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MISCELLANEOUS ELUTION STUDIES

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ABSTRACT

An investigation was made of the variables involved in a 5M NaCl - H₂O elution scheme. The most promising procedure was used in a cyclic ion exchange system.

Studies were also made on the effect of iron to phosphate ratios on uranium ion exchange and the effect of temperature on elution.

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INTRODUCTION

An elution scheme using 5M NaCl and H₂O was first reported in DOW-22 and later in MITG A-97, DOW-57, and DOW-59. The basis for this scheme is the fact that an anionic uranyl chloride complex, probably (UO₂Cl₄)⁻², is formed in strong chloride solutions (greater than 3M). This uranyl chloride complex ion is capable of being adsorbed on a strong base anion exchange resin such as Amberlite IRA-400. If, after the adsorbed uranium has been converted to the chloride complex, water is passed through the resin, the chloride is diluted causing the complex to dissociate. The uranium is probably a cation in dilute chloride solutions, and therefore is immediately desorbed and appears in the eluate as a sharp band at the chloride-water interface.

It has been reported in the above-mentioned reports that from 20 to 35 per cent of the uranium appears in the 5M NaCl portion of the eluate. A typical example of the uranium distribution is taken from DOW-59 and presented below.

Uranium Distribution

<u>Eluate Fractions</u>	<u>Per Cent of Total Uranium Desorbed</u>
10 Bed Volumes 5M NaCl	21
10 Bed Volumes H ₂ O	61
10 Bed Volumes 0.1M HCl ^{1/}	18

^{1/} The 0.1M HCl was used to remove the uranium remaining on the resin after the H₂O fraction.

As can be seen in the above table and in the work presented in this report, the uranium is not completely eluted with the 5M NaCl and H₂O. To effect the complete elution of uranium, the sulfate must be completely removed from the resin prior to the introduction of the water. According to DOW-57, at least six bed volumes of 5M NaCl, passed through the resin at a two-minute retention time, are required for complete removal of the sulfate. This excessive salt requirement has been minimized in the following investigation by allowing the 5M NaCl to remain in contact with the resin for extended periods of time.

This elution scheme would theoretically appear to be advantageous in that the elution time and the amount of alkali required for

neutralization would be greatly reduced in comparison to the usual salt plus acid eluting solutions. Therefore, it was decided to investigate further and attempt to improve the elution procedure described.

SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

After examination of the variables in an elution scheme in which 5M NaCl was followed by water, the following procedure was found to be the most effective. One bed volume of 5M NaCl was passed through the resin column. The latter half of this eluant was allowed to remain in the column for one-half hour. Four bed volumes of water were then passed through the column. This, in turn, was followed by four bed volumes of 1M H₂SO₄. A typical breakdown of the uranium removed by each eluant is presented below:

	<u>U₃O₈ Eluted Per Cent</u>
First one-half bed volume of 5M NaCl	21.1
Second one-half bed volume of 5M NaCl	9.5
Four bed volumes of H ₂ O	62.3
Four bed volumes of 1M H ₂ SO ₄	7.1

The uranium is not completely eluted by the 5M NaCl and H₂O. It would be displaced from the resin, and appear in the effluent of the succeeding exhaustion cycle. To prevent this loss, the 1M H₂SO₄ eluant was used to convert the resin and any residual uranyl chloride complex to the sulfate form. This conversion decreased the uranium concentration in the barren solution to an acceptable value. The 1M H₂SO₄ eluate was recycled to the pregnant solution.

In order to lower the chloride consumption, the first half bed volume of NaCl eluate was precipitated along with the four bed volumes of H₂O. The second half bed volume of NaCl, which was reduced to about 4M NaCl, was used in the first part of the succeeding elution cycle.

This scheme has advantages and disadvantages compared to the usual salt plus acid eluants, e.g., NaCl + H₂SO₄. One advantage is the lower cost of precipitation resulting from the use of a neutral eluting solution. The pH of these eluates is in the range of 2.1 to 2.4, whereas the pH of an eluate produced by an acidic eluant is approximately 1.1. The precipitation cost would also be lowered because of the smaller eluate volume. The eluate volume is 4.5 bed volumes which is approximately one-half the volume resulting from a salt plus acid eluant using a split elution technique. Another advantage would be the total time required for elution. This elution scheme would require 255 minutes as compared to approximately 450 minutes for the usual elution. A disadvantage is that the chloride consumption is one and one-half

times the consumption of the conventional elution procedure. This elution scheme does not make full use of the total resin capacity. Six or seven per cent of the capacity is not utilized by returning the 1M H_2SO_4 portion of the eluate to the feed solution. The complexity of using three different eluants may also be considered a drawback; however, the potential cost savings are of a sufficient magnitude to warrant testing the procedure more completely.

It is therefore recommended that the elution scheme described on page 20 be tested in the CCD-IX Column Pilot Plant in Grand Junction so as to obtain operating information on the cost of elution and precipitation. Based upon laboratory test work and current Grand Junction prices, an elution and precipitation cost of five cents per pound of U_3O_8 produced is indicated at a resin loading of 60 grams of U_3O_8 per liter of wet settled IRA-400 resin. In addition, the laboratory data show that the elution procedure described results in a higher overall recovery of uranium.

The combined effect of iron and phosphate on uranium ion exchange was investigated. It was found that the eluant required for complete elution became excessive as the molar ratio of ferric iron to phosphate was decreased below the value of 1:1. These long elutions were accompanied by very high uranium loadings. As the ferric iron to phosphate ratio was increased to greater than 1:1, the number of bed volumes required for complete elution decreased to a normal value. The shorter elutions were accompanied by smaller breakthrough and saturation loadings.

Unlike the ferric ion, the ferrous ion did not form a complex with the phosphate ion. This left the phosphate free to be adsorbed on the resin as the uranium phosphate complex, giving rise to very high uranium loadings and long elutions.

This excessive eluant requirement was decreased to 19 bed volumes by eluting at a temperature of $62^\circ C$, compared with 31 bed volumes at $25^\circ C$.

PART IELUTION WITH 5M NaCl AND H₂OA. Examination of Variables

Columns containing 25 ml of Amberlite IRA-400 resin were used throughout this investigation. The columns were, without exception, loaded to saturation (average loading was 80 grams of U₃O₈ per liter of wet settled resin) using a three-minute retention time with a leach liquor prepared from Edgemont ore. The composition of this pregnant solution, which is relatively free from impurities, is as follows:

<u>pH</u>	<u>Emf(mv)</u>	<u>Leach Liquor Assay - Grams/Liter</u>					
		<u>U₃O₈</u>	<u>V₂O₅</u>	<u>Fe⁺⁺⁺</u>	<u>Fe⁺⁺</u>	<u>SO₄</u>	<u>Mo</u>
1.40	-440	0.93	0.38	0.34	0.22	10.7	Nil

Part I of this report includes the individual eluting tests that were made, varying such factors as the volume of 5M NaCl, the contact time of the salt solution and the water with the resin, the use of 6M NaNO₃, 12M NH₄NO₃, or acidified 5M NaCl in place of 5M NaCl, the use of dilute HCl and H₂SO₄ in place of H₂O, and the volume of 5M NaCl that was passed through the column before and after allowing it to stand in the column.

Test 1Procedure

One-half bed volume of 5M NaCl was passed through the column at a 10-minute retention time (R.T.) and allowed to stand one-half hour. Thereafter, one and one-half volumes of 5M NaCl and then six bed volumes of water were passed through the column at a 10-minute retention time.

Table I

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>Moles Cl/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	21.2	2.48	30.2
	2	1.79	4.74	32.7
H ₂ O	1	43.9	1.0	95.2
	2	2.2	0.03	98.0
	3	0.56		98.8
	4	0.31		99.2
	5	0.21		99.5
	6	0.13		99.7

Note: This column is probably not completely eluted.

Test 2Procedure

The water in the column was displaced with 5M NaCl and allowed to stand one-half hour. Sufficient 5M NaCl to make up a total of one bed volume was passed through the column at a 10-minute retention time. Seven bed volumes of H₂O were passed through at a 20-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table II

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1/2	32.9	23.0
	1	11.1	30.8
H ₂ O	1/2	67.0	77.5
	1	15.1	88.0
	2	2.9	92.0
	3	0.85	93.2
	4	0.40	93.8
	5	0.21	94.1
	6	0.13	94.3
	7	0.036	--
1N HCl	1	2.74	98.1
	2	1.1	99.6
	3	0.36	100.0

Test 3Procedure

The water in the column was displaced with 5M NaCl and allowed to stand one-half hour. Sufficient 5M NaCl, to make up a total volume of one bed volume, was passed through the column at a 10-minute retention time. Ten bed volumes of 0.1N HCl were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table III

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1/2	30.7	23.0
	1	11.1	31.3
0.1N HCl	1/2	43.8	64.1
	1	20.5	79.4
	2	5.90	88.2
	3	2.5	92.0
	4	1.5	94.2
	5	1.0	95.7
	6	0.83	97.0
	7	0.59	97.9
	8	0.56	98.7
	9	0.25	99.1
	10	0.19	99.4
1N HCl	1	0.22	99.7
	2	0.12	99.9
	3	0.061	100.0

Test 4

Procedure

One-half bed volume of 5M NaCl was placed in the column and allowed to stand one-half hour. Three bed volumes of water were passed through the column at a 10-minute retention time. Four bed volumes of 1N HCl were used as the scavenger eluant.

Table IV

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1/2	34.4	22.5
H ₂ O	1	33.2	66.0
	2	7.01	75.2
	3	3.4	79.7
1N HCl	1	8.68	91.1
	2	4.5	97.0
	3	1.8	99.3
	4	0.64	100.0

Test 5Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The last fraction of this eluant was allowed to remain in the column 15 minutes. Three bed volumes of water were passed through at a 10-minute retention time. Four bed volumes of 1N H₂SO₄ were used as the scavenger eluant.

Table V

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	21.7	32.8
H ₂ O	1	32.8	82.3
	2	4.1	88.5
	3	2.2	91.8
1N H ₂ SO ₄	1	3.94	97.8
	2	0.78	99.0
	3	0.38	99.6
	4	0.32	100.0

Test 6Procedure

One bed volume of 6M NaNO₃ was passed through the column at a 10-minute retention time. The last part of this eluant remained in the column one-half hour. Nine bed volumes of water were passed through the column at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table VI

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
6M NaNO ₃	1	38.6	48.2
H ₂ O	1	28.1	83.4
	2	3.22	87.4
	3	1.5	89.3
	4	1.0	90.5
	5	0.70	91.4
	6	0.52	92.0
	7	0.45	92.6
	8	0.36	93.0
	9	0.29	93.4
1N HCl	1	3.62	97.9
	2	1.1	99.3
	3	0.50	100.0

Test 7

Procedure

One-half bed volume of 12M NH_4NO_3 was placed in the column and allowed to stand one-half hour. An additional bed volume of 12M NH_4NO_3 was passed through the column at a 10-minute retention time. Nine bed volumes of H_2O were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table VII

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g $\text{U}_3\text{O}_8/\text{l}$</u>	<u>% U_3O_8 Eluted</u>
12M NH_4NO_3	1/2	55.4	38.8
	1/2-1 1/2	13.2	57.3
H_2O	1	22.4	88.7
	2	2.44	92.1
	3	0.92	93.4
	4	0.41	94.0
	5	0.29	94.4
	6	0.20	94.7
	7	0.11	94.9
	8	0.11	95.0
	9	0.070	95.1
1N HCl	1	2.63	98.8
	2	0.67	99.8
	3	0.12	100.0

Test 8

Procedure

One bed volume of 5M NaCl , acidified to a pH of 0.5 with HCl , was passed through the column at a 10-minute retention time. The latter part of this eluant was allowed to remain in the column for one-half hour. Nine bed volumes of water were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table VIII

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl (+HCl-pH 0.5)	1	25.0	30.4
H ₂ O	1	46.4	86.8
	2	3.83	91.4
	3	1.4	93.1
	4	0.62	93.8
	5	0.45	94.3
	6	0.29	94.7
	7	0.20	94.9
	8	0.15	95.1
	9	0.12	95.2
1N HCl	1	2.29	98.0
	2	1.3	99.6
	3	0.39	100.0

Test 9Procedure

One-half bed volume of 5M NaCl was placed in the column and allowed to stand for two hours. An additional one-half bed volume of 5M NaCl was passed through the column at a 10-minute retention time. Six bed volumes of water were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table IX

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1/2	37.2	23.6
	1	11.0	30.6
H ₂ O	1	42.5	84.6
	2	4.56	90.4
	3	1.4	92.2
	4	0.74	93.1
	5	0.45	93.7
	6	0.28	94.0
1N HCl	1	3.04	97.8
	2	1.23	99.3
	3	0.50	100.0

Test 10Procedure

One-half bed volume of 5M NaCl was placed in the column and allowed to stand one-half hour. An additional bed volume of 5M NaCl was passed through at a 10-minute retention time. The first bed volume of eluate was made up as near as possible to its original chloride concentration (2.6M Cl⁻ to 4.7M Cl⁻) with NaCl and passed through the column again. Six bed volumes of water were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table X

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1(recycled)	17.0	21.4
	1/2	2.98	23.3
H ₂ O	1	45.3	80.3
	2	4.94	86.5
	3	2.27	89.4
	4	1.3	91.0
	5	0.90	92.1
	6	0.56	92.8
1N HCl	1	3.12	96.7
	2	1.80	99.0
	3	0.83	100.0

Test 11Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The last fraction of this eluant was allowed to remain in the column for a half hour. Two bed volumes of water were passed through at a 10-minute retention time. The first step was repeated. That is, a bed volume of 5M NaCl was passed through, allowing the last fraction to remain in the column for a half hour. Six bed volumes of water were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table XI

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	10.9	23.6
H ₂ O	1	21.7	70.5
	2	4.11	79.4
5M NaCl	1	0.16	79.7
H ₂ O	1	3.75	87.8
	2	0.23	88.3
	3	0.11	88.5
	4	0.075	88.7
	5	0.045	88.8
	6	0.045	88.9
1N HCl	1	4.11	97.8
	2	0.68	99.3
	3	0.27	100.0

Test 12Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The last fraction of this eluant was allowed to stand in the column for a half hour. Nine bed volumes of 1N HCl were passed through at a 10-minute retention time.

Table XII

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	22.8	28.2
1N HCl	1	36.5	73.4
	2	14.2	91.0
	3	4.66	96.8
	4	1.62	98.8
	5	0.54	99.5
	6	0.20	99.7
	7	0.092	99.8
	8	0.045	99.9
	9	0.025	100.0

Test 13

Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The last fraction of this eluant was allowed to stand in the column for one-half hour. Twelve bed volumes of 1M NaCl were passed through at a 10-minute retention time. Three bed volumes of 1N HCl were used as the scavenger eluant.

Table XIII

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	22.9	28.8
1M NaCl	1	26.0	61.5
	2	12.1	76.7
	3	5.91	84.2
	4	3.18	88.2
	5	1.64	90.3
	6	0.77	91.3
	7	0.43	91.8
	8	0.27	92.1
	9	0.19	92.3
	10	0.13	92.5
	11	0.086	92.6
	12	0.072	92.7
1N HCl	1	4.54	98.4
	2	0.89	99.5
	3	0.38	100.0

Incomplete Conversion to Chloride Complex

It can be seen that in all these variations of the 5M NaCl - H₂O elution scheme, the uranium is not completely eluted from the resin.

Approximately five to 10 per cent of the uranium remains on the resin after the H₂O elution, and would be bled into the barren solution on the succeeding exhaustion cycle. This incomplete elution is attributed to the incomplete conversion of the uranyl sulfate complex to the uranyl chloride complex. This theory was substantiated by a test in which uranium, adsorbed on the resin from a 5M NaCl solution, was completely eluted with water.

The detection (by spot tests) of sulfate in the scavenger eluates demonstrated the incomplete conversion of the sulfate complex to

the chloride complex. As pointed out in the introduction, an excessive amount of salt solution is required for a complete conversion to the chloride complex. Therefore, this approach was not attempted in this investigation. Instead, it was decided to follow up the H_2O elution with a few bed volumes of H_2SO_4 . Although this amount of H_2SO_4 does not completely elute the uranium, it prevents the leakage in the subsequent exhaustion cycle. The H_2SO_4 fraction of the eluate could be recycled to the leaching circuit.

The test work, from this point on, was an attempt to prove the feasibility of this approach. The resins were partially reloaded after elution to note the uranium loss in the barren.

Test 14

Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The latter half of this eluant was allowed to remain in the column for one-half hour. Four bed volumes of water were passed through, followed by four bed volumes of 1M $(NH_4)_2SO_4$ at a 10-minute retention time.

Table XIV

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U_3O_8/l</u>	<u>% U_3O_8 Eluted</u>
5M NaCl	1	22.6	27.4
H_2O	1	52.8	91.4
	2	4.55	96.9
	3	1.49	98.7
	4	1.01	99.9
1M $(NH_4)_2SO_4$	1	0.11	100.0
	2	0.069	
	3	0.0018	
	4	0.0066	

Eight bed volumes of Edgemont leach liquor were then passed through the column at a five-minute retention time. The eight bed volumes of barren solution averaged 0.0045 gram U_3O_8 per liter.

Test 15

Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The first half of this eluant was allowed to stand in the column overnight. Four bed volumes of water were passed through, followed by four bed volumes of 1M H₂SO₄ at a 10-minute retention time.

Table XV

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	25.0	29.5
H ₂ O	1	40.9	77.8
	2	9.28	88.8
	3	1.55	90.6
	4	1.14	92.0
1M H ₂ SO ₄	1	4.17	96.9
	2	1.22	98.4
	3	0.77	99.3
	4	0.61	100.0

The effluent from the 15 bed volumes of Edgemont leach liquor, which were passed through the column at a five-minute retention time, averaged 0.0029 gram U₃O₈ per liter.

Four bed volumes of 1M H₂SO₄ were used in this test because that is the volume required to remove virtually all of the chloride from the resin. Theoretically, this means that all the uranium adsorbed on the resin existed as the sulfate complex and would not be eluted by the pregnant solution.

Test 16

Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The last half of the eluant was allowed to stand in the column for one-half hour. Three bed volumes of water were passed through followed by four bed volumes of 1M H₂SO₄ at a retention time of 10 minutes.

Table XVI

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	21.8	27.2
H ₂ O	1	44.7	83.2
	2	4.21	89.0
	3	1.78	91.2
1M H ₂ SO ₄	1/2	5.67	94.7
	1	3.86	97.1
	1 1/2	1.73	98.2
	2	0.87	98.7
	3	0.76	99.6
	4	0.69	100.0

Twenty bed volumes of Edgemont leach liquor were spiked with NaCl to a chloride concentration of 0.41 gram per liter and passed through the column at a 10-minute retention time. This would be the chloride concentration in the Edgemont leach liquor if the 1M H₂SO₄ fraction of the eluate had been added to it. The 20 bed volumes of barren solution averaged 0.0027 gram U₃O₈ per liter, demonstrating that this low chloride concentration does not interfere with the exhaustion cycle.

Test 17Procedure

One bed volume of 5M NaCl was passed through the column at a 10-minute retention time. The latter half of this eluant was allowed to remain in the column for one-half hour. Three bed volumes of water were passed through followed by four bed volumes of 2M H₂SO₄ at a 10-minute retention time.

Table XVII

<u>Eluant</u>	<u>Bed Volumes</u>	<u>g U₃O₈/l</u>	<u>% U₃O₈ Eluted</u>
5M NaCl	1	22.1	28.5
H ₂ O	1	42.2	83.0
	2	4.18	88.4
	3	1.73	90.6
2M H ₂ SO ₄	1/2	3.68	93.0
	1	2.51	94.6
	1 1/2	2.39	96.1
	2	1.77	97.3
	3	1.1	98.7
	4	0.91	100.0

Twenty bed volumes of Edgemont leach liquor were then passed through the column at a 10-minute retention time. The first bed volume of barren solution contained 0.072 gram U_3O_8 per liter; however, the following 19 bed volumes averaged 0.0021 gram U_3O_8 per liter.

The barren solutions in these tests had higher uranium assays than are usually encountered in these barren effluents when the columns have been completely eluted with salt plus acid eluting solutions, but these assays were still much lower than break-through values. In cases where the water eluant is not followed by another eluant, the subsequent barren assays become intolerable. For example, the four bed volumes of barren effluent, immediately following the elution in Test 1, averaged 0.56 gram U_3O_8 per liter.

B. Cyclic Testing

The 5M NaCl - H_2O elution has also been tested on a cyclic basis in the leaching and ion exchanging of Edgemont ore (Sample 156-1) containing 0.287 per cent U_3O_8 . As previously reported, the 5M NaCl and H_2O did not give complete elution, giving rise to an excessively high uranium bleed in the barren effluent of the succeeding exhaustion cycle. This condition was remedied by following the H_2O elution with four bed volumes of 1M H_2SO_4 , which removed most of the residual uranium and permitted a barren solution to be obtained at the start of the next exhaustion cycle.

The elution scheme used in this investigation consisted of three stages and was carried out at a 10-minute retention time. The first part of the eluant was one bed volume of 5M NaCl, the second half of which was allowed to remain in the column for one-half hour. The second part was four bed volumes of H_2O . The third part was four bed volumes of 1M H_2SO_4 which was recycled to the leaching circuit. The assays from the fourth cycle are presented below as being typical.

Three-Stage Elution - Cycle Four Assays

	Grams/Liter			pH
	U_3O_8	Cl	SO_4	
First 1/2 bed volume of 5M NaCl	33.1	27.7	122.0	2.4
Second 1/2 bed volume of 5M NaCl	14.9	137.0	50.6	2.4
Four bed volumes of H_2O	12.2	10.0	Nil	2.1
Four bed volumes of 1M H_2SO_4	1.40	10.0		0.0

The use of 50 pounds of H_2SO_4 per ton of feed in the leach gave consistent uranium extractions of 97 per cent. The leaching was done at 50 per cent solids and the resultant pregnant solution was diluted 3:1. Before ion exchange, the leach liquor was reduced from minus 610 mv to minus 440 mv with $FeSO_4$ and the pH was raised to 1.40 with a very small amount of NH_4OH . A total of eight cycles were completed in which varying weight charges of ore were leached and the resulting leach liquors ion exchanged. It was not until seven cycles were completed, however, that a uranium balance was reached between the leaching and the ion exchange circuits. At this point, 44 per cent of the acid requirement for leaching was supplied by the H_2SO_4 eluate. The H_2SO_4 eluate, which assayed about 1.5 grams U_3O_8 per liter, increased the uranium concentration in the feed liquor by six or seven per cent to a level of 1.0 gram U_3O_8 per liter.

The ion exchange was done in a two-column system using 25 ml of IRA-400 resin per column. The exhaustion retention time was three minutes. The system was said to have reached a uranium balance if the first column was saturated with uranium and the second column reached breakthrough when all of the prepared leach liquor had been passed through both columns. The first four bed volumes of barren effluent assayed 0.006 to 0.007 gram U_3O_8 per liter, and the remaining composite barren (approximately 90 bed volumes) assayed 0.002 to 0.003 gram U_3O_8 per liter. The H_2SO_4 eluate, which was recycled to the leach, contained approximately 10 grams of chloride per liter and increased the chloride concentration in the feed liquor to 0.5 gram per liter. However, this did not appear to affect the breakthrough loadings or the saturation loadings, which were in the order of 80 grams of U_3O_8 per liter of wet settled resin.

The primary drawback to this 5M NaCl - H_2O - 1M H_2SO_4 elution scheme was the rather high chloride requirement if the bed volume of 5M NaCl were precipitated along with the four bed volumes of H_2O . In order to lower the chloride consumption, the first half bed volume of NaCl eluate was precipitated along with the four bed volumes of H_2O ; the second half bed volume of NaCl, which was reduced to about 4M NaCl, was used in the first part of the succeeding elution cycle. This scheme slightly lowered the amount of uranium eluted in the first two stages and raised the uranium concentration in the H_2SO_4 eluate to two grams per liter; however, it did cut the chloride consumption in half.

The data from these tests indicate that one pound of U_3O_8 can be eluted with approximately 2.1 pounds of NaCl and 0.3 pound of H_2SO_4 , while precipitation consumes 0.27 pound of MgO per pound of U_3O_8 .

C. Elution of Resin Loaded With Mt. Isa Leach Liquor

This elution scheme was also used in the ion exchange of two Mt. Isa leach liquors which had high phosphate concentrations. There was a slight modification, however, in that 0.1N HCl was used in place of H₂O to remove phosphate that might have precipitated within the resin bed. The results of this elution scheme are compared to elutions made with an eluant consisting of a 1M NaCl solution acidified to a pH of 1.0 with sulfuric acid and spiked with magnesium sulfate to a sulfate concentration of 100 grams per liter. The ion exchange took place in columns containing 25 ml of IRA-400 resin. The head assays of the two solutions are given below:

Mt. Isa Feed Liquor - Sample 191-1

<u>pH</u>	<u>Emf(mv)</u>	<u>Grams/Liter</u>					
		<u>U₃O₈</u>	<u>P₂O₅</u>	<u>Fe</u>	<u>SO₄</u>	<u>V₂O₅</u>	<u>Mo</u>
1.75	-405	1.54	4.05	9.26	62.8	0.25	0.001

Mt. Isa Feed Liquor - Sample 191-2

<u>pH</u>	<u>Emf(mv)</u>	<u>Grams/Liter</u>					
		<u>U₃O₈</u>	<u>P₂O₅</u>	<u>Fe</u>	<u>SO₄</u>	<u>V₂O₅</u>	<u>Mo</u>
1.55	-275	0.60	9.81	6.86	58.9	0.50	0.001

The 1M NaCl - H₂SO₄ elution of the column loaded with Sample 191-1 leach liquor required 19 bed volumes of eluant for complete elution, and the elution curve exhibited a normal peak. The 5M NaCl elution scheme was very efficient in this case. The assays are presented below:

5M NaCl Elution - Sample 191-1

	<u>g U₃O₈/l</u>
1 bed volume 5M NaCl	26.6
4 bed volumes 0.1N HCl	12.3
4 bed volumes 1N H ₂ SO ₄	0.38
4 bed volumes 1M HCl <u>1/</u>	Nil
<u>1/</u> Scavenger eluant.	

The 1M NaCl - H₂SO₄ elution of the column loaded with Sample 191-2 leach liquor required 23 bed volumes of eluant for complete elution, and the elution curve was extremely flat with virtually no peak. The 5M NaCl - 0.1N HCl elution was also a very poor one as shown by the assays below:

5M NaCl Elution - Sample 191-2

	<u>g U₃O₈/Liter</u>
1 bed volume 5M NaCl	1.36
4 bed volumes 0.1N HCl	5.69
4 bed volumes 1N H ₂ SO ₄	6.53
4 bed volumes 1N HCl ^{1/}	3.47

^{1/} Scavenger eluant.

The 5M NaCl - H₂O elution scheme was also used to elute a column loaded with Dakota Lignite leach liquor in an attempt to remove the adsorbed molybdenum. This test was unsuccessful in that very little Mo was eluted.

PART II

ION EXCHANGE OF HIGH PHOSPHATE LEACH LIQUORS

A. Effect of Iron and Phosphate on Elution and Loading

Prompted by the numerous reports of phosphate interferences in the ion exchanging of acid leach liquor, an investigation of this problem was initiated, examining the effect of varying iron to phosphate ratios on the loading and elution of uranium.

Fifteen synthetic solutions containing uranium, iron, phosphate, and sulfate were tested in four series. In all the tests, the uranium and sulfate concentrations were held constant at 1.0 gram per liter and 25 grams per liter, respectively. Solution Numbers 9 and 15 were exceptions in that an excess of H_2SO_4 was needed to dissolve the iron. In the first series of tests, the P_2O_5 concentration was held constant at 4.0 grams per liter and the ferric iron concentration was varied from 1.77 to 8.74 grams per liter. In the second series, the P_2O_5 concentration was 8.2 grams per liter and the ferric iron concentration varied from 3.67 to 17.3 grams per liter. In the third series, the iron concentration was constant at five grams per liter and the P_2O_5 concentration was varied from 2.99 to 23.6 grams per liter. The fourth series consisted of two tests in which ferrous iron was used rather than ferric iron. The two ferrous iron concentrations were 3.70 and 18.2 grams per liter while the phosphate concentration was approximately 8.2 grams per liter.

To prevent the precipitation of ferric phosphate before and during ion exchange, these artificial leach liquors were prepared at a pH of 1.0, and 1M H_2SO_4 was run through the resin columns before exhaustion. Columns containing 10 ml of wet settled Amberlite IRA-400 resin were used. The retention time was three minutes on exhaustion and 10 minutes on elution. The columns were loaded to saturation and eluted with a 1M NaCl solution acidified to a pH of 1.0 with H_2SO_4 and spiked with $\text{MgSO}_4 \cdot 7 \text{H}_2\text{O}$ to a sulfate concentration of 100 grams per liter. The results of these tests are presented in Table XVIII on the following page.

According to Salmon (Salmon, J.E., Chem. Soc. of London, 2644, Sept. 1953) the predominant ferric phosphate complex existing in acid solution is $(\text{FeHPO}_4)^+$, representing an iron to phosphate ratio of 1:1. There is also the anionic complex $[\text{Fe}(\text{PO}_4)_3]^{-6}$; however, this complex is formed only when the phosphate to iron ratio approaches 10:1 and this condition is not met in any of these artificial solutions. When the iron to phosphate ratio is 1:1 or less, the number of bed volumes for complete elution is excessive and the elution curve is flat, exhibiting no peak. These long

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Table XVIII

Effect of the Iron to Phosphate Ratio on Uranium Ion Exchange on IRA-400 Resin

Solution Number	Solution Assays Grams/Liter				pH	Emf(mv)	Molar Ratio Fe : PO ₄	Bed Volumes To:			Loading g U ₃ O ₈ /l
	Fe ⁺⁺⁺	P ₂ O ₅	U ₃ O ₈	SO ₄				Breakthru	Saturation ^{1/}	Elution	
1	--	--	1.04	26.3	1.00	-500 ^{1/}	--	48	100	18	61.8
2	1.77	4.02	1.04	24.4	1.00	-560	0.56:1	56	160	31	102.0
3	3.22	4.02	1.04	23.0	1.00	-570	1:1	52	160	28	91.8
4	5.00	4.02	1.04	24.1	1.00	-610	1.6:1	44	120	22	69.8
5	8.74	4.2	1.04	23.3	1.00	-630	2.7:1	40	120	19	64.5
6	3.67	8.40	1.08	24.8	1.00	-550	0.56:1	44	170	31	98.2
7	6.28	8.20	1.04	24.1	1.00	-580	1:1	37	160	26	78.7
8	9.69	8.40	1.04	27.7	1.00	-610	1.5:1	35	120	21	63.0
9	17.3	8.20	1.04	40.9	1.00	-710	2.7:1	29	120	18	55.8
10	4.64	23.6	1.05	25.4	1.00	-420	0.26:1	27	180	35	88.9
11	5.04	11.8	1.06	25.0	1.00	-420	0.55:1	30	180	33	89.8
12	5.14	5.95	1.04	26.3	1.00	-600	1.1:1	30	140	27	78.2
13	5.20	2.99	1.04	24.4	1.00	-630	2.2:1	34	120	20	62.7
	<u>Fe⁺⁺</u>										
14	3.70	8.10	1.03	24.8	1.00	-280	0.58:1	61	190	38	121.0
15	18.2	8.24	1.06	38.4	1.00	-280	2.8:1	55	180	36	115.0

^{1/} Approximately

elutions are accompanied by very high loadings. This phenomenon can be explained by the fact that the uranium is held on the resin as a uranyl phosphate complex (probably $[\text{UO}_2(\text{H}_2\text{PO}_4)_5]^{-3}$) with a smaller charge than the uranyl trisulfate. There was no visible precipitation in the columns during the loadings or the elutions, and no explanation was found for the long elution cycles.

As the iron to phosphate ratio is increased to a value greater than 1:1, the number of bed volumes for complete elution decreases to 18 to 20 bed volumes. This is the usual solution volume required by this $\text{NaCl} - \text{H}_2\text{SO}_4$ eluting solution. The elution curves also exhibited their usual peaks, i.e., 10 to 15 grams U_3O_8 per liter. The shorter elutions were, unfortunately, accompanied by smaller breakthrough loadings, due to the increase in ferric iron concentration in the pregnant solution. The saturation loadings decreased to normal values, i.e., 60 to 70 grams U_3O_8 per liter of wet settled resin at a pH of 1.0, as the iron to phosphate ratio increased. Presumably, the iron is tying up the phosphate as the $[\text{FeHOP}_4]^{+1}$ complex and preventing the formation of the uranyl phosphate complex.

Unlike the ferric ion, the ferrous ion does not form a complex with the phosphate ion. This leaves the phosphate free to become adsorbed on the resin as the uranium phosphate complex, giving rise to very high uranium loadings and long elutions.

B. Effect of Temperature on Elution

An investigation was made of the effect of temperature on the elution of IRA-400 resin loaded with a synthetic leach liquor of the composition tabulated below:

<u>Synthetic Pregnant Solution</u>						<u>Molar Ratio</u>
<u>pH</u>	<u>Emf (mv)</u>	<u>Grams/Liter</u>				
		<u>U₃O₈</u>	<u>P₂O₅</u>	<u>Fe⁺⁺⁺</u>	<u>SO₄</u>	<u>Fe:PO₄</u>
1.00	-580	1.04	4.2	1.77	24.3	0.56:1

The columns were loaded to saturation and eluted at a 10-minute retention time with a 1M NaCl solution acidified to a pH of 1.0 with H_2SO_4 and spiked with MgSO_4 to a total sulfate concentration of 100 grams per liter. The elutions were carried out in glass-jacketed columns through which water was circulated at a constant temperature.

The elution results at three temperatures are presented in Table XIX. It can be seen that increasing temperature is definitely advantageous. These tests should be compared to the elution of a column loaded with a phosphate free leach liquor. This phosphate-free elution required 18 bed volumes of eluant.

A 62°C elution was also made on a column loaded with Hidden Splendor leach liquor in an attempt to elute the adsorbed molybdenum. The test was unsuccessful.

Table XIX
Effect of Temperature on Elution

Test Number	1	2	3
Temperature, °C	25	45	62
Loading, g U ₃ O ₈ /l	102	104	104
Bed Volumes for Complete Elution	31	23	19

C. Effect of Ammonium Sulfate on Elution

It was reported in ACCO-33 that the presence of (NH₄)₂SO₄ in the eluant appreciably decreased the bed volumes of eluant required for complete elution. The leach liquor investigated in ACCO-33 contained 0.2 gram P₂O₅ per liter. Consequently, it was decided to duplicate this elution on a column loaded with a high phosphate leach liquor. Solution 2 (see Table XVIII) was used.

The eluting solution was identical to that described on page 26 except that (NH₄)₂SO₄ was used in place of MgSO₄ to increase the sulfate concentration to 100 grams per liter. The ammonium content of this eluant was 30.5 grams per liter.

This elution required approximately 40 bed volumes as compared to 31 bed volumes required by the eluant containing MgSO₄. This increase in eluant requirement may be due to the formation of insoluble UO₂NH₄PO₃. During the elution, a slight precipitation was observed within the resin bed.

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