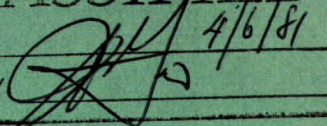


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OTTAWA

MINES BRANCH INVESTIGATION REPORT IR 60-95

PRODUCTION OF HIGH PURITY AMMONIUM DIURANATE BY THE SULPHURIC ACID ELUTION-AMINE EXTRACTION PROCESS

by

A.J. GILMORE, V.M. McNAMARA, H.W. PARSONS & R. SIMARD

EXTRACTION METALLURGY DIVISION

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A. J. Gilmore^{*}, V. M. McNamara^{*}, H. W. Parsons^{*}
and R. Simard^{**}

SUMMARY OF RESULTS

Uranium in leach solutions obtained from the treatment of Milliken Lake ore was recovered from solution by anion exchange resins and then eluted from the resin effectively by 14 bed volumes of 10% sulphuric acid. The eluate, containing 6-7 g U_3O_8 /l, was extracted with 5% Alamine (tertiary amine) in kerosene, and the uranium stripped in 15% ammonium sulphate at a controlled pH. Continuous precipitation of the uranium with gaseous ammonia produced an ammonium diuranate suitable for the fabrication of high density ceramic UO_2 pellets. The main impurity above nuclear grade specification was molybdenum. Reagent consumptions were low and savings are indicated in replacing acidified nitrate with 10% sulphuric acid for resin elution.

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INTRODUCTION

In the process of sulphuric acid leaching of Canadian uranium ores, uranium is recovered from solution by anion exchange resins which are then eluted with acidified chloride or nitrate solutions. The eluate is neutralized to pH 3.5 with lime, filtered, and then uranium is precipitated from the eluate with magnesia, sodium hydroxide or ammonia. The barren eluate is recycled to ion exchange. This constitutes the established flowsheet of most uranium leach plants. The dried product or "yellow cake" is then shipped to a custom refinery for retreatment by liquid-liquid extraction with tri-butyl phosphate (TBP) and production of a nuclear grade trioxide.

In an effort to incorporate the refining step within the leach plant, various flowsheets have been proposed ⁽¹⁾. Direct extraction of uranium from nitrate eluates with TBP or commercially available dialkyl alkylphosphonates was studied here, as was a procedure consisting of strong neutral sodium chloride-water elution followed by hydrogen peroxide precipitation of the water eluate ⁽²⁾. These projects will be reported separately.

The process investigated in this case consisted of recovering the uranium from leach solution on an anion exchange resin, eluting the uranium from the resin with 10% sulphuric acid, treating the sulphuric acid eluate by amine extraction, followed by controlled pH stripping of the uranium and precipitation with NH_3 of a near

nuclear grade product. This study was suggested from data (3) gathered on sulphuric acid elution from anion exchange resins, and the use of tertiary amines (4) (5) as selective extractants of uranyl sulphate from leach solutions. The process would be relatively simple in that it would require only a solvent unit to treat an eluate product which could be produced from existing facilities.

In defining the operating conditions as shown in the flowsheet of Figure 1, the data available from previous investigations were helpful. The concentration of sulphuric acid for elution was set at 8 - 10% w/v H_2SO_4 in keeping with efficient elution of the resin and subsequent ease of extraction with tertiary amines. A kerosene solution containing 5% Alamine 336* was adopted for this work because it is commercially available, highly selective, and proven in practice. Various ammonium salts, the nitrate, chloride or carbonate can be used for stripping, to produce solutions suitable for the precipitation of ammonium diuranate, but for reasons of economy (6) it was felt that ammonium sulphate solutions at a controlled pH should be tested first. A 15% $(NH_4)_2 SO_4$ solution was suggested from a preliminary study made on the effect of pH and sulphate concentration.

*General Mills Inc., Chemical Division, Kankakee, Illinois.

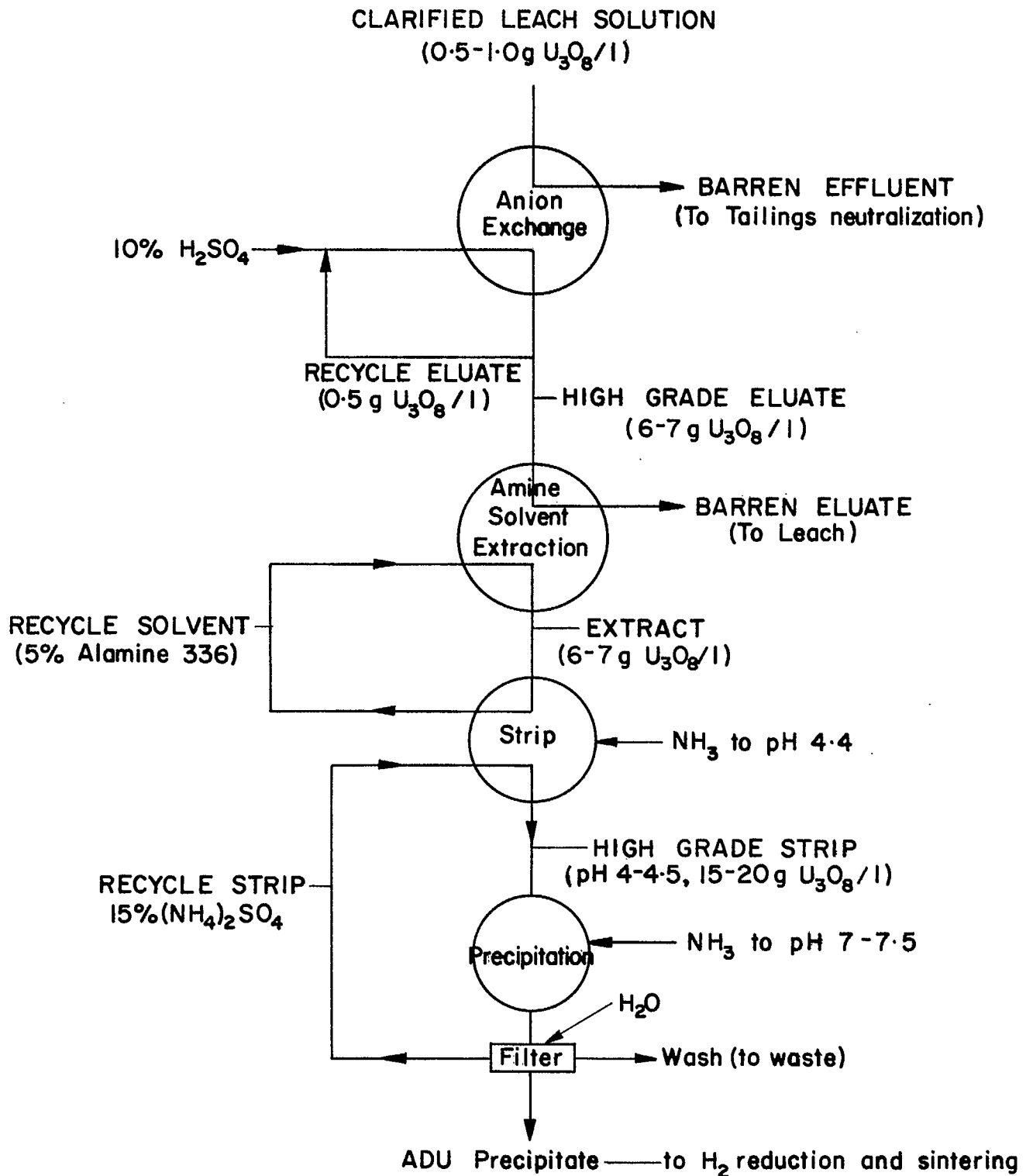


FIGURE I

FLOWSHEET OF
SULPHURIC ACID ELUTION
AMINE EXTRACTION PROCESS

The points to be investigated further in continuous pilot plant equipment were therefore 1) the suitability of the resin and amine as applied to a 10% sulphuric acid eluate, 2) the feasibility of ammonium sulphate stripping in continuous operation and finally 3) the possibility of producing a nuclear grade ammonium diuranate as a source of ceramic UO_2 by continuous precipitation with gaseous ammonia.

For this investigation, the feed solution to ion exchange was produced in a series of pilot plant two-stage leach tests carried out on 40 tons of ore from Milliken Lake Uranium Mines Ltd., Elliot Lake, Ontario. Leaching procedure and results are described in a Mines Branch report (7).

EQUIPMENT AND PROCEDURE

Leach Solution Preparation

Unclarified solution from the leach pilot plant drum filter was pumped to a 2000 litre rubber-lined tank in order to settle most of the slimes, then pumped through a Sethco four-leaf clarifier to a similar storage tank. When pH adjustment was required, lime was added to the solution in the first storage tank where the gypsum settled before clarification.

Ion Exchange

A two-column ion exchange circuit as shown in Figures 2 and 3 was used for the sulphuric acid elution study. This included two 4 in. dia by 6 ft. Pyrex pipes with flanged ends; each column had a capacity of 7 litres of wet-settled resin. The flowmeter, and suitable valve arrangement to carry out the cyclic operation are indicated in Figure 2. Leach solution was fed at a set rate from a 600-litre storage tank, through a Sigma pump and a surge bottle. Water and eluate were fed from pressurized 50-litre carboys.

Operation of the two-column circuit was as follows:

1. Adsorption on columns A and B in series through valves 2, 6, 4 and 10.
2. At uranium breakthrough on column B, influent changed from leach solutions to water for one bed volume, through same valves.
3. Column A backwashed with water through valves 9 and 11.
4. After resin settled, column A eluted through valves 2 and 9.
5. Column A flushed with one bed volume of water through valves 2 and 9.
End of first cycle.
6. With columns B and A in series, adsorption is resumed through valves 1, 5, 3 and 9.

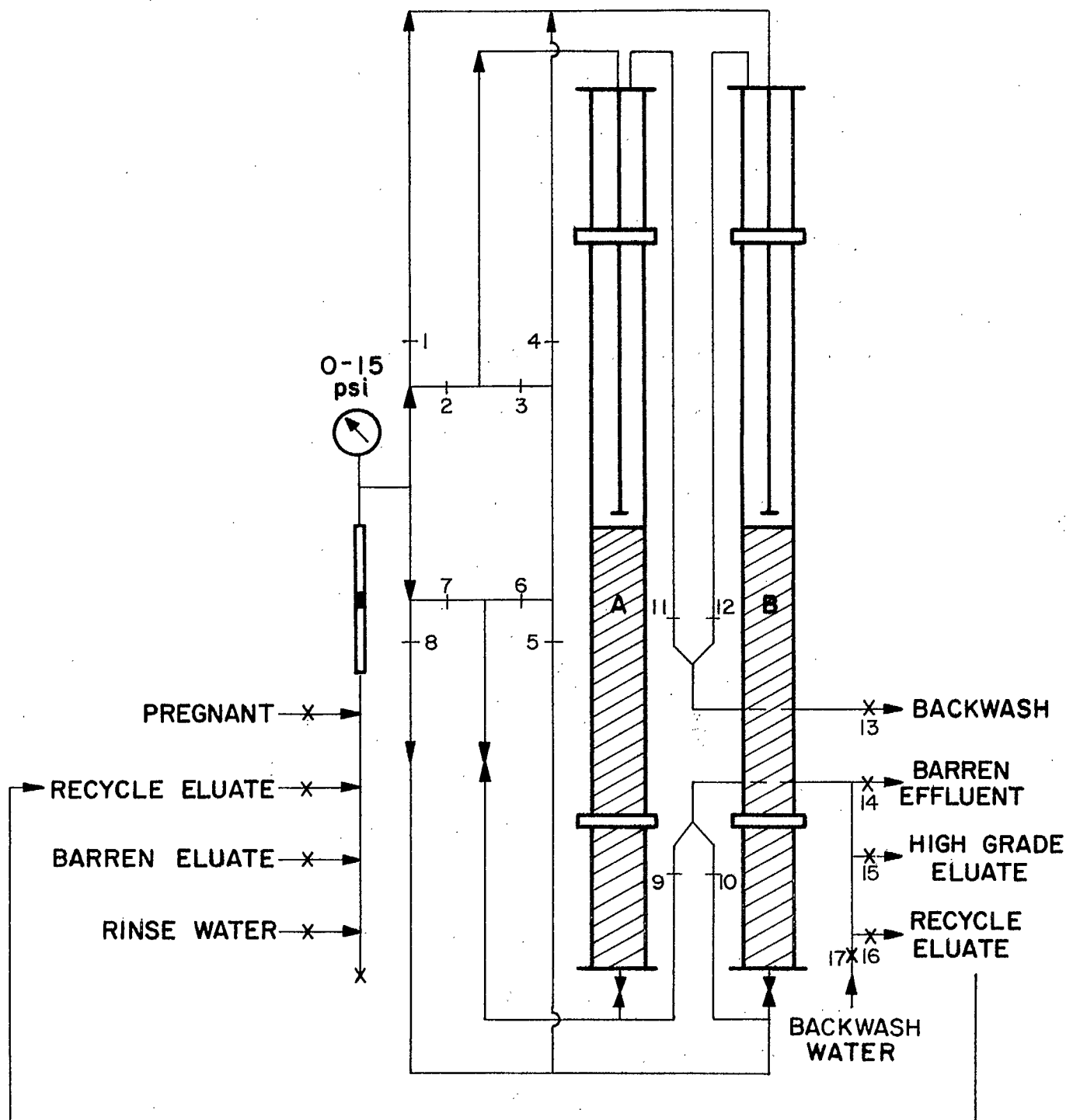


FIGURE 2
TWO-COLUMN ION EXCHANGE CIRCUIT

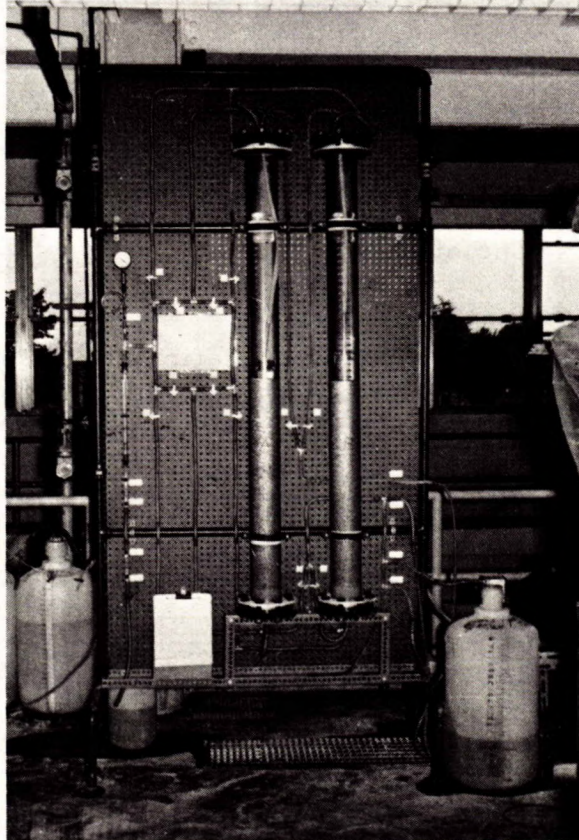


FIGURE 3

TWO-COLUMN ION EXCHANGE CIRCUIT

7. At uranium breakthrough on column A, influent changed to water for one bed volume through same valves.
 8. Column B backwashed through valves 10 and 12.
 9. After resin settled, column B eluted through valves 1 and 10.
 10. Column B flushed with one bed volume of water through valves 1 and 10.
- End of 2nd cycle.

Barren effluent after neutralization with lime to pH 5.5 - 6.0 was discarded to the tailings circuit. Commercial sulphuric acid and tap water were used for barren eluate make up. Any excess recycle eluate from individual cycles was stored separately for uranium recovery, while high grade eluate was accumulated for liquid-liquid extraction.

Liquid-Liquid Extraction

Two four-stage mixer-settler units as shown in Figures 4 and 5 were used for continuous test work. The ion exchange eluate, stored in a 600-litre tank, was fed by gravity through a flowmeter. Eighteen litres of solvent was made up from General Mills Alamine 336 diluted to 5% v/v in Imperial Oil kerosene. To prevent emulsification and third-phase formation n-decyl alcohol was added to a 2% v/v concentration. An Adjust-o-feeder pump rated at 0 - 700 ml/min was used to meter the solvent from an 8-litre surge bottle to the fourth-

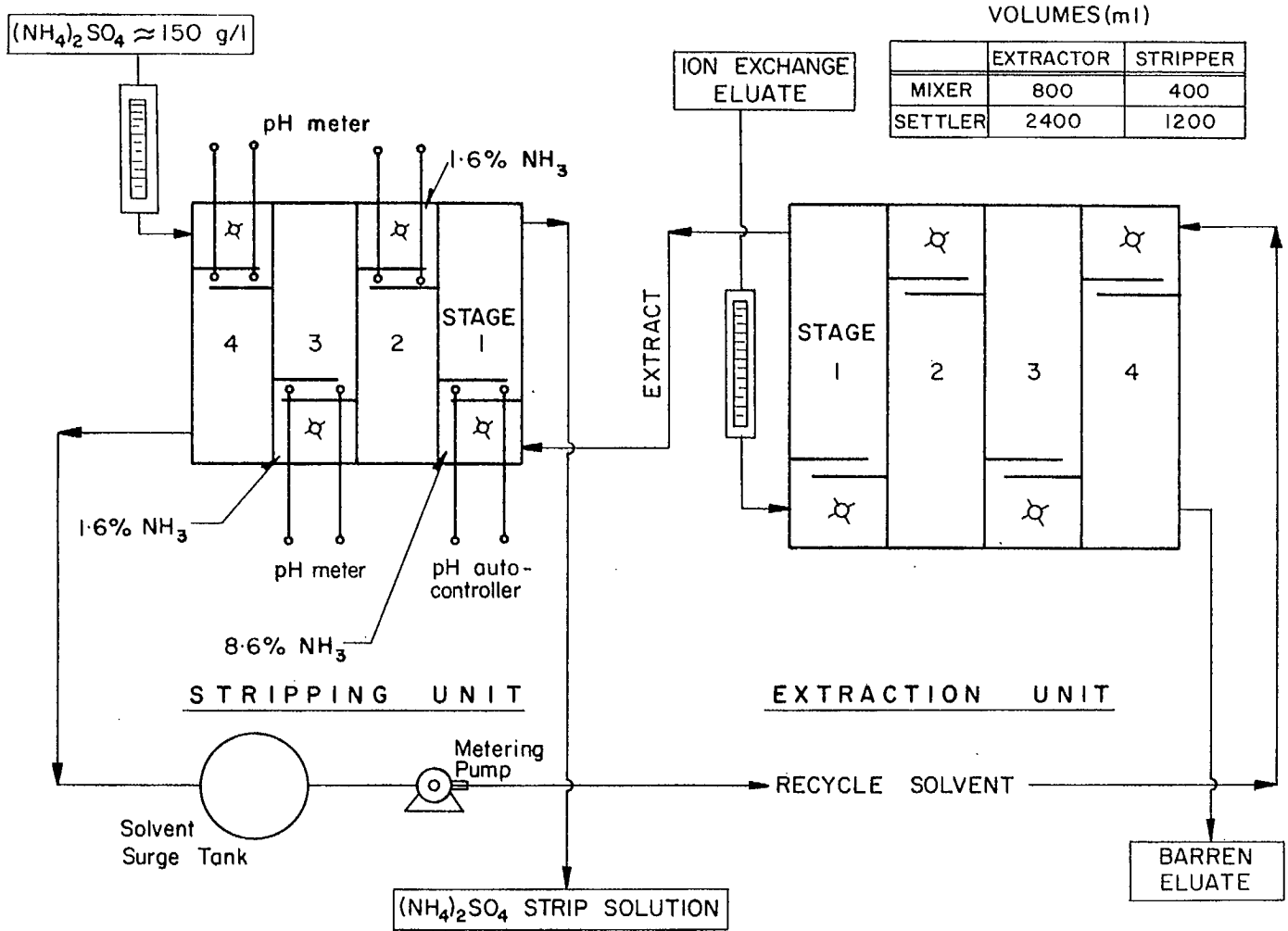


FIGURE 4

FLWSHEET OF EXTRACTION AND SULPHATE STRIP CIRCUITS

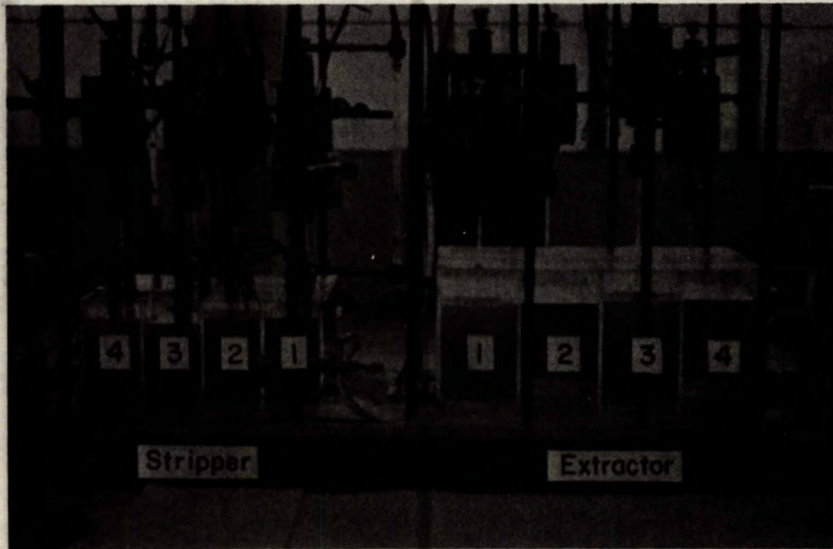


FIGURE 5
MIXER-SETTLER UNITS

stage extractor. The eluate feed solution was fed to the extraction countercurrent to the solvent flow, as shown in Figure 4.

For pH control in the first stage of stripping, a pH recorder-controller operated a titrimeter valve feeding 8.6% NH_3 ^{w/v} solution. Manual control was used to feed a weaker (1.6% NH_3) solution to the second and third stage. The fourth stage did not require ammonia when the recycling barren ammonium sulphate was adjusted to a pH of 7.0. The pH electrodes in the first stage were set below the mixed phases, in a semi-settled zone of the double baffle. During operation it was found desirable to operate the first stage mixer under a continuous aqueous phase condition in order to allow direct reading of the pH in the mixed phases. By this procedure the control lag, due to the distance between point of ammonia addition and pH electrodes, was minimized and provided a closer control of pH, within ± 0.1 pH unit.

For each run, the circuit was operated at constant flowrates for 6 to 7 hours. This allowed approximately four complete solvent cycles. Before shut-down, representative samples were taken of barren eluates, extract, recycle solvent and final strip solution. A composite barren eluate was also taken for kerosene and amine determination and the recycle solvent was titrated for amine content. Ammonia consumption was determined from the initial and final volume readings of the head tanks.

Continuous Precipitation

Strip solution collected from each extraction run was fed continuously to a precipitation circuit as shown in Figure 6. Flowrate was held constant at 150 ml/min, and ammonia was introduced from a cylinder at the rate required to maintain pH in the desired range.

Conditions which were varied to determine their effect on the composition and physical characteristics of the precipitate were:

1. pH: from 6.5 to 7.5
2. Temperature: from 30°C to 80°C
3. Retention time during agitation was varied, from 20 to 40 minutes, by removing one or more of the surge tanks
4. Holding time of slurry before filtration: from 0 to 92 hours
5. Washing and repulping procedure on the filter cake: different agitation times and temperatures
6. Addition of flocculant: nil versus 3 ml/min of 0.05% Superfloc 16*

The barren strip solution from each run was returned to the extraction circuit. Displacement wash and repulp solution were discarded. The precipitate, after drying for 48 hours at 115°C, was sampled, pulverized and sent for chemical analysis. Representative

* Product of American Cyanamid Company,
30 Rockefeller Plaza,
New York 20,
N. Y., U. S. A.

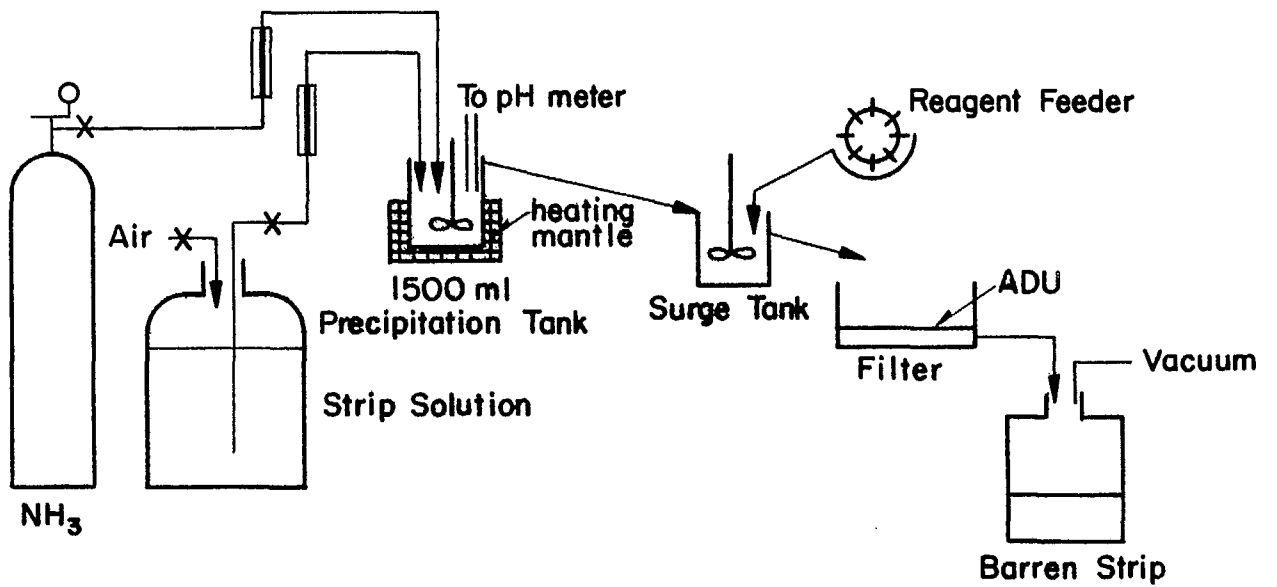


FIGURE 6
CONTINUOUS PRECIPITATION CIRCUIT

samples were also submitted to the Mineral Sciences Division of the Mines Branch and to the Research and Development Division of Eldorado Mining and Refining Ltd., Ottawa, for hydrogen reduction tests. Quantitative spectrographic analyses were also done on two samples.

RESULTS

Ion Exchange

Preliminary 50-ml column laboratory tests

Four commercial resins were first evaluated in 50-ml columns to compare the rates of elution with 1 M H_2SO_4 . The resin used in most mills, Amberlite IRA-400 from Rohm and Haas Co., was compared with three other resins and results are presented in Table 1 and Figure 7. As a point of reference, a nitrate elution curve was also determined for the IRA-400 resin. However, since retention time for the IRA-400 resin was 20 minutes as against 30 minutes for other resins, the results are not directly comparable. IRA-400 was selected for the pilot plant. Because of the fast elution rate of Dowex 21K, this resin was chosen for a comparative study with IRA-400 in the pilot plant four-inch diameter columns.

TABLE 1

Comparison of Uranium Elution Rates
on 50 ml Wet-settled Resin Laboratory Tests

Resin:	IRA-400	IRA-400	Dowex 21K	Permutit SK	Zerolit FF
Eluant:	0.25N HNO ₃ 0.75N NaNO ₃	1M H ₂ SO ₄	1M H ₂ SO ₄	1M H ₂ SO ₄	1M H ₂ SO ₄
Retention Time:	20 min	20 min	30 min	30 min	30 min
No. Bed Volumes	g U ₃ O ₈ /litre eluate				
0	2.96	0.055	13.12	2.15	4.76
0.25	9.37	17.23	24.40	10.75	12.12
0.50	25.01	37.16	36.2	22.86	18.70
1.0	46.84	36.68	38.36	30.91	25.69
1.25	43.47	26.59	36.20	31.00	22.19
2	35.50	15.59	23.08	29.90	20.92
3	22.48	11.82	13.96	14.27	15.25
5	1.65	7.92	3.31	6.81	7.17
6	0.57	3.36	1.14	3.16	2.21
8	0.073*	--	0.20	0.90	0.68
10	0.012	0.68	0.033*	0.29	--
12	0.002	0.31	0.007	0.12*	--
14	--	0.098*	0.004	0.050	--
16	--	0.030	0.001	0.016	--
18	--	0.007	--	0.005	--
20	--	0.002	--	0.003	--
22	--	0.002	--	0.003	--

* passed nilspot (< 0.1g U₃O₈/l)

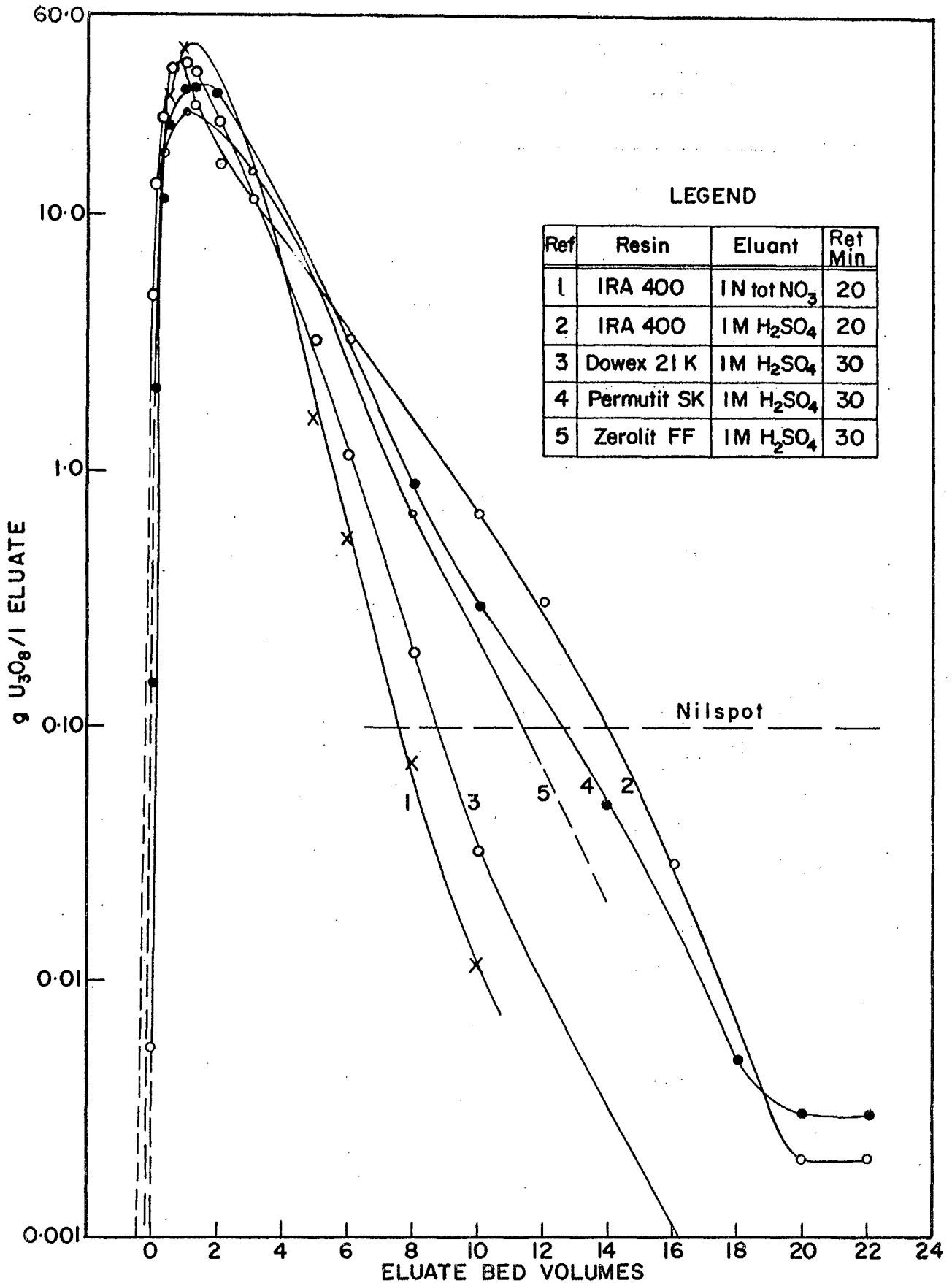


FIGURE 7
RESIN ELUTION DATA
50-ml Column Tests

Pilot Plant Cyclic Tests in 4-in. dia columns

Eleven adsorption-elution cycles were completed on Dowex 21K resin, followed by nine cycles on Amberlite IRA-400. A summary of operating data is given in Table 3. Feed solution as supplied from the leach pilot plant was analysed in two composite lots and the data are presented in Table 2.

TABLE 2

Analyses of Composite Leach Solutions

Leach No.	89	90
pH	1.6	1.3
Analysis g/l		
U ₃ O ₈	0.7	0.52
Fe ²	2.96	2.10
Fe ³	0.80	0.82
ThO ₂	0.12	0.095
Mo	0.0002	0.0005
Ti	0.055	0.050
Free H ₂ SO ₄	3.90	4.4
SO ₄ Total	17.4	18.6
SiO ₂	0.66	0.48
As and P ₂ O ₅	0.048	0.067
Na ₂ S ₄ O ₆	0.01	0.005

From cycle 1 to 19, leach solution was used without pH adjustment. In cycle 20, lime was added to a pH of 1.8 before clarification to reduce free acid and increase the uranium loading capacity from 45 to 70 g U_3O_8 /l. w. s. r. This in turn yielded a higher grade eluate of 7.83 g U_3O_8 /l as against 5 to 6 g U_3O_8 /l in previous cycles. During two cycles, effluent samples were taken at the start of loading to detect any "royal barren". The uranium analyses of the effluent did not show this increase as usually occurs after nitrate elution.

In order to confirm the elution data obtained in the 50-ml column tests, a series of elution curves was determined during four cycles at various retention times. The data are presented graphically in Figure 8. No significant difference in elution rate can be detected between the two resins at equal retention times. The curves indicate that optimum retention time for efficient elution is in the order of 12 to 15 minutes.

TABLE 3

Summary of Ion Exchange Data
(Average loading and elution results)

Resin (7 litres w. s. r.)	Dowex 21K		IRA-400	
Cycle Nos.	1 to 7	8 to 11	12 to 19	20
<u>Loading</u>				
Leach Soln. No.	89	90	90	90
pH	1.4	1.2	1.5	1.8
U ₃ O ₈ g/l	0.71	0.81	0.51	0.40
Retention Time, min	2.3	3.0	2.4	2.1
Barren Effluent				
U ₃ O ₈ g/l	0.03	0.005	0.003	0.001
Total Vol. litres	553	400	735	1425
Lead Column Effluent				
U ₃ O ₈ g/l	0.70	0.76	0.45	0.41
<u>Elution</u>				
Eluant, % H ₂ SO ₄	10	8	10	10
Retention Time, min.	8.7	14.1	15.1	15.0
Recycle Eluate, entering				
U ₃ O ₈ g/l	0.61	0.58	0.58	0.37
High Grade Eluate				
Volume litres	59.3	61.3	56.7	60.
U ₃ O ₈ g/l	5.29	5.81	6.05	7.83
Recycle Eluate, leaving				
Volume litres	69.3	62.5	64.4	68.0
U ₃ O ₈ g/l	0.59	0.38	0.61	0.60
Total Eluate Volume to Nilspot, litres	15.6	14.6	15.0	17.0
Calculated Uranium Loading, g U ₃ O ₈ /l l. w. s. r.	45.4	48.7	46.6	69.8

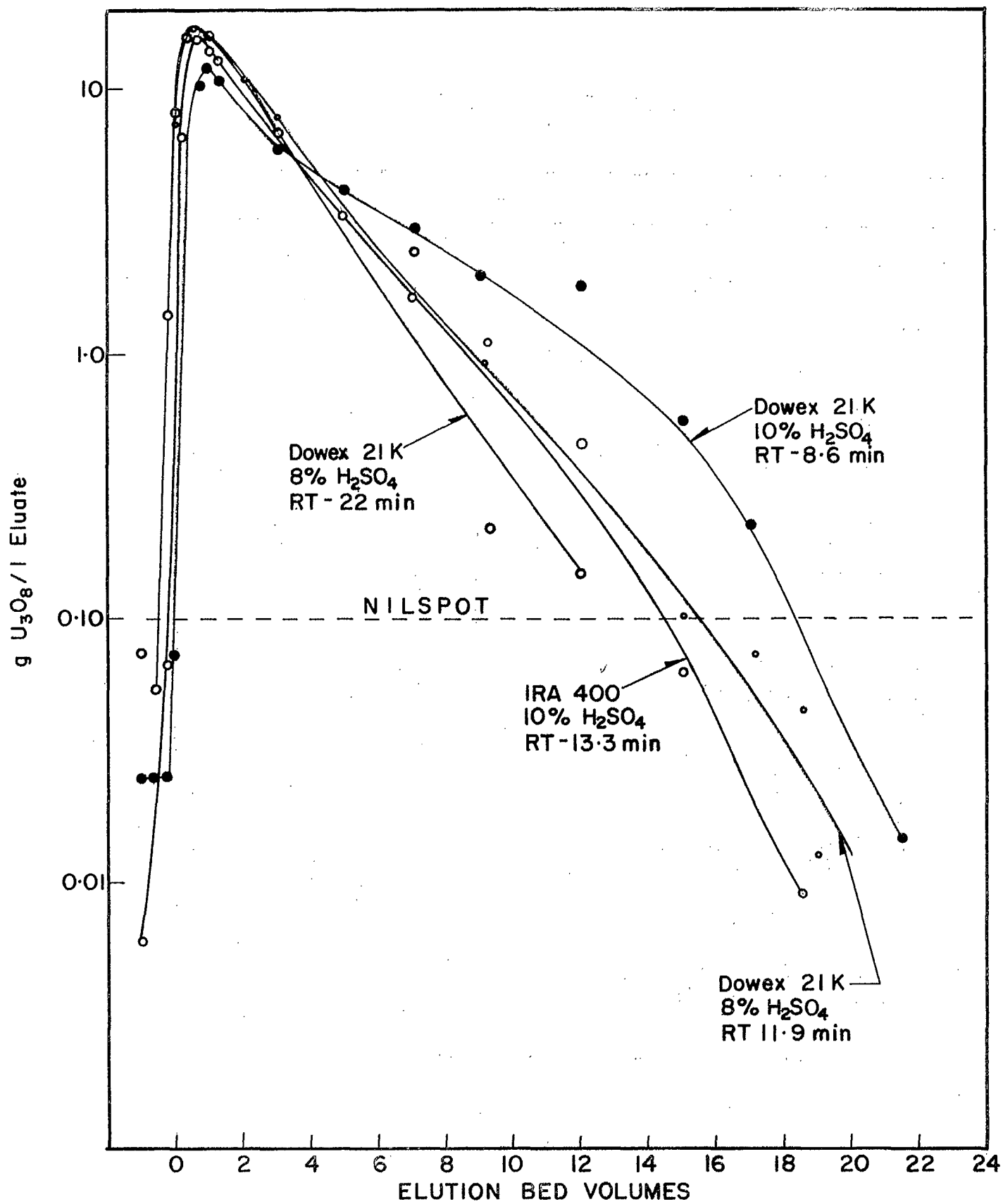


FIGURE 8
RESIN ELUTION DATA
(Four-inch column cyclic tests)

Amine Extraction and Stripping

Fifteen continuous runs were completed in the liquid-liquid extraction circuit with the composite eluate produced during the 20-cycle ion exchange operation. A run of four hours was first done to condition the solvent and approach equilibrium in the various stages. Table 4 summarizes operating conditions and results of subsequent runs.

Extraction

By maintaining a feed eluate-to-solvent flow ratio of 1 to 1, barren eluates containing less than 0.01 g U_3O_8 /l were obtained in the fourth stage, as shown in Table 4. Due to some fluctuations of uranium in the eluate feed and in the recycle solvent, some runs were done at a higher saturation level at the expense of recovery. Where the barren eluate is to be recycled to leaching, values of 0.1 g U_3O_8 /l could be tolerated. Extraction equilibrium data as calculated from the results of run No. 466 are represented graphically in Figure 9.

Stripping

The pH of the aqueous phase in the four-stage stripper required close control to avoid precipitation. In previous work, where sodium sulphate was used, a pH of 4.5 to 5.0 could be used in the first stage, with adjustment to 5.5 in the later stages. However with ammonium sulphate, the limit of 4.4 could not be exceeded in the first stage but could be raised to 5.5 - 6.0 in the last stage, thus improving

TABLE 4

Continuous Extraction and Stripping Results

Run No.	453	454	455	456	457	458	459	460	461	463	464	465	466	467	468
Operating Time,hr	6.5	6.5	6.75	6.75	6.5	7.	6.75	6.75	7.0	6.5	7.5	7.75	6.25	6.75	7.0
Flowrates, ml/min															
Eluate Feed	190	190	192	192	197	200	195	196	200	203	197	191	203	200	200
Solvent (5% Alamine)	260	260	267	198	199	253	241	210	223	150	206	207	209	198	153
Strip (15%(NH ₄) ₂ SO ₄)	73	72	78	75	74	78	81	80	75	52	73	77	77	82	51
Analyses, g U ₃ O ₈ /l															
Eluate Feed	6.46	6.34	6.45	6.31	6.45	6.62	6.70	7.37	7.35	5.99	6.24	6.05	6.74	7.68	4.16
Effluent Eluate Stage 1	6.02	4.72	1.64	6.31	6.45	5.30	3.51	7.13	7.33	5.46	5.97	2.87	5.47	7.68	3.71
" " " 2	3.33	1.28	0.14	6.31	6.45	1.25	0.41	5.13	6.47	2.01	3.57	0.24	1.47	7.56	1.75
" " " 3	0.42	0.14	0.012	4.78	5.38	0.16	0.032	0.85	2.47	0.15	0.53	0.024	0.11	5.81	0.24
" " " 4	0.037	0.046	0.007	>0.4	>0.4	0.03	0.006	0.025	0.083	0.007	0.036	0.010	0.014	0.75	0.031
Composite Final Barren	0.046	0.053	0.021	0.08	>0.40	0.15	0.009	0.008	0.057	0.006	0.13	0.02	0.012	0.49	0.12
Extract	6.60	5.88	5.08	6.04	5.96	5.84	5.64	6.19	6.32	6.17	5.90	5.21	6.04	6.62	6.16
Strip Solution	20.65	18.63	16.53	14.78	15.00	19.72	17.44	15.02	20.09	17.95	16.44	15.26	17.37	15.64	13.44
Recycle Solvent	0.48	0.58	0.27	0.46	0.50	0.53	0.053	0.29	0.22	0.055	0.047	0.18	0.14	0.061	0.22
Strip Solution Composite															
Volume, litres	30	26.4	29.2	28.1	28.5	32.0	31.7	30.5	29.7	26.7	29.2	32.9	29.4	29.9	20.3
Total U ₃ O ₈ ,g	619.5	492	483	415	427	631	553	457	597	479	480	502	511	468	273
pH of Stripping Stage 1	4.1	4.3	4.3	4.4	4.4	4.4	4.3	4.4	4.4	4.4	4.5	4.4	4.4	4.3	4.4
" " 2	4.3	3.9	4.3	4.3	4.5	4.4	4.3	4.3	4.4	4.4	4.2	4.2	4.6	4.4	4.4
" " 3	4.3	3.6	-	-	3.8	3.7	5.1	5.4	5.6	5.1	5.2	5.5	5.4	5.5	5.1
" " 4	6.0	5.8	4.9	6.6	6.2	5.4	5.8	6.3	6.0	5.5	5.8	5.5	5.6	5.5	4.6
Ammonia Consumption g NH ₃ /g U ₃ O ₈	-	0.258	0.329	0.287	0.269	0.311	0.346	0.345	-	0.313	0.365	0.291	0.295	0.27	-
Final Amine Normality	0.100	0.099	0.099	0.099	0.099	0.102	0.101	0.101	0.102	0.101	0.100	0.102	0.099	0.099	0.101

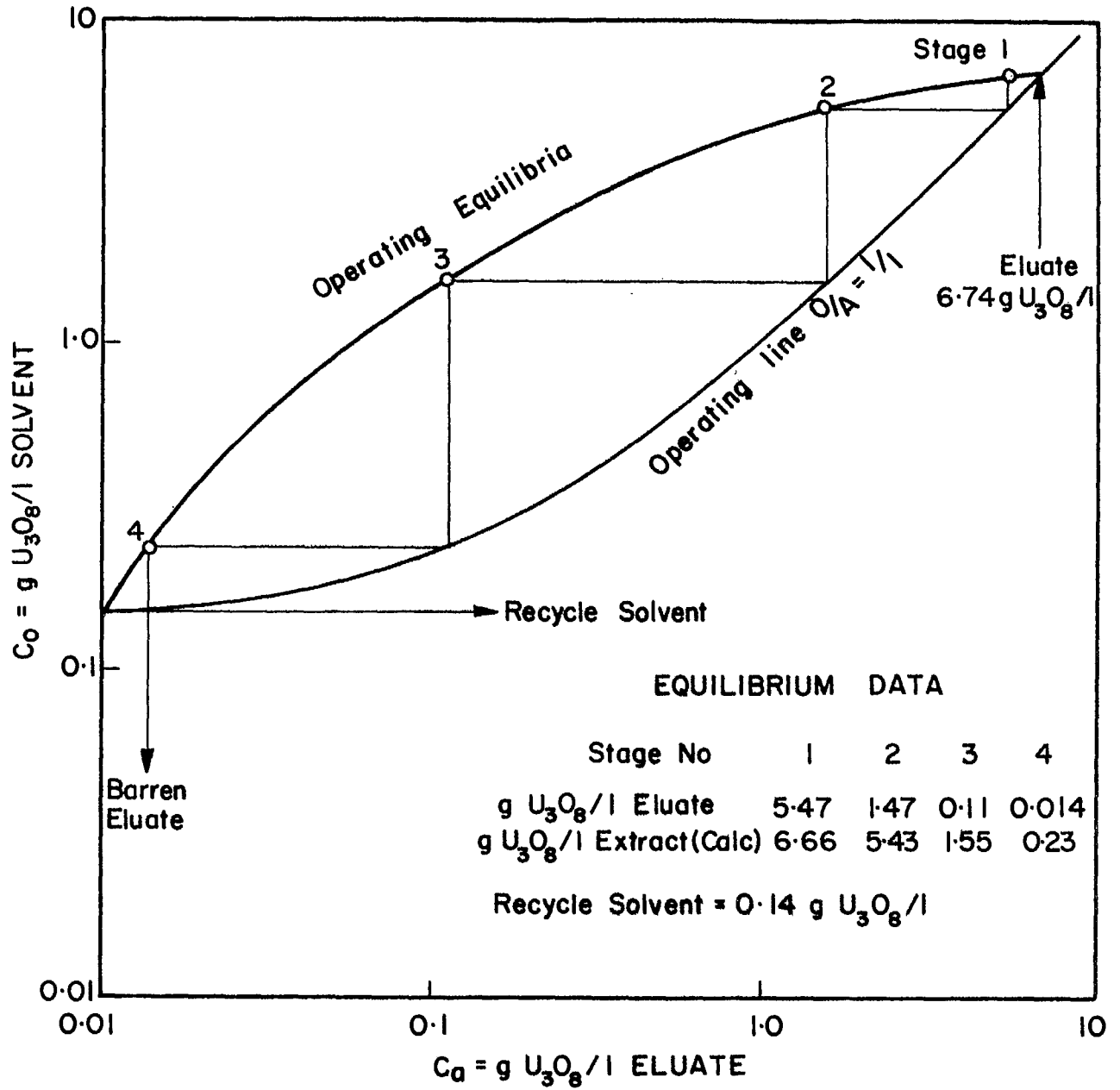


FIGURE 9
OPERATING EXTRACTION EQUILIBRIA

stripping efficiency. Allowable uranium concentration in the recycle solvent being dictated by the extraction equilibria, it will be seen from Figure 9 that 0.1 to 0.2 g U_3O_8/l in the solvent can be allowed without greatly reducing the efficiency of the last stage of extraction.

An accumulation of interface sludge over long periods in the settler compartments was screened out, filtered and ignited. A chemical analysis showed the following contents:

	<u>U_3O_8</u>	<u>ZrO_2</u>	<u>Al</u>	<u>Fe</u>	<u>Ti</u>	<u>Mo</u>	<u>ThO_2</u>
%	93	0.5	0.25	0.08	0.05	0.04	0.02

When a portion of this sludge was leached in sodium carbonate, the residue after ignition was submitted for spectrographic analysis with the following results:

	<u>ZrO_2</u>	<u>SiO_2</u>	<u>Fe</u>	<u>Ca</u>	<u>P, Mg, Al, U, Th</u>
%	> 10	> 10	5-10	5-10	1-5

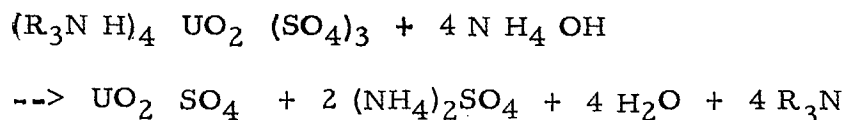
Incidentally, this points out the good extraction coefficient for zirconium with tertiary amine at low pH. Other impurities found could be partly due to entrained eluate in the extract.

Reagent Consumption

Ammonium sulphate concentration in the recycle strip was maintained at 15 - 16% through a balance of sulphate produced, water added from the dilute ammonia, and solution retained in the filtration and washing of the ADU precipitate. No sulphate make-up was therefore necessary after the initial amount was prepared from

commercial sulphuric acid and ammonia.

Ammonia consumed as shown in Table 4 was close to 0.3 lb NH₃/lb U₃O₈, which is higher than the theoretical amount of 0.24 lb/lb calculated from the following equation



This higher NH₃ consumption indicates the presence of some bisulphate anion in the extract as would be expected from the higher acidity of the eluate feed.

Solvent soluble loss, if determined by the drop in amine normality throughout the 15 runs, was not detectable. Actual kerosene and amine determinations on a composite barren eluate were respectively 0.001 lb and < 0.003 lb per lb U₃O₈.

Precipitation

Conditions and results of 18 continuous precipitation runs are presented in Table 5. In an effort to lower the sulphate content of the ADU, a study was made on the effect of pH, temperature, mixing time and filtration procedure.

As will be noticed, final pH of the barren is in most cases higher than the maximum point of control by 0.3 to 0.5 units. Hydrolysis of the ammonium diuranate during filtration and washing is the most probable explanation of the rise in pH. On relating final

TABLE 5

Continuous Precipitation Data
Feed rate 150 ml/min

Run No.	453	454	460	461	463	455	456	457	458	464	465A	465B	467	468	469	470	471	472	
Feed																			
pH	2.70	3.40	3.45	4.10	4.20	3.65	4.30	4.0	4.0	4.0	4.2	3.5	3.5	3.7	3.7	3.7	4.0	4.1	
U ₃ O ₈ , g/l	14.3	17.5	16.0	18.9	14.0	17.4	15.35	15.3	17.9	16.4	15.2	15.2	16.2	16.2	16.2	18.0	18.0	18.0	
Vol, litres	26.4	28.0	30.3	30.8	27.0	28.0	25.9	29.4	32.0	26.0	14.0	14.0	10.0	10.0	10.0	10.0	10.0	10.0	
Precipitation																			
pH	7-7.5	7-7.5	6.5-7	6.5-7	6.5-7	6.5-7	6.5-7	6.5-7	6.5-7	6.5-7	7-7.5	7-7.5	7-7.5	7-7.5	7-7.5	7-7.5	7-7.5	7-7.5	
Temperature, °C	38	38	38	38	38	60	60	60	60	38	38	38	45	50	50	50	50	38	
Mixing time, min	40	40	40	40	40	40	40	40	40	20	20	20	20	20	20	20	20	20	
Filtration and Washing																			
Holding time, hr	24	24	24	92	24	24	68	92	92	24	0	0	0	0	0	0	0	0	
Repulp vol, litres	0	0	0	0	0	0	0	0	0	0	0	1x0.5	1x1.0	1x1.0	1x2.0	1x2.0	1x2.0	2x2.0	
Repulp temp °C	-	-	-	-	-	-	-	-	-	-	-	19	19	19	19	75	19	19	
Wash vol litres	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.5	2.0	1.0	1.0	1.0	1.0	1.0	0.75	
Barren Strip																			
pH	7.5	7.3	7.05	7.0	7.0	8.15	8.65	7.95	7.80	7.35	7.90	7.90	7.90	7.90	7.90	7.90	7.90	7.90	
U ₃ O ₈ , g/l	0.002	0.003	0.003	0.002	0.003	0.002	0.001	0.004	0.006	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	
(NH ₄) ₂ SO ₄ , g/l*	138	154	158	165	158	-	150	158	166	162	162	162	152	152	152	152	152	152	
Precipitate																			
Dry wt, g	418	-	-	-	-	-	-	-	-	492.5	176.5	187.6	173	192	207	167	201	220	
U ₃ O ₈ , %	84.8	88.3	83.2	85.0	87.0	81.9	81.1	87.8	88.4	86.1	88.2	90.8	88.95	88.95	88.4	88.9	87.9	89.5	
NH ₃ , %	2.91	2.14	2.96	2.98	2.08	3.64	1.48	2.50	2.17	2.48	1.86	1.50	2.29	2.62	2.40	2.45	2.38	2.00	
SO ₄ , %	4.08	3.18	7.26	4.65	1.62	9.15	0.75	2.53	2.11	1.38	1.14	0.81	1.02	1.92	1.77	2.64	1.89	0.63	

* Determined from Specific Gravity of Solution

pH of the solution and sulphate content of the precipitate, the higher pH in general produced a lower sulphate content in the product. A minimum of 0.75% SO_4 was obtained without repulping.

In general the precipitates formed at higher temperature (60°C) contained less sulphate and filtered better. Mixing time, when reduced from 40 to 20 minutes by removing the second and third agitators, gave somewhat less sulphate. Keeping the slurry overnight or longer before filtration produced some fluctuation in the composition of the precipitate. This variable was eliminated in the later runs by filtering immediately during the test.

Reslurrying the precipitate lowered the sulphate content slightly. On the last test this was done twice and gave the lowest sulphate (0.63% SO_4). Variations in the temperature of the wash water, and time of reslurrying had little effect.

The ammonia content of the product cannot be related to any of the conditions of precipitation. In most cases the NH_3 content accounts for only 40 to 50% of the U_3O_8 as $(\text{NH}_4)_2\text{U}_2\text{O}_7$.

Samples from runs 455 and 458 were submitted for rare earths, thorium, boron and molybdenum chemical analyses and for a complete quantitative spectrographic analysis. Results are presented in Table 6 together with specifications for nuclear grade ceramic UO_2 , as listed by Atomic Energy of Canada Ltd. in September, 1959.

TABLE 6

Chemical and Quantitative Spectrographic Analyses
of ADU Precipitates

Element	ppm, U basis		Specifications
	Sample No.		
B chem	455 <0.1	458 1.2	0.2-0.3
B spect	2	2	"
Th chem	16	17	10
RE ₂ O ₃ chem	34	20	
As spect.	20	20	
Be "	<0.05	<0.1	
Bi "	20	20	
Cd "	< 5	< 5	0.2
Co "	<20	<20	20.
Cr "	100	< 5	20
Fe "	100	75	50
Ge "	<0.5	<0.5	
In "	5	5	
Mn "	<10	<10	5-10
Mo chem	30	50	1-2
Ni spect.	< 2	10	15
Pb "	50	20	
Sn "	10	5	
Y "	<20	<20	
Cu "	200	20	10-20

Some erratic results in the cases of B, Cr, Ni and Cu suggest that contamination in handling is the likely cause of the high values. For other elements where the limit of detection is above that of the specification, determination of the total neutron capture cross-section will be necessary for a final evaluation of the product. Molybdenum is reported much above specification in both samples. This can be expected in view of the high extraction coefficient of hexavalent molybdenum with tertiary amines.

Reduction and Sintering

Samples of the ammonium diuranate were submitted to the Mineral Sciences Division of the Mines Branch for thermogravimetric, DTA, pelletizing, and sintering tests⁽⁸⁾. In a number of tests the pellets showed some cracking and/or bloating. High densities of 10.5 or greater were nevertheless obtained on many samples. ~~Three samples were also tested by the Research and Development~~ Division of Eldorado Mining and Refining Ltd., Ottawa and satisfactory pellets were produced. The sintered densities obtained are listed in Table 7.

No clear relationship can be established between composition of the precipitate and sintering properties. In most cases the reduced powders were pyrophoric, except those reduced at 900°C by the Eldorado laboratory, in which case partial sintering was evident and resulted in a much lower density.

TABLE 7

Sintered Density of UO₂ Pellets

Reduction Temperature °C	Mines Branch				Eldorado	
	900°				600°	900°
Forming pressure psig	40,000		20,000		40,000	40,000
Sintering Cycle	R*	S**	R	S	R	R
Sample No. 453	10.01	9.95				
461	10.09	9.89				
462	10.37	10.61				
460	-	-			10.55	
466	10.28	-	10.22	10.54	-	
472	10.74	-	10.75	10.8	-	
455	10.17	10.49	-	-	10.50	7.98
456	10.41	10.18	10.35	-	10.57	9.45
458	10.56	10.68	-	-	-	
467	10.05	-	10.22	10.54	-	
471	10.68	-	10.67	10.77	-	
468	10.24	-	10.11	10.33	-	
469	10.23	-	10.14	10.42	-	
470	10.15	-	9.75	10.77	-	

* Regular Cycle: 350°C per hour to 1700°C, soaked in hydrogen for 30 minutes, cooled at 900°C per hour.

** Slow Cycle: Pellet heated slowly to 1020°C, soaked overnight, then heated at 150°C per hour to 1700°C, soaked 30 minutes, cooled at 250°C per hour.

CONCLUSIONS

A review of the conditions and results obtained from the investigation of the flowsheet as proposed in Figure 1, suggests the following:

1. The use of 10% sulphuric acid as an eluant for IRA-400 or Dowex 21K resins in place of acidified ammonium nitrate is practical. Total elution volume is increased from 8 to 14 bed volumes while uranium concentration in the strong eluate was reduced from 15 to approximately 8 g U_3O_8/l . By allowing a retention time of 15 minutes in current plant practice, the total elution cycle will not be changed. Since the "royal barren" is absent in the first part of adsorption, recycling of such a barren to leaching will not be required.
2. The long term effect of sulphuric acid elution on resin life has not been determined but on the basis of past experience, it would appear advantageous in reducing silica, titanium and uranium phosphate poisoning.
3. Liquid-liquid extraction of uranium from the eluate with a commercial tertiary amine, General Mills Alamine 336, can be done effectively in four stages. Disposal of the barren eluate as leach acid is recommended in order to avoid the build-up of impurities in the eluant. Since the barren eluate will be equivalent to 12 - 14% of the ore weight, recycling to leaching will require

dewatering of the neutral pulp to 80% solids in order to maintain the leach pulp at the present level of 70% solids in the agitators.

4. Stripping of the amine extract with a controlled-pH ammonium sulphate solution was effective and practical. But in view of the high molybdenum values in the final precipitate, an ammonium chloride strip⁽⁹⁾ is recommended for selective stripping of the uranium. This will involve regeneration of part of the recycle solvent with sodium carbonate to remove molybdenum.

5. Continuous precipitation with gaseous ammonia produced an ADU that filtered well and can be washed to less than 1% SO_4 in the product. A higher sulphur content on the other hand was not objectionable in the reduction and sintering to a high density UO_2 pellet.

6. In view of the uncertainty of the effect of certain impurities in the product, in-reactor evaluation will be required to determine overall neutron absorption and thermal properties of the fabricated uranium dioxide pellets.

Cost of reagents for this process as compared to the nitrate elution followed by two-stage precipitation is given in Table 8.

Prices of reagents are based on present quotations from leach plant operators in the Elliot Lake area, Ontario.

TABLE 8

Comparison of Reagent Costs

Process	Reagent			Cost	
	Used	Price cents/lb	Consumption lb/lb U ₃ O ₈	cents/lb U ₃ O ₈	
Sulphuric Acid Elution	H ₂ SO ₄	1.2	1.2	1.44	
	Amine	130.	0.003	0.40	
	Amine Extraction	Kerosene	2.0	0.001	0.002
	Ammonia Precipitation	NH ₃ for strip	4.5	0.3	1.35
		" for pptn	4.5	0.3	1.35
		Total			4.54
Nitrate Elution	HNO ₃	5.5	1.70	9.35	
	Lime	1.0	1.50	1.50	
	Two-stage Lime-Ammonia Precipitation	NH ₃	4.5	0.35	1.57
		Total			12.42

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