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PROGRESS REPORT

on

REFINING OF MgX AND OTHER URANIUM-BEARING MATERIALS

by

R. A. Ewing
R. L. Belcher
S. J. Kiehl, Jr.
A. E. Bearse

September 30, 1950

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For The Atomic Energy Commission

H. F. Canale
Chief, Declassification Branch

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R. A. Ewing, R. L. Belcher, S. J. Kiehl, Jr., and A. E. Bearse

ABSTRACT

The effects of solution concentration and acidity on extraction of uranium by diethyl ether have been investigated. Data on the transference of vanadium and molybdenum to the ether phase were obtained in some tests. Continuous extractions were made with a Scheibel one-inch laboratory column at feed rates of 500 to 3000 ml./hr., and stirrer speeds of 1800 to 3400 r.p.m.

The approximate solubility of vanadium pentoxide in nitric acid was determined.

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INTRODUCTION

The direct slurry-extraction process for the recovery of uranium from MgX and pitchblende continues to exhibit promise, and the work of the past month has been largely in connection with the development of this process. / This work included study of the effects of acidity and solution concentration on uranium extraction, as well as on the concurrent extraction of vanadium and molybdenum. In earlier tests, synthetic solutions had been used for preliminary evaluation. All of the recent tests have been conducted on process, rather than synthetic, solutions.

Previous work at Battelle on the refining of MgX and pitchblende was reported in BMI-246 (August 31, 1950) covering the period May 1, to August 31, 1950. The present report describes work carried out during the month of September.

SUMMARY

/ Further testing has clarified the anomalous results previously reported on the effects of the specific gravity of the feed solution on the extraction of ^Uuranium. Definite increases in extractive efficiency were observed as the specific gravity was increased from 52° Bé to 62° Bé. / There were, however, some inconsistencies. Temperatures were not controlled during these tests, and since temperatures are known to have a major influence on distribution coefficients, there is reason to believe that part of the inconsistencies arose from this cause.

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The effects of acidity on ~~uranium~~^U extraction were investigated, when some of the results above indicated that acidity might have been influencing the results. However, ^{but} over the range studied, the acidity of the system did not appear to be an important factor.³ Although other effects may have been partially responsible, the best extractions were obtained with feed solutions in the range from zero excess acid to pH 1. At a solution acidity of pH 2, there was apparently some precipitation of uranium-bearing compounds, which redissolved only slowly.

Study of the effect of acidity on the extraction of vanadium and molybdenum was begun. Complete results are not yet available, but those at hand indicate³ that the distribution coefficient of ~~vanadium~~^V, like that of ~~molybdenum~~^{Mo}, decreases with decreasing acidity.⁴ Minimum vanadium transfer to the ether phase was obtained when the acidities of both the feed and the ether were low. Vanadium transfer was reduced from one-half to two-thirds under optimum conditions.

⁴ Additional continuous-extraction tests with a Scheibel laboratory column confirmed previous results which had indicated that low flow rates (500 ml./hr. of feed) lowered extractive efficiency. Optimum conditions for maximum ~~uranium~~^U extraction with this column appear to be a feed rate of approximately 1000 ml./hr. and a stirrer speed of 2500-3000 r.p.m. Under these conditions, ~~99 percent~~^{99%} extraction can be obtained with slurry feeds containing 260 to 270 g. of ~~uranium~~^U/liter.⁵ Only one test has been made with the aqueous phase continuous; results of this test were inconclusive.

X-ray diffraction studies on several ignited samples of synthetic MgX disclosed the presence of one common major phase, as yet unidentified.

A few preliminary tests were made of the possibility of recovering combined nitrates from raffinates by displacement with ~~sulfuric acid~~^{+H₂SO₄} and extraction with neutral ether. The data indicated that distribution coefficients varied in approximately direct proportion to the acidity, and ranged from a high of 0.4 to a low of 0.04.

The solubility of ~~vanadium pentoxide~~^{V₂O₅} in ~~nitric acid~~^{HNO₃} solutions was determined approximately. ~~Vanadium~~^V solubility passed through a maximum in the neighborhood of 3N acid. At the maximum, ~~vanadium~~^V concentration was nearly 20 g./liter. ⁶ _{cent}

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

Ether-Extraction Studies

Process Solutions

Additional tests were run on Process Solution No. 5269-72 adjusted to various specific gravities, in an attempt to clarify the anomalies observed in the tests described in the previous report (BNI-246). As shown by Table 28, more consistent results were obtained from these tests which exhibited the expected increase in extractive efficiency with increasing specific gravity. For example, even with the high sulfate content of Solution No. 5269-72 (about 26 per cent of the uranium), increasing the specific gravity from 56° to 62° Bé reduced the uranium content of the raffinate from 6.8 to 0.8 grams/liter.

Similar tests were conducted on a process solution of the same composition, in which the pitchblende and MgX portions were concentrated

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TABLE 28. EFFECT OF SPECIFIC GRAVITY ON EXTRACTION OF URANIUM FROM A PROCESS SOLUTION

Specific Gravity - Degrees Baumé(1)										Specific Gravity - Degrees Baumé(2)													
52			56(3)			60(3)			62			56			60			62					
Specific gravity at 60°F.			1.56			1.62			1.71			1.75			1.62			1.71			1.75		
Excess acid, g./l.			35±			40			46			53			68			64			71		
Shakeout(4)	Uranium			Uranium			Uranium			Uranium			Uranium			Uranium			Uranium				
	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d		
1	102	48.5	0.94	139	59.0	1.4	177.6	64.8	1.9	197	67.3	2.1	137	59.3	1.5	179	64.4	1.8	195	66.0	1.9		
2	42.8	68.7	0.65	44.4	77.9	0.86	51.5	81.2	1.2	60.3	87.8	1.7	45.6	79.1	0.95	57.0	85.0	1.4	58.6	85.8	1.4		
3	22.2	79.2	0.50	22.9	87.6	0.78	21.5	92.1	0.97	21.2	95.0	1.4	21.0	88.3	0.78	18.9	91.7	0.82	23.0	93.5	1.2		
4	13.0	85.4	0.42	11.1	92.7	0.61	11.5	95.8	0.98	9.3	98.1	1.7	10.9	93.0	0.68	11.3	95.8	0.97	9.5	96.7	1.0		
5	8.6	89.5	0.39	7.0	95.3	0.64	5.9	97.8	1.02	3.7	98.7	2.1	6.2	95.7	0.62	5.9	97.9	1.0	4.7	98.3	0.94		
6	6.0	92.3	0.37	4.1	97.1	0.60	2.6	98.8	0.81	1.0	99.74	1.3	3.6	97.2	0.57	2.8	98.9	0.97	2.2	99.0	0.74		
Raffinate	16.2			6.8			3.2			0.76			6.3			2.9			2.9				
Total, g.	210.8			235.3			273.8			293.3			230.6			277.8			295.9				

- (1) Combined process solution No. 5269-72 boiled down to desired specific gravity.
(2) Pitchblende and MgX solutions boiled down separately to desired specific gravity before combining.
(3) Average of two experiments.
(4) 50-ml. samples; extracted with equal volume of 1N acid ether; 1½-min. time cycle. Results reported to 1-liter basis.

separately to the desired specific gravity before combining. When the solutions were concentrated separately, the loss of acid appeared to be less, so that the excess acid of the final combined solution was increased. A sample of the standard 56° Bé solution was adjusted to comparable acidity and extracted for comparison. As shown by Table 28, there appeared to be no major differences in the results when the solutions were boiled down separately.

The preliminary indications of the foregoing series of tests were that acidity was a variable which exerted a greater effect on uranium extraction than finally proved to be the case. In order to investigate this further, as well as to study the effects of acidity on the transfer of vanadium to the ether phase, two additional series of experiments were made in which the acidities of both the feed solution and the ether were varied. The results of these tests, shown in Tables 29 and 30, indicated that, over the range tested, neither solution nor ether acidity influenced uranium extraction appreciably, where the solution had some excess acid. Maximum uranium extractions were obtained with solutions in the range of zero excess acid to pH 1.0, with both 1N and 0.5N acid ether.

It was observed that a slight precipitate formed when the solutions were adjusted to pH 2.1. With 1N ether, this precipitate redissolved on the second shakeout and did not reappear. With 0.5N ether, the precipitate dissolved only gradually and the final sulfate precipitate masked its eventual disappearance, if it did completely redissolve. Judging by the uranium content of the raffinate, this precipitate did not go back entirely into solution.

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TABLE 29. EFFECT OF ACIDITY ON EXTRACTION OF URANIUM FROM
PROCESS SOLUTION BY 1N ETHER(1)

	Approximate Excess HNO ₃ , g./l. or pH																	
	87 g./l.			68 g./l.			40(2) g./l.			0 g./l.			pH 1			pH 2.1(3)		
Specific gravity at 60°F.	1.61			1.62			1.62			1.62			1.63			1.59		
Shakeout(4)	Uranium			Uranium			Uranium			Uranium			Uranium			Uranium		
	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d
1	136.	60.7	1.5	137.	59.3	1.5	139.	59.0	1.4	148.	62.7	1.7	155.	65.8	1.9	120.	52.8	1.1
2	45.5	81.0	1.1	45.6	79.1	0.95	44.4	77.9	0.86	49.0	83.5	1.3	49.0	86.5	1.5	54.8	76.6	1.0
3	20.3	90.0	0.91	21.0	88.3	0.78	22.9	87.6	0.78	21.9	92.8	1.3	18.4	84.3	1.4	26.3	88.4	1.0
4	9.3	94.2	0.71	10.9	93.0	0.68	11.1	92.7	0.61	9.4	96.8	1.2	7.9	87.7	1.4	12.9	94.0	1.0
5	5.1	96.4	0.63	6.2	95.7	0.62	7.0	95.3	0.64	4.2	98.5	1.2	3.3	99.07	1.5	6.9	97.0	1.0
6	3.3	97.9	0.69	3.6	97.2	0.57	4.1	97.1	0.60	1.9	99.35	1.2	1.4	99.63	1.5	3.5	98.6	1.1
Raffinate	4.7			6.3			6.8			1.5			0.9			3.3		
Total U, g.	221.2			230.6			235.3			235.9			235.9			227.7		
Excess Acid in Raffinate, g./l.	48			-			39			31			26			31		

Notes:

- (1) Process solution No. 5269-72. Excess acids below 40 g./l. obtained by neutralizing with MgO.
- (2) Average of two tests.
- (3) 5M NaOH used to neutralize from pH 1 to pH 2.1. Slight precipitation occurred..
- (4) 50-ml. samples; extracted with equal volume of 1N acid ether; 1½-min. time cycle.
Results reported to 1-liter basis.

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TABLE 30. EFFECT OF ACIDITY ON EXTRACTION OF URANIUM FROM
PROCESS SOLUTION BY 0.5N ETHER(1)

Approximate Excess HNO ₃ , g./l. or pH																				
87 g./l.			68 g./l.			40 g./l.			0 g./l.			pH 1			pH 2.1 ⁽²⁾					
Specific gravity at 60°F.			1.61			1.61			1.62			1.62			1.63			1.59		
Shakeout ⁽³⁾	Uranium			Uranium			Uranium			Uranium			Uranium			Uranium				
	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d	Conc., g./l.	Extracted, Cum. %	K _d		
1	134	60.7	1.5	140	61.3	1.6	142	59.0	1.4	152	63.0	1.7	140	61.3	1.6	88.0	39.9	0.66		
2	43.5	79.6	0.93	41.4	79.4	0.87	47.0	78.4	0.90	45.5	81.7	1.0	48.4	82.5	1.2	50.5	62.6	0.71		
3	19.6	88.1	0.72	18.2	87.2	0.62	20.8	87.0	0.66	19.9	90.1	0.80	21.6	91.9	1.2	35.0	77.7	0.73		
4	10.3	92.6	0.61	10.4	91.7	0.55	11.4	91.7	0.57	10.7	94.4	0.78	9.5	96.1	1.1	20.0	87.4	0.71		
5	6.4	95.4	0.60	6.3	94.5	0.49	7.2	94.7	0.56	5.9	96.8	0.75	4.6	98.1	1.1	11.3	92.4	0.67		
6	3.8	97.0	0.53	4.5	96.4	0.54	4.6	96.6	0.57	3.3	98.1	0.73	2.0	99.0	0.90	7.0	95.6	0.71		
Raffinate	6.9			8.3			8.2			4.5			2.3			9.8				
Total U, g.	224.5			229.1			241.2			241.8			228.4			221.6				
Excess Acid in Raffinate, g./l.	20			19			8			12			4			2				

Notes:
(1) Process Solution 5269-72.
(2) 5M NaOH used to neutralize from pH 1 to pH 2.1. Slight precipitation occurred.
(3) Standard procedure.

In report BMI-246, it was noted that spectroscopic analysis of the first ether extract from two slurry extractions showed that the transference of vanadium, molybdenum, silicon, and phosphorus was much reduced when the acidity of the feed was reduced to a pH of 2. The effect of acidity on vanadium transfer was explored further as a part of the above tests, with partial results contained in Table 31 and Figure 9.

More complete results will be required to establish optimum conditions for obtaining low vanadium transference without unduly sacrificing uranium extraction. The evidence, based on the available results, is that low system acidity definitely tends to suppress vanadium transfer. The most promising results were those in which the acidity of the ether was low.

Additional tests which were made on a similar process solution showed the same general trends, although differing somewhat in details. The results of these tests, shown in Table 32 and Figure 10, indicated also that the behavior of molybdenum closely paralleled that of vanadium. In these tests, when 1N acid ether was used, varying the acidity of the feed solution from 40 g./l. excess acid to pH 1 or 2 did not appreciably change the total carry-over of either vanadium or molybdenum. With a high-acid feed, the transference was at a maximum during the first shakeout, decreasing thereafter. With a low-acid feed, transference was at a low level during the first shakeout, increased markedly during the second shakeout, and then decreased thereafter.

The indications of both series of tests are that, with optimum conditions of both feed and ether acidities, it may be possible to reduce

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TABLE 31. EFFECT OF ACIDITY ON EXTRACTION OF VANADIUM

	Test No. (1)																	
	1			2			3			4			5			6		
	Approximate Excess Acid, g./l. or pH			90 g./l.			40 g./l.			40 g./l.			40 g./l.			pH 2.1		
	Normality of Ether			1.0			1.0			0.5			Neutral			1.0		
Shakeout	Vanadium			Vanadium			Vanadium			Vanadium			Vanadium			Vanadium		
	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d
1	3.4	6.0	0.063	5.0	9.2	0.10	5.0	9.5	0.11	3.2	5.8	0.061	0.6	1.2	0.012	0.4	0.7	0.007
2	2.9	11.0	0.057	1.9	12.7	0.040	0.65	10.7	0.014	0.5	6.7	0.010	1.5	4.2	0.032	0.6	1.8	0.011
3	2.6	15.6	0.054	1.4	15.2	0.030	0.78	12.2	0.017	0.5	7.6	0.010	2.3	8.9	0.051	0.6	2.8	0.011
4	1.8	18.8	0.039	0.90	16.9	0.020	0.78	13.7	0.017	0.5	8.5	0.010	2.8	14.5	0.066	0.6	3.9	0.011
5	1.2	20.9	0.027	0.78	18.3	0.018	0.78	15.2	0.017	0.4	9.2	0.008	1.6	17.7	0.039	0.6	5.0	0.011
6	1.2	23.0	0.027	0.50	19.2	0.011	0.65	16.2	0.015	0.4	9.9	0.008	0.9	19.5	0.022	0.6	6.0	0.011
Raffinate	44			44.0			44.0			50			40			53		
Total V, mg.	57.1			54.5			52.6			55.5			49.7			56.4		
Total U ext., mg.	10,960			11,470			11,650			10,595			11,237			10,586		
V in Extract, % of U	0.119			0.092			0.108			0.052			0.086			0.032		
Excess Acid in Raffinate, g./l.	48			40			8			pH 0.8			18			2		

Note:
(1) All tests except No. 4 correspond to those in Tables 29 and 30.

FIGURE 9. EFFECT OF FEED AND ETHER ACIDITIES ON EXTRACTION OF VANADIUM BY DIETHYL ETHER

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TABLE 32. EFFECT OF SOLUTION ACIDITY ON EXTRACTION OF VANADIUM
AND MOLYBDENUM BY IN ACID ETHER(1)

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Shakeout	Approximate Acidity, g./l. or pH											
	40 g./l.			40 g./l.			pH 1.0(2)			pH 2.1(2)		
	Uranium			Uranium			Uranium			Uranium		
	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d
1	7,250	64.7	1.8	7,360	63.2	1.7	5,815	52.2	1.1	5,185	47.5	0.9
2	2,310	85.3	1.4	2,420	84.0	1.3	2,625	75.8	1.0	2,350	69.0	0.7
3	920	93.5	1.3	1,023	92.8	1.3	1,330	87.8	1.0	1,670	84.3	1.0
4	372	96.8	1.0	466	96.8	1.3	631	93.5	0.9	826	91.9	0.9
5	200	98.6	1.3	210	98.6	1.3	338	96.8	0.9	403	95.6	0.9
6	90	99.4	1.3	88	99.4	1.2	172	98.3	0.9	228	97.7	0.9
Raffinate	70			73			189			249		
Total U, mg.	11,212			11,640			11,100			10,911		
Raff. XS Acid, g./l.	44			33			19			25		

Shakeout	Vanadium			Vanadium			Vanadium			Vanadium		
	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d
1	5.7	8.2	0.09	6.0	8.2	0.09	2.4	3.4	0.04	1.3	1.8	0.02
2	2.4	11.7	0.04	3.0	12.3	0.05	4.8	10.2	0.08	4.5	8.1	0.07
3	1.8	14.3	0.03	2.1	15.2	0.03	3.0	14.5	0.05	3.8	13.5	0.06
4	1.4	16.3	0.02	2.1	18.1	0.03	1.9	17.2	0.03	2.1	16.5	0.04
5	1.5	18.5	0.03	1.9	20.7	0.03	0.8	18.3	0.01	1.2	18.2	0.02
6	1.4	20.5	0.03	1.7	23.0	0.03	1.3	20.2	0.02	1.2	19.9	0.02
Raffinate	55.0			56.0			56.0			56.8		
Total V, mg.	69.2			72.8			70.2			70.9		
V Extracted, % of U Extracted	0.13			0.15			0.13			0.13		

Shakeout	Molybdenum			Molybdenum			Molybdenum			Molybdenum		
	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d	mg.	Cum. %	K _d
1	43.9	32.1	0.47	40.8	29.4	0.42	12.9	9.3	0.10	5.4	4.2	0.04
2	12.5	41.2	0.15	19.4	43.4	0.25	27.6	29.1	0.28	29.2	26.9	0.31
3	10.1	48.6	0.14	12.6	52.5	0.19	15.2	40.0	0.18	19.9	42.4	0.27
4	5.7	52.8	0.09	6.0	56.8	0.10	6.7	44.8	0.09	7.7	48.4	0.12
5	5.1	56.5	0.09	4.7	60.2	0.08	3.0	47.0	0.04	3.0	50.7	0.05
6	4.4	59.7	0.08	2.1	61.7	0.04	1.8	48.3	0.03	2.0	52.3	0.03
Raffinate	55.1			53.4			71.9			61.5		
Total Mo, mg.	136.1			139.0			139.1			128.7		
Mo Extracted, % of U Extracted	0.73			0.75			0.62			0.63		

Notes:

- (1) 50-ml. samples of process solution No. 5269-81 extracted with equal volume of 1 N ether; 1½-min. time cycle.
- (2) pH adjusted with 20% NaOH solution, thereby reducing solution concentration somewhat.

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FIGURE 10. EFFECT OF SOLUTION ACIDITY ON EXTRACTION OF VANADIUM AND MOLYBDENUM BY DIETHYL ETHER

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materially the transfer of such ions as vanadium and molybdenum. Since silicon and phosphorus presumably also are being transferred as complexes with the molybdenum and/or the vanadium, optimum conditions of acidity should also reduce the transfer of these components. Acidity may also have some bearing on the ease of back-washing these components from the ether extract.

Column-Extraction Tests

Two factors that control the efficiency of the Scheibel extraction column are flow rate and stirrer speed. A study of these factors has been made, with the results contained in Table 33. These results indicated that, with an ether:feed ratio of 1.8:1, optimum operating conditions were a feed rate of about 1000 ml./hr., and a stirrer speed of 2500-3000 r.p.m. In order to obtain stirrer speeds in this range, it was necessary to replace the original electric motor drive with a Cenco air motor. This motor is capable of speeds up to 6000 r.p.m., using 100 p.s.i.g. air. Under these conditions, the motor is rated at 1/6 H.P.; at the 25 p.s.i.g. available in the laboratory, the horsepower is correspondingly reduced, but is still ample to drive the stirrer at high speeds.

The low extractive efficiencies observed earlier at low flow rates have been confirmed. Evidently, these are characteristic of this particular size and type of column and of the liquids being used. It has been surmised that there is excessive cross-mixing at low feed rates.

All of the tests described in Table 33 were made with ether as the continuous phase. One test was made with the aqueous phase continuous, with inconclusive results. Additional tests are to be made using a continuous aqueous phase.

TABLE 33. CONTINUOUS EXTRACTION TESTS ON PROCESS SLURRIES IN A SCHEIBEL ONE-INCH EXTRACTION COLUMN

Column Operating Conditions

Slurry acidity = 60 g. excess acid/l.
 Ether acidity = 60 g. HNO_3 /l.
 Ether temperature = 0-10°C.
 Feed temperature = 20-25°C.
 Ether phase continuous

<u>Slurry Feed⁽¹⁾</u>			Ratio, Ether: Feed	Stirrer Speed, r.p.m.	<u>Uranium</u>		
Slurry No.	U, g./l.	ml./hr.			In Raffinate, g./l.	Extracted, Per Cent ⁽²⁾	Metal Bal., Per Cent
3	275	463	1.6:1	1300	14	94.8	110
6	270	523	1.7:1	1800	5	98.2	109
6	270	1066	1.5:1	1800	4.5	98.3	97
6	270	1840	1.8:1	1800	2.5	99.1	75
6	270	2850	2.2:1	1800	2.9	98.9	104
6	270	543	1.8:1	2500	6.7	97.5	93
6	270	938	1.7:1	2500	0.3	99.2	108
4	262	1980	1.8:1	2500	0.8	99.7	108
4	262	475	1.7:1	3400	10.3	96.2	118
4	262	1000	1.7:1	3400	3.7	98.6	89
4	262	1822	1.9:1	3400	0.6	99.8	96

(1) Slurry feeds prepared from pitchblende blend A-1 and MgX blend B-1, so that U ratio was 2:1.
 All approximately 55-56° Bé.

(2) Based on feed and raffinate analyses.

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Vanadium Solubility Studies

The approximate solubility of vanadium pentoxide in simple nitric acid solutions has been determined, with the results as shown in Table 34 and Figure 11. Vanadium solubility apparently increases with increasing acid concentration, reaching a maximum in about 3N acid; beyond this point, it decreases with further increases in acid concentration. At the maximum, the solubility is nearly 20 grams of vanadium/liter.

The filtrates from the equilibrated solutions above were heated to 80-90°C. and maintained there for 24 hours. Any solid phase then present was filtered off and the filtrates assayed. Vanadium solubility was slightly lowered, although still exhibiting a maximum in the neighborhood of 3N nitric acid.

Additional vanadium solubility studies are being conducted in process solution, using uranyl vanadate, sodium uranyl vanadate, and vanadium pentoxide.

Attention has recently been turned towards the "boil-down" precipitate obtained during concentration of MgX digest liquor as one possible means of handling the vanadium problem of MgX. This had not been considered a feasible approach earlier because it was believed that the uranium loss to the precipitate might be excessive, and because of the difficult filtration problem presented. Adoption of a slurry-type extraction eliminated the necessity of a filtration step. Further study of boil-down precipitates indicated that the boil-down precipitate is primarily a compound of iron, vanadium, phosphorus, and sometimes calcium, but with

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TABLE 34. SOLUBILITY OF VANADIUM IN DIFFERENT CONCENTRATIONS
OF NITRIC ACID

Ten grams of V_2O_5 was added to 100 ml. of each solution and then shaken mechanically for 72 hours.

Temperature = $25 \pm 5^\circ C$.

pH		Normality of HNO_3	Vanadium Concentration, g./Liter	Vanadium Concentration, g./Liter ⁽¹⁾
Initial	Final			
5.6	2.5	-	0.60	No solid phase.
4.0	2.5	-	0.50	Slight amount of solid phase.
2.0	2.0	-	0.26	Ditto
0.6	0.8	0.25	3.44	1.87
0.3	0.5	0.50	6.54	4.06
0.2	0.2	0.75	9.58	5.38
0.0	0.1	1.0	12.04	7.08
-	-	1.5	15.92	10.50
-	-	2.0	17.96	12.75
-	-	3.0	19.74	19.25
-	-	4.0	18.00	Slight amount of solid phase.
-	-	5.0	15.42	No solid phase.
-	-	8.7 ⁽²⁾	5.40	No solid phase.

(1) Filtrates from $25^\circ C$. test were heated in water bath at $80-90^\circ C$. for 24 hours and solid phase which formed was filtered off.

(2) 45 per cent HNO_3 .

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FIGURE 11. SOLUBILITY OF VANADIUM IN NITRIC ACID SOLUTIONS

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A 15x5 grid of dots forming a stylized drawing of a person with arms raised in a 'V' shape.

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uranium present only as a minor impurity. Analysis of a recently prepared boil-down precipitate from P-92 MgX is shown below (in comparison with one earlier presented which was obtained from P-88 MgX):

	Analysis, Per Cent			
	Boil-Down Precipitate		MgX	
	P-92(1)	P-88	P-92	P-88
Fe	11.5	14.9	2.40	3.52
V	29.8	25.8	0.43	0.35
PO ₄	1.3	9.1	1.71	3.38
U	0.36	1.7	39.4	33.3
Alk. earth oxides	Ca and SO ₄ being analyzed.		-	-

(1) Spectrographic analysis of other constituents of this precipitate was:

Per Cent					
<u>Ca</u>	<u>Mg</u>	<u>Mo</u>	<u>Cu</u>	<u>Ti</u>	<u>Al</u>
10-40	0.1-1.0	1-5	0.1-1.0	0.1-1.0	<0.1

In both precipitates, the iron, phosphorus, and vanadium were in good balance for a mixed precipitate of ferric phosphate and ferric vanadate. With a well-washed cake, uranium losses to the precipitate should be negligible. It has been observed in the laboratory that the precipitate itself is readily washed, after its separation from the viscous digest liquor. The difficulty in filtration appears to arise primarily from the viscosity of the liquor.

If the boil-down precipitate does not carry down any significant quantity of uranium (as the above analyses suggest), it may be possible to tie up much of the vanadium in a non-ether-soluble form by boiling down

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MgX slurry until a boil-down precipitate is formed. This approach to the vanadium problem is to be investigated further.

X-Ray Diffraction Studies

Three samples of synthetic MgX, which had previously been examined by X-ray diffraction without success, were analyzed chemically, with the following results:

	Per Cent						
	<u>U</u>	<u>Mg</u>	<u>Fe</u>	<u>Cu</u>	<u>SO₄</u>	<u>PO₄</u>	<u>L.O.I.</u>
E6-10-1	45.2	3.6	9.5	-	1.4	12.4	10.6
E6-10-2	48.1	7.3	3.0	-	0.8	12.2	11.8
E6-10-3	40.3	8.9	2.6	6.8	1.4	10.2	13.8

Samples of each were ignited at 800°C. and the ignited samples re-examined by X-ray diffraction. All three samples had a common major pattern, indicating a common major phase. This has not yet been identified. A pattern of uranyl phosphate is being prepared for comparison. Sample E6-10-1 also showed indications of the presence of Fe_3O_4 or MgFe_2O_4 (spinel form). Sample E6-10-2 showed a similar pattern; a trace of MgO was evident in addition. Sample E6-10-3 indicated the presence of some fused $\text{Cu}_3(\text{PO}_4)_2$ and MgO. None of the above were major phases.

Nitrate Recovery

Provisions are being made in the revised Plant 6 flowsheet to recover the free nitric acid in the raffinate from the acid ether-extraction column by means of a neutral ether scrub. It appeared likely that

some of the combined nitrates remaining after this operation might be displaced by a cheap acid such as sulfuric and extracted with neutral ether. This possibility was examined very briefly, with the results shown in Table 35 and Figure 12. The sulfuric acid added was about 50 and 100 per cent of stoichiometric, based on the nitrate present. The distribution coefficient appeared to vary almost in direct proportion to the solution acidity; it was quite low at low acidities.

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	65-80
5269	81-95
5270	84-100
5531	1-12

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TABLE 35. RECOVERY OF COMBINED NITRATE IN RAFFINATE BY ETHER EXTRACTION

Procedure: Raffinate from Scheibel column extractor given four shake outs with neutral ether, reducing acidity to pH 0.4 (zero XS acid); 94-ml. aliquots (containing 22.0 g. NO_3) were extracted with neutral ether after addition of sulfuric acid.

Shakeout	g. of NO_3	NO_3 Extracted, Cum. %(1)	K_d	XS Acid Before Ext., g./l.(2)
<u>7.75 g. H_2SO_4 Added</u>				
1	3.29	17.2	0.21	84
2	1.99	27.6	0.14	52
3	1.11	33.4	0.086	32
4	0.73	37.3	0.061	17
5	0.50	39.8	0.043	9
Raffinate	11.5			3
Total NO_3 , g.	19.12			
NO_3 bal., %	87			
<u>15.5 g. H_2SO_4 Added</u>				
1	5.45	28.8	0.40	175
2	3.03	44.6	0.29	122
3	2.00	55.2	0.24	86
4	0.52	58.0	0.065	63
5	0.87	62.5	0.12	49
6	0.64	66.0	0.10	43
Raffinate	6.44			35
Total NO_3 , g.	18.95			
NO_3 bal., %	86			

(1) Based on nitrate found

(2) As measured by standard method and expressed as HNO_3 .

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FIGURE 12. EXTRACTION OF COMBINED NITRATES FROM RAFFINATE IN THE PRESENCE OF ADDED SULFURIC ACID

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