BMI-JDS Topical Report

AEC RESEARCH AND DEVELOPMENT REPORT

Topical Report

Contract No. W-38-094-eng-27

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memo fr. D P Kuntz, D R M
by authority of *Wash. Dtd 3/5/56*
by *J. C. Ridenour* TISOR, date *3/26/58*

TOPICAL REPORT

on

CHEMICAL PROCESS TO RECOVER URANIUM FROM PHOSPHATE ROCK

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SUMMARY

This report summarizes research done on dissolving uranium from phosphate rock and superphosphate and recovering it from solution in a more concentrated form. It covers the period from February 1 to November 15, 1947, and is a continuance of the topical report submitted at the end of January, 1947.

Because of the desire to develop a process of uranium recovery, which may readily be fitted into existing commercial superphosphate operations, most attention has been given to treatment of phosphate rock, particularly with sulphuric acid, and to water leaching superphosphate, together with treatment of the resulting solutions to recover the uranium. All results reported, except where otherwise noted, were obtained by chemical analysis.

The net result of the work on extraction, reported here and in the topical report of January, 1947, is to show (1) that with sulphuric acid, even in considerable excess, it has proved impossible to solubilize more than about 55 per cent of the uranium in either of the two raw Florida rocks investigated or more than about 60 to 65 per cent of that in the raw Idaho rock, (2) that more uranium, up to 100 per cent, was dissolved with other acids not now used to any great extent in processing raw phosphate rock, and (3) that, in preliminary experiments, apparently between 80 and 85 per cent of the uranium was extracted with sulphuric acid from calcined Idaho rock.

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The amount of uranium extracted by water leaching of commercial superphosphate varied with the origin of the superphosphate. Water extracted 25 to 30 per cent of the uranium in Sacco brand commercial superphosphate, bought on the market, and from 40 to 50 per cent of that in a Florida superphosphate obtained from International Minerals and Chemical Corporation. Extractions from both could be raised to 50 to 55 per cent by pretreating the superphosphate with mineral acids or by such treatment of the leach residue and releaching with water.

By making triple superphosphate from Idaho rock and leaching with water 60 to 70 ~~per cent~~ of the uranium was extracted. /^e

The best possibility with sulphuric acid thus seems to be leaching of calcined rock. This is being followed. Another possibility under study is separate treatment of the leach residue.

With respect to recovery of the uranium from solution to date only two methods offered promise of success. / They are solvent extraction and precipitation with an amine. Extraction with ethyl ether removed 100% per cent of the uranium but needed the presence of 30% per cent ferric nitrate as a salting-out agent. The high concentrations of ferric nitrate in the extracted solution made it virtually impossible to recover the P₂O₅ in fertilizer form. ¹¹ ^{Fe(NO₃)₃}

Amine precipitation seemed to offer the best means for uranium recovery. AM-Coco-B, a coconut oil amine, was the best reagent. In

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Sacco superphosphate solutions, containing 8 mg./l^{iter}, it was possible to precipitate all but 4 to 5 mg. of ~~uranium~~ per liter (4 to 5 parts per million). In a Florida superphosphate solution containing 12 mg./l^{iter}, 6 to 8 mg./l^{iter} was left (6 to 8 parts per million).

The amine precipitation data on superphosphate leach solutions is somewhat erratic because some of it tends to show that the fraction of uranium precipitated bears a constant ratio to that in solution and that a similar fraction may be recovered from filtrates. This is still imperfectly known because reprecipitation of filtrates and the use of larger ratios of amine to uranium have not yet been studied sufficiently. These matters and other means to better the precipitation conditions, such as inactivation or removal of organic matter and fluoride ion, are under investigation. More sensitive uranium precipitants are also being sought.

RAW MATERIALS

Up to late in May, 1947, the only raw materials available for this work were a series of four samples of Idaho phosphate rock, one sample of Florida pebble phosphate concentrates, and a sack of Sacco brand superphosphate. The Idaho rock was secured by the U.S. Geological Survey in the field and the Florida concentrates from International Minerals and Chemical Corporation. The superphosphate was bought locally. Since May, at intervals, through the agency of the U.S. Geological Survey,

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samples of phosphate rock in various stages of concentration and of superphosphate have been received. At present there are on hand four samples of Idaho and twenty samples of Florida phosphate rock, which because of their P_2O_5 content may be considered suitable for making phosphoric acid or superphosphate. Five samples of commercial, 18 to 20 per cent, superphosphate, exclusive of the sample of Sacco brand, are on hand. In Tables 1 and 2 a short description of these materials is given.

Because most of the materials have been received only recently analyses are incomplete. For the same reason only a few of them have yet been used in the present research work.

More detailed analyses of the rocks and superphosphates which have served as subject for uranium extraction are given in Table 3.

SUMMARY OF EARLIER WORK

The results of early chemical work were reviewed in a topical report dated January, 1947. The raw materials available for this work were four phosphate rocks from Idaho and a sample of pebble phosphate rock concentrates from Florida. The richest Idaho material No. 1090-8 and the Florida rock No. 1090-11 were selected for investigation. The compositions of these rocks are given in Table 3.

The rocks were ground, usually to pass 90 per cent through 100 mesh, and were then attacked with a variety of reagents. It was found

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TABLE 1. HIGH-GRADE PHOSPHATE ROCKS ON HAND, OCTOBER, 1947

No.	Received	U, %	P ₂ O ₅ , %	Nature	Source ⁽¹⁾
<u>Idaho Phosphate Rocks</u>					
1090-3	Aug., 1946	0.006	-	Phosphate Rock	U.S. Geological Survey
-5	Ditto	0.010	-	Ditto	Ditto
-6	"	0.013	-	"	"
-8	"	0.013	29.7	"	"
<u>Florida Phosphate Rocks</u>					
1090-11	Aug., 1946	0.020	31.3	Washed Pebble	International, Mulberry, Florida
14	May, 1947	0.010	32.2	Ditto	International, Peace Valley Plant
16	Ditto	0.006	35.5	Flotation Concentrate	Ditto
18	"	0.010	34.4	Ground Phosphate Rock	International, East Point Acidulation Plant, derived from Peace Valley Plant
23	July, 1947	0.017	30.1	Washed Pebble	Davison, Bonny Lake Plant
26	Ditto	0.014	30.3	Flotation Concentrate	Ditto
30	"	0.012	-	Ground Phosphate Rock	Davison, Curtis Bay Plant
32	Sept., 1947	0.009	-	Washed Pebble	Cyanamid, Saddle Creek, Florida
33	Ditto	0.007	-	Flotation Concentrate	Ditto
36	"	0.012	-	Ground Phosphate Rock	"
37	"	0.010	-	Phosphate Matrix	Coronet, Eleanor Mine
38	"	0.011	-	Raw Pebble Phosphate	Coronet, Hopewell Mine
39	"	0.012	-	Flotation Concentrate	Ditto
42	"	0.012	-	Raw Ground Phosphate	"
43	"	0.007	-	Defluorinated Ground Phosphate	"
45	"	0.008	-	Washed Pebble	Amer. Agr., Boyette Mine
46	Oct., 1947	0.009	-	Flotation Concentrate	Ditto
50	Ditto	0.013 ⁽²⁾	-	Washed Pebble	Virginia-Carolina, Nichols, Florida
51	"	0.010 ⁽²⁾	-	Flotation Concentrate	Ditto
54	"	0.014 ⁽²⁾	-	Ground Rock	"

Footnotes appear on the following page.

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TABLE 1 (Continued)

Footnotes:

- (1) International is International Minerals and Chemical Corp.
 Davison is Davison Chemical Corp.
 Cyanamid is American Cyanamid Co.
 Corconet is Coronet Phosphate Co.
 Amer. Agr. is American Agricultural Chemical Co.
 Virginia-Carolina is Virginia-Carolina Chemical Corp.
- (2) Analysis by B-count

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A 10x10 grid of dots forming a stylized letter 'A'. The grid is 10 columns wide and 10 rows high. The letter 'A' is formed by dots, with the top row being a solid horizontal line of 10 dots. The two slanted sides of the 'A' are formed by dots, with the right side being a solid vertical line of 10 dots. The bottom row is a solid horizontal line of 10 dots. The interior of the 'A' is mostly empty, with a few dots forming a small 'V' shape in the center.

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TABLE 2. NORMAL(1) SUPERPHOSPHATES ON HAND OCTOBER, 1947

No.	Received	U, %	P ₂ O ₅		Nature	Source(2)
			Total, %	Avail-able, %		
1090-20	May, 1947	0.006	19.5	18.5		International, East Point Acidulation Plant, supposedly derived from Rock No. 1090-18
-28	July, 1947	0.008	-	-	Run of pile	Davison, Curtis Bay Plant, supposedly derived from Rock No. 1090-30
-29	Ditto	0.009	-	-	Granulated	Ditto
-55	Oct., 1947	0.007 ⁽³⁾	-	-		Virginia-Carolina, Nichols, Florida
-56	Ditto	0.007 ⁽³⁾	-	-		Ditto
Sacco	Apr., 1947	0.008	20.5	19.1		Product of Smith Agricultural Chemical Co. bought on local market

- (1) Normal superphosphate is superphosphate containing 18 to 20 per cent of total P₂O₅ and about 1 per cent less than this of available P₂O₅.
- (2) International is International Mineral and Chemical Corp.
Davison is Davison Chemical Corp.
Virginia-Carolina is Virginia-Carolina Chemical Corp.
- (3) Analysis by B-count.

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TABLE 3. COMPOSITIONS OF PHOSPHATE ROCKS AND SUPERPHOSPHATES
USED IN LEACHING TESTS

No.	Composition, %										
	U	CaO	Fe ₂ O ₃	Al ₂ O ₃	P ₂ O ₅ , Total	P ₂ O ₅ , Avail-	SiO ₂	F	CO ₂	H ₂ O	LOI
<u>Phosphate Rocks</u>											
1090-8	0.013	38.3	1.63	2.62	29.7	-	12.0	2.77	1.57	-	8.7
-11	0.020	44.5	1.27	1.49	31.3	-	7.14	3.46	4.42	-	7.4
-18	0.010	48.9	0.98	0.55	34.4	-	6.97	3.81	2.11	-	4.0
<u>Superphosphates</u>											
1090-20	0.006	-	-	-	19.5	18.5	-	-	-	9.0	-
Sacco	0.008	27.7	-	-	20.5	19.1	-	-	-	10.0	-

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that in order to extract any appreciable amount of uranium it was necessary to decompose the rock. Reagents which did not decompose the rock extracted less than about 20 per cent of the contained uranium.

Mineral acids were most effective in dissolving the uranium. Thus, with enough acid to decompose the rock to make phosphoric acid from 59 to 96 per cent of the uranium in the Idaho rock was dissolved and from 38 to 99 per cent of that in the Florida rock. The effectiveness varied with the acid. Nitric acid and hydrochloric acids were most effective probably because they left only a small insoluble residue. Sulphuric acid was less effective but extracted up to 60 per cent of the uranium from the Idaho phosphate rock and up to 44 per cent from the Florida rock.

When superphosphates were made with sulphuric acid or with phosphoric acid and the products leached with water the results were in general similar.

EXTRACTION OF URANIUM FROM PHOSPHATE ROCK

Guided by the earlier results, which showed that mineral acids were the most effective reagents for extracting the uranium, most of the later efforts have been devoted to rock extractions with acid, or to superphosphate extraction with water, or with water and acids.

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The rock extraction with acid, except when otherwise noted, was done at room temperature by stirring the mixture of about 100 g. of minus 100-mesh rock with the desired amount of acid. Acid concentrations, amounts, and lengths of time of stirring are shown in the tables below. The mixture was then filtered on paper on Buchner funnels under a vacuum. The residue was washed with water in small portions. About 150 to 200 cc. of water was used in washing.

When the rock was first made into superphosphate and then water leached the procedure was essentially as follows: One hundred grams of rock was mixed quickly with the desired amount of acid in a glass container. After about two or three minutes the mixture had set to a hard mass. After a short time the mass was broken into small fragments with a spatula and allowed to cure by sitting overnight, or longer if desired. After curing, the superphosphate was made into a slurry with about 200 cc. of water and stirred for 1/2 to 2 hours (The length of time did not seem to be critical because about the same amount of uranium was dissolved.). The mixture was filtered by suction and washed with about 300 cc. of water in small portions. Variations of this procedure are noted in the separate sections.

Other procedures, where used, are described in the text.

The percentage extraction given in the tables is based on chemical analysis of the extraction solution because it was felt that solution

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analyses offered the best accuracy. The degree of precision is indicated with each value.

Metal balances, i.e. comparisons of the sum of the uranium, found by chemical analyses in the leach solution and leach residue, with that similarly found for the head sample, i.e. the phosphate rock or superphosphate, were made. These usually were reproducible to better than ± 20 per cent and were accurate to this value if the analysis of the head sample was assumed to be correct. Only a few metal balances outside this limit were obtained and these were high. Repetition of the analyses usually brought them within the limit.

ACID TREATMENT OF RAW PHOSPHATE ROCK

Two Florida phosphate rocks, Nos. 1090-11 and 1090-18, were used. Both are described in Table 3. The effect of sulphuric acid, both in the concentration used commercially in the manufacture of superphosphate and in more dilute strength, was determined. Illustrative data are given in Table 4.

By making superphosphate from Florida rock No. 1090-11, which contains 0.020 per cent of uranium, and leaching the product an average of about 33 per cent of the uranium, 7 mg. out of 20 per 100 g. of rock, was extracted. The same process on Florida rock No. 1090-18 resulted in an extraction of about 50 per cent of the uranium, 5 mg. out of 10 per 100 g. of rock.

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TABLE 4. ACID TREATMENT OF PHOSPHATE ROCK
100 g. rock used in each test

No.	Sulphuric Acid		Residue Wt., g.	Volume of Extract and Washings, cc.	Uranium Extracted		Remarks
	g.	Theoretical,% Conc.,%			mg.	%	
<u>1090-11, 20 mg. U, 75°F., 24 Hours(3)</u>							
2940-26-1	73.5	100	79.5 (4)	470	6.9 + 0.5	35	--
2940-26-2	73.5	100	79.5 (4)	472	7.2 + 0.5	36	--
2940-26-3	78.5	107	79.5 (4)	478	6.2 + 0.5	31	--
2940-26-4	78.5	107	79.5 (4)	478	6.5 + 0.5	33	--
2940-26-5	83.5	114	79.5 (4)	490	6.8 + 0.5	34	--
2940-26-6	83.5	114	79.5 (4)	485	7.0 + 0.5	35	--
2940-26-7	88.5	121	79.5 (4)	485	6.7 + 0.5	34	--
2940-26-8	88.5	121	79.5 (4)	485	6.6 + 0.5	33	--
2940-27-1	73.5	100	41.6 (4)	115	5.0 + 1.0	25	--
2940-27-2	73.5	100	41.6 (4)	112	5.8 + 1.0	29	--
2940-27-3	73.5	100	26.6 (4)	175	10.1 + 1.0	51	--
2940-27-4	73.5	100	26.6 (4)	190	11.0 + 1.0	55	--
2940-27-5	73.5	100	19.5 (4)	235	10.9 + 1.0	55	--
2940-27-6	73.5	100	19.5 (4)	230	10.6 + 1.0	53	--
2940-27-7	73.5	100	15.4 (4)	310	11.6 + 1.0	58	--
2940-27-8	73.5	100	15.4 (4)	310	10.9 + 1.0	55	--
2758-51-1	(1)	(1)	(1) 6.5	545	20.4 + 2.0	100	--
<u>1090-18, 10 mg. U, 75°F., 2 Hours</u>							
2940-45-4	73.5	100	12.7 (4)	483	5.2 + 0.5	52	--
2940-45-1	73.5	100	79.5 (4)	370	3.0 + 0.5	30	110 g. NaCl added
2940-45-2	73.5	100	79.5 (4)	478	4.0 + 0.5	40	16 g. NaCl added
2940-45-3	73.5	100	12.7 (4)	463	4.6 + 0.5	46	16 g. NaCl added
2940-41-2	72.5	100	79.5 114	460	6.1 + 1.0	61	1 g. HNO ₃ added
2940-41-1	(2)	(2)	(2) 14	460	10.0 + 1.0	100	--

- (1) The sulphuric acid was replaced by 42% nitric acid.
 (2) The sulphuric acid was replaced by 60% nitric acid.
 (3) Twenty-four hours in the sulphuric acid tests; 3 hours with nitric acid.
 (4) Residues not weighed; the residues in a large number of similar tests weighed 115 to 125 g.

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By diluting the acid before treating the rock, which process resulted in a slurry of decomposed rock and solution, more uranium, 10 to 11 mg. out of 20, was extracted from No. 1090-11. This is the highest yield obtained from this rock with sulphuric acid. It was also attained by using less water, one third to one half of that necessary in leaching superphosphate. That this amount of water was enough, to get maximum extraction, is shown by later experiments in the same series in which the amount of water was nearly doubled with no increase in extracted uranium.

Addition of sodium chloride to the sulphuric acid decreased the uranium extraction. Substitution of 1 per cent of the sulphuric acid by nitric acid increased the extraction from about 50 per cent to about 60 per cent.

When all of the sulphuric acid was substituted by nitric acid all of the uranium in both rocks was extracted.

The residue weight from 100 g. rock, when sulphuric acid was used, was 115 to 125 g. When nitric acid was used it averaged about 10 g. (the two examples given show 6.5 and 14 g.).

ACID TREATMENT OF CALCINED PHOSPHATE ROCK

A portion of Rock No. 1090-8 was ignited first, over an open burner for six hours, and then in a muffle furnace for 15 hours at 700°C. The loss in weight was 8.9 per cent.* The calcined ore was agitated for

* The loss in weight by ignition at 1000°C. on a previous sample was 8.7 per cent.

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24 hours at room temperature with dilute sulphuric acid, or with a mixture of dilute sulphuric and phosphoric acids. After filtering and washing analysis of the extracts showed that approximately 11 mg. out of 13 per 100 g. of rock, or over 80 per cent of the uranium had been extracted. Details are given in Table 5.

WATER LEACHING OF SUPERPHOSPHATE

Two commercial superphosphates have been studied with regard to the effect of varying the amount of leach water used. They are Sacco brand of the Smith Agricultural Chemical Company, Columbus, Ohio, and Florida No. 1090-20, a product of International Minerals and Chemical Corporation. Both are described in Table 3.

One hundred and ninety-gram samples were used for leaching since this is approximately equivalent to 100 g. of phosphate rock. Important details of the leaching are shown in Table 6.

First it will be noted that water leaching alone brought at best 50.0 per cent of the uranium into solution regardless of the amount of water. Thus an increase in the amount of leach water did not bring a corresponding increase in uranium extraction. Some means other than water leaching will be necessary to get more uranium into solution.

The data suggest that centrifuging and decanting may be a little more effective than filtration.

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TABLE 5. EFFECT OF CALCINING PHOSPHATE ROCK ON EXTRACTION OF URANIUM WITH ACID AND WATER

Basis: 100 g. Idaho No. 8 rock — 13 mg. U.

No.	Acid	Per Cent of Theoretical*	Uranium Dissolved	
			mg.	%
2758-70-1	24% H_2SO_4	94	10.7	82
2758-73-1	22% H_2SO_4 16% H_3PO_4	94	10.9	84

* Based on that required to make superphosphate.

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TABLE 6. WATER LEACHING OF SUPERPHOSPHATE

190 g. superphosphate in each test =
100 g. rock

No.	Total Volume of Leach Water, ml.	Uranium			P ₂ O ₅ Extracted, %
		Total in Sample mg. $\pm$ 1	Extracted mg.	%	
<u>Sacco, Smith Agricultural Chemical Co., Leach, Filter and Wash</u>					
2940-22-1	300	15	3.0 $\pm$ 0.3	20	--
2940-22-2	500	15	3.8 $\pm$ 0.5	25	--
2940-22-3	800	15	5.0 $\pm$ 0.8	33	--
2940-29-7	700	15	3.2 $\pm$ 0.6	21	--
2940-29-8	700	15	3.1 $\pm$ 0.6	20	--
2940-29-1	1000	15	2.8 $\pm$ 0.9	18	--
2940-29-2	1000	15	2.6 $\pm$ 0.9	17	--
2940-29-3	1500	15	3.2 $\pm$ 1.4	21	--
2940-29-4	1500	15	3.2 $\pm$ 1.4	21	--
2940-29-5	2000	15	3.9 $\pm$ 2.0	26	--
2940-29-6	2000	15	3.5 $\pm$ 2.0	23	64
<u>1090-20, International Minerals and Chemicals Corp., Leach, Filter and Wash</u>					
2940-34-1	500	11.4	4.1 $\pm$ 0.5	36	89
2940-34-2	500	11.4	4.2 $\pm$ 0.5	37	--
2940-34-3	1000	11.4	5.2 $\pm$ 0.5	45	--
2940-34-4	1000	11.4	4.9 $\pm$ 0.5	43	--
2940-34-5	1500	11.4	4.6 $\pm$ 0.5	40	--
2940-34-6	1500	11.4	4.6 $\pm$ 0.5	40	92
<u>1090-20, Centrifuged and Decanted</u>					
2940-35-1	570	11.4	5.7 $\pm$ 0.5	50	87
2940-35-2	570	11.4	5.7 $\pm$ 0.5	50	--
2940-35-3	760	11.4	4.6 $\pm$ 0.5	40	--
2940-35-4	760	11.4	4.6 $\pm$ 0.5	40	--
2940-35-5	950	11.4	5.7 $\pm$ 0.5	50	--
2940-35-6	950	11.4	5.3 $\pm$ 0.5	46	87

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SULPHURIC ACID TREATMENT OF SUPERPHOSPHATE
PRIOR TO LEACHING

Sulphuric acid was applied as a pretreatment to the superphosphate before water leaching. The acid was applied in a fairly concentrated form with just enough water to wet the superphosphate and the mixture was allowed to stand for 24 hours at room temperature before leaching with water.

The data showed that for Sacco superphosphate the acid pretreatment doubled the uranium extraction, but did not extend it beyond 50 to 60 per cent. There was evidence that the 50 to 60 per cent level was the upper limit. See Table 7.

LEACHING SUPERPHOSPHATE WITH ACIDIFIED WATER

When sulphuric, phosphoric, or nitric acid was added to the leach water there was a slight improvement in uranium extraction over plain water leaching but the improvement was not as great as if (1) the superphosphate were treated with the same amount of more concentrated acid and then leached or (2) the residue from a water leach were acid treated and re-leached.

ACID TREATMENT OF THE SUPERPHOSPHATE RESIDUE

Water leaching left a large portion of the uranium in the residues. The residues were treated with various acids at room temperature and at

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TABLE 7. SULPHURIC ACID TREATMENT OF SUPERPHOSPHATE
PRIOR TO LEACHING

Sacco superphosphate, 100 g. = 15 mg. U.
190 g. used in each test = 100 g. rock

Test No.	Anhydrous H ₂ SO ₄ , g. (1)	Uranium Extracted	
		mg.	%
2939-45-1	0	3.7±0.5	25
2939-48-1	1.0	3.9±0.5	26
2939-48-2	1.9	5.0±0.5	33
2939-49-1	4.8	5.4±0.5	36
2939-49-2	9.6	6.8±0.5	45
2939-50-1	14.4	7.9±0.5	53
2939-50-2	24.0	7.5±0.5	50
2940-30-1	9.6	6.6±0.5	44
2940-30-2	9.6	6.6±0.5	44
2940-30-3	14.4	7.7±0.5	51
2940-30-4	14.4	7.0±0.5	47
2940-30-5	24.0	7.4±0.5	49
2940-30-6	24.0	9.3±0.5	62
2940-30-7	33.6	8.6±0.5	57
2940-30-8	33.6	8.5±0.5	57

(1) The acid was diluted to a volume just great enough
to wet the superphosphate.

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about 200°F. Sacco and 1090-20 were both treated but most of the work was on Sacco as shown in Table 8.

The results show that considerable uranium may be extracted from the residue by this method but the total uranium extracted from the superphosphate was no higher, 45 to 59 per cent, than by acid treatment of the superphosphate and a single water leaching.

MISCELLANEOUS TREATMENTS OF LEACHED
SUPERPHOSPHATE RESIDUES

Water leaching of commercial superphosphate, in the absence of pretreatment with acid, usually extracted less than 50 per cent of the contained uranium. The residue thus retained more than half the uranium in the original rock. Methods were sought to extract it.

One method was to treat the residue with a strong solution of ammonium or sodium carbonate. By this means the residue was converted to a water-soluble fraction containing practically no uranium and a nearly 100 per cent acid-soluble fraction which presumably carried 90 per cent or more of it. Roasting with alkali carbonates and leaching produced similar results. Roasting with sodium sulphate also seemed to decompose the residue to some extent. The analytical results of these and other attacks on the residue are not yet available. Details of the processes will be described in later reports when analyses can be given.

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TABLE 8. ACID TREATMENT OF SUPERPHOSPHATE LEACH RESIDUE

Procedure = 190 g. superphosphate leached with 700 cc. of water at room temperature.
Residue treated with 80% sulphuric acid as shown below and leached with 700 cc. of water at room temperature.

No.	Amount of Acid, Anhydrous, g.	Extracted From Residue, mg.	Uranium	
			Total Extracted From Superphosphate and Residue	
			mg.	%
<u>Sacco Residue, 75°F., 24 Hours, Sulphuric Acid</u>				
2940-31-1	9.6	3.9 + 0.8	7.0	47
2940-31-2	9.6	4.3 + 0.8	7.4	49
2940-31-3	19.2	5.5 + 0.8	8.6	57
2940-31-4	19.2	5.6 + 0.8	8.7	58
2940-31-5	33.6	5.7 + 0.8	8.8	59
2940-31-6	33.6	4.8 + 0.8	7.9	53
<u>Sacco Residue, 200°F., 4 Hours, 75°F. 20 Hours, Sulphuric Acid</u>				
2940-32-1	9.6	3.7 + 0.7	6.8	45
2940-32-2	9.6	4.1 + 0.7	7.2	48
2940-32-3	19.2	5.4 + 0.7	8.5	57
2940-32-4	19.2	4.8 + 0.7	7.9	53
2940-32-5	33.6	3.7 + 0.7	6.8	45
2940-32-6	33.6	3.9 + 0.7	7.0	47
<u>1090-20 Residue, 750°F., 30 Minutes, Various Acids</u>				
2940-37-R-1	19.2(1)	2.0 + 0.5	6.2	54
2940-37-R-2	24.5(2)	2.2 + 0.5	6.4	56
2940-37-R-3	14.5(3)	2.1 + 0.5	6.3	55
2940-37-R-4	(4)	1.9 + 0.5	6.1	54
<u>1090-20 Residue, 212°F., 30 Minutes, Nitric Acid</u>				
2940-40-3	100(5)	3.0 + 0.5	7.2	63

(1) 80% sulphuric acid

(4) 18.2 g. anhydrous H₂SO₄, 1 g. anhydrous HNO₃, in 43% solution

(2) 50% nitric acid

(5) 70% nitric acid

(3) 37% hydrachloric acid

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LEACHING TRIPLE SUPERPHOSPHATE

A series of triple superphosphates was made from Idaho phosphate rock with various amounts, ranging from a considerable excess to a deficiency, of phosphoric acid. One set of the products was leached with water after aging for one day. The other was leached after one week. The results are shown in Table 9.

Maximum uranium extraction in the first set was 78 per cent and in the second 85 per cent. This was achieved with 170 per cent of the theoretical acid. When the amount of acid was decreased below this amount the extraction decreased in proportion to the decrease in acid but faster in the set aged for one week. In the set aged for one day about 70 per cent of the uranium (by interpolation) was extracted by the theoretical amount of acid and in the set aged for one week a little less than 60 per cent.

RECOVERY OF URANIUM FROM SOLUTION

The recovery of uranium has been attempted by the following principal methods:

- (1) Precipitation
- (2) Solvent extraction
- (3) Ion exchange

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TABLE 9. EXTRACTION OF URANIUM FROM BATTELLE-MADE
TRIPLE SUPERPHOSPHATE

100 g. Idaho No. 1090-8 Rock = 13 mg. U

No.	Phosphoric Acid		Uranium		Triple Superphosphate Aged Prior to Leaching
	78%, g.	% of Theoretical	Extracted, mg., ±1	%	
2758-52-1	224	170	10.1	78	One day
54-1	168	127	9.8	75	Ditto
55-1	112	85	8.8	68	"
55-2	56	43	5.5	42	"
2758-60-1	224	170	11.0	85	One week
62-1	168	127	7.5	58	Ditto
62-2	112	85	7.5	58	"
63-1	56	43	4.8	37	"

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The method which seemed to offer greatest recovery of uranium with least interference with other phosphate operations was precipitation. Therefore such methods received greater attention than others.

SPECIFICATIONS FOR URANIUM PRECIPITANTS

In the present instance it is desirable to remove uranium down to 1 to 2 parts per million (1 to 2 mg./l.) or less because the leach solutions are dilute. The uranium concentrations encountered so far have ranged from 8 to 60 mg./l. but have usually been about 10 to 15 mg./l. Unless richer rock or superphosphate than those presently treated are encountered it is unlikely that concentrations much higher than 25 mg./l. will be reached. The first requirement of the reagent is therefore that it should have a sensitivity of 2 to 3 parts per million.

The second requirement is that the reagent must remove uranium from an acid solution high in phosphate and without material change in pH. The pH of the present commercial solutions lies between 2.5 and 3.0. Changing the pH is difficult because (1) the solution is highly buffered and requires a large amount of reagent to change it materially, and (2) an increase of more than 2 or 3 tenths of a pH unit causes heavy calcium phosphate precipitation. A satisfactory precipitant must, therefore, have high sensitivity for uranium and work successfully on the unaltered leach solution without simultaneous large precipitation of calcium phosphates.

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A review of available project and other literature revealed practically nothing that contributed directly toward selection of a reagent for the present purpose. All reagents described, with the exception of cupferron and hydrogen peroxide, require neutral or slightly alkaline solutions. Cupferron will work in an acid solution but requires reduction of uranium to the quadrivalent state. Hydrogen peroxide fails in the presence of considerable sulphate and is decomposed in the presence of ferric ions unless the latter are inactivated by considerable additions of, for example, malonic acid. Furthermore, the sensitivity of most of the reagents described, even under optimum conditions, is too low for the present purpose.

In the absence of specific leads, except for cupferron and hydrogen peroxide, a systematic testing program of organic compounds was begun.

SELECTION OF ORGANIC PRECIPITANTS

Approximately 100 organic compounds, including many types known to be precipitants for uranium or related metals, were tested. Among these were amines, alkaloids, amino alcohols, amino ethers, amino phenols, hydroxy acids, quinones, thio compounds, dyes, alcohols, etc. Preliminary tests in synthetic uranium nitrate-phosphoric acid and synthetic calcium phosphate solutions weeded out all but a few of the amines.*

* See progress reports for April, 1947, and subsequent ones.

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Among these were 2 amino-pyridine, ethylene diamine, hexamethylene tetramine, tetraethylene pentamine, and a number of coconut oil amines. Further tests in raw superphosphate leach solutions eliminated all but the coconut oil amines.

One observation made during these tests was that phosphate ion was necessary to amine precipitation of uranium at the low pH, 2.5 to 2.8, of a superphosphate solution.

Many ways of making the precipitation, such as adding the amine directly, adding a solution of the amine, dropwise addition, heating the solution during precipitation, and others were tried. The most consistently successful method was to (1) make a dilute aqueous solution of the amine, with an acid such as acetic, if necessary; (2) add the desired amount of amine solution with stirring at room temperature, (3) let the mixture set for 24 hours to coagulate and settle, and (4) filter and wash with water.

PRECIPITATION WITH COCONUT OIL TYPE AMINES

A series of 10 coconut oil amines and amine mixtures was obtained from Armour and Company and two rosin amines from Hercules Powder Company. These were added as 1 per cent solutions in 1 per cent acetic acid in varying amounts to Sacco and International Minerals and Chemical Corporation superphosphate leach solutions. The results of typical tests on the

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unaltered leach solutions and on similar solutions with added uranium are reported in Table 10. Uranium was added with the hope that a larger precipitate would help to make precipitation more complete.

From the Sacco superphosphate solution the various amines removed 10 to 48 per cent of the uranium, with most of the values above 30 per cent, and left 4 to 7 mg./l. of an original 7.75 mg./l. in solution.

From the International Minerals and Chemical Corporation superphosphate solution the uranium recoveries were from 6 to 49 per cent but only a third were above 20 per cent. From 6 to 11 mg./l. was left in solution. There thus seemed to be a noticeable difference in the amount of uranium recoverable from the leach solutions of these two commercial superphosphates.

The experiments were repeated after adding more uranium, as the nitrate, to the solutions. The Sacco solution was increased to 32 mg./l. and the other to 36.5 mg./l.

The recoveries from the Sacco solution were again the highest with 14 out of 18 above 30 per cent and 7 above 60 per cent. The recoveries from the International Minerals and Chemical Corporation solution were all less than 25 per cent. The amount of uranium left in solution in the fortified Sacco solution was 9 to 31 mg./l. and in the other 27 to 35 mg./l.

A comparison of the different amines showed that the AM-Coco series (AM-Coco-B, AM-Coco-C, and their acetates) consistently left less

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TABLE 10. URANIUM PRECIPITATION FROM COMMERCIAL SUPERPHOSPHATE LEACH SOLUTIONS WITH COCONUT OIL TYPE AMINES

400 cc. of solution used = 100 g. raw phosphate rock

No.	Amine	Amount, mg.	Uranium		
			Precipitated, mg.	%	Left in Solution, ⁽¹⁾ mg./l.
<u>Sacco Superphosphate Leach Solution, pH 2.8, 7.75 mg. U/l.</u>					
2939-78-3	Hexadecylamine	-	1.0±0.1	32	5
4	"	-	0.7±0.1	23	6
91-1	AMAC-Coco-B	100	0.9±0.1	30	5
3	"	250	1.5±0.1	48	4
92-1	AM-Coco-C	100	0.5±0.1	16	7
2	"	250	1.2±0.1	39	5
3192-9-1	AM-118.5-C	250	1.3±0.1	42	4
12-5	AM-1181.2-B	250	0.3±0.1	10	7
13-5	AM-1181.5-B	250	0.6±0.1	20	6
14-5	AMAC-118.5-B	250	1.0±0.1	32	5
15-5	AMAC-118.5-C	250	1.1±0.1	35	5
16-5	Rosin Amine D Acetate	250	1.1±0.1	35	5
17-5	Rosin Amine D	250	0.8±0.1	26	6
18-5	AM-1120	250	1.4±0.1	45	4
<u>International Minerals and Chemical Corporation Superphosphate (1090-20) Leach Solution, pH 2.6, 12 mg. U/l.</u>					
3192-9-3	AM-118.5-C	250	0.9±0.2	19	10
5	"	250	1.0±0.2	21	9
8	"	250	0.5±0.1	13	9
11-3	12-NAM-118.5-C	250	0.8±0.1	17	10
12-1	AM-1181.2-B	250	0.4±0.1	8	11
3	"	500	0.6±0.1	13	10
13-1	AM-1181.5-B	250	0.3±0.1	6	11
3	"	500	0.5±0.1	10	11
14-1	AMAC-118.5-B	250	0.3±0.1	6	11
3	"	500	0.8±0.1	17	10

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TABLE 10 (Continued)

No.	Amine	Amount, mg.	Uranium		
			Precipitated, mg.	%	Left in Solution, (1) mg./l.
3192-15-1	AMAC-118.5-C	250	0.5±0.1	11	11
3	"	500	0.9±0.1	19	10
16-1	Rosin Amine D Acetate	250	0.4±0.1	8	11
3	Ditto	500	2.3±0.1	48	6
17-1	Rosin Amine D	250	1.6±0.1	33	8
3	Ditto	500	0.7±0.1	15	10
18-1	AM-1120	250	0.9±0.1	19	10
7-1	AM-Coco-B	250	1.1±0.1	24	9
8-5	"	250	0.8±0.1	18	9
7-3	"	500	2.2±0.1	49	6
8-7	"	500	1.5±0.1	30	7

Sacco Superphosphate Leach Solution, pH 2.8, 32 mg. U/l.
(Extra Uranium Added as Uranium Nitrate)

2939-76-2	Heptylamine	-	1.7±0.1	13	28
77-1	AMAC-Coco-C	-	4.2±0.5	33	22
3192-9-2	AM-118.5-C	250	6.1±0.5	47	17
11-2	12-NAM-118.5-C	250	0.8±0.5	6	31
12-6	AM-1181.2-B	250	5.8±0.5	45	18
13-6	AM-1181.5-B	250	3.9±0.5	30	23
14-6	AMAC-118.5-B	250	3.8±0.5	30	23
15-6	AMAC-118.5-C	250	4.0±0.5	31	22
16-6	Rosin Amine D Acetate	250	3.7±0.5	29	23
17-6	Rosin Amine D	250	3.6±0.5	28	24
18-6	AM-1120	250	4.9±0.5	38	20
4-1	AM-Coco-B	250	7.7±0.5	60	13
8-1	"	250	7.7±0.5	60	13
4-3	"	250	8.0±0.5	62	12
4-2	"	500	8.7±0.5	67	10
8-2	"	500	8.4±0.5	65	11
5-1	"	500	8.9±0.5	69	10
4-4	"	1000	9.4±0.5	73	9

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TABLE 10 (Continued)

No.	Amine	Amount, mg.	Uranium		Left in Solution, (1) mg./l.
			Precipitated, mg.	%	
<u>International Minerals and Chemical Corporation Superphosphate (1090-20) Leach Solution, pH 2.6, 36.5 mg. U/l.</u> <u>(Extra Uranium Added as Uranium Nitrate)</u>					
3192-9-4	AM-118.5-C	250	1.8±0.5	12	32
6	"	250	1.2±0.5	8	34
11-4	12-NAM-118.5-C	250	1.2±0.5	8	34
12-2	AM-1181.2-B	250	1.2±0.5	8	34
4	"	500	3.2±0.5	22	29
13-2	AM-1181.5-B	250	1.1±0.5	8	34
4	"	500	1.8±0.5	12	32
14-2	AMAC-118.5-B	250	0.8±0.5	5	35
4	"	500	2.1±0.5	14	31
15-2	AMAC-118.5-C	250	1.3±0.5	9	33
4	"	500	2.7±0.5	18	30
16-2	Rosin Amine D Acetate	250	1.0±0.5	7	35
4	Ditto	500	2.0±0.5	14	32
17-2	Rosin Amine D	250	1.0±0.5	7	35
4	Ditto	500	1.9±0.5	13	32
18-2	AM-1120	250	2.9±0.5	20	29
4	"	500	1.8±0.5	12	32
7-2	AM-Coco-B	250	2.7±0.5	19	29
4	"	500	3.3±0.5	24	27

Note: All the above amines are insoluble in water and must be converted to salts before using. They were used as 1 per cent solutions in 1 per cent acetic acid. The amines designated AMAC are the AM amine acetates supplied by Armour and Company which are soluble in water.

The suffix letter B indicates a chemically pure grade and C a technical grade.

The nature of these amines is more fully described on pages 249 and 250 of the progress report for August, 1947.

(1) By difference

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uranium in solution than did the others. This series, therefore, was singled out for further investigation.

PRECIPITATION WITH AM-COCO AMINES

Most of the work with AM-Coco-B and its acetate AMAC-Coco-B was done in the leach solutions from an International Minerals and Chemical Corporation superphosphate (No. 1090-20). Typical results are shown in Table 11. They confirm the previous results but do not demonstrate that these amines can strip the solution of uranium down to the level necessary, 2 to 3 mg./l. The extraction was, however, in general higher than with the other coconut oil amines. Again the phenomenon previously observed with the other coconut oil amines was manifest, namely that the amount of uranium precipitated was a more or less constant fraction of the amount in solution. For example, about 30 per cent of the uranium was precipitated by 500 mg. of amine whether the solution contained 12 mg. of uranium per liter or 35 mg./l. The process could be repeated with the same result on many of the filtrates.

A large number of modifications of the tests reported in Table 11 were made but the results did not better the recovery. They, therefore, are not listed in that table but will be discussed briefly.

Heating the solution during precipitation with the amine and afterward was harmful to uranium recovery.

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TABLE 11. PRECIPITATION OF URANIUM WITH AM-COCO-B FROM INTERNATIONAL MINERALS AND CHEMICAL CORPORATION SUPERPHOSPHATE SOLUTION - pH 2.6

400 cc. solution used = 100 g. raw rock

No.	Amine, mg.	Uranium			Left in Solution, mg./l.	Remarks
		In Solution, mg./l.	Precipitated mg.	%		
3192-7-1	250	11.25	1.1±0.1	24	8.5	Amine solution added rapidly
8-5	250	11.25	0.8±0.1	18	9.0	Ditto
7-3	500	11.25	2.2±0.1	49	7.0	"
8-7	500	11.25	1.5±0.1	30	7.5	"
25-1	500	12.0	1.4±0.1	29	8.5	"
2	500	12.0	1.5±0.1	31	8.0	"
3	500	12.0	1.4±0.1	29	8.5	"
4	500	12.0	1.9±0.1	39	7.0	"
26-1	500	12.0	1.6±0.1	33	8.0	Amine solution added dropwise
3	250	12.0	0.9±0.1	19	10.0	Ditto
5	100	12.0	0.3±0.1	6	11.0	"
7-2	250	35.25	2.7±0.5	19	28.0	Amine solution added rapidly
7-4	500	35.25	3.3±0.5	24	27.0	Ditto
25-5	500	35.75	4.5±0.5	31	24.0	"
6	500	35.75	4.7±0.5	33	24.0	"
7	500	35.75	4.7±0.5	33	24.0	"
8	500	35.75	4.7±0.5	33	24.0	"
26-2	500	35.75	4.8±0.5	34	24.0	Amine solution added dropwise
4	250	35.75	2.2±0.5	15	30.0	Ditto
6	100	35.75	0.7±0.5	5	34.0	"

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When the pH of the solution was raised to 3.0 and the precipitation then made the uranium recovery was not increased as would have been expected on the basis of the results obtained with the ammonium phosphate solutions (described later). Apparently there are other complex formers, besides phosphate, that nullify the effect of the higher pH.

Addition of other materials to decrease the solubility of the uranium precipitate or to aid in carrying it down were of no benefit. Both pH variation and variation in solution temperature were tried in these tests too but to no avail.

COMPOSITION OF AMINE PRECIPITATES

The composition of the amine-uranium precipitate from a uranium nitrate solution containing 2.0 g. U/l. was determined. One gram of tetraethylene pentamine per gram of uranium was used in each test. In order to check the reproducibility of composition under different conditions of precipitation the precipitations were made in the following three ways. The uranium was precipitated (1) by adding phosphoric acid to the solution of uranium nitrate and amine, (2) by adding amine solution to the uranium nitrate-phosphoric acid solution and (3) by adding the uranium nitrate solution to the amine-phosphoric acid solution. The compositions of the oven-dried precipitates are shown in Table 12.

The composition of the organic part of the precipitate could not be identified with the composition of tetraethylene pentamine.

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TABLE 12. COMPOSITION OF URANIUM-AMINE PHOSPHATE PRECIPITATES
OBTAINED WITH TETRAETHYLENE PENTAMINE

Constituent	Weight Per Cent ⁽¹⁾		
	1	2	3
Ash ⁽²⁾	83.3	82.2	83.1
H ₂ O	1.7	2.2	1.5
C	5.38	4.69	4.66
H	2.50	2.33	2.20
N(Kjeldahl)	0.77	1.00	0.70
N(Total)	3.11	3.23	3.36
P ⁽²⁾	8.36	8.37	8.62
Uranium ⁽²⁾	52.2	51.2	51.0

- (1) The composition is that of the precipitate dried in an oven at 110°C.
- (2) The composition of the ash corresponded roughly to that of uranyl pyrophosphate, (UO₂)₂P₂O₇.

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EFFECT OF PHOSPHATE IONS AND pH ON AMINE PRECIPITATION

It has been observed throughout this work that both phosphate ion and pH affect the uranium precipitation with amines. The observations have been mostly qualitative. In order to gain some quantitative knowledge of the effects three series at different pH values and with varying amounts of phosphate were run. Interference by precipitation of calcium phosphates was avoided by using ammonium phosphate and adjusting the pH with phosphoric acid and ammonia. The results are shown in Table 13.

The largest amount of P_2O_5 , at pH 2.0 and 3.0, approximates the amount found in commercial leach solutions.

At pH 2.0 no uranium was recovered when the P_2O_5 concentration was 23 g./l. or higher. At pH 2.5 the uranium recovery dropped from 85 per cent at a P_2O_5 concentration of 0.5 per cent to zero at the P_2O_5 concentration of a leach solution. At pH 3.0 the uranium recovery first dropped with increase in P_2O_5 concentration and then increased as the P_2O_5 increased. When the P_2O_5 was about that in a leach solution uranium was insoluble without the addition of amine. This indicates that in a pure ammonium phosphate solution, at least, it is possible to remove the uranium quantitatively at approximately the concentrations and acidities of natural leach solutions.

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TABLE 13. EFFECT OF P_2O_5 AND pH ON PRECIPITATION OF URANIUM WITH TETRAETHYLENE PENTAMINE

24 mg. uranium in solution
250 mg. tetraethylene pentamine used
One liter of solution used

No.	pH	P_2O_5 , g./l.	Uranium		
			Recovered mg.	%	Left in Solution mg./l.
2939-88-1	2.0	1.2	20.0±0.5	84	4.0
2	2.0	13.0	13.7±0.5	57	10.3
3	2.0	23.0	No precipitate	0	24.0
4	2.0	32.0	Ditto	0	24.0
5	2.0	41.7	"	0	24.0
6	2.0	63.8	"	0	24.0
2939-88-7	2.5	0.5	20.5±0.5	85	3.5
8	2.5	8.5	18.5±0.5	77	5.5
10	2.5	23.5	16.5±0.5	69	7.5
11	2.5	32.0	15.7±0.5	66	8.3
12	2.5	51.2	12.5±0.5	52	11.5
19	2.5	81.5	No precipitate	0	24.0
2939-88-13	3.0	Trace	20.3±0.5	85	3.7
14	3.0	7.0	20.0±0.5	84	4.0
15	3.0	14.5	18.0±0.5	75	6.0
16	3.0	24.0	18.7±0.5	78	5.3
17	3.0	27.8	19.3±0.5	80	4.7
18	3.0	44.5	23.0±0.5	96	1.0
20	3.0	81.5	24*	100*	0*

* When the uranium nitrate solution was added the uranium precipitated quantitatively without addition of amine. In all other cases no precipitate was obtained unless amine was added.

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EFFECT OF FLUORIDE ION ON AMINE PRECIPITATION

Fluoride ion, as HF, was added to some of the ammonium phosphate solutions with pH 2.5. The lowest amount tried was 1.25 g./l. of fluoride ion. This prevented precipitation of uranium completely.

Later experiments, in a synthetic calcium phosphate-phosphoric acid solution of about the composition of a natural leach solution, it was found that fluoride concentrations of 0.1 to 0.25 g./l. would materially lower uranium recoveries.

Attempts have been made to coprecipitate fluoride with uranium by means of a barium salt. Preliminary experiments were inconclusive with respect to uranium but the amount of fluoride was decreased to about 0.02 g./l.

PRECIPITATION OF URANIUM WITH HYDROGEN PEROXIDE

Attempts to precipitate uranium from leach solutions with hydrogen peroxide in the pH range 1.5 to 3.0 were unsuccessful. It required considerable reagent to lower the pH much and raising it above 3.0 caused calcium phosphate precipitation. Therefore the possibilities outside this pH range were not explored.

The leach solutions are known to contain some ferric iron. Ferric iron is known to decompose hydrogen peroxide and to make it ineffective as a precipitant for uranium unless a material like malonic acid is used to tie up the iron. This remedy is being tried.

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PRECIPITATION OF URANIUM WITH CUPFERRON

Quadrivalent uranium is precipitated by cupferron in a fairly strong acid solution. Superphosphate solutions which had been enriched to 25 mg. U/l. were reduced with aluminum and treated with cupferron but no uranium precipitated.

RECOVERY OF URANIUM BY SOLVENT EXTRACTION

Direct extraction of the uranium from superphosphate leach solutions was successful with ethyl ether when a salting-out agent was used. By making the solution up to 30 per cent with ferric nitrate and 3 per cent with nitric acid 100 per cent of the uranium was extracted at room temperature, in one hour, in a continuous extractor. The solution contained 4.4 mg. uranium and 18.7 g. P_2O_5 per 100 ml. When the amount of ferric nitrate was reduced to 15 per cent the recovery of uranium dropped to 25 per cent but was raised again to 45 per cent by extracting at $0^\circ C$.

The drawback to this process is that so much iron salt was added to the solution that P_2O_5 recovery was difficult. When the extracted solution was put back on the leached residue, or was evaporated, it formed a gel. Any calcium phosphates which could be recovered would be high in iron salts. At best they would contain large amounts of hygroscopic ferric and calcium nitrates.

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RECOVERY OF URANIUM BY ION EXCHANGE

Uranium recovery from solutions with ion-exchange methods was not so successful as precipitation with amines. Two commercial cation-exchange materials, Zeo-Karb, a natural coal base material, and Amberlite XE3, a synthetic resin, were used. Recovery from dilute, unacidified uranyl nitrate solutions containing 30 mg./l. uranium was about 40 per cent for the Zeo-Karb and 66 per cent for the Amberlite. This recovery rapidly decreased the addition of phosphoric acid. Practically no uranium could be recovered from superphosphate leach solutions probably because of the large amount of calcium ion. Table 14 summarizes the tests on the uranyl nitrate-phosphoric acid solutions.

P₂O₅ RECOVERY FROM LEACH SOLUTIONS

To date two methods have been tested for recovery of P₂O₅. One was evaporation of the leach solution either in contact with the leach residue or alone. The other was chemical precipitation using calcium oxide (CaO) to give a final product which was mostly dicalcium phosphate. The dicalcium phosphate was only very slightly soluble in water, but almost completely available as determined by the citrate solubility test. Table 15 shows typical results.

Evaporation of the leach solution in contact with the residue gave a final product almost identical with the original superphosphate.

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TABLE 14. RECOVERY OF URANIUM BY ION EXCHANGE FROM PHOSPHORIC ACID SOLUTIONS CONTAINING 30 mg./l. U

Test No.	H_3PO_4 , %	Uranium Recovery	
		mg.	%
<u>Zeo-Karb</u>			
2758-80	0	12.4+1.0	41.0
87	5	13.3+1.0	44.0
88-1	10	0.4+0.1	1.3
88-2	15	0.2+0.1	0.6
90-1	23	0.1+0.1	-
90-2	41	0.1+0.1	-
<u>Amberlite XE3</u>			
2758-89-1	0	19.9+1.0	66.0
89-2	5	0.5+0.1	1.6
91-1	10	0.3+0.1	1.0
91-2	15	0.2+0.1	-
92-1	23	0.1+0.1	-
92-2	41	0.2+0.1	-

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TABLE 15. P₂O₅ RECOVERY FROM LEACH SOLUTIONS

Based on 190 gm. superphosphate =
100 g. rock

Sacco — a product of the Smith Agricultural Chemical Company

1090-20 — a product of International Minerals and Mining Company

No.	P ₂ O ₅					
	<u>In Superphosphate</u>		<u>Recovered in Product</u>		<u>Analysis of Product</u>	
	Total, Available, g.	Total, Available, g.	Total, Available, g.	Total, Available, g.	Total, Available, %	Total, Available, %
<u>Evaporation of Leach Solution on the Residue From Sacco</u>						
2940-24-1	39.0	36.2	39.0	36.2	20.7	19.1
2939-40-1	39.0	36.2	41.0	37.0	21.7	19.5
<u>Evaporation of Leach Solution Alone From Sacco</u>						
2939-41-1*	-	36.2	24.8	24.8	53.5	53.5
<u>CaO Precipitation — 20 gm. CaO Used for Precipitation Solution From No. 1090-20</u>						
2940-44-1	34.3	33.4	33.6	31.9	39.4	37.1
2940-44-4	34.3	33.4	32.7	32.7	39.4	39.4

Note: The product obtained by CaO precipitation contained 0.2 per cent F. Similar products obtained in other experiments contained even less.

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The evaporation of leach solution alone did not recover all of the P_2O_5 because the P_2O_5 in the residue is lost if the residue is not used. The product, however, was much like triple superphosphate.

The calcium oxide precipitation went rapidly to completion when a slight excess of calcium oxide was used. The final product after drying was granular and easily handled. It contained 39 per cent of available P_2O_5 .

DISCUSSION

The sulphuric acid treatment of raw Idaho and Florida phosphate rock have demonstrated that it will probably be impossible to get much more than about 55 per cent of the uranium into solution by making phosphoric acid or by manufacture of superphosphate and leaching it with water. The results in water leaching commercial superphosphate were less encouraging because water alone on Sacco superphosphate removed only about 25 to 30 per cent of the uranium. Slightly better was done on commercial Florida material but it was necessary to acidify the superphosphate in order to bring the extraction up to the 55 per cent obtained on the rock.

Slightly better results were obtained, 60 to 70 per cent extraction, by making triple superphosphate from Idaho rock, or by calcining the rock to destroy organic matter, making superphosphate and then water leaching. The extraction after calcining, based on experiments which need checking, was about 80 per cent.

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These results show that if more uranium is to be extracted either the rock will have to be attacked by reagents other than the sulphuric acid used in superphosphate manufacture or the leached residue will have to be processed separately. Nitric acid may be used to leach the rock or to make a nitrate superphosphate. In either case 100 per cent of the uranium was made water soluble. From the standpoint of ease of handling, and fitting into the present phosphate industry, this solution is not very attractive.

The other alternative, that of treating the leached residue, is free from further interference with the superphosphate process. The choice of reagents and process are not restricted but the entire cost of treatment will be borne by the uranium. A study of methods for extracting uranium from the residue is under way. Only a few incomplete results are yet available.

With respect to uranium recovery from leach solutions, ether extraction and amine precipitation have given the highest yields, 100 per cent and about 50 per cent, respectively. The first has the drawback that a large amount of salting-out agent, which interferes with P_2O_5 recovery, is necessary. The presently used amines are not sensitive enough, at least on leach solutions from raw rock, to remove uranium down to 2 to 3 mg./l. in a single precipitation with up to 170 times as much amine as uranium by weight. The best that has been done is to leave 5 to 6 mg./l. Repeated precipitation has not been tried sufficiently yet to appraise its value.

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Several ways to improve recovery are under study. They are among others (1) use of larger ratios of amine to uranium, (2) repeated precipitation, (3) improvement in precipitation conditions by removing organic matter and removing or complexing the fluoride, and (4) constant search for a better and more sensitive reagent.

A uranium recovery process based on present data and designed to interfere as little as possible with present phosphate practice would have about the following steps and would recover about 25 per cent of the uranium in the rock:

- (1) Acid treatment of the rock to make superphosphate or a liquid slurry. The slurry would be preferable because only filtration and washing would be necessary. About 55 per cent of the uranium and 75 to 90 per cent of the P_2O_5 would dissolve.
- (2) Precipitate uranium from the filtrate with a coconut oil amine, filter and wash. About 40 to 60 per cent of the dissolved uranium would be precipitated and recovered.
- (3) Recover the P_2O_5 from the solution by evaporation or by precipitation with CaO . By evaporation on the residue 100 per cent of the P_2O_5 may be recovered as superphosphate with 19 to 20 per cent available P_2O_5 . Precipitation with CaO produces a dicalcium phosphate with 38 to 40 per cent available (citrate soluble) P_2O_5 .

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The process described is not entirely satisfactory largely because of the low recovery of uranium from the rock. It needs to be improved by some one or more of the means discussed above.

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December 16, 1947

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