

THE UTILIZATION OF URANIUM INDUSTRY
TECHNOLOGY AND RELEVANT CHEMISTRY
TO LEACH URANIUM FROM MIXED-WASTE SOLIDS

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MASTER

ABSTRACT

Methods for the chemical extraction of uranium from a number of refractory uranium-containing minerals found in nature have been in place and employed by the uranium mining and milling industry for nearly half a century. These same methods, in conjunction with the principles of relevant uranium chemistry, have been employed at the Oak Ridge National Laboratory (ORNL) to chemically leach depleted uranium from mixed-waste sludge and soil. The removal of uranium from what is now classified as mixed waste may result in the reclassification of the waste as hazardous, which may then be delisted. The delisted waste might eventually be disposed of in commercial landfill sites. This paper generally discusses the application of chemical extractive methods to remove depleted uranium from a biodegradation sludge and a storm sewer soil sediment from the Y-12 weapons plant in Oak Ridge. Some select data obtained from scoping leach tests on these materials are presented along with associated limitations and observations which might be useful to others performing such test work.

INTRODUCTION

For nearly half a century, the uranium industry has been chemically extracting uranium from ores containing various types of uranium-containing minerals. These minerals are many times bound in silica-based matrices that are quite refractory toward chemical removal methods. Such methods have, however, been developed despite this refractory nature. The chemical removal processes usually utilized in the uranium industry most often employ crushing and grinding to expose bound uranium to the leachant solution. In some ways, the extraction of uranium from such ores is a much more challenging task than the removal of uranium from mixed-waste solids, as will be discussed in this paper. However, despite this generalization, the leaching of uranium from mixed-waste solids and sludges can present some special problems stemming from the nature of this type of material.

ACID VERSUS ALKALINE-BASED LEACHING SCHEMES

In an effort to develop a leaching scheme for the removal of uranium from a waste solid, one must first have some idea about the chemical form(s) of the uranium present in the solid. This is extremely important because the chemistry that will successfully oxidize and complex the uranium is highly dependent upon the form of the uranium in the waste. The same is true in the uranium industry; only certain types of minerals are amenable to uranium extraction in alkaline solution, while others require aggressive acid-based solutions (1). Therefore, some insight as to the form(s) of the uranium should be established by either employing rigorous X-ray diffractive techniques (which may be limited) or indirectly by leaching the solid under various acidic and alkaline-based conditions. By performing scoping tests under proper leaching conditions which are conducive to solubilizing uranium, using both acidic and alkaline routes, one may surmise in

what form the uranium exists. Such tests will also generate process data which may be useful for actual process implementation.

In the uranium industry, acid-based leachants, such as sulfuric acid, and an oxidant, such as sodium chlorate, are most commonly used. With some uranium ores, alkaline-based leachants containing sodium carbonate and bicarbonate together with oxygen or hydrogen peroxide may also be employed. These two types of leaching schemes are the most common, and the necessary conditions for each are discussed in many texts and journal articles (1,2,3).

For those forms of uranium that are soluble in alkaline solutions, we receive a definite advantage because many other metals and nonmetals are not coextracted with the uranium. In this way, we obtain a solution that contains primarily uranium and little else. Using the acidic route, such as with sulfuric acid, selectivity is no longer observed; and the uranium-containing solution becomes loaded with many other species, of which many will be hazardous under current regulations. The result may be that we produce a new mixed-waste solution containing our uranium and unwanted hazardous components. With this in mind, it would appear that for almost any type of waste solid we would prefer to be able to extract uranium in alkaline solution, rather than in acid, when possible.

As already mentioned, depending upon the predominant form(s) of the uranium in the waste solid, the scoping tests will give insight into the most probable form of the uranium, based upon known chemical properties of uranium under different conditions in various forms. For example, since uranium metal is machined at our Y-12 weapons plant, metallic uranium could be present. It is known, however, that metallic uranium will slowly react with water to form hydrogen gas and the insoluble uranium IV cation. In acid this reaction is rapid, and we would expect metallic uranium to quickly react in acid, resulting in a good extraction in this medium

when an oxidant is present. In an alkaline solution, such metal could only react slowly with the water and may never be extracted to a satisfactory extent.

As a second example, uranium is also burned to various oxides at our Y-12 Plant and may, therefore, be in the soil in this form; that is, as some mixture of oxides of UO_2 and UO_3 , commonly called U_3O_8 or $\text{UO}_2 \cdot 2 \text{UO}_3$, depending upon the ratios of these oxides. The solubility of any burned oxides of uranium is highly dependent upon the calcining temperature and the time at that temperature. Some oxide will be soluble in only oxidizing acids, such as nitric acid, and only sparingly soluble in sulfuric acid. Such a refractory, calcined oxide will usually not be extractable in any alkaline solution. If one were to leach with nitric acid, you might expect to be successful because the oxide is soluble.

In addition to the form(s) of the uranium, the pH of the waste is also important. If a waste solid is highly alkaline, as is the case with both of the wastes to be discussed in this paper, then the addition of vast amounts of acid only add unwanted anions to the waste process solutions. The anions may react with other cations present, such as calcium, and form new insoluble solids which may be quite voluminous, such as calcium sulfate (gypsum). This can occur when sulfuric acid is used with a solid containing large amounts of calcium.

INDUSTRY AND LABORATORY PROCESS EQUIPMENT

Most commonly in the U S uranium industry, open vats are used to leach uranium from various types of ores that have been crushed and screened (1,4). The choice of equipment is, however, a function of the ore and mineral form and sometimes requires the use of high-pressure autoclaves for leaching at temperatures above the solution boiling point. In addition, leached solids may be reground between leaching stages if it becomes necessary to break down surface

coatings or to further expose bound uranium to fresh solution. Such attrition may require the use of rod or ball mills.

Such unit operations may be viewed as too costly when a competitive situation exists for a marketable uranium oxide, otherwise known as "yellow cake." In the waste treatment business, however, the costs associated with disposal are those that dictate what may be considered costly. Options considered too costly in the uranium industry when a saleable product is involved may not be thought of as such when treating solid wastes. As a result, more options may be available to an engineer or researcher working in the waste treatment area as opposed to those available to someone selling a marketable product.

OBJECTIVES OF SCOPING LEACH TESTS

The objectives of such a scoping test program, as described in this paper, have centered around some 50 leach tests split between 2 different types of mixed waste and various leaching schemes (acid vs alkaline). The objectives of such a test program can be generally summarized as follows:

- (1) To determine the most probable form of the uranium present in the solid waste by observing the extraction efficiency under different conditions in various types of leachants, while at the same time achieving our 95 ppm uranium goal.
- (2) To generate process data that may be useful to engineers and environmental staff.

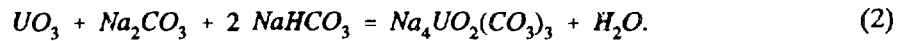
- (3) Although once a leaching scheme has been decided upon kinetics of the extraction should logically follow, this has not been one of the more important aspects of these scoping tests; however, some kinetic data may be generated.
- (4) To establish the extent of practical limits in terms of reagent or equipment use, and how this may impact final disposal of the leached residue or coproduction of unwanted side streams.

FUNDAMENTAL URANIUM CHEMISTRY

A thorough, more in-depth discussion of the chemistry of uranium than will be discussed here can be found in many journals and books on the topic (4,5,6). The fundamental chemistry of uranium can be summarized, however, into two necessary conditions that must occur in the following order:

- (1) Uranium must first be oxidized from its most common reduced oxidation state of U IV to U VI. The uranium must remain in the U VI state and must not be reduced back to U IV at any time during the leaching or washing process; otherwise, it may hydrolyze and precipitate or be irreversibly adsorbed onto a solid surface, such as clay.
- (2) There must be a sufficient supply of complexing anion, such as carbonate, sulfate, chloride, or nitrate, to stabilize the oxidized uranium and maintain it as a soluble species.

As an example of the oxidation and complexation sequence that occurs, the following simplified reactions can be written for a carbonate/bicarbonate system containing oxygen as the oxidant, where reaction (1) is the oxidation reaction and reaction (2) the necessary complexation.



Similar, analogous reactions may be written for other types of leaching schemes with the various acids except that the cyclic oxidation of Fe II to Fe III will be involved in acid solutions (1).

NECESSARY ADDITIONAL CONDITIONS FOR ACID AND ALKALINE LEACHING

For acid-based leaches using sulfuric or hydrochloric acid, an oxidant must be present, such as sodium chlorate. The oxidant itself "can not" oxidize the uranium, and at least 100 ppm of soluble iron must be in solution at all times, at a minimum oxidation potential of -450 mv versus the saturated calomel electrode. This is very important because the Fe III can efficiently effect the oxidation of uranium. It can not be assumed that a waste soil or solid contains the iron in a soluble form, and, therefore, it is usually wise to add soluble iron when this is uncertain. When leaching with nitric acid, control of iron concentration will no longer be of importance. For a more in-depth discussion of this important point and the control of other factors such as pH, we suggest references 1 and 4.

When leaching in the alkaline mode, using the more common sodium carbonate and bicarbonate mixture in addition to an oxidant such as potassium permanganate or hypochlorite,

one must ensure that the pH is maintained within a proper range. Generally, a pH range between 9.5 to 10 is desired; in this range, a sufficient amount of carbonate is present to complex U VI, and enough bicarbonate occurs to prevent hydrolysis and loss of uranium from solution. In such solutions, the oxidant itself must oxidize the uranium; thus, iron is not necessary because it would precipitate from solution. It is for this reason that leaching in the alkaline mode can be much slower than in acid and, as a result, may require elevated temperatures or longer leaching durations.

THE POTENTIAL BENEFITS OF ATTRITION

As already mentioned, in the uranium industry it is usually necessary to crush and grind ore in ball or rod mills to expose uranium minerals to the leachant solution. In addition to exposing uranium to the solution, surface coatings which build up on solid surfaces can be removed between leaching stages, if more than one stage is involved. For a soil such as the one to be discussed in this paper, ball milling was shown to enhance the final extraction efficiency. Such ball milling may provide some benefit for a material such as a soil, but is of limited value for sludges and may only make washing and filtration very difficult. Unfortunately, a large amount of waste containing uranium is in the form of high-water-content sludge at many government sites around the nation.

ALL IMPORTANT WASHING OF THE LEACHED TAILS

It is the authors' opinion that, above all, the efficient and complete washing of leached residues, also referred to as tails, is as important as, or more important than, the leaching process itself. This is especially true for sludges in which the task of exchanging water containing complexed uranium in the sludge, with wash water on the outside, is more difficult than thought

by most. With a pasty sludge, this task is much more difficult than it would be for a soil or uranium industry ore. Similar problems might be expected when clays are present as well. Generally, a few useful guidelines can be followed to facilitate more efficient washing.

- (a) At least 3 washes of the filtered tails, capable of exchanging the volume of bound water in the filtered solids at least 10 times, should be employed for sludges and clay-containing materials. Optimum wash volumes should be established by performing washing efficiency tests.
- (b) The chemistry of the wash water should usually match that of the leachant solution.
- (c) For difficult sludges and clay-containing waste materials, remixing the filtered solids with wash water in multiple stages may be necessary, with sufficiently long enough mixing time in each stage for wash water exchange to occur. Elevated-temperature wash water may speed up the wash time and efficiency with some types of waste solids.

THE "PHOSPHATE CURSE"

Of the possible chemical species which may be present in a waste solid or slurry that can limit the extent of uranium extraction, phosphate is by far the worst. Phosphate combines with uranium to form *highly insoluble* minerals, such as hydroxylapatite, which are only sparingly soluble in hot, concentrated acid. This is a well known fact in the phosphate mining industry, which is well established in Florida, Idaho, and Montana. During the reaction of hot,

concentrated sulfuric acid with crushed phosphate-based ore, not all of the uranium is recoverable. As a result, it is difficult to buy a container of phosphoric acid that does not contain uranium.

In our studies, phosphate was found to be present in a biodenitrification sludge, which will be discussed below, along with our other laboratory test work. When uranium is bound with this anion, alkaline leaching will be of no value, especially for that portion of the uranium which may be bound in this way. Even aggressive acid leaching will yield little benefit at the price of putting many other hazardous species in solution under such condition. Processes that employ the use of phosphate should be planned so that this species is kept away from uranium-containing solutions at all cost.

EXPERIMENTAL

The remainder of this paper will be devoted to summarizing a selected amount of data obtained from some of our scoping tests, performed on two mixed wastes from our Y-12 weapons facility here in Oak Ridge. More emphasis will be placed upon our observations rather than upon the fine details of how each test was performed. We feel this may be of more value to those doing similar work, since specific conditions will have to be adjusted to each and every type of waste solid tested.

WASTE MATERIALS AND CHARACTERISTICS

Storm Sewer Soil Sediment

Operations at the Y-12 facility over many years have resulted in some soils being contaminated with uranium. These soils eventually were washed by the rains into storm sewers,

which have been recently cleaned out and the soil stored for future treatment to remove the uranium. The storm sewer soil sediment (SSSS) is contaminated with trace amounts of mercury and some other heavy metals, in addition to 354 ppm of depleted uranium. As such, the SSSS is classified as a mixed waste, and it shall be our objective to lower the uranium content to at least 95 ppm, or 32 pCi of dry solid. This is a locally imposed limit and is undergoing revision at present. This uranium activity is based upon the use of a specific activity of 0.333 $\mu\text{Ci/g}$ of uranium. This target was the same for both types of waste materials discussed in this paper.

The SSSS contained only 0.5 wt % water and was highly alkaline, as are most of the karst-type soils in this area. Calcium carbonate was present at high enough concentrations that this material was able to consume more than a tonne of sulfuric acid per tonne of SSSS. As expected, copious evolution of carbon dioxide and foaming was a major problem when using any of the acids with this mixed waste.

Biodenitrification Sludge

Of the two solid mixed wastes studied, this material was the most interesting for it was the residue remaining from anaerobic, biological denitrification processing at Y-12. In this process, nitrate laden solution was reduced to nitrogen gas and water by bacteria. The bacteria were fed calcium acetate as a carbon source and subsequently formed calcium carbonate, which makes up most of the sludge mass. In addition, trisodium phosphate was added to the solution to maintain the bacteria that require phosphate to manage energy storage and transport in their bodies.

The bacteria were able to concentrate uranium and heavy metals in their bodies, with uranium reaching as much as 15 wt % of their dry body weight. Eventually, this diet became fatal to the bacteria. Because this was an anaerobic process, most of the metals and uranium were

present inside these bacteria in their most chemically reduced state, as were those metals in the surrounding solution.

The biodenitrification sludge contained 40 wt % solids and was shown to contain 3711 ppm uranium based upon the dry weight. The sludge was nearly completely soluble in nitric acid at room temperature except for a small amount of residue which was found to contain about 10% of the total uranium and some bacterial fatty acid mass.

Equipment Setup and Methods

All tests were performed in 1-L, agitated, glass resin kettles which were placed in a temperature-controlled water bath, as described in reference 5. Some tests were performed in a 1-L Fluitron autoclave at 40 psig air pressure and 120°C. A select number of leach residues were ground in a ceramic ball mill containing a charge of ceramic balls to investigate the affect of attrition upon the leaching efficiency.

The solids, once leached, were filtered using ceramic filter funnels and remixed with wash solution in resin kettles prior to being refiltered a number of times. This process was continued in stages until it was determined that the washing was sufficient.

The oven-dried tails were pulverized to a fine powder and 30- to 50-g samples were removed in triplicate for chemical digestion. The samples were repeatedly taken to dryness in Teflon beakers in a double boiler using a mixture of concentrated nitric and hydrofluoric acid. The solids were washed repeatedly and the filtrate diluted to 500 cc for uranium analysis using a new analytical technique less prone to interferences, that is, ICP mass spectrometry.

RESULTS

Tabulated results of our scoping tests are presented in the following two tables for each type of mixed-waste material tested.

OBSERVATIONS

Storm Sewer Soil Sediment

A quick scan of the data shown in Table 1 above reveals that our objective of 95 ppm uranium in the tails is achievable by a number of different leaching schemes. However, as already discussed, our preferred leaching scheme is based upon the alkaline leachant composed of carbonate and bicarbonate salts. Utilization of this scheme will afford us the opportunity to cleanly leach the uranium into solution without solubilizing many other metals. Therefore, it appears that we would likely choose to use a carbonate-based leachant at $\sim 50^{\circ}\text{C}$ over 48 h in a stirred open-vat-type leach with potassium permanganate as an oxidant. It does appear that use of the ceramic ball mill has been able to lower the uranium tails content by 50 % due to some benefit from attrition of the soil surfaces. This attrition may be exposing uranium to the solution and/or it may be removing cemented calcium carbonate deposited from ground water over years of weathering.

Biodenitrification Sludge

Initial scoping test results obtained from early leaching tests, using a carbonate/bicarbonate-based leachant were very disappointing, as can be seen in Table 2. The largest benefit obtained with this sludge was realized upon preleaching the sludge with sodium

hydroxide to saponify all bacterial fatty acids. It was only a supposition that the bacterial mass might be hindering our efforts with this material. Early tests had revealed that the pH of the leach solutions was continuously dropping, and we attributed this to the hydrolysis of metal cations that were oxidized. Although this probably was part of the reason, apparently bacterial mass composed of complex fatty acids was also consuming alkalinity as a result of probable saponification of this material. Whatever the exact effect of the presaponification, it appears to be beneficial.

Additionally, it also appears that some added benefit can be gained by leaching in an autoclave at elevated temperatures, as compared with open-vat leaching; however, other engineering-related factors may preclude this option based upon desired throughput.

CONCLUSIONS

Storm Sewer Soil Sediment

This soil was found to be quite amenable to the extraction of uranium in both acid and alkaline leaching schemes, while meeting our target minimum of 95 ppm uranium. It appears that a minimum of 90% of the uranium contained in this mixed-waste solid is in the form of oxidizable uranium IV, probably bound as an insoluble, hydrolyzed carbonate and/or sulfate.

The use of an acid-based leachant will only result in the coextraction of many other metals and consume vast amounts of acid. This was shown by performing ICP scans on the resulting uranium-bearing solution for coextracted metals (data not presented). Tests with sulfuric acid have shown that the volume increase in the leached tails is quite substantial due to the formation of insoluble gypsum from the reaction of the acid with calcium carbonate in the soil. The use of

nitric acid could be considered only if one were able to accept the large amount of nitric acid necessary and the coextraction of other waste species.

Although hydrochloric acid was used in the scoping test program on a limited basis, it is far too corrosive and likely impractical as a realistic choice if forced to use an acid-based leaching scheme.

Biodenitrification Sludge

Early in the test program it was observed that nearly all of the calcium carbonate-based sludge was found to be soluble in nitric acid. The fraction not soluble in nitric acid was found to be rich in phosphorous and uranium. X-ray diffraction tests are being performed on this material as of this writing. This fact might lead one to consider dissolving the sludge and then removing the uranium by solid or liquid ion exchange. However, again we are faced with the penalty of co-dissolving all other hazardous species, some of which will be carried along with the uranium via the exchange processes. For this reason, only the alkaline-based leaching scheme has been considered for this sludge despite the fact that we were not able to lower the uranium content of the sludge to 370 ppm uranium.

As data in Table 2 show, the best results were obtained using the higher temperatures associated with the autoclave leaching experiments. However, the 370-ppm tail was obtained on material that had already been leached in open top resin kettles following saponification, in which tails of 440 ppm were obtained previously. Such a material as this might well require multiple stage leaching, as was found to give the best results in these scoping tests. This approach is oftentimes employed in the uranium industry. Such an approach, however, must take into consideration the number of new waste streams that are cogenerated and their characteristics.

It would appear that with this type of mixed-waste sludge, saponification prior to alkaline leaching is preferred. Despite our best efforts with this material, and after many different approaches, we have not been able to remove approximately the last 10% of the uranium. We feel that our efforts to obtain 95 ppm uranium with this mixed waste have been limited by the uranium's association with phosphate: the "phosphate curse" as we have referred to above. The soluble portion of the U in this mixed waste is most probably hydrolyzed uranium IV in association with carbonate and possibly some organic matter.

**Table 1. Some Selected Results of Scoping Leaching Tests
of Storm Sewer Soil Sediment**

Uranium Tail Leach Test Description	Assay, ppm (dry)
Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ , 52° C, 48 h, kettle	85
NaHCO ₃ , NaOCl, 52° C, 48 h, kettle	87
HNO ₃ , 52° C, 24 h, kettle	37
H ₂ SO ₄ , FeSO ₄ , NaClO ₃ , 52° C, 48 h, kettle	29
Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ , 80° C, 48 h, kettle	102
Na ₂ CO ₃ -NaHCO ₃ , KMn ₄ , 26° C, 48 h, ball mill	45

**Table 2. Some Selected Results of Scoping Leaching Tests
of Bionitrification Sludge**

Uranium Tail Leach Test Description	Assay, ppm (dry)
Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ , 52° C, 48 h, kettle	1,080
Na ₂ CO ₃ -NaHCO ₃ , NaOCl, 52° C, 24 h, kettle	2,370
NaOH saponification in autoclave, 120° C, 25 h Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ , 12 h, kettle then autoclaved again at 120° for 7 h	460
NaOH saponification in kettle, 80° C, 24 h Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ , 80° C, 24 h, kettle	440
Previous test tails, Na ₂ CO ₃ -NaHCO ₃ , KMnO ₄ autoclave, 120° C, 24 h	370

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