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QUARTERLY PROGRESS REPORT

on

REFINING OF MgX AND OTHER URANIUM-BEARING MATERIALS

by

R. A. Ewing
S. J. Kiehl, Jr.
R. E. Sharpe
A. E. Bearse

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ABSTRACT

Results are presented which suggest the possibility of satisfactorily extracting uranium from pitchblende feeds with neutral ether, without the necessity of removing sulfate, by the addition of a sufficient quantity of iron to the feed.

The effect of adding minimal quantities of iron on extraction with neutral ether was investigated for a number of MgX feeds, with and without V-20 soda salt added.

The effect of temperature on extraction of uranium with a Scheibel column was studied and qualitatively evaluated.

Arsenic was traced through both primary and secondary extraction stages in two tests; results indicate that arsenic is satisfactorily rejected by a two-stage extraction, even from feeds relatively high in arsenic content.

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INTRODUCTION

This report describes the work performed from July 1, 1951, to September 30, 1951, on problems associated with the use of MgX and other feed materials at the Plant 6 uranium refinery operated for the A.E.C. by Mallinckrodt at St. Louis. Previous work has been reported in BMI-250, BMI-253, and BMI-254.

Emphasis during the period was on exploring the possibilities of a neutral-ether primary extraction, by the addition of iron to complex unwanted and interfering components of the feed. It was shown that the addition of iron could eliminate the need for the barium precipitation of sulfate from pitchblende feeds. However, large quantities of iron are necessary to accomplish this, and the economic feasibility is still open to question.

The addition of moderate quantities of iron (10 to 20 g./l.) to either MgX or pitchblende digest filtrate (sulfate removed) made extraction with neutral ether entirely feasible. At 20 g./l. of added iron, raffinates consistently equalling or bettering those with acid ether were obtained. Transfer of molybdenum and phosphate to the extract was substantially reduced — for certain, rather unusual feeds, the reductions were striking. Transfer of vanadium with neutral ether appeared generally lower than with acid ether, although some anomalous results were obtained. The over-all reduction was such that scaling and precipitation problems should be materially reduced in a neutral re-extraction system, where neutral ether and iron are used for the primary extraction.

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SUMMARY

Test results show that it is possible to obtain satisfactory raffinates by a neutral-ether primary extraction of pitchblende feeds, without removal of sulfate, by the addition of sufficient iron to the feed. Addition of the iron at the ore-dissolution step is inadvisable, since the effectiveness of a given quantity of iron is materially reduced by the unavoidable losses of iron leaving the system with the digest cake. In addition, the iron tends to solubilize unwanted components, particularly lead sulfate, further reducing the effectiveness of the iron, and also promoting carry-over of radioactive components to the column feed.

Addition of iron in a 1:1 molar ratio to the sulfate (added to the digest filtrate) appeared to produce a satisfactory raffinate (0.11 g./l. of U), but gypsum scaling did not appear to be entirely overcome.

Increasing the ratio of iron to sulfate to 2:1 reduced the uranium content of the raffinate to 0.01 g./l. and gypsum scaling appeared to be eliminated. The data indicated that a ratio of 1-1/2:1 might be feasible, but this would have to be demonstrated, on larger scale equipment. The chemical costs at a 2:1 ratio were calculated to be comparable to the chemical costs of barium sulfate precipitation; the over-all costs are thus estimated to be of the same order as those of precipitation.

One feature of the pitchblende-iron tests was the low molybdenum content of extracts from feeds high in molybdenum. The results indicated that precipitation of uranyl molybdate in the digest cake could be avoided,

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without jeopardizing the quality of the extract. This might have practical significance, since absence of uranyl molybdate in the digest cake could lead to a substantial improvement in the efficiency of the C-3 process.

Study of the behavior of a high-molybdenum MgX (Lot P-163) confirmed the results obtained when this lot was extracted at Plant 6. Using acid ether, extremely high molybdenum contents were found in the extract, and this molybdenum was essentially unscrubbable (up to 4000 p.p.m. in the scrubbed extract). Using neutral ether for the primary extraction, the molybdenum transfer was much reduced, although still relatively high, and the uranium content of the raffinate was doubled. With neutral ether and 20 g./l. of iron added to the feed, the uranium loss to the raffinate decreased to 0.11 g./l., and the scrubbed extract contained only 10 p.p.m. of molybdenum. The use of neutral ether, plus iron, appeared to be very effective on an MgX feed of this type.

In connection with the study of V-20 soda salt feed materials, it was shown that straight V-20 could be satisfactorily extracted with neutral ether, with iron and a salting agent added to the feed. Iron in stoichiometric equivalency to the total sulfate, phosphate, and vanadate appeared to be ample.

The arsenic associated with V-20, as such, does not appear to pose a problem in the refining of uranium. Mixed feeds containing normal percentages of V-20 were "spiked" with additional arsenic and extracted. No consistent increase in the amount of uranium lost to the raffinate was

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found with increasing arsenic content, though the arsenic content of the extract did increase. However, two neutral re-extraction tests indicated satisfactory rejection of arsenic, even from NOK liquor which was high in arsenic. The indications of these tests were that arsenic could probably be tolerated in V-20 at levels of at least up to 5 per cent (uranium basis) without causing difficulty at Plant 6.

In connection with the proposed larger scale tests at Plant 6 on neutral-ether extraction, a number of MgX feeds from different lots were tested at ^{1e}iron-addition rates embracing the probable practical plant range. Although addition of ^{1e}iron at the rate of 10 g./l. gave satisfactory results for some lots of MgX, this rate was insufficient for others. Addition of iron to the extent of 20 g./l. (0.167 lb./gal.) proved to be sufficient for all MgX feeds tested. This was true even when V-20 was also incorporated into the feed. Since the Scheibel column, as used here, with 12 mechanical stages, appears to be somewhat less efficient than the Plant 6 column, it seems probable that satisfactory raffinates may be attainable in the plant at iron addition rates less than the 20 g./l. required for the 12-stage Scheibel column.

A study of the degree of reproducibility of results attainable with the Scheibel column confirmed the importance of temperature on the extraction of uranium by ether. Differences in column temperature of no more than 10°F. were found to cause wide variations in raffinate assays. Approximate temperature control during Scheibel column tests was maintained by control of incoming-ether temperature, plus some external

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cooling of the column. Complete control would require the use of a jacketed column. The test data indicated that results could be adequately reproduced with a Scheibel column, where temperatures were held constant.

In connection with the addition of iron to pitchblende feeds, the effect of ~~iron~~ on calcium solubility was determined approximately. Although the results were not consistent, due primarily to analytical difficulties in the calcium assays, they showed that calcium solubility increased with increasing iron. At a 1:1 ratio of ~~iron~~:sulfate, for example, 5-10 g./l. of calcium could be held in solution, even after removal of the uranium.

EXPERIMENTAL DETAILS AND DISCUSSION OF RESULTS

Extraction Studies

Effect of Iron Addition on Pitchblende Feed

Iron, due to its complexing action, appeared to be a possible substitute for the relatively costly precipitation of sulfate from pitchblende feeds with barium. Pitchblende Blend A-2 was used for the test work exploring this possibility; this pitchblende assayed about 13 per cent sulfate, and the sulfate content of the digest (Feinc) filtrate assayed approximately 95-100 g./l. SO_4 , or about 1 mol/liter. The effect of adding iron was tested at three molar ratios of iron to sulfate: 2:3, 1:1, and 2:1. In one series of tests, the iron was introduced at the ore-dissolution step; in the other, it was added to the digest filtrate. Extraction was with neutral ether in all cases.

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Where the iron was added at the ore-dissolution step, the digest filtrates had extremely high molybdenum contents; dissolution of the molybdenum appeared to be virtually complete. The high molybdenum contents in these tests are attributed to the complexing action of the iron, although it is known that such factors as high digestion acidity and low digestion temperature may also result in high molybdenum contents of digest filtrates.

Suppression of the normal precipitation of uranyl molybdate resulted in low uranium and molybdenum contents in the digest cakes. Analyses of several thoroughly washed digest cakes illustrate the effect of adding iron at the pitchblende-dissolution step:

Solution No.	Iron Added, g./l.	Digest Cake, Per Cent. Dry Basis			Digest Filtrate, g./l. Mo
		U	Mo	Fe	
23	0	2.2	1.8	0.8	0.5
17	20	0.7	0.96	0.8	5.5
18	50	0.05	0.07	0.9	6.6
22	120	0.11	0.09	1.2	5.0

Addition of the iron at this point is subject to two serious objections. At the rates of iron addition required to produce acceptable raffinates, lead sulfate also tends to be solubilized. In the test in which iron was added at a 2:1 molar ratio to the sulfate, a fine white crystalline precipitate was observed in the extraction raffinate, which spectrographic analysis indicated was essentially lead sulfate. Tests on

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the precipitate showed it to be strongly radioactive. The possibility of having radium distributed throughout the extraction system argues against the introduction of the iron at the ore-dissolution step. The other objection to the introduction of iron at this point is that all of the iron is not effectively utilized in the extraction. Some is diverted to such unprofitable uses as solubilizing the lead sulfate; more important is the actual physical loss with the mother liquor carried out by the digest cake, which would be lost in the subsequent C-3 treatment.

The summarized results of the effect of iron on the neutral extraction of straight pitchblende feeds are as follows:

Run No.	Fe Added, g./l.	<u>Digest Filtrate</u>		Raffinate, U, g./l.	<u>Scrubbed Extract,</u> <u>p.p.m. (U Basis)</u>			<u>Scaling</u>
		<u>Mo,</u> <u>g./l.</u>	<u>U,</u> <u>g./l.</u>		<u>PO₄</u>	<u>Mo</u>	<u>V</u>	
<u>Iron Added to Ore</u>								
94	0	5.75	256	49.3	605	6460	315	Heavy
116	0	0.48	-	57.5	<10	4	80	Heavy
93	20	5.45	246	15.9	35	485	35	Slight
98	40	6.20	224	11.1	<10	20	8	Very slight
99	60	6.38	220	1.7	<10	4	15	Very slight
100	120	5.00	173	0.024	<15	3	20	Negligi- ble

<u>Iron Added to Digest Filtrate</u>								
95	40	4.9*	220	1.4	<10	7	40	Very slight
96	60	4.6*	205*	0.11	<15	3	20	Very slight
97	120	3.8*	170*	0.012	<15	5	30	Negligi- ble

* Calculated values.

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The initial blank test with no iron (Run 94) showed extremely high transfer of molybdenum. Scrub distribution coefficients for both the PO_4 and Mo were >1 , indicating a phospho-molybdate complex of high ether solubility. The molybdenum content of the pitchblende feed liquor was high (5.75 g./l.), presumably as a result of excessive acidity during digestion, or an unduly low digestion temperature, both of which factors have been shown earlier to suppress the precipitation of uranyl molybdate. A duplicate batch of feed was prepared, with these factors corrected, which assayed only the normal 0.5 g./l. of molybdenum. Extraction of this feed with neutral ether produced only the normal transfer of contaminants (Run 116).

The addition of one-half the stoichiometric requirement of iron (1 mole Fe to 3 moles SO_4) to the ore was insufficient, although the uranium content of the raffinate and the transfer of contaminants were both markedly reduced (Run 93). The addition of iron to the ore in stoichiometric equivalency to the sulfate (2 moles Fe to 3 moles SO_4) (Run 98) was effective in minimizing transfer of contaminants. Scaling was very slight in this test; the stainless steel column packing and agitator appeared to acquire a dull gray cast, rather than a definite scale. Increasing the iron to 50 per cent excess above stoichiometric (1 mole Fe to 1 mole SO_4) (Run 99) gave similar results, with a lower uranium content in the raffinate.

Adding iron at the ore-dissolution step in 100 per cent excess above stoichiometric (Run 100) appeared to eliminate scaling, and produced a raffinate containing only 0.02 g./l. of U. However, the raffinate

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precipitate from this test was radioactive, indicating the presence of radium.

Where the iron was added to the digest filtrate, the uranium content of the raffinate was much lower than in the corresponding test where the same quantity of iron was added at the ore-dissolution step. The addition of iron at 50 per cent above stoichiometric (Run 96) produced a raffinate containing only 0.11 g./l. of U; with the addition of a 100 per cent excess, the raffinate contained 0.012 g./l. of U. In comparison, the same pitchblende feed, without iron, but with sulfate removed, produced raffinates containing 0.18-0.22 g./l. of U, when extracted with neutral ether (Runs 67 and 103). In all three tests with added iron, transfer of contaminants was low. Details of the iron-pitchblende tests are shown in Table 1.

The exceptionally low transfer of molybdenum from column feeds containing from 4-6 g./l. of molybdenum is of interest. The indications of the pitchblende tests are that molybdenum can be rejected with the raffinate, and that rejection as uranyl molybdate in the digest cake is hence not a prerequisite for low molybdenum contents in the extract. Carrying the molybdenum through to the raffinate would minimize the load on the C-3 process.

Raffinate precipitates were filtered off in several of the tests and analyzed spectrographically, with the following results:

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TABLE 1. EXTRACTION OF URANIUM FROM PROCESS FEEDS WITH A SCHEIBEL COLUMN (1)

Run No	Feed Used (2,3)	U, g./l.		Excess Acid, g./l.			Raff. pH	Run No	p.p.m. (Uranium Basis)								Scrub Distribution Coeff, E_A^0 (6)				
		Raff.	Ext.	Feed	Ether	Ext.			Unscrubbed Extract				Scrubbed Extract (4)				Scrub Distribution Coeff, E_A^0 (6)				
									PO ₄	Mo	V	As	PO ₄	Mo	V	As	PO ₄	Mo	V	As	U
93	PB + 20 g./l. Fe (to ore) [PB17]	15.9	112	30	Neut.	20	0.8	93	35	395	60	--	35	485	35	--	0.28	1.3	0.08	--	0.31
94	PB alone [PB19]	49.3	100	37	Neut.	20	0.9	94	475	5060	270	--	605	6460	315	--	1.4	1.4	0.6	--	0.27
95	PB + 40 g./l. Fe (to filt) [PB19]	1.4	103	34	Neut.	26	0.6	95	<20	20	55	--	<10	7	40	--	(0.1)	0.04	0.13	--	0.32
96	PB + 60 g./l. Fe (to filt) [PB19]	0.11	96	34	Neut.	31	0.5	96	<20	10	50	--	<15	3	20	--	(0.1)	0.03	0.04	--	0.32
97	PB + 120 g./l. Fe (to filt) [PB19]	0.012	78	34	Neut.	39	0.1	97	<20	15	65	--	<15	5	30	--	(0.1)	0.04	0.06	--	0.33
98	PB + 40 g./l. Fe (to ore) [PB20]	11.1	108	33	Neut.	18	0.5	98	<15	25	25	--	<10	20	10	--	(0.1)	0.11	0.04	--	0.27
99	PB + 60 g./l. Fe (to ore) [PB21]	1.7	108	37	Neut.	33	0.4	99	<15	15	35	--	<10	4	15	--	(0.1)	0.03	0.05	--	0.34
100	PB + 120 g./l. Fe (to ore) [PB22]	0.024	83	40	Neut.	43	0.4	100	<20	10	45	--	<15	3	20	--	(0.1)	0.03	0.04	--	0.35
101	PB alone (SO ₄ out) [PB14]	0.043 (5)	125	34	0.6 N	57	10 g./l.	101	60	170	70	--	20	195	40	--	0.04	1.4	0.08	--	0.41
102	MgX alone [MgX14]	0.34	76	32	0.6 N	53	0 g./l.	102	190	370	835	--	70	400	110	--	0.04	0.7	0.01	--	0.44
103	PB alone (SO ₄ out) [PB14]	0.22	117	34	Neut.	17	0.9	103	25	15	60	--	5	12	30	--	0.02	0.17	0.06	--	0.33
104	V-20 + Mg (NO ₃) ₂	11.6	134	72	Neut.	39	0.2	104	2300	<2	1080	1430	450	<1	170	300	0.02	(0.1)	0.01	0.02	0.48
105	MgX alone (filtrate) [MgX14]	0.38	102	32	Neut.	24	0.3	105	35	50	315	--	10	45	40	--	0.04	0.28	0.011	--	0.35
106	P-163 (filtrate)	0.063 (5)	127	33	Neut.	21	0.7	106	30	320	140	--	25	350	30	--	0.13	0.55	0.02	--	0.36
107	V-20 + Mg(NO ₃) ₂ + Fe (1:1 mol ratio)	0.015 (5)	104	54	Neut.	37	--	107	<15	<3	1040	<35	<10	<2	80	<20	(0.1)	(0.1)	0.007	--	0.40
108	V-20 + Mg(NO ₃) ₂ + Fe (2:1 mol ratio)	0.006	97	50	Neut.	40	0.3	108	<15	<3	950	<35	<10	<2	60	<20	(0.1)	(0.1)	0.006	--	0.45
109	PT-2 (filtrate)	0.26 (5)	94	36	Neut.	25	0.4	109	<20	40	385	--	<10	35	45	--	(0.1)	0.23	0.01	--	0.34
110	MgX + V-20 + As (2 x As) [MgX24]	0.69 (5)	115	30	Neut.	22	0.4	110	15	15	440	<40	10	10	30	<10	(0.1)	0.07	0.005	(0.2)	0.31
111	MgX + V-20 + As (4 x As) [MgX24]	0.64	104	30	Neut.	21	0.4	111	35	10	325	<70	15	6	35	<20	0.1	0.08	0.008	(0.03)	0.30
112	MgX + V-20 + As (10 x As) [MgX24]	1.50 (5)	111	34	Neut.	26	0.4	112	<130	7	300	<145	<10	4	35	<10	0.04	0.07	0.009	(0.01)	0.29
113	MgX + V-20 + As (2 x As) [MgX24]	0.44	113	30	0.6 N	42	--	113	80	125	455	250	35	125	70	275	0.06	0.37	0.01	0.62	0.37
114	MgX + V-20 + As (4 x As) [MgX24]	0.50	106	30	0.6 N	45	5 g./l.	114	240	85	380	<60	30	85	40	<10	0.01	0.38	0.10	(0.1)	0.39
115	MgX + V-20 + As (10 x As) [MgX27]	0.55	118	34	0.6 N	46	2 g./l.	115	290	45	405	<100	45	35	65	110	0.02	0.20	0.02	(0.1)	0.38
116	PB - SO ₄ in (check Run 94) [PB23]	57.5 (5)	108	34	Neut.	12	0.8	116	<20	10	85	--	<10	4	80	--	(0.1)	0.04	0.22	--	0.25
117	PB - SO ₄ in (10% Scheibel scrub) [PB23]	84.1	88	34	Neut.	25	0.7	117	<20	<4	<25	--	<15	<3	25	--	(0.1)	(0.1)	(0.2)	--	0.20
118	P-163 (filtrate)	0.014	120	33	0.6 N	46	4 g./l.	118	280	2420	325	--	240	2620	230	--	0.25	3.5	0.14	--	0.46
119	PB + V-20 (diss. W/ore) (check Run 70) [PB26]	1.04 (5)	136	36	Neut.	18	0.7	119	<80	10	35	<45	<10	6	10	<8	(0.01)	0.08	0.02	(0.02)	0.32
120	MgX + 20 g./l. Fe (check Run 84) [MgX25]	0.163	92	31	Neut.	28	0.3	120	<20	<10	410	--	<15	<3	20	--	(0.1)	(0.03)	0.004	--	0.31
121	P-163	0.54	124	31	Neut.	28	0.5	121	80	620	300	--	75	650	65	--	0.27	0.46	0.02	--	0.36
122	P-163	0.23	137	31	0.6 N	44	2 g./l.	122	285	3460	655	--	325	4120	430	--	1.0	1.9	0.11	--	0.39
123	P-163 + 10 g./l. Fe	0.22 (5)	121	32	Neut.	23	0.1	123	20	110	310	--	10	115	50	--	(0.1)	0.13	0.01	--	0.33
124	P-163 + 20 g./l. Fe	0.11 (5)	109	31	Neut.	28	0.1	124	<15	15	310	--	<10	10	40	--	0.12	0.46	0.01	--	0.32
125	P-163 + V-20	0.81 (5)	122	34	Neut.	22	0.2	125	60	330	275	<15	30	320	45	<10	0.06	0.29	0.01	(0.1)	0.32
126	P-163 + V-20	0.25 (5)	129	34	0.6 N	47	7 g./l.	126	275	2260	575	50	230	2680	300	30	0.19	1.7	0.07	0.07	0.39

Footnotes on next page.

FOOTNOTES

- (1) One-inch x 6-foot Scheibel column; 12 mechanical stages; agitator speed, approximately 3300 r.p.m.; ether phase, continuous; specific gravity about 56° Baumé. Feed rate, approximately 1500 ml./hr.; ether/aqueous ratio, 2/1.
- (2) Feeds prepared from A-2 blend of pitchblende; B-2 blend of MgX and V-2 blend of V-20 soda salt. Analyses of numbered feeds were as follows:

Soln. No.	Description	Component, g./l.						
		U	Mo	V	SO ₄	PO ₄	Fe	As
PB14	PB alone	247	0.90	0.41	0.28	3.74	5.24	--
MgX14	MgX alone	163	0.97	2.42	34.9	14.4	13.5	--
PB17	PB + 20 g./l. Fe (to ore)	246	5.45	--	--	--	19.3	--
PB18	PB + 50 g./l. Fe (to ore)	223	6.60	--	--	--	36.6	--
PB19	PB alone	256	5.75	--	--	--	5.3	--
PB20	PB + 40 g./l. Fe (to ore)	224	6.20	--	--	--	30.4	--
PB21	PB + 60 g./l. Fe (to ore)	221	6.38	--	--	--	39.4	--
PB22	PB + 120 g./l. Fe (to ore)	173	5.00	--	--	--	64.3	--
PB23	PB alone	--	0.48	--	--	--	--	--
MgX25	MgX alone	133	1.04	2.29	--	15.7	--	--
PB26	PB + V-20 (to ore)	284	1.58	0.64	--	3.37	--	--
MgX27	MgX + V-20 + 10 x As + NG	220	0.81	2.60	--	12.1	--	2.71

- (3) All MgX tests in this series included 140 ml. of NG liquor (600 g. of U/l.) / 1000 ml. of MgX (simulating a recycle of approximately 25 per cent of plant uranium throughput).
- (4) Ten per cent batch-wise scrub.
- (5) Precipitate in portion of raffinate was filtered off, and, solid and liquid phases were separately analyzed for uranium:

Run No.	Uranium, g./l.			
	Raff. Ppt. Sample			Equilibrium
	Solid Phase	Liquid Phase	Total	Raff. Sample
101	0.004	0.05	0.05	0.04
106	0.003	0.07	0.07	0.06
107	0.007	--	--	0.02
109	0.02	0.23	0.25	0.26
110	0.12	0.57	0.69	0.69
112	0.30	0.92	1.22	1.50
116	1.2	51.5	52.7	57.5
119	0.57	0.46	1.03	1.04
123	0.01	0.18	0.19	0.22
124	0.002	0.08	0.08	0.11
125	0.01	0.79	0.80	0.81
126	0.005	0.25	0.25	0.25

- (6) Figures in parentheses indicate approximate distribution coefficients

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Run No.	Constituent, Per Cent							
	Fe	Ca	Mo	V	Pb	Na	P	
95	5-25	10-50	1-5	0.05-0.5	0.1-1	0.1-1	1-5	} Al, Mg, Si, Mn, Ti, Ni, Co, Cu all <0.1 per cent
96	10-30	10-50	1-5	0.05-0.5	0.1-1	0.1-1	1-5	
97	10-30	0.1-1	1-5	0.01-0.1	0.1-1	0.1-1	1-5	
100	-	-	-	-	Majority	-	-	

The raffinate precipitates represented only small percentages of the total weight of raffinate.

Extraction of Uranium From V-20 Soda Salt

Earlier tests had indicated that incorporation of V-20 soda salt into a column feed adversely affected uranium extraction. As a part of the study of V-20 soda salt, several neutral extraction tests were made on straight V-20 feed. V-20 soda salt (Blend V-2) was dissolved in nitric acid, and the very slight (<0.5 per cent) acid-insoluble fraction, containing only negligible amounts of vanadium and uranium, was filtered off. The combined washings and filtrates were boiled down to gravity, and the resultant slight precipitate also was filtered off. The appearance and analysis of this precipitate indicated that it was probably a mixture of uranyl vanadate and vanadium pentoxide. Magnesium nitrate was added (ca. 900 g./l. of $Mg(NO_3)_2 \cdot 6H_2O$) as the salting agent, diluting the V-20 solution from its original 300 g. of U/l. level to about 200 g./l.

Extraction of the straight V-20 feed with neutral ether produced a raffinate containing 11.6 g./l. of U. During the test, a heavy precipitate formed in the column, which spectrographic analysis showed consisted chiefly of uranium and vanadium. The phosphate content of Blend V-2 was 1.15 per cent, the sulfate content - 5.3 per cent, and

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the vanadium content - 1.5 per cent, all on a uranium basis. Addition of iron in a 1:1 molar ratio to these components (approximately 20 g./l. of Fe) reduced the raffinate to 0.015 g. of U/l. Increasing the iron ratio to 2:1 reduced the raffinate to 0.006 g. of U/l. In the latter two tests, a reddish-brown mirror formed on the column walls, which spectrographic analysis indicated consisted primarily of ferric vanadate.

The addition of iron also either reduced the transfer of contaminants (phosphate and arsenic) or rendered them more scrubable (vanadium), as shown in the following summary (for other details see Table 1):

Run No.	Mole Ratio* of Added Iron	Raff., U, g./l.	p.p.m. in Extract (U Basis)							
			Unscrubbed				Scrubbed			
			PO ₄	Mo	V	As	PO ₄	Mo	V	As
104	0	11.6	2300	<2	1080	1430	450	<1	170	300
107	1:1	0.015	<15	<3	1040	<35	<10	<2	80	<20
108	2:1	0.006	<15	<3	950	<35	<10	<2	60	<20

* Mole ratio of iron to phosphate, sulfate, and vanadate.

Torbernite MgX

Only one test (Run 109, Table 1) was made on torbernite MgX (Blend PT-2). No appreciable differences were observed in uranium content of the raffinate or in contaminant transfer from usual MgX lots. Spectrographic analysis of the raffinate precipitate, however, showed that it contained, in addition to the elements usually found, appreciable percentages of Ca, Ni, and Mo.

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Effect of High Molybdenum Content in MgX

The usual MgX appears to contain about 0.1 per cent of molybdenum, or less. Lot P-163 had, however, a much higher molybdenum content, 0.45 per cent. Considerable difficulties were reported with molybdenum carry-over when this lot was processed at Plant 6, and a sample of this lot was studied in the laboratory in order to observe more closely the behavior of high-molybdenum MgX.

A batch of P-163 slurry was prepared according to the usual procedure. This was filtered, to provide clear filtrate for the preliminary tests. Upon boiling down the combined filtrate and washings to gravity, precipitation occurred. Analysis of the precipitate indicated that it was essentially uranyl vanadate. This was the first MgX boil-down precipitate of this composition obtained here; all of the previous ones have appeared to consist of ferric phosphate and ferric vanadate, with very little uranium. Approximately one per cent of the uranium in the solution and approximately 45 per cent of the vanadium were carried out by the precipitate. Extraction of this feed with neutral ether produced a raffinate containing 0.063 g./l. of U (Run 106). The total loss, including that lost to the MgX boil-down precipitate, was calculated to represent approximately 2.5 g./l. of U. Molybdenum transfer was high and the scrub K_d was >0.5 , so that the scrubbed extract contained 350 p.p.m. of Mo (on a uranium basis). Extraction of the same feed with 0.6N ether (Run 118) gave an unscrubbed extract containing 2220 p.p.m. of Mo, and a scrub K_d of 3.5, indicating that the molybdenum was virtually unscrubbable.

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An additional quantity of P-163 slurry was prepared. Digestion was kept at a minimum, in order to minimize the possibility of uranyl vanadate precipitating. When this feed was extracted with neutral ether (Run 121), the raffinate contained 0.54 g./l. of U. Molybdenum transfer was again high. Extraction with 0.6N ether (Run 122) reduced the uranium content of the raffinate to 0.23 g./l., but the molybdenum content of the unscrubbed extract reached 3460 p.p.m. (U basis); the scrub K_d was 1.9. Presumably, this is about the same situation that was encountered when P-163 was extracted with acid ether in the plant.

The addition of 10 g./l. of iron to the slurry reduced the uranium in the raffinate to 0.22 g./l., and reduced the Mo in the unscrubbed extract to 110 p.p.m. (U basis) (Run 123). The addition of 20 g./l. of iron further reduced the raffinate to 0.11 g./l. of U, and the extract to only 15 p.p.m. of Mo (Run 124). The use of iron and neutral ether appears to be extremely effective on troublesome feeds such as P-163.

The effect of adding V-20 to P-163 feed was studied in two tests, using MgX slurry (Runs 125 and 126). With neutral ether, the uranium content of the raffinate increased from 0.54, in the absence of V-20, to 0.81 g./l.; the increase with 0.6N ether appeared negligible.

The summarized results of the P-163 tests are as follows (for other details, see Table 1):

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Run No.	Ether	Additive(1)	Raff., U, g./l.	p.p.m. in Extract (U Basis)					
				Unscrubbed			Scrubbed		
				PO ₄	Mo	V	PO ₄	Mo	V
<u>P-163 Filtrate(2)</u>									
106	Neutral	-	0.06	30	320	140	25	350	30
118	0.6N	-	0.01	280	2220	325	240	2620	230
<u>P-163 Slurry</u>									
121	Neutral	-	0.54	80	620	300	75	650	65
122	0.6N	-	0.23	285	3460	655	325	4120	430
123	Neut.	10 g./l. Fe	0.22	20	110	310	10	115	50
124	Neut.	20 g./l. Fe	0.11	<15	15	310	<10	10	40
125	Neut.	V-20	0.81	60	330	275	30	320	45
126	0.6N	V-20	0.25	275	2260	575	230	2680	300

(1) N.G. liquor added in all tests.

(2) After removal of MgX boil-down precipitate.

Effect of Arsenic in MgX Feeds

Earlier hand-shakeout tests had indicated that arsenic did not adversely affect uranium extraction, and that present arsenic levels in V-20 soda salt could probably be permitted to increase without experiencing difficulties. This was investigated further in a series of Scheibel column tests in which V-20 was added to a B-2 MgX feed, plus sufficient additional arsenic (added as sodium arsenate) to raise the arsenic level in the feed to 2, 4, and 10 times that obtained upon the addition of usual percentages of V-20 to the feed. When these high-arsenic feeds were extracted with neutral ether (Runs 110, 111, and 112) arsenic transfer was low, and it was readily scrubbed, so that the scrubbed extract contained <20 p.p.m. arsenic. Increasing the arsenic level appeared to have no effect on uranium loss to the raffinate (the

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high result in Run 112 is discounted as being a result of high column temperatures, described elsewhere in this report).

The transfer of arsenic was somewhat greater when the three feeds were extracted with 0.6N acid ether. Although the results were not entirely consistent, the arsenic appeared to be less readily scrubbed from acid ether.

Results of the arsenic tests are contained in Table 1; the highlights are summarized below:

Run No.	As Level	Raff., U, g./l.	p.p.m. in Extract (U Basis)							
			Unscrubbed				Scrubbed			
			PO ₄	Mo	V	As	PO ₄	Mo	V	As
<u>Neutral Ether</u>										
110	x2	0.69	15	15	440	<40	10	10	30	<10
111	x4	0.64	35	10	325	<70	15	6	35	<20
112	x10	1.5	<130	7	300	<145	<10	4	35	<10
<u>0.6N Acid Ether</u>										
113	x2	0.44	80	125	455	250	35	125	70	275
114	x4	0.50	240	85	380	<60	30	85	40	<10
115	x10	0.55	290	45	405	100	45	35	65	110

Neutral Re-Extraction Tests Involving Arsenic

In order to better follow the path of arsenic through the neutral extraction to OK liquor, two neutral batch extractions were performed on arsenic-containing NOK liquor. In the first test, a quantity of primary extract (NOK liquor) was "spiked" with approximately 900 p.p.m. of arsenic (added as sodium arsenate). This was added during the initial stages of boiling down while the excess acidity was still high; it went into solution readily. Upon further boiling down, NOK precipitates were

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observed. Three successive precipitates were filtered off; the analyses were as follows:

	<u>Component, Per Cent (Dry Basis)</u>			
	<u>U</u>	<u>V</u>	<u>Mo</u>	<u>As</u>
Precipitate I	60.8	6.9	0.02	3.8
Precipitate II	58.0	3.7	0.02	4.8
Precipitate III	61.1	3.2	<0.01	9.3

The arsenic contained in these boil-down precipitates represented about 1/4 of that added to the NOK liquor. These were the first NOK boil-down precipitates to contain significant percentages of arsenic. Presumably these were high in arsenic as a result of the abnormally high arsenic level in the NOK liquor.

The results of the neutral re-extraction test are summarized in Table 2. They show an effective rejection of arsenic, even from a feed containing in excess of 600 p.p.m. The extraction K_d for arsenic was 0.013; the scrub K_d was 0.082. The arsenic content of the scrubbed extract (one five-per-cent batch scrub) was 15 p.p.m.

In a second test, the arsenic "spike" was added to the MgX column feed, in order to permit the formation of any possible heteropoly arsenic complexes which might be more difficult to reject. The arsenic content of the column feed for the primary extraction was about 1.25 per cent on a uranium basis, or approximately 5-10 times that obtained upon the normal rate of addition of V-20. This feed was used for Run 115 (0.6N ether), which was extended several hours to provide sufficient extract for a neutral re-extraction test. Analysis of a sample of the

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TABLE 2. NEUTRAL RE-EXTRACTION OF NOK FEED "SPIKED" WITH ARSENIC⁽¹⁾

	Total, mg.					p.p.m. (U Basis)			
	U	Mo	V	PO ₄	As	Mo	V	PO ₄	As
Boil-down ppt. I (2.895 g.)	1760	0.6	20	-	110				
Ditto II (1.440 g.)	835	0.3	5.3	-	69				
" III (1.970 g.)	<u>1205</u>	<u><0.2</u>	<u>6.3</u>	<u>-</u>	<u>183</u>				
Total	3800	<1.1	31.6	-	362				
NOK feed (after BD ppt.)	1,670,000	60.4	45.5	73.7	1070	36	27	44	642
<u>Neutral Re-Extraction</u>									
OK extract	1,194,000	2.8	21.0	3.0	18	2.3	17.6	2.5	15
Scrub ⁽²⁾	147,500	5.3	1.1	2.7	11	36	7.5	18.3	75
Raffinate	<u>268,100</u>	<u>56.5</u>	<u>31.0</u>	<u>37.5</u>	<u>1057</u>	211	115	140	3980
Total mg. found	1,609,600	64.6	53.1	43.2	1086				
Extraction K _d						0.072	0.356	0.08	0.013
Scrub K _d						0.026	0.95	0.05	0.082

(1) Approximately 1300 ml. of warm NOK liquor ("spiked" with arsenic) was extracted with chilled neutral ether (2:1 ratio).

(2) Five per cent batch-wise scrub.

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unscrubbed extract from Run 115 indicated <100 p.p.m. of arsenic. Analysis of the NOK liquor itself indicated about 200 p.p.m. of arsenic, however. The arsenic balance tended to support the latter value.

The results of this neutral re-extraction test are shown in Table 3. As in the previous test, they indicate effective re-jection of arsenic. The extraction K_d was 0.019; the scrub K_d was 0.15; and the arsenic content of the scrubbed OK liquor was 7 p.p.m.

In all three neutral re-extraction tests performed here, vanadium has been the most difficult contaminant to reject, and has been the largest single contaminant in the OK extract.

The contaminant levels in the OK extracts prepared here have been, in general, somewhat higher than would be anticipated from a plant-scale continuous neutral re-extraction. On this basis, it appears that arsenic can probably be tolerated in V-20 at levels of up to 5 per cent (uranium basis) without causing difficulty at Plant 6, where the proportion of V-20 feed is not markedly increased above present levels. Or, an arsenic content of 1.25 per cent (U basis) in the feed is still below the point at which the arsenic content of OK liquor becomes excessive.

Effect of Temperature on Extraction of Uranium With a Scheibel Column

Run 115 was extended beyond the normal length of run (1000 ml. of feed) in order to provide sufficient NOK extract for a neutral re-extraction test, and to provide data on the reproducibility of Scheibel results. Approximately 3 liters of feed was extracted the first day; the run was continued the following day and an additional 5 liters of

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TABLE 3. NEUTRAL RE-EXTRACTION OF NOK FEED CONTAINING ARSENIC

	U	Total, mg.				P.P.M. (U Basis)			
		Mo	V	PO ₄	As	Mo	V	PO ₄	As
Run 115 - unscrubbed extract ⁽¹⁾						45	405	290	<100
Boil-down ppt. (9.249 g.)	5,560	-	560	280	130				
NOK feed (after BD ppt.)	1,552,000	84	83	332	357	54	53	210	230
<u>Neutral Re-Extraction⁽²⁾</u>									
OK extract	1,077,000	<1	30	<0.5	7.5	<1	28	<0.5	7
Scrub ⁽³⁾	130,000	3.8	3.6	2.3	2.5	30	30	20	20
Raffinate	309,000	81	84	358	265	260	270	1160	86.5
Extraction K _d						<0.03	0.20	0.004	0.019
Scrub K _d						<0.01	0.47	0.01	0.15

- (1) NOK feed was unscrubbed extract from Run 115. Feed for primary extraction contained 200 g./l. of U and 2.7 g./l. of As. Extracted with 0.6N ether (2:1 ratio).
- (2) Approximately 1275 ml. of NOK liquor was extracted with neutral ether at room temperature (2:1 ratio).
- (3) Five per cent batch-wise scrub.

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feed was extracted. Raffinate samples were taken over the last 100-200 ml. of each liter of feed. The analyses of the raffinate samples were as follows:

<u>Date</u>	<u>Raff. Sample</u>	<u>U. g./l.</u>
7/18/51	115-1	1.00
	-2	0.65
	-3	0.40
7/19/51	115-4	0.55
	-5	0.39
	-6	0.12
	-7	0.13
	-8	0.15
Raffinate composite		0.60

Although the indicated reproducibility was poor, a definite downward trend to a plateau toward the end of the run was evident.

Consideration of the variations suggested that temperature, an uncontrolled variable, was the most likely cause. As ambient temperatures had increased seasonally, it had become necessary to cool the ether in order to minimize boiling of the ether and to prevent vapor locks in the column. Initially, an ice-bath in the ether feed line was used. With further increases in ambient temperatures, this did not furnish sufficient cooling, and a dry ice-acetone bath was substituted. Also, a small cup was formed about the column, several inches above the feed plate; dry ice placed in this cup assisted in minimizing the boiling

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of the ether extract in the top of the column. In Run 115, the column was rapidly filled with ether (the continuous phase) to start; very little cooling of the ether occurred and the column temperature was at a relatively high level at the beginning of the run. At the normal ether flow rates (2000 ml./hr.) during the run proper, effective cooling was obtained, and the ether left the cooling coil at from -5 to -25°F. Presumably, the column cooled down as the run progressed, thus reducing the uranium content of the raffinates.

The effects of temperature on the distribution of uranium between ether and aqueous phases are known to be significant. In some of the early project literature, it was reported that, in a pure system, where uranium concentrations were in the 135-240 g./l. range, reducing the temperature from 79 to 55°F. approximately doubled the distribution coefficient.

The effects of temperature on Scheibel results were explored in a limited investigation in which a series of tests at various ether temperatures were made on aliquots of one feed solution. Temperatures of the column were measured by thermometers inserted through the available openings; one at the fifth stage below the feed plate and one at the fifth stage above the feed plate. The temperature of the ether at the cooling-coil exit was also measured. The data, summarized in Table 4, show, in a semi-quantitative way, the variation in raffinate assay with temperature.

The column temperature at the fifth stage below the feed plate appeared to be the most significant of those measured. A plot of this

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TABLE 4. EFFECT OF TEMPERATURE ON EXTRACTION OF URANIUM FROM A PROCESS SOLUTION IN A SCHEIBEL COLUMN(1)

Run No.	U in Raff., g./l.	Temperature, °F. (2)			Remarks
		Ether	Below Feed Plate	Above Feed Plate	
128A	0.39	-20 to -40	76-78	57-62	Ether cooled by dry ice-acetone bath.
	0.29	-20 to -40	77-78	56-58	
	0.22	-20 to -40	77-78	58	
	0.31	-20 to -40	77-78	58	
128-B	0.28	37-61	79-81	55-58	Dry ice-acetone bath replaced by water-ice bath
	0.54	59-61	81-84	58-62	
	0.60	61-64	85-86	60	
	0.62	64	86	60	
	0.72	79	80-83	62-64	Ice bath removed.
	0.80	81	83-85	61-63	
131	0.43	77	78-80	60-63	Ether at room temperature.
	0.48	77-79	80-81	63-71	
	0.51	79	81-82	71-75	
	0.55	79	83	76	
	0.55	79	83	77	
132	0.19	-22 to -31	74-75	80-83	Ether cooled by dry ice-acetone.
	0.19	-31 to -35	75-76	79-80	Minimum cooling above feed plate.
	0.29	-22 to -31	74-76	79-80	
	0.18	-22 to -31	74-75	80-82	
	0.20	-18 to -31	74-78	80-82	
	0.22	-22 to -31	77-78	81-82	
133	0.41	5-26	80-83	84-86	Start with cold ether.
	0.64	25-39	83-84	84-85	Cooling removed and ether temperature allowed to increase. Minimum cooling above feed plate.
	0.51	50-59	83	80-82	
	1.8	81-84	90-91	90-91	
	2.3	84	90	88-90	
	1.2	84	88-89	86-87	
134	0.61	77-73	83-85	88-89	Start with ether at room temperature. Cooling coil then immersed in dry ice-acetone bath and ether temperature progressively reduced.
	0.63	73-32	84	85-88	
	0.37	-7 to -24	82-83	69-78	
	0.36	-34 to -42	76-78	62-67	
	0.37	-36 to -42	72-74	62	
	0.31	-36 to -40	72-74	60	
	0.25	-36 to -40	72-73	58-60	
	0.22	-36 to -40	72-73	54-58	

See next page for Footnotes.

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TABLE 4. (CONTINUED)

Footnotes

- (1) One-inch x six-foot Scheibel column; twelve mechanical stages; agitator speed, approximately 3300 r.p.m.; ether phase, continuous; neutral ether at 2:1 ratio.
- (2) Temperature range during period raffinate sample was being withdrawn.

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temperature against the raffinate assay is shown in Figure 1. For plotting purposes, the column was assumed to be at temperature equilibrium over the period when the raffinate sample was being collected, although this was not strictly true, since the temperatures were changing progressively. Inclusion of these non-equilibrium points considerably increased the spread of the results. However, a consistent correlation of raffinate assay and column temperature was apparent.

The results indicate that temperature is an important variable with respect to uranium content of Scheibel raffinates, and that raffinate assays may vary widely with a change in temperature of no greater than 10°F. However, they indicate further, that, at a constant temperature, good reproducibility of results may be attained with the Scheibel column. The inlet temperature of the ether may be controlled quite satisfactorily. The actual column temperature is more difficult to control, since the rate of dissipation of the heat of reaction depends largely on the ambient temperature, which is not subject to control. A jacketed column would be desirable for a higher degree of precision.

Column temperatures were recorded for subsequent Scheibel tests, and were controlled to as near a constant temperature as was possible, subject to the ambient-temperature limitations described above. With respect to the previous Scheibel tests, fortunately the standard operating procedure which was used minimized the possibility of gross temperature variations, so that, in most cases, the results were comparable. Undoubtedly some of the anomalous results obtained occasionally can be traced to this cause.

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FIGURE I. URANIUM CONTENT OF RAFFINATE VERSUS TEMPERATURE OF SCHEIBEL COLUMN, FIVE STAGES BELOW FEED PLATE

Effect of Iron Addition on MgX Feeds

In anticipation of planned larger scale extraction tests with neutral ether and added iron at Plant 6, a number of Scheibel column tests were made to examine the behavior of various lots of MgX and their response to differing rates of iron addition. Extraction procedures have been described in previous reports. The principal change was that temperatures were controlled as closely as possible, although some variations were still experienced. Each MgX feed was extracted with 0.6N acid ether, neutral ether, and with neutral ether plus varying amounts of added iron in the aqueous feed. Detailed results are shown in Table 5, which also includes data from earlier tests previously reported. The uranium results are summarized below:

MgX Used	Uranium in Raffinate, g./l.					
	Acid Ether, 0.6N	Neutral Ether				
		No Added Fe	5 g./l. Fe	10 g./l. Fe	20 g./l. Fe	30 g./l. Fe
B-1 Blend	0.68	0.98		0.91	0.58	
B-2 Blend	0.34	0.46		0.24	0.13	
P-88	0.15	0.58		0.17	0.11	
P-92	0.27	1.12		0.32	0.16	
P-75	0.31	- (1)	0.42	0.16	0.15	0.21(2)
P-163	0.23	0.54		0.22	0.11	
PT-2 Blend	0.22	0.46		0.49	0.17	

- (1) Inoperable with neutral ether in absence of added iron; raffinate plugged bottom of column.
- (2) Average column temperatures were slightly higher (4-5°F.) than for corresponding tests at 10 and 20 g./l. Fe, overcoming the benefits of the increased iron level.

TABLE 5. EXTRACTION OF URANIUM FROM MgX FEEDS WITH A SCHEIBEL COLUMN (1)

Run No.	Feed Used (2)	U, g./l.		Fe Added, g./l.	Excess Acid, g./l.				pH	p.p.m. (U Basis)						Scrub Distribution Coeff., E_A^0 (5)			
		Raff.	Ext.		Feed	Ether	Ext.	Raff.		Unscrubbed Extract			Scrubbed Extract ⁽³⁾			Scrub Distribution Coeff., E_A^0 (5)			
										PO ₄	Mo	V	PO ₄	Mo	V	PO ₄	Mo	V	U
140	B-1 MgX	0.98	92	--	30	Neut.	23	--	0.6	<50	<5	80	<15	<3	40	(0.02)	0.07	0.06	0.27
141	B-1 MgX	0.66	104	--	30	0.6 N	49	0	0.0	160	20	115	25	8	75	(0.01)	0.05	0.11	0.45
142	B-1 MgX	0.91	94	10	37	Neut.	28	--	0.5	25	<6	110	<10	<2	70	(0.05)	(0.04)	0.09	0.33
143	B-1 MgX	0.58	95	20	32	Neut.	30	--	--	<20	<3	600	<10	<3	45	(0.1)	(0.2)	0.006	0.32
166	B-1 MgX	0.39	96	30	34	Neut.	33	--	0.4	<20	<5	660	<10	<1	65	(0.1)	(0.02)	0.009	0.36
144	P-88 MgX	0.58	102	--	48	Neut.	28	--	0.5	175	10	50	25	2	35	0.01	0.02	0.12	0.30
145	P-88 MgX	0.15	104	--	48	0.6 N	59	0	0.0	320	40	70	45	30	50	0.01	0.15	0.15	0.44
146	P-88 MgX	0.17	105	10	44	Neut.	33	--	0.5	<25	<6	275	<10	<2	35	(0.06)	(0.04)	0.01	0.36
147	P-88 MgX	0.11	103	20	46	Neut.	21	--	0.1	<20	<8	360	<10	<2	45	(0.1)	(0.03)	0.01	0.35
148	P-92 MgX	0.10 (4)	119	--	33	Neut.	27	--	0.5	<15	55	290	<10	45	30	0.08	0.2	0.09	0.36
149	P-92 MgX	0.27	122	--	38	0.6 N	49	4	--	135	290	365	45	300	95	0.04	0.5	0.03	0.43
150	P-92 MgX	0.32	125	10	32	Neut.	28	--	0.3	<15	20	365	10	15	45	(0.1)	0.13	0.01	0.37
151	P-92 MgX	0.16	119	20	34	Neut.	28	--	0.2	<15	<6	350	<10	<2	65	(0.1)	(0.03)	0.02	0.37
152	P-75 MgX	0.31	86	--	35	0.6 N	57	0	--	120	12	1080	35	3	125	0.03	0.03	0.01	0.53
153	P-75 MgX	0.42	65	5	31	Neut.	23	--	0.1	<40	8	930	<30	<5	90	(0.1)	(0.1)	0.007	0.24
154	P-75 MgX	0.16	73	10	34	Neut.	33	--	0.4	<25	<5	950	<20	<3	90	(0.1)	(0.1)	0.007	0.28
155	P-75 MgX	0.15	68	20	37	Neut.	37	--	0.2	<25	<5	1110	<15	<3	100	(0.1)	(0.05)	0.007	0.33
156	P-75 MgX	0.21	68	30	35	Neut.	39	--	0.2	<25	<5	905	<15	<3	85	(0.1)	(0.05)	0.007	0.32
121	P-163 MgX	0.54	124	--	31	Neut.	28	--	0.5	80	620	300	75	650	65	0.27	0.5	0.02	0.36
122	P-163 MgX	0.23	137	--	31	0.6 N	44	2	--	285	3460	655	325	4120	430	1.0	0.9	0.11	0.39
123	P-163 MgX	0.22	121	10	32	Neut.	23	--	0.1	20	105	310	10	115	50	(0.1)	0.13	0.01	0.33
124	P-163 MgX	0.11	109	20	31	Neut.	28	--	0.1	<15	15	310	<10	10	40	0.12	0.46	0.01	0.32
159	PT-2 MgX	0.46	96	--	32	Neut.	28	--	0.2	<75	10	285	<10	10	30	(0.01)	0.2	0.01	0.30
160	PT-2 MgX	0.22	94	--	32	0.6 N	53	0	--	195	100	380	40	105	40	0.02	0.5	0.01	0.40
161	PT-2 MgX	0.49	92	10	32	Neut.	29	--	0.3	55	<6	355	<10	<2	25	(0.04)	(0.05)	0.006	0.31
162	PT-2 MgX	0.17	85	20	30	Neut.	30	--	0.3	<25	<7	360	20	<3	50	(0.1)	(0.05)	0.01	0.28
68	B-2 MgX	0.46	95	--	31	Neut.	21	--	0.6	110	45	350	<10	45	40	(0.01)	0.3	0.01	0.31
102	B-2 MgX	0.34	76	--	32	0.6 N	53	0	--	190	370	835	70	400	110	0.04	0.7	0.01	0.44
163	B-2 MgX	0.24	94	10	33	Neut.	26	--	0.4	30	<5	335	25	20	30	0.15	(0.7)	0.007	0.33
120	B-2 MgX	0.16	92	20	31	Neut.	28	--	0.3	<20	<8	410	<15	<3	20	(0.1)	(0.04)	0.004	0.31

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Footnotes

- (1) One-inch x 6-foot Scheibel column; 12 mechanical stages; agitator speed approximately 3300 r.p.m.; ether phase continuous; ether; aqueous ratio about 2:1; Feed approx. 56° Bé, feed rate 1500 ml./hr.
- (2) MgX slurry; 140 m.l. of NG liquor (@ 600 g./l. of U) added per 1000 m.l. of slurry (simulating a recycle of 25 per cent of total plant throughput).
- (3) Ten per cent batch-wise scrub.
- (4) Value seemed high. Repeat test gave 1.12 g./l. of U, however.
- (5) Values in parentheses indicate approximate distribution coefficients, based on "less than" figures.

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In the absence of added iron, the uranium contents of the raffinates from neutral-ether extraction were, in general, from 1-1/2 to 4 times as large as those from 0.6N ether. With some lots of MgX, the addition of 10 g./l. of iron reduced the raffinates to the 0.6N ether level, although with others there appeared to be very little effect. The addition of 20 g./l. of iron quite consistently reduced the uranium assay of the raffinate to the 0.11-0.17 g./l. level; this was invariably lower than the level attained with 0.6N ether.

MgX Blend B-1 appeared to be a special case. Results with it were consistently high, although the cause of the difference is not apparent. The discrepancy has not been further investigated, since Blend B-1 was composed principally of the earliest MgX lots (P-1 to P-12) and is not considered representative of MgX feeds apt to be encountered in the future.

The addition of 20 g./l. of iron was extremely effective in reducing molybdenum transfer for those feeds which were high in molybdenum and in which molybdenum transfer was a problem. Phosphate transfer was normally reduced when iron was added to the feed. The picture on vanadium is not so clear. Less vanadium transferred with neutral ether than with 0.6N ether. The addition of iron did not reduce it further (unlike Mo and PO_4); in a few tests there was a slight increase. However, the vanadium content of the scrubbed extract, using 20 g./l. of iron and neutral ether, was in all cases <100 p.p.m.

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Effect of Iron Addition on Mixed MgX:V-20 Feeds

Since the current practice at Plant 6 is to combine the V-20 soda salt with the MgX and to extract them together, the effect of iron addition on mixed feeds was also studied in a series of tests similar to those on straight MgX feed. The results are contained in Table 6. The summarized uranium results compare with the corresponding tests without V-20 as follows:

<u>Feed Used (1)</u>	<u>Ether, N</u>	<u>U, g./l.</u>	<u>U, g./l. (Without V-20)</u>
P-88	Neutral	0.82	0.58
P-88	0.6N	0.29	0.15
P-88 + 10 g./l. Fe	Neutral	0.32	0.17
P-88 + 20 g./l. Fe	Neutral	0.09	0.11
P-92	Neutral	1.00	1.10
P-92	0.6N	0.71	0.27
P-92 + 10 g./l. Fe	Neutral	0.40	0.32
P-92 + 20 g./l. Fe	Neutral	0.22	0.16
B-2	Neutral	0.71	0.46
B-2	0.6N	0.40	0.34
B-2 + 10 g./l. Fe	Neutral	0.46	0.24
B-2 + 20 g./l. Fe	Neutral	0.16	0.13

(1) V-20 added equivalent to about 8 per cent of total plant feed.

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TABLE 6. EXTRACTION OF URANIUM FROM MIXED MgX : V-20 FEEDS WITH A SCHEIBEL COLUMN (1)

Run No.	Feed Used (2)	U, g./l.		Fe Added, g./l.	Excess Acid, g./l.				pH Raff.	p.p.m. (U Basis)								Scrub Distribution Coefficient, E_{Δ}^0 (4)			
		Raff.	Ext.		Feed	Ether	Ext.	Raff.		Unscrubbed Extract				Scrubbed Extract (3)				PO ₄	Mo	V	As
										PO ₄	Mo	V	As	PO ₄	Mo	V	As				
167	P-88 + V-20	0.82	115	--	44	Neut.	31	--	0.5	<130	<7	310	30	<10	<2	40	20	(0.07)	(0.03)	0.011	0.10
168	P-88 + V-20	0.29	120	--	44	0.6 N	52	0	--	280	30	340	40	40	22	35	15	0.01	0.2	0.009	0.05
169	F-88 + V-20	0.32	111	10	41	Neut.	31	--	0.4	<25	4	330	25	<10	<2	25	<10	(0.04)	(0.05)	0.006	0.04
170	P-88 + V-20	0.09	107	20	42	Neut.	33	--	0.3	<15	<5	350	<20	<10	<2	30	<10	(0.1)	(0.05)	0.007	(0.05)
171	P-92 + V-20	1.00	138	--	33	Neut.	21	--	0.6	30	15	430	<12	<8	10	70	<8	(0.02)	0.10	0.015	(0.1)
172	P-92 + V-20	0.71	136	--	32	0.6 N	41	6	--	80	215	570	40	30	230	140	20	0.04	0.7	0.026	0.06
173	P-92 + V-20	0.40	140	10	38	Neut.	27	--	0.5	<10	6	670	<15	<8	3	245	<10	(0.1)	(0.02)	0.040	(0.06)
174	P-92 + V-20	0.24	140	20	33	Neut.	32	--	--	<10	<6	910	25	<8	2	135	10	(0.1)	(0.02)	0.014	0.06
175	B-2 + V-20	0.65	119	--	31	Neut.	21	--	0.6	20	15	510	70	<10	10	50	25	(0.1)	0.08	0.008	0.04
176	B-2 + V-20	0.40	112	--	40	0.6 N	50	0	--	160	200	660	<20	35	210	100	<10	0.02	0.8	0.015	(0.06)
177	B-2 + V-20	0.46	113	10	33	Neut.	28	--	0.4	20	7	650	<15	10	<2	100	<10	(0.1)	(0.02)	0.013	(0.1)
178	B-2 + V-20	0.16	106	20	33	Neut.	26	--	0.4	<20	10	500	35	10	1	50	25	(0.1)	0.02	0.008	0.1
179	P-163 + V-20 (5)	0.61	122	--	34	Neut.	22	--	0.2	60	330	275	<15	30	320	45	<10	0.06	0.29	0.01	(0.1)
180	P-163 + V-20 (5)	0.25	129	--	34	0.6 N	47	7	--	275	2260	575	50	230	2660	300	30	0.19	1.7	0.07	0.07

(1) One-inch x six-foot Scheibel column; 12 mechanical stages; agitator speed, approx. 3300 r.p.m.; ether phase, continuous; feed rate, 1500 ml./hr.; ether/aqueous ratio of 2/1; feed at room temperature; ether cooled.

(2) MgX slurry; V-20 soda salt (Blend V-2) added at the rate of 58.5 g. per liter of slurry, simulating the addition of about 3 per cent of total U as V-20 140 ml. of N.G. liquor (6.600 g./l. of U) added to simulate a recycle of 25 per cent of plant throughput.

(3) Ten per cent batch-wise scrub.

(4) Values in parentheses indicate approximate distribution coefficients, based on "less than" values.

(5) Insufficient P-163 MgX available to complete the series.

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Based on data from some earlier tests, it had been expected that incorporating V-20 into the feed would result in increased uranium losses to the raffinate and would probably increase slightly the iron demand. The data indicate that in the absence of iron, there is usually a definite increase with both neutral and acid ether. However, when 20 g./l. of iron was added to the feed, the differences observed were not significant. It is concluded that 20 g./l. of iron is a satisfactory rate of addition for MgX feeds, either with or without V-20 soda salt present.

The contaminant data indicated that the addition of V-20 had very little effect on the behavior of B-2 and P-88 MgX. Except for vanadium, this was also true for P-92 MgX. The increase in vanadium content of the extract of the P-92 + V-20 feed, plus its greater resistance to removal by scrubbing, was not expected. The analyses of these lots of MgX were quite similar. However, one point of difference was in the PO_4 content: P-88 assayed about 3.0 per cent and P-12 assayed only 1.5 per cent. Results of some earlier work on heteropoly acids had indicated that not only the Mo-to-V ratio, but also the PO_4 -to-V ratio, influenced both the extraction and scrub distribution coefficients. The effect of increasing the PO_4 level of P-92 to that of P-88 is to be checked, in the hope that a better understanding of the factors controlling vanadium transfer may result. From a contaminant point of view, transfer of vanadium is the least improved by a neutral-ether - iron type of extraction procedure; further study appears to be required to develop methods of reducing vanadium to the low levels such as are readily attainable with the other important contaminants.

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Effect of Iron Addition on Calcium Solubility

In connection with the studies on the use of iron as a possible substitute for the BaSO_4 precipitation of pitchblende feeds, some data were obtained on the effect of iron on calcium solubility in pitchblende digest filtrates and raffinates. The results of this work are shown in Table 7. Reproducibility was rather poor, due primarily to the difficulties encountered in analyzing for calcium in this system. It was necessary in some cases to repeat the test and average the results. Calcium solubility increased with increasing iron concentration; the addition of 60 g./l. of iron made it possible to hold from 5-10 g./l. of calcium in solution. Small squares of Type 304 stainless steel were present in each flask to provide a metallic surface for precipitation. Calcium scaling was absent, however, except that a negligible scale was observed on the digest filtrate sample at 37 g./l. excess acid.

Addition of 120 g./l. of iron produced high uranium distribution coefficients, remarkably high for a pitchblende feed originally containing about 70-75 g./l. of sulfate. After two shakeouts with neutral ether, the raffinate contained only 0.53 g./l. of U, for an indicated average distribution coefficient of about 17. The indicated distribution coefficient where 60 g./l. of iron was added appeared to be about 4. In the absence of iron, the average coefficient for the first two shakeouts was approximately 0.6.

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TABLE 7. EFFECT OF IRON ON SOLUBILITY OF CALCIUM IN PITCHBLEND
FILTRATE AND RAFFINATE(1)

Excess Acid, g./l.	Iron Added, g./l. of Digest Filtrate	Solution Assay	
		Ca, g./l.	U, g./l.
<u>Digest Filtrate</u>			
37	0	1.8	237
55	0	1.2	237
36	5	1.9	237
35	10	0.6	233
35	20	5.6	214
32	40	8.8*	214*
35	60	9.6*	196*
35	120	12.8*	159*
<u>After 2 Shakeouts</u>			
	0	2.0	94.2
	0	0.02	93.5
	5	0.6	93.5
	10	2.0*	69.7
	20	2.7	55.8
	40	4.1*	21.2*
	60	5.2*	7.4*
	120	11.5*	0.53*
<u>After 6 Shakeouts</u>			
	0	0.4	40.8
	0	1.0	47.5
	5	1.5	36.3
	10	2.1*	25.5
	20	2.6	15.7
	40	3.5*	0.85*
	60	7.1*	0.045*
	120	10.4*	<0.002

(1) Fitchblende Solution No. 19 (A-1 ore) containing 5.0 g./l. of Ca was given equal volume shakeouts with neutral ether. The resultant aqueous phase was equilibrated with excess CaSO_4 on a mechanical shaker for 1 week at 70°F.

* Average of two tests.

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PLANS FOR FUTURE WORK

The mass of data accumulated, on a variety of feeds, indicates that the substitution of neutral for acid ether in the primary extraction is now fairly well worked out, and that it will be necessary to devote only minor attention to this phase of the problem in the future. A limited number of tests on the effects of minimal quantities of iron on straight pitchblende feeds is planned.

The absolute maximum contents of vanadium and molybdenum tolerable in NOK liquor without encountering precipitation upon neutral re-extraction have never been definitely established. Further, precipitation and scaling has at times been experienced in the triple-effect evaporators, during the boiling down of primary extracts to NOK liquor. Although the replacement of acid ether by neutral ether plus iron may minimize both of these problems, additional information on the upper limits appears to be desirable. A general study of the solubility of vanadium, molybdenum, and phosphate, and their inter-effects, in solutions of uranyl nitrate at varying acidities and uranium concentrations should define the maximum allowable concentrations of these contaminants.

Additional data on the solubility of molybdenum during pitchblende digestion and in digest filtrates may assist in explaining its sometimes erratic behavior at this point, and point the way towards improvements in the digestion and C-3 processes. Results of the neutral-ether + iron tests suggest that molybdenum at high levels can be tolerated in the

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column feed; such a procedure, if practical, could materially improve the efficiency of the C-3 process.

Some study of the causes of emulsions and methods of preventing their formation is planned, as time permits.

An attempt is to be made to develop a simple, but more reliable, method for determining free acid in uranyl nitrate and process feed solutions than the ones presently used. It may be necessary to secure such a method in order to complete the solubility studies of NOK liquor; there is reason to believe that acidity is one of the most important variables affecting solubility of these components in highly concentrated uranyl nitrate solutions.

Other problems for study include the effect of iron on radium solubility and the behavior of boron as a possible constituent of heteropoly acids.

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