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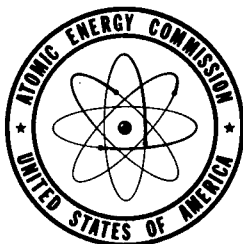
STUDIES OF RECOVERY PROCESSES FOR WESTERN  
URANIUM BEARING ORES

III. The Recovery of Uranium and Vanadium from Acid  
Leach Liquor Liquors of Carnotite Ores

By  
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November 25, 1949

Carbide and Carbon Chemicals Corporation, Y-12



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### ABSTRACT

Tests are reported on hydrolytic precipitation of uranium and precipitation of uranyl, arsenate, and vanadate; uranium peroxide; uranous fluoride, oxalate, and p-toluenesulfinate; and ferrous, ferric, and lead vanadates.

### CHEMISTRY

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THE RECOVERY OF URANIUM AND VANADIUM FROM  
ACID LEACH LIQUORS OF CARNOTITE ORES

INTRODUCTION

This report covers a part of the work of the Y-12 laboratories on methods of recovery of uranium and vanadium from acid leach liquors. The scope of the investigation was originally set forth in a memorandum (RMD:AJB, July 12, 1948, E. F. Wilson to Ned Williams) as follows:

"III Study of Recovery of Uranium and Vanadium Salts from Acid Leach Liquors:

(a) A study of equilibrium conditions and solubilities of salts.

(b) The present methods of winning the uranium from the solutions consist of a series of precipitations and filtrations.

(1) Could the recovery of uranium be effected by the direct precipitation of uranium organic compounds, heavy metal uranates such as lead uranate, or organic solvent extraction methods."

Subsequent conferences indicated that part (a) was not intended to be limited to the process used at present (Figure 1), but was to include any other compounds and reactions, as suggested in (b)(1), which could be useful in improved processes, and that part (b) should receive the major attention.

A series of studies was made using reagents which were known to precipitate uranium or vanadium. These included, besides hydrolytic precipitation, arsenate, vanadate, and peroxide for uranyl ion; fluoride, oxalate, and p-toluenesulfinate for uranous ion; iron(II), iron(III), and lead for vanadate; and phosphate for vanadic ion.

The investigations were organized as studies of "unit processes",

each precipitation being examined for possible service in one or more tentative flowsheets. The extent of study of each was limited by time and laboratory capacity, governed by expediency.

#### Head Solutions

Synthetic. In the absence of analytical data on acid leach liquors at the time the recovery investigations were started, "synthetic leach" solutions were made up on basis of the mineralogical information available. The leach liquors were expected to be dilute hydrochloric or sulfuric acid solutions containing the acid-soluble metals in about the same percentages as they occur in the ores. Accordingly, the following concentrations were assigned: 0.2 w/v\* percent U, 0.3 percent V, 1.0 percent Fe, and 0.5 percent Al. For some tests 0.1 percent phosphate was added. The iron and aluminum concentrations were the highest thought probable, so chosen to represent the worst solution likely to be encountered. Both sulfuric and hydrochloric acids were used, and the respective solutions will be referred to as "sulfate synthetic" and "chloride synthetic".

It was expected that these synthetics would soon be replaced by actual plant solutions, or at least by more realistic synthetics based on actual analyses. However, such a solution was not obtained until December, 1948; hence the foregoing synthetics were used for a large proportion of the tests.

Plant Leach Solutions. During December, 1948, and January, 1949, a series of samples of acid leach liquors was received from an operat-

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\* "Weight on volume" %, i.e., grams constituent per 100 ml of solution.

ing plant. The first of the series (R-1) was supplied in sufficient volume to serve as a stock solution for recovery tests. Description and analyses are given in Table 1. Acid-base titration curves are shown in Figure 2. In appearance the solutions varied from blue-green to brown, with a finely-divided residue of brown or white solids in each.

#### PRECIPITATION OF URANOUS ION

##### Uranous Fluoride

In the presence of sufficient fluoride ion, ferrous ion will reduce uranium to form insoluble uranous fluoride. This reaction was examined for recovery of uranium from acid liquors. In all tests with the synthetic leach solutions, the sample was reduced with metallic iron just to zero ferric ion by thiocyanate test. It is assumed that at this point the vanadium was all plus four, and the uranium still plus six.

Hydrofluoric Acid. The amount of HF required was estimated on the assumption that each iron, aluminum, and vanadium ion would complex with six fluoride ions. Samples treated with much less than this theoretical amount gave no precipitate. With about the theoretical amount, a very small precipitate was formed after long boiling. With larger amounts (up to ten times the estimated theoretical) a small precipitate was formed, about the same amount in each, appearing more quickly with the larger amounts of acid. The precipitates consisted of fine powder with the typical color of green salt. Large amounts of uranium remained in the filtrates, decreasing slightly as the fluoride was increased.

Ammonium Fluoride. A constant amount of hydrofluoric acid (slightly over the estimated theoretical) was added to each of a series of samples containing ammonium hydroxide ranging from zero to one-half the amount equivalent to the acid. (This amount of ammonia gave a permanent precipitate, which quickly dissolved on addition of the acid.) On boiling, precipitates slowly formed, resembling those obtained with hydrofluoric acid alone. The amount of uranium in the filtrate was decreased with increased ammonia, but the lowest level found was 100 ppm.

Each filtrate was treated with calcium chloride solution. Precipitates were obtained in all except the most acid. The resulting filtrates showed lowest uranium (about 20 ppm) in the most basic solution. The final pH's were not measured because of probable injury to a glass electrode.

Potassium Fluoride. When the first tests were repeated with potassium fluoride instead of the acid, voluminous, gelatinous precipitates were obtained immediately, and the filtrates contained less than 5 ppm uranium. Potassium fluoride gave a similar precipitate with aluminum but not with iron or vanadium or the two combined. Hence, it is assumed that the voluminous precipitate involved aluminum, probably as  $K_3AlF_6$ , and that this precipitate was effective in sweeping the uranium. Similar results were obtained when potassium chloride or carbonate was added to the sample, followed by hydrofluoric acid.

Some of the precipitates were washed by decantation with volumes of water equal to the original filtrates. The filtered washes showed less than 5 ppm uranium.

Aging. An attempt was made to improve the uranium recovery with smaller amounts of fluoride by aging. Samples were reduced as described

above, treated with 40 percent and 80 percent of the theoretical fluoride (based on the assumption of six fluoride ions for each iron, aluminum, and vanadium ion), and allowed to age for twelve days in plastic beakers. Slight precipitates were formed in each. The uranium concentrations found in the filtrates were about 800 and 400 ppm, respectively.

Tests with Plant Leach Solution. After samples of the actual leach solution were received and analyzed, the expected consumption of fluoride was estimated, and tests were made similar to those above.

The expected fluoride (or oxalate) consumptions, and the requirements for reduction, are shown in Table 2. If direct acid dissolution of iron could be avoided, its use as a reductant would increase the fluoride consumption (measured as HF) only from 26 to about 32 grams per liter. The effect of zinc ion in these precipitations was not measured; formation of a tetrafluoride complex would increase the fluoride consumption by nearly the same amount as would iron. Sulfur dioxide should not directly increase fluoride consumption, and hence it was used instead of iron in tests with the plant leach solution.

Reduction with Sulfur Dioxide. When sulfur dioxide was passed through the leach solution (R-1) at room temperature, color changes showed rapid reduction of vanadium, but the thiocyanate test for ferric ion remained strong even after an hour. When the temperature was raised to boiling, the ferric test became negative in about 20 minutes.

Eight 100-ml samples thus reduced were treated with quantities of 48 percent hydrofluoric acid ranging from 1 to 30 ml. Precipitates formed immediately in all but the first two samples (with 1 and 2 ml HF), and settled slowly. They appeared similar to the "cryolite" precipitates

obtained from the synthetic leach solutions in the presence of alkali. The results, Table 3, show that the estimated fluoride consumption was nearly correct, but that the uranium precipitation was far from complete, and became worse with large excess of hydrofluoric acid.

Separation from Aluminum. Three methods were examined qualitatively for recovery of uranium from the uranium-aluminum fluoride cake: (1) slurry with ammonium hydroxide and hydrogen peroxide to produce soluble uranyl fluoride; (2) fuse with sodium potassium carbonate to produce soluble sodium aluminate and fluoride, leaving uranous oxide; (3) dissolve in concentrated sulfuric and nitric acid, dilute, and separate aluminum as alum. None of the three appeared useful in the brief tests made.

An attempt was made to avoid the aluminum contamination by adding hydrofluoric acid and removing the "cryolite" before reduction of the solution. The usual voluminous precipitate formed immediately, and was filtered off after aging and settling for about 20 hours. The filtrate was treated with an excess of fine iron powder, digested for about one hour, and filtered. The aluminum precipitate and the final filtrate contained 7.5 and 2.6 percent of the uranium, respectively.

Fluoride Recovery. The only method examined for recovery of the excess fluoride ion from the effluent was by precipitation with calcium ion. The calcium fluoride formed was very gelatinous and difficult to retain in a filter.

#### Uranous Oxalate

Precipitation of uranous oxalate was found to be similar to precipitation of uranous fluoride in that ferrous ion was sufficient for the

reduction of uranyl ion, and that enough excess oxalate must be supplied to complex all iron, aluminum, and vanadium present (see Table 5).

Reduction of the uranium with zinc amalgam before the addition of oxalic acid did not decrease the amount of reagent needed. Addition of calcium ion caused redissolution of a part of the precipitate, rather than sweeping of the solution.

#### Uranous p-Toluenesulfinate

Thomas, and Krishna and Singh have reported precipitation of iron(III) with arylsulfonic acids, and Feigl has reported that uranium(IV), as well as some other quadrivalent ions, forms insoluble arylsulfonates stoichiometrically. Ferrous iron, aluminum, cobalt, and nickel were reported not to form precipitates. Preliminary tests in this laboratory confirmed these points, except that a reported titration of ferric ion with arylsulfonic acid was not successfully repeated.

Early tests with uranium were erratic: in one precipitation from the chloride synthetic the uranous p-toluenesulfinate was ignited to  $U_3O_8$  of better than 99 percent purity, with 96 percent recovery, while in some other tests the recovery was as low as 85 percent. Subsequent studies of the reduction step (cf Y-501) indicate that incomplete reduction could have caused the variations; instability of the reagent under some conditions may also have been involved.

Satisfactory reduction of the uranium was obtained by iron, aluminum, zinc, or zinc amalgam. Reduction by sulfur dioxide or ferrous ion in the presence of the sulfinate was not satisfactory, in contrast to the

results obtained with fluoride or oxalate. Some typical precipitation results are shown in Tables 6 and 7. No interference was found from vanadium, but large amounts of sulfate interfere as shown in Table 8.

Reagent. Sodium p-toluenesulfinate was prepared satisfactorily by zinc reduction of p-toluenesulfonyl chloride (Organic Syntheses I:492). The purity was checked by a hypochlorite titration (Ackerman, Ind. Eng. Chem., Anal. Ed., 18, 2 and 3 (1946)), which gave precisions within  $\pm 0.5$  percent.

Sodium o-toluenesulfinate was prepared from o-methylaniline by the Gattermann reaction (prepared by R. Woodard). No difference was found between precipitations with it and with the para reagent.

#### PRECIPITATION OF URANYL ION

##### Uranyl Arsenate and Arsenite

Precipitation of uranyl arsenate from slightly acid solution has been described as a satisfactory quantitative procedure (Rice, dissertation, Columbia University). Both arsenate and arsenite precipitations were tested. Neither showed any real advantage over simple hydrolytic precipitation. Typical results are shown in Table 12.

##### Uranyl Vanadate

When carbonate solution is used for leaching of carnotite ore, neutralization of the resulting solution of sodium vanadate and sodium uranyl carbonate causes precipitation of "yellow cake", which is considered to be a synthetic carnotite, sodium uranyl vanadate. Some other

carnotite processes have involved precipitation of a "yellow cake", which may be the same, by neutralization of an acid leach solution after removal of some contaminants. Such a precipitation was studied briefly, particularly in connection with possible modifications of the acid process which involved precipitation by sodium carbonate; the "yellow-cake" tests were suspended when the latter precipitation proved unsatisfactory.

Analyses of "yellow cakes" have been variously reported as 22%  $V_2O_5$ : 44%  $U_3O_8$ , 20%  $V_2O_5$ : 50%  $U_3O_8$ , 20%  $V_2O_5$  : 45% U, and 22% V : 41% U. Since none of these approach the U:V ratio of the conventional carnotite formula ( $K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$ ), samples of "yellow cake" obtained in the tests above were analyzed. These precipitates were obtained at about pH 5, from solutions containing 0.13% U, 0.72%  $NaVO_3$ , and 3%  $Na_2CO_3$ . A sample dried at 120°C showed 11.8% V (21.0%  $V_2O_5$ ) and about 53% U (62%  $U_3O_8$ ). A sample similarly dried and then ignited at successively higher temperatures to 900°C lost 4% of its weight, but did not appear to decompose. The final vanadium content was 12.7% V (22.7%  $V_2O_5$ ).

The formula  $Na_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$ , analogous to the carnotite formula, indicates 11.7% V (20.9%  $V_2O_5$ ), 54.8% U (64.6%  $U_3O_8$ ), and 6% water. Subsequent studies of "yellow cake" precipitation from carbonate leach liquors indicate that the average composition of the precipitate varies with that of the solution, with either a sodium uranate or a sodium vanadate accompanying the sodium uranyl vanadate.

#### Uranium Peroxide

Peroxide precipitation from nitric acid solution has been used for recovery and purification of uranium. The precipitation

is also feasible, although less satisfactory, from hydrochloric acid solution. The chief difficulty encountered is decomposition of the peroxide reagent, especially catalytic decomposition by iron and many other ions.

Attempts were made to precipitate uranium peroxide from the synthetic leach solution after removal of vanadium as lead or iron vanadate (see Precipitation of Vanadium, below). With either lead or iron, the vanadate precipitate began to form at pH 1.5. The precipitations were slow and incomplete, with at most 90 to 95 percent of the vanadium precipitated. Lead showed no better results than iron. Treatment of a solution containing 0.03 percent vanadium and 0.2 percent uranium with hydrogen peroxide at pH 2 precipitated some uranium peroxide, but the corresponding solution obtained by removal of vanadate from the synthetic leach gave no precipitate even on seeding.

Attempts were also made to produce a uranium concentrate by simultaneous precipitation of iron vanadate and uranium peroxide. The resulting precipitate contained only about 20 percent of the uranium. In all the foregoing tests, decomposition of the hydrogen peroxide was very rapid whenever both iron and vanadium were present.

#### Hydrolytic Precipitation of Uranium

Past and present processes for recovery of uranium from acid leach liquors start with a hydrolytic precipitation of most of the metals present, the resulting precipitate being known as "green sludge". In these processes the precipitation is considered merely a concentration step rather than a means of separation. The precipitate is typically voluminous, slimy, and

very difficult to filter. No washing is attempted. Formerly, the acid leach liquor was partially reduced with scrap iron before the green-sludge precipitation; however, according to more recent information, the reduction step has been abandoned.

Green-Sludge Precipitation. Investigation was started of the green-sludge precipitation with several objectives in view, principally determination of the optimum pH range for uranium recovery, improvement of filtration, and establishment of separations from contaminants. However, the investigation was interrupted when only the effects of pH and redox state had been studied.

Qualitative tests of hydrolytic precipitation from the chloride synthetic leach showed satisfactory uranium recovery only after nearly all other metal ions had been precipitated, which occurred slightly below pH 3 in oxidized solutions and slightly above pH 3 in partially reduced solutions (containing uranyl, vanadyl, ferrous ions).

Titration curves for the green-sludge precipitation are shown in Figure 2. These curves were obtained by titration of leach liquor R-1, first with ammonia to pH 4.5, then with concentrated sulfuric acid back to pH 0.4, and finally with solid sodium carbonate to pH 8. The sulfuric acid was transferred by Mohr pipet from a weighing bottle, and the total volume used was checked against the net weight. The sodium carbonate was added in weighed increments of about 0.1 gram until effervescence ceased and about 0.5 gram thereafter.

Results of precipitation studies are shown in Table 13. The pH adjustment was made with 1:1 ammonium hydroxide or with ammonia gas.

The latter gave better and also more reproducible results. Precipitation of uranium was essentially complete from either oxidized or reduced (uranous, vanadic, ferrous) solutions at pH 4.5, but less than 70 percent of the uranium was precipitated at that pH from partially reduced solution (uranyl, vanadyl, ferrous).

Raising the pH from 4.5 to 5.0 decreased the residual uranium in the filtrate from about 0.2 percent to about 0.02 percent of the original uranium. The total mass of the precipitate rose from about 15 grams (wet) per 100 ml of liquor at pH 4.0 to about 20 grams at pH 4.5, with little further change at pH 5.0 or 5.5. The water content of the centrifuged cakes was less affected, staying close to 85 percent.

#### Modifications of the Present Processes

The acid process shown in Fig. 1 consists essentially of a hydrolytic precipitation to eliminate water, followed by redissolution of the green sludge in sulfuric acid, oxidation and precipitation of iron vanadate, a carbonate separation from iron and aluminum, and finally precipitation of sodium diuranate. Several possible modifications of this process were considered: (1) Treatment of oxidized leach liquor with sodium carbonate to precipitate iron and aluminum, leaving a solution of uranium and vanadium to be handled as in the carbonate-leach processes. (2) Hydrolytic precipitation as in the present process, followed by a carbonate leach of the precipitate. (3) Reduction and hydrolytic precipitation followed by thorough washing to remove most of the iron (ferrous) and ammonia, and leaching with concentrated sodium hydroxide to dissolve the alumina

Preliminary tests eliminated the first two suggestions, but the third procedure showed some promise and was investigated more fully.

The solution was reduced with iron powder just to the disappearance of ferric ion. Extensive washing was required for effective removal of the ferrous iron; it was also important to wash out excess ammonium ion, since it interfered with the subsequent caustic leach. A small amount of sodium sulfate in the wash water suppressed peptization of the alumina, which otherwise increased the difficulty of filtration. Dilution of the original leach liquor proved to be more effective in aiding the separation of iron than did washing of the precipitate with the same additional volume of water.

The minimum amount of sodium hydroxide found necessary to remove all the aluminum was close to two moles of hydroxide for each mole of aluminum. More hydroxide was needed in the presence of carbonate or ammonium ion. All iron in the green sludge remained in the final uranium residue, together with part of the vanadium and a trace of aluminum. Oxalic acid readily removed the residual iron, aluminum, and vanadium, leaving nearly pure  $UO_2$  with better than 95 percent over-all recovery; however, the oxalic acid consumption was large.

A batch process was devised on basis of the foregoing relationships, and tested as shown in Table 14. This process consisted of the following steps:

1. Reduction of the acid liquor with iron to zero ferric ion.
2. Dilution with wash water from the preceding batch.
3. Precipitation with ammonia at pH 5.0 to 5.5, at 70 to 90°C.  
Filtrate discarded.
4. Countercurrent washing (two stage) with one volume of water per volume of original liquor.

5. Countercurrent leaching (two stage) with caustic containing two moles of sodium hydroxide per mole of aluminum. The residue from this step is the uranium dioxide product.

The following steps for vanadium recovery were also used in this test, although a process less wasteful of reagents should be possible:

1. Acidification of the spent caustic with sulfuric acid.
2. Oxidation with sodium chlorate.
3. Precipitation of iron vanadate at pH 3.

In spite of the good uranium recovery, the procedure showed several major disadvantages. The difficult filtration of the green sludge was emphasized by the necessity for thorough washing; the vanadium content was split between a residue and a solution, and the uranium residue still required further purification, as by oxalic acid.

Reduction of Uranium in Basic Solution In the foregoing procedure, vanadium was oxidized by uranyl ion, presumably during the caustic treatment, and also by air. (The possibility of reduction of uranyl ion by the metallic iron was avoided by removing the metal as soon as all ferric ion had disappeared.) To prove the redox reaction between uranium and vanadium, a sample containing only those metals was reduced with metabisulfite, the excess sulfur dioxide being boiled off, and the subsequent steps were carried out under nitrogen. The redox balance and vanadium balance are shown in Table 15. The uranium balance could not be checked because the original filtrate was lost. In each fraction the total reduced material was determined by permanganate titration, total vanadium by subsequent ferrous titration.

## PRECIPITATION OF VANADIUM

Vanadates

Iron Vanadates. In various processes, vanadium has been removed from basic (carbonate) solution as iron vanadate, and ferrous ion is reported to be more effective than ferric for the precipitation. An iron vanadate is also precipitated from the acid uranium liquor in the present acid process. Recovery data for the latter application have not been available.

The precipitate obtained is called "ferrous vanadate" in the reports available, but it probably has not been characterized. In moderately strong acid solution, ferrous ion reduces vanadate quantitatively to vanadyl; hence if the "ferrous vanadate" is actually a ferrous compound it must be formed under conditions in which the redox reaction is much slower than the precipitation.

When a solution of sodium metavanadate (1 percent vanadium) at pH 3 was treated with excess ferrous sulfate, the solution immediately turned green, indicating partial reduction to vanadyl. A yellow precipitate slowly formed, leaving a blue solution (vanadyl) which contained no vanadate. Further tests with ferrous, ferric, and chlorate ions corroborated that precipitation was obtained with ferric rather than ferrous ion. Precipitation was very slow, even from hot solution, and filtration was difficult. The best recoveries approached 90 percent of the vanadium. No effect was found from the presence of excess chlorate.

Table 16 shows the relative effects of oxidant, iron, and pH on vanadium recovery. In each test, vanadium (205 mg in 25 ml) at the pH

shown was treated with solid sodium chlorate and with the amount of ferrous sulfate shown. The ferrous sulfate was dissolved in 25 ml of water, adjusted to pH 2.5. The iron vanadates were precipitated from hot solutions and were allowed to age overnight at room temperature before filtration.

Tests comparing precipitations by ferric and ferrous ions from neutral to basic solutions are shown in Table 17. The ferrous precipitates were dark green; the ferric precipitates were light brown, resembling all the precipitates obtained from more acid solutions.

Lead Vanadate. Brief tests were made of precipitation of vanadate by lead chloride. The best result (about 90 percent precipitation of vanadium) was no better than had been obtained with iron. Some difficulty was encountered in recovery of all the vanadium from the lead precipitate.

Calcium Vanadate. Presence of calcite in the salt roasting of carnotite ore interferes with the subsequent water leaching of vanadium, presumably by formation of an insoluble calcium vanadate. The vanadium so held is dissolved by a moderately strong acid leach. Brief tests were made of possible precipitation of a calcium vanadate at weaker acidities; however, no precipitate was obtained below pH 6 by treating solutions of oxidized vanadium chloride, sodium metavanadate, or sodium orthovanadate with calcium chloride solution.

## SUMMARY

An investigation of uranium and vanadium solution chemistry has been conducted which was primarily intended to develop improvements in or a replacement for the present recovery process, which is based on a hydrolytic precipitation of uranium and vanadium together with other constituents.

The conditions for the reduction, green-sludge precipitation, and iron vanadate precipitation steps of present processes were examined. Modifications were considered, especially one using a caustic wash after hydrolytic precipitation. Separation of aluminum was good and of iron, fair, but vanadium separation was poor.

Precipitation of uranyl arsenate, or arsenite showed no real advantage over hydrolytic precipitation. Precipitation of uranium peroxide was completely unsuccessful, even after removal of most of the vanadium.

Precipitation of uranous fluoride or oxalate showed some advantages, which were outweighed by high reagent consumption. Precipitation of uranous p-toluenesulfinate appeared nearly as successful as precipitation of uranous phosphate, and may eventually prove better. Further study of sulfinate reagents is planned.

Only fair results were obtained in the precipitation of ferric vanadate from weakly acid solutions. Ferrous vanadate could not be precipitated at pH 3 or below because of reduction of the vanadate. Lead vanadate showed no advantage under the same conditions. No precipitate of calcium vanadate was obtained below pH 6.

## ACKNOWLEDGMENT

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Table 1  
Comparison of Plant Leach Liquors

No.	<u>R-1*</u>	<u>R-2</u>	<u>R-4</u>	<u>R-6</u>	<u>R-7</u>
Date Sampled		Dec. 16, 1948	Dec. 21, 1948	Jan. 6, 1949	Jan. 9, 1949
Sp. Gr.	1.04	1.032	1.026	1.024	1.047
pH	1.2	1.6	1.5	1.7	1.4
Free acid, titrated to					
pH 2.0	0.115 <u>N</u>	0.030 <u>N</u>	0.055 <u>N</u>	0.017 <u>N</u>	0.068 <u>N</u>
pH 2.5	0.156 <u>N</u>	0.072 <u>N</u>	0.091 <u>N</u>	0.062 <u>N</u>	0.135 <u>N</u>
Potential, volts (Pt-sat'd calomel)	0.790	0.596	0.586	0.523	0.577
Uranium, %	0.280	0.155	0.169	0.165	0.306
Vanadium, %	0.227	0.142	0.139	0.154	0.288
Iron, %	0.10	0.077	0.095	0.114	0.183
Aluminum, %	0.165	0.022	0.026	0.019	0.034
Calcium, %	0.20	0.077	0.102	0.148	0.223
Silica, %	0.293	0.137	0.149	0.144	0.325
Chloride, %		1.74	1.32	1.76	2.38
Fluoride, %		0.0096	0.0083	0.012	0.011
Sulfate, %	0.88	1.23	0.86	0.63	0.73
Phosphate, %	0.08	0.046	0.051	0.041	0.080

\*Separate carboys, -- R-1A, R-1B, R-1C -- showed minor differences in composition.

Samples R-3 and R-5 were lost in transit.

Table 2

Estimated Consumption of Fluoride, Oxalate, and Reductants by R-1

	W/V %	M	Moles reagent/liter solution					
			<u>Fluoride</u>	<u>Oxalate</u>	<u>Fe</u>	<u>Zn</u>	<u>Al</u>	
U	0.28	0.012	0.048	0.024	0.012	0.012	0.008	
V	0.23	0.045	0.27	0.14	0.022	0.022	0.015	0.022
Fe	0.10	0.018	0.11	0.06	0.009	0.009	0.006	0.009
Al	0.18	0.067	0.40	0.20				
Ca	0.21	0.052	0.10	0.05				
MP	0.10	0.041	0.08 ?	0.04 ?				
SiO <sub>2</sub>	0.30	0.050	0.30					
Total moles/liter solution:			1.31	0.51	0.043	0.043	0.029	0.031
g/liter solution:			26	64	(as H <sub>2</sub> C <sub>2</sub> O <sub>4</sub> •2H <sub>2</sub> O)			
			(as HF)					

Table 3Fluoride Precipitation after SO<sub>2</sub> Reduction

100 ml. of R-1

<u>ml. of 48% HF</u>	<u>g. HF*</u>	<u>mg. U in Filtrate</u>	<u>% U pptd</u>
1	0.6	260	0
2	1.2	260	0
4	2.4	91	65
6	3.6	33	87
10	5.9	49	81
15	8.9	68	74
20	11.8	62	76
30	17.8	85	67

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\* Estimated theoretical fluoride - 2.6

Table 4

Uranous Fluoride Precipitations

Head Solution	ml	Reductant	Reagent	g	ml	Filtrate ppm U	% pptd
0.17% U	120	FeSO <sub>4</sub>	Sat'd KF	-	15	< 5	100
Sulfate Synthetic	100	Fe	Sat'd KF		25	< 5	100
Sulfate Synthetic	50	Fe	48% HF		5	500	75
					6	1200	40
					7	1000	50
					12	300	85
Sulfate Synthetic	25	Fe	48% HF plus 15 N NF <sub>4</sub> OH		5	600	70
					0	400	80
					1	300	85
					2	200	90
					2.5	200	90
					3	100	95
					3.5	200	90
					4	200	90
					4.5	200	90
Sulfate Synthetic	25	Fe	KF, 63 W/V %		2	50	97
					6	< 5	100

Table 4 (continued)

Head Solution	ml	Reductant	Reagent	g	ml	Filtrate ppm U	% pptd
Sulfate Synthetic	50	Fe	48% HF plus - NaCl Na <sub>2</sub> CO <sub>3</sub> KCl K <sub>2</sub> CO <sub>3</sub>	3.8 3.4 4.8 4.4	5	10 15 5 5	99 99 100 100
Sulfate Synthetic	50	Fe	48% HF plus - Na <sub>2</sub> CO <sub>3</sub> (wash K <sub>2</sub> CO <sub>3</sub> (wash	3.4 4.4	5	100 10) 20 5)	95 99
Chloride Synthetic	50	Fe	48% HF plus - NaCl (wash (wash	2 3 4.5 6	5	60 60) 15 5 5 10)	97 99 100 100

Table 5Uranous Oxalate Precipitations

Head Solution: Chloride Synthetic (ml.)	Reductant	Oxalic Acid Dihydrate (g.)	Filtrate (ppm U)	% pptd
100	Fe	15	10	99
100	Zn	15	20	99
50	Fe	5	100	95
	(Repeat)		10	99
50	Fe	4	300	85
		2	trace of ppt	
		1	no ppt	
		0.5	no ppt	
37.5 12.5	Fe ) unreduced )	5	no ppt	
25 25	Fe ) unreduced )	5	no ppt	
12.5 37.5	Fe ) unreduced )	5	no ppt	

Table 6  
Precipitation of Uranous and p-Toluenesulfinate

Run No.	Reductant	pH after Reduction	Potential*	Adjusted to	Sulfinate ppt.	Filtrate (ppm)
VS-9	Fe	(1.8)	-0.391	(2 )	yes	3
VS-10	Fe	(2.5)	-0.165	(2.9)	yes	10
VS-12	Al	3.3	-0.088	2.0	no	
VS-14	Fe	1.9	-0.405	(2.2)	yes	1
VS-18	Fe	(1.5)	-0.119	(2 )	no	
VS-19	Fe	2.9	-0.185	(2 )	no	
VS-20	Fe	1.0	-0.360	(2 )	yes	
VS-21	Al	2.7	-0.275	(2 )	yes	

\*Potential measured by platinum - saturated-calomel electrode system.

Table 7Precipitation of Uranous Sulfinat

<u>Head Solution</u>	<u>Reductant</u>	<u>Quantity of Reagent (g./100 ml)</u>	<u>pH</u>	<u>Pptn %</u>
Chloride Synthetic	Jones Reductor	2.3		100
Chloride Synthetic	Jones Reductor	2.0		91
R-1	Zn/Hg (liquid)	2.0	1.0	91
R-1	Zn	2.0	1.0	100

Table 8Sulfate Interference

0.1% U in 1 N acid buffered to pH 1.5

50% excess p-toluenesulfinate acid

% HCl	100	80	50	20	0
% H <sub>2</sub> SO <sub>4</sub>	0	20	50	80	100
% U ppt'd	96	81	68	47	36

Table 12Precipitation of Uranyl Arsenate and Arsenite

## Sulfate Synthetic Leach

No.	Reagent	g./100 ml.	pH	Filtrate	
				U(mg.)	V(mg.)
S-448	NaAsO <sub>2</sub>	12	2.0	300	20
S-449		12	3.1	200	2
S-457		25	2.0	150	
S-458		25	3.0	140	
S-453	Na <sub>2</sub> HAsO <sub>4</sub> ·7w	25	1.9	200	
S-455		25	4.0	42	

Table 13Hydrolytic Precipitation from Leach Solution R-1

Room Temperature

A. Precipitations with 7N NH<sub>4</sub>OH

pH	U in Filtrate (ppm)	Weight of Cake/100 ml.		
		Wet (g.)	Dry (g.)	Ratio (Dry/Wet)
4.0	24	16.0	2.33	0.145
4.0	27	15.2	2.27	0.149
4.2	9			
4.4	6	19.7	2.76	0.141
4.5	1	23.7	3.15	0.132
4.6	7	19.4	2.73	0.139
5.0	1	20.6	2.89	0.140
5.9	1	25.1	3.18	0.126

(partially-reduced leach solution: reduced as far as possible by iron without additional acid)

4.0		16.5	2.15	0.131
4.0	1700	19.3	2.71	0.140
4.0		21.0	2.84	0.135
4.4	370	18.7	2.71	0.145
4.5	840	19.0	2.77	0.146
5.0		24.0	2.66	0.111
5.0	850	20.2	2.95	0.147
5.5	1	27.9	3.27	0.117

Table 13 (continued)

pH	U in Filtrate (ppm)	Weight of Cake/100 ml.		
		Wet (g.)	Dry (g.)	Ratio (Dry/Wet)
(leach solution as received)				
4.0	160	10.64	1.87	0.175
4.4	5	15.15	2.65	0.174
5.0	0.5	18.19	2.84	0.156
(partially reduced leach solution: reduced with iron just to absence of Fe <sup>+++</sup> )				
4.0	1700	15.28	2.06	0.135
4.4	810	23.38	2.76	0.118
5.4	6	22.02	2.86	0.136
(partially-reduced leach solution: equal parts of solution as received and solution reduced just to absence of Fe <sup>+++</sup> )				
4.0	240	13.93	2.27	0.163
4.5	8	23.08	2.88	0.125
5.2	1.4	19.64	2.82	0.144
(completely-reduced leach solution)				
4.0	50	15.36	2.35	0.153
4.5	12	20.36	2.86	0.140
4.9	0.5	19.71	2.86	0.145

Table 14Caustic Washing of Green Sludge

Multiple-Batch Test with Recycle Head Solution:  
Chloride Synthetic Leach plus 0.1%  $P_2O_5$ .

Batch No.	1	2	3	4
Filtrate from Green Sludge				
pH	5.1	5.0	5.0	4.0
V, mg.	0	0	0	6.5
U, mg.	0.1	0.1		
Water Wash of Green Sludge				
U, mg.	0.2	0.2	0.2	0.1
Caustic Wash 1				
V, mg.	18.8	9.1	23.3	116.4
U, mg.	0.4	0.2	0.3	3.0
Caustic Wash 2				
V, mg.	92.2*	132.1*	175.9*	170.8
U, mg.	0.3	0.3	0.3	0.3
UO <sub>2</sub> Cake				
Weight, wet, g.	15.8	25.5	19.1	10.8
dry, g.	1.52	2.43	2.52	1.48
V, g.	0.15	0.22	0.20	0.14
Fe(VO <sub>3</sub> ) <sub>3</sub> Cake				
V, mg.	20	9	25	105

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\* Intermediate vanadium contents by difference.

Initial vanadium - 1.06 g.  
Vanadium accounted for - 1.08 g.

Table 15  
Reduction of Uranium in Basic Solution

<u>Fraction</u>	<u>Total Reduced</u>	<u>V(IV)</u>	<u>V(V)</u>	<u>Total V</u>	<u>U(IV)</u>	<u>U(VI)</u>	<u>Total U</u>
Head	-			2.60	-		2.10
Filtrate	0			0			? <sup>c</sup>
First NaOH	0.33	0.33	1.35	1.68	-	-	-
Second NaOH	0.10	0.10	0.20	0.30	-	-	-
Residue	2.15	0.58	0 <sup>b</sup>	0.58	1.57	(0.18)	1.75
	2.58		1.55	2.56	1.57		?

(quantities in milliequivalents)<sup>a</sup>

<sup>a</sup> Total reduced, total V, and total U by analysis; other quantities calculated.

<sup>b</sup> Assumed to be zero because of rapid extraction of V(V). This assumption does not affect the redox balance.

<sup>c</sup> Solution lost before analysis.

Table 16

Precipitation of Iron Vanadate

205 mg. Vanadium

50 ml. final volume

<u>Initial pH</u>	<u>NaClO<sub>3</sub> Added (mg.)</u>	<u>Potential (volts)</u>	<u>Fe Added (mg.)</u>	<u>pH of Filtrate</u>	<u>Potential of Filtrate (volts)</u>	<u>% V ppt'd</u>
3	0	0.440	500	2.54	0.303	51
3	125	0.470	500	2.45	0.425	54
3	250	0.485	500	1.48	0.650	88
3	500	0.485	250	2.00	0.660	84
3	500	0.485	500	1.80	0.685	82
3	500	0.485	750	1.80	0.664	84
1.5	500	0.670	500	1.72	0.692	63
2.5	500	0.585	500	1.89	0.664	86
3.5	500	0.470	500	1.90	0.680	88

Table 17Precipitation of Iron Vanadate

<u>Initial pH</u>	<u>Precipitant</u>	<u>Final pH</u>	<u>% V Precipitated</u>
6.5	Ferric	2.2	81
	Ferrous	3.5	82
7.5	Ferric	2.2	80
	Ferrous	3.5	85
8.5	Ferric	2.2	86
	Ferrous	4.1	93

Head solution contained 108 g.  $\text{Na}_2\text{SO}_4$ , 2.1 g.  $\text{NaCl}$ , and 1.23 g. V per liter, adjusted to pH indicated with  $\text{H}_2\text{SO}_4$  or  $\text{Na}_2\text{CO}_3$ . Precipitation was by  $\text{FeSO}_4$  or  $\text{Fe}_2(\text{SO}_4)_3$  (hydrates), 0.36 g. Fe per liter, at  $70^\circ\text{C}$ ., with digestion for one hour.

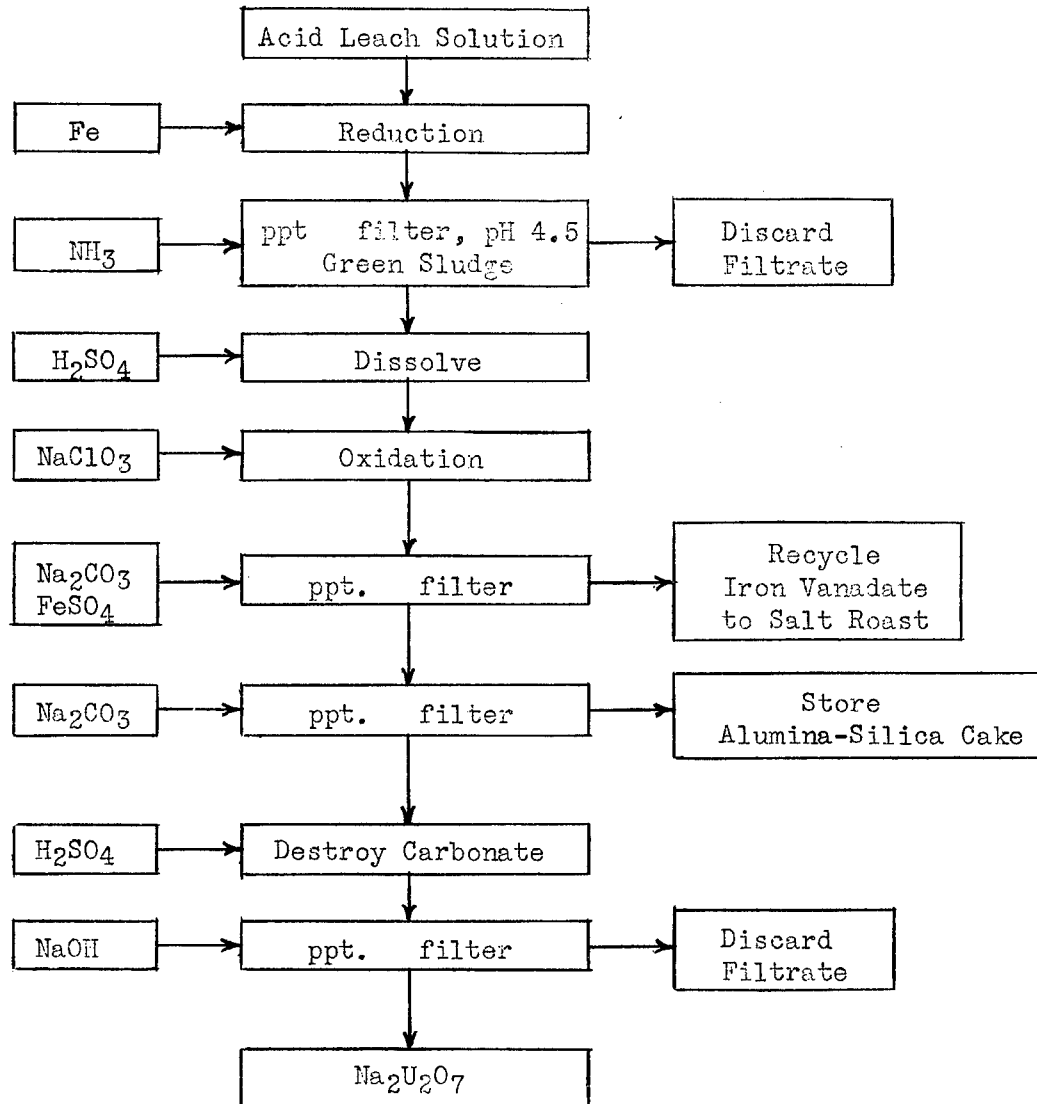


Figure 1

Flowsheet of an Acid Solution Process

