Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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Fathi Habashi[a]; Farouk T. Awadalla[a]
[a] DEPARTMENT OF MINING&METALLURGY, LAVAL UNIVERSITY, QUEBEC CITY, QUEBEC, CANADA

To cite this Article Habashi, Fathi and Awadalla, Farouk T.(1986) 'The Recovery of Uranium during the Purification of Phosphoric Acid by Organic Solvents', Separation Science and Technology, 21: 4, 327 — 337
To link to this Article: DOI: 10.1080/01496398608057165
URL: http://dx.doi.org/10.1080/01496398608057165

SEPARATION SCIENCE AND TECHNOLOGY, 21(4), pp. 327-337, 1986

The Recovery of Uranium during the Purification of Phosphoric Acid by Organic Solvents

FATHI HABASHI and FAROUK T. AWADALLA

DEPARTMENT OF MINING & METALLURGY
LAVAL UNIVERSITY
QUEBEC CITY, QUEBEC, CANADA G1K 7P4

Abstract

When wet process phosphoric acid is purified by extraction with isobutanol, *sec*-butanol, or tributyl phosphate (TBP), the raffinate is enriched in the impurities. Uranium can be recovered from the raffinate by precipitation with ammonia. An upgraded precipitate can be obtained if the bulk of impurities is first crystallized at 200°C. *sec*-Butanol is a more effective extractant than isobutanol and TBP.

INTRODUCTION

The use of low grade phosphate rock in the manufacture of phosphoric acid by the conventional H_2SO_4 route is increasing, and under such conditions the amount of metal impurities in the acid produced increases. The presence of such impurities is undesirable because they lower the quality of the fertilizer produced from such acid, they increase the acid viscosity and cause formation of slow-settling sludge, and they cause a loss in ammonia due to the formation of insoluble metal ammonium phosphates when the acid is ammoniated.

A process that could produce pure phosphoric acid from low grade material would be attractive. This would have the added advantage of eliminating the ore beneficiation cost and increase the P_2O_5 recovery since P_2O_5 losses in flotation would be eliminated. Also, many phosphate deposits not now economical for production of phosphoric acid could be used, thus extending the phosphate reserves. Another aspect of purifying

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wet-process phosphoric acid is to produce clear solution fertilizers that can be stored for extended periods without precipitation of solids.

About 80% of the phosphate rock is destined for the manufacture of fertilizers; the remaining 20% is used for the production detergents, metal surface treatment reagents, chemicals for the food industry, and phosphorus compounds. The nonfertilizer materials are usually prepared from electric furnace phosphorus because of the high purity required. The thermal route, however, is expensive and is associated with pollution problems. There is, therefore, a tendency to purify the wet process acid to meet certain levels of the purity required for the different industries, and even a tendency to modify the method of production of wet process acid to yield a pure product. Numerous processes have been proposed (*1–3*), the most important is the extraction of H_3PO_4 by organic solvents such as *n*-butanol, isobutanol, isopropyl ether, tributyl phosphate, and others (*4, 5*). The plant capacities of purified acid by this route in West European countries was estimated in 1980 at 365,000 tonnes/year (*6*). Since the wet process phosphoric acid (30% P_2O_5) contains about 0.1 g/L uranium, it was considered worthwhile to study the behavior of uranium in such a circuit and to propose a method for its recovery (*7*).

EXPERIMENTAL

The technical acid used was obtained from a manufacturer in New Brunswick, who treats Florida phosphate by the dihydrate process. Pertinent data on the analysis of acid are given in Table 1. Reagent grade tributyl phosphate, isobutanol, and *sec*-butanol were used as extractants (Table 2). Due to the mutual solubility of the alcohols and water there

TABLE 1
Analysis of Phosphoric Acid

	g/L
P_2O_5	607.8
Al	6.1
F (calculated)	26.2
Fe	14.7
Mg	4.4
Mn	0.45
Si	6.4
Ca	2.3 ppm
U	145 ppm

TABLE 2
Data on Solvents Used

	Isobutanol	*sec*-Butanol	Tributyl phosphate
Formula	$CH_3 \cdot CH(CH_3) \cdot CH_2 \cdot OH$	$H_3C \cdot CH(OH) \cdot CH_2 \cdot CH_3$	$[CH_3(CH_2)_3O]_3P(O)$
Manufacturer	Anachima	Aldrich	Aldrich
Purity, %	Reagent grade	99.5	99.9
Boiling range, 760 mmHg, °C	107.9	98.9–100.3	180–183[a]
Specific gravity at 20°C	0.8032	0.8109	0.979
Vapor pressure at 20°C, mmHg	8.8	12.5	—
Solubility of solvent in water, %	8.5	18.0	0.6
Solubility of water in solvent, %	16.4	—	7.0

[a]22 mmHg.

were great changes in the volumes of the organic and the aqueous phases after equilibration; this was taken into consideration when evaluating the results. Some tests were conducted using alcohol saturated with water to minimize changes in volume. Extraction tests were performed in beakers with magnetic agitation for 20 min. Separation of phases was done in separatory funnels. Crystallization experiments were conducted in a Teflon-lined electrically heated pressure reactor.

Since technical phosphoric acid contains appreciable amounts of Si and F, it was considered worthwhile to study their behavior during extraction. For this purpose a sample of technical acid was reacted with the stoichiometric quantity of sodium carbonate to precipitate sodium fluorosilicate according to (*8*)

$$2Na^+ + SiF_6^{2-} \rightarrow Na_2SiF_6$$

Variable amounts of reagent grade H_2SiF_6 were then added equivalent to the amount usually found in the acid. One hundred milliliters of the samples so prepared were agitated for 20 min at ambient temperature with 100 mL solvent. The mixture was then transferred in a separating funnel, allowed to settle, the two phases separated, their volume measured, and then analyzed for P_2O_5, U, and SiF_6^{2-} ion. The raffinate was extracted two more times with 100 mL portions of solvent following the same procedure, and the same was repeated at 0°C to study the effect of temperature and also at 150 mL solvent to study the effect of the organic/aqueous ratio. A material balance was calculated for each series.

The recovery of uranium from the raffinate was attempted in two ways:

(1) Direct precipitation by ammonia
(2) Heating at 200°C in an autoclave to crystallize and separate the major part of the impurities, then adding ammonia

Tests were also conducted using iron powder (*9, 10*) and potassium ferrocyanides as precipitants. Uranium was analyzed spectrophotometrically using arsenazo I after a prior enrichment on anion-exchange resin Amberlite IRA 400 in the sulfate form (*11*), P_2O_5 was determined gravimetrically by the phosphomolybdate method (*12*), fluorosilicate ion was also determined gravimetrically by precipitation as Na_2SiF_6, and the metallic impurities were determined by atomic absorption.

The phosphomolybdate method was tested for possible interference by the fluorosilicate ion and was found to be free from error.

RESULTS AND DISCUSSION

Distribution of H_3PO_4

Table 3 shows a comparison between the extraction of defluorinated technical phosphoric acid by tributyl phosphate, isobutanol, and *sec*-butanol. It can be seen that *sec*-butanol is a more effective extractant for H_3PO_4 than the other solvents. More data are shown in Fig. 1 in the form of distribution isotherms. These curves were constructed using a single step extraction at the following phase ratios (by weight): 2/1, 1/1, 1/2, 1/4, and 1/8. These curves also show that the transfer of H_3PO_4 to the organic phase is favored from a concentrated acid.

Effect of Fluorosilicic Acid on Extraction

Table 4 shows the results of extraction of a mixture of H_2SiF_6 and technical phosphoric acid. It can be seen that H_2SiF_6 is co-extracted with H_3PO_4, and with increasing amount H_2SiF_6 the extraction of H_3PO_4 increases, then becomes constant. However, since the use of solvent is aimed at obtaining a pure phosphoric acid, therefore in light of these

TABLE 3
Comparison between *sec*-Butanol, Isobutanol, and Tributyl Phosphate as Extractants for Defluorinated Technical Phosphoric Acid (607.8 g/L P_2O_5) (organic/aqueous ratio 1.5/1, 20 min contact, two-stage extraction at ambient temperature)

	sec-Butanol	Isobutanol	Tributyl phosphate
Aqueous phase:			
Initial volume, mL	100	100	100
Final volume, mL	24	39	57
Final concentration of P_2O_5, g/L	627.6	607.8	511.2
Organic phase:			
Initial volume, mL	150	150	150
Final volume, mL	376	361	344
Concentration of P_2O_5, g/L	121.6	102.7	92.0
Distribution of P_2O_5, %:			
Aqueous phase	24.8	39.0	47.9
Organic phase	75.2	61.0	52.1

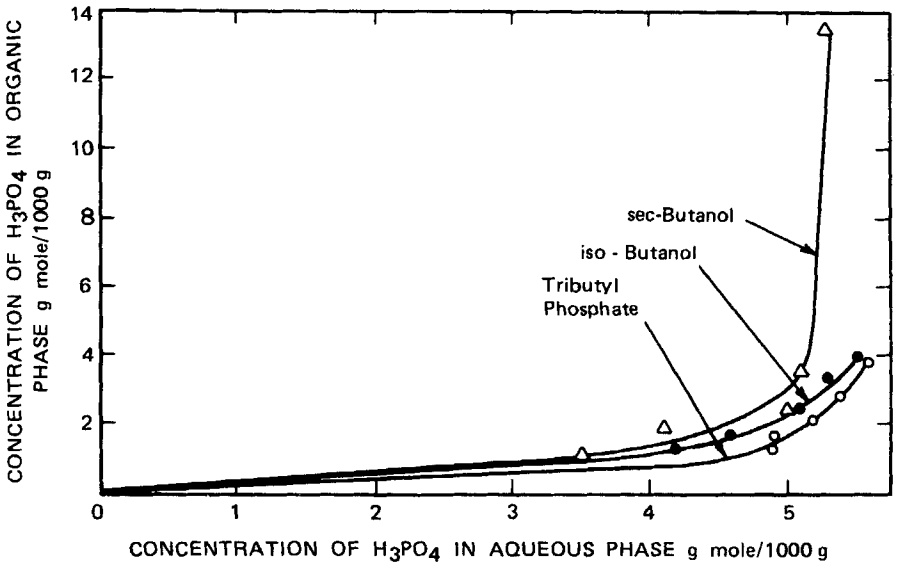


FIG. 1. Distribution of H_3PO_4 between SiF_6^{2-}-free technical phosphoric acid (607.8 g/L P_2O_5) and different organic solvents at ambient temperature.

results it would be an advantage to remove H_2SiF_6 from the technical acid prior to extraction, e.g., by precipitation with Na_2CO_3 or Na_3PO_4.

Behavior of Uranium

When technical phosphoric acid is extracted by organic solvents, negligible amounts of uranium are co-extracted. Due to the decrease in the volume of the aqueous phase, the concentration of uranium increases. For example, when 100 mL technical acid was extracted in three stages with 150 mL portions of isobutanol at ambient temperature, the volume of the aqueous phase decreased to 62, 40, and finally to 26 mL while that of the organic phase increased to 186, 168, and then 156 mL. The concentration of uranium in the aqueous phase increased from 145 to 455 ppm while that of phosphoric acid increased from 594 to 635 g/L P_2O_5 (Table 5). A material balance showed that about 82% of the uranium and about 28% of the phosphoric acid remained in the aqueous phase. Table 5 shows more details on the behavior of uranium as well as

TABLE 4
Extraction of Phosphoric and Fluorosilicic Acid Mixtures by Isobutanol (one-stage extraction)

H_2SiF_6 added (mL)	H_3PO_4 extracted (%)	H_2SiF_6 extracted (%)
0	44.6	0
2	47.4	6.2
3	49.3	8.8
4	49.5	8.4

TABLE 5
Behavior of Uranium and H_3PO_4 during the Extraction of Defluorinated Technical Phosphoric Acid by Isobutanol and Tributyl Phosphate (three-stage extraction, only aqueous phase analyzed: values for organic phase obtained by difference)

	Isobutanol				Tributyl phosphate
Temperature, °C	0	25	0	25	25
Phase ratio, organic/aqueous	1/1	1/1	1.5/1	1.5/1	1.5/1
Aqueous phase:					
Initial P_2O_5 concentration, g/L	594	594	594	594	543
Initial U concentration, ppm	145	145	145	145	140
Initial volume, mL	100	100	100	100	100
Final P_2O_5 concentration, g/L	594.1	667.8	570.7	635.0	377.7
Final U concentration, ppm	314	331	423	455	273
Final volume, mL	39	37	28	26	44
Organic phase:					
Total final volume, mL	355	355	517.5	510.0	506.0
P_2O_5 concentration, g/L	102.0	99.4	84.0	84.1	74.5
U concentration, ppm	6.3	6.3	5.1	5.2	4.0
Distribution of P_2O_5, %:					
Aqueous phase	39.0	41.6	26.9	27.8	30.6
Organic phase	61.0	59.4	73.1	72.2	69.4
	100	100	100	100	100
Distribution of uranium, %:					
Aqueous phase	84.5	84.5	81.7	81.7	85.7
Organic phase	15.5	15.5	18.3	18.3	14.3
	100	100	100	100	100

phosphoric acid during extraction at two different temperatures and at two different phase ratios. At a phase ratio of 2/1, extraction was not possible because of increased viscosity of the organic phase that led to difficulty in phase separation. Temperature has little effect on extraction; results at 0°C were practically the same as at ambient temperature. Table 5 also shows that tributyl phosphate is less effective than isobutanol in the extraction of H_3PO_4, and also less uranium is co-extracted. Table 6 shows data on extraction by *sec*-butanol. It can be seen that practically all the impurities, including uranium, remain in the raffinate.

Recovery of Uranium

Since uranium was enriched in the aqueous phase, its recovery would be feasible by extraction with the same solvents presently used for its extraction from the black and green acids (*7*). Attempts, however, were made to find other routes. The addition of ammonia resulted in the formation of a precipitate at pH 2.1 containing the bulk of uranium (about 75%) but analyzing only 0.09% U. This precipitate did not differ much from the one obtained when the initial acid was treated with

TABLE 6
Behavior of Impurities during the Extraction of Defluorinated Technical Phosphoric Acid by *sec*-Butanol, (organic/aqueous = 1.5/1 two-stage extraction, only aqueous phase analyzed: values for organic phase obtained by difference)

	Acid feed[a]	Raffinate	Organic extract
Volume, mL	100	24	376
Analysis:			
P_2O_5, g/L	607.8	627.5	121.6
Fe, g/L	14.7	60.5	0.53
Mg, g/L	4.4	18.0	0.21
Mn, g/L	0.45	1.9	0
U, ppm	145	496	7
Distribution, %:			
P_2O_5	100	24.8	75.2
Fe	100	98.6	1.4
Mg	100	98.2	1.8
Mn	100	100.0	0
U	100	82.0	18.0

[a]No calcium was detected.

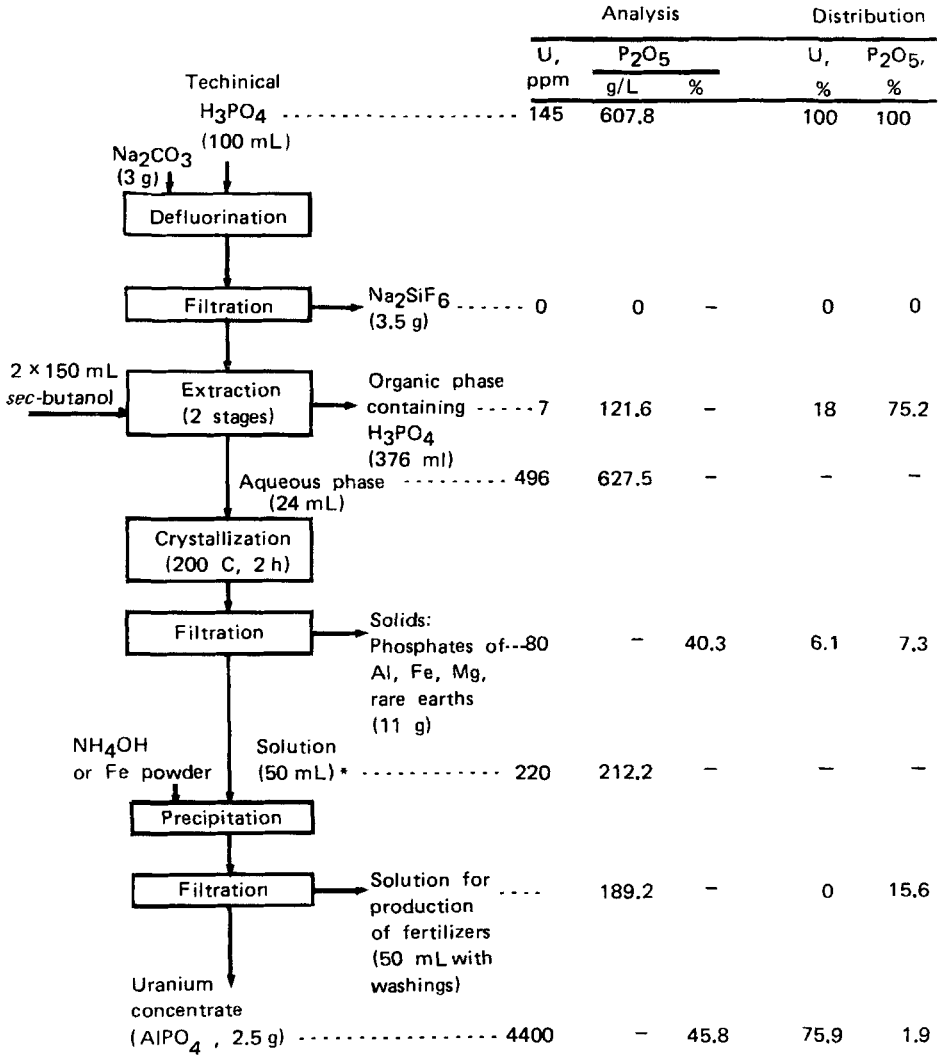
ammonia. It was therefore considered necessary to upgrade the precipitate. Heating the aqueous phase at 200°C in an autoclave to crystallize as much as possible of the impurities, which can then be removed by filtration before precipitating the uranium, was therefore considered (*13*).

Heating the raffinate for 1/2, 2, and 6 h deposited 8.9, 11, and 12 g of impurities, respectively. X-ray diffraction analysis revealed that this deposit was mainly phosphates of iron, aluminum, magnesium, and rare earths. Chemical analysis revealed the presence of a negligible amount of uranium, and the amount of coprecipitated uranium increased with increased time of heating. Two hours was considered to be optimal since the coprecipitate contained a minimum amount of uranium (Fig. 2). The volume of filtrate decreased considerably (from 24 to about 7 mL). The deposit was washed with water and the washings added to the filtrate, then uranium was precipitated. The following methods of precipitation were used:

(1) Precipitation by ammonia. When NH_4OH was added until pH 2.1, the precipitate obtained contained the major part of uranium (76%) and analyzed 0.4% U (Fig. 2). It was amorphous to x-rays but after ignition it lost about one-third of its weight and the product was identified as $AlPO_4$ and analyzed 0.6% U.
(2) Precipitation by iron powder. When 2 g iron powder was added and the solution allowed to stand for 6 h, a precipitate was obtained from which the unreacted iron could be separated by a magnet; it contained the major part of uranium (76%) and analyzed 0.5% U.
(3) Precipitation by potassium ferrocyanide. When a limited amount of $K_4[(Fe(CN)_6]$ solution was added, a precipitate was formed which contained about 60% of the uranium present.

CONCLUSIONS

1. The extraction of H_3PO_4 from technical phosphoric acid by *sec*-butanol is better than by isobutanol or tributyl phosphate.
2. Fluorosilicic acid is co-extracted together with H_3PO_4. To obtain a pure H_3PO_4 from technical phosphoric acid, it is advisable to remove fluorosilicate ion by precipitation as a sodium salt before extraction.
3. The bulk of impurities including uranium are left behind in the raffinate. Uranium can be recovered by precipitation with ammonia, but a higher grade product can be obtained if the major impurities (Fe, Al, and Mg phosphates) are first crystallized at 200°C and separated before



* Originally 7 mL, washings added, and volume adjusted to 50 mL

FIG. 2. Scheme for the recovery of uranium during the purification of technical phosphoric acid by *sec*-butanol.

the addition of ammonia. The product obtained was identified (after ignition) as $AlPO_4$ and contained 0.6% U. The recovery was about 76%.

4. Instead of ammonia, iron powder or potassium ferrocyanide can be used for precipitating uranium, resulting in nearly similar results.

REFERENCES

1. J. F. McCullough, "Phosphoric Acid Purification," *Chem. Eng., 83*(26), 101–103 (1976).
2. J. P. Cuer and A. Floreancig, "Nouvelle Source d'Acide Phosphorique très Pur. Procédé Double Solvant," in *Proceedings of the 2nd International Congress on Phosphorus Compounds*, Institut Mondial du Phosphate, Paris, 1980, pp. 529–540.
3. R. Fitoussi and J. Helgorsky, "Purification de l'Acide Phosphorique," *Ind. Min.—Tech., 3*, 225–234 (1982).
4. F. Habashi, *Principles of Extractive Metallurgy, Vol. 2, Hydrometallurgy*, Gordon & Breach, New York, 1970 (reprinted 1980), pp. 371–373, 410–413.
5. R. Blumberg, "Industrial Extraction of Phosphoric Acid," *Solvent Extraction Rev., 1*(1), 93–104 (1971).
6. H. Harnisch, Opening Speech, in *Proceedings of the 2nd International Congress on Phosphorus Compounds*, Institut Mondial du Phosphate, Paris, 1980, pp. 3–8.
7. F. Habashi, "The Recovery of Uranium from Phosphate Rock. Progress and Problems," in *Proceedings of the 2nd International Congress on Phosphorus Compounds*, Institut Mondial du Phosphate, Paris, 1980, pp. 629–660.
8. F. Habashi and F. T. Awadalla, "The Removal of Fluorine from Wet Process Phosphoric Acid," *Sep. Sci. Technol., 18*(5), 485–491 (1983).
9. E. M. El-Shazly et al., "Recovery of Uranium from In-Process Phosphate Fertilizers," in *Congress of Phosphate in Arab Republic of Egypt*, Cairo, Egypt, 1972, pp. 272–284.
10. E. M. El-Shazly et al., "Preparation of Sodium Diuranate from the Uraniferous Iron Phosphate Concentrate," in *Congress of Phosphate in Arab Republic of Egypt*, Cairo, Egypt, 1972, pp. 303–314.
11. F. T. Awadalla and F. Habashi, "Spectrophotometric Determination of Uranium in Technical Phosphoric Acid by Arsenazo 1," In Press.
12. H. N. Wilson, "The Determination of Phosphate in the Presence of Soluble Silicates, Application to the Analysis of Basic Slag and Fertilizers," *Analyst, 75*, 535–546 (1954).
13. F. Habashi, K. Naito, and F. T. Awadalla, "Crystallization of Impurities from Black Phosphoric Acid at High Temperature," *J. Chem. Technol. Biotechnol., 33A*, 261–265 (1983).

Received by editor April 24, 1985