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TECHNOLOGY—FEED MATERIALS

THE REMOVAL OF POLYBENZENE FROM SOLUTIONS OF UALYL

NITRATE PREPARED FROM PITS ALLIANCE

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THE REMOVAL OF MOLYBDENUM FROM SOLUTIONS OF URANYL
NITRATE PREPARED FROM PITCHBLENDE

I. INTRODUCTION

In processing pitchblende ore by nitric acid digestion and ether extraction under acid conditions, purification is practically complete except for molybdenum and excess nitric acid. The nitric acid can be readily removed by steam sparging the purified liquors, or if not present to a sufficient extent to cause corrosion of the evaporating pots, can be driven off during the formation of UO_3 from $\text{UO}_2(\text{UO}_3)_2$. Special treatment, however, is required to get rid of the molybdenum.

At the time this work was begun, it was well known that no difficulty would be encountered from molybdenum if feed liquors containing no excess nitric acid were fed to ^{the} extraction column. This would, however, entail the separate processing of a substantial proportion of the uranium which would be precipitated by the phosphate present. The only other suggested methods of handling the problem had been tried at Yale University in Professor Earned's laboratory; ^{namely}, removal of the Mo from the acid solution of the ore by treatment with hydrogen sulfide, or the addition of ferric nitrate to the solution fed to the extractor to complex the phosphorous and thus prevent the extraction into ether of phosphomolybdic acid. Later, several of the present authors tried adsorption of the polyacid on activated charcoal, while working in the Yale laboratory. These methods

were checked and developed considerably in the present study, except the sulfide treatment, which was virtually ruled out because of difficulties associated with the sulfide precipitate, and because of the well known incompleteness of precipitation of Mo by H_2S .

In considering these and possible new methods, the following points in the process at which Mo might be removed were suggested:

- 1) During ore processing
- 2) From the ore solutions by chemical treatment
- 3) Retention in the raffinate
- 4) Removal from the unwashed ether extract
- 5) Retention in the ether extract on re-extraction into water
- 6) Removal from the purified water solution.

II. DISCUSSION

In ore processing variation in the nature and amount of acid used affects the Mo content of the liquors formed. It was found that more Mo was present in liquors made using sulfuric and nitric acids for digestion than in those made by digestion with nitric acid alone⁽¹⁾. Molybdic acid was found to be more soluble in sulfuric acid ^{and} in sulfuric-nitric acid mixtures than in nitric acid alone, so that the result on the ore is what might be expected. The Mo was still high, however, when only nitric acid was used.

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It was thought that since an excess of many heteropoly acids will completely precipitate alkaloids and certain other nitrogenous compounds, perhaps the reverse might be effective, particularly since the ether extractable Mo is presumed to be present as a heteropoly acid. Precipitates were obtained from moderately dilute phosphomolybdic acid solutions with narcotine, thebaine, quinine, quinoline, trimethylamine, ethylene ~~diamine~~, and others, but no precipitate could be obtained in pitchblende digest liquors with any of these reagents. Similar negative results were obtained with synthetic mixtures made from phosphomolybdic acid and uranyl nitrate.

Retention of Mo in the raffinate ^{and} ~~is~~ exemplified by the low acidity feed already mentioned, and by the iron-phosphate complex. Further study of the iron method showed it to be practicable both in laboratory experiments and in the pilot plant. It has other advantages in that it increases the extraction efficiency of uranium, and decreases the precipitation of barium sulfate in the extraction column (2).

Another possibility of retaining the Mo in the raffinate is to tie it up in a stronger complex than the phosphomolybdic acid, which complex must also be much more soluble in water than in ether. The hydroxy aliphatic acids (3) and the polyhydric alcohols (4) form complexes with molybdic acid. Since the former are generally appreciably ether soluble, it was considered likely that compounds such as mannitol, sorbitol, or glycerol would be more promising. Most of the work was

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done with mannitol because it was the most effective, and it seemed least likely to nitrate or oxidize. After searching the literature, it was decided that the nitration hazard was negligible, except that in a plant operation the tailings from ether purification would have to be checked for organic nitrates. The oxidation of mannitol proved to be troublesome, particularly in hot concentrated uranyl nitrate solutions, in which the oxidation product was oxalic acid and a precipitate of uranyl oxalate would form on extended heating. Under proper conditions, the method was successful in bringing Mo down to around 50 ppm in the unwashed ether extract, and this could be readily washed down to less than 5 ppm. The possibility of ^{obtaining} more efficient removal by adding mannitol to the wash water was ^{explored} ~~tried~~, but *this method* ^{from D.D.} ~~was~~ no more successful than washing with plain water. The main disadvantages of using mannitol are its relatively high cost, and the undesirability of organic material in the raffinate from the standpoint of $\text{Ca}(\text{NO}_3)_2$ recovery.

Extensive work on the adsorption of the molybdenum from unwashed ether extracts with activated charcoal proved this method to be as good as early experiments promised. Some variability was encountered, but this was accountable for by variations in the amount of Mo present, as might be expected in an adsorption method. The handling of the charcoal worked out well in pilot equipment. The main disadvantages of the method are the relatively costly equipment required and the high cost of suitable charcoal.

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Another way of removing Mo via the wash water might be ^{provided} if the Mo polyacid could be converted to molybdate in the unwashed ether extracts. The Mo xanthate complex is quite unstable in ether, and forms a water soluble molybdate on decomposing. This method worked very well on synthetic mixtures of the presumed composition of the extract, but trouble was encountered when it was tried on natural extracts. This may have been due to the presence of other impurities not yet removed.

As indicated above, the Mo xanthate is not sufficiently stable to be retained in the ether extract during stripping, decomposition being appreciable in 5-7 minutes. Addition of toluene to the extract should facilitate the stripping and tend to stabilize the xanthate complex, and such proved to be the case. However, complete stability is only of the order of 15 minutes, and this was considered too short a time to be safe in plant operations. Also, the danger of contamination of the purified liquor is as great as in treating the liquor directly, as below.

The possibility of extracting Mo from the purified liquor as the xanthate was investigated, using chloroform, at first, and later toluene, as the immiscible solvent. This was successful in separatory funnels, but some difficulties were encountered in a column. These could probably be overcome, but the impurities introduced by the xanthate

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(Na, SO_4 , and possibly others) would require a second set of columns for their removal. While this could be done, it is much more feasible to neutralize the liquor prior to the second set of extractions, and this was the method finally adopted.

While this paper describes several methods which would probably be feasible in plant operation, only one seems worth consideration as an alternative to the double extraction. The iron method can compete as to cost and is simple to use. Its main disadvantage would lie in the fact that the plant would be in trouble should a feed be encountered on which iron would not work. The Mo is not acted upon directly, but is held in the raffinate solely because phosphate is kept out of the sphere of action. It is conceivable that under some circumstances other Mo polyacids might be present and could go into the ether extract. On the other hand, if a similar situation should be encountered in using the double extraction, it would be quite likely that an iron addition to the feed would help.

III. EXPERIMENTAL

A few typical experiments are given below to illustrate the methods employed in 1) the use of polyhydric alcohols, 2) the use of ferric nitrate, 3) the use of activated charcoal, and 4) the use of double extraction. No attempt will be made to give the complete data on which the conclusions are based.

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1) Polyhydric alcohols - To each of a series of 50 ml portions of a pitchblende digest liquor a different quantity of mannitol was added. After 15 minutes stirring at room temperature each portion was extracted with four successive 100 ml portions of acidulated ether. The combined unwashed extracts from each portion were analyzed for uranium and molybdenum with the results shown in Table 1 and Figure 1.

TABLE 1

Sample #	1	2	3	4	5
g. Mannitol used	0	0.025	0.25	0.63	1.00
mg MoO_3	8.62	7.45	2.16	0.71	0.29
g U	7.85	7.85	7.85	7.85	7.85
ppm $\frac{\text{MoO}_3}{\text{U}}$	1098	950	275	90	37

In similar experiments using glycerol and sorbitol in the same molar concentration (approximately 0.05 M) and under the same conditions as mannitol the results shown in Figure 2 were obtained.

2) Ferric Nitrate * Each of a series of 100 ml portions of pitchblende acid digest liquor was extracted using four successive 200 ml. portions of acidulated ether. The various portions contained different ratios of Fe to Ca, ^{the} ~~and~~ ⁱⁿ NO_3 ~~in~~ concentration being constant throughout. The combined ether extracts were each washed with ten successive 5 ml portions of distilled water. The results shown in Table 2, while not entirely consistent, are striking evidence of the effectiveness of this treatment.

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FIGURE 1

EFFECT OF MANNITOL IN FEED LIQUOR ON MOLYBDENUM
IN TIL. UNWASSED ETHER EXTRACT

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FIGURE 2

MOLYBDENUM REMOVAL BY VARIOUS POLYHYDRIC ALCOHOLS

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TABLE 2

Portion #	1	2	3	4	5	6
g $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	0	11.2	14.9	22.4	33.6	44.8
g $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	40.0	30.0	26.6	20.0	10.0	0
Volume (ml)	200	200	200	200	200	200
ppm MoO_3/U in unwashed ether extract 1930		110	61	72	48	69
ppm MoO_3/U in washed ether extract 2018		105	L 10	10	L 5	L 5

Since ferric nitrate is effective by virtue of its action on the phosphate, and mannitol acts on the molybdate, it was expected that the two together would be much more effective than either. The improvement realized, however, proved to be too slight to be worthwhile in practice.

3) Activated Charcoal - On the theory that heteropoly acids have properties resembling organic compounds it was considered possible that the Mo in the ether extract could be selectively absorbed on charcoal, alumina, or silica gel. Not only did the adsorption on charcoal prove very effective, but it was found that the charcoal could be rejuvenated by leaching with a strong sodium hydroxide solution. The experiments were carried into pilot plant equipment and the variables involved were studied carefully. It was only after the proving in of a still better method that plans for the use of charcoal were dropped.

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FIGURE 3

MOLYBDENUM REMOVAL FROM ETHER EXTRACTS BY ACTIVATED CHARCOAL

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ppm Mo Remaining in Ether Extract

Grams Charcoal Per 250 ml. Ether Extract

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15 IV. SUMMARY

A study of the removal of Mo from liquors ^{sanitized for} ~~originating with~~ pitchblende was made using the following methods, with the results as indicated:

- a) Precipitation of Mo present as heteropoly acids with a cheap alkaloid or other nitrogenous organic compound. Removal was incomplete.
- b) Retention of Mo in the raffinate by forming a complex between molybdic acid and a polyhydric alcohol such as mannitol. This succeeded but was more costly than other methods.
- c) Retention of Mo in the raffinate by forming a complex between phosphate and iron. This succeeded apparently because most of the ether extractable molybdenum is present as phosphomolybdic acid. This is a worthwhile alternative method to the one chosen.
- d) Adsorption of the Mo polyacid from the ether extract with activated charcoal. This was very successful but was more costly and harder to adapt to plant practice than the method chosen.
- e) Conversion of the Mo polyacid to molybdate in the ether extract and removal by washing. Sodium ethyl xanthate was used as reagent, the resulting compound being unstable in ether. Other impurities not yet washed out interfered.

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- f) Removal of Mo from the purified uranyl nitrate solution by extraction as the xanthate. This was successful in laboratory experiments but would require additional columns. Hence, it was abandoned in favor of the method chosen.
- g) Neutralization of the purified uranyl nitrate solution and subsequent re-extraction. This was completely effective, and had the advantage of safeguarding against other impurities which might not be completely removed by the first extraction. The neutralization, in practice carried out by steam sparging, was required anyway, prior to evaporation of the purified uranyl nitrate solution, in order to reduce corrosion of the evaporation vessels.

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