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BROWN OXIDE BY-PRODUCT RECOVERY - V

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BROWN OXIDE BY-PRODUCT RECOVERY-V

Introduction

The problem of recovering uranium in the residues from the brown oxide process has been the object of considerable work. Recently a new scheme was proposed for recovering a large part of the uranium which in the past has gone into the residues. The plan as outlined was to involve the following steps:

1. All of the very impure material in the plant, such as NG 3 liquor, acid press cake, and recovery press cake, was to be slurried with nitric acid and adjusted to a pH of 2.85 (1:100).
2. This material was then to be placed in an extractor which would extract the uranium from the water solution by bubbling ether through it.
3. The uranium in the ether layer could then be removed by scrubbing with water, by evaporation, or by some other suitable means.

Presumably this method would recover practically all of the uranium which was soluble in nitric acid at a pH of 2.85 (1:100).

Object

To determine the feasibility of the proposed process for recovering most of the uranium which at present goes into brown oxide process residues.

Conclusions

1. The amount of uranyl nitrate which can be extracted from a water layer by washing with ether depends very critically upon the amount of water present. Approximately 98% of the uranium can be removed from uranyl nitrate hexahydrate in which the water is not more than approximately 20%.
2. The extraction of uranyl nitrate from nitric acid-treated brown oxide process residues by the ether-wash method is not very satisfactory because of the difficulties involved in getting a good mixture of sludge and ether.
3. Nitric acid is concentrated in the ether layer during an extraction of this kind and precautions should be taken so the acid concentration is not sufficiently great to cause an explosive reaction.

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4. Organic material is concentrated in the ether layer, most of which apparently is not sufficiently soluble in water so that it can be readily washed out. It is questionable whether this would render the ether solution unsuitable for further use.
5. Since presumably any ether-soluble material in this process is also water-soluble, it appears that the over-all reduction of uranium in the finally discarded residues would not be appreciably decreased below the amount discarded by using our present process.
6. Work done up to the present time indicates that any advantages over the present recovery process which might be gained by installing the proposed process are not sufficiently great to warrant the installation of the special equipment which would be required to carry out this process.

Discussion

The proposed process was to consist essentially of extracting uranium from a water solution by bubbling ether through it. The relatively pure uranium could then be recovered from the ether by scrubbing with water, by evaporation, or by other suitable means.

A study of the distribution curve of uranyl nitrate between water and ether shows that the practical limit to which the uranium content of a water solution can be reduced by scrubbing with ether is about 25%. This means that the amount of water in the initial charge in the proposed special extractor would have to be very small in order to get appreciably good yields of uranium into the ether layer, even though large quantities of ether were used. Since the amount of water in uranium nitrate hexahydrate is about 21-22%, it is necessary, in order to get good extraction yields by the proposed method, that the amount of water in the water layer be in the neighborhood of the amount of water in uranyl nitrate hexahydrate. Since the freezing point of uranyl nitrate hexahydrate is about 65°C, it is obvious that a water solution cannot be used, but instead the material to be extracted would necessarily be practically solid or crystalline. This condition might not be particularly bad when the "water layer" is nearly all uranyl nitrate, but when the soluble uranium salt is mixed with considerable amounts of insoluble material, such as is found normally in the residue cake and acid press cake in our present process, the "water layer" then becomes a heavy sludge, the physical nature of which makes it very difficult to mix with ether.

The three most likely materials which would be used in this process are:

1. NG 3 liquor
2. Acid press cake
3. Recovery cake

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A brief discussion of each type of material follows:

1. NG 3 Liquor.

Since it was found that an emulsion formed when hex made from unfiltered NG 2 liquor was used in the special extraction process, it was presumed that hex made from unfiltered NG 3 would behave the same way or possibly worse. In the present plant process, NG 3 liquor is treated with sodium hydroxide to a pH of 2.3, filtered, and the uranium in the filtrate is then precipitated as low sodium salt, a nitric acid solution of which is extractable. It seems likely that the special extractor would work with hex made from the filtrate from a similarly sodium hydroxide treated solution. However, if it is necessary to make this sodium hydroxide treatment on liquor for the proposed process, it seems unlikely that it would be economically feasible to build a special extractor, inasmuch as the present process works fairly satisfactorily with this type of liquor.

2. Acid Press Cake.

At present the acid press cake is slurried with water and nitric acid, and the resulting soluble uranium is filtered and precipitated as low sodium salt which is extractable. Experiments with acid press cake in the special extraction process indicate that this material would be quite difficult to extract directly with ether, inasmuch as when mixed with ether it forms a very gummy mass, so that the cake does not readily mix intimately with ether to effect the most efficient extraction. It seems likely that the liquor obtained by treating this cake in the present process (slurrying with water and filtering) when boiled down to hex would be extractable in the special extractor. However, since a fairly satisfactory process has already been worked out, namely, precipitating extractable low sodium salt, it does not seem particularly advisable to build special equipment to extract this material.

3. Recovery Press Cake.

A similar line of reasoning is applied to the recovery cake process as was used for the acid press cake. In order to get the uranium in a form which is extractable by the special process, it is necessary to go through steps very similar to those required to get the uranium in a form in which it can be precipitated as extractable low sodium salt.

It might be said in general that since presumably the ether-extractable uranium in any of these materials is also water-extractable, and since in general the water solutions are considerably easier to handle than the ether solutions, it does not seem that the special extraction process holds sufficient advantage over our present process to warrant its installation.

Nitric Acid Concentration in Ether Layer.

There is some evidence that nitric acid is washed out of the water layer by ether faster than is the uranium trioxide. In any continuous process for extracting with ether, precautions should be taken that the acid concentration in the ether layer does not become high enough to cause an explosion hazard.

Experimental Details.

Experiment 43.-- The object of this experiment was to determine the general conditions necessary to effect the extraction of uranyl nitrate from a water solution by washing with ether. Five hundred ml of a solution of uranyl nitrate hexahydrate in water (44.7% uranyl nitrate hexahydrate) was placed in a cylindrical vessel. A glass tube with small openings at the bottom was placed inside the vessel so that the end with the small openings was near the bottom of the vessel, and the top which was arranged in the form of a funnel, extended several inches above the top of the vessel. When ether was poured through the tube it came out of the bottom in the form of small bubbles which passed through the water layer containing the uranyl nitrate, removing some of the uranyl nitrate into the ether layer. When ether was poured continuously into the funnel arrangement, the level of the ether layer in the extraction vessel rose until it overflowed into a side arm and was collected in a graduated cylinder. A total of 2200 ml of ether was used in this experiment to extract the uranium from the water layer as described above. The specific gravity of the ether discharging from the apparatus was measured from time to time, and from this the amount of uranyl nitrate in the ether could be determined from a previously prepared graph of specific gravity of ether layer versus per cent uranyl nitrate. Table I gives the pertinent data recorded in this experiment and Chart I shows the amount of uranyl nitrate extracted versus volume of ether used.

Table I

Data From Experiment 43

Uranyl nitrate hexahydrate in water layer before extraction.	44.7%
Amount uranyl nitrate hexahydrate in water layer before extraction.	356 grams
Specific gravity of water layer before extraction.	1.454
Amount of ether used for extraction.	2200 ml
Temperature of mixture during extraction.	24°C
Uranyl nitrate hexahydrate in water layer after extraction.	34%
Specific gravity of water layer (ether free) after extraction.	1.280
Amount of uranyl nitrate hexahydrate in water layer after extraction.	200 grams
Uranyl nitrate hexahydrate recovered by extraction.	44%
pH of water layer before extraction.	2.70
pH of water layer after extraction.	2.97

Conclusion

The extraction efficiency in this experiment was very low, presumably due to the amount of water in the water layer. A study of Chart II shows that the minimum concentration of uranyl nitrate in water which can be obtained by washing with reasonable amounts of ether is in the neighborhood of 25%. This means that the amount of water in the water layer must be very small so that a 25% solution of uranium in this amount of water will represent only a small percentage of the total amount of uranium which was in the water layer* before the extraction was started.

Experiment 45.

Since a very poor extraction was obtained in Experiment 43, presumably due to the relatively large amount of water in the water layer, it was decided to try the extraction with uranyl nitrate hexahydrate crystals in which the amount of water is about 20%. The same apparatus was used in this experiment as was used in Experiment 43 with the addition of a motor stirrer. The crystals were placed in the bottom of the cylindrical vessel, and the ether was passed through in the manner described previously. The specific gravity of the effluent ether was measured from time to time. Table II gives pertinent data obtained in this experiment, and Chart III shows the amount of uranium extracted versus the amount of ether used.

Table II

Data From Experiment 45

Uranyl nitrate hexahydrate in water layer before extraction.	100%
Amount of uranyl nitrate hexahydrate in water layer before extraction.	561 grams
Amount of ether used for extraction.	4600 ml
Uranyl nitrate hexahydrate in water layer after extraction.	20%
Weight of uranyl nitrate hexahydrate in water layer after extraction.	8.8 grams
Specific gravity of water layer after extraction.	1.135
Uranyl nitrate hexahydrate recovered by extraction.	98.4%

Conclusions

98.4% of the uranium present at the beginning of the extraction was recovered in the ether layer. A study of Chart III shows that the first 2000 ml of ether removed most of the uranyl nitrate, while the remaining 2600 ml was used to remove the uranyl nitrate at a time when the concentration of uranyl nitrate in the water layer was such that the distribution between ether and water was becoming progressively and rapidly more favorable

* In this report the term "water layer" is used to define the uranium containing material from which the uranium is being extracted with ether.

towards the water layer. It appears, however, if only a very small amount of water is present in the initial water layer, that fairly good yields of uranyl nitrate can be obtained in the ether before the amount of ether used becomes prohibitive.

Experiment 46.

In the factory boil-down tanks (for hex liquor before extraction) considerable sludge is produced. This sludge is about 97% uranyl nitrate with probably some insoluble uranium salts, such as phosphates, vanadates, and molybdates, and other insoluble material, but practically no "free" water. In this experiment this sludge was extracted the same way as the uranyl nitrate crystals were extracted in Experiment 45 with very similar results. Table III shows the pertinent data obtained in this experiment. The uranyl nitrate which was extracted with ether in this experiment was recovered from the ether by extraction with water, after which the water layer was boiled down to hex and the regular laboratory extraction test performed. In this extraction test the layers separated very quickly and both were clear.

Table III

Data from Experiment 46

Uranyl Nitrate Hexahydrate in water layer before extraction.	97%
Weight of uranyl nitrate hexahydrate in water layer before extraction.	587 grams
Volume of ether used for extraction.	4600 ml
Weight of hex in water layer after extraction.	31 grams
Uranyl nitrate hexahydrate removed by extraction.	95%

Conclusions

About 98% of the uranium was removed by ether extraction when pure hex was used as the starting material (Experiment 45). Since about 95% was removed in this experiment, and since the amount of water in the original material was approximately the same as that in the starting material when pure hex was used (Experiment 45), the reason that less material was extracted in this case is probably because some of the uranium was tied up as insoluble uranium salt, such as phosphate, etc.

Experiment 47.

One of the materials from the plant process which contains considerable uranyl nitrate, a large per cent of which now goes into brown oxide process residues, is acid press cake. The original idea was to slurry this acid press cake with nitric acid and adjust the pH to 2.85 (1:100), after which uranium could be extracted by bubbling ether through. However, since it was

learned previously that the amount of water present in the water layer determined the efficiency of the extraction, it was decided that after the slurry of press cake had been adjusted to a pH of 2.85 (1:100), it should be concentrated by boiling off most of the water before the extraction was performed.

Nine and three-quarter pounds of acid press cake were treated with nitric acid until a sample of the slurry when diluted 100 to 1 with water gave a pH of 2.65. The slurry was then evaporated to a very thick, pasty, gummy mass. The evaporation was very difficult to carry out because the steam coil continually became very badly caked. The evaporated material was placed on stainless steel trays to cool. The material in one of the trays appeared to be slightly more moist than the material in the other tray, which contained a considerable amount of the cake which had baked on the steam coil. Both the "dry" material and the "moist" material were extracted with ether by mixing several portions of ether by mixing several portions of ether with the sludge, and decanting. The extraction was stopped when the specific gravity of the ether reached 0.72. Table IV gives the pertinent data obtained from the extraction of the "dry" material and Table V gives the pertinent data obtained from the "moist" material.

Table IV

Data From Extraction of "Dry" Sludge

Uranium in water layer before extraction.	38%
Weight uranium in water layer before extraction.	380 grams
Volume of ether used.	2150 ml
Uranium in water layer after extraction.	26%
Weight of uranium in water layer after extraction.	151 grams
Uranium removed by extraction.	60%

Table V

Data From Extraction of "Moist" Sludge

Uranium in water layer before extraction.	33.2%
Weight of uranium in water layer before extraction.	332 grams
Volume of ether used.	2300 ml
Uranium in water layer after extraction.	26.6%
Weight of uranium in water layer after extraction.	150 grams
Uranium removed by extraction.	54%

The ether layers from these extractions were dark brown in color. When the uranium was extracted from this ether by washing it with water, the brown-colored material stayed in the ether layer. This is probably some sort of organic material, since it seems to be soluble in ether and insoluble in water. The water layer containing the uranium was then boiled down to hex, after which the hex was tested by the regular extraction test. The two layers separated rapidly, and both were clear.

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Conclusions

The physical nature of the sludge made it extremely difficult to get the intimate mixture with ether which is necessary for good extraction. The amount of uranium extracted was only about one-half of the total amount of uranium in the cake before the extraction was attempted. It appears that the extraction of acid press cake is likely to be a very unsatisfactory procedure, both from the standpoint of the amount of uranium recovered and the difficulties which might be involved in designing and operating an apparatus to carry out the extraction of a sludge with the physical properties exhibited by the acid press cake.

Experiment 48.

It was found in Experiment 47 that only about one-half of the uranium originally in acid press cake was extracted with ether. This might be due to either or both of the following conditions:

1. Poor extraction obtained because of the physical nature of the material extracted.
2. A large part of the uranium in the acid press cake may have been insoluble in ether because it existed as uranium phosphate, vanadate, or molybdate.

This experiment was designed to check the latter of the two conditions. It was thought that if lead nitrate were added to the slurry of acid press cake, the phosphates, etc., might be precipitated as a lead salt and the uranium converted to soluble uranyl nitrate.

Nine pounds and twelve ounces of acid press cake were slurried with water and nitric acid to obtain a pH of 2.67 on a sample which was diluted with water to a concentration of one part of slurry to 100 parts of water. One hundred grams of lead nitrate dissolved in 500 ml of water was mixed with the slurry, after which a mixture was evaporated to a thick sludge by aid of a steam coil. The sludge was placed on two stainless trays and the contents of one of these trays were evaporated further by heating and stirring. After standing overnight, the tray of material which had been given the extra evaporation was fairly dry. One hundred grams of this "dry" cake was extracted with ether by mixing successive portions of ether with it and decanting. Table VI shows the pertinent data obtained from this extraction.

Table VI

Uranium in water layer before extraction	35.7%
Weight uranium in water layer before extraction.	357 grams
Volume of ether used.	2400 ml
Uranium in water layer after extraction.	23.5%
Weight of uranium in water layer after extraction.	129 grams
Uranium removed by extraction.	64%

The ether layer from this extraction was dark brown in color. When the uranium was extracted from this ether by washing it with water, the brown-colored material stayed in the ether layer. This is probably some sort of organic material, since it seems to be soluble in ether and insoluble in water. The water layer containing the uranium was then boiled down to hex, after which the hex was tested by the regular laboratory extraction test. The two layers separated rapidly, and both were clear.

Conclusions

The only additional conclusion which may be drawn from this experiment is that the lead treatment did not materially help to extract a greater amount of uranium from the cake. The failure of the extraction may still be due to one or both of the two conditions outlined in conclusions of Experiment 47.

Experiment 49.

In the present factory process, NG 3 liquor ordinarily is not extractable as such, but must be given a special treatment, and precipitated as low sodium salt. One of the possibilities seen in the proposed extraction method was to recover the uranium from NG 3 liquor by scrubbing with ether, thereby eliminating the above-mentioned treatment and precipitation. However, since the amount of water in the water layer for the proposed extraction process should be very small, it would be necessary to concentrate the NG 3 liquor to a point where the water content approximated that in uranyl nitrate hexahydrate. At the time these experiments were done, there was no NG 3 liquor available in the factory, but there was some NG 2 liquor available and it was assumed that if any difficulties were encountered in the extraction of the NG 2, these difficulties would at least be equal to and probably greater in the extraction of NG 3. NG 2 liquor which had been adjusted to a pH of 2.85 (1:100) was obtained from the factory, and was concentrated by boiling with a steam coil to a boiling point of approximately 118°C, after which it was crystallized by cooling and stirring. These crystals were placed in the special extraction vessel and were extracted with ether as described in Experiment 45 (Extraction of Pure Hex). A very stable emulsion formed which persisted for eleven minutes. At the end of this time it was partially broken by intermittent slow stirring. Ether was bubbled through the solution as in previous experiments, and was collected and measured in the usual way.

Pertinent data obtained in this experiment are given in Table VII. The uranium which was collected in the ether layer was recovered by extracting with water, after which this water layer was concentrated to hex and tested in the regular laboratory extraction procedure. In this test the layers separated rapidly: the ether layer was clear, and the water layer was slightly cloudy.

Table VII

Uranium in water layer before extraction	35.6%
Weight of uranium in water layer before extraction.	250 grams
Volume of ether used.	4900 ml
Uranium in water layer after extraction.	12.1%
Weight of uranium in water layer after extraction	26 grams
Uranium removed by extraction.	89%

Conclusions

Although NG 3 liquor would presumably form an emulsion even more stable than that produced in this experiment, it is possible that the proposed extraction process could be made to work with fair success.

CHART I
 $\% \text{ UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ REMOVED
 VS.
 AMOUNT ETHER USED

STARTING MATERIAL - SOLUTION
 $\% \text{ UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ IN STARTING MATERIAL - 44

PERCENT REMOVED OF ORIGINAL PRESENT

12

70 IN
WATER
LAYER

CHART II
DISTRIBUTION OF $\text{Li}_2\text{O}(\text{H}_2\text{O})_x$
BETWEEN WATER AND ETHER

138112

SECRET

CHART III

% $UO_2(NO_3)_2 \cdot 6H_2O$ EXTRACTED

VS

AMOUNT OF ETHER USED

STARTING MATERIAL - CRYSTAL

% $UO_2(NO_3)_2 \cdot 6H_2O$ IN STARTING MATERIAL 2.10%

100

80

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13

0

200

600

1000

1400

1800

2200

2600

2800

3000

3200

13

CC ETHER USED