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RAW MATERIALS PROCESS TESTING

**Engineering Section Progress Report for
April 1956**

By
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July 17, 1956

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This is a continuation of studies reported in ORNL-2112.

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**COUNTERCURRENT EXTRACTION OF MOLYBDENUM LIQUORS BY
THE AMEX PROCESS WITH CHLORIDE STRIPPING**

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COUNTERCURRENT EXTRACTION OF MOLYBDENUM LIQUORS BY
THE AMEX PROCESS WITH CHLORIDE STRIPPING

H. F. Bauman

The study, reported in ORNL-2112, of the effect of molybdenum and vanadium in leach liquors on uranium extraction in the Amex process with chloride stripping, was continued. The previous work showed that: (1) molybdenum is not appreciably stripped from the organic by chloride, and, therefore, tends to build up in the organic phase, (2) the molybdenum--amine complex has limited solubility (0.5 to 1.0 g/l as molybdenum) in kerosene-amine organic, but considerably greater solubility (over 8 g/l) in Amsco G--amine organic, (3) build-up of molybdenum in the organic decreases the organic phase uranium capacity, and (4) liquors containing at least as much as 0.3 g/l molybdenum can be successfully extracted with Amsco G--amine organic with chloride stripping, by employing secondary stripping with sodium carbonate (which strips the molybdenum). To continue this study, one run was made to determine whether or not low molybdenum liquor (0.01 g/l) can be processed without secondary stripping, and one run was made to determine whether molybdenum liquor in the range 0.02 to 0.2 g/l can be extracted successfully with kerosene--amine organic by using secondary stripping. This latter run was continued for 100 cycles of the organic phase so that in addition to the data on the effect of molybdenum, data was obtained on organic loss, amine loss, and uranium recovery for a long-term run. Previously such data for the Amex process was available only for carbonate stripping (ORNL 2034).

PROCESSING MOLYBDENUM LIQUOR WITHOUT SECONDARY STRIPPING

One run was made, in the countercurrent test array used in previous tests (ORNL-2112), in which a synthetic liquor containing 0.01 g/l molybdenum and 0.9 g/l vanadium(V) was extracted with a 0.11M solution of amine 9D-178 in Amsco G, and the organic stripped with 1M sodium chloride 0.05M sulfuric acid solution. The run was continued for 36 cycles of the organic phase so that the build-up of molybdenum in the organic could be observed.

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Molybdenum Build-up

The molybdenum concentration built up slowly in the organic during the run, until at the end of 36 cycles it was 0.18 g/l. There was no appreciable build-up of vanadium. A material balance at the end of the run showed that of the molybdenum which entered in the feed, about 60% went out in the raffinate and an additional 20% in the loaded strip solution, leaving 20% still accumulating in the organic phase (equivalent to an organic molybdenum concentration rise of 0.005 g/l per cycle).

Uranium Extraction

The uranium extraction was normal during the first half of the run, with a raffinate uranium concentration of 0.002 g/l, but became progressively more incomplete during the second half, until at the end of 36 cycles the uranium concentration in the raffinate reached 0.040 g/l. At this point, the organic molybdenum concentration (0.18 g/l) was not high enough to account for the interference with uranium extraction, since in a previous run (ORNL-2112) satisfactory uranium extraction was obtained at an organic molybdenum concentration as high as 1.1 g/l.

Analyses were made for chloride in the organic extract, which showed that the chloride concentration increased steadily all during the run, to 0.82 g/l at 36 cycles (sufficient to combine with 25% of the amine and thus interfere with the uranium extraction). In previous (short term) runs, all the chloride in the organic was replaced by sulfate or uranyl sulfate in the extraction section. No reason has been found for this build-up of "unreplaceable" chloride in the organic phase. However, the chloride can be readily stripped from the organic with an alkaline stripping agent, such as sodium carbonate.

The foregoing results indicate that some degree of secondary stripping should be provided in the Amex process with chloride stripping, even for liquors low in molybdenum. This may be done by treating the entire organic inventory with an alkaline stripping agent periodically (every 10 or 20 cycles), or by treating a side stream of organic (5 or 10% of the total organic flow) continuously.

PROCESSING MOLYBDENUM LIQUOR WITH SECONDARY STRIPPING

Two runs were planned, using feeds containing molybdenum concentrations of 0.02 and 0.2 g/l, to determine the approximate range of molybdenum concentration over which extraction is practical using kerosene--amine organic, with chloride stripping followed by secondary stripping. The 0.02 g/l molybdenum run was completed, using 10% secondary stripping with 1M sodium carbonate solution.

The run was made in a countercurrent test array that contained three mixer-settlers in the extraction section, four in the primary stripping section, and one in the secondary stripping section, as shown in Fig. 1.

The operating and sampling procedures were the same as for previous runs (ORNL 2035, et al.), except that the amine concentration was readjusted to 0.11M at the end of every 20 cycles. The raffinate from each 10 cycles' operation was collected and allowed to stand at least 16 hours; any organic which separated was returned to the system. The operating conditions are given in Table 1, and the composition of the entering streams in Table 2.

The extraction and stripping data are shown in Tables 3 and 4, the uranium and molybdenum material balances in Table 5, the organic phase material balance in Table 6, and the amine loss in Table 7. The composition of the uranium strip solution and product are reported in Table 8, and the chemicals consumption in Table 9.

Steady State

The extraction and stripping data at 10-cycle intervals, given in Table 3, show that the system was at steady state after 50 cycles (and the extraction and chloride stripping sections earlier).

Uranium Extraction and Stripping

As shown in Tables 3 and 4, the uranium extraction was complete in three stages, the same as for a run with a standard nonmolybdenum liquor under similar conditions. The raffinate uranium concentration was consistently less than 0.001 g/l. The material balance, Table 5, showed that less than 0.09 percent of the uranium entering in the feed was lost in the raffinate.

* SAME AS SHOWN IN FIG. 5, ORNL CF 56-4-79, BUT WITHOUT ORGANIC RECYCLE LINES.

** AS SHOWN IN FIG. 2, ORNL 1970.

FIG. 1-EXTRACTION AND STRIPPING FLOW DIAGRAM

As was desired, practically all the uranium was stripped from the organic in the primary stripping section; the average uranium concentration of the chloride stripped organic was 0.013 g/l. This was somewhat higher than obtained in runs with nonmolybdenum liquors, but agrees well with the results of previous molybdenum runs. The fraction of uranium passed on to be secondary stripped was only 0.03%. By difference, greater than 99.88% of the uranium entering in the feed liquor was recovered in the primary strip.

Molybdenum Extraction and Stripping

In previous work it was observed that the molybdenum extraction coefficient was comparatively low at low organic molybdenum concentrations. The molybdenum coefficient in this run conformed to this observation; it was 13 at an organic molybdenum concentration of 0.29 g/l, compared with 33 at 1.1 g/l in a previous run. As a result, about 65% of the molybdenum in the feed went out in the raffinate; another 15% went out in the chloride strip, leaving only 20%, which was stripped by the carbonate.

As a result of the low coefficient, the molybdenum concentration in the extract was only about 0.3 g/l at steady state, which indicates that 10 percent secondary stripping is on the safe side in processing a 0.02 g/l molybdenum liquor. In practice, probably as little as 5% secondary stripping would be adequate.

Chloride

The carbonate stripped organic was free of chloride (<0.05 g/l), and the chloride concentration in the organic extract was only about 0.09 g/l, equivalent to about 4% of the amine combined as chloride complex. This low chloride concentration did not appreciably interfere with uranium extraction.*

Loss of Organic Phase

The organic phase material balance, given in Table 6, shows that 121 ml of organic phase, equivalent to 0.140 ml/l raffinate, was lost during the run. Less than 61 ml organic

*The effect of organic chloride concentration on extraction is discussed on p. 3.

was lost due to entrainment** in the raffinate; the remaining loss was probably due to evaporation, leakage, and spray.

The total loss of amine was 0.075 mole, equivalent to 31 ppm of aqueous phase, of which 0.013 mole was associated with the 121 ml of organic phase lost. The remaining 0.062 mole, equivalent to 26 ppm, represents the amine lost through solubility or degradation.

The amine loss per cycle, reported in Table 7, was estimated by assuming that the volume loss was evenly distributed over the run. The losses were equivalent to 55 ppm of aqueous phase for the first 20 cycles, after which they were roughly constant at an average of 25 ppm.

The amine loss in this run averaged about 10 ppm less than in the previous long-term run (with carbonate stripping, ORNL-2034). About a third of this reduction was due to improved technique, which reduced the volumetric organic loss to 0.14 from 0.25 ml/l raffinate in the earlier run.

Uranium Product

The uranium was precipitated from the chloride strip solution with ammonia, filtered, washed, dried, and calcined at 600°C. The compositions of the loaded strip solution and uranium product are shown in Table 8. The product was 82% uranium as U_3O_8 and no impurity (except sulfate) exceeded 1%.

Chemicals Consumption

The consumption of chemicals during the run is shown in Table 9. The total chemicals cost was 5.9 cents per pound of U_3O_8 . This is less than half the cost (16.1 cents) in the previous long-term run. Most of the saving is due to the use of chloride rather than carbonate stripping. The cost of carbonate in the earlier run was 8.0 cents per pound of U_3O_8 , plus an additional 3.8 cents required for sulfuric acid to neutralize the carbonate in the precipitation step.

**The entrainment was <0.07 ml/l by steam distillation.

FUTURE WORK

One additional 100-cycle run is planned to determine whether or not a kerosene--amine organic can be successfully used to extract a 0.2 g/l molybdenum and 1.0 g/l vanadium(IV) liquor, with chloride stripping, by employing 100% secondary stripping with calcium hydroxide.

TABLE 1. OPERATING CONDITIONS

Run time, hours	44.3
Number of cycles of organic	100
Flow rates, ml/min	
Head liquor	316
Total organic	105
Primary stripped organic	94.5
Secondary stripped organic	10.5
Chloride strip	15.8
Carbonate strip	0.64
Stripping agent excess, %	
Chloride	50
Carbonate	10
Mixer speed, units 101 to 103,	600 rpm
Continuous phase, extraction	Aqueous

TABLE 2. COMPOSITION OF ENTERING STREAMS

Concentrations in g/l except as noted

Head liquor	
Uranium	1.2
Iron	2.1
Aluminum	2.9
Vanadium(IV)	1.0
Molybdenum	0.02
Sulfate	42
Phosphate	2.2
pH	1.0
Organic	
Amine 9D-178 in kerosene, <u>M</u>	0.1078
(also see Table 6)	
Chloride strip	
Sodium chloride, <u>M</u>	1.0
Sulfuric acid, <u>M</u>	0.05
Carbonate strip	
Sodium carbonate, <u>M</u>	1.0

TABLE 3. EXTRACTION AND STRIPPING DATA AT TEN-CYCLE INTERVALS

Cycle	Concentration, g/l													
	Extraction					Chloride Stripping					Carbonate Stripping			
	Aqueous, stage			Organic Extract		Loaded Strip		Chloride Stripped		Organic	Loaded Strip		Carbonate Stripped	
	101	102	103(a)	(Stage 101)		Solution(a)		Organic			Solution(a)		Organic	
	U	U	U	U	Mo	U	Mo	U	Mo		U	Mo	U	Mo
10	0.15	0.005	0.002	3.1	0.17	20.7	0.048	0.015	0.17	-	-	-	0.002	0.031
20	0.33	0.010	0.001	3.7	0.22	23.0	0.062	0.008	0.20	0.16	1.1	-	0.001	0.047
30	0.13	0.004	0.001	3.4	0.26	23.3	0.065	0.013	0.24	0.17	1.6	-	0.002	0.060
40	0.15	0.004	0.001	3.5	0.27	22.5	0.063	0.015	0.26	0.20	2.0	-	0.002	0.064
50	0.14	0.004	0.001	3.2	0.25	23.6	0.060	0.014	0.27	0.19	2.2	-	0.002	0.10
60	0.15	0.004	0.001	3.5	0.27	23.1	0.060	0.015	0.30	0.19	2.2	-	0.006	0.22
70	0.25	0.005	0.001	3.7	0.26	23.3	0.058	0.012	0.31	0.16	2.3	-	0.002	0.15
80	0.21	0.007	0.001	3.4	0.27	23.5	0.056	0.010	0.28	0.16	2.4	-	0.002	0.14
90	0.13	0.005	0.001	3.3	0.28	23.1	0.059	0.015	0.30	0.13	2.4	-	0.002	0.15
100	0.13	0.005	0.001	3.4	0.28	23.6	0.065	0.017	0.30	0.13	2.3	-	0.003	0.13

(a) Analyses of aqueous solutions collected over ten cycles intervals.

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TABLE 4. EXTRACTION AND STRIPPING DATA AT STEADY STATE

Section	Mixer- Settler Number	Composition(a), g/l						Distribution, org/aq	
		Aqueous			Organic			U	Mo
		U	Mo	Cl	U	Mo	Cl		
Extraction									
	Feed liquor	1.2	0.02	0	-	-	-	-	-
	101	0.18(b)	0.022	0.16	3.4(b)	0.29(b)	0.089	19	13
	102	0.005(b)	0.014	0.40	0.48	-	0.53	96	-
	103	<0.001(b)	0.013	1.0	0.037	0.26(c)	1.3	-	20
Chloride Stripping									
	121	23 (b)	0.061(b)	14	0.78	-	-	1/30	-
	122	6.9	0.044	31	0.12	-	-	1/58	-
	123	0.93	0.042	36	0.042	-	-	1/22	-
	124	0.19	0.039	37	0.013(b)	0.28(c)	3.5(c)	1/15	7.2
Carbonate Stripping									
	131	0.14(b)	2.28(b)	56	0.002(b)	0.15(b)	<0.05	-	1/15

(a) Composition of samples taken at the end of the run, except as noted.

(b) Average of analyses of samples taken at 10-cycle intervals during the steady state portion of the run.

(c) Calculated by material balance.

TABLE 5. URANIUM AND MOLYBDENUM MATERIAL BALANCES

	Uranium		Molybdenum	
	Wt, g	%	Wt, g	%
In				
Feed liquor	1039		17.2	
Out				
Raffinate	< 0.9	< 0.09	11.3	65.7
Chloride strip	1043	100.3	2.69	15.7
Carbonate strip	0.3	0.03	3.53	20.5
Out/In		100.4		101.9

TABLE 6. ORGANIC PHASE MATERIAL BALANCE

	Volume, ml	Amine Concen- tration, M	Moles of Amine	Amine Loss, ppm of Aqueous
In				
Initial inventory	2,800	0.1078	0.302	
Additions				
at 20 cycles	57	.5219	.029	
	100	.1078	.011	
at 40 cycles	34	.5219	.018	
	100	.1078	.011	
at 60 cycles	11	.5219	.006	
	50	.1078	.005	
at 80 cycles	41	.5219	.021	
	3,193		0.403	
Out				
Samples	50	.0995	0.005	
	50	.1046	.005	
	50	.1077	.005	
	50	.1043	.005	
Final inventory	2,872	.1071	.308	
	3,072		0.328	
Loss				
Volumetric	121(a)	.1073	.013	
Solubility, etc. (by diff.)			.062	26
Total amine loss (by diff.)			0.075	31

(a) Equivalent to 0.140 ml/liter raffinate.

TABLE 7. AMINE LOSS

Cycles	Amine Concentration in Organic, M		Loss per Cycle, g	Loss as ppm of Aqueous Phase
	Analysis	Adjusted to		
0	0.1078			
20	.0995	0.1080	0.482	55
40	.1046	.1098	.226	26
60	.1077	.1092	.158	18
80	.1043	.1095	.305	35
100	.1073		.164	19
Average, cycles 20 to 100:				25

TABLE 8. COMPOSITION OF URANIUM
STRIP SOLUTION AND PRODUCT

Constituent	Chloride Strip Solution		%	Product	
	g/l	g/100 g U		g/100 g U	
Uranium					
as U	22.5	-	69.5	-	
as U ₃ O ₈	26.5	-	82.0	-	
Iron	-	-	0.30	0.43	
Molybdenum	0.058	0.26	0.14	0.20	
Vanadium	0.01	0.04	< 0.4	< 0.6	
Aluminum	-	-			
Phosphate	-	-	0.76	1.1	
Sulfate	-	-	12.7	18.3	
Ammonia (as NH ₃)	-	-	< 0.05	< 0.07	
Chloride	-	-	< 0.05	< 0.07	

TABLE 9. CHEMICALS CONSUMPTIONBasis: 2.70 lb U_3O_8 processed

Operation and Chemical	Consumption		Unit Price, Cents per lb	Cost per lb U_3O_8 , Cents
	Total, lb	per lb U_3O_8 , lb		
Extraction				
Amine	0.0615	0.0228	85.0	1.94
Kerosene	.226	.0838	2.0	0.17
Stripping				
Sodium chloride	5.60	2.08	0.75	1.56
Sulfuric acid	0.469	0.174	1.50	0.26
Sodium carbonate	0.414	0.153	2.25	0.34
Precipitation				
Ammonia	0.783	0.290	5.75	<u>1.67</u>
Total				5.9

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