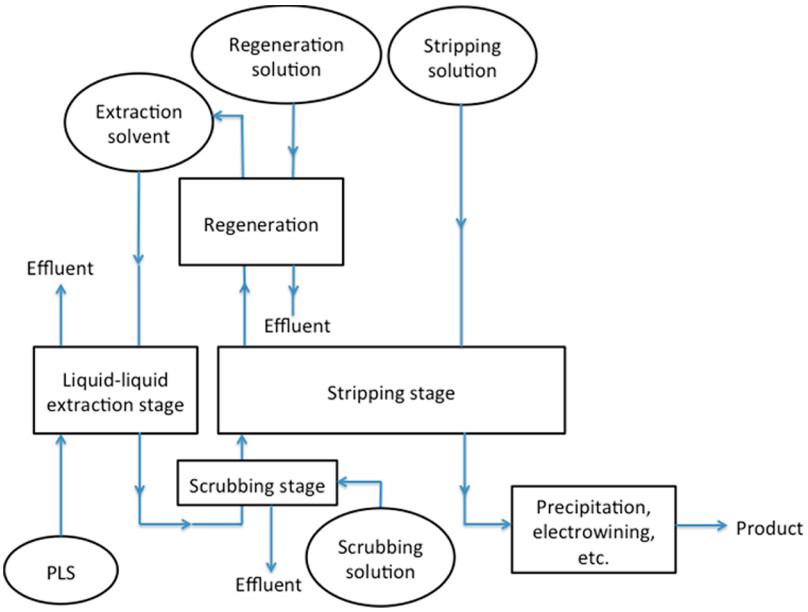


Figure 1. General flowsheet of liquid−liquid extraction.

attractive, as a large part of the capital expenditure and the operational expenditure of mining, including ore preparation and leaching, has already been borne by the phosphate industries. The research driven by these incentives over several decades led to the development of three solvent extraction processes[5−8] and one process based on precipitation.[9,10]

The chronology of uranium market prices and uranium production from WPA as shown in Figure 2 reflects demand

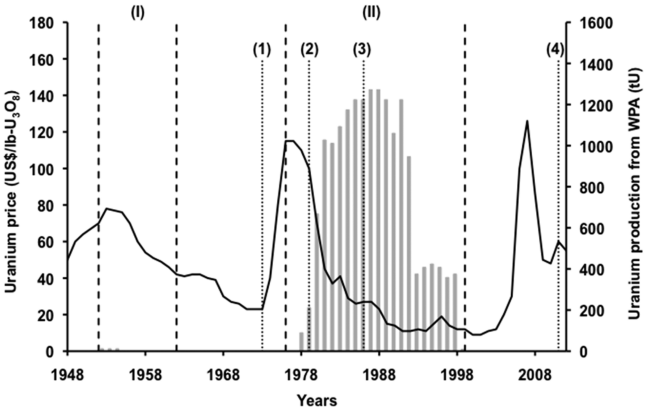


Figure 2. Uranium production (tU) from WPA (gray square from ref 12) and uranium spot price history (black line). Adjusted for inflation to January 2009 dollars (1948−1967 from US DoE; since 1967 from ref 25). (I and II) Uranium production from WPA at industrial scale. (1) First Oil Crisis. (2) Three Mile Island Accident. (3) Chernobyl Accident. (4) Fukushima Accident.

from military and energy sectors. Little data concerning uranium production from WPA before 1952 are available because uranium was produced for military applications, and published reports are so few that they coincide with the baseline in the plot reported in Figure 2. Between 1952 and 1962, the arms race stimulated the production of 17 150 tons of uranium from WPA in the U.S. by precipitation and solvent extraction processes for military needs.[4] Blockson Chemical Co. developed the first process implemented for the recovery of uranium from WPA in Florida in 1952. Uranium(VI) was precipitated and calcined as U_3O_8 with a global yield of 60−70% and a purity of 40−60%.[9−11] The second process implemented by US Phosphoric Products and International Mineral & Chemical Corp. used a solvent extraction stage.[5,6] Both processes are described in greater detail later in this Review.

In 1973, the rapid rise of the fossil-fuel price due to the oil crisis was responsible for an increase of both the uranium demand and the uranium price (Figure 2). In response to the uranium demand, several solvent extraction plants started to operate in 1976 for recovering uranium from WPA. Between 1976 and 1999, the OPPA, D2EHPA/TOPO, and OPAP processes were implemented. These processes recovered 16 000 tons of uranium from WPA in several countries.[12] After the Three Mile Island and Chernobyl accidents in 1979 and 1986, respectively, the world uranium demand decreased, and many uranium mines were closed. The last plant producing uranium from WPA closed in 1999. Table 1 gathers the names of the plants that were operated between 1952 and 1999 to recover uranium from WPA, as well as the corresponding uranium and phosphoric acid capacities.[1,2,13]

From the current perspective, the global uranium demand is expected to rise to between 97 000 and 137 000 tons of uranium per year by 2035, since the world's nuclear reactor fleet should expand despite the Fukushima accident. Altogether, there are 435 operable nuclear power plants in 30 countries, 71 are under construction in 14 countries including China and India, and 484 are on order or proposed in 44 countries).[4] Demand can be expected to be met from conventional mining operations possibly augmented by unconventional sources such as seawater[14] or phosphate rocks. Whether or not they are actually utilized, unconventional sources serve at least as supply security and diversification, which can provide an effective cap on uranium price. In particular, phosphate rock appears to be one of the most attractive resources of uranium for the next decades for the following reasons:

(i) The extraction technologies are mature and fairly cheap to implement.

Table 1. Past Plants Built for the Recovery of Uranium from WPA[a]

country	location	operator/process	capacity P_2O_5 (t/year)	capacity U (t/year)	year start	year close
United States	Jolliet (IL)	Blockson Chemical Co.	100 000	31	1952	1961
		uranium precipitation				
	Bartow (FL)	International Minerals & Chemicals Corp.	100 000	31	1955	1961
		DPPA				
	Tampa (FL)	US Phosphoric	200 000	62	1957	1961
		OPPA				
	Bartow (FL)	United Nuclear Corp.	330 000	(127)	1976	1980
		OPAP	(333 000)	101		
	Pierce (FL)	Wyoming Mineral Corp.	450 000	(173)	1978	1981
		D2EHPA/TOPO		138		
	Convent (Los Angeles, CA)	Freeport Uranium Recovery Co.	820 000 (675 000)	(265)	1978	1998
		D2EHPA/TOPO	950 000	291		
	Tampa (FL)	Gardinier	450 000 (500 000)	(163)	1979	1982
		OPPA		138		
	New Wales (FL)	International Minerals & Chemicals Corp.	1 500 000 (840 000)	(290)	1980	1992
		D2EHPA/TOPO	1 700 000	500		
	Plant City (FL)	International Minerals & Chemicals Corp.	750 000 (680 000)	(231)	1980	(1985)
		D2EHPA/TOPO		166		
	Bartow (FL)	International Minerals & Chemicals Corp.	600 000 (720 000)	(254)	1980	(1985)
		D2EHPA/TOPO		279		
	Donaldsonville (Los Angeles, CA)	Freeport Uranium Recovery Co.	480 000 (360 000)	(162)	1981	1998
		D2EHPA/TOPO	540 000	166	1980	
Canada	Calgary (Alberta)	Earth Science Inc.	110 000 (144 000)	(40)	1980	1981
		OPAP		33		
	Calgary (Alberta)	Earth Science Inc.	110 000		1983	1987
		D2EHPA/TOPO				
Belgium	Puurs and Engis	Umipray S.A.	130 000	43	1980	1998
		D2EHPA/TOPO	140 000			
Taiwan	Lung Tan	Institute of Nuclear Research	33 000	10	1981	1985
		D2EHPA/TOPO				
Iraq		SOM	90 000	28	1984	1991
		D2EHPA/TOPO				

[a]Normal style: data from ref 1. In parentheses: data from refs 2,13.

(ii) Phosphate rocks contain enough uranium to supply 11 000 tons of uranium per year,[4] and the phosphate supply is diversified among multiple producers and likely stable in the long term.[15]

(iii) The cost of mining and processing of the ore has already been borne by the phosphate industry.

(iv) Other byproducts such as rare earths could also be recovered.

(v) Uranium recovery from phosphate rocks may be beneficial in terms of environmental stewardship, as phosphate rocks include about 16 elements potentially hazardous to human health, such as arsenic, cadmium, and uranium. These elements are being redistributed within the environment via fertilizer products and related production processes and may present radiological and toxic risks to human health and the environment.[16,17]

(vi) Technologies have been developed and are in place to respond rapidly to future demand; furthermore, research developments will likely result in improved efficiency in uranium extraction from WPA. Competition from other unconventional resources seems unlikely because phosphate rock is the only resource from which significant amounts of uranium have been recovered and found to be economically viable.[4] Nevertheless, long-term contracts must be put in place to create a safe investment space, as the uranium price is subject to volatility. Ulrich et al. recently published an interesting SWOT analysis that shows the strengths and weaknesses of uranium recovery from phosphate rocks.[16]

Many strategies have been developed to recover uranium from WPA based on the development of biopolymeric microcapsules,[18] liquid−liquid supported membranes,[19−21] precipitation,[22] ion exchange resins,[23−26] solvent extraction, etc. However, only solvent extraction and precipitation have been used to recover uranium from WPA at the industrial scale. After describing briefly the wet processes used to produce phosphoric acid, we give an overview of the main solvent extraction processes that were implemented at the industrial scale to recover uranium from WPA. Particular attention is paid to the physicochemistry involved in such processes as well as the extractant molecules that have been developed to improve the extraction efficiency and the selectivity of the process. In the last part of this Review, different routes to improve the cost-effectiveness of these processes are discussed.

2. WET PROCESS FOR THE PRODUCTION OF PHOSPHORIC ACID

Wet phosphoric acid (WPA) is produced by leaching phosphate rocks rich in calcium phosphate minerals such as apatite $Ca_{10}(PO_4)_6(F,OH)_2$ or francolite $Ca_{10}(PO_4)_{6-x}(CO_3)_x$-

Table 2. Typical Composition of Phosphate Rocks[27]

composition	origin				
	Russia	S. Africa (Phalaborwa)	Morocco (Khouribga)	United States (Florida)	Senegal
P_2O_5 (wt %)	38.9	36.8	33.4	34.3	36.7
CaO (wt %)	50.5	52.1	50.6	49.8	50.5
SiO_2 (wt %)	1.1	2.6	1.9	3.7	5.0
F (wt %)	3.3	2.2	4.0	3.9	3.7
CO_2 (wt %)	0.2	2.5	4.5	3.1	1.8
Al_2O_3 (wt %)	0.4	0.2	0.4	1.1	1.1
Fe_2O_3 (wt %)	0.3	0.3	0.2	1.1	0.9
MgO (wt %)	0.1	1.1	0.3	0.3	0.1
Na_2O (wt %)	0.4	0.1	0.7	0.5	0.3
SO_3 (wt %)	0.1	0.2	1.6	0.1	
Cl (wt %)			0.1		
rare earth metals (ppm)	6200	4800	900	600	
U_3O_8 (ppm)	11	134	185	101	124
As (ppm)	10	13	13	11	18
Cd (ppm)	1.2	1.3	15	9	53
Cr (ppm)	19	1	200	60	6

Table 3. Concentrations of Major Radionuclides for Different Phosphate Rocks[32]

country	uranium		thorium		^{226}Ra	^{228}Ra
	Bq/kg	ppm	Bq/kg	ppm	Bq/kg	Bq/kg
FSU	44−90		78−92		30−70	
U.S.	259−3700	62−156	3.7−22.2		1540	
Florida	1500−1900		16−59		1800	
South and Central Florida	847−1980				881−1980	
North Florida	241−981				229−884	
Idaho	1850		30		300	
Wyoming	2300		10		1200	
Brazil	114−880	22−71	204−753	55−185	330−700	350−1550
Chile	40		30		40	
Algeria	1295		56		1150	
Morocco	1500−1700		10−200		1500−1700	
Senegal	1332		67		1370	
South Africa	163−180		483−564			300−500
Tanzania	5000				5000	
Togo	1360		110		1200	
Tunisia	590		92		520	
Egypt	1520		26		1370	
Israel	1500−1700					
Jordan	1300−1850					
Australia	15−900		5−47		28−900	

$(F,OH)_{2+x}$. Phosphate rocks contain many impurities, and their nature and their concentration vary considerably from one phosphate rock to another as shown in Table 2.

Following mineral preparation that includes crushing, grinding, and beneficiation, WPA is produced by leaching the phosphate mineral concentrate with hydrochloric acid, nitric acid, or sulfuric acid:[27]

$$Ca_{10}(PO_4)_6F_2 + 20HCl \rightleftharpoons 6H_3PO_4 + 10CaCl_2 + 2HF \quad (1)$$

$$Ca_{10}(PO_4)_6F_2 + 20HNO_3 \rightleftharpoons 6H_3PO_4 + 10Ca(NO_3)_2 + 2HF \quad (2)$$

$$Ca_{10}(PO_4)_6F_2 + 10(H_2SO_4 \cdot nH_2O) \rightleftharpoons 6H_3PO_4 + 10(CaSO_4 \cdot nH_2O)_s + 2HF \quad (3)$$

About 75% of the global phosphoric acid production involves the use of sulfuric acid for leaching phosphate rocks. Indeed, sulfuric acid is very satisfactory from an industrial viewpoint because calcium is simultaneously precipitated as calcium sulfate and removed by filtration during the leaching.[28,29] Conversely, the use of hydrochloric acid or nitric acid leads to the formation of aqueous-soluble calcium nitrate or calcium chloride, respectively, which can be removed only by implementing costly additional purification stages such as solvent extraction, ion exchange, or crystallization.[30,31] Hydrochloric acid and nitric acid also efficiently liberate the comineralized radionuclides, uranium, thorium, and radium, along with their shorter-lived daughters (Table 3). In particular, the fate of radiotoxic radium in processing and its disposal can therefore arise as a serious concern. With sulfuric acid leaching, however, the bulk of the radium (roughly 80%) reports to the phosphogypsum, while

uranium and thorium mostly follow the phosphoric acid into fertilizer production.[32]

Calcium sulfate is crystallized as gypsum dihydrate ($CaSO_4 \cdot 2H_2O$), hemihydrate gypsum ($CaSO_4 \cdot 0.5H_2O$), or gypsum anhydrite ($CaSO_4$) depending on the crystallization temperature (Table 4). Therefore, WPA production generates a huge amount of gypsum; that is, the recovery of 1 ton of P_2O_5 produces nearly 5 tons of gypsum. After solid/liquid separation, phosphoric acid is concentrated by evaporation to increase the P_2O_5 content up to 50 wt % (Figure 3).

Table 4. Crystallization Temperatures To Form Gypsum ($CaSO_4 \cdot nH_2O$)

n	process	temp (°C)	acid concentration
2	dihydrate	70−80	26−32% P_2O_5
1/2	hemihydrate	90−110	40−52% P_2O_5
0	anhydride	120−130	50−55% P_2O_5

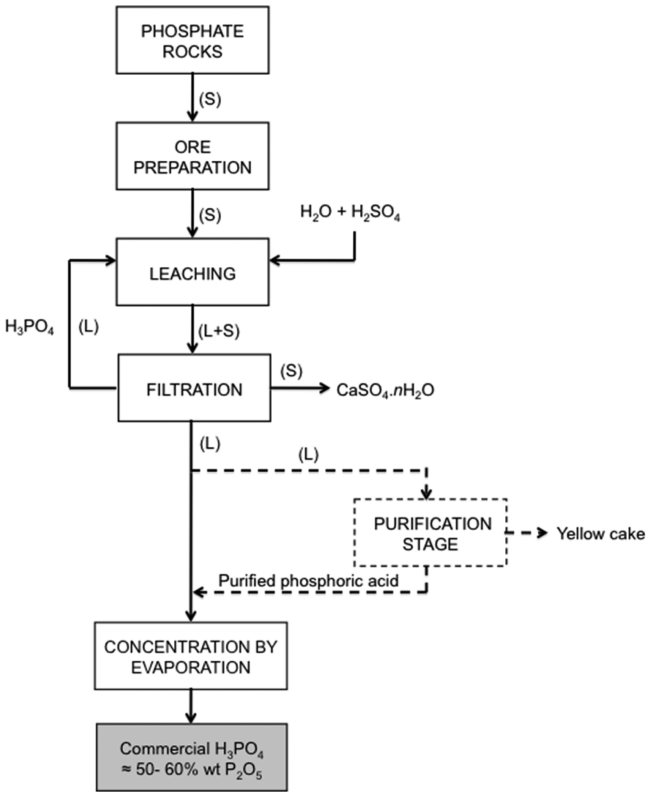


Figure 3. Global flowsheet for the production of commercial phosphoric acid by the hydrometallurgical route. The purification stage is described in Figure 4. L: liquid. S: solid. $CaSO_4 \cdot nH_2O$ with n = 0, 0.5, or 2.

Phosphoric acid must be purified, as many impurities such as iron, magnesium, arsenic, aluminum, uranium, etc., are solubilized into WPA during the leaching stage (Table 5). The degree of purification needed depends on the industrial applications. For instance, high-grade phosphoric acid must be produced for food and pharmaceutical industries, whereas low-grade phosphoric acid is sufficient for fertilizers. Several strategies for purification may be employed, involving manipulation of the conditions of any of the steps from mineral preparation to treatment of the clarified WPA. Options for treating the WPA include removal of the impurities from the WPA or extraction of phosphoric acid itself from the WPA. By employing the former approach, cadmium,[36−39] arsenic,[38,40,41] and fluorine[37,38,41,42] can be removed from WPA by volatilization, chemical precipitation, or extraction to produce animal-grade phosphoric acid. Liquid−liquid extraction is a mature technology commonly used to purify WPA to produce food- or pharmaceutical-grade phosphoric acid. In liquid−liquid extraction of phosphoric acid, WPA is contacted with an immiscible organic phase that extracts the phosphoric acid with high selectivity versus metal impurities. For instance, diisopropylether (DIPE)/tri-n-butyl phosphate (TBP),[41,43] TBP/methyl isobutyl ketone (MIBK),[44] isoamyl alcohol,[45,46] and 1-butanol and 1-heptanol[47,48] were reported as attractive extraction solvents.

Table 5. Typical Composition of WPA[a]

	concentration			
	WPA 1	WPA 2	WPA 3	WPA 4
origin:	United States	Taiwan	Iranian	Syrian
P_2O_5	30%	30%	29%	28%
U (g L^{-1})	0.165	0.067	0.083	0.06
Fe (g L^{-1})	9.0	1.22	6.6	1.3
Ca (g L^{-1})	0.8	4.56	1.5	0.85
Mg (g L^{-1})	n.d.	1.24	n.d.	5.0
Al (g L^{-1})	2.4	0.76	1.0	0.76
Si (g L^{-1})	<0.1	5.65	n.d.	n.d.
V (g L^{-1})	0.2	0.065	n.d.	n.d.
F^-	1.7 g L^{-1}	23.6 g L^{-1}	1.3 g L^{-1}	1.8 wt %
Cl^-	n.d.	0.41 g L^{-1}	n.d.	0.125 wt %
SO_4^{2-}	19 g L^{-1}	5.4 g L^{-1}	30 g L^{-1}	2.0 wt %

[a]WPA 1 from ref 7; WPA 2 from ref 33; WPA 3 from ref 34; WPA 4 from ref 35.

In the 1970s, Prayon developed a process to produce food-grade phosphoric acid from WPA.[41] A TBP/DIPE mixture was used to extract phosphoric acid at 5−25 °C with four mixers-settlers (extraction efficiency = 65%). High selectivity was attempted versus the impurities present in WPA except fluorine, sulfate, and arsenic, which were removed by implementing a pretreatment (Figure 4). In this pretreatment, phosphate rock or barium was added to the leaching solution to remove the sulfate ions.[38,41,43] Silica and defoamer were also added to remove sulfate and fluoride, and Na_2S was used to eliminate arsenic. The loaded extraction solvent was then washed with water at 5−25 °C, and phosphoric acid was stripped with distilled water at 50 °C. Heat was applied to evaporate the residual traces of solvent, and phosphoric acid was then discolored by using adsorbents. The phosphoric acid concentration was then increased by evaporation to produce food-grade phosphoric acid. The same flowsheet as in Figure 4 was also implemented to produce pharmaceutical-grade phosphoric acid, except that fluorine was removed by using steam. The resulting fluorine concentration was less than 10 ppm, while fluorine concentration in food-grade phosphoric acid is usually close to 150−200 ppm.[41,43]

3. WET PROCESSES FOR URANIUM RECOVERY FROM WPA

Blockson Chemical Co. developed the first process implemented for the recovery of uranium from WPA in Florida in 1952. In this process (Figure 5), phosphate rocks were calcined, crushed, and leached with sulfuric acid to produce phosphogypsum and phosphoric acid. The leaching solution was treated with chlorine to oxidize uranium(IV) to uranium(VI) so that no uranium

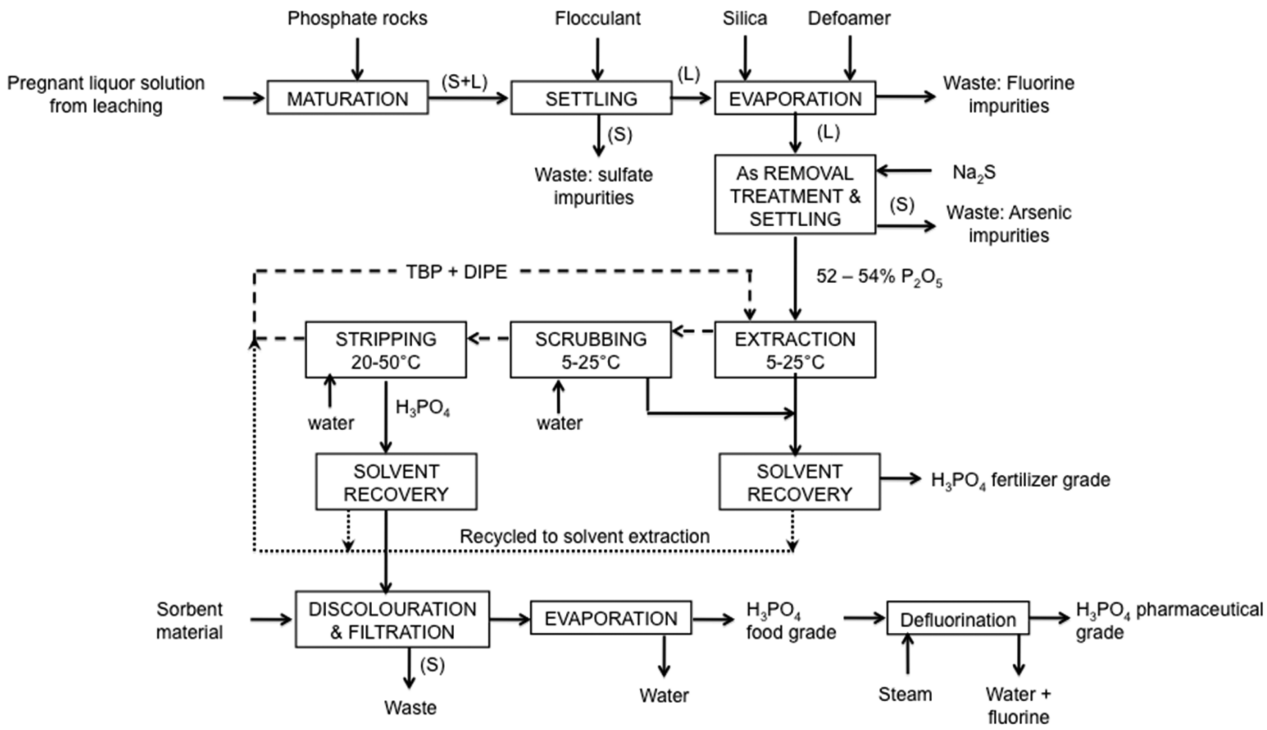


Figure 4. Prayon flowsheet for the purification of WPA.[41] L: liquid. S: solid.

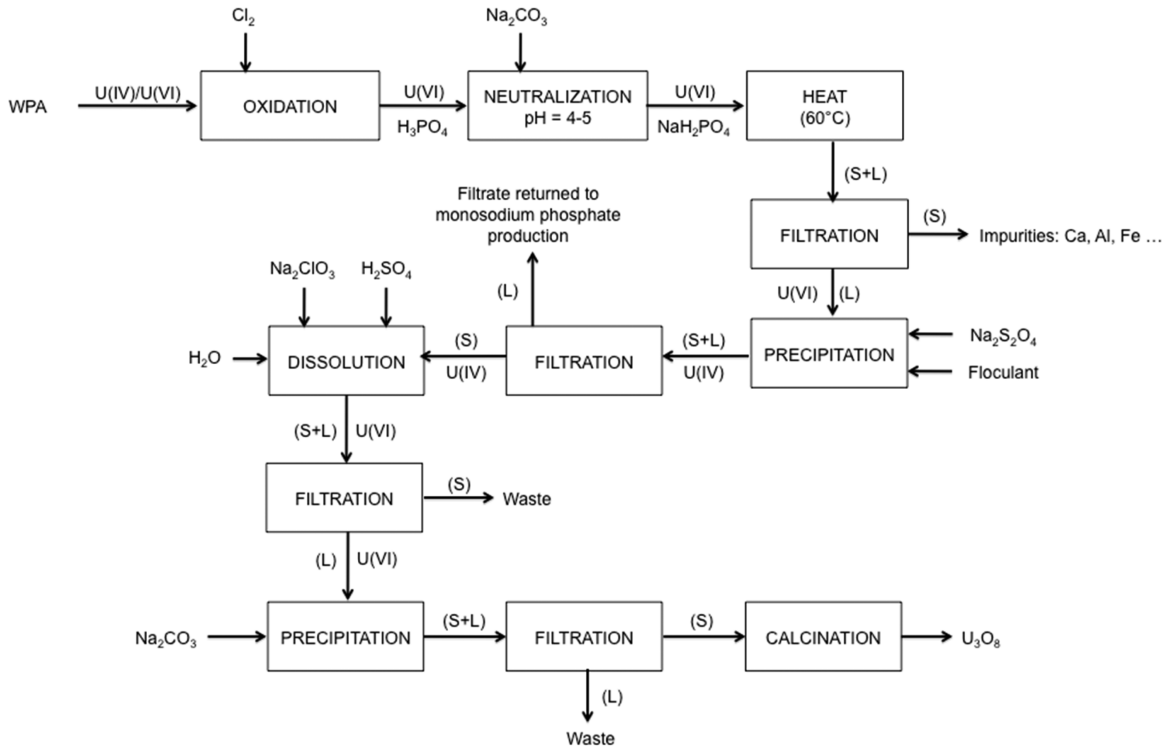


Figure 5. Flowsheet of the Blockson Chemical process.[9] L: liquid. S: solid.

precipitation occurs at pH 4−5 by adding sodium carbonate, while impurities such as calcium, iron, and aluminum precipitate as phosphates and silicates. After solid−liquid separation, uranium(VI) contained in the filtrate was precipitated and reduced to uranium(IV) by using sodium hydrosulfite ($Na_2S_2O_4$).

Uranium(IV) precipitate was then dissolved and oxidized in sulfuric acid in the presence of sodium chlorate. Uranium(VI) was then precipitated and calcined as U_3O_8 with a global yield of 60−70% and a purity of 40−60%.[9−11] The second process implemented by US Phosphoric Products and International Mineral & Chemical Corp. used a solvent extraction stage, which is described in detail later in this Review.[5,6]

In the 1950s through the late 1990s, the recovery of uranium from WPA has been performed at the industrial scale by using different extraction solvents depending on the process.

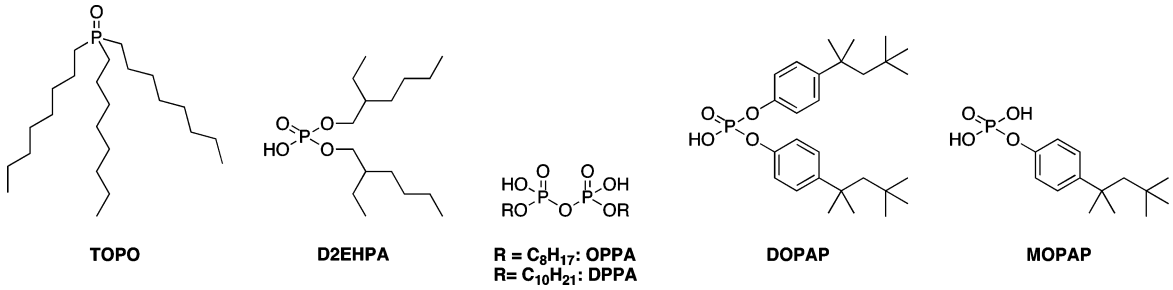


Figure 6. Chemical structure of the extractants used in OPAP, OPPA, and D2EHPA/TOPO (Oak Ridge) processes.

Extractants employed were all organophosphorous compounds used singly or in synergistic mixtures, as shown in Figure 6. Synergistic extraction usually occurs when a cationic exchanger is mixed with a solvating agent. The use of mixtures of extractants may increase the extractability and selectivity of metals by increasing the hydrophobicity of the extracted metal complexes and removing water molecules belonging to the solvation shell of metal ion:

$$M^{z+} + z\overline{HL} + b\overline{B} \rightleftharpoons \overline{ML_{z-a}(HL)_aB_b} + (z-a)H^+$$

where M^{z+} is the metal ion, HL is the cation exchanger, and B is the solvating agent. The bar means that the species is in the organic phase, whereas the absence of bar means that the species is in the aqueous phase.

However, the opposite effect may occur with certain mixtures (antagonism effect) when interactions between extractant molecules in the mixture are so strong that the metal distribution ratio dramatically decreases as compared to the single systems because less extractant molecules are available to extract metal ions. Because the two extractants generally do interact with one another to some extent in the organic phase, the formation of the mixed-extractant metal product species must be strong enough to overcome this competing effect for net synergism to be observed.

Process extractants included a mixture of bis(2-ethylhexyl)-phosphoric acid (D2EHPA, also abbreviated in the literature as DEHPA, DEPA, or HDEHP) and tri-*n*-octylphosphine oxide (TOPO),[7] a mixture of di(octylphenyl) phosphoric acid (DOPAP) and mono(octylphenyl) phosphoric acid (MOPAP),[8,49] and dioctylpyrophosphoric acid (OPPA)/didecylpyrophosphoric acid (DPPA) in kerosene.[5,6] Processes employing mixtures of D2EHPA and TOPO emerged as dominant and were considered the state of the art into the 1990s.[50]

In any of the commercialized processes, the recovery of uranium from WPA by liquid−liquid extraction takes place after the filtration stage and before the evaporation stage (Figure 4). As the uranium(VI)/uranium(IV) ratio in phosphate rocks varies from 40% to 90% depending on the origin of the ore,[7] a redox treatment is implemented before solvent extraction so that the totality of uranium is converted to uranium(IV) or uranium(VI) depending on the choice of the type of extractant used in the liquid−liquid extraction stage.[5,7−9,51] Oxidants include air, oxygen, hydrogen peroxide, chlorine, or $NaClO_3$. Reduction is generally carried out using ferrous iron or sodium hydrosulfite. Oxidation during the acidulation of the phosphate rock was shown to increase the fraction of uranium reporting to the WPA, while reducing conditions in acidulation favor uranium retention in the phosphogypsum.[1,52]

An important issue encountered in the development of processes for uranium recovery from WPA is interference due to humic substances liberated during the acidulation of the phosphate rocks. If allowed to proceed directly into liquid−liquid extraction, the humic matter is partly extracted, leading to operational problems in extraction and stripping due to crud (or "gunk") formation, emulsions, and foam.[7,53−58] To avoid such problems, organic matter is removed by calcining the phosphate rock before leaching, by contacting WPA with clay or activated carbon, or using flocculants after leaching. Other benefits of removing humic material include increased stripping kinetics and resultant reduction in equipment size,[59] decreased losses of acid and extractant,[1,53] increased yield,[54] improved precipitation of ammonium uranyltricarbonate,[7] and likely decreased consumption of redox reagents for control of the uranium oxidation state in the feed.

3.1. Oak Ridge and Urphos Processes

A research team led by Hurst (Figure 7) at Oak Ridge National Laboratory developed the first process for the recovery of uranium(VI) from WPA at the end of 1960s, continuing with further study and improvement into the 1980s. This process uses a mixture of 0.5 mol L^{-1} D2EHPA and 0.125 mol L^{-1} TOPO diluted in an aliphatic kerosene[7,60] (Figure 8). The corresponding flowsheet for the recovery of uranium(VI) from 4−6 mol L^{-1}

Figure 7. Fred Hurst tests the DEPA-TOPO process in a cascade of bench-scale mixer-settlers at Oak Ridge National Lab (Courtesy of the Oak Ridge National Laboratory, U.S. Department of Energy). Reproduced with permission from Oak Ridge National Laboratory, The ORNL Chemical Technology Division 1950−1994, Report ORNL/M-2733/R1, Oak Ridge National Laboratory, Oak Ridge, TN 37831, October 1994; p 4-3.

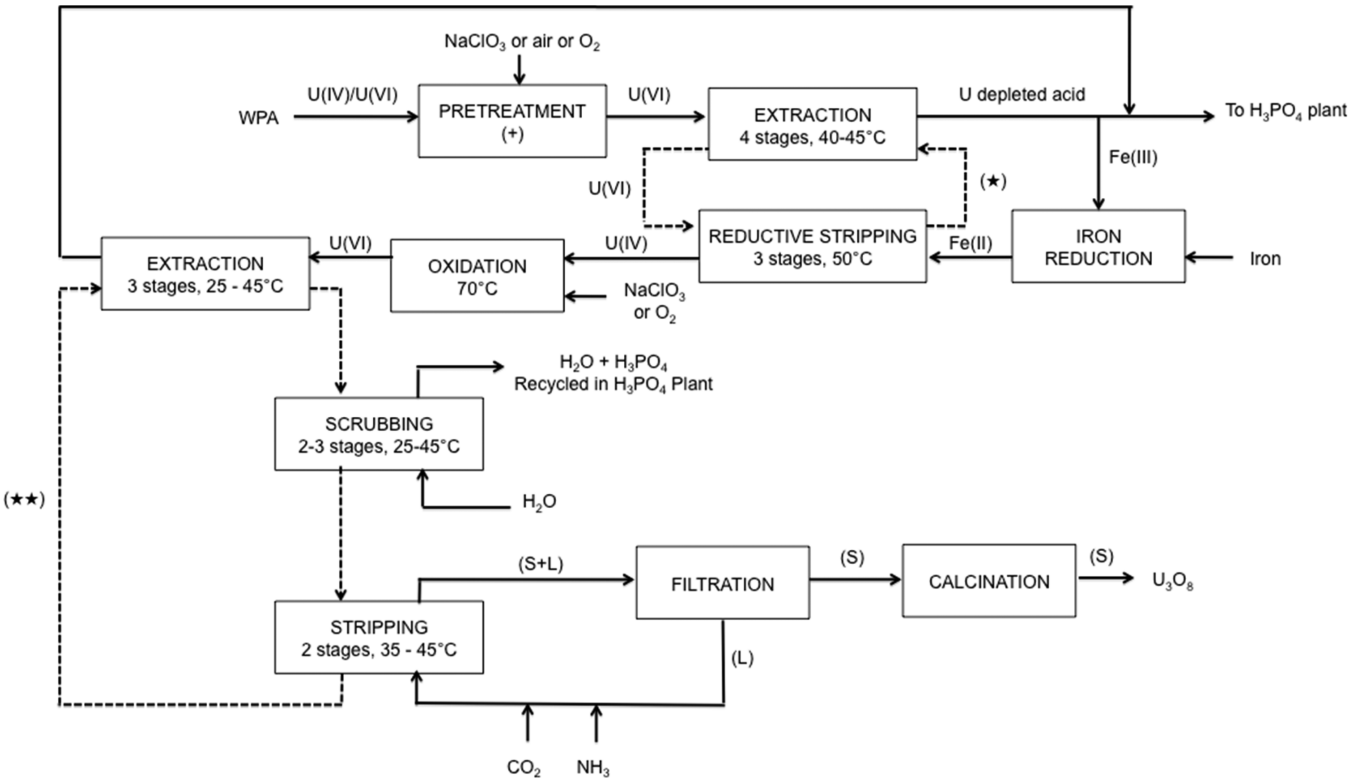


Figure 8. Simplified flowsheet of the Oak Ridge D2EHPA−TOPO process.[7] (*) 0.5 M D2EHPA + 0.125 M TOPO in Amsco 450, (**) 0.3 mol L^{-1} D2EHPA + 0.075 mol L^{-1} TOPO in Amsco 450. L: liquid. S: solid. (+) oxidation, cooling, and organic removal.

phosphoric acid is shown in Figure 8. Uranium from WPA is first oxidized to uranium(VI) at 50 °C by using $NaClO_3$ or air. The feed solution is then cooled to 40−45 °C before liquid−liquid extraction, because low temperature improves the extraction efficiency of uranium(VI) by D2EHPA−TOPO; cooling the feed below 40 °C is cost-prohibitive. About 96% of the uranium is recovered from the WPA in four stages. A reductive stripping of uranium(VI) according to eq 4 is then performed at 50 °C by using 4−6 mol L^{-1} phosphoric acid in the presence of about 15 g L^{-1} ferrous iron.[7,61] For this purpose, a portion of the raffinate treated with iron metal was employed as the stripping solution. Because of the high solubility of oxygen in the solvent, sparging of the solvent with inert gas is required. The use of 10 mol L^{-1} phosphoric acid borrowed from the evaporator effluent was subsequently recommended[62] to gain improved kinetics and reduce the amount of ferrous iron required.

$$\overline{UO_2(HL_2)_2TOPO} + 2Fe^{2+} + (6 - x)H^+ + xH_3PO_4 \rightleftharpoons U(H_2PO_4)_x^{4-x} + 2Fe^{3+} + 2H_2O + 2\overline{(HL)_2} + \overline{TOPO} \quad (4)$$

where the overbar means that the species are in the organic phase and the absence of overbar denotes species in aqueous phase. Two or three stages are required to recover about 95% or more of the uranium from the loaded extraction solvent.

Oxidation of uranium(IV) to uranium(VI) by adding $NaClO_3$ or air in the stripping solution at 70 °C is then performed, and a second liquid−liquid extraction loop is implemented at 25−45 °C by using 0.3 mol L^{-1} D2EHPA and 0.075 mol L^{-1} TOPO. Three mixers-settlers are required to recover nearly 99% of the uranium. The extraction solvent is then scrubbed by water with three mixers-settlers at 25 °C, and uranium is stripped with two mixers-settlers by using 2 mol L^{-1} ammonium carbonate,[7] resulting in the direct precipitation of ammonium uranyltricarbonate $(NH_4)_4UO_2(CO_3)_3$ according to the following equation:

$$\overline{UO_2(HL_2)_2TOPO} + 5(NH_4)_2CO_3 \rightleftharpoons (NH_4)_4UO_2(CO_3)_{2(s)} + 2NH_4HCO_3 + \overline{TOPO} + 4\overline{NH_4L} \quad (5)$$

The precipitate is then filtered, washed with ammonium hydroxide (NH_4OH), and then calcined to U_3O_8, while the purified phosphoric acid is concentrated by evaporation to produce commercial phosphoric acid at about 50 wt % P_2O_5. During the stripping step, the final product is contaminated with iron(III) due to the simultaneous precipitation of a minor amount of iron(III) carbonate. However, the degree of contamination is considered acceptable, and an excellent feed for UF_4 production is obtained.[7]

While a one-cycle process potentially offers economy, a two-cycle system was adopted in the Oak Ridge DEHPA−TOPO process.[7] In early development using one cycle with ammonium carbonate stripping, problems were encountered with the precipitation of copious amounts of iron hydroxide, which proved difficult to filter and separate from the uranium product. Humic substances extracted from the WPA feed interfered with uranium precipitation, and a high-quality ammonium uranyltricarbonate product could not be obtained. Such difficulties were avoided with the two-cycle system described above, which also provided a greater concentration of uranium in the second strip effluent, thereby reducing the consumption of ammonia for stripping in the one-cycle scheme. It may be added that the use of the same extractants in the first and the second extraction loops is advantageous, because there is no risk of contamination of the second solvent extraction loop by solubility and entrainment losses from the first solvent extraction loop.

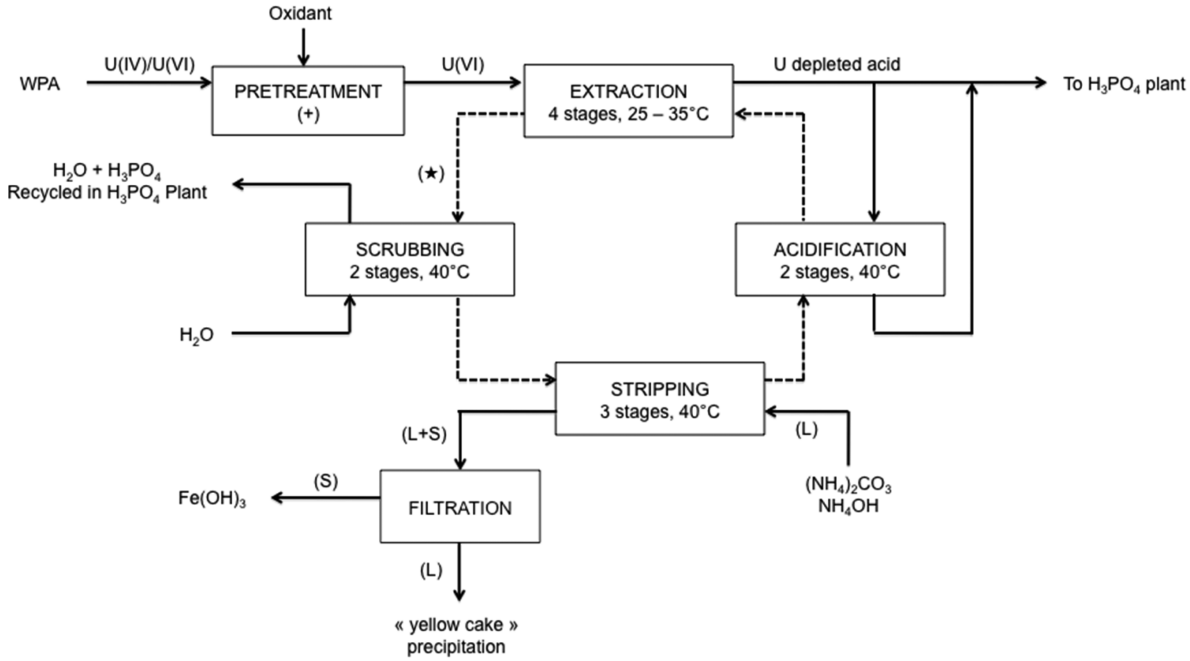


Figure 9. Simplified flowsheet of the Urphos process.[55,63] (*) 0.5 mol L^{-1} D2EHPA + 0.125 mol L^{-1} TOPO in kerosene. L: liquid. S: solid. (+) oxidation, cooling, and organic removal.

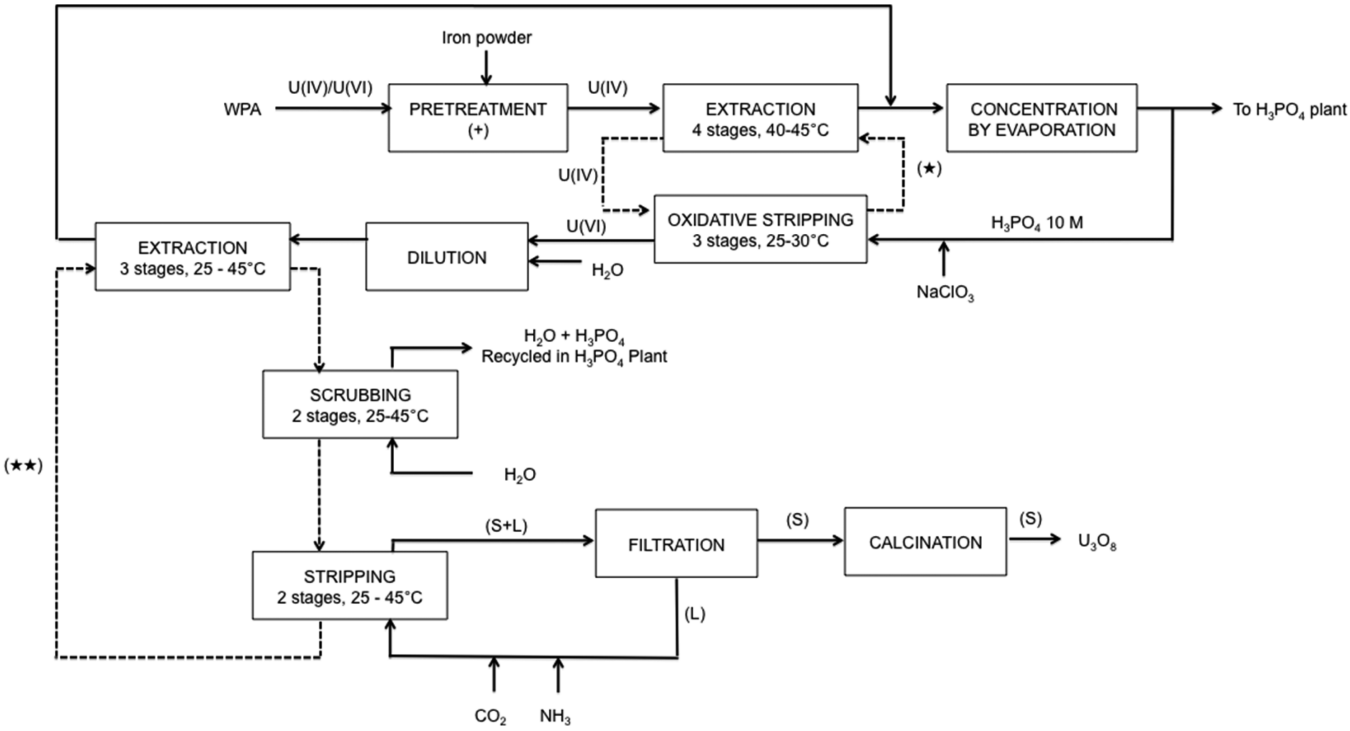


Figure 10. Simplified flowsheet of the OPAP process.[7,8] (*) 0.4–0.3 mol L^{-1} OPAP in Amsco 450, (**) 0.3 mol L^{-1} D2EHPA + 0.075 mol L^{-1} TOPO in Amsco 450. L: liquid. S: solid. (+) reduction, cooling, and organic removal.

Cogema (Compagnie Générale des Matières Nucléaire) developed the Urphos process described in Figure 9.[55,63] By contrast to the Oak Ridge process, one solvent extraction loop is implemented in this process. After oxidizing uranium(IV) to uranium(VI) by bubbling air or adding chlorate, uranium(VI) is extracted at 40 °C from WPA by 0.5 mol L^{-1} D2EHPA and 0.125 mol L^{-1} TOPO diluted in kerosene. Four mixers-settlers are necessary to extract about 99% of the uranium from WPA. The solvent is then scrubbed with water at 40 °C in two mixer-settlers. Uranium is then stripped at 40 °C by contacting the extraction solvent with ammonium carbonate at pH 8–8.5 in one mixer-settler to precipitate ferric hydroxide. The precipitated $Fe(OH)_3$ is then separated by filtration, and uranium(VI) can then be precipitated with sodium hydroxide in the presence of hydrogen peroxide.[63] The extraction solvent is then contacted with fresh phosphoric acid to reprotonate D2EHPA and to remove

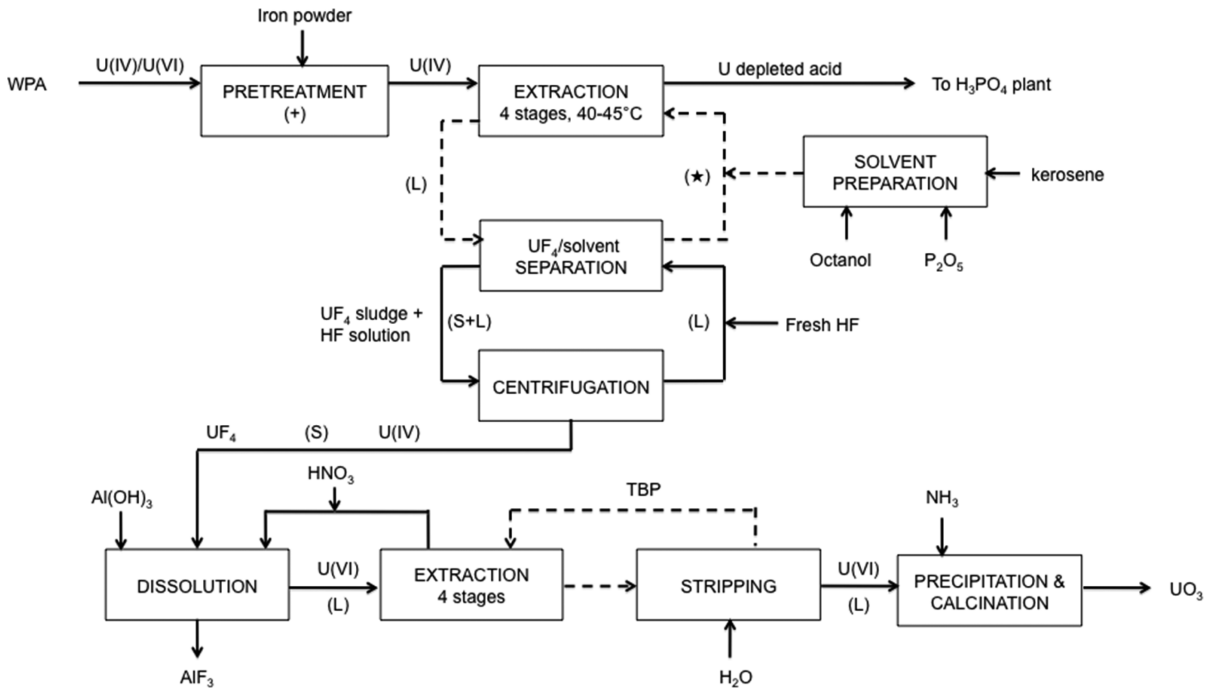


Figure 11. Simplified flowsheet of the OPPA process.[64] (★) 3% v/v OPPA in kerosene. L: liquid. S: solid. (+) reduction, cooling, and organic removal.

ammonium ion from the extraction solvent, as ammonium is coextracted into the organic phase during the stripping stage. Unfortunately, this process was never implemented at the industrial scale, precluding a comparison of the one- and two-cycle flowsheets in full-scale practice.

At the end of the 1970s, Prayon and Union Minière developed their own process based on the utilization of D2EHPA/TOPO extractants and started recovery of uranium from WPA in May 1980 in two plants in Belgium.[54] The process used was a modification of the Oak Ridge process, using two liquid–liquid extraction loops in which a solvent regeneration step was introduced after the stripping step of the second cycle as in the Urphos process. Various process improvements increased efficiency, which contributed to the longevity of the Belgium plants even against unfavorable uranium market conditions in the 1990s (Table 1). A total of 686 tU was produced in Belgium from Moroccan WPA from 1980 to 1998.

3.2. OPAP Process

The OPAP process was based on the liquid–liquid extraction of uranium(IV) from WPA by a mixture of mono- and dioctylphenyl phosphoric acid (OPAP) diluted in an aliphatic diluent. Uranium(IV) is mainly extracted by monooctylphenyl phosphoric acid (MOPAP), but the addition of dioctylphenyl phosphoric acid (DOPAP) is necessary to increase the solubility of MOPAP and avoid important solubility loss to the WPA.[64,65] This extraction solvent was very attractive initially, as it opened the way to the direct extraction of uranium(IV) without any oxidation step. In addition, the extractants are less expensive than D2EHPA–TOPO and extract uranium more strongly, which allows a higher concentration factor. In this process, uranium(VI) from WPA was first reduced to uranium(IV) by iron powder. Next, 0.3–0.4 mol L^{-1} OPAP was used to extract about 90% of the uranium(IV) from 5–6 mol L^{-1} WPA at 40–45 °C by means of four mixers-settlers in series (Figure 10).[62,66]

Oxidative stripping was then performed at 30 °C in three mixers-settlers by using a stripping solution containing H_3PO_4 at 10 mol L^{-1} in the presence of sodium chlorate. Although the distribution ratio of uranium(IV) between the organic phase containing OPAP diluted in kerosene and WPA is 3–4 times higher than that obtained with D2EHPA–TOPO in kerosene and WPA, the poor uranium(IV) selectivity of OPAP toward iron(III) is a major drawback. As a result, separation of uranium from iron was only possible by implementing a second liquid–liquid extraction stage using a mixture of 0.3 mol L^{-1} D2EHPA and 0.075 mol L^{-1} TOPO diluted in kerosene as in the Oak Ridge process (Figure 8).

3.3. OPPA Process

Dialkylpyrophosphoric acids such as didecylpyrophosphoric acid (DPPA) and dioctylpyrophosphoric acids (OPPA) (Figure 6) were used in similar flowsheets at the industrial scale to recover uranium from WPA.[5,6,67] These extractants can be prepared easily onsite by condensation of P_2O_5 with the desired long-chain alcohol to give the dialkyl esters, an attractive feature. In the OPPA process, uranium(VI) was reduced to uranium(IV) by adding iron powder to the WPA, and uranium(IV) was then extracted at 40–45 °C in four mixer-settlers with 3 vol % OPPA diluted in kerosene (Figure 11).[64] The loaded extraction solvent was then contacted with hydrofluoric acid to precipitate uranium(IV) as hydrated uranium tetrafluoride ($UF_4{\cdot}2H_2O$) called green cake:[68]

$$\overline{U(R_2HP_2O_7)_4} + 2H_2O + 4HF = UF_4{\cdot}2H_2O + \overline{4R_2H_2P_2O_7} \quad (6)$$

$$\overline{U(R_2P_2O_7)_2} + 2H_2O + 4HF = UF_4{\cdot}2H_2O + \overline{2R_2H_2P_2O_7} \quad (7)$$

However, this process does not produce nuclear grade hydrated uranium tetrafluoride due to the low selectivity of OPPA toward impurities present in WPA. Therefore, before conversion to UF_6 for uranium enrichment, the crude hydrated uranium tetrafluoride had to be purified. For this aim, the hydrated uranium tetrafluoride was dissolved in nitric acid in the

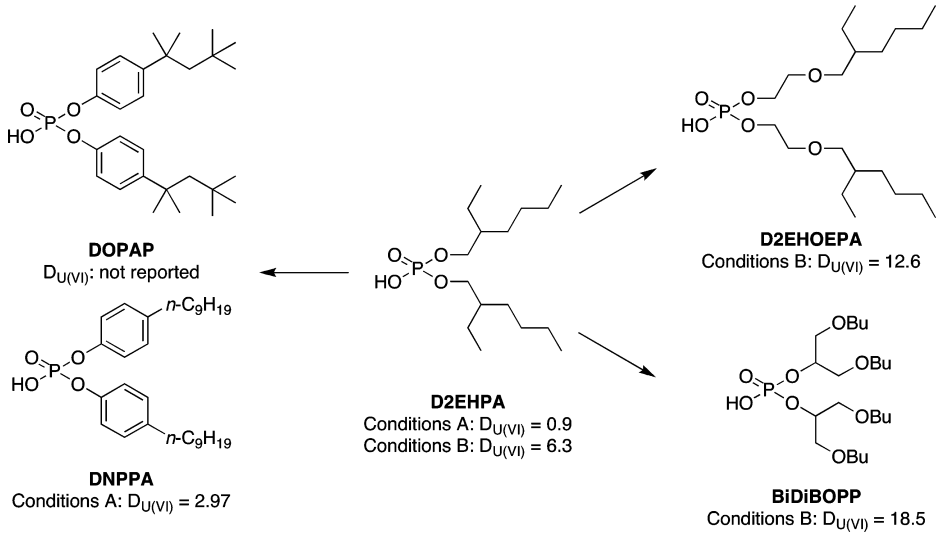


Figure 12. Chemical structure of the extractants developed to improve upon D2EHPA affinity for uranium(VI). Conditions A: Distribution ratio of uranium(VI) between a 5.8 mol L^{-1} phosphoric acid solution and 0.2 mol L^{-1} D2EHPA + 0.05 mol L^{-1} TOPO (optimized ratio) or 0.2 mol L^{-1} DNPPA + 0.1 mol L^{-1} TOPO (optimized ratio) in kerosene.[76] Conditions B: Distribution ratio of uranium(VI) between a 6 mol L^{-1} phosphoric acid solution and 0.5 mol L^{-1} cation exchanger + 0.125 mol L^{-1} TOPO diluted in kerosene.[82]

presence of $Al(OH)_3$ to remove fluoride by precipitating AlF_3 and oxidize uranium(IV) in uranium(VI).[67] After solid/liquid separation, uranium(VI) was then recovered from the nitrate solution by using tri-*n*-butyl phosphate (TBP) diluted in kerosene with four mixers-settlers in series. After the loaded extraction solvent was stripped with water, uranium(VI) was precipitated with ammonia as ammonium diuranate $(NH_4)_2U_2O_7$, and the extraction solvent was then reengaged.

The efficiency of the liquid−liquid extraction stage in the OPPA process is significantly better than that of the OPAP process or the D2EHPA−TOPO processes. In particular, the distribution ratio ($D_{U(IV)}$) of uranium between 28−30 wt % P_2O_5 and the extraction solvent reaches 100 for the OPPA process, whereas it is 25−30 for the OPAP process and 4−10 for the D2EHPA−TOPO process.[69] This allows for high concentration factors, an advantage in view of the dilute uranium concentration in the feed.

Unfortunately, the OPPA process was not as attractive overall as the D2EHPA−TOPO processes or the OPAP process despite the high distribution ratio of uranium. OPPA is quickly degraded by hydrolysis into monoalkylorthophosphoric acids.[70] This degradation quickly leads to low uranium production, and an extraction solvent unit production had to be built to produce fresh OPPA to rejuvenate the extraction solvent.[71] The degradation was so high that the extraction solvent was changed every 24 h.[10] This problem and the necessity to purify the uranium recovered by the process led to its abandonment.

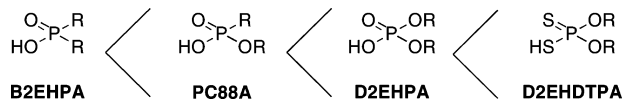
4. DEVELOPMENT OF NEW EXTRACTANTS

Despite the successes achieved in uranium recovery from WPA, the above three commercialized processes leave considerable room for improvement, inspiring new research. Major drawbacks to the developed processes are classical: insufficient selectivity and insufficient ability to treat the dilute concentration of uranium in the feed. The OPAP and OPPA processes are very attractive in terms of uranium extraction efficiency from WPA, but the presence of iron(III) in WPA is responsible for a strong decrease of the distribution ratio of uranium(VI) as well as an increase of iron content in the yellow cake.[7,8,72] The OPAP process had to be followed by a single D2EHPA−TOPO cycle to achieve the needed product purity. The D2EHPA−TOPO process as commercialized employed a two-cycle scheme to deal with the rather low extraction strength and problems with iron contamination. All of the processes required that the WPA feed be cooled due to decreasing extraction strength with increasing temperature. Finally, all of the processes were not effective at high phosphoric acid concentration.

As a result of the above limitations, considerable research has focused on the development of new efficient, selective, and robust extraction solvents that could successfully replace the standard D2EHPA−TOPO system without increasing the cost of the uranium extraction process. This section discusses the main cation exchangers and solvating agents that were developed to formulate new synergistic mixtures.

4.1. Liquid Cation Exchangers in Mixtures with TOPO

All of the cation exchangers developed for the recovery of uranium(VI) from WPA are phosphorus compounds. Among them, bis(2-ethylhexyl) phosphinic acid (BEHPA),[73] (2-ethylhexyl) phosphonic acid mono-2-ethylhexyl ester (PC88A),[74] dibutyl dithiophosphoric acid (DBDTPA),[75] and bis(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA)[76] mixed with TOPO were the subject of many papers for the recovery of uranium(VI) from WPA. These studies showed that the extraction efficiency of uranium(VI) from WPA by these molecules in mixture with TOPO follows the following order (R = 2-ethylhexyl alkyl chains):



The replacement of the phosphoric acid function of D2EHPA by a dialkyl phosphinic acid (B2EHPA) decreases strongly the extraction efficiency of uranium(VI), because the distribution ratio of uranium(VI) between 5.3 mol L^{-1} H_3PO_4 and 0.5 mol L^{-1} cation exchanger mixed with 0.125 mol L^{-1} TOPO in Isane IP 185 decreases from 9.2 to 0.2 when the cation exchanger D2EHPA is replaced by B2EHPA, respectively. Conversely, the replacement of D2EHPA by dialkyl dithiophosphoric acids

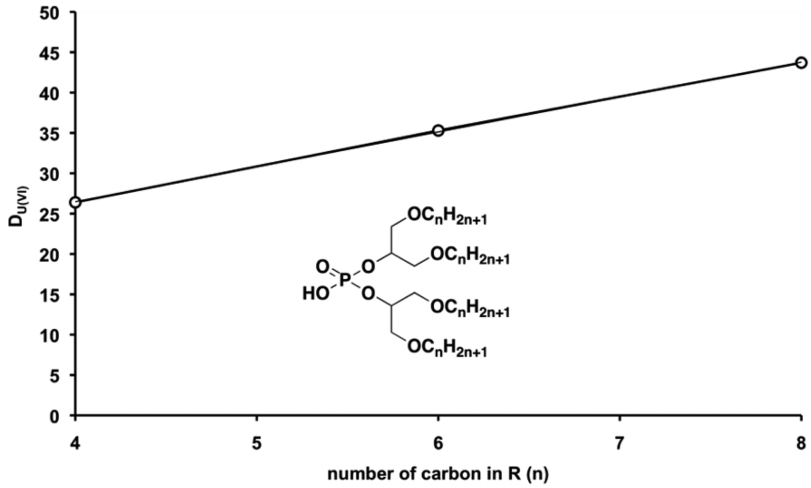


Figure 13. Distribution ratio of uranium(VI) between a 5.3 mol L^{-1} H_3PO_4 containing 0.34 g L^{-1} uranium(VI) and an organic phase containing 0.5 mol L^{-1} cation exchanger bis(1,3-dialkyloxypropan-2-yl) phosphoric acid + 0.125 mol L^{-1} TOPO diluted in Isane as a function of the number of carbon atoms in the alkyl chain; T = 25 °C, $V_O/\underline{V}_a$ = 1.[81]

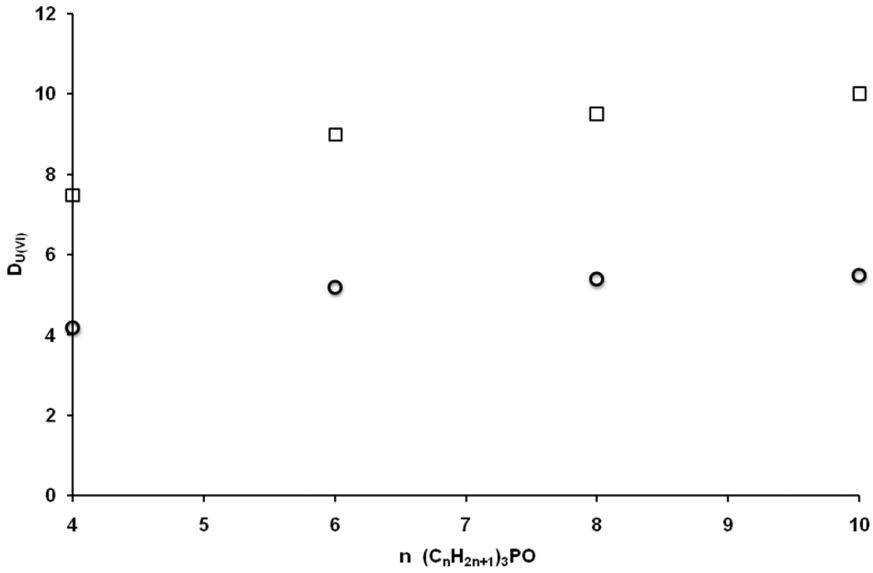


Figure 14. Distribution ratio of uranium(VI) between a 5.3 mol L^{-1} H_3PO_4 containing 0.34 g L^{-1} uranium(VI) and an organic phase containing 0.5 mol L^{-1} D2EHPA + 0.125 mol L^{-1} tri-*n*-alkylphosphine oxide diluted in Isane as a function of the number of carbon atoms in the alkyl chain. ○, T = 40 °C; □, T = 25 °C; V_O/V_a = 1.[92]

(D2EHDTPA) significantly increases $D_{U(VI)}$, which reaches 21.3.[73] Unfortunately, D2EHDTPA cannot be used in a solvent extraction process due to its low chemical stability, as D2EHDTPA can be easily hydrolyzed in acidic media and oxidized in the presence of iron(III) to $(RO)_2P(S)SS(S)P(OR)_2$.[77]

The influence of the alkyl chains on the distribution ratio of uranium(VI) was also investigated as shown in Figure 12.[73,78−85] For instance, Krea[78] and Singh[79] investigated the influence of the presence of octylphenyl (DOPAP) and nonylphenyl (DNPPA) chains on the extraction properties of uranium(VI). New dialkoxyphosphoric acids, such as phosphoric acids containing oxygen atoms in the hydrophobic part of the cation extractant, were also synthesized.[73,82−84] The presence of an ether function in the hydrophobic part of the cation extractant increases the distribution ratio of uranium(VI) as $D_{U(VI)}$ = 6.3 for D2EHPA, $D_{U(VI)}$ = 12.6 for D2EHOEPA, and $D_{U(VI)}$ = 18.5 for BiDiBOPP (phosphoric acid concentration = 5.3 mol L^{-1}; 0.5 mol L^{-1} cation exchanger + 0.125 mol L^{-1} TOPO).[82] It seems that the presence of oxygen atoms in the lipophilic moiety of the extractant increases the acidity of the cation extractant by an inductive effect, which is all the more important because the oxygen atom is close to the phosphoryl group. A recent study showed that the affinity of bis(1,3-dialkyloxypropan-2-yl) phosphoric acid such as BiDiBOPP toward uranium(VI) is significantly improved by increasing the length of the *n*-alkyl chains (Figure 13).[81]

4.2. Solvating Agents in Mixtures with D2EHPA

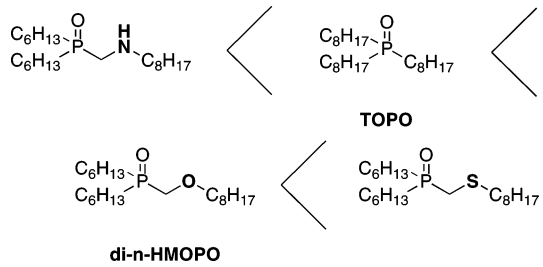
Many papers reported the substitution of TOPO in D2EHPA−TOPO mixtures by other synergistic reagents such as tri-*n*-butylphosphate (TBP) or di-*n*-butyl butyl phosphate (DBBP).[33,79,86−90] These studies showed that the distribution ratio of uranium(VI) between WPA and the synergistic mixture increases as follows:

$$\text{D2EHPA/TBP} < \text{D2EHPA/DBBP} < \text{D2EHPA/TOPO}$$

It seems that the solvating agent is bonded to uranium(VI) through the phosphoryl oxygen atom and that the strength of the bond increases in the same sequence as the electron-donor power of the phosphoryl oxygen atom, the basicity as reported by Blake.[91] The increase of the length of the alkyl chain of tri-*n*-alkylphosphine oxide is responsible for an increase of the distribution ratio of uranium(VI), as $D_{U(VI)}$ rises from 7.5 for tri-*n*-butylphosphine oxide to 10.3 for tri-*n*-decylphosphine oxide[92] (Figure 14).

The introduction of oxygen atoms in one of the alkyl chains of the phosphine oxide influences significantly the extraction properties of uranium(VI). For instance, the use of di-*n*-HMOPO instead of TOPO in mixture with D2EHPA increases the distribution ratio of uranium(VI) by a factor 1.5.[82−84] Conversely, if the phosphine oxide contains three octoxymethyl radicals, the $D_{U(VI)}$ is twice lower than those obtained with TOPO, likely due to a decrease of the extractant basicity when the number of octoxymethyl radicals increases.

One study was completed by introducing one nitrogen atom or one sulfur atom in one of the three hydrophobic chains of the solvating agent.[93] The extraction efficiency of uranium(VI) from 0.2 to 2 mol L^{-1} phosphoric acid by the resulting molecules, dihexyl *S*-*n*-octylmercaptomethyl phosphine oxide and dihexyl *N*-*n*-octylaminomethyl phosphine oxide, in mixture with D2EHPA, was evaluated and compared to those obtained with di-*n*-HMOPO:



4.3. Other Extraction Systems

The extraction efficiency of uranium(VI) from WPA by other synergistic systems containing a cation exchanger such as dibutyl dithiophosphoric acid (DBDTPA), bis(2-ethylhexyl) dithiophosphoric acid (D2EHDTPA), bis(1,3-dibutoxyprop-2-yl) phosphoric acid (BiDiBOPP), dinonylphenyl phosphoric acid (DNPPA), or (2-ethylhexyl) phosphonic acid mono-2-ethylhexyl ester (PC88A) and a neutral synergistic molecule such as di-*n*-hexyl-methoxyoctylphosphine oxide (di-*n*-HMOPO), dibutyl butyl phosphonate (DBBP), tri-*n*-butyl phosphate (TBP), or octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl methyl phosphine oxide (CMPO) was investigated by several authors (Table 6). It was shown that such synergistic systems are interesting providing that a first solvent extraction stage was implemented to concentrate uranium before the second solvent extraction stage to minimize the impurities concentration in the yellow cake (Table 7).[8]

In the 1980s, COGEMA modified the Urphos process by replacing D2EHPA/TOPO by BiDiBOPP/di-*n*-HMOPO.[93,94] With this latter system, the uranium concentration in the extraction solvent was 4 times higher than the D2EHPA/TOPO system (Table 8). Unfortunately, the selectivity toward iron(III) of this system was lower than that of the D2EHPA/TOPO system, as the iron(III) concentration in BiDiBOPP/di-*n*-HMOPO was 2.5 times greater than that in the D2EHPA/TOPO solvent. It was then necessary to scrub out the iron(III) selectively by washing the loaded extraction solvent with a mixture of phosphoric acid and sulfuric acid (Figure 15). The use of oxalic acid was also studied to scrub iron(III) from the extraction solvent.[98,100] The CAPEX of this process was estimated to be 10% lower than the Urphos CAPEX, but this process was not developed at the industrial scale due to the drop of the uranium price in the 1990s.

Table 6. Other Studied Synergistic Systems[a]

HL	T	refs
DBDTPA	di-*n*-HMOPO	75
D2EHDTPA	di-*n*-HMOPO	76
	TBP	75
BiDiBOPP	di-*n*-HMOPO	76
		94
DNPPA	DBBP	80,95
	TBP	95
PC88A	DBBP	90
	TBP	96
	CMPO	97

[a]HL and T refer to cation exchange extractants and neutral phosphorus reagents, respectively.

Research also focused on the development of extraction systems employing extractants possessing two or more functional groups.[34,40,93] For instance, polyalkylphosphasene (PN-1200) at 0.075 mol L^{-1} in kerosene leads to the same distribution ratio of uranium(VI) as that obtained with 0.2 mol L^{-1} D2EHPA in the presence of 0.05 mol L^{-1} TOPO in kerosene (Figure 16).[34,40] Autosynergistic molecules, which are bifunctional extractants containing both phosphine oxide and phosphoric acid groups, such as *O*-methyldihexylphosphine oxide *O*′-hexyl-2-ethyl phosphoric acid (Figure 16), were also tested for the recovery of uranium(VI) from WPA.[93] This molecule diluted at 0.1 mol L^{-1} in *n*-dodecane extracts uranium(VI) more efficiently from 2 mol L^{-1} synthetic phosphoric acid ($D_{U(VI)}$ = 110) than D2EHPA at 1 mol L^{-1} mixed with 0.1 mol L^{-1} di-*n*-HMOPO ($D_{U(VI)}$ = 13.1). Nevertheless, the formulation of this extraction solvent must be improved, as third-phase formation occurs during the extraction,[93] and the distribution ratio of uranium(VI) significantly decreases in the presence of iron(III) in the phosphoric acid solution.

Table 7 reports the different steps implemented in the main processes reported in the literature for the recovery of uranium from WPA. Only the Urphos and Urphos Bis processes use one extraction stage, whereas the other processes include both two extraction stages and one stripping stage as initially implemented in the Oak Ridge process. This table shows that extractant concentration varies significantly from one extraction solvent to another one depending on their extraction capacity. For instance, the use of TBP instead of TOPO is responsible for an important increase of the D2EHPA concentration from 0.5 mol L^{-1} in the presence of TOPO in the Oak Ridge process[7] to 1.5 mol L^{-1} in the presence of TBP.[88] Beyond a strictly economic viewpoint, the increase of D2EHPA concentration increases dramatically the iron(III) coextraction.[101,102]

More recently, the extraction properties of carbamoylphosphonic acid were investigated for the recovery of uranium(VI) from industrial 5 mol L^{-1} phosphoric acid containing 250 mg/L of U(VI) and 2500 mg/L of Fe(III) [Figure 16].[103−105] The extraction properties of this class of ligands appear very interesting. Indeed, they lead to high distribution ratios of uranium(VI) even when the phosphoric acid concentration is 5 mol L^{-1}, at low concentration of extracting ligands and in the

Table 7. Comparison between Different Processes Developed for the Recovery of Uranium(VI) from WPA

first cycle				second cycle			
extraction	stripping	intermediate step	extraction	scrubbing	stripping	ref
0.5 M D2EHPA + 0.125 M TOPO	20−10 g L^{-1} Fe^{2+} in 6 M H_3PO_4 (50 °C)	oxidation	0.3 M D2EHPA + 0.075 M TOPO	water	2 mol L^{-1} $(NH_4)_2CO_3$	7
			0.5 M D2EHPA + 0.125 M TOPO	water	1 mol L^{-1} $(NH_4)_2CO_3$	63
			0.5 M BiDiBOPP + 0.125 M di-*n*-HMOPO	(1) 4 N H_3PO_4 + 12 N H_2SO_4; (2) water scrubbing	1 mol L^{-1} $(NH_4)_2CO_3$	94
0.5 M DNPPA + 0.25 M DBBP	10 g L^{-1} Fe^{2+} in 8−10 M H_3PO_4 (55−60 °C)	dilution + oxidation	0.3 M D2EHPA + 0.075 M TOPO	diluted sulfuric acid	1 mol L^{-1} $(NH_4)_2CO_3$	89
0.6 M DNPPA + 0.2 M TBP	15 g L^{-1} Fe^{2+} in 12 M H_3PO_4 (65 °C)	dilution + oxidation	1.5 M D2EHPA + 0.2 M TBP	30% H_2SO_4	160 g L^{-1} Na_2CO_3	95
1.5 M D2EHPA + 0.2 M TBP	?? g L^{-1} Fe^{2+} in 11−14 M H_3PO_4 (50−60 °C)	dilution + oxidation	1.2 M D2EHPA + 0.15 M TBP	5.5 M H_2SO_4 (25−30 °C)	10−20 wt %/vol % Na_2CO_3	88
0.8 M PC88A + 0.5 M DBBP	10 g L^{-1} Fe^{2+} in 11 M H_3PO_4 (60−70 °C)	dilution + oxidation	0.3 M D2EHPA + 0.075 M TOPO	5 M H_2SO_4	1 mol L^{-1} $(NH_4)_2CO_3$	99
1 M D2EHPA + 0.5 M DBBP	10 g L^{-1} Fe^{2+} in 8−10 M H_3PO_4 (60−70 °C)	dilution + oxidation	0.3 M D2EHPA + 0.075 M TOPO	5 M H_2SO_4	1 mol L^{-1} $(NH_4)_2CO_3$	90
0.6 M D2EHPA + 0.12 M DBBP	35 g L^{-1} Fe^{2+} in 4.7 M H_3PO_4 (60−70 °C)	oxidation	0.4 M D2EHPA + 0.08 M DBBP	water	2.5−2 mol L^{-1} $(NH_4)_2CO_3$	33
10% PN-1200	(1) washing with 5% H_2SO_4; (2) 20% $(NH_4)_2CO_3$	acidification to pH 1.5−1	10% Alamine 336	water	20% $(NH_4)_2CO_3$	39

presence of iron(III) as reported in Table 9. The highest uranium(VI) distribution ratio and uranium(VI) selectivity toward iron(III) is obtained with butyl-*N*,*N*-bis(2-ethylhexyl)-carbamoyl nonyl phosphonate (BDEHCNP) [$D_{U(VI)}$ = 117; $D_{U/Fe}$ = 2800 at room temperature with 5 mol L^{-1} phosphoric acid]. Such results are 90 times higher for uranium extraction and 150 times higher for the selectivity toward iron(III) than the synergistic D2EHPA/TOPO system without third-phase formation during the extraction and the stripping, which is totally achieved by using ammonium carbonate. Furthermore, this study shows that BDEHCNP at 0.1 mol L^{-1} in *n*-dodecane extracts selectively uranium(VI) from other species potentially present in natural phosphoric acid solutions such as molybdenum, aluminum, titanium, vanadium, and zirconium. Therefore, this class of molecules paves the way to new efficient extraction processes of uranium(VI) from concentrated phosphoric acid.

5. HIGHLIGHTS ON THE PHYSICOCHEMISTRY OF EXTRACTION OF URANIUM(VI) BY THE D2EHPA/TOPO SYSTEM

Although D2EHPA/TOPO is the most common extraction solvent for the recovery of uranium(VI) from concentrated phosphoric acid, the physicochemistry of the extraction of uranium(VI) by this synergistic extraction system is not completely understood. This is mainly due to the fact that the speciation of uranium(VI) in phosphoric acid and the nature of the extracted species are still subject to controversies. The main studies on the speciation of uranium(VI) in phosphoric acid and the physicochemistry of uranium(VI) from phosphoric acid are summarized in the following part of this Review.

5.1. Speciation of Uranium(VI) in Phosphoric Acid

Several studies report that uranium(VI) in phosphoric acid exists as neutral, charged, and uncharged complexes such as $UO_2H_3PO_4^{2+}$, $UO_2H_2PO_4^{+}$, $UO_2(H_2PO_4)_2$, $UO_2(H_2PO_4)H_3PO_4^{+}$, $UO_2(H_2PO_4)_2H_3PO_4$, $UO_2(H_2PO_4)(H_3PO_4)_2^{+}$, $UO_2(H_2PO_4)_3^{-}$, $UO_2(HPO_4)_2(H_2O)_2$, and $UO_2(HPO_4)_3(H_2O)_4^{2-}$ depending on pH and phosphoric acid concentration.[105−111] However, only three papers describe the speciation of uranium in concentrated phosphoric acid.[107,108] Thamer[108] suggested that uranium complexation by phosphate ligands leads to the formation of $UO_2(H_2PO_4)_2H_3PO_4$ and $UO_2(H_2PO_4)_2$ when phosphoric acid concentration is greater than 2 mol L^{-1}. At high phosphoric acid concentration (above 2 mol L^{-1} H_3PO_4), the predominant species was postulated to be $UO_2(H_2PO_4)_2H_3PO_4$. By contrast, Elyahyaoui et al.[107,112] reported that uranium(VI) exists mainly as $UO_2(H_2PO_4)(H_3PO_4)_2^{+}$ in 4 mol L^{-1} phosphoric acid.

The presence of anionic impurities in phosphoric acid seems to modify uranium(VI) speciation. One indication that this is true is that the distribution ratio of uranium(VI) between phosphoric acid and D2EHPA/TOPO diluted in kerosene is significantly affected by the presence of F^-, SO_4^{2-}, or Cl^- in phosphoric acid, while the presence of HSO_4^- in WPA has no impact on uranium(VI) speciation in phosphoric acid.[35,65,112,113] These anions have a negative impact, and the magnitude of the decrease of the uranium(VI) distribution ratio follows the order $Cl^- < SO_4^{2-} < F^-$. This phenomenon was attributed to the formation of $(UO_2X_a)^{(2-a)}$ complexes with X = Cl^-, SO_4^{2-}, or F^-.[35]

Table 8. Comparison between the Distribution Ratios of Uranium(VI) ($D_{U(VI)}$) and Iron(III) ($D_{Fe(III)}$), and the Organic-Phase Concentrations of Uranium $[U]_{org}$ and Iron $[Fe]_{org}$ in the Urphos and Urphos Bis Processes[82,94]

extractant (0.5 mol L^{-1})	phosphine oxide (0.125 mol L^{-1})	$D_{U(VI)}$	$D_{Fe(III)}$	D_U/D_{Fe}	$[U]_{org}$ (g/L)	$[Fe]_{org}$ (g/L)
D2EHPA	TOPO	4.47	0.04	112	0.35	0.5
BiDiBOPP	di-*n*-HMOPO	21.3	0.47	46	1.5	1.3

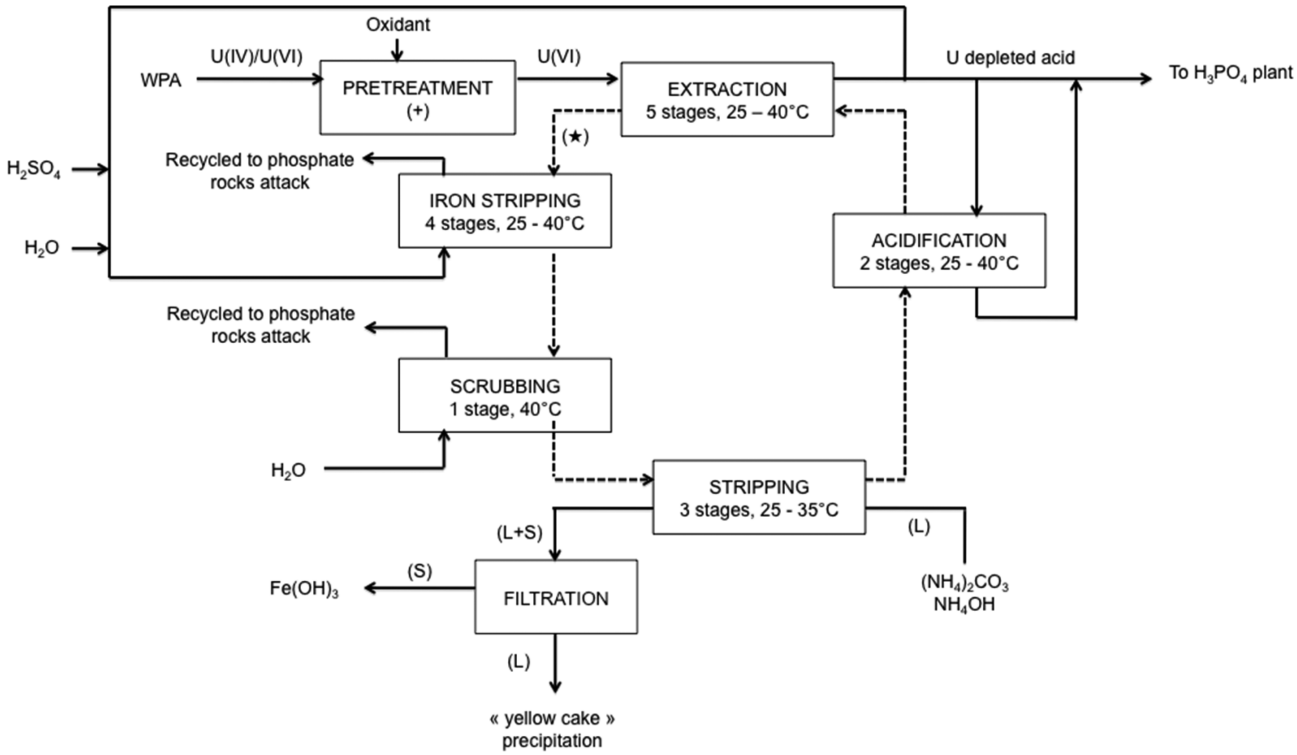


Figure 15. Simplified flowsheet of the Urphos Bis process.[91,95] (★) 0.5 M BiDiBOPP + 0.125 M di-*n*-HMOPO in kerosene. L: liquid. S: solid. (+) oxidation, cooling, and organic removal.

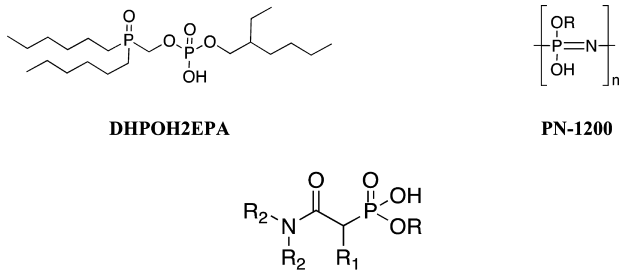


Figure 16. Chemical structure of the PN-1200, *O*-methyldihexylphosphine oxide *O′*-hexyl-2-ethyl phosphoric acid and carbamoyl phosphonic acid.

Table 9. Distribution Ratios of Uranium(VI) ($D_{U(VI)}$) and Separation Factor $S_{U/Fe} = D_{U(IV)}/D_{Fe(III)}$ between an Aqueous Phase Containing 250 mg/L U(VI) and 2500 mg/L Fe(III) in 5 mol L^{-1} H_3PO_4 and an Organic Phase Containing 0.25 mol L^{-1} Alkylcarbamoylnonyl Phosphonate in *n*-Dodecane[a]

R	R_1	R_2	abbreviation	$D_{U(VI)}$	$S_{U/Fe}$
H	Ph	2-ethylhexyl	DEHCBPA	8	80
Et	H	2-ethylhexyl		12.2	10
Et	Ph	2-ethylhexyl		65	1800
Bu	octyl	2-ethylhexyl	BDEHCNP	117	2800
D2EHPA/TOPO				3.8	200

[a]Phase volume ration O/A = 1; room temperature.

5.2. Extraction Equilibria of Uranium(VI) from Phosphoric Acid by D2EHPA/TOPO Diluted in Kerosene

Several studies concerned the extraction of uranium(VI) by D2EHPA/TOPO from phosphoric acid, but only a few of them were focused on the speciation in the organic phase and the equilibria involved in the recovery of uranium(VI) from concentrated phosphoric acid (4−8 mol L^{-1}). The addition of TOPO into D2EHPA increases significantly the distribution ratio of uranium(VI) between the extraction solvent and phosphoric acid (Figure 17). Hurst et al.[7] showed that the synergistic effect is maximal when the D2EHPA/TOPO ratio is equal to 4/1,[7] while an antagonistic effect appears at lower D2EHPA/TOPO ratio due to strong interaction between D2EHPA and TOPO leading to the formation of aggregates. The following reactions between TOPO and D2EHPA were observed by infrared spectroscopy and isopiestic experiments:[114]

$$(\overline{HL})_2 + 2\overline{TOPO} \rightleftharpoons 2\overline{HL{-}TOPO} \quad (8)$$

$$(\overline{HL})_2 + \overline{TOPO} \rightleftharpoons \overline{(HL)_2{-}TOPO} \quad (9)$$

where HL denotes D2EHPA.

More recently, Staszak and Prochaska[115] confirmed such interactions, but they did not report the stoichiometry of the D2EHPA−TOPO complexes, unlike Beltrami et al.[116] who

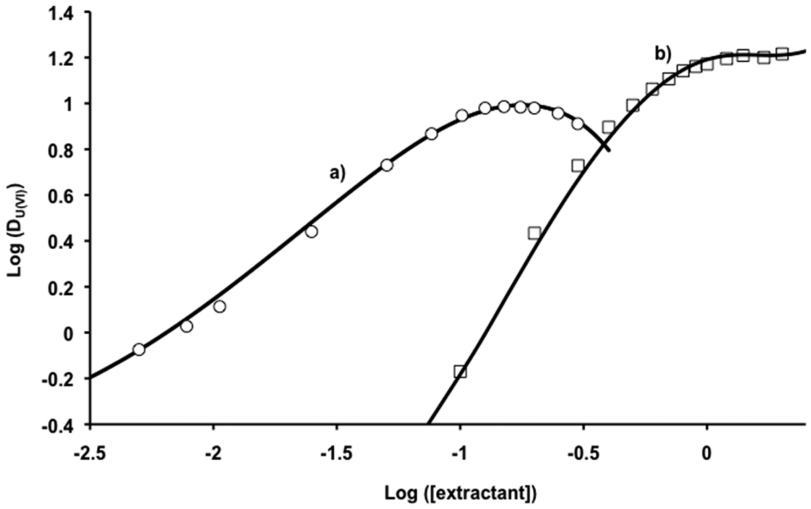


Figure 17. Logarithm of the distribution ratio of uranium(VI) at 25 °C between 5.3 mol L^{-1} phosphoric acid and D2EHPA/TOPO diluted in Isane IP 185 as a function of (a) the logarithm of initial TOPO concentration at constant initial D2EHPA concentration (0.5 mol L^{-1}), and (b) the logarithm of initial D2EHPA concentration at constant initial TOPO concentration (0.125 mol L^{-1}). Initial concentration of uranium = 1.43×10^{-3} mol L^{-1}, phase volume ratio O/A = 1. ○ and □: Experimental values. Continuous lines —: Calculated curves with the thermodynamic model of Beltrami et al.[116]

suggested the formation of higher aggregates such as $(HL)_5$—T by means of a thermodynamic model (see below):

$$\frac{5}{2}(\overline{HL})_2 + \overline{TOPO} \rightleftharpoons \overline{(HL)_5\text{—}TOPO} \tag{10}$$

Bunus et al.[118] suggested the formation of $UO_2(HL_2)_2(TOPO)_m$ complex as the major extracted species, where $m \leq 1$ depending on the TOPO concentration. Girgin et al.[84] proposed the two following extraction equilibria depending on the concentration of phosphoric acid:

$$UO_2(H_2PO_4)_2(H_3PO_4) + 3\,\overline{(HL)_2} + n\overline{TOPO} \rightleftharpoons \overline{UO_2L_2(HL)_4(H_3PO_4)_2(TOPO)_n} + H_3PO_4 \tag{11}$$

$$UO_2(H_2PO_4)_2 + (\overline{HL})_2 + n\overline{TOPO} \rightleftharpoons \overline{UO_2L_2(H_3PO_4)_2(TOPO)_n} \tag{12}$$

Therefore, literature data show that $UO_2L_2\cdot(HL)_4(H_3PO_4)_2(TOPO)_n$ may be the predominant complex in the organic phase in the range 1.5−2.4 mol L^{-1} phosphoric acid, while $UO_2L_2(H_3PO_4)_2\cdot(TOPO)_n$ may be the major species when phosphoric acid concentration is higher than 2.4 mol L^{-1}. Table 10 gathers the uranium(VI) species reported in the literature during the extraction of uranium(VI) from phosphoric acid at various ranges of phosphoric acid concentration by D2EHPA−TOPO.

More recently, Beltrami et al.[116] and Ali et al.[117] revisited the extraction equilibria involved in the recovery of uranium(VI) from 5.3 and 8 mol L^{-1} phosphoric acid by D2EHPA/TOPO

Table 10. D2EHPA/TOPO/UO_2 Complexes Extracted from Phosphoric Acid Solution by the D2EHPA/TOPO Solvent

extracted species	phosphoric acid concentration	refs
$UO_2(HL_2)_2T$	5.3 mol L^{-1}	116
$UO_2(HL_2)_2T_m$ with $m \leq 1$	4.3 mol L^{-1}	118
$UO_2L_2\cdot 2(HL)_2(H_3PO_4)_2T_n$	1.5−2.4 mol L^{-1}	84
$UO_2L_2(H_3PO_4)_2\cdot T_n$	>2.4 mol L^{-1}	
$UO_2(HL_2)_2T$	42% P_2O_5	117

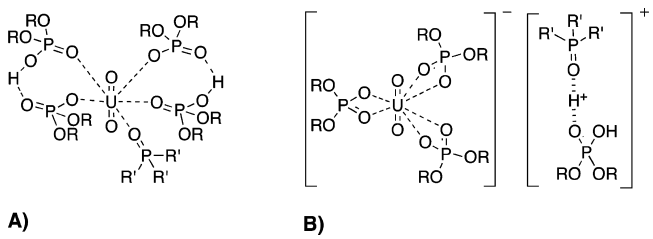


Figure 18. Speciation proposed for the D2EHPA/TOPO/U(VI) complex, (A) corresponding to Blake's model and (B) corresponding to Kennedy and Deane's model.

diluted in kerosene, respectively. Beltrami et al.[116] developed a thermodynamic model to fit the experimental distribution ratios for uranium(VI) between 5.3 mol L^{-1} phosphoric acid and D2EHPA/TOPO as a function of the concentration of D2EHPA and TOPO (Figure 17). This model permitted the deduction of the presence of aggregates such as $(HL)_2TOPO$, $(HL)_5TOPO$, and $(HL)_2(TOPO)_2$, and uranyl complexes such as $UO_2(HL_2)_2$, $UO_2(HL_2)_2TOPO$, and UO_2L_2TOPO. For the species $UO_2(HL_2)_2TOPO$ in the organic phase, TOPO has been shown to be located in the first coordination shell as deduced by time-resolved fluorescence spectroscopy (TRFS) coupled with DFT calculation.[119] Ali et al.[117] pointed out the presence of a few of these species in the organic phase by using the classical slope-analysis method.

Speciation of uranium(VI) in D2EHPA−TOPO was recently investigated by time-resolved laser fluorescence spectroscopy (TRLFS).[119] This study showed that the first coordination shell of the uranyl−D2EHPA−TOPO complex in kerosene is the same whatever the concentration of phosphoric acid in the feed solution in contact with the organic phase, at least when the phosphoric acid concentration in the aqueous phase varies between 0.73 and 7.08 mol L^{-1}.[119]

Thus, by taking into account the data reported in the literature and the models used by Bake et al.[114] and Kennedy and Deane,[120] which describe the uranyl ion in the D2EHPA−TOPO complexes, it can be inferred that the major complex $UO_2(HL_2)_2TOPO$ exists as uranyl complexed by two dimers

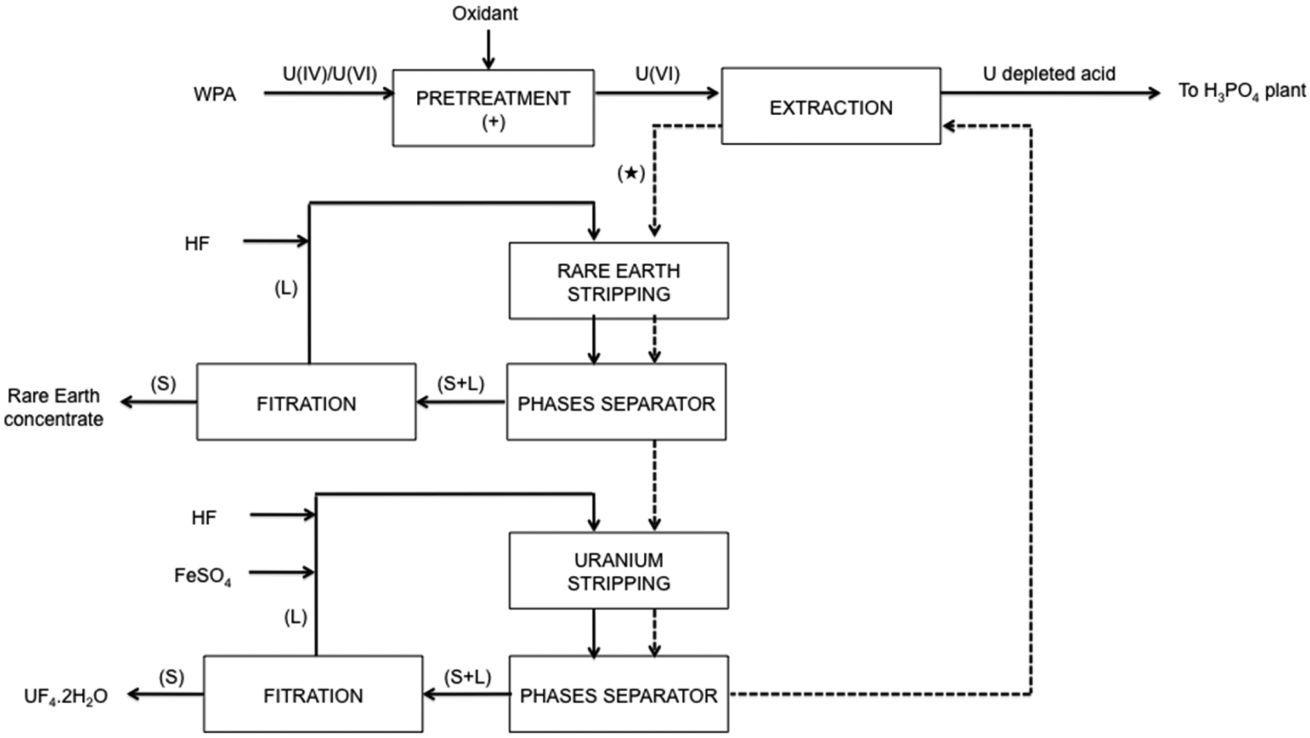


Figure 19. Simplified flowsheet of process developed for the simultaneous recovery of rare-earth and uranium from WPA.[87] (★) 1.2 mol L^{-1} D2EHPA + 0.1 mol L^{-1} TBP in kerosene. L: liquid. S: solid. (+) oxidation, cooling, and organic removal.

of D2EHPA and one molecule of TOPO or as an ion-pair as illustrated in Figure 18A and B, respectively.

6. HOW CAN THE COST-EFFECTIVENESS OF URANIUM EXTRACTION PROCESSES FROM WPA BE IMPROVED?

6.1. Simultaneous Recovery of Uranium(VI) and Rare Earth(III) from WPA

Nowadays, the uranium spot price is not high enough to consider the recovery of uranium from WPA as economically attractive in the short term, although the long-term prospects are good. However, even without a substantial price increase in uranium, the economics of its recovery can be improved in principle with the corecovery of other metal values present in WPA. Phosphate rocks contain between a few hundred to a few thousand ppm of rare earth (RE) metals depending on the origin of the ore (Table 2). Unfortunately, the REs split into various streams in the treatment of phosphate rocks, leaving on the order of only 10% in the WPA. A large fraction of the REs is lost to the tailings in beneficiation, and 60−70% of the REs are lost to the phosphogypsum during sulfuric acid acidulation. Some latitude exists to increase the yield of REs in the WPA during acidulation by manipulating process conditions, such as by increasing the sulfuric acid concentration.[123] Such changes would likely not be implemented in existing plants, whose processing has already been optimized for WPA production. Despite the limited overall yield of REs possible from WPA, their corecovery with uranium has still attracted interest, because the metals are already in solution form. The recovery of REs from phosphoric acid was investigated by using various extractant molecules, including D2EHPA, DNPPA,[121] D2EHPA/TBP,[87,89] D2EHPA/TOPO,[121] DOPPA/TOPO,[73] and DNPPA/TOPO[89] with the goal of simultaneous coextraction of uranium(VI) and REs followed by selective stripping. It was observed that the extraction efficiency of REs from 28% (wt) P_2O_5 phosphoric acid is greater.[121]

Bunus et al.[87] developed a process to extract both uranium(VI) and RE from WPA by 1.2 mol L^{-1} D2EHPA mixed with 0.1 mol L^{-1} TBP diluted in kerosene (Figure 19). An acidic fluoride medium was then used to strip the REs followed by a reductive stripping of uranium(VI) by using iron(II) in hydrofluoric acid according to the following reaction:

$$\overline{UO_2(HL_2)_2TBP} + 6HF + 2Fe^{2+} \rightleftharpoons UF_4{\cdot}2H_2O + 2FeF^{2+} + 2\,\overline{(HL)_2} + \overline{TBP} \quad (13)$$

Singh et al.[89] studied the recovery of yttrium(III) and uranium(VI) from WPA by D2EHPA−TBP and from merchant-grade phosphoric acid by DNPPA/TOPO. After the first extraction stage, a stripping solution containing 10% Na_2SO_4 mixed with 30−40% H_2SO_4 was contacted with the extraction solvent to achieve the separation of yttrium(III) and uranium(VI). Stripping of yttrium from the extraction solvent before the recovery of uranium seems to be essential to avoid yttrium contamination in the yellow cake.

Overall, given the low yield of REs to the WPA, it is an open question regarding the economics of recovering REs by solvent extraction after sulfuric acid leaching.[122,123] Viewed as a byproduct of uranium extraction, recovered REs may add value provided the extra processing costs are minimal. On the other hand, the use of nitric acid instead of sulfuric acid to leach phosphate rocks is an interesting alternative, as nitric acid solubilizes nearly 100% of the RE present in the phosphate rock.[121] As mentioned above, the liberation of radionuclides into the nitric acid presents its own set of challenges.

6.2. Recovery of Uranium from WPA with Ion Exchange Resins

Recovery of uranium from WPA by using ion exchange resins instead of solvent extraction is a good alternative because ion exchange resins are less sensitive to the temperature and ion exchange resins allow removing uranium from WPA even at low uranium concentration.[1,2,67] Thus, the implementation of ion exchange resins instead of liquid−liquid extraction may decrease the number of operations in the flowsheet and therefore improve the cost-effectiveness of the process.

The Minemet Recherche process[25] and the Israeli process[26,124] were developed to recover uranium(IV) from WPA with ion exchange resins, but these processes were never exploited at the industrial scale. The Minemet Recherche process used Duolite C464 hydroxy-phosphonic resins,[2] while the Israeli process used amino-phosphonic resins (Duolite ES467, Figure 20). Duolite C464 and Duolite ES467 extract uranium(IV) from WPA with high selectivity toward the other metals except iron(III).

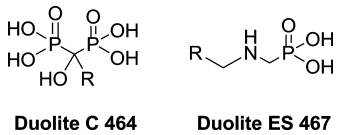


Figure 20. Chemical structure of the molecules that correspond to Duolite C464 and Duolite ES 467.

In the Israeli process (Figure 21), uranium and iron in WPA were reduced, respectively, into uranium(IV) and iron(II) by adding iron powder in the feed solution before uranium extraction with Duolite ES467. The ion-exchange resin was then washed with water to selectively strip WPA and impurities, and uranium was eluted with ammonium carbonate after removing the organic matter with ammonia. The yellow cake was produced by partial evaporation of the eluted solution. The final product was then dissolved in sulfuric acid and purified by selective precipitation with hydrogen peroxide.

Recently, Urtek developed another ion-exchange resin process.[24] The main difference between the Urtek process and the Israeli process concerns the implementation of ultrafiltration membranes to increase the uranium concentration in WPA as well as the precipitation of iron(III) by using ammonia before uranium extraction. Residual iron(III) was reduced into iron(II) by adding iron powder, and uranium(IV) was extracted by contacting the feed solution with ion-exchange resin. The resin was then scrubbed with water and ammonia and eluted with ammonium carbonate. Uranium ammonium carbonate was then extracted by a second ion exchanger column. Uranium was then eluted with sodium carbonate and precipitated as a yellow cake. This process was estimated to be cheaper than solvent extraction processes or other ion exchange processes. Indeed, it was reported in 2009 that this process permitted the production of U_3O_8 at 20−30 \$/lb, whereas the Oak Ridge, OPPA, and OPAP processes produced U_3O_8 at 40−80 \$/lb U_3O_8.

Urtek plans to build the first plant in 2015 based on resin technology. However, some issues must be solved before implementing such a technology: (i) resins are highly sensitive to chemical degradation in concentrated phosphoric acid; (ii) resins undergo mechanical stresses during sorption−desorption due to swelling phenomena; and (iii) resins are not as mature for the industrial-scale recovery of uranium from WPA as solvent extraction processes, especially regarding the iron(III) coextraction resulting in poisoning of the resins and a dramatic decrease in resin capacity.

6.3. Recommendations

Although solvent extraction seems to be easy to implement in hydrometallurgical processing and is regarded as a mature industrial separations technique, its implementation for uranium recovery from WPA leaves considerable room for technical improvement and cost reduction. During the operation of a plant, the evolution of the composition of the leaching solution or the deformulation of the extraction solvent due to chemical degradation, crud formation, extraction of humic material, or solubility losses can lead to a dramatic drop of the performance of the process and the quality of the product.[125,126] Therefore, toward reducing the production cost of yellow cake, it is of great interest to improve the chemistry of the process as well as to optimize its operation.

First, the chemistry of the process can be improved by optimizing the formulation of the extraction solvent. In particular, the influence of both the diluent and the nature of the extractant molecules on the extraction equilibria must be taken into account in the formulation of efficient extraction solvents. Extractant molecules presently used in solvent extraction are not adapted to treat WPA, because these molecules were developed more than 50 years ago for other applications. Therefore, the design of new efficient and selective extractant molecules appears to be a priority to improve the performance of solvent extraction processes. These molecules will have to extract uranium(VI) from WPA with high efficiency and high selectivity, in particular toward iron(III). The literature review reported above shows that mixtures of cationic exchangers and solvating agents as well as new single extractants like BiDiBOP, di-*n*-HMOPO, etc., exhibit attractive extraction properties. It is now necessary to explore the extraction properties of analogues of these molecules to identify other extracting agents having the greatest selectivity and highest uranium distribution ratio. For this goal, the development of QSPR calculations (structure−activity relationships) or other molecular-design methodology

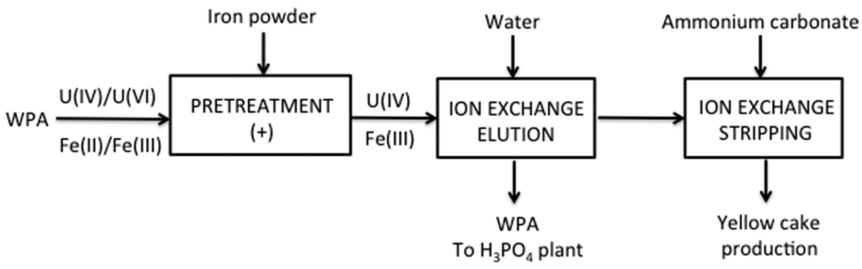


Figure 21. Simplified flowsheet of the Israeli process.[124]

could be beneficial. The most promising molecules could be used directly in solvent extraction or impregnated or grafted onto resins to develop new resin-ion exchange materials for the recovery of uranium from WPA.

In addition, solvent extraction conditions must be optimized to improve the efficiency of any deployed process, and the physicochemistry involved in the solvent extraction process must be adequately known. Thus, it appears essential to develop a tool to simulate the solvent extraction process under the range of expected conditions. Such a tool should include a thermodynamic model of the chemistry and the physics involved in solvent extraction of nonferrous hydrometallurgy (speciation, nonideality, extraction equilibria) and a database easily adaptable to the variety of WPA. Not only is it desirable to use such a tool for process optimization, but it is necessary to anticipate the process behavior to varying operating conditions (redox potential, ore composition, pH, etc.).

7. CONCLUSION

This Review gives an overview of the main processes that have been developed in the past to recover uranium from wet phosphoric acid: Oak Ridge, OPAP, OPPA, Urphos, and Urphos Bis processes. These processes rely on the use of solvent extraction and precipitation stages. The physicochemistry involved in these processes is very complicated, and many controversies are reported in the literature regarding the speciation of metal species, especially uranium(VI) and iron(III), in concentrated phosphoric acid as well as the equilibria involved during liquid−liquid extraction.

The major challenge for process on uranium recovery from WPA is to improve the uranium extraction efficiency and the uranium/iron separation in the extraction solvent stage to decrease the number of operations, the size of the plant, and the operating cost. Given that extraction solvents are at the center of liquid−liquid extraction processes, it appears crucial to identify new extractant molecules having high extraction efficiency (and high stripping efficiency) as well as high selectivity toward uranium over iron. Therefore, recent studies are focused on the selective and efficient extraction of uranium(VI) from WPA with rejection of iron(III). These studies are devoted to the search of new extractant molecules, especially organophosphorus cation exchangers, in a mixture with organophosphorus solvating agents to achieve a synergistic effect like that obtained in the reference system developed by Oak Ridge containing bis(2-ethylhexyl) phosphoric acid (D2EHPA) and tri-*n*-octylphosphine oxide. Among these molecules, a recent patent reports the development of alkylcarbamoylnonyl phosphonates, which appear as breakthrough extractants that give very high extraction efficiency and very high selectivity against iron(III) for the recovery of uranium(VI) from wet phosphoric acid.

The development of extraction processes based on the use of ion exchange resins is another interesting route even if no process is developed today at the industrial scale. The use of resins seems to be attractive because they can be used to extract uranium even at low concentration. Nevertheless, more studies are necessary to evaluate the industrial interest of such a technology for recovering uranium from WPA, and it seems mandatory to remove iron(III) before uranium extraction because coextraction of iron(III) is responsible for a dramatic decrease of the extraction capacity of current resins. Therefore, one salient challenge concerns the development of selective resins that reject iron(III) as for the extraction solvent technology.

In the future, uranium recovery from WPA may provide important ecological benefits and facilitate adherence to environmental laws as it contributes to sustainability of uranium resources even in the face of increasing long-term global uranium demand.

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Notes

The authors declare no competing financial interest.

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Dr. Denis Beltrami graduated from Université Pierre et Marie Curie (France) in 2009 after three years of research at the Ecole Nationale Supérieure de Chimie Paris (ENSCP) under the supervision of Professors Gerard Cote and Alexandre Chagnes. During his Ph.D. research, he worked on the development of new extractant molecules for the recovery of uranium(VI) from wet phosphoric acid in collaboration with Areva. In 2013, he joined Eramet Research as an R&D engineer to work on the development of new hydrometallurgical processes.

Gérard Cote, Professor at Chimie ParisTech has 38 years of experience in fundamental to applied research in solution chemistry and solvent extraction with 180 open-literature publications, 165 oral and poster presentations at local, national and international conferences, 6 patents and 35 PhD theses supervised or co-supervised. His researches are focused both on the production (primary mining) and recycling (urban mining) of strategic metals including Ge, Ga, In, Nb, Ta, U, PGM's, as well as on the processing of used nuclear fuels. He has developed a strong partnership with industrial companies including Areva, Eco-Systèmes, EDF, Eramet Research and Prayon and is presently co-responsible of the Chairs ParisTech "Nuclear Engineering" and "Urban mining" supported by AREVA and Eco-Systèmes, respectively.

Dr. Hamid Mokhtari performed his Ph.D. research at CEA Marcoule in the period 2005−2008 on the design of uranium/actinide fuels by a resin ion-exchange process for the generation IV reactors. After receiving his Ph.D., he accepted a position at Areva Mines as a research engineer working on unconventional resources. Presently, he is head of the pilote section at Areva Mine.

Bruno Courtaud was Engineering project manager at Areva for 16 years and hydrometallurgist at Areva mine for 11 years. He is an expert in solvent extraction and uranium precipitation, and he works as a hydrometallurgist at Eramet (niobium and rare earth project).

Dr. Bruce Moyer, Distinguished Scientist and Group Leader of Chemical Separations at Oak Ridge National Laboratory, has 35 years of experience in fundamental to applied research in separation science with more than 170 open-literature publications. He also leads the Diversifying Supply Focus Area of the Critical Materials Institute and the Sigma Team for Minor Actinide Science for the U.S. Department of Energy. Among other activities, he is co-Editor of the international journal *Solvent Extraction and Ion Exchange* and is also co-Editor of the book series *Ion Exchange and Solvent Extraction*.

Dr. Alexandre Chagnes published in the past decade 55 papers in peer-reviewed journals (41), proceedings with peer-review on the full text (10), and books and book chapters (4). He organized several conferences on extraction and recycling processes in the U.S. in the framework of the American Chemical Society. He works in the field of solvent separations applied to liquid−liquid extraction of strategic metals from mining and more recently from recycling. Since his arrival at Ecole Nationale Supérieure de Chimie Paris (ENSCP) in 2005, his research aims to develop fundamental knowledge to overcome technological barriers in hydrometallurgy. He is also Vice-President of the "Extractive Metallurgy" section of "Société des Industries Minérales" (SIM) and scientific consultant for several governmental institutes and companies.

ACKNOWLEDGMENTS

A. Chagnes and G. Cote thank the Chaire ParisTech "Ingénierie Nucléaire" funded by AREVA (AREVA France) for financial support. The contribution of B.A.M. was supported by the Critical Materials Institute, an Energy Innovation Hub funded by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Advanced Manufacturing Office.

ACRONYMS

BDEHCNP	butyl-*N*,*N*-bis(2-ethylhexyl)carbamoylnonyl phosphonate
BidiBOPP	bis(1,3-dibutoxyprop-2-yl) phosphoric acid
D2EHPA	bis(2-ethylhexyl) phosphoric acid
DBDTPA	dibutyldithiophosphoric acid
D2EHDTPA	bis(2-ethylhexyl) dithiophosphoric acid
DBBP	di-*n*-butyl butyl phosphate
CMPO	octyl(phenyl)-*N*,*N*-diisobutylcarbamoyl methyl phosphine oxide
DEHPA	same as D2EHPA
DEHCBPA	*N*,*N*-2-ethylhexylcarbamoylbenzylphosphonic acid
DIPE	diisopropylether
di-*n*-HMOPO	di-*n*-hexyl-methoxyoctyl-phosphine oxide
DNPPA	bis(dinonylphenyl) phosphoric acid
DOPAP	bis(octylphenyl) phosphoric acid
DPPA	didecylpyrophosphoric acid
MOPAP	mono(octylphenyl) phosphoric acid
OPAP	octylphenyl acid phosphate, a mixture of mono- and bis(octylphenyl) phosphoric acids
OPPA	dioctylpyrophosphoric acid
RE	rare earth elements
PC88A	bis(2-ethylhexyl) phosphonic acid mono-2-ethylhexyl ester
TBP	tri-*n*-butyl phosphate

TOPO	tri-*n*-octylphosphine oxide
WPA	wet process phosphoric acid

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