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MINES BRANCH INVESTIGATION REPORT IR 58-49

ION EXCHANGE TREATMENT OF SOLUTION PRODUCED IN ACID LEACHING OF URANIUM ORE FROM AMALGAMATED RARE EARTH MINES LIMITED, BANCROFT, ONTARIO.

Ref. No. 7/57-7

by

E. KORNELSEN and V. M. McNAMARA

RADIOACTIVITY DIVISION

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LIST OF ILLUSTRATIONS

Mines Branch Investigation Report IR 58-49

ION EXCHANGE TREATMENT OF SOLUTION PRODUCED IN ACID LEACHING OF URANIUM ORE FROM AMALGAMATED RARE EARTH MINES LIMITED, BANCROFT, ONTARIO.

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E. Kornelsen* and V.M. McNamara *

ABSTRACT

An ion-exchange study has been made of the effect of repeated loading, with solution produced in acid leaching of uranium ore from Amalgamated Rare Earth Mines Ltd., Ref. No. 7/57-7, and elution on Amberlite IRA-400 resin. A study of uranium precipitation from eluate produced by this ion exchange treatment has also been made. No evidence of serious resin poisoning has been observed. Uranium precipitates obtained were satisfactory except for the fact that their thorium content was somewhat high. It is suggested that under plant operating conditions this latter trouble might not be encountered.

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INTRODUCTION

The work described in this report was done for two purposes, namely:

A. To determine what effect repeated cycles of loading (with Amalgamated Rare Earth Mines leach liquor) and elution would have on anion exchange resin Amberlite IRA-400.

B. To make a study of uranium precipitation from ion exchange eluate produced during the loading and elution tests mentioned in A.

The present report is divided into two sections, A and B, dealing with these two purposes.

For the convenience of the reader, this introduction is followed immediately by a brief Review of Results covering the two sections, after which each section is treated in detail.

REVIEW OF RESULTS

Section A. - Ion Exchange Cycling Testwork

A total of 52 cycles of loading, washing and elution was carried out on a sample of Amberlite IRA-400 resin (Rohm and Haas Lot No. 1904), using Amalgamated Rare Earth Mines leach liquor produced in previous acid leaching testwork (1)(2).

Examination of the used resin showed that its uranium saturation capacity had remained essentially unchanged and its uranium breakthrough capacity had not decreased seriously (see Table 1).

TABLE 1

Resin Capacities Determined by Standard Loading and Elution Tests

Amberlite IRA-400 Resin	Saturation Capacity, g U_3O_8/1 resin		Breakthrough Capacity*	
	Determined by loading	Determined by elution	g U_3O_8/1 resin	Retention time, min
Unused resin	71	69	55	3.0
After 24 cycles	68	67	47	3.0
After 52 cycles	69	68	48	3.1

* Breakthrough was taken as the point at which barren effluent assay reached 0.05 g U_3O_8/1.

The resin manufacturer's report on examination of a portion of the used resin is to be found in Appendix II (page 42).

Section B. - Precipitation of High Grade Eluates

Three batch precipitations were done on the high grade eluate obtained from the ion exchange testwork. Precipitates obtained were satisfactory except for the thorium contained, which exceeded specification. This is partly due to the fact that in the present testwork only one column was used, so that there was no opportunity to continue contacting the resin with uranium-containing liquor as in 3-column operation. Such prolonged contact would reduce the thorium loading by displacing it with uranium.

The high thorium content of the product was also attributed to the eluate not being recycled as in normal plant practice. As a result, the sulphate content is low and does not provide sufficient gypsum to co-precipitate the thorium in the first stage of precipitation. One can be reasonably confident that under normal operating conditions the thorium content can be maintained below specification limits.

The following table summarizes the results obtained:

URANIUM PRECIPITATE (by MgO "90")

	Test 1	Test 2	Test 3
Precipitant			
1st stage	-	Lime to pH 3.5	Lime to pH 4.0
2nd stage (pH, 7.0)	MgO "90"	MgO "90"	MgO "90"
Product			
% U_3O_8	71.48	74.74	77.50
% ThO_2	2.69	2.00	1.80
Parts Th/100 U_3O_8	3.30	2.35	2.04
Reagent Consumption lb/lb U_3O_8			
Hydrated lime		0.342	0.424
MgO	0.553	0.314	0.246

A stable foam formed on the surface of the precipitation feed solution during the precipitation step. This is attributed to the flotation reagent used in ore concentration, which is believed to have been removed from the leach liquor by the resin and taken up by the eluting solution. This foam tended to disappear as pH 7 was approached.

SECTION A. - ION EXCHANGE CYCLING TESTS USING AMBERLITE IRA-400 RESIN

Details of Testwork

Apparatus-

A description of the apparatus used is given in Appendix I (page 38).

Reagents-

The leach liquor used was produced by acid leaching of ore from Amalgamated Rare Earth Mines Ltd. (see Radioactivity Division Report No. SR-483/57 (1) for leaching details). The acidity of the leach liquor received was adjusted to pH 1.75 by the addition of reagent grade sulphuric acid.

The eluting solution used to remove the uranium from the resin was 1N NaCl - 0.1N H_2SO_4.

The synthetic pregnant solution used for the standard loading tests was prepared from uranyl sulphate, magnesium sulphate, and sulphuric acid. The eluting solution used for standard elution was 1N NaCl - 0.1N H_2SO_4. Enough of this solution was prepared at the outset to permit use of the same solution for all three standard elution tests, thereby avoiding possible changes in eluting conditions caused by slight variations in solution composition. The same synthetic pregnant solution was used for the first and last standard loading tests, but the solution for the second test was prepared separately.

Procedure -

(a) Measurement of Resin Bed Volume

A quantity of Amberlite IRA-400 (Maker's Lot No. 1904) anion exchange resin was placed in the glass ion exchange column. Several litres of 1N NaCl - 0.1N H_2SO_4 eluting solution were pumped through the resin to condition it before use. The bed volume of the resin was then measured by the following three methods:

i) The resin bed was fluidized by backwashing with water, then water was drained off at about 10 ml/min until no further settling of the resin took place. The flow rate of the water was measured with a rotameter. This method gave bed volume values of 102, 102 and 103 ml - average, 102 ml. This value was used in all calculations of resin uranium capacity, etc.

ii) The resin bed was backwashed with water at a flow rate of about 20 ml/min until the resin bed volume was at a maximum. Then water was drained from the column at about 30 ml/min until the resin bed volume was at a minimum. This method gave bed volume values of 104, 104 and 104 ml- average value 104 ml.

iii) The glass column containing the resin in water was tapped with a hammer, consisting of a rubber stopper on a metal rod, until no further settling of the resin bed was observed. This method gave bed volume values of 94 and 94 ml - average, 94 ml.

(b) Standard Loading and Elution

To determine the uranium capacity of the resin before, during and after the life test, it was loaded using the synthetic pregnant solution.

The first 4450 ml of barren effluent from the standard loading tests was collected, mixed, and analysed for U_3O_8. The next 50 ml of barren was analysed for U_3O_8 and following this, a 50 ml sample of barren was taken after every 450 ml throughput until sufficient synthetic pregnant solution had been passed through the column to saturate the resin. Each 50 ml sample was assayed for uranium. The 450 ml portions were combined, mixed, and also assayed for uranium.

Following saturation of the resin, it was washed with water at the same flow rate as that of the synthetic pregnant solution.

After this, eluting solution was passed through the resin. The eluate was collected in 100 ml volumetric flasks for the first 500 ml throughput and in 250 ml volumetric flasks afterwards. In the case of the first standard elution the total volume of eluate collected was 2000 ml and in the case of the second and third, 2500 ml. A larger volume of eluate was collected in the later elutions to ensure removal of all uranium from the resin even if the elution rate had dropped due to deterioration.

For each standard elution, a composite eluate sample, consisting of 10 ml from each 100 ml fraction and 25 ml from each 250 ml fraction, was prepared and assayed for uranium. The individual fractions were also analysed for U_3O_8.

A standard loading and elution test was done at the beginning, and after 24 cycles and 52 cycles of loading with leach liquor.

(c) Loading with Amalgamated Rare Earth Mines Leach Liquor and Elution

The leach liquor received from the pilot plant was acidified with sulphuric acid to about pH 1.75, and samples from each batch used were assayed for various constituents.

The cycle of loading, washing, elution and washing consisted of:

i) Leach liquor flow - 11 hours at approximately 10 ml/min (retention time, about 4 min; total volume passed per cycle, about 67 bed volumes). The barren effluent during the first 200 min of loading was collected separately and reserved for any testwork that might be required. Breakthrough did not occur until after 200 min of loading.

ii) Water flow - 20 min at about 10 ml/min.

iii) Eluting solution flow - During the first 5 cycles, a total of 20 bed volumes of eluate was collected at a flow rate of about 4.2 ml/min (retention time about 9.7 min). The eluate was "split", i.e., the last 10 bed volumes of eluate from one cycle were used as eluting solution for the first 10 bed volumes of eluate of the following cycle. The eluting solution used while collecting the last 10 bed volumes of eluate was fresh 1N NaCl - 0.1N H_2SO_4 solution.

Starting with cycle No. 6, a total of 18 bed volumes was collected at a flow rate of about 4.1 ml/min (retention time about 10 min). In this case, the "split" was made at 9 bed volumes and the last 9 bed volumes of eluate were recycled. The eluate from the first "split" was collected and used in uranium precipitation studies (see Section B).

iv) Water flow - 40 min at about 10 ml/min.

Samples of barren effluent were taken at intervals to determine breakthrough or to note whether it occurred before or after 200 min of loading had taken place. From time to time, samples of eluate were taken to determine nil spot. When required, the resin bed was backwashed to remove foreign matter which collected. Several samples of the first "split" of eluate were assayed for uranium to determine the amount of uranium eluted per cycle.

After completion of the final standard loading and elution test, about 90 ml of the resin were sent to the manufacturer (Rohm and Haas) for testing, and the remainder was retained for moisture and sulphated ash determinations. The sulphated ash was analysed spectrographically.

The moisture in the resin was determined by drying the resin in a sintered glass,filtering crucible by suction for 5 minutes and then in a drying oven at 110°C for 24 hours. The loss in weight during drying in the oven, divided by the weight of the resin after drying by suction, was taken as the fraction of moisture in the sample.

The sulphated ash content of the resin was determined by moistening the dried resin from the moisture test with concentrated sulphuric acid in a Vycor dish. After charring on a hot-plate, the resin was ignited over a burner. The ash was moistened with sulphuric acid and again ignited over a burner. From this the ash content (based on the dry resin weight) was calculated.

Data and Results

Conditions and results of the three standard loading tests are shown in Tables 2 and 3. The standard loading curves are shown in Figure 1.

TABLE 2

Conditions of Standard Loading Tests

Particulars	Unused Resin	After 24 Cycles	After 52 Cycles
Synthetic Pregnant Solution:			
U_3O_8 assay -g/l	1.02	1.02	1.02
Volume pumped-litres	11.0	11.0	12.0
U_3O_8 content -g	11.2	11.2	12.2
pH	1.5	1.5	1.5
$SO_4^=$ -g/l	33.1	37.4	33.1
Resin Bed Volume - ml	102	102	102
Average Flow Rate - ml/min	13.4	13.5	13.2
Average R.T.* - min	3.0	3.0	3.1
Barren Effluent Composite:			
Volume -litres	5.85	5.85	6.75
U_3O_8 assay -g/l	0.59	0.64	0.67
U_3O_8 content -g	3.45	3.74	4.52
Water wash			
Volume -litres	0.20	0.20	0.20
U_3O_8 assay -g/l	0.81	0.59	0.67
U_3O_8 content -g	0.16	0.12	0.13

$$* \text{ R.T.} = \text{Retention Time} = \frac{\text{Void Volume}}{\text{Flow Rate}}$$

$$= \frac{\text{Bed Volume} \times 0.4}{\text{Flow Rate}}$$

TABLE 3

Results of Standard Loadings of Resin

Fraction of Barren Effluent		Barren Effluent from Unused Resin		Barren Effluent from Resin after 24 Cycles		Barren Effluent from Resin after 52 Cycles	
ml	Bed volumes*	U_3O_8 assay, g/1	U_3O_8 content, g	U_3O_8 assay, g/1	U_3O_8 content, g	U_3O_8 assay, g/1	U_3O_8 content, g
0-4,450	-	0.0002	0.0009	0.003	0.0134	0.002	0.0089
4,450-4,500	43.9	0.002	0.0001	0.028	0.0014	0.020	0.001
4,950-5,000	48.8	0.012	0.0006	0.079	0.0040	0.072	0.0036
5,450-5,500	53.7	0.044	0.0022	0.17	0.0085	0.17	0.0085
5,950-6,000	58.6	0.15	0.0075	0.32	0.016	0.32	0.016
6,450-6,500	63.5	0.36	0.018	0.49	0.0245	0.48	0.024
6,950-7,000	68.4	0.58	0.029	0.60	0.030	0.62	0.031
7,450-7,500	73.3	0.75	0.0375	0.80	0.040	0.68	0.034
7,950-8,000	78.2	0.84	0.042	0.81	0.0405	0.78	0.039
8,450-8,500	83.1	0.88	0.044	0.89	0.0445	0.85	0.0425
8,950-9,000	88.0	0.95	0.0475	0.91	0.0455	0.84	0.042
9,450-9,500	92.9	1.03	0.0515	0.93	0.0465	0.83	0.0415
9,950-10,000	97.8	1.01	0.0505	0.95	0.0475	0.84	0.042
10,450-10,500	102.7	0.98	0.049	0.91	0.0455	0.91	0.0455
10,950-11,000	107.6	1.03	0.0515	0.95	0.0475	0.93	0.0465
11,450-11,500	112.5	-	-	-	-	0.92	0.046
11,950-12,000	117.4	-	-	-	-	0.91	0.0455
Total U_3O_8 Content of Leakage Samples			0.4318		0.4553		0.5175
Syn. Preg. Soln.		1.02		1.02		1.02	

* Bed volumes have been calculated to the "mid-point" of the sample, i.e., to 4,475 ml for the 4,450-4,500 ml fraction.

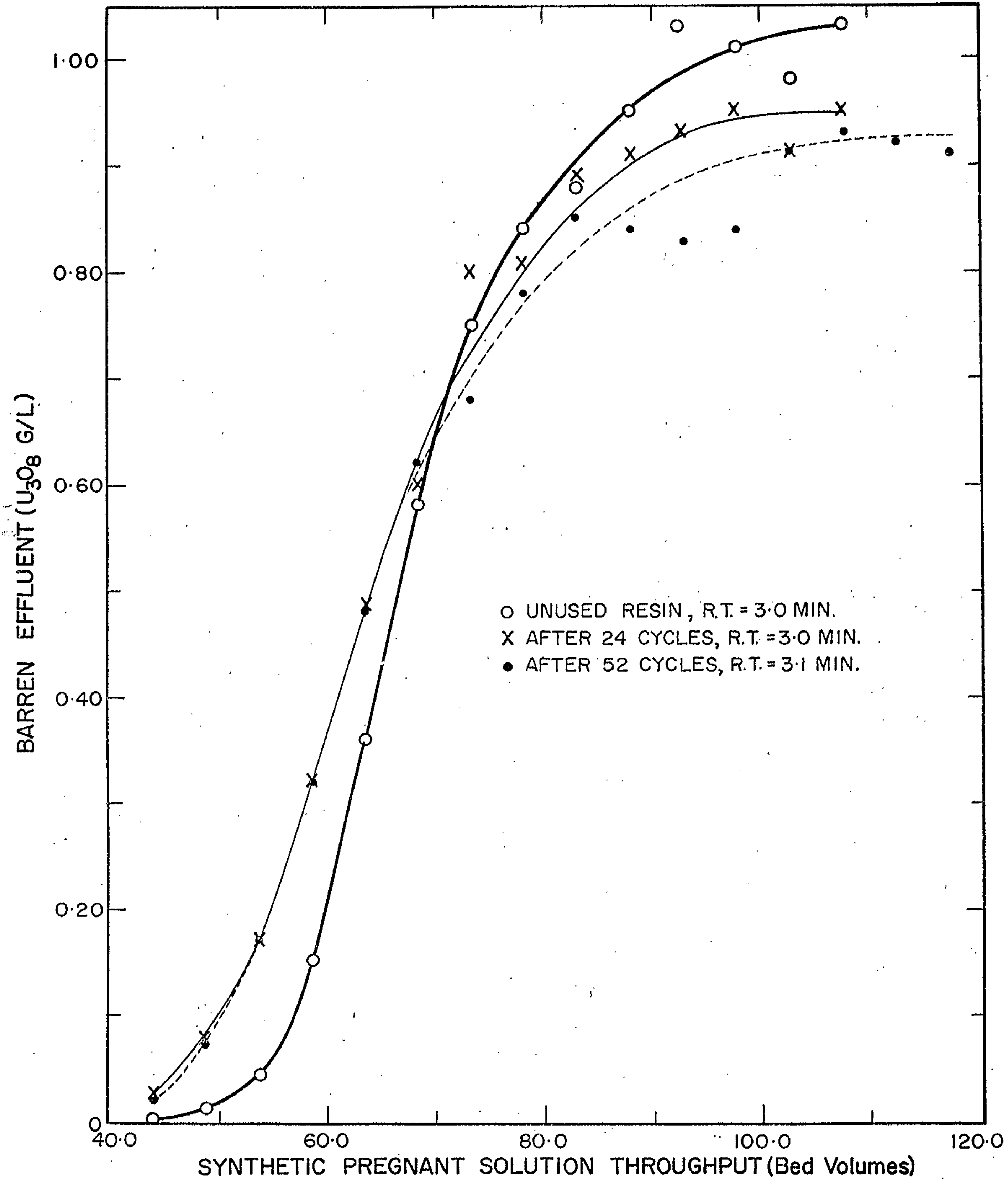

FIGURE I

LOADING CURVES, STANDARD LOADING TESTS

The calculation of the uranium capacity to breakthrough of the resin is shown in Table 4.

TABLE 4

Calculation of Uranium Capacity to Breakthrough *

Particulars	Unused Resin	Resin after 24 Cycles	Resin after 52 Cycles
Bed volumes of synthetic pregnant solution to breakthrough **	54	46	47
Volume of synthetic pregnant solution to breakthrough, litres	5.51	4.69	4.79
U_3O_8 content of synthetic pregnant solution to breakthrough, g	5.62	4.78	4.89
U_3O_8 capacity of resin to breakthrough, g U_3O_8/1 resin	55	47	48

* Breakthrough was taken as the point at which the U_3O_8 concentration of the barren effluent reached 0.05 g/1.

** These values are taken from Figure 1.

The calculation of the uranium (saturation) capacity of the resin, based on the (standard) loading stage, is shown in Table 5.

TABLE 5

Calculation of Uranium Capacity of Resin, Loading Stage

Particulars	Unused Resin		Resin after 24 Cycles		Resin after 52 Cycles	
	U_3O_8 Influent, g	U_3O_8 Effluent, g	U_3O_8 Influent, g	U_3O_8 Effluent, g	U_3O_8 Influent, g	U_3O_8 Effluent, g
Synthetic pregnant solution (see Table 2)	11.2		11.2		12.2	
Barren effluent composite (see Table 2)		3.45		3.74		4.52
Leakage samples (see Table 3)		0.43		0.46		0.52
Water wash (see Table 2)		0.16		0.12		0.13
Total U_3O_8 effluent		4.04		4.32		5.17
U_3O_8 held on resin, g	7.2		6.9		7.0	
U_3O_8 capacity of resin, g/l resin	71		68		69	

The results of elution of the resin loaded with synthetic pregnant solution are shown in Table 6. The elution curves are to be found in Figure 2.

The calculation of the uranium capacity of the resin based on the elution stage is shown in Table 7.

TABLE 6

Results of Elution of Resin Loaded with Synthetic Pregnant Solution (Eluting Solution, 1N NaCl - 0.1N H_2SO_4)

Fraction of Eluate		U_3O_8 Assay of Eluate Fraction, g/l		
ml	Bed volumes	Unused Resin*	Resin after 24 Cycles**	Resin after 52 Cycles***
0-100	0.49	0.53	0.40	0.46
100-200	1.47	12.67	13.39	12.50
200-300	2.45	20.46	18.83	18.77
300-400	3.43	14.40	14.11	13.35
400-500	4.41	9.11	8.67	8.73
500-750	6.13	4.00	4.05	4.27
750-1,000	8.58	1.08	1.18	1.33
1,000-1,250	11.03	0.28	0.33	0.42
1,250-1,500	13.48	0.077	0.12	0.16
1,500-1,750	15.93	0.013	0.039	0.039
1,750-2,000	18.38	0.003	0.021	0.016
2,000-2,250	20.83	-	0.028	0.008
2,250-2,500	23.28	-	0.025	0.004

* Average elution flow rate = 3.88 ml/min; R.T.= 10.5 min.
** Average elution flow rate = 3.89 ml/min; R.T.= 10.5 min.
*** Average elution flow rate = 3.99 ml/min; R.T.= 10.2 min.

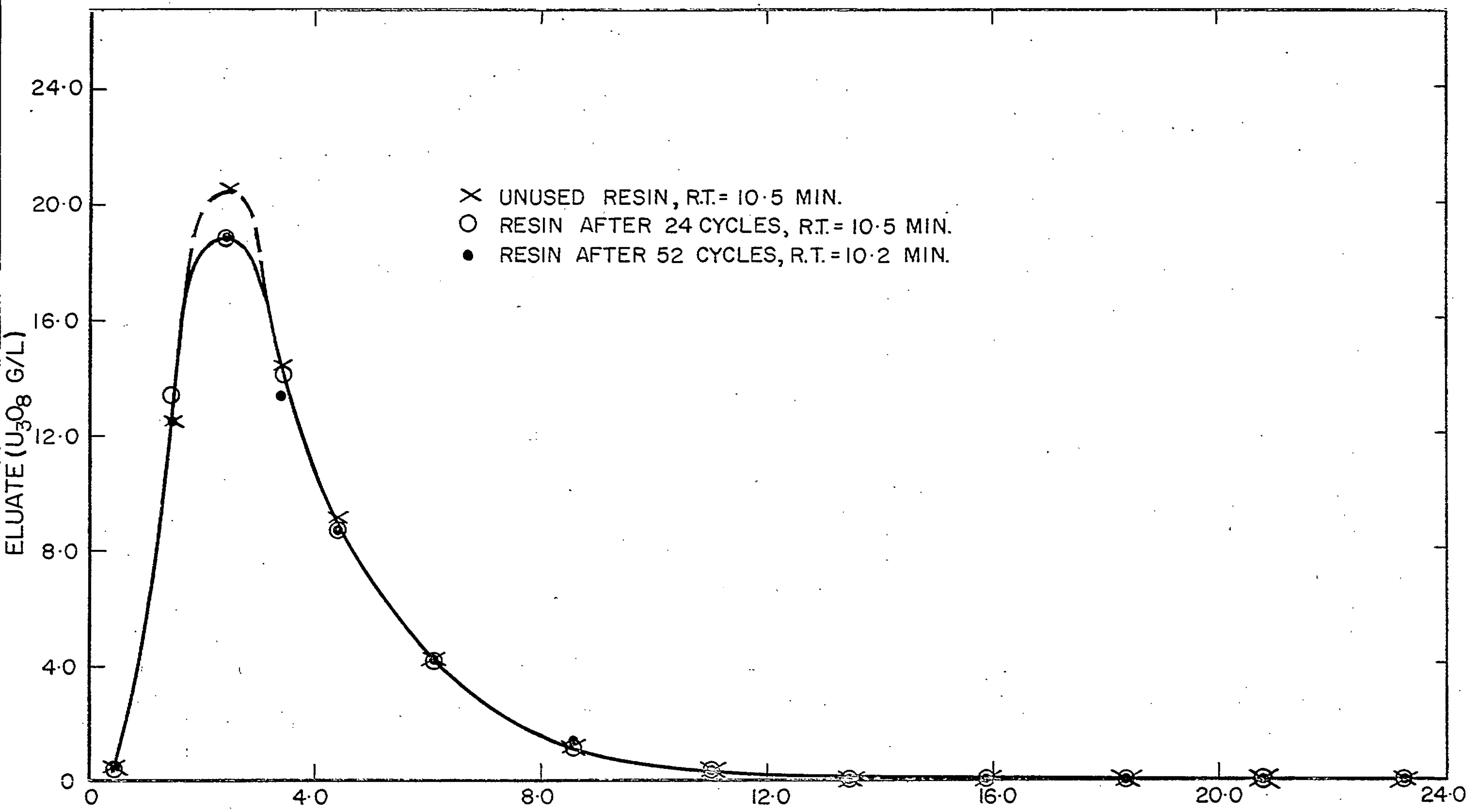

FIGURE 2

ELUTION CURVES, STANDARD LOADING TESTS

TABLE 7

Calculation of Uranium Capacity of Resin, Elution Stage

Particulars	Unused Resin	Resin after 24 Cycles	Resin after 52 Cycles
U_3O_8 assay of eluate composite, g/l	3.53	2.75	2.76
Total volume of eluate, litres	2.00	2.50	2.50
Total U_3O_8 content of eluate (calculated from eluate composite assay), g	7.06	6.88	6.90
U_3O_8 capacity of resin, g/l	69	67	68

Leach liquor assays of the batches used are given in Table 8. The results of semi-quantitative spectrographic analysis of the dissolved solids in Batches No. 1 and No. 2 are listed in Table 9. This latter table also shows the results of a similar analysis of the solids in the barren effluent collected during the first 200 min of each of cycles 29 to 39, inclusive.

The leach liquor of Batch No. 1 was produced during leaches 13 and 14 of the pilot plant run. (For leaching details, etc., see page 13, Radioactivity Division Report SR-483/57 (2).) Batches No. 2 and No. 3 of leach liquor were both taken from the combined liquor production of leaches 1 to 12 and 15 to 20.

TABLE 8

Leach Liquor Assays

Batch Number: Used in Cycles:	1 1 to 19 inc.	2 20 to 43 inc.	3 44 to 52 inc.
pH	1.73	1.74	1.75
Assays, g/1:*			
U_3O_8	3.12	2.60	2.66
ThO_2	1.94	1.81	1.83
Fe^{++}	0.90	0.52	-
Fe^{+++}	1.44	1.43	-
Total Fe	-	-	1.90
$Na_2S_4O_6$	0.038	0.04	0.06
V_2O_5	<0.01	<0.03	-
Mo	<0.001	<0.0002	-
$(R.E.)_2O_3$ **	1.10	1.10	0.89
F	0.17	0.095	-
P_2O_5	0.01	-	-
SiO_2	1.38	1.14	-
As	<0.01	-	-
As + P_2O_5	-	0.020	-
$SO_4^=$	19.5	18.1	18.1
Cl	0.29	0.27	-
Total solids	35.9*	34.4*	-

* For semi-quantitative spectrographic analysis, see Table 9.

** $(R.E.)_2O_3$ = rare earth oxides

TABLE 9

Results of Semi-quantitative Spectrographic Analysis of Leach Liquor Solids and Barren Effluent Solids

Element	Batch No. 1, %	Batch No. 2, %	Barren Effluent, * %
Al	5	2.5	2
Fe	7	6	6
Ca	1.5	1.5	2
Si	1.5	2	2
Mg	1.5	2	2
Th	2.5	8	5
U	2.5	3	N.D.
Ce	2	2.5	2.5
La	1	1	1
Mn	0.3	0.5	0.5
Bi	0.25	-	-
Pb	0.1	-	-
Y	0.35	0.4	0.4
Yb	0.1	0.1	0.1
Dy	0.07	0.04	0.05
Gd	0.04	0.05	0.05
Cu	0.04	0.06	0.05
Ti	0.03	0.03	0.03
B	0.01	0.01	0.01
Be	0.002	0.002	0.003
Cr	-	N.D.	0.01
V	-	N.D.	0.007

N.D. = none detected

* This was a sample of barren effluent collected during the first 200 minutes of loading of cycles 29 to 39 inclusive, using batch No. 2 of leach liquor.

Table 10 shows the amount of uranium eluted during a number of cycles, from which the uranium capacity of the resin has been calculated. These values are naturally higher than those obtained in the standard loading, due to the fact that the standard loading solution has a lower uranium concentration.

Table 10

Uranium Capacity of Resin Loaded with Amalgamated Rare Earth Leach Liquor

Cycle No.	U_3O_8 assay of feed liquor, g/l	Volume of first half of eluate, litres	U_3O_8 assay, g/l	U_3O_8 content, g	U_3O_8 capacity of resin, g U_3O_8/l resin
3	3.12	1.020	9.65	9.84	96
8	3.12	0.918	10.81	9.92	97
15	3.12	0.918	10.75	9.87	97
20	2.60	0.918	9.91	9.10	89
23	2.60	0.918	9.99	9.17	90
24	2.60	0.918	9.91	9.10	89
39	2.60	0.918	10.44	9.58	94
44	2.66	0.918	9.98	9.16	90
46	2.66	0.918	10.62	9.75	96
52	2.66	0.918	10.17	9.34	92

Note: 1 g/l = 0.0624 lb/cu ft, e.g., 90 g U_3O_8/l resin = 5.62 lb U_3O_8/cu ft.

In Table 11 are shown the results of assaying a number of barren effluent samples for uranium. The samples listed for cycles Nos. 17, 25 and 47 were taken, in each case, just before and just after 200 min of loading were completed. The results for cycles Nos. 1 and 26 have been plotted in Figure 3.

TABLE 11

Uranium Assay of Barren Effluent Samples (loading with Amalgamated Rare Earth Mines Leach Liquor)

Barren Effluent Portion		U_3O_8 Assay, g/l				
ml	Bed volumes	Cycle No. 1 (R.T.=4.1 min)	Cycle No. 17 (R.T.=4.1 min)	Cycle No. 25 (R.T.=4.0 min)	Cycle No. 26 (R.T.= 4.0 min)	Cycle No. 47 (R.T.=4.1 min)
0-50	0.2	-	-	-	0.003	-
50-100	0.7	-	-	-	0.002	-
100-150	1.2	-	-	-	0.0007	-
150-200	1.7	-	-	-	0.001	-
200-700	-	-	-	-	0.003	-
700-750	7.1	-	-	-	0.001	-
750-1250	-	-	-	-	0.0008	-
1250-1300	12.5	-	-	-	0.0008	-
1380-1430	13.8	0.0002	-	-	-	-
1300-1800	-	-	-	-	0.002	-
1800-1850	17.9	-	-	-	0.012	-
1880-1930	18.7	0.003	-	-	-	-
1920-1981	19.1	-	0.007	-	-	-
1930-1980	19.2	-	-	-	-	0.014
1981-2032	19.7	-	0.015	-	-	0.019
2000-2053	19.9	-	-	0.008	-	-
2053-2103	20.4	-	-	0.010	-	-
1850-2350	-	-	-	-	0.061	-
2350-2400	23.3	-	-	-	0.16	-
2380-2430	23.6	0.38	-	-	-	-
2400-2900	-	-	-	-	0.37	-
2880-2930	28.5	1.49	-	-	-	-
2900-2950	28.7	-	-	-	0.70	-
2950-3450	-	-	-	-	1.21	-
3380-3430	33.4	2.09	-	-	-	-
3450-3500	34.1	-	-	-	1.70	-
3880-3930	38.3	2.26	-	-	-	-

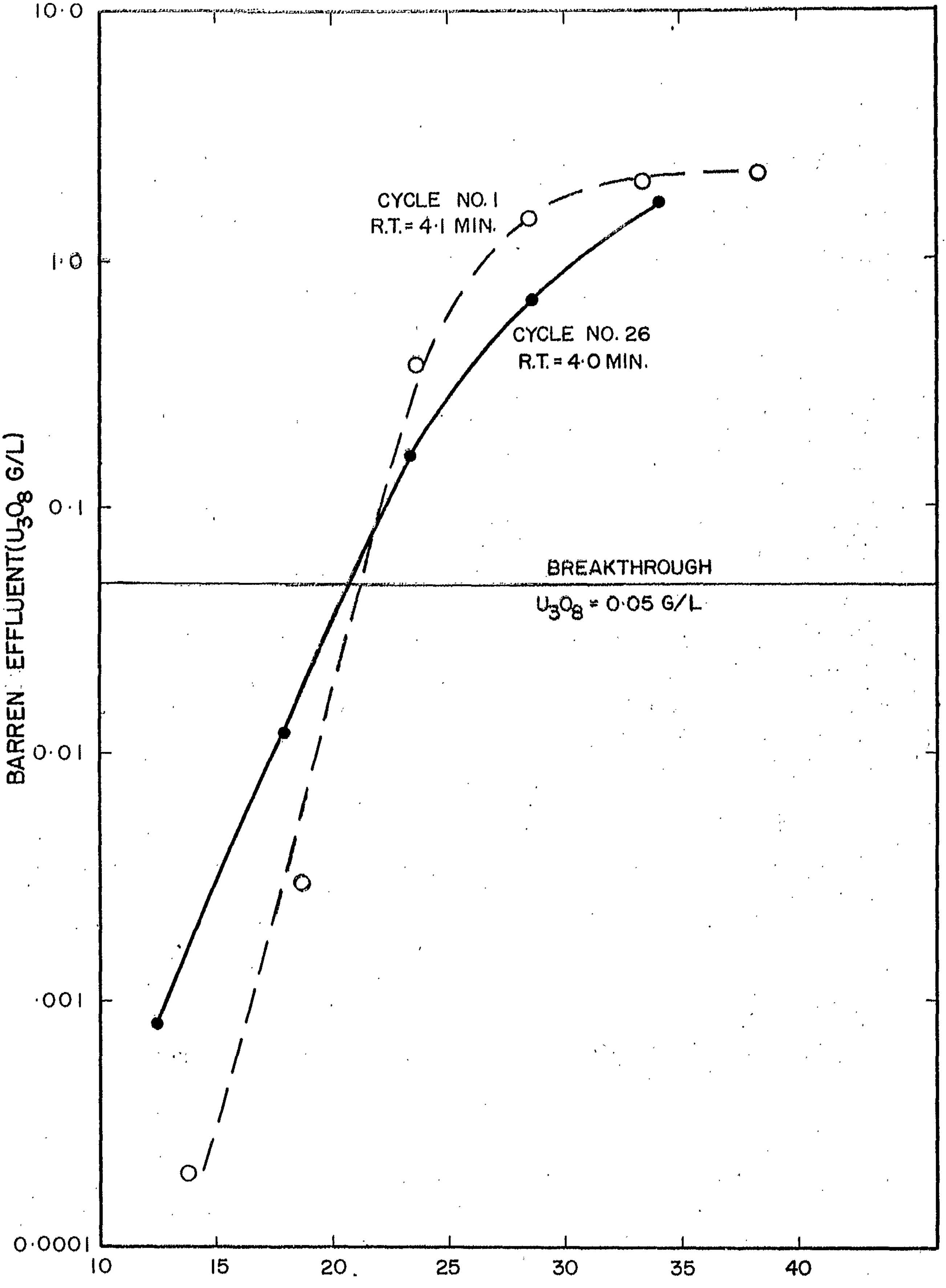

FIGURE 3

LOADING CURVES USING AMALGAMATED RARE EARTH MINES LEACH LIQUOR

Table 12 shows the uranium assay of eluate samples taken to determine "nil spot" and to see if any change occurred with use of the resin. The results for cycles No. 6 and No. 52 have been plotted in Figure 4.

TABLE 12

Uranium Assay of Eluate Samples taken for Nil Spot* Determination
(loading with Amalgamated Rare Earth Mines Leach Liquor)

Eluate Portion		U_3O_8 Assay - g/l					
ml	Bed Volumes	Cycle No. 1 (R.T. = 10.1 min)	Cycle No. 6 (R.T. = 10.1 min)	Cycle No. 19 (R.T. = 9.8 min)	Cycle No. 29 (R.T. = 10.1 min)	Cycle No. 40 (R.T. = 10.1 min)	Cycle No. 52 (R.T. = 10.1 min)
1000-1025	9.9	0.70	-	-	-	-	-
1150-1175	11.4	-	0.82	0.89	0.98	0.91	1.01
1375-1400	13.6	-	0.32	0.39	0.42	0.41	0.43
1500-1525	14.8	0.043	-	-	-	-	-
1600-1625	15.8	-	0.11	0.15	0.17	0.18	0.20
1750-1775	17.3	0.012	-	-	-	-	-
1825-1850	18.0	-	-	0.059	-	-	-
1836-1861	18.1	-	0.040	-	0.071	0.074	0.088
2000-2025	19.7	0.004	-	-	-	-	-
2225-2250	21.9	0.002	-	-	-	-	-

* At nil spot, the uranium concentration in the eluate is 0.1 gm U_3O_8/l.

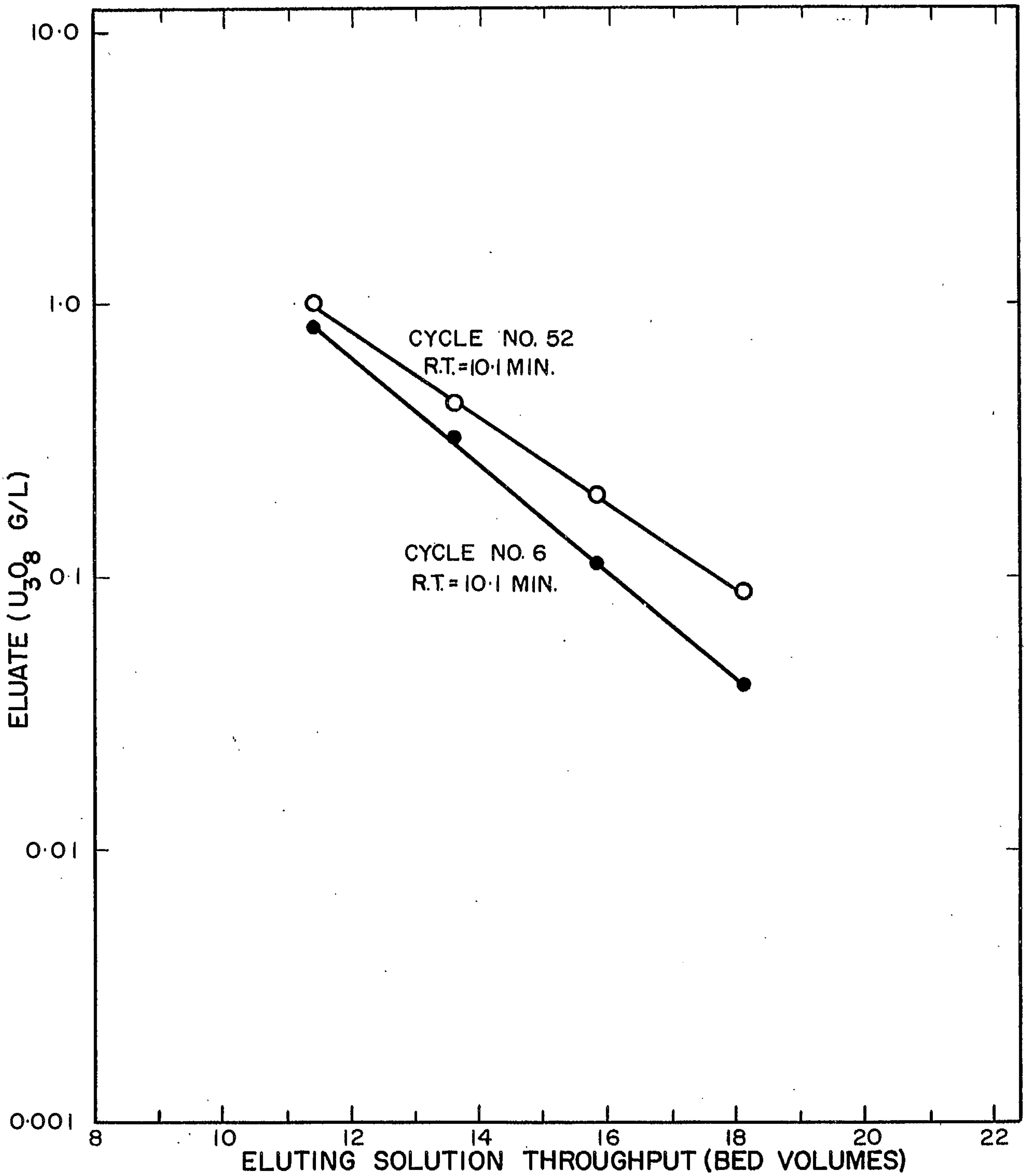

FIGURE 4

ELUTION CURVES FOR NIL SPOT DETERMINATION
LOADING WITH AMALGAMATED RARE EARTH MINES LEACH LIQUOR

Table 13 shows the results of analyses of barren effluent collected during the first 200 min of loading. These were obtained in order to see if any elements other than uranium were being adsorbed. (See Table 9 for the semi-quantitative spectrographic analysis of the solids (dissolved) in the leach liquor and in this sample of barren effluent.)

TABLE 13

Results of Analysis of Barren Effluent Collected During First 200 Minutes of Loading, Cycles 29 to 39 inclusive*

Constituent	Assay, g/1
U_3O_8	0.002
ThO_2	1.10
Fe^{++}	0.73
Fe^{+++}	1.36
$Na_2S_4O_6$	0.03
V_2O_5	<0.02
Mo	<0.0001
$(R.E.)_2O_3$**	0.92
F	0.095
SO_4	11.5
SiO_2	1.02
$As+P_2O_5$	0.015
Total Solids	22.7
Cl	2.47

* Used Batch No.2 leach liquor

** $(R.E.)_2O_3$ = rare earth oxides

The effluent collected while backwashing the resin was measured and assayed for uranium to see how much was removed durin this operation. These results are in Table 14.

TABLE 14

Uranium Removed from Resin by Backwashing

Cycle No.	Volume of Effluent, l	U_3O_8 Assay, g/1	U_3O_8 Content, g
7	1.66	0.31	0.51
20	1.55	0.24	0.37
23	1.05	0.28	0.29
24	1.22	0.24	0.29
27	0.80	0.35	0.28
32	0.89	0.31	0.28
38	0.80	0.34	0.27
44	0.88	0.30	0.26

The amount of sulphuric acid required to adjust the pH of the leach liquor as received from the pilot plant to pH 1.75 is indicated in Table 15.

TABLE 15

Sulphuric Acid Requirements of Leach Liquor for Adjustment of pH

Particulars	Batch No. 1	Batch No. 2	Batch No. 3
Weight of leach liquor, lb	325	400	400
Specific gravity	1.027	1.025	1.025
Initial pH	1.94	1.85	1.80
Final pH	1.73	1.74	1.75
Sulphuric acid added - ml*	70	35	23
- g*	129	64	42
- lb*	0.284	0.141	0.092
Acid consumption, lb H_2SO_4**/ton leach liquor	1.68	0.68	0.44

* Concentrated reagent grade sulphuric acid solution (assay, 95-98% H_2SO_4; specific gravity, 1.84).

** Calculated as pure H_2SO_4.

The moisture content of the unused resin was 46% and that of the resin after 52 cycles was also 46%. The sulphated ash content of the unused resin was 1.1%, and that of the used resin was 0.52%. The results of spectrographic analysis of resin ash are shown in Table 16.

TABLE 16

Results of Semi-Quantitative Spectrographic Analysis of Resin Ash

Element	Ash from unused resin	Ash from resin after 52 cycles
	%	%
Al	10	10
Si	0.1	10
Zr	N.D.	10
Na	N.D.	3
Fe	1	2.5
Mo	N.D.	3
Nb	N.D.	0.8
Mg	0.2	1
Ca	0.05	0.15
Zn	0.2	N.D.
Ti	0.001	0.1
Pb	0.009	0.09
Cu	0.05	0.03
Co	N.D.	0.02
B	0.001	0.002
Mn	0.003	0.007
Cr	0.006	0.009
Ni	0.01	N.D.

N.D. = none detected

Discussion of Results, and Conclusions

The uranium capacity of the resin, as calculated on the basis of uranium removed from the synthetic pregnant solution, was essentially unchanged after 52 cycles of loading with Amalgamated Rare Earth Mines leach liquor (see Table 5). Also, no significant change in capacity was found on the basis of uranium eluted from the resin (see Table 7).

No decrease in resin uranium capacity is shown by the loading values calculated from a number of cycles throughout the course of the test (see Table 10).

No significant change in leakage characteristics is indicated by the loading curves of Figure 1. The drop in breakthrough capacity from 55 to 48 grams per litre of resin is not thought to be serious, and no worsening of the effect occurred from 24 to 52 cycles (see Table 4). The elution characteristics, as shown by the elution curves of Figure 2, are also unchanged. Further evidence that the loading and elution characteristics of the resin have remained unaltered is to be found in Tables 10 and 11 and in Figures 3 and 4.

The moisture content of the resin was the same after 52 cycles of loading. The sulphated ash content of the used resin is about what might be expected and in its magnitude is not indicative of serious resin poisoning.

The results of the semi-quantitative spectrographic analysis of the resin ash show that the greatest increases in concentration have occurred in the case of the elements Si, Zr, Mo, and Ti. However, due to the low ash content, the actual amounts represented, on a dry resin basis, are quite low, and these concentrations appear to have had no noticeable effect on the resin characteristics studied.

SECTION B. - URANIUM PRECIPITATION FROM ION EXCHANGE ELUATE

Procedure

Three batch precipitations were carried out on high grade eluate obtained from the ion exchange testwork. Each precipitation feed represented several cycles of operation, since approximately one litre of eluate was obtained per cycle.

The three precipitations were carried out as follows:

I. Single-Stage.
 MgO "90" (Sample No. 5/57-14) to pH = 7.0

II. Two-Stage.
 Alcan hydrated lime to pH = 3.5
 MgO "90" to pH = 7.0

III. Two-Stage.
 Alcan hydrated lime to pH = 4.0
 MgO "90" to pH = 7.0

The small quantity of precipitate obtained from the lime addition was given a 25 ml water displacement wash into the filtrate, followed by two 100 ml water washes, which were discarded. The precipitate obtained from MgO "90" addition was washed with two 500 ml portions of 1/4% Na_2SO_4 solution and one wash of 500 ml water.

Lime was added as a slurry, 20 parts lime/80 parts water. MgO "90" was added dry.

Results and Discussion

Due to the fact that the eluate was not recycled in the ion exchange operation, there was a relatively low sulphate concentration in solution (16 g/1), and consequently there was a very small quantity of gypsum precipitate. From previous studies, as well as from this work, it is apparent that adequate thorium precipitation below pH 4.0 is dependent upon having a large gypsum precipitate which will co-precipitate the thorium. This condition is obtained in standard ion exchange operation where barren eluate is recycled and the sulphate concentration is greater than 100 g/l.

Tables 17 and 18 show the data and results of the precipitation batch tests. Tests 1 and 2 are standard single-stage and two-stage precipitation respectively. The percent thorium in the final precipitate was greater than specification in both tests. Therefore, precipitation 3 was performed in an attempt to bring down more of the thorium during the first stage of precipitation, and thus lower the amount appearing in the final precipitate.

Assays of the first precipitate for tests 2 and 3 are included in Table 17. Table 19 gives a complete list of the final product assays for single-stage and two-stage precipitation.

From the standpoint of product specifications, the only problem is the thorium. The only unusual condition noted in the precipitation tests was that of the foam produced during neutralization. This was undoubtedly due to the flotation reagent used during ore treatment, which is believed to have been adsorbed to some extent on the resin and subsequently stripped by the eluate.

TABLE 17

Precipitation Data and Results

Test	1	2	3
Eluate			
Volume, litres	14.78	14.42	8.00
pH	1.35	1.35	1.35
Assays (g/l)			
U_3O_8	10.49	10.23	10.24
ThO_2	0.38	0.36	0.34
Fe	0.080	0.088	-
SO_4	17.0	16.3	-
Precipitant			
Alcan lime (g)	-	51	34.5
MgO "90" (g)	85	47	20
Precipitate, 1st cake			
dry wt, g	-	28	24
Assays, %			
U_3O_8	-	0.84	0.78
Fe	-	2.06	-
ThO_2	-	2.20	3.60
SO_4	-	56.9	-
CaO	-	24.3	-
Precipitate, 2nd cake			
$\frac{\text{wet wt, g}}{\text{dry wt, g}}$	415/215	542/200	105 (dry)
Moisture, %	51.7	63.1	-
Assay, %			
U_3O_8	71.48	74.74	77.50
ThO_2	2.69 *	2.00*	1.80 *
Final Barren			
Assay g/l			
U_3O_8	0.0002	0.0007	0.0006
Reagent Consumption ($lb/lb\ U_3O_8$)			
Hydrated lime	-	0.342	0.424
MgO	0.553	0.314	0.246

* Over specification limit.

TABLE 18

Further Precipitation Data

Test	Precipitant (cumulative g)		pH	Observations
1			1.35	
	MgO	12	1.50	Very severe foam formation on surface during addition of MgO below pH = 7.0. This stable foam (1 1/4 in. thick on 9 in. liquid depth) disintegrated at the neutral point to about 1/4 in. of very light foam. Filtering was good.
		37	3.75	
		52	4.50	
		62	4.80	
		67	5.10	
		80	5.25	
		85	7.30	
2			1.35	
	Lime	30	1.85	
		50	3.35	Some light foam (1/4 in).
		51	3.50	
	MgO	40	5.50	
		41	5.50	Increase of light foam to 1/2 in.
		43	5.50	
		45	5.50	
		47	7.20	Foam almost disappeared.
3	Lime		1.35	
		25	2.60	
		26.5	2.90	
		27.5	3.20	
		32.5	3.90	Some light foam (1/4 in).
		34.5	4.00	
	MgO	20	7.20	Foam increased slightly, then gradually disintegrated.

TABLE 19

Precipitate Assays
%

1. Single-stage Lab.Sample No.R.D.2658		2. Two-stage Lab. Sample No. R.D.3628
71.48	U_3O_8	74.74
2.69	ThO_2	2.00
<0.02	V_2O_5	<0.02
0.0007	Mo	<0.001
0.004	B	0.003
0.03	Cl,Br,I	0.03
0.02	F	0.025
0.001	Cu	0.002
0.48	CO_2 (evol.)	0.36
0.008	NH_3	0.003
0.73	Fe	0.50
0.36	SO_4	0.39
0.63	CaO	2.31
0.74	MgO	0.66
2.01	H_2O	1.58
0.51	Ti	<0.10
1.63	SiO_2	1.07
0.13	$(RE)_2O_3$	0.09
2.0	Na	1.2
2.16	Acid Insol.	1.40
<0.001	Ni	0.002
<0.01	As	<0.01
0.047	P_2O_5	0.030

It should be noted that results and conclusions appearing in this report refer specifically to the work done in connection with this particular project. While these will be of value in estimating what will happen in actual plant operation, it must be remembered that plant conditions have not been duplicated.

For instance, the leach liquor pumped through the resin in the life tester had been stored for a considerable length of time, some of it for a few months. This storage could cause changes in the leach liquor, e.g. a decrease in the silica content. The total number of cycles completed is not very large and could be expected to disclose only more serious poisoning effects.

REFERENCES

(1) "Report on Pilot Plant Flotation of Amalgamated Rare Earth Uranium Ore Sample (Reference No. 7/57-7)", by W.R. Honeywell and C. Freitag. Special Report No. SR-480/57, Radioactivity Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, August 19, 1957.

(2) "Acid Leaching of Uranium-bearing Flotation Concentrate Produced from Amalgamated Rare Earths Mines Limited Ore (Reference No. 7/57-7)", by W.A. Gow and H.H. McCreedy. Special Report No. SR-483/57, Radioactivity Division, Mines Branch, Department of Mines and Technical Surveys, Ottawa, Canada, November 6, 1957.

EDK:VNM:(PES) DM

(Appendices I, II and III)
(follow, on pages 38 to 53.)

APPENDIX I

Apparatus

A block diagram of the apparatus making up the resin life tester is shown in Figure 5.

The Robotron Control, Type B 680, is an electrically operated timing device which turns the solenoid valves on and off in sequence. In this test, the Robotron did not control elution of the resin, only loading, washing and separation of the barren effluent into two fractions.

Opening solenoid valve V_1 causes loading of the resin and V_2, washing. Opening valve V_3 sends effluent from the column through one line, V_4, through another line and, keeping both valves V_3 and V_4 closed, sends the effluent through a third line. This permitted the separation of the first 200 minutes of barren effluent, the last 460 minutes of barren effluent and wash water effluent. For the first 200 minutes barren effluent was collected and reserved for possible testwork. For the last 460 minutes, the effluent was collected for volume measurement and then discarded. Wash water effluent was discarded directly.

The Robotron was not used during elution, because it was not possible to adjust the flow rate of eluting solution to a definite value automatically after the pump had been adjusted to pump leach liquor at the required rate of flow. Because it was desired to collect 18 bed volumes of eluate without much variation and at a set flow rate, this portion of the cycle was controlled manually. The eluting solution supply was connected to the pump only when required for elution.

A Sigmamotor pump was used to pump the various liquids through the column. The pump was driven by a variable-speed motor which permitted continuous (manual) adjustment of flow rates.

A chart recorder indicated the lengths of time during which valves V_1, V_2 and V_3 were energized.

A small centrifugal pump was used to pump water for backwashing the resin.

Leach liquor was stored in plastic-lined steel drums. Water was stored in a 12 litre aspirator flask. Eluting solution was prepared and stored in a 24 litre polyethylene carboy.

The pressure-operated safety valve and power cut-off is a glass U-tube with approximately 7 inches of mercury in each arm. One arm is connected to the ion exchange column and the other is connected to a small (approximately 100 ml capacity) polyethylene container resting on the spring-arm of a micro-switch. When pressure in the column builds up to the point where it can no longer be counterbalanced by the mercury in the U-tube, the polyethylene container fills, causing the micro-switch to open and the power supply to the Robotron Control and pump to cut off.

A detailed drawing of the ion exchange column is shown in Figure 6.

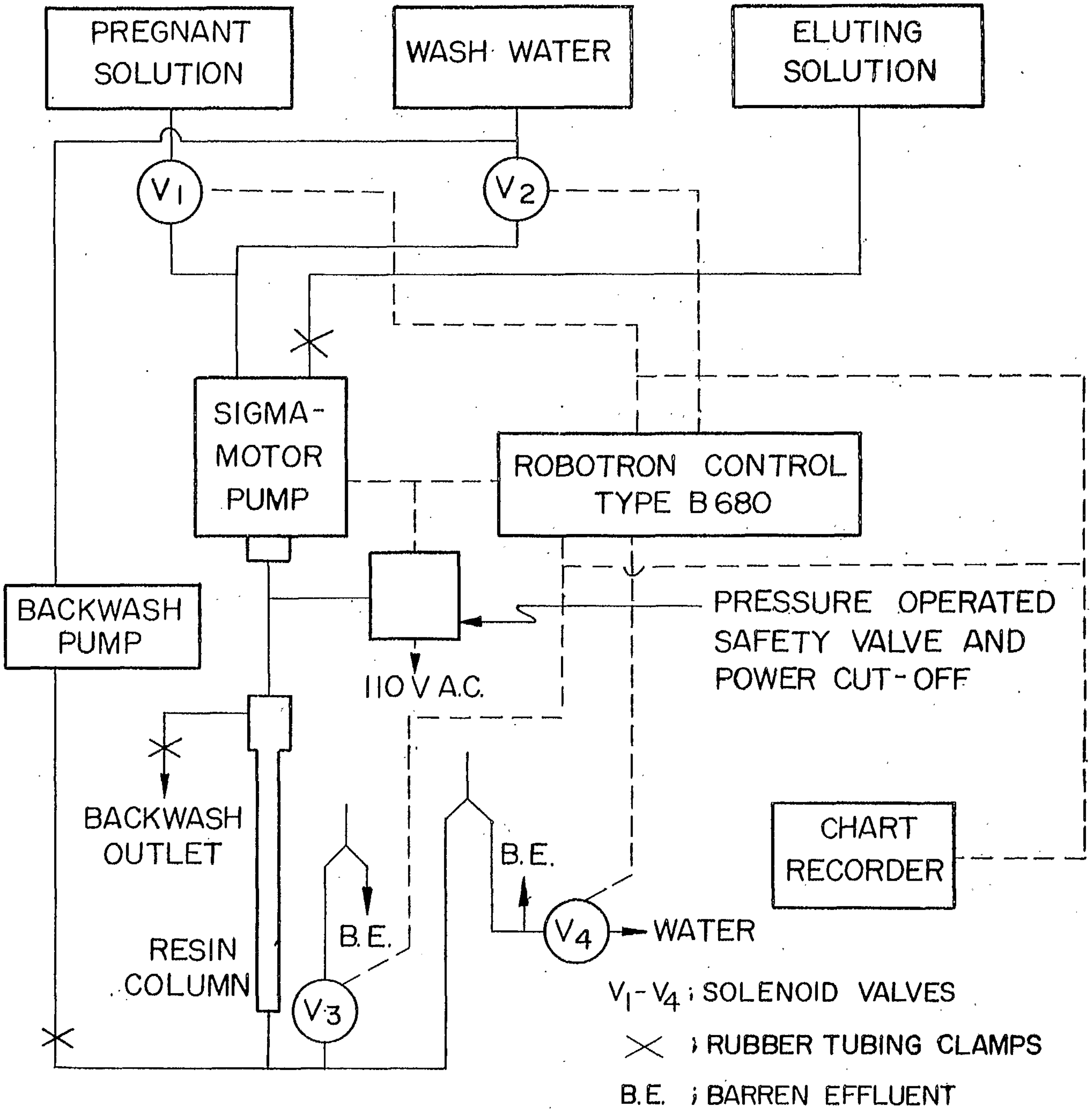

FIGURE 5

BLOCK DIAGRAM OF RESIN LIFE TESTER

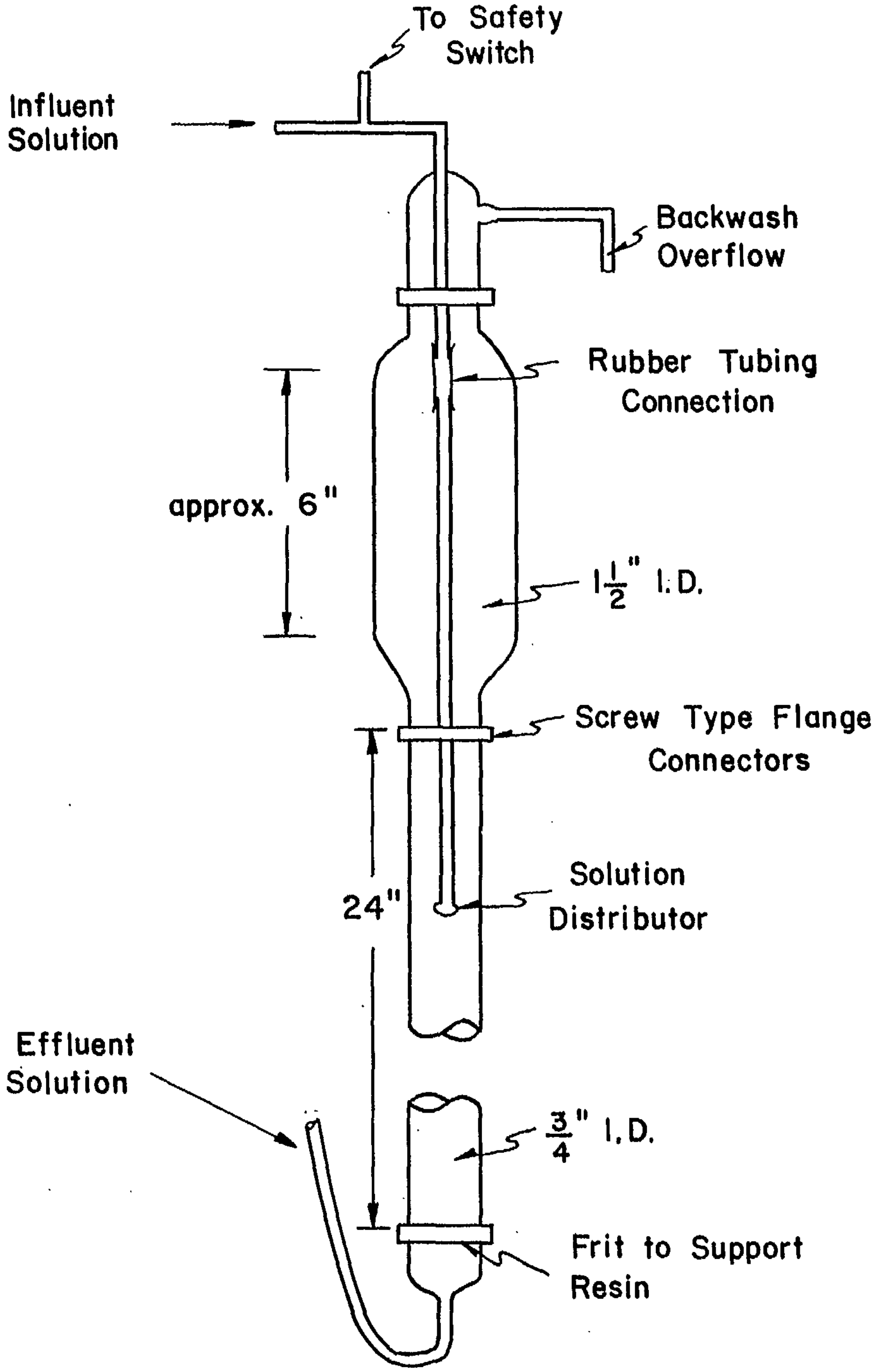

FIGURE 6

ION EXCHANGE COLUMN

APPENDIX II

Manufacturer's Report on Used Resin

The following is the manufacturer's report following examination of the used resin:

ROHM AND HAAS COMPANY

Export Department
Philadelphia 5, Penn. U.S.A.

March 13, 1958.

Dr. E.A. Brown
Chief, Radioactivity Division
Department of Mines and Technical Surveys
30 Lydia Street,
Ottawa, Ontario, Canada.

Dear Dr. Brown:

Re: Your letter 8 January 1958
Amalgamated Rare Earths
Mines Limited. Amberlite
IRA-400 Resin Sample

You will recall that you forwarded a sample of Amberlite IRA-400 used in your laboratories for the recovery of uranium from leach liquors from the ore of Amalgamated Rare Earths Mines Limited. You requested at that time that we make a routine evaluation of this sample. These results are now available and give every indication that this leach liquor should not at all be troublesome.

The resin sample was divided into two portions and the said evaluations were made in the following manner.

Treatment A

Sample was treated with 25 lbs. NaCl/ft^3 (as a 10% solution) acidified to pH 1.0 with concentrated HCl and rinsed. A portion of this material was saturated with the standard synthetic uranium solution and eluted with 1.0N NaCl in 0.1N H_2SO_4 to determine uranium capacity. This same portion was then rinsed and evaluated for total exchange capacity.

Some of this material was forwarded for spectrographic analysis and the results are given below.

Treatment B

Sample was regenerated with 25 lbs. of acidified NaCl/ft^3, rinsed, washed with 25 lbs. NaOH/ft^3 (95° F), rinsed, and regenerated with 25 lbs. of acidified NaCl/ft^3.

	Treatment A	Treatment B
% Moisture	43.76	45.48
Exchange Capacities		
Weak Base meq/gm	.77	.81
Strong Base meq/gm	2.78	2.97
Total Cap. meq/gm	3.55	3.78
Uranium Capacity		
gms U/L	47.6	-
gms U_3O_8/L	56.0	-
Breakthrough -Bed Volume	35.2	-
Elution Volume-Bed Volume	19.0	-
Polythionates % S as S_4O_6	nil	nil
% Sulfated Ash	0.35	0.20
% Silica	0.19	0.09
% Non-Silica	0.16	0.11

A spectrographic analysis of this sample showed the following:

Element	Approx. Concentration
Cu	not found
Fe	0.00x
Al	0.0x
Si	0.x (high)
Mg	0.000x
Ca	0.0000x
Ti	0.000x
Na	not found
Zr	0.00x
Th	not found

Other elements checked but not found: Sb, As, Ba, Be, B, Bi, Cd, Cr, Co, Ge, Au, Pt, Ag, Te, W, V, Zn, Mo, Cb, Pb, Ni, Sn, Ga, Mn, Sr, Ta, Ce, La.

The above results certainly indicate that the leach liquor used on this resin for 52 cycles is virtually trouble free. There is clearly no serious accumulation of metallic contaminants such as silica, thorium, titanium, etc., nor is there any accumulation of polythionate whatever. The uranium loading achieved with a synthetic solution, namely, 56.0 grams U_3O_8 per litre, is certainly in accord with these findings. However, you will notice that treatment with caustic shows some slight improvement in the strong base and total capacities and it might ultimately prove, if this leach liquor is actually used, that a very occasional treatment with caustic would have a beneficial effect in the plant.

In summary, we can certainly conclude that the resin is in excellent condition and, if the conditions in the laboratory are typical of those to be used in the plant, very little if any operating difficulty can be expected from the point of view of poisoning or fouling of the resin.

Sincerely,

ROHM AND HAAS COMPANY
Export Department

Paul F. Kirk

PEK:mdw

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APPENDIX III

Details of Test Methods Used by the Manufacturer for Evaluation of the Used Resin.

Introduction

Details of the manufacturer's test methods are included because they represent a considerable change over the methods previously used in evaluating this resin. The change in the uranium capacity method should be noted particularly, since it results in a reduced loading figure, and this must be taken into account in evaluating the results.

I. Uranium Capacity Determination

Reagents

Uranyl Sulfate	$3\ H_2O$ - (Purified)
Sodium Sulfate	A.C.S. Anhydrous Granular
Ammonium Nitrate	A.C.S. Granular (0.9 $MHNO_3$)
Sodium Carbonate	A.C.S. Anhydrous Fine Granular
Nitric Acid	C.P. grade (0.1M HNO_3)
Sulfuric Acid	C.P. grade (95.5 - 96.5%)

Preparation of Solutions

(1) Stock Uranium Solution (90 g U/l)

Dissolve 1110 g UO_2SO_4 - $3\ H_2O$/7 litres of H_2O.

(2) Synthetic Loading Solution (.85 g U/l or 1.0 g U_3O_8/l)

Weigh 800.0 g (±.1 g) Na_2SO_4 and transfer to a 3 litre beaker with tap water. Apply heat while stirring and pour dissolved Na_2SO_4 into an 18 litre bottle half filled with tap water.

Add 170 ml of stock uranium solution 90.0 g U/l or 105.88 g U_3O_8/l (Factor for conversion of U/l to U_3O_8/l = 0.85). If stock uranium solution is not exactly 90 g U/l, use proportion to determine the volume which must be added here:

(90 gm U/l) (170 ml) = (conc. of stock uranium solution) (ml needed)

Add approximately 90.0 ml conc. H_2SO_4. Add tap water to 18 litre mark and air agitate.

(3) Eluting Solution

On a torsion balance weigh into a 250 ml beaker 72.0 g of Ammonium Nitrate and add the weighed salt in small portions to approximately 200-250 ml of H_2O. Dissolve and transfer to a one litre volumetric flask, rinse the beaker several times with H_2O, and add the rinsings to the volumetric flask. Now add 6.3 ml of conc. HNO_3 to the flask. Shake several times and adjust volume to one litre. Stopper the flask and mix thoroughly. No standardization is required.

Determine the uranium and free acid content of the synthetic loading solution and adjust it to contain 1.0 g U_3O_8/l and to be 0.180 ± 0.005 N in free sulphuric acid. The pH should be 1.5 but is not used as a criterion.

Procedure

Preparation

Soak the resin in water for 1/2 hour. Transfer to a Buchner funnel and drain off excess water for 5 minutes. Accurately weigh out 13.46g of sample. Transfer this sample quantitatively to a 25 ml graduate and determine its volume. Remove the sample from the graduate and place in a 50 ml alkali burette. Backwash the bed and allow the beads to settle. Drain the burette until there is 1 ml of water above the sample bed, and, at the same time, lightly tap the column with the hand to help settle the sample bed.

Loading

Attach the siphon from the synthetic uranium solution to the top of the burette. Regulate the flow to 2.8 ml/min. Breakthrough is reached when one drop of effluent shows the slightest tinge of brown colour with one drop of 10% potassium ferrocyanide indicator. A minimum of 19 hours is required for saturation and the amount of effluent collected should be at least 3,300 ml. To determine whether the resin is saturated at this volume, pipette 5.0 ml of effluent and determine the concentration colorimetrically. If the assay of the effluent does not equal the assay of the influent, continue loading till it does so.

Quite infrequently it is desired to determine saturation volume. This may be done by collecting samples in 100 ml graduates and testing for the saturation point(i.e. the point where the effluent assay is equal to the influent assay). A close check must be kept on the number of samples taken to determine the volume.

Elution

Rinse the bed with 20 ml of water and drain the burette until only one ml of water remains above the sample bed.

Attach the siphon from the eluting solution to the top of the burette. Elute the resin at 50 ml/hr, collecting the effluent in a clean, dry 250 ml graduate. Spot plate checks should be taken every 15 minutes after 100 ml of effluent have been collected. The end point has been reached when one drop of effluent no longer gives a brown colour with one drop of the 10% potassium ferrocyanide indicator solution. The frequency of spot plate tests may be increased at the discretion of the analyst as the end-point is approached. When the spot test is negative, record the total volume of the effluent and transfer the effluent to a clean, dry 500 ml Erlenmeyer flask. Mix thoroughly and pipette 1 ml for colorimetric analysis.

Calculation of Capacity of Resin After Elution

Resin Capacity (Eluate), g/l U_3O_8

$$= \frac{\text{g/l } U_3O_8 \text{ in eluate} \times \text{vol. eluate, ml}}{\text{resin vol., ml.}}$$

II. Analytical Procedure

Transfer the treated sample to a Buchner funnel. Aspirate off excess water for five minutes. Store in tightly capped jar. All chemical analyses should be performed on the resin so treated. It is advisable to weigh out the samples for all analyses at the same time as the sample for solids determination.

1. Solids Determination

Weigh accurately an approximate 5.0 gram sample of the drained resin in a dry tared, weighing pan. Oven dry at 110°C for at least eight hours. Cool in a desiccator and reweigh.

Calculation

$$\frac{\text{g dry sample}}{\text{g wet sample}} \times 100 = \text{\% Solids}$$

$$100\% - \text{\% Solids} = \text{\% Moisture}$$

2. Strong Base Capacity

Weigh out a 5 g sample, and transfer to a glass filter tube, porosity A, supported on a 1 litre volumetric flask. Convert the sample to the OH-form by passing one litre of 4% NaOH through it at a rate slow enough to require thirty minutes. Rinse with water, and leach the rinsed sample with exactly one litre of 4% Na_2SO_4 (approx. 30 minutes), collecting the effluent in a clean 1 litre volumetric flask. Shake the flask well and titrate a 100 ml aliquot of the solution with standardized 0.1 N H_2SO_4, using methyl orange as the indicator (yellow to yellow orange).

Calculation

(a) Weight capacity

$$\frac{\text{ml } H_2SO_4 \times \text{N } H_2SO_4 \times 10}{\text{wt resin} \times \frac{\%\ \text{Solids}}{100}} = \text{meq/g dry resin}$$

(b) Volume capacity

$$\underset{\text{meq/g dry}}{\text{Weight capacity}} \times \underset{\text{g wet/ml wet}}{\text{Density}} \times \frac{\%\ \text{Solids}}{100} = \text{meq/ml}$$

3. Total Anion Exchange Capacity (AEC)

Weigh out a 5 g sample and transfer to a glass filter tube, porosity A. Put through the resin, in order, 1 litre of 4% HCl (weight basis), 1 litre of ethyl alcohol, and exactly 1 litre of 4% Na_2SO_4. Collect this last litre of effluent in a one litre volumetric flask; to be sure all chloride is leached from the resin, follow with another litre of 4% Na_2SO_4 and collect this also. Shake the flasks well, and remove

100 ml aliquots. Add 1 drop of methyl orange and, if pink, sufficient 0.1 N NaOH to change the indicator to yellow. Add 1 ml 1 M potassium chromate solution and titrate with standardized $AgNO_3$ until the color changes from yellow to yellow-orange.

Calculation

$$\frac{\text{ml } AgNO_3 \times \text{N } AgNO_3 \times 10}{\text{wt resin} \times \frac{\%\ \text{Solids}}{100}} = \text{meq/g dry resin}$$

4. Silica Determination

To the above residue is added approximately 25 ml of 48% HF and several drops of concentrated H_2SO_4. The HF is removed by placing the platinum dish on a steam bath and the H_2SO_4 by evaporation on a hot plate and finally heating over a Meker burner for 30 minutes (sample may be "hand-heated" provided extreme care is exercised so as to avoid splattering and consequent loss of sample.) This treatment is repeated a second time. The weight of the resulting residue is determined and, from the difference, silica based on dry resin can be determined.

Calculations

$$\frac{\text{wt residue after HF}}{\text{wt of dry sample}} \times 100 = \%\ \text{non-silica}$$

$$\%\ \text{sulfated ash} - \%\ \text{non-silica} = \%\ \text{silica}$$

5. Graduate Density

Where the amount of sample available is limited, or speed and simplicity of the operation are necessary, approximate density measurements may be made in a graduated cylinder.

Weigh out accurately the amount of sample available and soak in water for thirty minutes. Transfer to a graduate partially filled with water, and allow the bed to settle. Place the palm of the hand over the mouth, and invert the cylinder two or three times. Allow the bed to settle until the supernatant liquid is clear. The side of the cylinder is then tapped with a mallet until no further settling takes place. The volume of resin is then read.

Calculation

$$\frac{\text{g of sample}}{\text{ml of sample}} \times 62.4 = \text{density lb/ft}^3$$

6. Polythionate Poisoning

1. Charge approximately 10 ml of sample into a sintered glass column, porosity A.
2. Pass through 10% NaOH at a 0.75 gal/ft^3/min flow rate, and collect effluent in 100 ml graduates. Wash solution into 500 ml Erlenmeyer flask.
3. To each 100 ml of effluent add 5 ml of 40% formalin (formaldehyde).
4. Add 40 ml of 10% H_2SO_4, two drops of phenolphthalein, and continue addition of the H_2SO_4 until red color disappears. Then add 10 more ml of 10% H_2SO_4.
5. Titrate sample with standardized 0.1 N iodine to a starch endpoint. Note: collect 100 ml samples until iodine titer is less than 1 ml.
6. Rinse column, pass through 1 litre of 4% HCl, and rinse free of acid.
7. Transfer resin quantitatively to a tared weighing dish, dry overnight at 110°C, cool, and reweigh.

Calculation

$$\% \text{ S as } S_4O_6^{=} = \frac{\text{Total ml } 0.1 \text{ N } I_3^-}{\text{dry wt of resin}} \times 0.853 \times \frac{\text{N } I_3^-}{0.1}$$

7. To prepare solution of 0.1 N I_3^-

1. Dissolve 20 g KI in 30-40 ml of water in a 1 litre volumetric flask.
2. Weigh out about 12.7 g of I_2 on a watch glass, and transfer to flask by means of a dry funnel.
3. Shake until all I_2 has dissolved (overnight).
4. Dilute the solution to 1 litre. Look carefully for any undissolved particles of iodine; if any are apparent the solution must be filtered.
5. Transfer solution to a glass stoppered bottle, and store away from sunlight.

8. To standardize the 0.1 N I_3^-

1. Weigh out accurately about 0.17 g of pure arsenic trioxide into a 250 ml Erlenmeyer flask.
2. Dissolve in 10 ml of 1.0 N NaOH.
3. Add 12-15 ml of 1.0 N H_2SO_4.
4. Then add carefully a solution of 5 g $NaHCO_3$ in 50 ml water.
5. Add starch and titrate to blue endpoint.

Calculation

$$\text{N of } I_3^- = \frac{\text{Wt of } As_2O_3}{\frac{49.45}{1000} \times \text{ml of } I_3^- \text{ used}}$$

9. Ash Analysis

Weigh a 5.0 g sample into a tared platinum dish that has previously been ignited over a Meker burner for at least 15 minutes and desiccator cooled. Determine the dry weight of sample according to the procedure for solids determination. After weighing, moisten the sample by dropwise addition of concentrated H_2SO_4 until it is uniformly moistened but contains no excess liquid. Char at a low temperature until the liberation of sulfur trioxide fumes ceases. Continue the ignition over a Meker burner for 30-45 minutes. Allow the samples to cool in desiccator and weigh (open stopcork on desiccator slowly before removing lid to prevent rush of air and consequent loss of residue).

Calculation

$$\frac{\text{Wt ash}}{\text{orig. wt sample}} \times 100 = \%\ \text{sulfated ash}$$

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EK:VMM:(PES) DM