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LEACHING OF NITRATED MATERIALS WITH ORGANIC SOLVENTS

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Uranyl nitrate hexahydrate is soluble in diethyl ether and certain other organic solvents. One of the standard analytical methods for determining uranium involves the extraction by ethyl ether of a saturated aqueous nitrate solution containing free nitric acid. Under proper conditions for liquid-liquid extraction, uranium is separated from the other elements with which it is associated so that it can be subsequently determined colorimetrically or by oxidation and reduction titrations. The analytical procedure, however, is not quantitative in the presence of sulfates. Chlorides also interfere somewhat with uranium extraction but the main difficulty with chloride is that, in its presence, other elements such as iron are also extracted.

For the extraction of uranium from low-grade materials, the MIT Laboratory developed and recommended a direct-leaching process using an aqueous solution of cold dilute sulfuric acid and ferric iron as the solvent. Uranium is recovered from the leach liquor by neutralization with an alkali, such as magnesia, in the form of a low-grade precipitate containing considerably more iron, aluminum, and silica than uranium. To obtain a high-grade uranium product from this material a number of methods were tried, some of which proved successful. Among the unsuccessful methods was an attempt to dissolve the precipitate in nitric acid followed by ether extraction of the saturated aqueous solution obtained. Many difficulties were encountered, namely:

1. Upon addition of nitric acid, the silica present formed a gel.
2. When the precipitate was dried to dehydrate silica so that gel formation could be avoided, attempts at extraction gave unbreakable emulsions.
3. When the precipitate was dissolved with dilute nitric acid and the solution saturated with ammonium nitrate or when the precipitate was roasted to dehydrate the silica completely, emulsions were no longer formed but uranium extraction was poor, partly because of interference from the sulfate ions in the hydroxide precipitate.

It became clear, therefore, that no liquid-liquid extraction method could be used to up-grade concentrated liquors formed by dissolving in dilute acid the low-grade precipitates obtained by an aqueous leaching process using cheap reagents.

At this stage, parallel experiments were conducted on a different material with a view to exploring the possibilities of directly leaching a dry solid of medium grade (1 to 10 per cent) with nitrated ether.

These experiments were so successful that preliminary tests were made in which Rand precipitates were treated with nitric acid, dewatered to a paste or dried completely, then leached with ether. The ether used in these experiments contained some added nitric acid. It was found that substantially all of the uranium dissolved in the ether leach liquor.

These preliminary experiments led to the conception and realization of an entirely new process for uranium extraction in which a non-aqueous nitrated liquor is the solvent, and in which solids are extracted with this solvent in the absence of water or in the presence of a minor quantity only of an aqueous phase. This process or these processes do not seem to depend primarily on partition coefficients of uranyl nitrate between aqueous and non-aqueous liquors and are not aimed at exclusive extraction of uranium. The process or processes are aimed at extraction with general purification rather than at the ultimate purification of uranium.

The elements of novelty in leaching with a non-aqueous solvent are considerable, and the engineering problems are as yet unevaluated, let alone solved. But the metallurgical results are so good as to justify optimism regarding the final outcome. It is certain, however, that the problems will differ from those encountered in liquid-liquid partition processes on the one hand, and those encountered in aqueous leaching processes on the other hand.

MATERIALS TESTED

As the testing progressed, it seemed that this method of treatment might be of general usefulness, and to date the following materials have been tested:

1. Impure calcium uranate precipitated from Congo leach liquors with lime.
2. Eldorado gravity concentrate (Port Hope refinery feed)
3. Rand precipitate
  - a. high-iron using calcined dolomite as precipitant
  - b. low-iron using magnesite as precipitant
4. Rand flotation concentrate
5. Rand cyanide residue

There are many methods of obtaining precipitates from Rand leach liquors. The normal leach liquor can be precipitated, or the iron can first be oxidized and precipitated selectively and removed separately, to give on further neutralization a low-iron uranium precipitate, but the iron

removal step has an appreciable cost. The liquor can be precipitated with MgO which presumably would have to be imported or with calcined dolomite obtained from material mined in shaft-sinking operations on the Rand. The dolomite will give the cheaper precipitant but the precipitate will be diluted with gypsum. Testing has been concentrated on the two types of Rand precipitates listed.

EXPERIMENTAL WORK

Preparation of Material for Leaching

The Rand flotation concentrate and the Eldorado gravity concentrate were given a preliminary roast to oxidize sulfides which otherwise would consume nitric acid. The Rand precipitates were first dried at $110^{\circ}C$ to dehydrate silica and facilitate the elimination of excess water after nitration.

For nitration, in most tests, the material was pulped with 1:1 nitric acid as a laboratory convenience to insure proper mixing. The water added by this procedure is probably in excess of what is necessary. The quantity of nitric acid is usually somewhat less than stoichiometric for the oxides present. The normal nitration time involves heating for one hour. Analytical methods used in this laboratory have shown that leaching for one hour with 1:1 nitric acid quantitatively dissolves uranium from all of the materials tested. After nitration, the material is air-dried or dried in an oven at $80^{\circ}C$. This drying procedure has been done at low temperature to avoid decomposing the hydrated nitrate crystals. As uranyl nitrate is infinitely soluble in water, it should be the last substance to crystallize and hence it should not be locked in crystals of other nitrates. If the drying is stopped while the nitrated material is still damp, no further treatment is required before ether leaching. If the material is actually dry, it is ground to -100 mesh. The grinding step is not difficult unless drying has been insufficient.

Leaching with Ether

The damp or dry material is then leached with ether which contains nitric acid. Most of the work has been done with dry material. In most tests a concentration of 2 per cent HNO_3 in the ether has been used. The nitric acid in the ether is not essential if the material to be leached has been nitrated properly. However, it has been possible to extract uranium with ether from Rand precipitates which have not been nitrated, by utilizing the nitric acid in the ether for the formation of uranyl nitrate. Therefore, the presence of nitric acid in the ether will insure good extraction if by some chance the initial nitration is incomplete. Although there is considerable latitude as to where the nitration should be accomplished, it is believed that some nitric acid should be added to the material before leaching and some should be added to the ether.

Other variations in leaching have been in the amounts of ether used, in the time of leaching, and in the number of leaches and washes. After leaching, the ether is filtered from the dry material or decanted from the damp cake. The nitrated solids settle very readily and filtration is extremely rapid. The high filter rate appears to be due in part to the low viscosity of ether and in part to the flocculated nature of the nitrated pulp. In laboratory experiments the leaching, filtration, and subsequent displacement washing of the cake are carried out in one container. The filtration is done by vacuum. Ether losses are minimized by condensing the vapors from the filtrate in a tube surrounded by a dry ice-ether bath. The laboratory apparatus used for leaching dry material is sketched in Figure 1. With this apparatus it is possible to use various combinations of multiple leaches and washes.

Results of typical leaching tests on various materials are summarized in Table 1.

This table shows that extractions of uranium have ranged in general from 90 to 98 per cent. In two instances, the extraction exceeded 99 per cent while in one case it was less than 90 per cent. The quantities of ether and nitric acid are stated in terms of pounds of reagent added per pound of feed and per pound of U_3O_8 recovered. Of course, the quantity of reagent consumed is much smaller than the quantity added, as will appear below.

Precipitation of Uranium

To recover the uranium from the ether solution, consideration was first given to stripping this solution with water and precipitating the uranium from the water solution with an alkali. However, a simpler method was conceived and tried. When gaseous ammonia is passed into the pregnant ether solution, a fine white precipitate of ammonium nitrate is first formed. After neutralization of the nitric acid to ammonium nitrate, all the uranium precipitates as a yellow compound. The uranium precipitate clings to the wall of the vessel or settles rapidly to the bottom. Then the ether can be decanted or filtered off and is ready for reuse. The mixture of uranium precipitate and ammonium nitrate can be leached with a little water to dissolve the ammonium nitrate leaving a high-grade uranium product. The washed precipitate is then ignited to U_3O_8 . In our tests to date, this uranium product has assayed over 80 per cent U_3O_8 and in tests with feed materials low in iron such as Rand magnesia-precipitates it has assayed over 95 per cent. Whether the ammonia precipitate is uranyl hydroxide or ammonium uranate has not been determined.

The principal advantages of direct precipitation of uranium from ether are that ether recovery from the aqueous stripping solution is not required, that the filtration to recover the precipitate is much easier from ether than from the aqueous solution, and that nitrates can be recovered readily from the concentrated ammonium nitrate solution.

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Figure 1. Solvent Leaching Apparatus

Table 1. Metallurgical Results

Material	Remarks	Grade % U_3O_8	Reagent Addition				U_3O_8 Recovery %
			lb/lb of Feed		lb/lb of Recovered U_3O_8		
			Ether	HNO_3	Ether	HNO_3	
Congo CaO Ppt.	Dry-nitrated	27.5	6.1	0.70	22	2.5	99.7
Congo CaO Ppt.	Dry-nitrated	29.8	7.9	0.54	26	1.8	98.1
Congo CaO Ppt.	Dry-nitrated	28.2	5.7	0.69	20	2.5	97.8
Congo CaO Ppt.	no HNO_3 in ether	28.4	5.7	0.44	20	1.6	97.6
Eldorado Grav. Conc.	Dry-nitrated	8.6	5.3	1.75	65	21.3	95.6
Eldorado Grav. Conc.	Dry-nitrated	9.7	7.4	1.25	65	11.1	96.0
Hand Ppt. High-Fe Dol.	Dry-nitrated	0.7	9.4	1.0	1370	145	97.4
Hand Ppt. High-Fe Dol.	Dry-unnitrated	1.8	10.5	1.11	369	38.8	82.1
Hand Ppt. Low-Fe MgO	5% HNO_3 in ether	1.7	4.5	0.72	270	43.0	95.3
Hand Ppt. Low-Fe MgO	Dry-nitrated	3.6	6.4	0.82	200	25	99.6
Hand Ppt. High-Fe Dol.	Dry-nitrated	3.9	5.8	0.21	150	15	97.2
Flot. Conc.	Dry-nitrated	0.10	4.9	0.36	5150	383	92.9
Flot. Conc.	Damp-nitrated	0.10	2.8	0.47	2720	455	94.1
Cyanide Res.	Dry-nitrated	0.02	2.5	0.19	21000	1550	75.0
Cyanide Res.	Damp-nitrated	0.02	1.0	0.12	5130	592	91.3

Note: Unless otherwise indicated, ether used for leaching contained 2 per cent concentrated HNO_3 by volume.

Recovery

In order for this process to have economic possibilities, it is necessary to provide for recovery of the reagents used. In laboratory experiments, the use of the dry ice-ether condensers and the flashing of the ether from the final residue by evacuation has resulted in ether recoveries as high as 99 per cent. The concentrated ammonium nitrate solution obtained by washing the uranium precipitate has been treated with lime to evolve the ammonia used. The nitrated residue from ether leaching and the calcium nitrate solution after evaporation to dryness have been thermally decomposed. The NO and NO_2 evolved are equivalent to 93-97 per cent of the nitric acid used. No attempt has been made in the laboratory to convert these oxides to nitric acid. However, nitric acid is commercially produced from these oxides obtained by the catalytic burning of ammonia in small stainless steel towers at a pressure of about 100 lb/in². Operation under pressure is probably not justified for gasses evolved at normal pressure by thermal decomposition of nitrates. However, oxidation of these gasses to nitric acid has been accomplished at atmospheric pressure in considerably larger stoneware towers to obtain nitric acid of 45 per cent strength with efficiencies of about 95 per cent*.

On the basis of these tests then the process may be evaluated for application to the various materials on the assumption that 99 per cent of the ether and 90 per cent of the ammonia and nitric acid will be recovered and that the lime consumption will be less than half the stoichiometric equivalent of the total nitric acid used. Plans are under way for operation of the process on 10-kg batches.

Figure 2 is an abbreviated flowsheet of the nitrated ether leaching process which shows the principal steps for the recovery of a high-grade uranium product from the low-grade Rand precipitates. Figure 3 is a more elaborate flowsheet of the same process (Nitrated Ether Leaching Process) showing the proposed methods of recovering such reagents as ether, nitric acid and ammonia.

CONCLUSION

We are hoping that this process may be expanded to include other organic solvents, in addition to ether, as the extracting medium and also to include the extraction of various other salts in addition to uranium nitrate. The process in its present stage of development shows such promise that expansion to a larger scale seems justified and we hope eventually to operate it on a continuous basis.

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* Industrial and Engineering Chemistry, Vol. 23, No. 8, P. 60 (1931)

Figure 2. Nitrated Ether Leaching Process Flowsheet