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TECHNOLOGY—FEED MATERIALS

BMI-249

PROGRESS REPORT

on

REFINING OF MgX AND OTHER URANIUM-BEARING MATERIALS

by

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ABSTRACT

Results of tests investigating the effects of feed and scrub acidities on the extraction of uranium and contaminants from process slurries by tributyl phosphate-Gulfspray Naphtha in a Scheibel continuous extractor are described. Included are the results of tests on the effect of temperature on the re-extraction of uranium from the organic to the aqueous phase.

Studies on the fractional precipitation of MgX from a dilute sulfuric acid system throw considerable light on the probable constitution of MgX.

Further data on the effect of acidity on the extraction of molybdenum and vanadium into ethyl ether are presented.

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273

2

TABLE OF CONTENTS

	<u>Page</u>
INTRODUCTION.	133
SUMMARY	133
EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS.	135
Ether-Extraction Studies	135
Extraction of Vanadium and Molybdenum	135
Tributyl Phosphate Extraction Studies.	137
Column-Extraction Tests	137
Effect of Acid Concentration in the Feed	137
Effect of Scrub	139
Recovery of Uranium From the Organic Extract.	140
Effect of Temperature on Stripping	140
Vanadium and Molybdenum Solubility Studies	142
Study of the Constitution of MgX	143

DECLASSIFIED

34 13

INTRODUCTION

Experimental evidence has indicated that transfer of molybdenum may be a serious problem in the solvent extraction of uranium with tributyl phosphate, and Scheibel-column studies have been made to develop methods of overcoming this difficulty. Although these tests have not yet provided the complete answer to the problem, they have shown that control of acidities of the feed and scrub is of material assistance in reducing the transfer of molybdenum.

The problem of molybdenum in connection with the original dissolution of pitchblende is under investigation. Early indications are that molybdenum solubility increases with increasing solution acidity; also, that considerable supersaturation may exist in process filtrates.

Since the behavior of both molybdenum and vanadium in process solutions and slurries is important in several respects, this problem is being explored further.

SUMMARY

Study of the extraction of vanadium and molybdenum by diethyl ether has shown that reduction of system acidity tends to suppress their transfer to the ether. Preliminary data indicate that the acidity limits are not critical, and that it is possible to obtain reasonably low transfer in the presence of some excess acid.

In connection with the preparation of pitchblende solutions for extraction tests, it was observed that the solubility of molybdenum

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appeared to be largely dependent on solution acidity. It was also noted that considerable supersaturation existed, so that molybdenum levels in the solutions ranged between 5 and 7 grams/liter. Study of the factors controlling the solubility of molybdenum in process solutions is continuing.

Due perhaps to high molybdenum levels in the process slurries employed, molybdenum transfer has proved to be one of the most serious problems encountered in the investigation of extraction of uranium with a tributyl phosphate-naphtha solvent. Although insufficient data are available to specify the conditions required for complete elimination of molybdenum in the final extract, it has been found that molybdenum transfer decreases with increasing system acidities. The minimum value obtained to date in the preliminary Scheibel-column tests has been less than 25 p.p.m.; this was secured with a 3.6N feed slurry and an 8N HNO₃ scrub.

The results of one series of tests studying the re-extraction of uranium from tributyl phosphate-naphtha to water indicated that the scrub volume could be reduced 50 per cent when the temperature was increased from 25 to 45°C. The results of another test at 70°C. were somewhat anomalous; although a higher concentration in the final aqueous extract was obtained, the uranium concentration of the raffinate also was increased.

A fractional precipitation of P-1 MgX from a dilute sulfuric acid solution, simulating the original precipitation, was made in order to secure additional information on the constitution of MgX. This test

indicated that most of the phosphate precipitated with the iron, and also strongly suggested the existence of an aluminum silicate as one of the major components of MgX. There is nothing in the data to suggest that uranium is present in MgX as uranyl phosphate.

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

Ether-Extraction Studies

Extraction of Vanadium and Molybdenum

Previous tests have illustrated the effects of feed and ether acidity on vanadium and molybdenum extraction. Most of these tests were made in the acid-deficient range. Since the range of acidity above zero excess acid appeared to be of more practical interest, recent work has included process solutions at higher acidities. Molybdenum analyses have been obtained in a series of extraction tests made with a process solution filtrate which had been adjusted to about 10 grams/liter of excess acid. The data are presented in Table 45, in comparison with vanadium analyses previously reported. In the case of both vanadium and molybdenum, extraction increased as the acidity of the ether increased. However, even in the worst case, transfer of these components to the extract was much less than has been normally found when feed and ether acidities were in the 0.5-1.0N range. The effects of improvements of the quality of the NOK liquor (feed to the neutral ether extraction step) on the quality of the final neutral ether extract may be of interest for future investigation.

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TABLE 45. EFFECT OF ACIDITY ON EXTRACTION OF VANADIUM AND MOLYBDENUM FROM FILTERED PROCESS SOLUTION⁽¹⁾

Excess Acid		Ether Acidity	Extracted, mg.			Extracted, %			p.p.m. in Extract ⁽²⁾	
Feed, g./l.	Raff.		U	V	Mo	U	V	Mo	V	Mo
9.5	pH 0.9	Neutral	11,460	1.7	1.6	98.3	2.4	0.8	150	70
9.5	pH 0.3	0.1N	10,920	2.3	3.0	98.4	3.2	1.6	210	275
9.5	pH 0.0	0.25N	11,690	3.0	6.3	98.8	4.4	3.6	265	540

(1) Process solution 5269-81, prepared so that 2/3 of uranium was derived from pitchblende Blend A-1 and 1/3 was derived from MgX Blend B-1. Sp. gr. approximately 56° Bē in all tests. Acidity adjusted to 9.5 g./l. with MgO. 50-ml. samples given 6 shakeouts with equal volumes of ether, using the normal time cycle.

(2) Uranium basis.

-136-

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The extent of further improvement attainable by scrubbing the extract is to be investigated, using the Scheibel continuous extractor. This work was temporarily postponed pending completion of the tributyl phosphate-extraction studies with the Scheibel equipment.

Further tests have been made to determine the effects of digestion of digest slurries on vanadium extraction. In none of these tests were the strongly colored ether extracts obtained such as were observed during the initial tests. Analyses are not yet available on these tests.

Tributyl Phosphate Extraction Studies

Column-Extraction Tests

Some of the factors involved in the extraction of uranium from a process slurry feed into a 30-70 tributyl phosphate-Gulfspray naphtha solvent have been investigated. These factors are feed acidity, scrub acidity, and length of scrub section.

The recovery of uranium from the organic extract as a function of temperature and organic-aqueous ratio was studied.

In all of the extraction tests previously reported (BMI-248), molybdenum appeared to be extracted along with the uranium. Consequently, the tests reported below were designed to reduce the extraction of molybdenum.

Effect of Acid Concentration in the Feed. Tests 1, 2, 3, and 4 (Table 46) show that the molybdenum concentration in the extract was reduced from 210 to 75 p.p.m. parts of uranium as the feed acidity was increased from 2.5 to 4.7 normal.

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84 13

TABLE 46. CONTINUOUS EXTRACTION TESTS ON PROCESS SLURRIES WITH A TRIBUTYL PHOSPHATE SOLVENT

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Column Operating Conditions

Solvent = 30 per cent tributyl phosphate - 70 per cent Gulf Spray Naptha.

Feed = Test No. 1 through No. 6 from Process Slurry No. 5583-8⁽¹⁾. Tests No. 7 and 8 from Process Slurry No. 5268-94⁽²⁾. Test No. 9 feed was C.P. uranyl nitrate dissolved in nitric acid.

Stirrer speed = 2500 - 3000 r.p.m., except Tests No. 7 and No. 8 which were 1500 r.p.m.

Organic phase continuous.

Temperature = 25 ± 2°C.

Test No.	Ratio, Feed: Scrub: Organic	Length of Scrub Section in Mechanical Stages	Feed, ml./hr.	HNO ₃ Normality				Uranium Conc., g./l.			Feed, g./l.		Uranium	
				Feed	Organic	Scrub	Raff.	Feed	Extract	Raff.	Mo	V	Ext., %	Metal Bal., %
1	1.0:0.26:2.4	5	625	1.3	0.0	H ₂ O	1.0	232	93	0.49	2.5	1.3	99.8	100
2	1.0:0.25:2.6	5	800	2.5	0.0	H ₂ O	1.7	212	85	0.15	2.3	1.2	99.9	107
3	1.0:0.26:2.6	5	778	3.6	0.0	H ₂ O	2.9	198	84	0.12	2.1	1.1	99.9	101
4	1.0:0.25:2.5	5	800	4.7	0.0	H ₂ O	3.5	182	80	0.04	2.0	1.0	>99.9	112
5	1.0:0.27:2.5	10	775	3.8	0.0	H ₂ O	3.0	178	75	1.2	1.9	1.0	99.3	95
6	1.0:0.23:2.1	5	875	1.9	0.0	1N HNO ₃	1.8	205	80	0.20	2.2	1.2	99.9	84
7	1.0:0.26:2.5	10	725	4.5	0.0	1N HNO ₃	3.5	181	70	4.9	1.0	1.4	97.3	102
8	1.0:0.23:2.2	10	800	3.6	0.0	8N HNO ₃	3.8	111	61	4.6	0.8	1.1	95.9	86
9 ⁽³⁾	1.0:0.35:2.3	10	800	3.5	0.0	8N HNO ₃	3.5	~200	97.5	----	0.0	0.0	----	---

Spectrographic Analyses of Extract, Uranium Basis, p.p.m.

Test No.	Mo	V	P	B	Cd	Cu	Si	Fe	Cn	Pb	Ni	Co
1	95	<20	<50	<1	<0.5	10	25	<20	40	<10	<20	20
2	210	<10	50-100	1	4	70	>190	low	--	--	--	--
3	150	<10	50-100	1	<0.5	5	100	50-100	--	--	--	--
4	75	N.D.	50-100	1	<0.5	5	50	low	--	--	--	--
5	140	N.D.	50-100	1	<0.5	5	45	low	--	--	--	--
6	135	<20	<50	<1	<0.5	15	30	<20	<20	--	--	--
7	225	10	80	1	<0.5	10	30	15	--	<5	N.D.	--
8	<25 ⁽³⁾	N.D.	40	1	<0.5	10	25	20	--	5-10	N.D.	--
9	--	--	--	--	--	--	--	--	--	--	--	--

(1) Process Slurry No. 5583-8 prepared from Pitchblende A-192 and MgX P-92 with uranium in the ratio of 2:1.

Original excess acid of 65 g./l. adjusted to desired acidity by adding HNO₃.

(2) Process Slurry No. 5268-94 prepared from Pitchblende blend A-1 and MgX blend B-1, so that the excess acid was 56 g./l. Subsequently evaporated and additional acid added to increase the acidity to 4N.

(3) Determined by colorimetric method.

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The anomalous value shown for molybdenum in Test 1 may have been due to a "back salting" effect of the higher uranium concentration of the extract.

Effect of Scrub. Increasing the length of the aqueous scrub section from 5 to 10 mechanical stages failed to decrease the molybdenum contamination (Tests 3 and 5, Table 46). This suggests a very organic-soluble molybdenum complex.

When a water scrub was replaced by a 1N HNO₃ scrub (5 mechanical stages), the molybdenum concentration of the organic phase was reduced from 210 p.p.m. to 135 p.p.m. (Tests 2 and 6, Table 46). Tests 7 and 8, Table 46, on a different process slurry, show that, by further increasing the acid concentration of the scrub from 1N to 8N, the molybdenum was decreased from 225 to less than 25 p.p.m. For the latter test, the scrub section consisted of 10 mechanical stages.

Unfortunately, it was necessary to perform Tests 7 and 8 with a feed different from that used in Tests 1 through 6. Therefore, a valid comparison between the two sets of tests cannot be made. For example, it would be expected that Test 7 should show less molybdenum transfer than Test 4, since an acid instead of a water scrub was used, and the scrubbing section was twice as long. Nevertheless, the molybdenum concentration of the extract in Test 7 was greater than that of Test 4. This may have been the result of the different feed composition or of the dependency of molybdenum extraction on the uranium concentration in the organic extract. These factors require more investigation.

Test 9 was a blank determination which indicated that no molybdenum was being dissolved from the stainless steel calming sections of the Scheibel column.

Recovery of Uranium From the Organic Extract

The organic feed used for the tests reported in Table 47 was non-equilibrium material from the column-extraction experiments. Therefore, the molybdenum and vanadium analyses are higher than those reported in Table 46 for equilibrium material. Tests 1 and 2 indicate that significant amounts of molybdenum were stripped from the organic with the last traces of the uranium.

In actual practice, it might be more satisfactory to remove the last traces of uranium from the organic phase by treatment with sodium carbonate solution than to use large amounts of water or a longer column. An organic scrub was added to the aqueous strip, Test 5, in an attempt to remove the molybdenum. The result of the single experiment was not successful.

Effect of Temperature on Stripping. Elevated temperature favors the distribution of uranium to the aqueous phase. As it is desirable to have the final uranyl nitrate extract as concentrated as possible, hot strips were tried at 45°C. and 70°C. (Tests 3 and 4, Table 47). At 45°C, the volume of the aqueous strip required was approximately 50 per cent less than that required at 25°C. The lower recovery at 70°C. cannot be explained from the results of only one run. The uranium recovery may pass through a maximum with an increase in temperature.

TABLE 47. RECOVERY OF URANIUM FROM THE ORGANIC EXTRACT

Column Operating Conditions

Feed(1) = 30 per cent tributyl phosphate - 70 per cent Gulfspray
 Naptha from extraction column. 0.3N HNO₃

Extractant = Water

Stirrer speed = 1000 r.p.m. .

Point of entrance to column: Extractant - top

Feed - 10 mechanical stages below top

Aqueous phase continuous

Test No.	Ratio, Feed: Scrub: Extractant	Scrub	Feed, ml./hr.	Uranium, g./l.			Molybdenum(2), p.p.m. parts U		Vanadium(2), p.p.m. parts U		Uranium		Temp., °C.
				Feed	Extract	Raff.	Feed	Extract	Feed	Extract	Ext., %	Metal Bal., %	
1	1.0:0:2.2	None	720	74	38	0.04	255	70	275	80	>99.9	109	25 ± 2
2	1.0:0:1.0	None	1000	74	64	1.5	255	20	275	60	97.2	95	25 ± 2
3	1.0:0:0.97	None	825	74	57	0.14	255	110	275	35	99.8	82	45(3)
4	1.0:0:1.1	None	1050	74	80(?)	1.7	255	225	275	100	97.8	100	70(3)
5	1.0:0.21:1.0	T.B.P.-G.S.N.	764	56	40	11.5	65	30(4)	---	N.D.(4)	79	92	25 ± 2

(1) Nonequilibrium material from extraction column; therefore, molybdenum and vanadium analyses are higher than those reported in Table 46.

(2) Determined by chemical analysis.

(3) Temperature of stream 5 mechanical stages above feed entrance.

(4) Determined by spectrographic analysis.

(5) Introduced at bottom of column.

The presence of increasing amounts of molybdenum in the aqueous extracts as the temperature was raised from 25 to 45 and 70°C. (Tests 2, 3, and 4, Table 47) suggests either that temperature has a pronounced effect on molybdenum distribution coefficients or that the molybdenum-containing heteropolyacids, which presumably have a high solubility in the organic phase, are broken down at the elevated temperatures.

Vanadium and Molybdenum Solubility Studies

Previously reported data on the solubility of vanadium in process solutions covered excess nitric acid acidities up to 120 g./l., since this is the practical limit when extracting with diethyl ether. However, in view of the increased feed acidities which may be desirable if extraction is carried out with tributyl phosphate, these solubility data are being extended to the 300-g./l. level of excess acid.

Some preliminary tests have been conducted to examine the behavior of molybdenum in pitchblende solutions. In a series of dissolutions of A-1 blend of pitchblende (for analysis, see BMI-246, page 69), it was noted that the molybdenum and uranium contents of the digest residues were lower when the digest filtrate had a high excess acid (100-110 g./l.) than when the digest filtrate had only 40 g./l. excess acid. The molybdenum content of the filtrates ranged from 5-7 grams per liter. At room temperature, these filtrates appeared to be quite stable; no precipitation of molybdate was observed upon standing for several weeks. However, on adjusting samples of filtrate to varying levels of excess acid and digesting, a yellow precipitate, apparently

uranyl molybdate, was formed. The maximum quantity was found at zero excess acid. The quantity decreased with increasing acidities, and was slight at 160-200 g./liter.

On the basis of these preliminary tests, it appears that dissolution of pitchblende at high excess acid levels, as would presumably be the case in preparing a feed solution suitable for tributyl phosphate extraction, would result in feed solutions with a high molybdenum content. This might increase the problem of molybdenum in the extraction step, but would at the same time probably reduce the amount of molybdenum in the digest cake and might permit modifications of the C-3 process.

More work on the solubility of uranyl molybdate and the factors affecting it is planned.

Study of the Constitution of MgX

A study of the fractional precipitation of a dilute sulfuric acid solution of MgX was made to obtain information concerning the constitution of MgX.

A dilute sulfuric acid solution of P-1 MgX (for analysis, see BMI-246, page 69) was made containing 5 grams per liter of uranium, simulating the pregnant solution from which the MgX was originally precipitated. On filtration, a clear amber-colored solution was obtained. After one month, the solution was still clear. The insoluble residue from the dissolution step was 2.1 per cent of the original sample. Spectrographically, it was shown to consist chiefly of iron, silicon, and magnesium. It is quite possible that a large portion of the magnesium was derived from unreacted magnesia used in the precipitation.

A portion of the filtered solution was neutralized step-wise with one-molar ammonium hydroxide solution, at room temperature. Precipitates were filtered off at four different pH levels, 2.7, 4.5, 5.7, and 6.5. The analyses of these precipitates are shown in Table 48, and graphically in Figure 13. No substantial amount of uranium was found in the first two fractions. The data indicate that most of the phosphate is precipitated with the iron. The precipitate that formed first (pH 2.7) appeared to be mainly ferric phosphate, as might be expected. The second precipitate was high in silicon and aluminum, suggesting the possibility of an aluminum silicate precipitating. The third fraction (pH 5.7) consisted mainly of aluminum and uranium. However, there was an appreciable silicon content (1.7 per cent) in this precipitate. The final precipitate (pH 6.5) was mainly uranium, 60 per cent. It is interesting to note that the major portion of the vanadium was found in this last fraction.

The above data indicate that uranyl phosphate is unlikely to be present in MgX, at least in those batches which contain sufficient iron to combine with the phosphate

Notebook References

The original data for the work covered by this report are recorded in the following Laboratory Record Books:

<u>Notebook No.</u>	<u>Pages</u>
5268	90-98
5531	26-36
5583	19-26
5597	1-26

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16

TABLE 48. COMPOSITION OF PRECIPITATES FROM A FRACTIONAL PRECIPITATION OF MgX FROM A DILUTE SULFURIC ACID SOLUTION

pH of Precipitation	Precipitate ⁽¹⁾ Weight, mg.	Millimoles					
		U	Fe	Al	Si	P	V
2.7	359	0.024	2.03	<0.13	0.02	1.64	0.08
4.5	848	0.10	1.14	3.84	6.63	0.30	0.03
5.7	2463	4.38	0.32	9.32	1.48	0.04	0.18
6.5	1588	3.99	0.04	<0.59	0.18	<0.03	0.72

(1) Precipitates from 500 ml. of solution ignited at 600°C.

FIGURE 13. COMPOSITION OF PRECIPITATES OBTAINED BY A FRACTIONAL PRECIPITATION OF MgX FROM DILUTE SULFURIC ACID.

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