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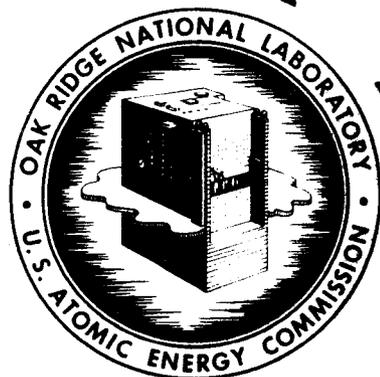


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ORNL-2245
Engineering *cy 4*

PROGRESS REPORT OF
PROCESS TEST SECTION
FOR OCTOBER, 1956

A. D. Ryon
K. O. Johnson



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CHEMICAL TECHNOLOGY DIVISION

PROGRESS REPORT OF

PROCESS TEST SECTION

FOR OCTOBER, 1956

A. D. Ryon and K. O. Johnsson

Date Issued
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ABSTRACT

Data is presented giving the results of the second 100 cycle continuous run using secondary stripping on uranium leach liquor containing molybdenum. The present run used liquor containing 0.2 g/l molybdenum and secondary stripping with carbonate solution of the total organic flow. The run was entirely successful.

NOTICE

The data presented in this report are preliminary, and are published in a formal report only to permit rapid dissemination of information to interested persons.

PROGRESS REPORT OF PROCESS TEST SECTION
OCTOBER 1956

AMEX PROCESSING, WITH SECONDARY STRIPPING, OF URANIUM LEACH
LIQUORS CONTAINING MOLYBDENUM

H. F. Bauman

Introduction

Previous work on the effect of the presence of molybdenum and vanadium in leach liquors on the extraction and stripping operations was reported in document ORNL CF 56-7-95. In that work a successful 100-cycle (of organic) run was made with secondary stripping (carbonate) of 10% of the organic flow starting with liquor containing 0.002 g/l molybdenum. The present run was based on using liquor containing 0.2 g/l molybdenum and secondary stripping of the total organic flow.

Equipment and Operation

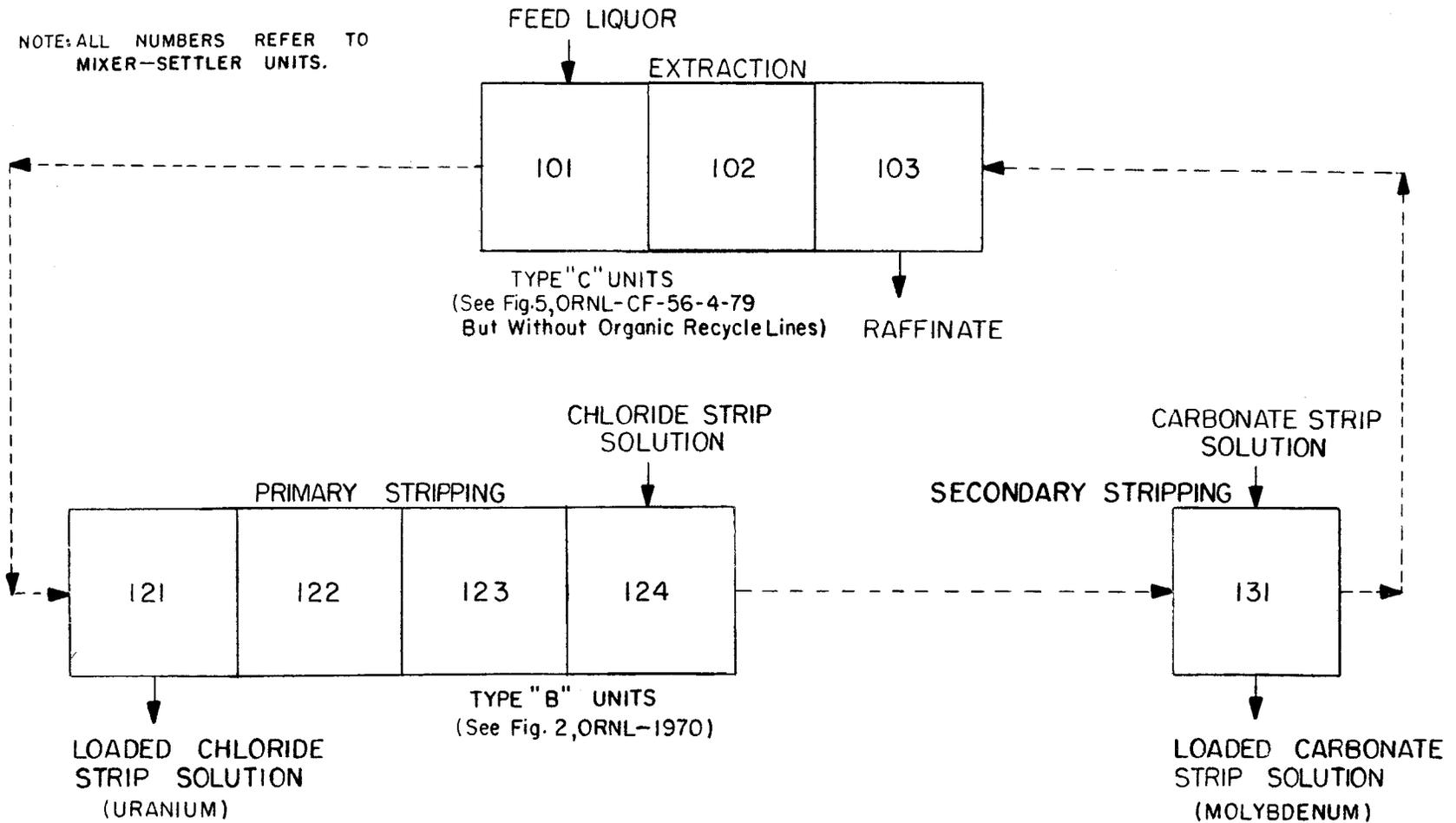
The run was made in the mixer-settler test array used for previous studies (CF 56-7-95), except that the entire organic stream was processed through the secondary strip section before recycle to the extraction section. This flow sheet is shown in Figure 1.

The compositions of the entering streams are shown in Table 1 and the operating conditions for the run are given in Table 2. As can be seen from the later tables giving the results, the system was at steady state after 20 cycles of organic.

Uranium

Extraction. As shown in Tables 3 and 4, the uranium extraction was complete in three stages, the raffinate uranium concentration was consistently less than 0.001 g/l. The material balance as given in Table 5, shows that less than 0.1% of the uranium entering in the feed was lost in the raffinate.

NOTE: ALL NUMBERS REFER TO MIXER-SETTLER UNITS.



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FIGURE 1 - EXTRACTION AND STRIPPING FLOW DIAGRAM

TABLE 1. COMPOSITION OF ENTERING STREAMS CONCENTRATIONS

(g/l except as noted)

<u>Head liquor</u>	
Uranium	1.1
Iron (III)	2.0
Aluminum	3.2
Vanadium (IV)	1.0
Molybdenum	0.21
Sulfate	38
Phosphate	2.2
pH	1.0
<u>Organic Phase</u>	
Amine 9D-178 in kerosene, <u>M</u>	0.1054
(also, see Table 8)	
<u>Chloride strip Solution</u>	
Sodium chloride, <u>M</u>	1.0
Sulfuric acid, <u>M</u>	0.05
<u>Carbonate strip Solution</u>	
Sodium carbonate, <u>M</u>	1.0

TABLE 2. OPERATING CONDITIONS

Run time, hours	44.6
Number of cycles of organic	100
Flow rates, ml/min	
Head liquor	316
Organic	105
Chloride strip	15.8
Carbonate strip	6.4
Stripping agent excess, percent	
Chloride	50
Carbonate	10
Mixer speed, units 101 to 103, rpm	600
Continuous phase, extraction	Aqueous

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

Concentration (g/l)

Cycle	Extraction					Chloride Stripping			Carbonate Stripping			
	Aqueous stage			Organic extract (Stage 101)	Loaded strip solution(a)	Chloride stripped organic	Strip loaded		Carbonate stripped			
	101	102	103(a)				U	Mo	U	Mo		
U	U	U	U	Mo	U	Mo	U	Mo	U	Mo		
10	0.26	0.005	0.002	3.5	0.85	18.0	0.064	0.006	0.168	6.2	0.002	0.30
20	0.24	0.004	<0.001	3.3	0.85	20.3	0.088	0.007	0.077	9.7	0.002	0.20
30	0.15	0.003	<0.001	3.5	0.88	20.8	0.077	0.014	0.123	10.2	0.006	0.32
40	0.13	0.003	<0.001	3.4	0.92	21.0	0.076	0.011	0.145	10.3	0.004	0.41
50	0.14	0.003	<0.001	3.6	0.97	20.7	0.076	0.015	0.143	9.9	0.005	0.22
60	0.11	0.002	<0.001	3.3	0.94	20.8	0.077	0.014	0.125	9.6	0.006	0.37
70	0.16	0.004	<0.001	3.5	0.95	20.9	0.080	0.010	0.135	11.1	0.005	0.35
80	0.18	0.003	<0.001	3.5	0.90	20.4	0.081	0.011	0.137	10.7	0.004	0.50
90	0.15	0.003	<0.001	3.4	1.1	20.0	0.080	0.017	0.134	9.5	0.007	0.41
100	0.17	0.003	<0.001	3.4	0.91	20.9	0.085	0.013	0.168	11.2	0.004	0.21

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

TABLE 4. EXTRACTION AND STRIPPING DATA AT STEADY STATE

Section	Mixer- Settler Number	Composition ^(a) , g/l						Distribution	
		Aqueous			Organic			org/aq	
		U	Mo	Cl	U	Mo	Cl	U	Mo
Extraction	Feed liquor	1.1	0.21	0	-	-	-	-	-
	101	0.17(b)	0.05	<0.05	3.4(b)	0.94(b)	-	20	20
	102	0.003(b)	0.02	<0.05	0.51(c)	0.47(c)	-	170	20
	103	0.001(b)	0.01	0.1	0.009(c)	0.37(c)	<0.05	-	40
Chloride stripping	121	20.6(b)	0.08(b)	13	1.1	-	-	1/19	-
	122	7.6	0.09	30	0.21(c)	-	-	1/36	-
	123	1.25	0.12	36	0.063(c)	-	-	1/20	-
	124	0.32	0.11	36	0.013(b)	0.93(c)	3.3(c)	1/25	-
Carbonate stripping	131	0.14(b)	10.3(b)	54	0.005(b)	0.34(b)	0.1	-	-

(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	
	<u>Wt, g</u>	<u>%</u>	<u>Wt, g</u>	<u>%</u>
In				
Feed liquor	926		178	
Out				
Raffinate	<0.9	<0.1	11.0	6.2
Chloride strip	897	96.9	3.3	1.9
Carbonate strip	2.3	0.25	167	93.6
Out/In		97.2		101.8

Stripping. As was desired, practically all of 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. The fraction of uranium passed on the secondary strip section was 0.25% of the uranium entering the primary strip section.

Product. The uranium was precipitated from the chloride strip solution with ammonia, filtered, washed, dried, and calcined at 600°C. The composition of the loaded strip solution and the uranium product are shown in Table 6. The product was 87.6% uranium as U_3O_8 and no impurity (except sulfate) exceeded 1%.

Molybdenum

The molybdenum concentration in the raffinate from this run was nearly identical to that in the previous run, but, since the feed concentration was ten times greater, the recovery of molybdenum on a percentage basis was much higher for this run. The material balance (Table 5) shows that about 92% of the molybdenum entering the feed was recovered in the carbonate strip, while 6% was left in the raffinate and 2% in the chloride strip.

The molybdenum was precipitated from a portion of the carbonate strip solution according to the following procedure: The sodium carbonate was neutralized with hydrochloric acid, the CO_2 driven off by boiling, and the molybdenum precipitated as $CaMoO_4$, washed, and dried. The compositions of the loaded strip solution and molybdenum product are given in Table 7.

TABLE 6. COMPOSITION OF URANIUM STRIP
SOLUTION AND PRODUCT

<u>Constituent</u>	<u>Chloride Strip</u> <u>Solution</u>		<u>Product</u>	
	<u>g/l</u>	<u>g/100 g U</u>	<u>%</u>	<u>g/100 g U</u>
Uranium				
as U	20.4	-	74.2	-
as U ₃ O ₈	24.1	-	87.6	-
Iron	0.094	0.46	0.38	0.51
Molybdenum	0.075	0.37	0.26	0.35
Vanadium	0.015	0.07	0.042	0.06
Aluminum	0.017	0.08	0.07	0.09
Phosphate	0.24	1.1	0.85	1.1
Sulfate	-	-	6.2	8.4
Ammonia (as NH ₃)	-	-	<0.05	<0.07
Chloride	-	-	<0.05	<0.07

TABLE 7. COMPOSITION OF MOLYBDENUMSTRIP SOLUTION AND PRODUCT

<u>Constituent</u>	<u>Carbonate Strip Solution</u>		<u>Product</u>	
	<u>g/l</u>	<u>g/100 g Mo</u>	<u>%</u>	<u>g/100 g Mo</u>
Molybdenum				
as Mo	9.6	-	34.1	-
as CaMoO ₄	-	-	71.0	-
Uranium	0.17	1.8	1.05	3.0
Vanadium	<0.01	<0.1	-	-
Sulfate	4.0	-	8.6	25
Chloride	-	-	<0.05	<0.15

Loss of Organic Phase

The organic phase material balance, Table 8, shows that 375 ml of organic phase, equivalent to 0.47 ml/l raffinate, was lost during the run. Less than 57 ml of organic 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 0.121 mole, equivalent to 51 ppm of aqueous phase, of which 0.040 mole was associated with the 375 ml of organic phase lost. The remaining 0.081 mole, equivalent to 34 ppm, represents the amine lost through solubility or degradation.

The amine loss per cycle, Table 9, was estimated by assuming that the volume loss was evenly distributed over the run. The losses were equivalent to 87 ppm of aqueous phase for the first 20 cycles, after which they were nearly constant at an average of 42 ppm.

The amine loss due to solubility was 8 ppm greater in this run than in the previous run (with 10% secondary stripping), but about equal to the loss in the earliest long-term run (with carbonate stripping). The organic loss due to evaporation, leakage, and spray was higher in this run than in either of the previous runs, due probably to losses during minor mechanical difficulties. However, the total amine loss in any of the runs was relatively low, and the differences in the runs are of minor significance.

Chemicals Consumption

The consumption of chemicals during the run is shown in Table 10. The total chemicals cost was 12.1 cents per pound of U_3O_8 . This is

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

TABLE 8. ORGANIC PHASE MATERIAL BALANCE

	Volume, ml	Amine Concen- tration <u>M</u>	Moles of Amine	Amine loss, ppm of aq.
In				
Initial inventory	2,800	0.1054	0.295	
Additions				
at 20 cycles	139	0.5219	0.073	
	100	0.1054	0.011	
at 40 cycles	27	0.5219	0.014	
at 60 cycles	9	0.5219	0.005	
	100	0.1054	0.011	
at 80 cycles	32	0.5219	0.017	
	<u>100</u>	<u>0.1054</u>	<u>0.011</u>	
	3,307		0.437	
Out				
Samples	50	0.0937	0.005	
	50	0.1090	0.005	
	50	0.1087	0.005	
	50	0.1053	0.005	
Final inventory	<u>2,732</u>	0.1082	<u>0.296</u>	
	2,932		0.316	
Loss				
Volumetric	375*	0.1077	0.040	18
Solubility, etc. (by diff.)			<u>0.081</u>	<u>36</u>
Total amine loss (by diff.)			0.121	54

* Equivalent to 0.47 ml/liter raffinate.

TABLE 9. AMINE LOSS

Cycles	Amine concentration in organic, <u>M</u>		Loss per cycle, g*	Loss as ppm Aqueous Phase
	Analysis	Adjusted to		
0	0.1054			
20	0.0937	0.1139	0.770	87
40	0.1090	0.1129	0.415	47
60	0.1087	0.1096	0.378	43
80	0.1053	0.1102	0.383	43
100	0.1082		0.300	34

* Including volumetric loss of 0.159 g/cycle.

TABLE 10. CHEMICALS CONSUMPTIONBasis: 2.40 LB U_3O_8 Processed

Operation and Chemical	Consumption Total, lb	Per lb U_3O_8 , lb	Unit price, cents per lb	Cost per lb U_3O_8 , cents
Extraction				
Amine	0.104	0.0434	85.0	3.69
Kerosene	0.735	0.306	2.0	0.61
Stripping				
Sodium chloride	5.65	2.36	0.75	1.77
Sulfuric acid	0.473	0.197	1.50	0.30
Sodium carbonate	4.04	1.68	2.25	3.78
Precipitation				
Ammonia	0.805	0.335	5.75	<u>1.93</u>
Total				12.08

about double that in the run with 10% secondary stripping (5.9 cents), but only about 75% of that in the run with carbonate stripping (16.1 cents). The chemicals cost was higher in this run because: (1) less uranium was processed with the same chemical consumption due to lower uranium in the feed, (2) higher loss of amine and kerosene, and (3) higher consumption of sodium carbonate for stripping of the entire organic phase each cycle. Direct comparison of chemicals cost shows that the cost of complete sodium carbonate strip should be 3.1 cents per lb U_3O_8 more than 10% strip giving a total chemicals cost of 9.0 cents per lb U_3O_8 . Note that these costs are based on the recovery of uranium only. It is possible that the recovery of molybdenum from secondary strip solutions may offset the increased cost of secondary stripping.