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throughout

AECD-3738

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RECOVERY OF URANIUM FROM WET PROCESS PHOSPHORIC ACID
Final Report

By
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The Economics of Iron Reduction

ABSTRACT

The state of reduction of wet process phosphoric acid determines largely the extractability of its uranium content.

This report defines the economic relationships involved over a wide range of reduction of the acid. Reductant consumption, penalties and capital investment as well as solvent consumption are evaluated.

The data presented here indicate:

1. It is economically advantageous to reduce the acid to about 210 mv.
2. Reduction below 150 mv is not feasible. If the acid is not reduced, solvent consumption is prohibitive; at about 170 mv, cost of iron addition becomes the controlling factor; at about 150 mv the efficiency of the iron as a reducing agent drops profoundly; at about 150 mv the solvent reaches peak efficiency. On either side thereof, efficiency decreases rapidly.

The Economics of Iron Reduction

Throughout the investigations of the feasibility of the solvent extraction process for the recovery of uranium values from phosphoric acid it has been recognized that the state of oxidation of the cations present largely determines the extractability of the uranium. The most promising solvents, those resulting from the condensation of one mole of P_2O_5 with about two moles of an octyl alcohol, are far more effective in extracting uranium from "reduced" phosphoric acid than from oxidized. Reduction may be carried out by the addition of metallic iron, aluminum, or zinc to the acid and the extent of reduction determined by measurement of the change in potential between two electrodes in the mixture. The salts of the metals added remain as contaminants in the solution and interfere with complete utilization of the acid in the manufacture of triple super phosphate.

It has also been recognized that the solvent (O.P.P.A.) declines in activity after preparation, at rates dependent upon storage conditions and possibly upon method of preparation; contact with acid, as HF or H_3PO_4 , affect the solvent adversely.

The purpose of this report is to show how the cost of uranium would vary with extent of reduction of the acid.

In the fall of 1952, the relationship of a solvent's ability to extract uranium from wet process phosphoric acid and the oxidative state of the acid, was investigated. The solvent used was a kerosene solution of the product of combination of one mole of phosphoric anhydride with two moles of Diisobutyl Carbinol. The active material was, apparently, a mixture of several compounds and was for convenience called D.P.P.A. Below in Table I are recorded some data derived from the investigation.

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TABLE I Extraction Coefficient of 100% D.P.P.A. (K*) vs Wet Process
Phosphoric Acid at Various Oxidation Levels

E.M.F. mv A_{w} vs St'd
C.E. as read on Model
G Beckman

Extraction Coefficient

Date of Test	A Before Reduction	B After Reduction	C As Rec'd	D After Reduced	E Ratio = $\frac{K^* \text{ Red.}}{K \text{ as Red.}}$	F Ratio x Ave. K*	G Change in E.M.F. mv	H Wt. of Iron Added g/L
7-21	344	178	—	—	—	—	166	4.7
7-22	332	113	—	—	—	—	219	9.1
7-28	323	253	325	534	1.64	523	70	2.2
7-29	329	205	292	1595	5.45	1740	124	3.4
7-30	319	171	257	5120	19.9	6350	148	5.1
7-31	323	158	214	7720	36.1	11500	165	8.7
8-1	323	139	312	4350	14.0	4480	184	—
8-4	322	136	386	3844	10.0	3860	186	7.0
8-5	330	-12	410	3800	9.3	2970	342	7.3
8-6	324	-48	566	4880	8.6	2740	372	13.0
8-7	321	170	418	2796	6.7	2140	151	7.1
8-8	326	153	380	2780	7.3	2300	173	6.2
8-11	327	24	306	3470	11.3	3610	303	13.6
8-12	329	82	141	2540	18.0	5750	147	13.2
8-13	331	120	267	2760	10.3	3290	211	8.2
8-14	327	-55	151	5170	34.2	10900	377	10.2
8-15	330	-32	362	2750	7.6	2420	—	—
8-18	322	114	310	1770	5.7	1820	—	—
Ave.	324		319				210	7.9

A graph of the data (Fig. 1), in which the activity of the solvent (as signified by a distribution coefficient K^* for the 100% solvent) is plotted against the e.m.f. of the acid just prior to extraction, is an S-shaped curve. A correction has been applied to minimize variations in activity from batch to batch of solvent. This and other data follow the same pattern. A fairly well defined curve is obtained between 330 mv and 150 mv (as read on a Beckman Model-G pH meter with gold and saturated calomel electrodes). When the acid is reduced below 150 mv, the results are very erratic but there appears to be a range of maximum extractability of uranium at 150 to 50 mv. At lower e.m.fs, extraction seems to drop off.

In the runs for which data are presented, reduction of the acid was carried out by pumping the acid through a column packed with nails. The loss in weight of the nails was determined for each reduction. The data are recorded in columns G & H, Table 1, and are represented graphically in Figure 2. One gram of iron reduces the e.m.f. of the acid 27 ± 9 mv in this case. About 4 grams of iron would be required to reduce the acid 100 mv.

In later work, acid for pilot plant extraction studies was reduced by circulation over scrap steel. Associated with the scrap were considerable amounts of rust and phosphate corrosion products. An average reduction of 23 ± 12 mv was obtained per gram of iron added per liter of acid. The iron added was determined by assay of the acid before and after reduction. The e.m.f. of the starting acid (plant acid) ranged between 270 and 326 mv and was reduced to about 230 mv (Au vs St'd C.E. as read on Beckman pH meter).

Over a period of nearly two years occasional small batches of acid have been reduced by the addition of weighed amounts of hydrogen-reduced iron powder. An average of about twenty such reductions in which the e.m.f. of the starting acid ranged from

FIG 2
REDUCTION OF PHOSPHORIC ACID

GM LOSS IN WT OF NAILS PER LITER
OF ACID
VS
REDUCTION IN MV.

FE Added g/l

REDUCTION IN L.P.P. MV

10-11-50

TABLE II Reduction of Phosphoric Acid With Scrap Iron - Iron Added Determined by Analysis of Phosphoric Acid Before and After Reduction

Date	E.M.F. Start	E.M.F. After Reduction	Gm/L Fe	Reduction in E.M.F.
12-6-52	305	233	2.85	72
"	305	239	1.36	66
"	310	238	1.88	72
"	310	211	4.62	99
2-2-53	315	226	4.78	89
"	297	226	2.91	71
"	297	227	2.25	70
2-7-53	272	209	2.95	63
2-9-53	278	224	2.88	54
"	278	234	1.79	44
2-13-53	275	225	2.75	50
"	275	226	1.94	49
"	272	243	1.62	29
2-14-53	270	222	2.41	48
"	270	229	2.63	41
2-20-53	270	224	3.11	46
"	270	224	2.47	46
"	277	235	1.36	42
"	277	232	1.77	45
2-21-53	271	232	2.06	39
"	271	229	2.02	42
3-3-53	294	222	2.69	72
4-15-53	288	230	2.19	58
5-19-53	323	241	3.37	82
"	326	239	2.13	87
Ave.			2.51	59

Note: $59 \div 2.51 = 24$

1.18

**TABLE III Reduction of Phosphoric Acid Solution With Hydrogen
Reduced Powdered Iron**

Date of Run	E.M.F. mv		Difference	Iron Added	
	As Rec'd	After Reduction		g/L	Kind
3-9-53	301	222	79	2	H ₂ Reduced Powder
"	311	228	83	2	" " "
"	288	225	63	2	" " "
"	288	218	70	2	" " "
10-3-53	282	224	58	2	" " "
"	282	249	33	2	Shavings
10-5-53	297	258	39	2	Shavings
"	297	235	62	2	H ₂ Reduced
10-6-53	297	231	66	2	" "
"	297	243	56	3	Shavings
10-7-53	299	230	69	4	Shavings
"	299	228	71	2	H ₂ Reduced
10-9-53	297	231	66	4	Fine Iron Shavings
"	297	232	65	4	Coarse Iron Shavings
3-26-54	334	236	98	3	H ₂ Reduced
"	334	224	110	3.4	" "
4-16-54	292	228	64	2	" "
"	292	190	102	4	" "
"	292	143	149	6	" "
"	292	125	167	8	" "
"	292	119	173	10	" "
"	292	112	180	12	" "
4-28-54	310	179	131	4	" "

Average of all H₂ reduced data above; 4.1 g Fe reduced the acid 102 mv or

1 g = 26 mv

Average of those where 4 g or less of Fe added; 1 g = 33 mv

GR Fe Added PER LITER OF ACID

FIG 3
REDUCTION OF PHOSPHORIC
ACID W. H₂-REDUCED
POWDERED IRON

GR Fe Added $\frac{1}{2}$
VS
 Δ E.M.F.

P.I.Q.
10-5-54

290 to 335 mv showed that one gram of iron powder added to a liter of acid reduced the e.m.f. 26 ± 9 mv. A plot of the data, mv reduction in e.m.f. vs. g iron added, shows that the relationship is not a straight line function but that as acid is more reduced, greater quantities of iron are required to reduce the acid a given number of millivolts. Partial reduction of the acid with iron is therefore more efficient. In the 14 runs in which 4 g or less of iron was added per liter of acid, average reduction was 33.5 ± 9 mv per gram of iron added. (Fig. 3).

The e.m.f. has been determined on a great many samples of wet process phosphoric acid as it comes from the filters in Armour's plant. In addition, tests have been run on acid from other plants. Most of the values range between 290 mv and 330 mv. Several extraction tests were carried out on acid as received from the plant. Not only was the extractability of the uranium low as is indicated by data presented in the first part of this report, the results were also quite erratic. It was concluded the acid should be reduced to some narrow range of e.m.f. before extraction to assume more uniform behavior. A range of 220 to 230 mv was selected and used as a standard level of reduction for many of the studies carried out in this laboratory. It was found that usually the amount of iron required for the reduction could be predicted if the initial e.m.f. were known.

The fact that partial reduction seemed to stabilize the acid to atmospheric oxidation was another factor in determining that partial reduction should be used.

The costs of iron reduction are: cost of iron, capital cost of reducing vessels and equipment and penalty for P_2O_5 neutralized by iron and therefore not available for freeing more P_2O_5 from rock.

The savings affected by iron reduction stem from reduced solvent requirements. Data obtained in this laboratory from the operation of a bench scale pilot plant

indicate that in one complete cycle through extraction and precipitation, solvent loses 50% of its effectiveness. If 3% active (O.P.P.A.) in kerosene is required to extract the uranium from phosphoric acid, then after precipitation of the uranium the kerosene solution behaves as though it contained 1-1/2% fresh solvent.

It was found necessary to add 100% O.P.P.A. to the extent of 1-1/2% of the oil stream to maintain the extractive ability of the solvent at a level that would give 90% extraction of uranium in 4 stages at a 1:10 oil to acid ratio.

Before proceeding with calculations of economics of iron reduction, data were compiled in a series of current runs (see Table IV).

Though the solvent used was made from iso octyl alcohol (Enjay) it nevertheless was found to fit data reported above. The amount of iron used in reduction was determined both by weight and by chemical assay.

Graphs (Fig. 4 & 5) of the data showed novel characteristics:

1. Below 150 mv iron is only one tenth as efficient reductant as above 150 mv.
2. The efficiency of the solvent not only increases as the acid is reduced, but peaks at 150 mv and then declines rapidly.

Because of the above facts and because highly reduced solutions re-oxidize rapidly, reduction below 150 mv is not warranted.

In making these runs the e.m.f. was measured 1/2 hour after reduction and later just before extraction. After extraction the e.m.f. of the raffinate was taken. The e.m.f. of the raffinate frequently duplicated the e.m.f. before extraction. The e.m.f.s taken earlier at the end of reduction were erratic and lower than those taken on the same samples later. The presence of hydrogen seems to give erroneous readings. The e.m.f.'s of the raffinates were taken as being most representative.

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TABLE IV Extractability of Uranium Values From Wet Process Phosphoric Acid @ Various E.M.Fs.

Shaker #	E.M.F. mv				Iron g/L			Uranium Mg/L			
	B	C	D	E	F	G	H	I	K*	K* !	
	% OPFA in Oil	At Time of Extn	Of Raffinate	Head E.M.F.-C Diff.	Wt. Red. Added	By Chemical Assay	Iron Added (By Assay)	Raff. Ca	Oil Layer Co.	$\frac{100}{\%OPFA}$	Adjusted
Run 1, 9/14/54 (Plant Acid Obtained 9/13/54 E.M.F. 274 mv)											
1	3	274	273	0	0	5.60	0.0	49	745	505	580
2	3	235	238	36	1	6.62	1.01	35	965	914	1050
3	3	212	213	61	2	7.50	1.90	30	1140	1300	1500
4	3	152	151	123	4	9.15	3.55	16	1320	2695	3100
5	1	132	139	135	8	11.91	6.31	37	965	2620	3000
6	1	125	131	143	12	14.62	9.02	46	789	1722	2000
7	1	111	119	165	16	18.10	12.50	46	789	1722	2000
8 Std.	3	223	223	0	0	---	0.0	53	1100	695	800
Run #2 9-17-54 (Plant Acid Obtained 9/16/54 E.M.F. 280 mv)											
1	3	280	278	2	0	5.92	0.0	44	698	526	530
2	3	243	238	42	1	6.84	0.92	33	718	730	730
3	3	210	212	68	2	7.82	1.90	28	860	1030	1000
4	3	145	145	135	4	9.40	3.48	12	985	2855	2900
5	1	111	129	151	8	12.09	6.17	34	780	2295	2300
6	1	90	124	156	12	14.24	8.32	34	738	2122	2100
7	1	83	116	164	16	18.29	12.37	34	655	1905	1900
8 Std.	3	218	223	-5	0	10.70	0.0	41	985	802	800
Run #3 9/21/54 (Plant Acid Obtained 9/20/54 E.M.F. 277 mv)											
1	3	277	277	0	0	5.70	0.0	50	880	586	600
2	3	248	246	31	1	6.65	0.95	35	1080	1045	1100
3	3	220	220	57	2	7.69	1.99	22	1200	1796	1850
4	3	159	152	127	4	8.86	3.16	10	1420	4640	4800
5	1	130	138	139	8	12.06	6.36	35	1080	3070	3150
6	1	103	128	149	12	16.14	10.44	40	1034	2630	2700
7	1	88	116	161	16	19.97	14.27	38	862	2270	2300
8 Std.	3	224	222	2	0	10.63	0.0	47	1080	772	800

TABLE IV (Cont.)

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Extractability of Uranium Values From Wet Process Phosphoric Acid @ Various E.M.Fs. (Cont.)

Shaker #	E.M.F. mv				Iron g/L			Uranium Mg/L			
	B	C	D	E	F	G	H	I	K*	K*1	
	% OPPA In Oil	At Time of Extn	Of Raffinate	Head E.M.F.-C Diff.	Wt. Red. Added	By Chemical Assay	Iron Added (By Assay)	Raff. C _a	Oil Layer C _o	$\frac{1 \times 100}{H \times \% \text{OPPA}}$	Adjusted
Run #4 9/23/54 (Plant Acid Obtained 9/22/54 E.M.F. 277 mv)											
1 PA	3	277	284	-7	0	5.89	0.0	48	1020	713	620
2	3	242	244	33	1	6.77	0.88	40	1040	867	950
3	3	216	214	63	2	7.66	1.77	28	1192	1435	1200
4	3	150	150	127	4	9.31	3.42	14	1385	3300	2900
5	1	124	134	143	8	13.00	7.11	42	1000	2410	2100
6	1	104	125	152	12	17.28	11.39	48	924	1935	1700
7	1	96	120	157	16	20.26	14.37	48	848	1780	1500
8 Std.	3	220	225	-5	0	10.85		37	1020	923	800

Ave. K* for Standard $\frac{695 + 802 + 772 + 923}{4} = 800$

$$K^{*1} = K^* \times \frac{800}{K^* \text{ for the standard for each run}}$$

SUMMARY REPORT

ABSTRACT

The results of investigations of processes for the recovery of uranium from Armour Fertilizer Works wet process phosphoric acid are described.

Details of a solvent extraction process are presented.

* * * * *

In October, 1951, work on the development of a feasible process for the recovery of uranium from phosphoric acid was begun.

The first process investigated was one involving ion exchange. Phosphoric acid containing uranium was to be pumped over an ion exchange resin. At an optimum time the flow of acid over the bed was to be interrupted and the uranium removed from the resin with the proper reagent, and recovered. The process was not satisfactory for the following reasons:

1. Phosphoric acid due to solids content does not pass through a resin bed readily.
2. All resins were too expensive.
3. There was too much dilution of the phosphoric acid stream.

A solvent extraction process was proposed. In about April, 1951, work was undertaken evaluating it. The work has culminated in a Cost Estimate and Plant Proposal (B.P. 115) for the recovery of uranium from phosphoric acid.

On the basis of data derived in laboratory scale investigations at Armour, the unit cost of uranium promises to be quite high. The estimate should now be checked by plant scale operation. In the next four months such data should be available and should establish whether uranium recovery at Armour is warranted.

When the by-product recovery program was undertaken it was proposed that processes for the recovery of uranium from Florida phosphate be investigated by the Armour group on a laboratory scale. Pilot plant work was to be done at U.S. Phosphoric Products Co., Tampa, and at I.M.C.C., Mulberry. There was to be free exchange of data and cooperation among the groups concerned.

The work done at this laboratory has been covered with weekly progress reports, and with occasional summary or topical reports. Attached to this report is a subject index of weekly progress (W.R. reports) and topical (B.P.) reports which cover the work done in this laboratory.

Phosphate rock as it comes to the plant contains varying amounts of uranium depending upon the grade of the rock and the location of the originating mine. The variation due to grade is illustrated by the data in Table I.

The table not only includes the rock assays but also the assays of acid derived from it. If it is assumed that 90% of the phosphate values of the rock are recovered in the acid, a means is provided of estimating the extent to which the uranium of the rock reports to phosphoric acid. This is shown in the last column of the table. It is 0.90 times the apparent percentage of uranium reporting to the acid, which in turn is determined from the ratios of U_3O_8 to P_2O_5 assays in the acid and in the rock.

By direct assay of samples of various streams in the plant, including waste streams, a rough check was obtained on the above figures.

As a general rule the better the operations in the plant are, the better the recovery of P_2O_5 and also the better the recovery of U_3O_8 . It is said that oxidizing agents in the digestors increase the recovery of uranium, rock to acid. None were

TABLE I Some Average Assays of Various Grades of Rock Supplied.
Armour and the Assays of Acid Derived From It

Rock					Phosphoric Acid			
A	B	C	D	(D/C) x 10 ³	E	F	F/C	$\frac{F/E}{D/C} \times 100 \times .9 =$
(% BPL) Grade	No Sample	% P ₂ O ₅	% U ₃ O ₈	Ratio x 10 ³	G/L P ₂ O ₅	mg/L U ₃ O ₈	Ratio	% Recovery
68	7	31.70	0.0158	0.485	309	136	0.44	81
77	5	35.07	0.0090	0.255	314	73	0.232	83
75	6	34.32	0.0094	0.259	314	64	0.202	70
73	8	33.21	0.0089	0.267	302	60.9	0.204	69
73	6	33.60	0.0085	0.260	311	59	0.190	66
72	7	32.70	0.0129	0.395	309	89.1	0.288	66
68	6	30.9	0.0210	0.682	296	164	0.555	82

tried here. Materials of construction in our plant do not lend themselves to further contamination of phosphoric acid.

After the uranium values are in phosphoric acid there are at least three possible methods of separating them. The uranium may be removed by ion exchange, precipitation or solvent extraction.

Precipitation procedures are used by Blockson and others who usually are required to separate "muds" from their wet-process acid anyway. For our operation the consumption of chemicals suggested to date has appeared excessive and contamination of the acid has been a hazard.

Ion exchange was tried but for reasons outlined earlier was not a feasible process.

Of the processes suggested, solvent extraction would appear to offer the most promise. Our efforts have been expended mainly on the development of such a process.

The process visualized would involve receiving and measuring the phosphoric acid from the factory, cooling it, reducing it, clarifying it, if necessary, and contacting it with a solvent to remove the uranium. The acid would then have to be metered back to the fertilizer plant.

The solvent stream would be subjected to treatment to remove the uranium, would be rejuvenated, and would be used again to extract more uranium from acid.

Phosphoric acid as produced by Armour is a coffee-colored solution containing about 23 to 25% P_2O_5 and U_3O_8 as recorded in Table I. As it comes from the filters its temperature is about 155 °F. In it are suspended solid particles of various

sizes. Upon cooling to 80 °F, 5 to 30 g/L (0.4 to 2.5%) of solids may precipitate from the acid. The acid contains about 2% fluorine (W.R. 86) present, mostly as fluosilicates. The E.M.F. (as measured on a Beckman Model G pH Meter, Au vs St'd calomel electrodes) ranges between 275 and 340 mv. Usually the E.M.F. will be about 320 mv.

The solvent or extracting medium is a solution of O.P.P.A. in kerosene. The active agent (called O.P.P.A. for convenience) is probably a mixture of unstable condensation products resulting from the addition of about two moles of an alcohol having 8 to 10 carbon atoms in the aliphatic skeleton to phosphorus pentoxide. The heat of reaction i.e., the heat evolved when the reagents are brought together, is about 35,000 gram calories per gram mole or about 65,000 B.T.U. per pound mole (W.R. 123)

Most of the solvents prepared in this laboratory have been prepared by placing two mole equivalents of the alcohol in a beaker in a water bath. To the alcohol under vigorous agitation is added one mole equivalent of P_2O_5 at a rate to keep the temperature below 130 °F. (55 °C).

A number of alcohols have been tested and evaluated (W.R. 123 & 126). About all that can be said is that on the basis of laboratory data, iso-octyl or capryl alcohols would be most economical to use. (See Table II).

Differences in reactivities of the alcohols are emphasized by the discrepancies in equivalent weight determinations by the two methods. The phthalic anhydride method is best as it is less subject to experimental error and it gives lower equivalent weights. On a plant scale, any differences that show up in laboratory tests might be erased by cooling difficulties, etc. Some of the alcohols dehydrate easily.

TABLE II Evaluation of Alcohols

From W.R. 126

Order	Alcohol	Source	Eq. Wt. By Acetic Anhydride Method	Eq. Wt.* By Phthalic Anhydride Method	\$ Cost/Lb.			% Req'd For 60% Ext'n	Equiv. Cost
					Alc	OPPA	K* Ave.		
1	Oxo Bottoms	Enjay	378	360	0.077	0.091	1018	1.42	0.11
2	Capryl	Hardesty	159	140	0.210	0.197	2264	0.66	0.13
3	Iso Octyl	Enjay	130	133	0.220	0.202	2257	0.67	0.13
4	Ethyl Amyl Carbinol	Shell	134	139	0.170	0.169	1647	0.91	0.16
5	CPS 224 (Decyl)	Enjay	172	162	0.228	0.210	1884	0.80	0.17
6	Capryl (85%)	Rohm & Haas	159	148	0.210	0.197	1682	0.89	0.18
7	N Octyl	Mathieson	152	132	0.325	0.274	2641	0.57	0.16
8	2 Ethyl Hexyl	Texas Eastman	153	134	0.220	0.202	1509	1.00	0.20
9	Di isobutyl Carbinol	Carbide & Carbon	153	153	0.185	0.180	1367	1.10	0.20

* Determined later and reported in W.R. 128

So far, the most satisfactory means of determining the activity or extractive ability of O.P.P.A. has been to actually carry out an extraction; no short cuts have been found. Such a test would require about an hour under optimum conditions.

Titration of the strong and weak $[H^+]$ from O.P.P.A. has not proven a means of measuring activity.

O.P.P.A. is most active as a solvent for uranium at the time it is made up or within about four hours afterwards. Thereafter its activity declines as much as 50% in 24 hours. This decline is so marked that the group at U.S.P.P. have considered making up solvent continuously and/or refrigerating the material after it is made up (W.R. 44 & 143).

Efforts to eliminate variables in the preparation of O.P.P.A. have met with only partial success. The value of the distribution coefficient K^* may vary by a factor of two from batch to batch of solvent though the same combination of raw materials are used. Because of this variability, studies such as the one above require much repetitions work.

The temperature at which O.P.P.A. is made has a profound effect on its subsequent activity. As a consequence, temperature during the addition of P_2O_5 to alcohol is held in the 90 °F to 130 °F range. (W.R. 143). In the plant scale operations this single consideration will be very important. The heat evolved in the preparation (65,000 B.T.U./# mole) must be carried away rapidly or an inferior solvent containing dehydration products and phosphoric acid will be produced.

Investigations aimed at determining optimum ratio of alcohol to P_2O_5 have shown only that it is near the 2 to 1 ratio. Probably an excess of P_2O_5 , say 10% in the above proportion will be desirable as there usually is some moisture pick-up

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during handling. Tests have shown that the activity of the solvent is largely proportional to the kerosene-soluble phosphorus compounds. Both phosphoric anhydride and its hydration products are lost to the aqueous phase upon contact and are ineffective as active solvent.

The kerosene portion of the extracting solution is there simply as a diluent and carrier for the O.P.P.A. Within the limits of experimental error little difference was found between samples of kerosene. It is believed that any aliphatic hydrocarbon mixture such as kerosene would be satisfactory. The advantages possessed by kerosene are: its comparatively low price, its availability, its viscosity, its flash point, and its immiscibility in aqueous solutions.

Diluent superior to kerosene may be available but as long as an entrainment loss of solvent of the order of 2% of the solvent stream (W.R. 112) is anticipated, the unit price of the material must be kept low. Fuel oil is ruled out because of its tendency to form stable emulsions at 80 - 100 °F.

If O.P.P.A. is made by slurring P_2O_5 in kerosene and then adding alcohol, the kerosene then must be quite inert to P_2O_5 and must have little entrained water. This method of preparing O.P.P.A. would be simpler to follow on plant scale but would lead to waste of O.P.P.A. and diluent. By this method the product is about 30% O.P.P.A. and 60% kerosene. If O.P.P.A. requirements are met during operations then the diluent requirements are exceeded; spent solvent tends to accumulate and would have to be utilized.

Of the factors which influence the extractability of uranium from phosphoric acid with O.P.P.A., the most important one is the state of reduction of the acid. The relationship is well illustrated in Table III (B.P. 120). The state of reduction of the acid is determined by means of the E.M.F. set up between gold and saturated calomel electrodes immersed in the acid. The E.M.F. recorded is taken directly from the reading in millivolts on a Beckman Model G pH meter, Thus a high (ca. 300 mv) positive value indicates an "oxidized" or unreduced sample.

Of the methods of reduction available, only a few have been examined in this laboratory.

Sulfur dioxide was unsatisfactory because even after extensive treatment with it the uranium values were held in phosphoric acid as tenaciously as though no reduction had been attempted. W.R. 56 & 57.

Metallic zinc was not used.

The possibility of using electrolytic reduction has been suggested and a small experimental cell was obtained from Rohm & Haas. No work has yet been done with this unit.

The use of iron as a reductant has been investigated extensively. A report has been written covering the Economics of Iron Reduction. (B.P. 120).

Reduction of phosphoric acid, while it involves capital investment for equipment, a cost for iron actually added and a cost for P_2O_5 tied up as iron salts and no longer available as phosphoric acid for acidulation of rock, decreases substantially the solvent requirements. The result is that it is economical to partially reduce the phosphoric acid to say 220 mv before extraction. B.P. 120

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TABLE III Extractability of Uranium Values From Wet Process Phosphoric Acid @ Various E.M.Fs.

		E.M.F. mv			Iron g/L			Uranium mg/L			
		B	C	D	E	F	G	H	I	K*	K*
Shaker #	% OPPA in Oil	At Time of Extrn	of Raffinate	Head E.M.F.-C Diff.	g Redu't Added	By Chemical Assay	Iron Added (By Assay)	Raff. C _a	Oil Layer C _o	I x 100 H x OPPA	Adjusted
Run 1, 9/14/54 (Plant Acid Obtained 9/13/54 E.M.F. 274 mv)											
1	3	274	273	0	0	5.60	0.0	49	745	505	580
2	3	235	238	36	1	6.62	1.01	35	965	914	1050
3	3	212	213	61	2	7.50	1.90	30	1140	1300	1500
4	3	152	151	123	4	9.15	3.55	16	1320	2695	3100
5	1	132	139	135	8	11.91	6.31	37	965	2620	3000
6	1	125	131	143	12	14.62	9.02	46	789	1722	2000
7	1	111	119	165	16	18.10	12.50	46	789	1722	2000
8 Std.	3	223	223	0	0	---	0.0	53	1100	695	800
Run 2 9-17-54 (Plant Acid Obtained 9/16/54 E.M.F. 280 mv)											
1	3	280	278	2	0	5.92	0.0	44	698	526	530
2	3	243	238	42	1	6.84	0.92	33	718	730	730
3	3	210	212	68	2	7.82	1.90	28	860	1030	1000
4	3	145	145	135	4	9.40	3.48	12	985	2855	2900
5	1	111	129	151	8	12.09	6.17	34	780	2295	2300
6	1	90	124	156	12	14.24	8.32	34	738	2122	2100
7	1	83	116	164	16	18.29	12.37	34	655	1905	1900
8 Std.	3	218	223	-5	0	10.70	0.0	41	985	802	800
Run 3 9/21/54 (Plant Acid Obtained 9/20/54 E.M.F. 277 mv)											
1	3	277	277	0	0	5.70	0.0	50	880	586	600
2	3	248	246	31	1	6.65	0.95	35	1080	1045	1100
3	3	220	220	57	2	7.69	1.99	22	1200	1796	1850
4	3	159	152	127	4	8.86	3.16	10	1420	4640	4800
5	1	130	138	139	8	12.06	6.36	35	1080	3070	3150
6	1	103	128	149	12	16.14	10.44	40	1034	2630	2700
7	1	88	116	161	16	19.97	14.27	38	862	2270	2300
8 Std.	3	224	222	2	0	10.63	0.0	47	1080	772	800

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TABLE III (Cont.)

Extractability of Uranium Values From Wet Process Phosphoric Acid @ Various E.M.Fs. (Cont.)

E.M.F. mv					Iron g/L			Uranium Mg/L			
B		C	D	E	F	G	H	I	K*	K*'	
Shaker #	% OPPA In Oil	At Time Of Extrn	Of Raffinate	Head E.M.F.-C Diff.	g Reduc't Added	By Chemical Assay	Iron Added (By Assay)	Raff. Ca	Oil Layer Co	$\frac{1 \times 100}{H \times \% OPPA}$	Adjusted
Run 4 9/23/54 (Plant Acid Obtained 9/22/54 E.M.F. 277 mv)											
1 PA	3	277	284	-7	0	5.89	0.0	48	1020	713	620
2	3	242	244	33	1	6.77	0.88	40	1040	867	950
3	3	216	214	63	2	7.66	1.77	28	1192	1435	1200
4	3	150	150	127	4	9.31	3.42	14	1385	3300	2900
5	1	124	134	143	8	13.00	7.11	42	1000	2410	2100
6	1	104	125	152	12	17.28	11.39	48	924	1935	1700
7	1	96	120	157	16	20.26	14.37	48	848	1780	1500
8 Std.	3	220	225	-5	0	10.85		37	1020	923	800

Ave. K* for Standard $\frac{695 + 802 + 772 + 923}{4} = 800$

K*' = K* $\frac{800}{K^* \text{ for the standard for each run}}$

The addition of one pound of iron to phosphoric acid reduces subsequent triple production by 1.2 lb (W.R. 135).

The temperature at which extractions are carried out must be given consideration. At higher temperatures the oil is less viscous and is less inclined to form stable emulsions but the life of the solvent is greatly shortened and the distribution coefficient (hence extractability of uranium) is lowered (W.R. 53-55). Furthermore if the temperature of the acid is falling during the extraction operation, solids tend to precipitate out and increase emulsion or mayonnaise difficulties.

Two methods have been suggested for cooling acid. Flash evaporation under vacuum has been suggested but costs, especially initial costs, for such a system are high. The acid may be cooled by counter-current contact with air over a tower. The latter method, though tested here and proposed for Armour's installation, may be objectionable because of excess windage losses. W.R. 71

Any approach to the recovery of uranium from phosphoric acid, to be feasible, must circumvent or overcome the effects of the solids in the acid. Their presence rendered the ion exchange process impracticable. In the solvent extraction process a stable colloid composed of finely divided solids and oil in acid tends to form and hang up at oil-acid interphases. This is a more serious problem in solvent extraction than was at first supposed and even yet threatens the process.

The problem can to a certain extent be circumvented. It is proposed that a Sharples "Nozljector" centrifuge be used instead of a mixer-settler. This approach holds high promise. It possesses the double-barreled advantage of taking the acid with its solids content as it comes from the filter or cooler and of bringing solvent and

acid together and then separating them again in a matter of seconds. Its disadvantages are that the units are expensive and maintenance on them is likely to be high. moreover, there is no guarantee that they will separate every "mayonnaise" mixture to be encountered.

Reduction of the uranium from the plus six to the plus four valence state is a time consuming reaction at the phosphoric acid concentrations we are dealing with - if there is no fluoride ion present (See ORNL 1581 C.F. Baes, Jr.) In a centrifuge plant the kinetics should be considered.

Another means of circumventing the mayonnaise problem would be the use of emulsion breaking agents when the mayonnaise forms. (W.R. 102.) This approach showed little promise and should be considered a last resort.

Since the mayonnaise or emulsion forming materials seemed to be associated with some of the solids in the acid, it was reasonable to attempt separation of the offending material either by filtration or by settling. (W.R. 89)

Filtration is not attractive because of the volume of acid to be handled and because of the amount of slimy solid, 0.4 to 5.0% solids, to be removed. It would be a difficult and expensive operation.

Extensive work has been done evaluating another alternative - separation of the solids by settling, B.P. 92. This method, when carried out in conjunction with additives such as about 0.005% of U-Det 90-95 or Regal, gives some promise but it is doubtful if the mayonnaise problem could be completely eliminated by this means alone and the installation would be expensive. B.P. 115

Emulsion or mayonnaise formation is not directly proportional to solids content but varies depending on the history of the acid. In any event, the solids content must

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be reduced from 0.4 to 5% to about 0.01%. A rough expression of the solids content is:

% retained of initial solids = $10T^{.51}$ at settling rates of
1 foot per hour
T is in minutes

It would probably be better to use Nozljectors than to try to clarify the acid sufficiently for mixer-settlers.

Another factor that influences the extractability of uranium is the concentration of the phosphoric acid; the more concentrated the acid is, the more difficult it is to extract the uranium. Table IV. About ten times as much O.P.P.A. is required to extract uranium from acid assaying 50% P_2O_5 as from acid assaying 25% P_2O_5 . The saving in solvent due to the handling of less total volume, is more than off-set by the increased requirements.

The uranium is removed from the oil layer by precipitation with HF. Other means of separation have been tried but precipitation as the fluoride has appeared to be most practical.

The concentration of HF used is determined by the following considerations: Strong HF is very detrimental to O.P.P.A. Weak acid solutions permit solution of O.P.P.A. in the aqueous layer and lead to rapid hydrolysis and emulsion formation. Intermediate strengths of HF are less harmful to O.P.P.A. The higher the HF concentration, the better the precipitating agent.

In this laboratory, a 15% concentration of HF was used to which 15% H_2SO_4 was also added. This gave an aqueous layer which was effective in removing UF_4 from the oil, which did not lead to emulsion formation and which did not lead to rapid deterioration of the solvent.

TABLE IV Extraction of U_3O_8 From Concentrated Phosphoric Acid
Summary

Run No.	Made	OPPA Made From	% P_2O_5	Mg U_3O_8/L	E.M.F. After Concentration mv	E.M.F. Adjusted to mv	K*	% OPPA Req'd in Kerosene @ 1:10 Oil:Acid Ratio
1	1/21/54	Iso Octyl Alcohol	25.56	60	300	198	1915	.8
			36.98	94	295	200	726	2.1
			40.88	112	272	209	388	3.9
			45.25	118	271	207	398	5.0
			49.86	125	240	206	189	8.0
2	2/4/54	N-Octanol	25.10	58	308	224	2863	.5
			28.40	71	302	227	2212	.7
			34.00	91	282	228	940	1.6
			37.90	95	258	222	515	2.9
			41.25	126	218	220	333	4.5
3*	2/17/54	Iso Octyl Alcohol	26.12	65	312	233	1838	.8
			30.41	78	304	234	959	1.6
			32.55	84	295	236	578	2.6
			38.71	109	287	235	377	4.0
			49.59	132	265	228	216	7.0

* In this run the acid was evaporated under $23\frac{1}{2}$ in Hg vacuum

We also used a dilute sulfuric acid (15%) wash of the solvent stream before and after the precipitation step. The first wash removed calcium as gypsum from the oil stream and permitted a higher grade product cake; the second removed HF from the oil stream and permitted the recovery of some of the entrained product cake before the solvent stream was recycled in the extraction cycle. (W.R. 75, 84, 85)

In this pilot plant, there was no means of rapidly contacting the oil stream with the precipitating solution. In the U.S.P.P. pilot plant, there was. A Sharples centrifuge was used for the separation. There, it is reported, rapid contact and separation with 50% HF was secured. Degradation of the solvent was held to a minimum. An advantage of that system is the simplicity. Disadvantages would be lower grade product cake and hazards of handling 50% HF solutions.

The actual execution of extractions in the laboratory has been accomplished with a variety of equipment. By far the larger percentage of the extractions were carried out by "hand shaker" technique. The bulk of the remainder were carried out in one of the two pilot plants, the packed towers and the mixer-settlers.

In the hand shaker procedure acid and solvent, usually in the proportion 100 cc of acid to 10 cc of a 3% solution of O.P.P.A. in kerosene, were placed in a 250 cc separatory funnel and shaken vigorously for one minute. After five minutes settling, the layers were separated and analyzed.

The pilot plants accomplished the same thing, contact and separation of a stream of acid and a stream of oil. In the tower plant, the oil was introduced at the bottom of a 2-1/2 inch diameter column while acid was introduced at the top. Because of the difference in specific gravity, the streams contacted each other counter-currently. Oil was drawn off at the top of the column and acid at the bottom. Initial experiments were carried out with the columns packed for 30 inches of their length with a variety

of 1/2 inch packing. Eventually a bed of berl saddles, 90 inches deep, was used. With the volume ratios used, 4 to 10 of acid to 1 of oil, only one theoretical stage was obtained in the column.

The column pilot plant was easy to operate and furnished uranium bearing solvent for precipitation studies. The promise of early success in developing data for the design of a full scale plant using towers was not as apparent as for a mixer-settler type plant. Efforts were devoted to mixer-settler study.

The heart of the pilot unit we used for most of our pilot studies was a two-stage mixer-settler unit. Acid entered "A" mixer, contacted oil and separated from it in "A" settler; it flowed to "B" mixer, to "B" settler, and thence out of the system. Oil was fed to "B" mixer along with the once extracted acid, flowed with mixed stream to "B" settler, was pumped to "A" mixer, separated in "A" settler and sent to the precipitation chain. In the precipitation chain, it was washed in a 1 to 1 ratio with three solutions; First with 15% H_2SO_4 , then with 15% H_2SO_4 - 15% HF precipitating solution and lastly with a 10-15% H_2SO_4 solution.

The capacity of the pilot plant was 1 liter of acid and 100 cc of oil per minute. A comprehensive description of the unit, its mode of operation and the kind of data obtained from a run, is described in W.R. 79. Other runs and data obtained from them, are described in W.R. 63 to 89.

From the operation of the pilot plant in our laboratory and from data developed at the pilot plant at U.S.P.P., an estimate of raw materials consumption was made. It was found that the consumption of raw materials was determined by the magnitude of the phosphoric acid stream processed and ~~not~~ by the amount of uranium recovered.

Raw Material Consumption

Iron: To reduce Armour's acid to E.M.F. of 230 to 220 mv, between 2 and 6 g of iron are required per liter (W.R. 75). For estimating purposes 4g/L is the figure used.

Solvent: To maintain a solvent activity in our two-stage system equal to 3% O.P.P.A. in kerosene solution, it was found necessary to use 50% make-up of the 3% O.P.P.A. or, on the basis of the flow of the oil stream, for every 100 cc of solvent pumped, 1-1/2 cc of 100% O.P.P.A. had to be added. The O.P.P.A. which has a specific gravity of about 1.0 is made from octyl alcohol and P_2O_5 in the proportion of 2 moles to 1 or 1.4g to 1.

Examples of data upon which the 1.5% solvent make-up figure is based are:

60%	extraction	U_3O_8	in Run 4-28 (e.m.f.-238)	where 3% & 33% make-up was used
65%	"	"	" " " 4-29 (e.m.f.-243)	" 3% & 33% " " "
74%	"	"	" " " 4-16 (e.m.f.-230)	" 3% & 50% " " "
85%	"	"	" " " 4-19 (e.m.f.-204)	" 3% & 50% " " "
92%	"	"	" " " 4-3 (e.m.f.-234)	" 3% & 50% " " "

It was noted that to maintain the activity of solvent equal to that of fresh 3% O.P.P.A., 1-1/2% (or 50% of 3%) of active must continually be added to the oil stream.