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TOPICAL REPORT

on

REFINING OF MgX AND OTHER URANIUM-BEARING MATERIALS

by

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ABSTRACT

A study of the effect of feed and ether acidity on the extraction of vanadium and molybdenum from process solutions by ethyl ether is described. Results of batch and continuous extraction tests on the extraction of uranium from process slurries by tributyl phosphate-Gulf Spray naphtha are presented, including studies of the effects of feed and scrub acidities on the concurrent extraction of molybdenum. The effect of temperature on the stripping of uranium from tributyl phosphate was studied briefly.

Results from fractional precipitation of MgX from dilute sulfuric acid solutions indicate that, in the presence of sufficient iron, phosphate is precipitated as ferric phosphate, and not as uranyl phosphate.

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INTRODUCTION

This report summarizes the work performed from September 1, 1950, to December 31, 1950, under Contract No. AT-30-1-Gen-228 on problems related to the use of MgX as a feed material in the Mallinckrodt Plant 6 uranium refinery. The work of the preceding period (May 1, to August 31, 1950) was described in BMI-246. Also, the following monthly progress reports on this subject have been submitted:

BMI-247	September 30, 1950
BMI-248	October 31, 1950
BMI-249	November 30, 1950

Research on the refining of pitchblende, MgX, and other high-grade feed materials is being continued.

Study of the problems associated with the incorporation of MgX precipitates as a part of the feed to the Mallinckrodt refinery was initiated at Battelle Memorial Institute late in April, 1950. In the period covered by this report, much of the effort was devoted to an investigation of the direct slurry extraction process developed by the M.C.W. group. One of the main phases included was a study of the problems introduced by the presence of vanadium and molybdenum in feed materials. The experimental data indicate that reduction of acidities in the ether extraction process, from present levels, can materially reduce the vanadium and molybdenum contents of the uranium extract. Although it does not now appear feasible to produce specification

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uranium by a one-step ether extraction, production of uranium nearly meeting specifications appears a possibility.

The application of tributyl phosphate to the direct slurry extraction process has been studied. Although higher uranium distribution coefficients are obtained with tributyl phosphate than with ether, so that extremely low uranium losses to the raffinate can be readily attained, there are some questionable features connected with its use which need additional consideration. Chief of these, perhaps, is the difficulty in meeting molybdenum specifications via a one-step extraction. The work here has indicated that molybdenum contamination may, in the case of certain types of feed solution, pose a serious problem. Since results from research carried on elsewhere indicate that the problem is not insoluble and that molybdenum transfer can be held below tolerable limits, it appears that additional study of the factors involved will supply the information required.

SUMMARY

Study of the effects of acidity on the extraction of vanadium and molybdenum by diethyl ether shows that a considerable dependency exists. The data indicate that the minimum acidity of both feed and ether, consistent with satisfactory uranium extraction, is the most desirable from the viewpoint of minimum transfer of these components. For example, extraction of a feed solution containing 10 g./l. of excess acid by 0.1N ether resulted in the transfer of only 3.2 per cent of the V and 1.6 per cent of the Mo to the extract.

The uranium in this unscrubbed extract contained only 210 and 275 p.p.m. of vanadium and molybdenum, respectively. Addition of an aqueous scrub of the extract would presumably have resulted in a substantial improvement in the purity of the extract. Study of the factors controlling the effectiveness of scrubbing of ether extracts is now under way. There is some reason to believe that a suitable combination of carefully controlled acidities in the extraction system, plus a satisfactory scrub, may make possible the production of a near-specification uranium extract from the primary (acid) extraction.

The application of a Scheibel laboratory-scale countercurrent continuous extractor to the extraction of uranium from slurry feeds by diethyl ether was briefly investigated. Uranium extractions of 99+ per cent were obtained on high-sulfate slurries containing 260 to 270 grams of uranium per liter. It was found that anomalous results were obtained at low feed rates (500 ml./hr. or below); optimum conditions for this column appeared to include a feed rate of approximately 1000 ml./hr., and a stirrer speed of 2500-3000 r.p.m. Even under these conditions, the 48-inch Scheibel extractor did not appear to possess quite enough stages for complete extraction of the uranium from the feed slurries used. Most of the Scheibel tests with ether were performed with the organic phase continuous; several tests with the aqueous phase continuous gave rather inconclusive results.

Only uranium extraction was considered in the Scheibel tests described above. Methods of controlling the transfer of molybdenum and vanadium are to be investigated, using this equipment; this work was postponed temporarily to permit completion of the tributyl phosphate extraction studies.

Among the serious disadvantages of extraction by diethyl ether are the hazard, and the deleterious effects on efficiency of such extractants as sulfate and phosphate. Also, the degree of flexibility with respect to maximum permissible acid concentrations is quite limited. The Commission is interested in other extractants not subject to these disadvantages and one of the most attractive of these, tributyl phosphate, has been investigated. Both batch and column extraction tests have confirmed the superior distribution coefficients possessed by a tributyl phosphate-kerosene extractant.

Virtually complete extraction was obtained on a typical feed slurry using three hand-shakeouts with equal volumes of a 50:50 tributyl phosphate-Gulfspray naphtha extractant. With 0.7N acid feed, the raffinate contained 1.1 grams of uranium/liter; increasing the HNO₃ normality of the feed to 2.7 and 3.7 decreased the uranium contents of the raffinates to 0.84 and 0.12 gram/liter, respectively. Similarly, in several typical column tests, using a feed:scrub:organic ratio of 1.0:0.25:2.5, the uranium concentration of the raffinates decreased from 0.49 to 0.04 gram/liter as the feed normality was increased from 1.3 to 4.7.

The indications of the batch extractions were that maintaining total nitric acid concentration above 0.5N minimized the transfer of molybdenum to the organic phase. Column tests also showed that molybdenum transfer decreased with increasing acid concentration. However, even under rather rigorous conditions of acidity, molybdenum transfer to the organic phase was more than was desirable, even with the inclusion of a strongly acid scrub. For example, in one column test, in

which a 3.6N feed and an 8N scrub were used, the molybdenum content of the uranium extract was less than 25 p.p.m. Molybdenum contents as low as 5 p.p.m. have not been attained under any of the conditions tested. This is not in complete agreement with results reported from other installations. One factor which is suspected is the slurry feed itself; it is believed that the method of preparation may have a bearing on both the amount and the species of molybdenum present. The feed slurries used here have all been laboratory prepared and may have contained excessive quantities of molybdenum. Since molybdenum transfer appears to be one of the critical points in connection with the feasibility of obtaining specification uranium in a one-step extraction, this problem merits further investigation.

The re-extraction of uranium from tributyl phosphate into water was the subject of a limited number of column tests. Although there is a temperature dependency, it is much less than is the case for ether. Test results indicated that the quantity of water required to strip the uranium from the organic phase was reduced 50 per cent (from 2 volumes to an equal volume) as the temperature was increased from 25 to 45°C. The results of a similar test at 70°C. were anomalous and require confirmation.

The approximate solubility of vanadium pentoxide in nitric acid solutions was determined; maximum solubility was attained in about 3N acid, at which point nearly 20 grams of vanadium per liter was in solution. At points below 3N acid concentration, the solubilities at 90°C. appeared to be lower than those at 25°C.; however, at 3N, no appreciable decrease was observed.



The solubility of vanadium pentoxide in one pitchblende-MgX process solution was virtually constant at 1.65 ±0.10 gram of vanadium per liter (equal to approximately 0.75 per cent on a uranium basis) over the range from 3 to 272 grams of excess acid/liter. In the same process solution, the solubilities of uranyl vanadate and sodium uranyl vanadate (artificial carnotite) increased from 0.4 gram to 8.5-9.0 grams of vanadium/liter as the acid concentration was increased to 225-235 grams of excess acid/liter. Most of this increase occurred over the range from 0-150 grams of excess acid/liter.

Study of the vanadium-containing "boil-down" precipitate encountered in concentrating MgX solutions disclosed that it consisted essentially of iron, vanadium, and phosphorus, and that uranium appeared to be present only as a minor constituent or impurity.

Preliminary study of the behavior of molybdenum in pitchblende solutions indicated that the solubility of molybdenum increased with increasing acidity. At an excess acidity of 160 grams/liter, it was possible to hold 5.6-6.0 grams of molybdenum/liter in solution, even after prolonged digestion at the boiling point.

All attempts to identify the phases present in MgX by means of X-ray diffraction techniques were unsuccessful. Although ignition of MgX was effective in providing a crystalline pattern, rather than the amorphous pattern of oven-dried MgX, it did not make possible the identification of any of the major phases by X-ray diffraction.

Fractional precipitation of MgX from dilute sulfuric acid solutions, similar to those from which it was originally precipitated, is providing interesting clues as to the constitution of MgX. The data

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Table 1—EFFECT OF SPECIFIC GRAVITY ON EXTRACTION OF URANIUM FROM A PROCESS SOLUTION

	Specific Gravity—Degrees Baumé*									Specific Gravity—Degrees Baumé†											
	52			56‡			60‡			62			56			60			62		
	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
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 [§]	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	95.6	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	0.51	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		

* Combined process solution No. 5289-72 boiled down to desired specific gravity.

† Pitchblende and MgX solutions boiled down separately to desired specific gravity before combining.

‡ Average of two experiments.

§ 50-ml. samples: extracted with equal volume of 1N acid ether; 1¼-min. time cycle. Results reported to 1-liter basis.

In some of the foregoing tests, the combined pitchblende-MgX solutions were boiled down together. Several similar tests were also made in which the individual solutions were boiled down separately to the desired specific gravity before combining. Other than a slight difference in final solution acidities, there appeared to be no major differences in the results.

Effect of Acidity. The preliminary indications of the foregoing series of tests were that acidity was a variable which exerted a greater effect on uranium extraction than later proved to be the case. Additional tests were conducted to investigate this, as well as to study the effects of acidity on vanadium transfer. The uranium extraction results, presented in Tables 2 and 3, indicated that, over the range tested, neither solution nor ether acidity influenced uranium extraction appreciably, where the feed solution contained some excess acid. Maximum uranium extractions were obtained in the neighborhood of zero excess acid, with both 1N and 0.5N ether.

In an earlier report (BMI-246), it was noted that spectroscopic analyses of the first ether extract from two slurry extractions showed much lower transference of vanadium, molybdenum, silicon, and phosphorous when a low-acid feed (pH 2) was used. The ether extracts from several of the above tests were analyzed for vanadium; several additional tests were also made to extend the test range. These results, shown in Table 4, indicated that low system acidity was a prerequisite for minimum vanadium transference. With a feed acidity of pH 2.1, 0.5N ether extracted only 6 per cent of the vanadium. Additional tests were made on a similar process solution, in which the acidity of the ether was maintained at 1N



Table 2—EFFECT OF ACIDITY ON EXTRACTION OF URANIUM FROM PROCESS SOLUTION BY 1N ETHER*

Specific gravity at 60°F.	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 [‡]		
	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
1.61	136.0	60.7	1.5	137.0	59.3	1.5	139.0	59.0	1.4	148.0	62.7	1.7	155.0	65.8	1.9	120.0	52.8	1.1
1.62	45.5	31.0	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	76.8	1.0
1.62	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
1.62	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
1.62	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
1.62	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:

* Process solution No. 5269-72. Excess acids below 40 g./l. obtained by neutralizing with MgO.

† Average of two tests.

‡ 5M NaOH used to neutralize from pH 1 to pH 2.1. Slight precipitation occurred.

§ 50-ml. samples; extracted with equal volume of 1N acid ether; 1½-min. time cycle. Results reported to 1-liter basis.

Table 3—EFFECT OF ACIDITY ON EXTRACTION OF URANIUM FROM PROCESS SOLUTION BY 0.5N ETHER*

Specific gravity at 60°F.	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†		
	1.61			1.61			1.62			1.62			1.63			1.69		
Shakeout‡	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	0.76	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	0.78	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:

* Process Solution 5269-72.

† 5M NaOH used to neutralize from pH 1 to pH 2.1. Slight precipitation occurred.

‡ Standard procedure.

Table 4—EFFECT OF ACIDITY ON EXTRACTION OF VANADIUM

	Test No.*																			
	1			2			3			4			5			6				
	Approximate Excess Acid, g./l. or pH			40 g./l.			40 g./l.			40 g./l.			pH 2.1			pH 2.1				
Normality of Ether			1.0			1.0			0.5			Neutral			1.0			0.5		
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	0.089	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	0.089	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			52.8			55.5			49.7			56.4				
Total U ext., mg.	10,960			11,470			11,650			10,595			11,237			10,586				
V in Ext. act, % 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:
* All tests except No. 4 correspond to those in Tables 2 and 3.

and the acidity of the feed was varied. Vanadium extraction was 20 per cent, even when the feed was adjusted to pH 2.1. As shown in Table 5 and Figure 1, the behavior of molybdenum closely paralleled that of vanadium. With 1N ether, there appeared to be no advantage in reducing the acidity of the feed. Only the peak of the transference curve shifted; the cumulative total of vanadium or molybdenum extracted remained virtually unchanged.

However, maintenance of both the feed solution and the ether at low acid levels reduced the transference of vanadium and molybdenum to less than 5 per cent. As shown in Table 6, extraction of a process feed solution containing 9.5 g./l. of excess acid with 0.1N acid ether resulted in the extraction of only 3.2 per cent of the vanadium and 1.6 per cent of the molybdenum. The vanadium and molybdenum contents of the extract were 210 and 275 p.p.m., respectively.

It should be noted that all of the ether extraction tests described in this report were made on feed solutions or slurries from which none of the sulfate had been removed. This condition was established in accordance with the procedure which has been proposed for handling slurry feeds; i.e., pitchblende sulfate is precipitated only to the extent required to remove completely any remaining radium from the pitchblende digest filtrate. With no sulfate removed, the feed solutions have frequently contained sulfate to the extent of approximately 25 per cent of the uranium. It was pointed out in a previous report (BMI-246) that the presence of uncomplexed sulfate had a rather considerable adverse effect on uranium extraction. The tests shown in Table 6 had low uranium

Table 5—EFFECT OF SOLUTION ACIDITY ON EXTRACTION OF VANADIUM AND MOLYBDENUM BY 1N ACID ETHER*

Shakeout	Approximate Acidity, g./l. or pH											
	40 g./l.			40 g./l.			pH 1.0†			pH 2.1†		
	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	8.4	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	66.8	0.10	6.7	44.8	0.09	7.7	48.4	0.12
5	5.1	56.6	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:

* 50-ml. samples of process solution No. 5269-81 extracted with equal volume of 1 N ether; 1½-min. time cycle.

† pH adjusted with 20% NaOH solution, thereby reducing solution concentration somewhat.

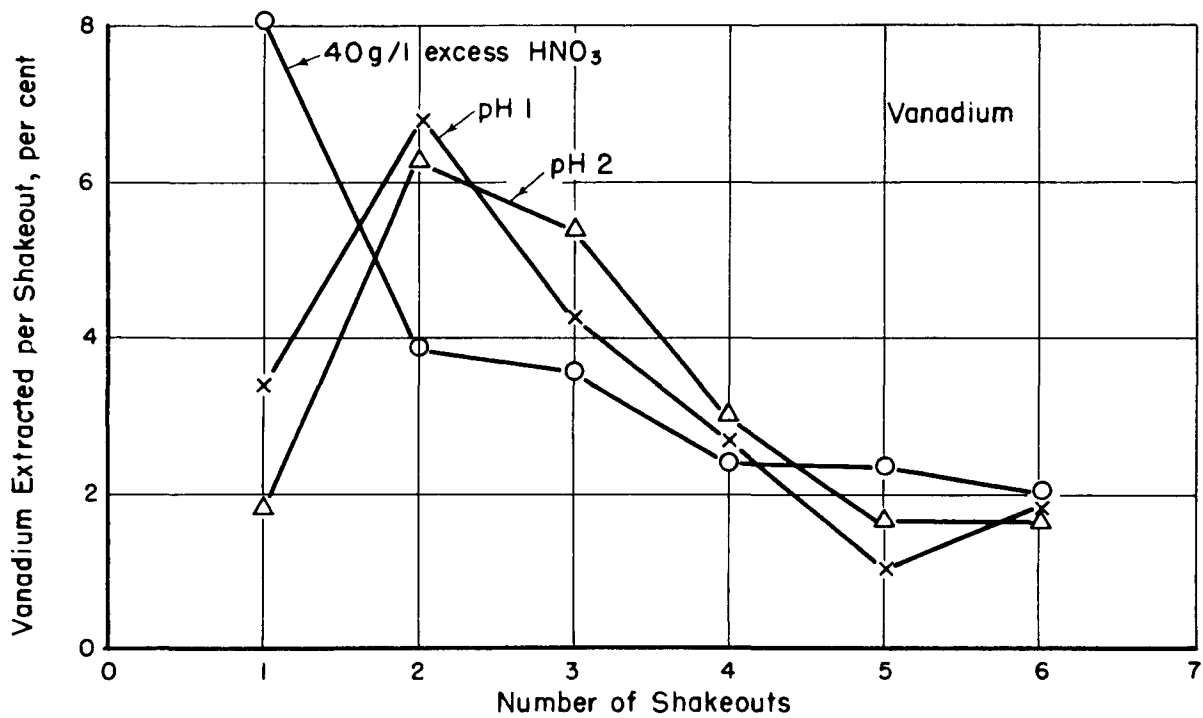
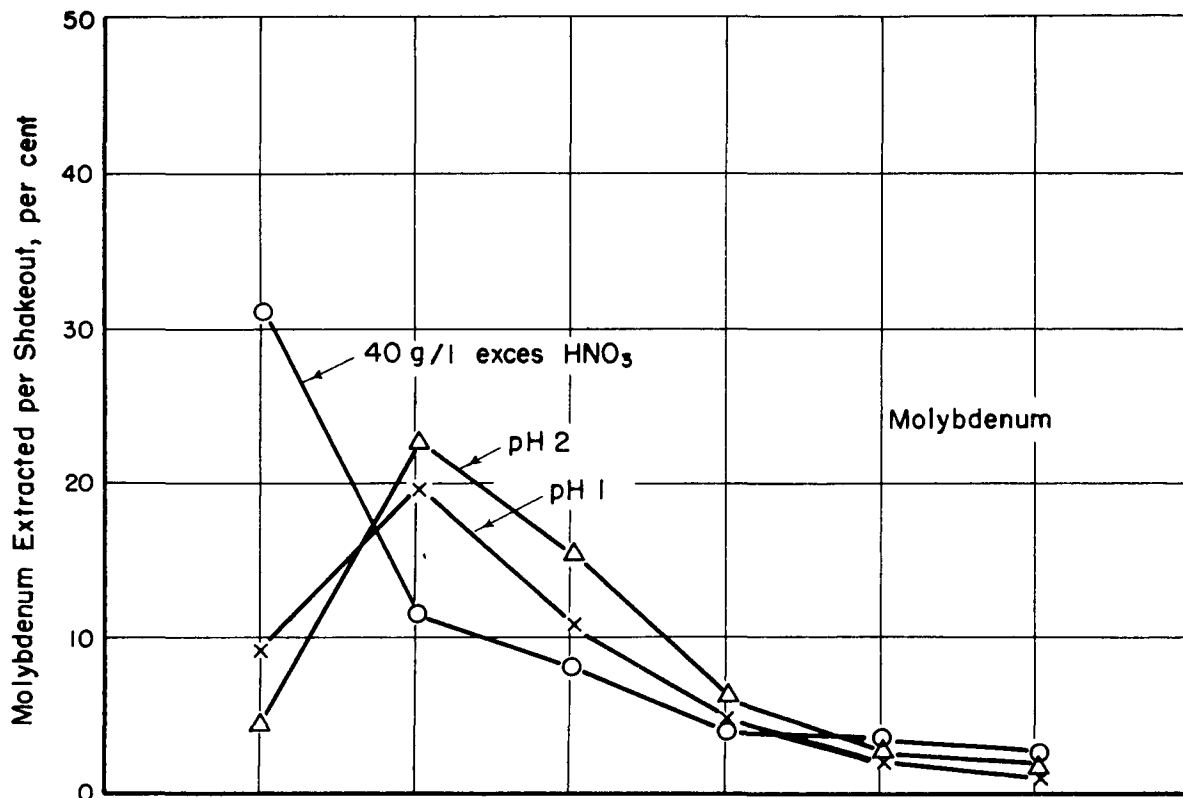


FIGURE 1. EFFECT OF SOLUTION ACIDITY ON EXTRACTION OF VANADIUM AND MOLYBDENUM IN DIETHYL ETHER



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TABLE 6. EFFECT OF ACIDITY ON EXTRACTION OF VANADIUM AND MOLYBDENUM FROM FILTERED PROCESS SOLUTION⁽¹⁾

Excess Acid		Extracted, mg.			Extracted, % ⁽²⁾			p.p.m. in Extract ⁽³⁾	
Feed	Raffinate	U	V	Mo	U	V	Mo	V	Mo
<u>Neutral Ether</u>									
9.5 g./l.	pH 0.9	11,460	1.7	1.6	98.3	2.4	0.8	150	70
pH 0	pH 1.0	11,400	1.6		95.9	2.5		145	
pH 0.5	pH 1.5	10,230	1.8		90.1	3.3		175	
pH 1.1	pH 2.0	9,700	2.4		81.0	3.1			
<u>0.1N Ether</u>									
9.5 g./l.	pH 0.3	10,920	2.3	3.0	98.4	3.2	1.6	210	275
pH 0	pH 0.2	10,200	1.7		98.7	2.9		165	
pH 0.5	pH 0.2	11,570	1.8		98.2	3.8		155	
pH 1.1	pH 1.7	10,060	2.1		84.9	2.9			
<u>0.25N Ether</u>									
9.5 g./l.	pH 0	11,690	3.0	6.3	98.8	4.4	3.6	265	540
pH 0	pH 0	11,250	1.8	<1.5	99.0	3.0	<1.0	160	<135
pH 0.5	pH 0	11,360	2.2		99.0	3.5		195	
pH 1.1	pH 0.5	11,920	3.0		97.0	3.7		250	

(1) Process solution 5269-81, prepared so that 2/3 of uranium derived from pitchblende Blend A-1 and 1/3 from MgX Blend B-1. Sp. gr. approximately 56° Be in all tests. Acidity adjusted with MgO. 50-ml. samples extracted 6 times with equal volumes of ether by usual procedure.

(2) Per cent of total metal found.

(3) Uranium basis.

extractions. However, upon comparing similar tests (Tables 2 and 3) with those of Table 6, it can be seen that, even with 40 g./l. excess acid in the feed and 1N acid ether, uranium extractions were also low. As a matter of fact, in those two series of tests, maximum uranium extractions were obtained when low-acid feeds were used. It is believed that the low uranium extractions shown in Table 6 resulted primarily from the high sulfate content of the solutions, and were not a result of the low acidities used. Additional work will be necessary to clarify this point, and to demonstrate that minimum vanadium and molybdenum extractions can still be obtained when uranium extraction is complete.

The problem of extract scrubbing was not investigated as a part of the foregoing tests. This study can best be conducted on continuous extraction equipment, and most of the experimental data will be obtained from tests using the Scheibel continuous extractor.

Effect of Boil-Down Precipitates. In boiling down MgX slurries or solutions to obtain the desired specific gravity for solvent extraction, a reddish-brown vanadium precipitate is formed. There was some fear that this precipitate might tie up uranium in a form unavailable for extraction. Although other analytical data indicated that uranium was not a component of this precipitate, some extraction tests were run on feed solutions in which boil-down precipitates were present. MgX slurry (P-1) was filtered and the filtrate was concentrated by boiling until a boil-down precipitate was visible. The slurry was diluted to 56° Bé and extracted by the usual procedure. The solid phase in the raffinate was filtered off and analyzed separately, with the results shown in Table 7. Less than 0.002 per cent of the uranium reported in the boil-down

TABLE 7. EFFECT OF ACIDITY ON THE EXTRACTION OF VANADIUM FROM MgX FEED SOLUTIONS CONTAINING BOIL-DOWN PRECIPITATES(1)

Ether Normal-ity (HNO ₃)	Excess Acid in Feed, g./l.	Vanadium			Total mg. Found	Uranium			Total mg. Found
		Per Cent in Ether Ext.	Per Cent in Raffinate Ppt.	Per Cent in Raffinate Filt.		Per Cent in Ether Ext.	Per Cent in Raffinate Ppt.	Per Cent in Raffinate Filt.	
Neutral	14	3.0	89.4	7.6	156.7	99.99	<0.002	0.009	10,440
0.1N	16	1.9	80.8	17.3	149.9	99.99	<0.001	0.003	10,320
0.25N	13	3.0	63.0	34.0	176.3	99.98	0.002	0.022	9,950

(1) 100-ml. samples of P-1 MgX-digest filtrate were boiled down until a boil-down precipitate was formed. Solutions were then adjusted to 56° Be, and extracted by the usual procedure.

precipitate. Low acidities of feed and ether were employed, and vanadium transfer to the extract amounted to only 3 per cent. The behavior of MgX solution was comparable in this respect to the behavior of the combined pitchblende-MgX process solutions described earlier.

Much higher uranium distribution coefficients were observed on these MgX-extraction tests than have been obtained on combined pitchblende-MgX feeds. Available data are insufficient to provide a definite explanation of the difference. However, one hypothesis, based on the assumption that salting strengths are comparable, is that the interfering components (such as sulfate and phosphate) are satisfactorily complexed in MgX, as opposed to pitchblende.

Additional study of the boiling-down operation showed that, when a combined process solution, consisting of A-1 pitchblende and P-1 MgX, was boiled down, no precipitate was formed. When the two components were boiled down separately, the usual precipitate was obtained in the MgX solution. Solutions prepared by boiling down separately and together were extracted with ether. As indicated by Table 8, vanadium transfer appeared to be unaffected, even when from 1/3 to 2/3 of the vanadium was tied up as a boil-down precipitate.

The indications of the experimental work with boil-down precipitates were that uranium losses to such a precipitate would be negligible, and that no interference with uranium extraction need be expected. However, although deliberate formation of a boil-down precipitate materially reduced the amount of vanadium in solution in the feed, there appeared to be no corresponding reduction in vanadium transfer.

TABLE 8. EFFECT OF ACIDITY AND BOIL-DOWN PRECIPITATE ON EXTRACTION OF VANADIUM FROM PROCESS SOLUTIONS

Ether Normality (HNO ₃)	Vanadium Distribution				Uranium Distribution			
	Per Cent in			Total mg. Found	Per Cent in			Total mg. Found
	Ether Ext.	Raffinate Ppt.	Filt.		Ether Ext.	Raffinate Ppt.	Filt.	
(A) Solutions Boiled Down Separately ⁽¹⁾								
Neutral	5.4	59.1	35.5	84.6	96.3	0.1	3.6	15,050
0.1N	5.6	30.0	64.4	93.2	98.1	0.02	1.9	14,510
0.25N	5.4	30.9	63.7	100.4	98.3	0.02	1.7	15,360
(B) Solutions Boiled Down Together ⁽²⁾								
Neutral	4.0	-	96.0	110.4	96.6	-	3.4	15,460
0.1N	7.6	-	92.4	79.0	98.1	-	1.9	14,990
0.25N	5.7	-	94.3	89.1	98.6	-	1.4	15,660

- (1) 50-ml. samples of P-1 MgX-digest filtrate were boiled down until a boil-down precipitate was formed. 59-ml. samples of A-1 pitchblende digest liquor were boiled to sp. gr. of 2.0; no precipitate formed. Solutions were mixed, adjusted to 56° Bē, and 30 g./l. excess acid, and extracted by usual procedure.
- (2) 50-ml. samples of P-1 NgX-digest filtrate were combined with 59-ml. samples of A-1 pitchblende digest filtrate (giving a uranium ratio of 1:2) and boiled to a sp. gr. of 2.0; no precipitate formed. Solutions were adjusted to 56° Bē, and 30 g./l. excess acid, and extracted by usual procedure.

It is hypothesized that it is the amount of vanadium-containing heteropolyacids in solution, rather than the total amount of vanadium, that is governing.

All of the preceding tests were made using filtered MgX solutions, so that the formation of boil-down and other precipitates could be followed visually. One series of tests was performed to observe the behavior of MgX slurries when treated similarly. P-1 MgX was digested, with no added heat, and the resultant slurry was boiled down until almost pasty. There was apparently some boil-down precipitate present at this stage. The slurry was diluted to approximately 56° Bé, (excess acid = 19 g./l.) and ether-extracted. A moderate to strong reddish color was observed in all extracts after the first or second. As indicated by the tabulation below, vanadium transfer to the extract was from 30-40 per cent:

<u>Normality of Ether</u>	<u>Uranium Extracted, Per Cent</u>	<u>Distribution of Vanadium, Per Cent</u>		
		<u>Extract</u>	<u>Raffinate</u>	
			<u>Liquid</u>	<u>Solid</u>
Neutral	99.0	31	54	15
0.1N	99.9	39	53	8
0.25N	99.0	43	54	3

The high vanadium transfer was surprising, since the conditions of acidity were those which had resulted in low vanadium transfer in previous tests. The explanation might be that the conditions used in this test were in some manner more favorable for the formation of an ether-soluble heteropolyacid than in other similar tests. Another series of tests was run in an attempt to duplicate the above results; however, the highly colored extracts were not obtained, and vanadium extraction was only of the order of 10 per cent.

The results of the study of vanadium extraction suggest that the species of vanadium in solution is a more important factor than the actual concentration of vanadium in solution. If this is the case, the species may be quite responsive to acidity, and can, perhaps, be controlled thereby.

Control of solution and ether acidities appears to offer promise as one means of reducing the transfer of vanadium and molybdenum to the ether extract. Since silicon and phosphorus are also presumably being transferred as complexes with the vanadium and/or the molybdenum, optimum acidity conditions should likewise minimize the transfer of these components. It is expected that conditions of acidity will also have some influence on the ease with which these undesired components may be scrubbed from the extract. The extent of extract purification attainable by scrubbing is to be investigated, using principally the Scheibel continuous extractor. This work was temporarily postponed pending completion of the tributyl phosphate extraction studies with the Scheibel equipment.

Column-Extraction Tests

It is highly advantageous to supplement batch equilibration data with continuous, countercurrent column extraction tests, which more nearly reproduce actual plant operating conditions. The experiments herein reported were made with a Scheibel liquid-liquid extraction column that was available in this laboratory, using process slurries prepared from pitchblende and MgX as described in the Appendix.

The Scheibel extractor used here is a glass column approximately 1-inch inside diameter x 48 inches in height, containing 14 mixing sections, each consisting of a 4-bladed impeller on a common shaft, and 15 calming sections, each loosely packed with stainless steel wire. Openings are provided at the top and bottom for introduction and removal of the liquid phases; several alternative feed inlets are also provided part way up the column. The mixing shaft is driven by 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 25 p.s.i.g., the horsepower is correspondingly reduced, but is still ample to drive the stirrer at high speeds.

Some mechanical difficulties were met in standardizing the extraction procedure. Initially, gravity feed was employed for both the feed slurry and the organic solvent. The solid particles present in the slurry feed were large enough to prevent the use of a stopcock for regulating the feed rate. This difficulty was satisfactorily avoided by forcing the feed into the column by controlled air pressure. Due to the high specific gravity of the organic-uranium phase in the column, a higher head was required for gravity feeding of the organic extractant than the ceiling height permitted. The organic extractant was, therefore, converted to a gas-pressured (nitrogen) system with the rate of flow controlled by a needle valve. This arrangement has operated satisfactorily. Both the aqueous feed and the organic extractant are withdrawn from graduated containers and the volumes and flow rates are measured directly. A diagrammatic sketch of the equipment was shown in Figure 8 of BMI-246 (page 60).

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 9. These results indicated that, with an ether:feed ratio of 1.8:1.0, optimum operating conditions were a feed rate of about 1000 ml./hr., and a stirrer speed of 2500-3000 r.p.m. These tests were made with the ether phase continuous.

In an attempt to obtain longer contact times between the organic and aqueous phases, several tests were run with the Scheibel column in which the aqueous phase was continuous. Results of these tests are compared in Table 9 with similar ones, in which the organic phase was continuous. Phase separation was observed at several sections of the column. This separation was probably a result of the viscous nature of the feed, which prevented the uniform flow of ether through the column. Under these conditions, it is doubtful if the laboratory column can be relied on to reach a state of equilibrium. As a result of these tests, it was decided that all future runs should be made with the ether phase continuous.

It was suggested that longer calming sections would improve the operation of the column. For Tests Nos. 16 and 17, the column was modified so that the calming sections were increased about 50 per cent in length. This necessitated reducing the number of calming sections from 15 to 11, and the number of mixing sections from 14 to 10. Comparison of Tests Nos. 15 and 16 with 10 and 17, respectively, show that differences in results were negligible, and the column subsequently was changed back to the original design.

TABLE 9. CONTINUOUS EXTRACTION TESTS ON PROCESS SLURRIES IN A SCHEIBEL ONE-INCH EXTRACTION COLUMN

Column Operating Conditions

Slurry acidity = 60 g. excess acid/liter.
 Ether acidity = 60 g. HNO₃/liter.
 Ether temperature = 0-10°C.
 Feed temperature = 20-25°C.
 Feed introduced at top of column.

Run No.	Slurry Feed ⁽¹⁾			Contin- uous Phase	Number of Mechanical Stages	Ratio, Ether: Feed	Stirrer Speed, r.p.m.	Uranium	
	Slurry No.	U, g./l.	ml./hr.					In Raffinate, g./l.	Extracted, Per Cent ⁽²⁾
1	3	275	493	Ether	14	1.4:1	1300	20	94
2	3	275	465	Ditto	14	1.6:1	1300	14	95
3	3	275	596	"	14	1.4:1	1300	14	96
4	3	275	463	"	14	1.6:1	1300	14	95
5	6	270	523	"	14	1.7:1	1800	5	98
6	6	270	1066	"	14	1.5:1	1800	4.5	98
7	6	270	1840	"	14	1.8:1	1800	2.5	99
8	6	270	2850	"	14	2.2:1	1800	2.9	99
9	6	270	543	"	14	1.8:1	2500	6.7	98
10	6	270	938	"	14	1.7:1	2500	0.3	99.2
11	4	262	1980	"	14	1.8:1	2500	0.8	99.7
12	4	262	475	"	14	1.7:1	3400	10.3	96
13	4	262	1000	"	14	1.7:1	3400	3.7	99
14	4	262	1822	"	14	1.9:1	3400	0.6	99.8
15	4	262	433	Aqueous	14	1.8:1	2500	3.3	99
16	7	234	900	Ditto	10	2.1:1	2500	<0.1	>99.9
17	7	234	1000	Ether	10	2.0:1	2500	3.2	99.8

See page 30 for Footnotes.

Calculations have indicated that for standard operating conditions⁽¹⁾, using the column with 14 mixing sections, the column efficiency was about 40 per cent. No figures are available for the column with the modified 11-mixing-section arrangement.

Tributyl Phosphate Extraction

During a meeting at Mallinckrodt Chemical Works on October 2, 1950, it was decided that solvents other than ether, particularly tributyl phosphate, warranted consideration. Earlier work at Battelle Memorial Institute on the extraction of thorium and uranium from monazite sand⁽²⁾ and more recent work at other installations has shown that tributyl phosphate in the presence of a hydrocarbon diluent is an extremely effective solvent, and a preliminary investigation of its application to the problem of refining MgX and pitchblende was initiated. The scope of the investigation included only the application of tributyl phosphate to the contemplated direct-slurry-extraction process at Plant 6. The method of preparing a typical slurry is described in the Appendix.

Batch-Extraction Tests

Several batch extractions, using equal volumes of solvent and aqueous phase, were conducted on typical samples of pitchblende-MgX process slurry. The solvent was a 50:50, by volume, mixture of tributyl phosphate and a refined kerosene (Gulf Spray naphtha). The results of these tests, shown in Table 10, indicated that three equilibrations effectively removed over 99 per cent of the uranium.

-
- (1) 1000 ml. of feed/hr.; ether:feed ratio of 1.6:1; 3000-r.p.m. stirrer speed; 56°-Bé slurry; ether phase continuous.
 - (2) BMI-JDS-151, November 15, 1948.

TABLE 10. EXTRACTION OF URANIUM FROM PROCESS
SLURRY WITH TRIBUTYL PHOSPHATE

Tributyl phosphate - Gulfspray Naphtha⁽¹⁾ (50:50 by volume).
Equal volumes of organic and aqueous.
Agitation time = 1 minute.
Phase separation time = 1-1/2 minutes (approximately).
Temperature = 25 ±2°C.

Uranium in Feed, g./l.	Shakeout	Normality of HNO ₃		Distribution g./l.			Ext., Per Cent (2)	Metal Balance, Per Cent
		Org.	Aq.	Org.	Aq.	E _A ^o		
<u>Test No. 1</u>								
276	1	0.7	0.7	172	71	2.4		
	2	0.3	0.3	63	1.1	58		
	3	0.3	-	1.1	0.56	2.0	99.8	86
<u>Test No. 2</u>								
213	1	0.6	2.7	152	46	3.3		
	2	0.2	1.7	56	1.1	51		
	3	0.9	0.7	0.84	0.56	1.5	99.7	98
<u>Test No. 3</u>								
208	1	0.7	3.7	156	56	2.8		
	2	0.2	2.5	38	10.2 ⁽³⁾	3.7		
	3	1.2	1.3	0.32	0.48	0.7	99.8	93

(1) Gulfspray Naphtha is a highly refined kerosene fraction obtained from the Gulf Oil Company.

(2) Based on raffinate and feed analyses.

(3) This value appears quite questionable.

The extraction of uranium appeared to be a function of both acid and uranium concentrations. This confirms data obtained during the monazite investigation⁽¹⁾.

Spectrographic analyses of the extracts from the above tests showed the uranium to be of high purity, as illustrated by Table 11. The data indicated that maintaining total nitric acid concentration above 0.5N minimized the extraction of molybdenum.

Column-Extraction Tests

The promising results obtained on the preliminary batch extractions were confirmed by several continuous-extraction tests made with the Scheibel column. The results of these tests, tabulated in Table 12, show that control of total acidity and inclusion of a scrub of the extract are important factors in reducing the concentration of the contaminants in the uranium extract.

In Test No. 1, tributyl phosphate, diluted with an equal volume of naphtha, was the solvent. In another run, under the same conditions, attempts were made to scrub the extract with 0.5N nitric acid. Due to the slight difference in density between the scrub and the organic extract, the scrub rose to the top of the column. In order to overcome this difficulty, the solvent composition for the remainder of the tests was changed to a 30:70 ratio of tributyl phosphate to naphtha. This lower density solvent mixture had good operating characteristics, and permitted the use of a scrub.

(1) See Figures 6 and 7, BMI-JDS-225, February 15, 1950.

TABLE 11. SPECTROGRAPHIC ANALYSES OF URANIUM FROM BATCH
EXTRACTIONS WITH TRIBUTYL PHOSPHATE

Test No.	Shakeout No.	Uranium Basis, p.p.m.							
		Mo	V	Pb	Cu	Ni	Fe	Si	Mn
1 ⁽¹⁾	1	20-100	<20	<40	<10	<50	<20	8-40	<5
	2	>500	<20	<40	<10	<50	<20	8-40	<5
2	1	20-100	<20	<40	<10	<50	<20	40-200	<5
3	1	20-100	<20	<40	<10	<50	<20	8-40	<5

(1) See Table 10 for other data.



TABLE 12. CONTINUOUS-EXTRACTION TESTS ON PROCESS SLURRIES WITH A TRIBUTYL PHOSPHATE SOLVENT

Operating Conditions

Feed = 200-250 grams of uranium/liter.
 Solvent = 30 per cent tributyl phosphate - 70 per cent Gulf Spray Naphtha, except in Test No. 1.
 Temperature = 25 ±2°C.
 Stirrer speed = 2500 r.p.m.
 Point of entrance to column: scrub - top,
 feed = 5 mechanical stages below top.
 Organic phase continuous.

Test No.	Ratio Feed:Scrub: Organic	Feed, ml./hr.	HNO ₃ Normality			Raff. (1)	Raffinate U Conc., g./l.	Uranium	
			Feed (1)	Organic	Scrub			Ext., % (2)	Metal Bal., %
1(3)	1.0:-:1.1	960	4.1	0.0	None	3.5	0.02	>99.9	93
2	1.0:0.25:2.3	757	4.3	0.0	0.5	3.4	0.09	99.9	92
3	1.0:0.26:2.4	625	1.3	0.0	0.0(4)	1.0	0.49	99.8	100
4	1.0:0.21:2.4	840	1.3	0.34	0.0(4)	1.4	4.9	97.9	84

Test No.	Spectrographic Analyses Uranium Basis, p.p.m.											
	Mo	V	P	Cr	Co	Ni	Pb	B	Fe	Si	Cd	Cu
1	30(5)	90(5)	-	-	-	-	-	-	-	-	-	-
2	20-100	<20	N.D.	N.D.	N.D.	<50	<40	<1	<20	10-50	N.D.	<10
3	95	<20	<50	40	<20	<20	<10	<1	<20	25	<0.5	10
4	50	<20	<50	40	<20	<20	<10	<1	<20	25	<0.5	10

- (1) Excess HNO₃ expressed as normality.
- (2) Based on raffinate and feed analyses.
- (3) Solvent composed of tributyl phosphate and Gulf Spray Naphtha in ratio of 50:50 by volume of Test No. 1.
- (4) Water scrub.
- (5) Chemical analysis.

In all of the extraction tests reported above, substantial amounts of molybdenum were extracted along with the uranium. Consequently, the following tests were designed to reduce the extraction of molybdenum.

Effect of Acid Concentration in the Feed. Tests 1, 2, 3, and 4 (Table 13) 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.

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). This suggests a very organic-soluble molybdenum complex.

By replacing the water scrub with 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). Tests 7 and 8, 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.

TABLE 13. CONTINUOUS EXTRACTION TESTS ON PROCESS SLURRIES WITH A TRIBUTYL PHOSPHATE SOLVENT

Column Operating Conditions

Solvent = 30 per cent tributyl phosphate - 70 per cent wulfspray Naphtha.

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

Test No. 10 from Process Slurry No. 5268-95. Test No. 11 and 12 from Process Slurry No. 5501-2.

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 Extract, Per Cent
				Feed	Organic	Scrub	Raff.	Feed	Extract	Raff.	Mo	V	
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
2	1.0:0.25:2.6	5	800	2.5	0.0	H ₂ O	1.7	212	55	0.15	2.3	1.2	99.9
3	1.0:0.26:2.6	5	778	3.6	0.0	H ₂ O	2.9	196	84	0.12	2.1	1.1	99.9
4	1.0:0.25:2.5	5	800	4.7	0.0	H ₂ O	3.5	162	80	0.04	2.5	1.0	>99.9
5	1.0:0.27:2.5	10	775	3.8	0.0	H ₂ O	3.0	175	75	1.2	1.5	1.0	99.3
6	1.0:0.23:2.1	5	575	1.9	0.0	1.0	1.8	205	60	0.20	2.2	1.2	99.9
7	1.0:0.26:2.5	10	725	4.5	0.0	1.0	3.5	181	70	4.9	1.0	1.4	97
8	1.0:0.23:2.2	10	800	3.6	0.0	8.0	3.5	111	61	4.6	0.8	1.1	96
9	1.0:0.35:2.3	10	800	3.5	0.0	8.0	3.5	~200	98	---	0.0	0.0	---
10	1.0:0.22:1.1	10	751	4.5	0.0	1.0	3.9	223	79	33.6	1.6	1.2	58
11	1.0:0.00:1.3	5	900	4.1	0.0	None	4.0	194	110	37.3	1.5	1.1	81
12	1.0:0.17:1.2	5	900	4.1	0.0	6.0	4.3	194	89	41.9	1.5	1.1	76

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

Test No.	Mo	V	P	B	Cd	Cu	Si	Fe	Cr	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	>100	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	N.D.	40	1	<0.5	10	25	20	---	5-10	N.D.	---
9	---	---	---	---	---	---	---	---	---	---	---	---
10	20	<5	90	0.2	<0.2	10	<10	<10	<10	<2	<5	---
11	70	15	80	0.4	<0.5	---	45	55	---	---	40	---
12	20	<5	65	<0.5	<0.5	---	<0.2	15	---	---	<5	---

(1) Process Slurry No. 5583-6 prepared from Pitchblende A-192 and MgX P-32 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.

This could either be a result of the different feed composition or of the dependency of molybdenum extraction on the uranium concentration in the organic extract.

Test 11 shows the "back salting" effect of a nearly saturated organic phase. The addition of a 6N nitric acid scrub to Test 11 (see Test 12) materially reduced the concentration of the uranium contaminants. However, in view of the other tests shown in Table 13, it is doubtful whether a longer scrubbing section would remove the last trace of the molybdenum.

Test 9 was a blank determination which indicated that the molybdenum being dissolved from the stainless steel calming sections and agitators of the Scheibel column was negligible.

Recovery of Uranium From the Organic Extract

The organic feed used for the tests reported in Table 14 was non-equilibrium material from column-extraction experiments. Therefore, the molybdenum and vanadium analyses are higher than those reported in Table 13 for equilibrium material. Tests 1 and 2 indicate that significant amounts of molybdenum were stripped from the organic phase with the last traces of the uranium.

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

Table 14—RECOVERY OF URANIUM FROM THE ORGANIC EXTRACT

Column Operating Conditions

Feed* = 30 per cent tributyl phosphate-70 per cent Gulf Spray
Naphtha 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:		Feed, ml./hr.	Uranium, g./l.			Molybdenum [†] , p.p.m. parts U		Vanadium [†] , p.p.m. parts U		Uranium		Temp., °C.
	Extractant	Scrub		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 [‡]
4	1.0:0:1.1	None	1050	74	80(?)	1.7	255	225	275	100	97.8	100	70 [‡]
5	1.0:0.21:1.0	T.B.P.-G.S.N.	764	56	40	11.5	65	30 [§]	---	H.D. [¶]	79	92	25 ± 2

* Nonequilibrium material from extraction column; therefore, molybdenum and vanadium analyses are higher than those reported in Table 13.

† Determined by chemical analysis.

‡ Temperature of stream 5 mechanical stages above feed entrance.

§ Determined by spectrographic analysis.

¶ Introduced at bottom of column.



possible, hot strips were tried at 45°C. and 70°C. (Tests 3 and 4, Table 14). 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.

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 14) 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 Solubility

The approximate solubility of vanadium pentoxide in simple nitric acid solutions was determined. As shown by Table 15 and Figure 2, the solubility increased with increasing acid concentration, reaching a maximum in about 3N acid, but decreased with further increases in acid concentration. At the point of maximum solubility, the solution contained nearly 20 grams of vanadium per liter.

The filtrates from these equilibrated solutions were heated to 80-90°C. and held there for 24 hours. Any solid phase then present was filtered off and the filtrates re-analyzed. As illustrated by Table 15, although the solubility was slightly decreased in acid concentrations below 3N, the maximum solubility was still nearly 20 grams of vanadium per liter in 3N acid.

TABLE 15. 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./l.	Vanadium Concentration After Heating ⁽¹⁾ , g./l.
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 .

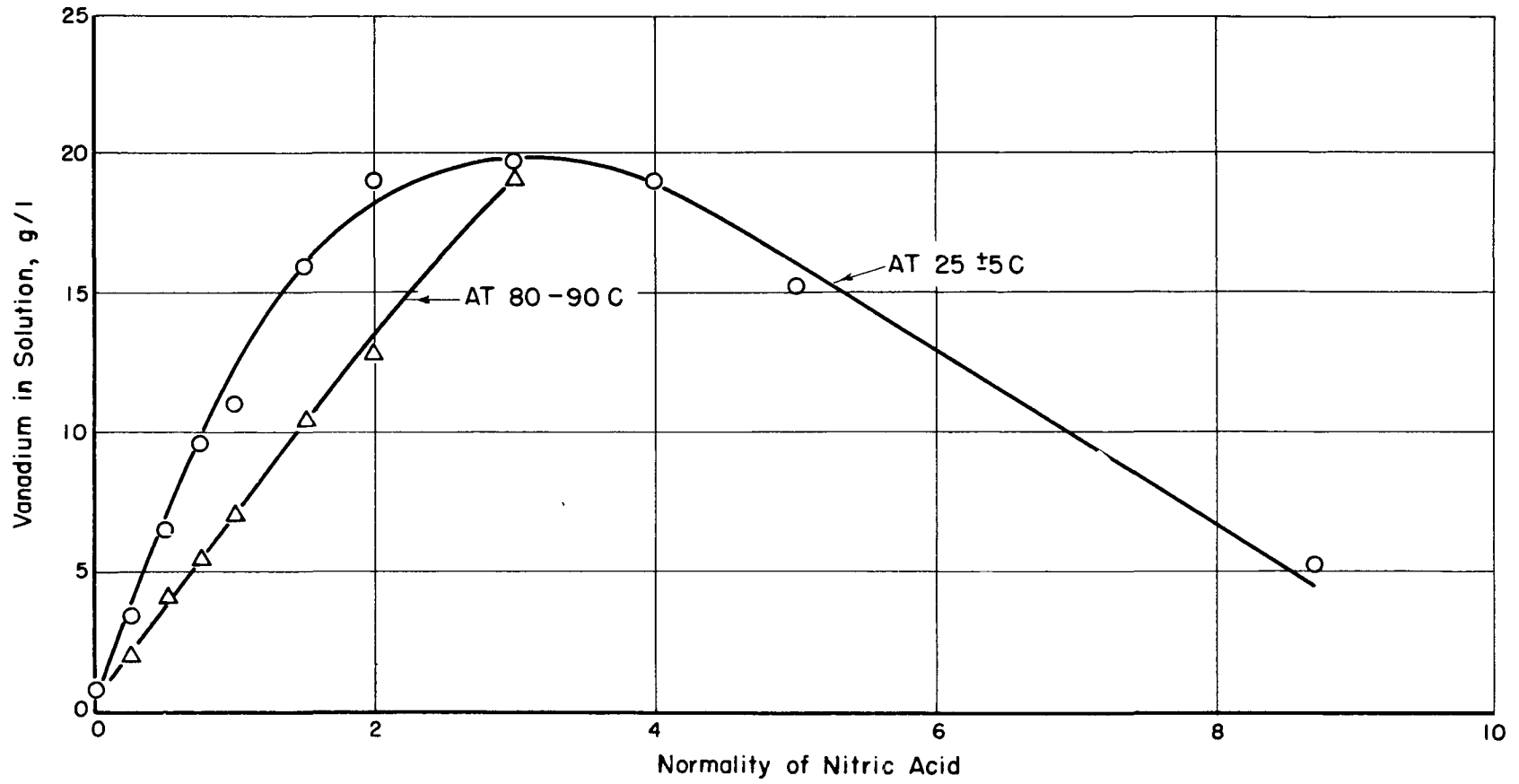


FIGURE 2. SOLUBILITY OF VANADIUM PENTOXIDE IN NITRIC ACID SOLUTIONS

The effects of solution acidity on the solubility of vanadium pentoxide, uranyl vanadate, and sodium uranyl vanadate in process solution have been studied, over the range from zero to 270 grams of excess acid/liter. The test results are presented in Table 16 and Figure 3. In contrast to its behavior in a simple nitric acid system, vanadium pentoxide was soluble only to the extent of about 1.6 grams of vanadium per liter, over the entire range. The explanation for the difference is at present not apparent. The solubility of sodium uranyl vanadate and uranyl vanadate increased with increasing acidity, although at acid concentrations above 2N, both appeared to level off at about 8.5-9.0 grams of vanadium/liter.

The data indicate that, where a more acid process feed is feasible (as with tributyl phosphate extraction), it should be possible to tolerate larger amounts of vanadium-bearing uranium compounds in the feed.

Analysis of Boil-Down Precipitate

During the concentration of MgX solutions to the desired specific gravity for ether extraction, a slight quantity of a reddish-brown "boil-down" precipitate is often obtained, which is essentially a vanadium precipitate. The original assumption was that uranium was also a constituent and that uranium losses to this precipitate might be excessive. Further study of the nature of this precipitate indicated, however, that it is primarily a compound of iron, vanadium, phosphorous, and calcium, with uranium present only as a minor constituent. Analyses of two such precipitates were as follows:



TABLE 16. EFFECT OF SOLUTION ACIDITY ON THE SOLUBILITY OF VANADIUM COMPOUNDS IN PROCESS SOLUTION(1)

Procedure: Excess solid phase was equilibrated with process solution by shaking mechanically for 140 hours at room temperature (25 ±5°C.).

Original XS Acid, g./l.	Analyses of Equilibrated Filtrates							
	No Sulfate Removed				Pitchblende Sulfate Removed(2)			
	Grams/Liter		V, as %		Grams/Liter		V, as %	
	XS Acid	U	V	of U	XS Acid	U	V	of U
<u>Vanadium Pentoxide</u>								
0	2	214	1.45	0.68	3	215	1.54	0.72
30	34	214	1.49	0.70	28	226	1.59	0.70
60	50	207	1.64	0.79	62	236	1.61	0.68
120	121	206	1.60	0.78	118	228	1.69	0.74
179					153	213	1.76	0.83
224					205	218	1.73	0.79
298					272	204	1.52	0.75
<u>Sodium Uranyl Vanadate(3)</u>								
0	0	224	1.21	0.54	3	210	0.38	0.18
30	19	218	4.17	1.91	9	238	1.57	0.66
60	40	220	4.28	1.95	46	240	4.18	1.74
120	100	234	5.00	2.14	97	224	4.92	2.20
179					109	262	9.0	3.4
224					142	236	8.2	3.5
298					215	237	8.7	3.6
<u>Uranyl Vanadate(3)</u>								
0	5	204	1.26	0.62	1	222	1.28	0.58
30	22	208	1.67	0.80	24	218	1.73	0.79
60	51	208	2.39	1.15	58	221	2.44	1.10
120	103	206	4.18	2.03	102	236	4.46	1.89
179					147	204	8.6	4.2
224					208	228	8.2	3.6
298					267	212	8.7	4.1

- (1) Process solution (No. 5269-87B) prepared with 2/3 of U derived from pitchblende Blend A-1 and 1/3 derived from MgX Blend B-1.
- (2) Sulfate precipitated from pitchblende digest liquor before combining with MgX solution.
- (3) Preparation and analysis of these compounds is described on pages 75-76 of BMI-246.

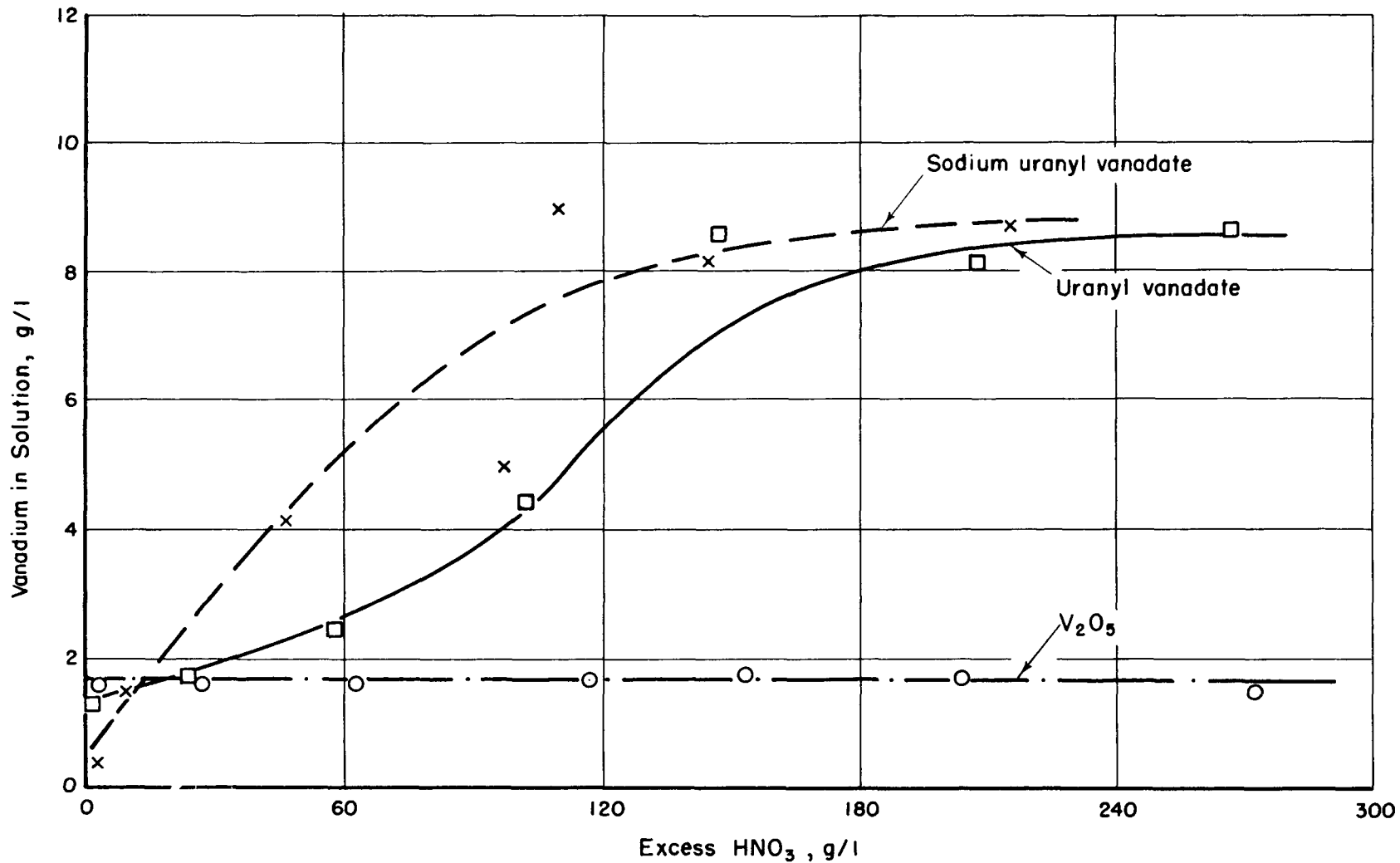


FIGURE 3. SOLUBILITY OF VANADIUM COMPOUNDS IN PITCHBLENDE-MgX PROCESS SOLUTION AT 25 C



	Analysis, Fer Cent			
	Boil-Down Precipitate		Original MgX	
	P-92(2)	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
CaO	2.2	0.5 ⁽¹⁾	0.43	0.71
U	0.36	1.7	39.4	33.3

(1) Total alkaline earth oxides.

(2) Spectrographic analysis of other constituents of this precipitate:

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

In both precipitates, the iron, phosphorous, and vanadium were in good balance for a mixed precipitate of ferric phosphate and ferric vanadate. Since the boil-down precipitate did not carry down any significant quantity of uranium, it was thought that it would be possible thus to tie up much of the vanadium in a non-ether-soluble form, prior to the ether extraction step, by deliberately forming such a precipitate. This proved to be entirely feasible. However, as described earlier (Table 8), vanadium extraction was equally as high when 1/3 to 2/3 of the vanadium was present as a precipitate, as when all of the vanadium was in solution.

Molybdenum Solubility

Some preliminary tests have been conducted to examine the behavior of molybdenum in pitchblende solutions. In connection with a series of dissolutions of A-1 pitchblende made during the preparation of

feed slurries for tributyl phosphate-extraction tests, 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. of excess acid. The molybdenum content of the filtrates ranged from 5-7 grams/liter. At room temperature, these filtrates appeared to be quite stable; no precipitation of molybdate was observed on standing a month. However, on adjusting portions of filtrate to varying levels of excess acid and digesting, a yellow precipitate, apparently uranyl molybdate, was formed. The quantities obtained from 100-ml. samples of filtrate were as follows:

<u>Excess Acid, g./l.</u>		<u>Precipitate</u>			<u>Filtrate</u>
<u>Before</u>	<u>After</u>	<u>Wt.,</u>	<u>Mo,</u>	<u>U,</u>	<u>Mo,</u>
<u>Digestion</u>	<u>Digestion</u>	<u>mg.</u>	<u>mg.</u>	<u>mg.</u>	<u>g./l.</u>
0	0	514	117	223	4.2
36	24	411	217	147	3.9
53	42	193	40	77	5.7
110	83	99	4.7	6.2	6.0
210	160	672*	3.1	6.6	5.6

* Principally a crystalline sulfate.

The data indicate that the original pitchblende filtrate (53 g./l. excess acid) was supersaturated with respect to molybdenum, as were all filtrates of lesser acidities. Digestion at higher excess acidities appeared to produce no serious loss of uranium.

Study of the Constitution of MgX

X-Ray Diffraction Tests

Attempts were made to determine the constitution of MgX by X-ray diffraction methods. Samples of actual and synthetic, laboratory-prepared MgX, both dried and ignited, were examined. All of the oven-dried MgX samples were amorphous, and identification of the phases was not possible.

The synthetic MgX samples were ignited (800°C.) and analyzed chemically, with the following results:

	<u>Per Cent</u>						
	<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	Nil	1.4	12.4	10.6
E6-10-2	48.1	7.3	3.0	Nil	0.8	12.2	11.8
E6-10-3	40.3	8.9	2.6	6.8	1.4	10.2	13.8

Re-examination of the ignited samples by X-ray diffraction disclosed the presence of a common major phase, designated as "X", which was unidentifiable. As shown in Table 17, the same major phase was common to the ignited samples of P-88 and P-92 MgX. The pattern of the original lot of MgX (Lot P-1) was unlike that of P-88 and P-92, although also unidentifiable by available diffraction data. Table 17 also shows the results of examining samples of uranyl phosphate and uranyl vanadate.

Fractional Precipitation of MgX

In another approach towards obtaining more information on the constitution of MgX, fractional precipitation from a dilute sulfuric acid solution of MgX was utilized.

TABLE 17. PHASE IDENTIFICATION OF MgX SAMPLES FROM X-RAY DIFFRACTION DATA

Sample	Description	Phases Present
EC-10-1	Synthetic MgX precipitate	Amorphous
EC-10-2	Ditto	Amorphous, trace Mg(OH) ₂
EC-10-3	"	Amorphous, trace Mg(OH) ₂
EC-10-1 ignited(1)	"	X ⁽²⁾ , trace Fe ₃ O ₄
EC-10-2 ditto	"	X ⁽²⁾ , trace Fe ₃ O ₄ , MgO
EC-10-3 "	"	X ⁽²⁾ , trace fused (Cu) ₃ (PO ₄) ₂ , MgO
P-88	MgX precipitate	Amorphous
P-92	Ditto	Amorphous
P-88 ignited	"	X ⁽²⁾
P-92 ditto	"	X ⁽²⁾
P-1 "	"	Crystalline(3)
5269-92A	Synthetic uranyl vanadate	Crystalline(3)
5269-92B	Ditto	Ditto
5597-2A (ignited)	Synthetic uranyl phosphate	"
5597-2B (ditto)	Ditto	"
4268-741	Fe-V boil-down precipitate	"

(1) Ignited at 800°C.

(2) X-phase is an unidentified crystalline phase.

(3) Phase is not identifiable by available diffraction data.



A dilute (5 per cent) sulfuric acid solution of P-1 MgX was prepared which contained approximately 5 grams/liter of uranium, simulating the pregnant solution from which the MgX was originally precipitated. On filtration, a clear amber-colored solution was obtained (this solution was still clear after standing several months). The insoluble residue from the dissolution step amounted to 2.1 per cent of the original sample. Spectrographically, it was found to consist chiefly of iron, silicon, and magnesium. A 500-ml. portion of the filtered solution was neutralized step-wise with one-molal ammonium hydroxide, at room temperature. Precipitates were filtered off at four pH levels, 2.7, 4.5, 5.7, and 6.5. The analyses of these precipitates are shown in Table 18 and graphically in Figure 4. The data indicate that most of the phosphate precipitated with the iron; the first precipitate appeared to be mainly ferric phosphate. The second precipitate (pH 4.5) was high in silicon and aluminum, suggesting the possibility of an aluminum silicate. The final precipitate (pH 6.5) was mainly uranium, 60 per cent. The bulk of the vanadium was found in the last two precipitates.

The test was repeated with a larger portion (2000 ml.) of the same solution of P-1 MgX, in order to permit sharper pH cuts. The results, presented in Table 19 and Figure 5, confirmed those of the first test for the most part. Precipitates were filtered off at pH levels 2.6, 4.2, 4.7, 5.7, 6.5, and 8.0. The precipitate at pH 2.6 again appeared to be essentially ferric phosphate. As in the first test, there was a sharp break between the first two precipitates; no precipitation occurred after removal of the ferric phosphate precipitate until a pH of approximately 4.0 was reached. The character of the precipitate at

TABLE 18. 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.

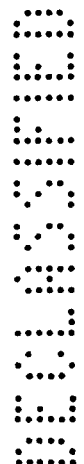


TABLE 19. COMPOSITION OF PRECIPITATES FROM A FRACTIONAL PRECIPITATION FROM A DILUTE SULFURIC ACID SOLUTION

pH of Precipitation	Precipitate ⁽¹⁾ Weight, mg.	Millimoles						
		U	Fe	Al	SO ₄	Si	P	V
2.6	1192	0.24	7.62	<0.04	0.23	0.04	5.19	0.20
4.2	2766	0.56	4.36	2.86	1.08	27.75	1.71	0.04
4.4	2137	0.31	1.41	16.91	6.55	2.14	0.58	0.04
4.75	1884	0.54	0.57	14.76	5.71	1.53	0.26	0.02
5.7	11570	36.1	0.38	<0.45	5.58	0.96	0.68	1.90
6.5	2336	5.64	-(2)	0.59	0.56	0.07	-(2)	1.51
8.0	10± ⁽²⁾	-	-	-	-	-	-	-

(1) Precipitates from 2000 ml. of solution (equivalent to approximately 40 grams of F-1); ignited at 600°C.

(2) Not analyzed.



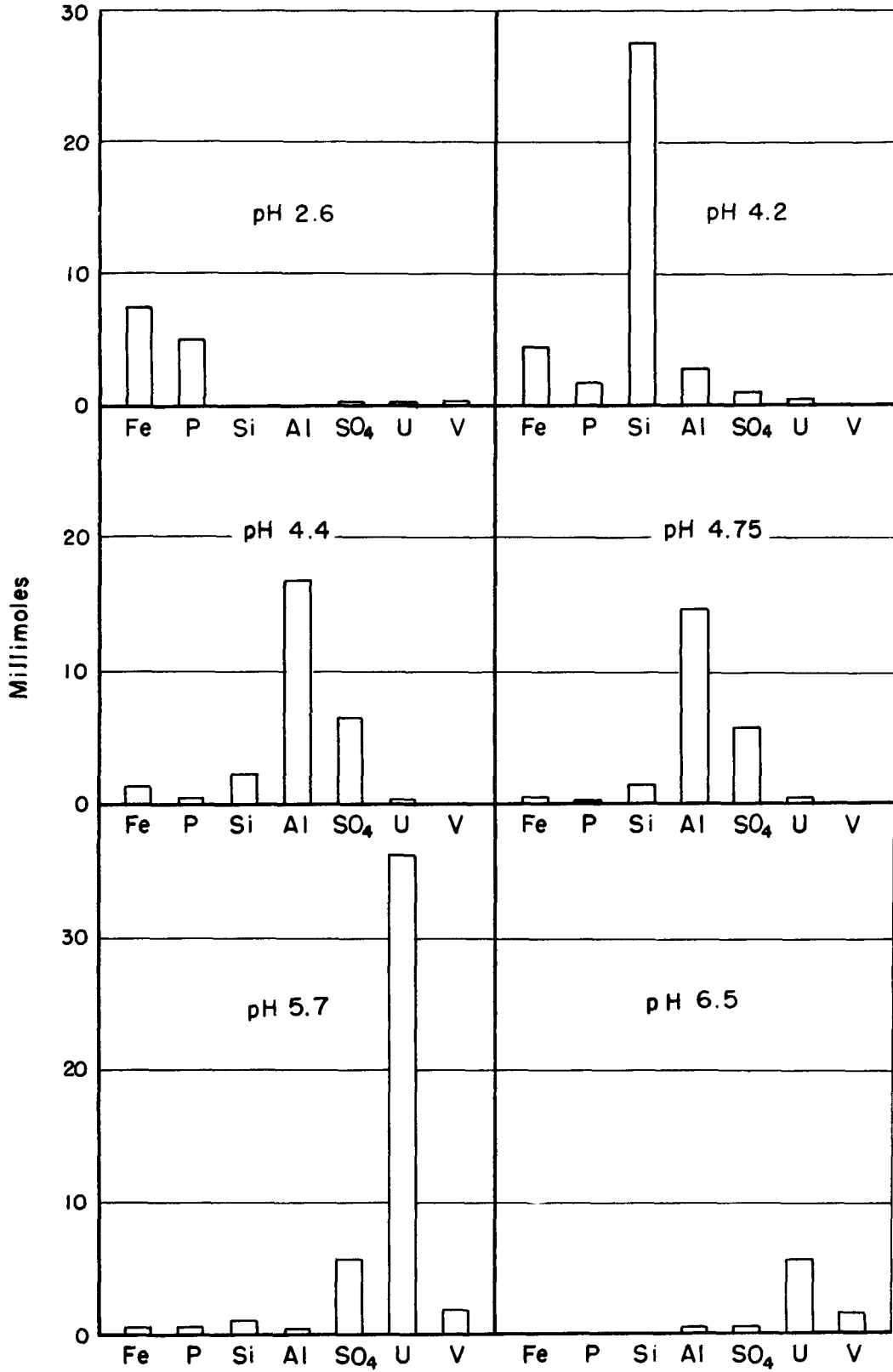


FIGURE 5. COMPOSITION OF PRECIPITATES OBTAINED BY A FRACTIONAL PRECIPITATION OF MgX FROM DILUTE SULFURIC ACID



pH 4.2 in the second test was quite different from the one at pH 4.5 in the first test, both in physical appearance and in filtration characteristics. It appeared to consist primarily of silica, which was borne out by the analytical data. Sulfate analyses were obtained on the second set of precipitates. Inspection of the results indicates that basic sulfates of aluminum and uranium were precipitated. The bulk of the vanadium appeared in the precipitates at pH 5.7 and 6.5. It is of interest to note that this is the pH range in which artificial carnotite precipitates.

The data from both tests suggest that uranyl phosphate is unlikely to be formed during the original precipitation of MgX, at least from solutions 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	65-100
5269	81-100
5270	84-100
5531	1-36
5581	1-3
5583	1-35
5597	1-29



APPENDIX

Method of Preparation of Process Slurries

The same general procedure was followed in preparing process slurries and solutions for batch-and column-extraction tests. The following description of the preparation of Slurry No. 5583-8 is typical of the procedure used throughout:

Three 1200-gram batches of unground pitchblende ore were dissolved in sufficient hot, 45 per cent nitric acid to produce a slurry containing 40-60 g./l. of excess acid (1500 ml./1200 grams of A-192 in the case of Slurry No. 5583-8). The slurry was digested for 3 hours at 180-190°F. and immediately filtered. The digest cake from each 1200-gram batch was washed with two 100-ml. portions of 1-2 per cent nitric acid, the washings being combined with the filtrate. No sulfate precipitation was made.

Three 1120-gram batches of P-92 MgX were dissolved in sufficient 45 per cent nitric acid (at room temperature) to produce a slurry containing approximately 40-60 g./l. of excess acid (1500 ml./1120 grams of P-92 for Slurry No. 5583-8). This slurry was digested for 3 hours, with continuous stirring, with no heat added. The three MgX slurries were combined and added to the combined pitchblende filtrates and washings to produce Slurry No. 5583-8. The excess acid of

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the final slurry was 65 g./l.; the specific gravity, which required no boiling down to attain, was 1.624 (60°F.).

The same procedure, except that relatively greater quantities of nitric acid were used, was followed in preparing Process Slurry No. 5583-15 and others derived from Fitchblende Blend A-1 and MgX Blend B-1. Slurries more acid than 1N were prepared by boiling down a standard 40-60 g./l. excess acid slurry such as that above, and making up to the original volume with concentrated nitric acid, so that uranium concentration was maintained approximately constant.

All Scheibel tests were made on process slurries. In the case of process solutions, used for solubility tests and for some of the batch-extraction tests, the same general procedure was followed, except that the solids were filtered from the MgX slurry before combining the MgX with the pitchblende filtrate.



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