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LABORATORY STUDIES ON LEACHING OF LOW GRADE
URANIUM ORES AND TREATMENT OF LOW LEVEL
LIQUID WASTE GENERATED BY LEACHING
EXPERIMENTS

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July, 1980

Philippine Atomic Energy Commission
Don Mariano Marcos Avenue
Diliman, Quezon City

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ABSTRACT

Acid leaching experiments of preconcentrated uranium ore were carried out at a pulp density of 50% solids, using sulfuric acid with sodium chlorate as oxidant. The different leaching parameters considered in this work were temperature, oxidant level and leaching time.

In the experimental procedure, the concentration of oxidant and the temperature were varied to determine how they affect the leaching process. Experimental results are illustrated in tabulated form for better interpretation. Uranium analyses were done by fluorimetric and delayed-neutron activation analysis.

An anion exchange method using Dowex 1 x 8, 200-400 mesh (Cl^-) was used in treating the low-level liquid waste generated by leaching experiments. The purpose of this treatment was to minimize radioactive contamination in the waste materials and also to recover some of the uranium left in the liquid waste.

INTRODUCTION

For the past several years, the Nuclear Fuels Research Division (NFRD) of the Philippine Atomic Energy Commission (PAEC) has been engaged in the recovery of uranium from local ores, particularly from the complex ore deposit found in Larap, J. Panganiban, Camarines Norte. An amenability test has been conducted and preliminary laboratory studies using physical beneficiation and chemical processes have been done to recover uranium for yellow-cake production. The results of these experiments which were discussed in a technical paper,⁽¹⁾ are very encouraging with high uranium recovery being obtained from the chemical processes.

In this paper, a number of experimental data on leaching or dissolution of uranium are given. The additional leaching experiments were deemed essential. These laboratory studies allow a greater number of parameters to be examined at relatively less cost. Emphasis is given to leaching because this is one of the most important unit operations in processing uranium-bearing ores.⁽²⁾ The different leaching parameters considered in this work are temperature, oxidant level or EMF (oxidation potential) and leaching time.

In the conduct of leaching experiments, the NFRD could not ignore the wash solutions that can be collected from cleaning the ore pulp. About three (3) liters of wash solution per leaching experiment can be obtained. Fluorimetric analyses of these liquids show that their uranium content ranges from 10 to 60 ppm. To be able to utilize the uranium from these washing solutions, a treatment process making use of anion-exchange resin was adapted. Chemical treatment of liquid waste consequently eliminates or reduces considerably the radioactivity of these solutions prior to disposal. Thus, pollution or possible contamination is minimized in the discharging area.

EXPERIMENTAL PART

A. Leaching of Low-Grade Uranium Ores

Ores containing about 200 ppm had to undergo beneficiation processes prior to acid leaching. Physical beneficiation of ores, which were selectively collected from Larap mines, has been described elsewhere.⁽¹⁾ There were, however, modifications made on different beneficiation methods applied. Tabling was eliminated due to the low uranium content of the ore ; furthermore, a considerable amount of uranium could be lost at this stage. Results of grinding tests showed that eight (8) minutes ball milling (Denver ball mill, 12 x 5) and 1:3/4 pulp density (1 kg. ore : 750 ml water) minimize the slime formation at a low power consumption. Separation of magnetites was done utilizing a wet-type drum magnetic separator which prevents the loss of uranium and inhalation of dust that could be experienced when using a dry-type separator. In the flotation process, a combination of two collectors was used to separate the sulfides. The above operations produced a preconcentrate, the ore feed, for the leaching experiments.

Leaching experiments were conducted for eight (8) continuous hours. Four (4) leaching test were simultaneously done in one day. About 500 to 1700 grams of preconcentrate (ground ore without sulfides and magnetites) were placed in 2 or 4

liter beakers. Water was added to the preconcentrate ore at a ratio of 1:1 giving a pulp density of 50% solids. The mixture was agitated for eight (8) hours continuously by a motor or magnetic stirrer. To maintain the pH at 1.5, concentrated sulfuric acid was added every 10 to 15 minutes for the first two (2) to three (3) hours from burettes placed over the beakers. Initial and final readings of sulfuric acid in the burettes were noted to obtain the acid consumption as follows -

$$\text{Acid Consumption, (kg/ton)} = \frac{\text{acid added (ml)} \times 1.84}{\text{weight of leach sample (kg)}}$$

The oxidant, sodium chlorate (NaClO_3), was added to the mixture after taking the initial measurements of the EMF oxidation potential or redox, the temperature and pH. Readings of the pH value, temperature and EMF were taken every 15 minutes for the first four (4) hours and every thirty (30) minutes for the succeeding four (4) hours.

An aliquot of 5 to 10 ml of the pulp was taken after 1.5, 3, 6 and 8 hours. The pulp was filtered and washed twice with slightly acidified water (dilute sulfuric acid, pH 4). The filtered cake was then repulped, filtered and washed again twice with dilute sulfuric acid. The filtered cake was finally dried, weighed and analyzed for its uranium content by the fluorimetric method or by delayed-neutron activation analysis. The final re-

sidue obtained after eight (8) hours leaching was likewise determined for its uranium content. Percent extraction efficiency was calculated using the formula,

$$\text{Extraction Efficiency (\%)} = \frac{\text{Uranium in ore feed} - \text{Uranium in residue}}{\text{Uranium in ore feed}} \times 100$$

With the above procedure, two leaching parameters, temperature and the amount of oxidant were varied. The experimental data are shown in Tables I to IV.

Table I. Leaching Conditions and Results for Preconcentrate Containing 150 to 250 ppm U_3O_8

Leach No.	Amount kg.	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	%U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-1	0.85	1.0	32.36	30	430	23	54	72	84
LE-2	1.20	1.66	31.12	50	465	6	62	71	89
LE-3	1.20	1.66	31.42	50	475	4	25	86	91
LE-4	1.20	1.66	27.59	50	470	-	60	76	93
LE-5	1.20	1.66	37.87	50	450	11	70	95	95
LE-6	0.85	2.35	19.47	33	485	-	10	45	74
LE-7	0.85	2.35	24.12	34	450	-	-	-	28
LE-8	0.85	2.35	19.48	34	490	38	70	73	86
LE-9	0.85	2.35	31.38	34	490	44	62	68	88

Leach No.	Amount kg.	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	% U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-10	0.85	2.35	30.52	34	460	-	22	55	90
LE-11	0.85	2.35	30.12	34	485	-	10	60	95
LE-12	0.85	2.35	28.19	36	490	-	19	72	93
LE-13	0.85	2.35	26.19	52	480	2	18	84	94
LE-14	1.20	2.50	17.79	48	490	7	44	93	92
LE-15	1.20	2.60	38.01	32	360	22	5	30	26
LE-16	1.20	2.60	21.76	32	475	3	36	55	77
LE-17	1.50	3.00	19.62	32	485	45	18	53	79
LE-18	1.50	3.00	19.74	33	490	-	41	68	85
LE-19	0.85	3.00	19.22	35	455	4	5	4	67
LE-20	0.85	3.00	18.57	35	470	-	20	52	80
LE-21	0.85	3.00	20.95	35	480	13	51	75	86
LE-22	0.85	3.00	20.52	36	480	-	26	61	83
LE-23	1.50	5.00	51.22	33	520	-	3	24	74
LE-24	1.50	5.00	49.00	33	505	-	7	47	80
LE-25	0.85	5.00	38.96	37	535	-	5	36	81
LE-26	0.85	5.00	32.47	37	540	-	33	51	86
LE-27	1.20	5.00	29.67	50	580	68	74	95	95

Table II. Leaching Conditions and Results for Preconcentrate
Containing 300 to 350 ppm U_3O_8

Leach No.	Amount kg	$NaClO_3$ kg/ton	H_2SO_4 kg/ton	T °C	Redox mv	% U_3O_8 Extraction			
						1.5h	3h	6h	8h
LE-1	0.85	0.53	28.35	30	405	-	-	18	23
LE-2	1.20	2.35	89.70	33	290	17	13	19	16
LE-3	1.20	2.35	39.55	32	410	3	8	1	4
LE-4	1.20	0.50	34.88	50	425	-	10	15	23
LE-5	1.20	1.00	31.43	49	460	21	30	61	-
LE-6	1.60	1.00	39.50	49	465	31	44	87	93
LE-7	1.20	2.50	24.53	50	460	-	74	96	95
LE-8	1.20	2.50	25.60	50	460	59	94	95	95
LE-9	0.85	3.50	30.73	50	475	-	70	97	92
LE-10	0.85	3.50	30.73	55	465	60	97	94	91
LE-11	0.675	4.63	13.77	50	510	8	59	83	96.
LE-12	0.675	4.63	14.58	52	505	15	38	82	95
LE-13	0.50	5.00	21.90	48	500	30	35	48	88
LE-14	1.00	5.00	15.36	48	510	59	68	95	97
LE-15	1.00	5.00	16.00	48	515	39	84	92	97
LE-16	1.00	5.00	11.40	49	515	19	73	88	97
LE-17	1.00	5.00	12.51	49	505	15	50	93	97
LE-18	0.50	5.00	10.30	50	520	82	67	93	97
LE-19	1.20	5.00	14.94	50	525	26	73	86	97

Leach No.	Amount kg	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	% U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-20	1.20	5.00	14.94	50	530	76	74	93	97
LE-21	1.60	5.00	20.06	50	530	80	93	93	97
LE-22	1.60	5.00	20.06	50	530	76	85	96	98
LE-23	1.00	5.00	12.79	50	515	28	75	97	99
LE-24	0.85	5.00	14.85	51	515	25	80	89	97
LE-25	0.85	5.00	17.64	51	530	63	83	93	97
LE-26	0.85	5.00	17.64	51	540	53	93	93	97
LE-27	0.85	5.00	17.53	53	545	53	86	97	93
LE-28	0.85	5.00	15.41	53	520	35	71	95	97
LE-29	0.85	5.00	17.53	53	530	63	86	96	97
LE-30	0.80	5.50	12.76	47	510	35	60	94	96
LE-31	0.80	5.50	11.44	49	515	8	67	93	96
LE-32	0.80	5.50	12.47	50	515	44	72	96	98

Table III. Leaching Conditions and Results for Preconcentrate Containing 350 to 400 ppm U₃O₈

Leach No.	Amount kg.	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	% U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-1	1.60	0	39.84	50	350	52	68	55	59
LE-2	1.20	0	38.25	51	360	20	4	-	4
LE-3	0.85	0	56.93	59	330	-	-	-	41

Leach No.	Amount kg.	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	% U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-4	0.85	0	46.75	66	330	20	-	10	47
LE-5	1.20	0.50	32.04	50	425	15	37	55	55
LE-6	0.85	0.53	29.54	30	410	9	26	14	22
LE-7	1.20	0.83	22.39	50	430	24	79	94	96
LE-8	1.20	1.66	21.31	50	440	39	83	89	96
LE-9	1.20	2.35	38.32	31	440	13	16	11	12
LE-10	0.85	2.35	16.23	51	440	28	77	88	94
LE-11	1.20	2.50	16.79	50	425	38	51	86	84
LE-12	1.20	3.33	19.62	50	440	-	25	89	94
LE-13	0.85	5.00	29.00	32	510	18	14	33	30
LE-14	0.85	5.00	34.96	35	510	23	5	48	52
LE-15	0.85	5.00	41.23	35	530	41	67	83	88
LE-16	1.20	5.00	29.36	47	510	57	83	96	95
LE-17	1.60	5.00	29.67	47	510	75	92	97	98
LE-18	0.85	5.00	31.28	48	510	78	90	96	96
LE-19	0.85	5.00	32.79	48	510	79	88	95	95
LE-20	1.60	5.00	20.87	49	535	72	86	97	97
LE-21	1.20	5.00	23.99	49	515	-	42	97	97
LE-22	1.20	5.00	45.38	50	545	77	95	97	98
LE-23	1.20	5.00	46.00	50	540	92	95	98	98
LE-24	0.85	5.00	28.89	56	530	86	51	96	99
LE-25	0.85	5.00	25.11	57	520	-	79	97	97

Table IV. Leaching Conditions and Results for Preconcentrate
Containing 400 to 450 ppm U_3O_8

Leach No.	Amount kg.	NaClO ₃ kg/ton	H ₂ SO ₄ kg/ton	T °C	Redox mv	% U ₃ O ₈ Extraction			
						1.5h	3h	6h	8h
LE-1	1.20	0	36.03	50	370	19	30	43	44
LE-2	1.60	0	35.77	50	380	54	60	66	54
LE-3	1.20	0	48.45	50	380	48	20	63	56
LE-4	1.60	0	45.88	50	390	54	31	51	63
LE-5	0.85	0.288	58.33	51	365	-	33	60	57
LE-6	0.85	0.288	50.43	53	370	10	13	-	33
LE-7	0.85	2.35	23.59	50	440	23	50	94	94
LE-8	1.20	2.50	15.33	48	485	19	63	-	91
LE-9	0.85	3.50	14.94	51	490	31	40	92	93
LE-10	0.85	3.50	15.80	54	435	-	56	76	90
LE-11	0.85	3.50	17.75	55	435	30	61	80	91
LE-12	0.85	3.50	17.31	55	490	38	84	93	94
LE-13	0.85	5.00	44.26	32	440	32	34	34	67
LE-14	1.20	5.00	16.10	50	530	52	83	89	94
LE-15	0.80	5.00	20.12	50	520	48	85	93	94
LE-16	1.70	5.00	17.70	50	520	63	91	81	97
LE-17	0.80	5.00	19.09	53	520	76	75	95	98
LE-18	1.20	5.00	30.36	50	580	57	94	98	98

B. Treatment of Low-Level Liquid Waste Generated by Leaching Experiments

Acid leaching of 3 to 3.5 kg. of preconcentrate yielded three (3) liters of leach liquor and three (3) liters of low-level liquid waste. The leach liquor containing an average amount of amount of 200 ppm uranium was processed to recover uranium as ammonium diuranate (yellow-cake). The liquid waste collected from washing the ore pulp contained copper (0.05%-0.1%), iron (0.1-0.4%) and uranium (10-60ppm). It was decided to recover uranium from these wash solutions, considering the importance of uranium and following the practice in some uranium mill plants in other countries⁽³⁻⁷⁾. Treatment of the liquid waste would likewise minimize pollution or contamination in the disposal of the wastes.

Dowex anion-exchange resin, 1 x 8, 200-400 mesh (Cl^-) was used. Transformation of the resin into sulfate form was done by washing the resin with sulfuric acid (2N, 1N and 0.005N). Silver nitrate solution was utilized for testing the completeness of conversion.

A glass column with an inside diameter of 1.25 cm was used in the initial trials. A 50 mesh resin was packed in this column with glass wool placed at the bottom and on top of the resin. Ion-exchange columns with an inside diameter of 2.54 cm and 200-400 mesh resin were used in the subsequent experiments.

Copper sulfate pentahydrate (1-3 mg) and ferric sulfate (3-7 mg) were used as carriers. Two (2) to three (3) liters of liquid waste were passed thru the columns. Copper was very slightly adsorbed by the column, while most of the iron was. The adsorbed copper, iron and uranium were eluted with 0.005N H_2SO_4 , 1N H_2SO_4 , and 4N H_2SO_4 respectively. Some of the experimental data obtained are shown in Tables V and VI.

Table V. Sequential Elution of Copper, Iron and Uranium without Carriers

Liquid Waste : 2 liters, 45 ppmU
No carriers added

Eluants : 100 ml 0.005N H_2SO_4
200 ml 1N H_2SO_4
100 ml 4N H_2SO_4
200 ml dist. water

			ppm Cu	ppm Fe	ppm U
Eluate	A	500 ml, green	5	4	ND
	B	500 ml, green	880	825	ND
	C	500 ml, green	1240	130	ND
	D	500 ml, green	685	945	ND
	1	50 ml, very light yellow	8	590	ND
	2	50 ml, yellow	2	1160	ND
	3	50 ml, orange	1	924	ND
	4	50 ml, orange	0.4	800	ND

			ppm Cu	ppm Fe	ppm U
Eluate	5	20 ml, light orange	ND	500	ND
	6	60 ml, colorless	ND	165	0.5
	7	10 ml, colorless	ND	100	9
	8	50 ml, yellow	ND	3	1425
	9	25 ml, yellow	ND	2	2475
	10	75 ml, colorless	ND	ND	110
	11	40 ml, yellowish	ND	ND	ND
	12	70 ml, colorless	ND	ND	ND

Table VI. Sequential Elution of Copper, Iron and Uranium with Carrier

Liquid Waste : 2.8 liters, 55 ppm U

Carriers : 3.5 mg $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$
7.0 mg $\text{Fe}_2(\text{SO}_4)_3$

Eluants : 150 ml, 0.005 N H_2SO_4
150 ml, 1 N H_2SO_4
100 ml, 4 N H_2SO_4
100 ml, dist. water

			ppm Cu	ppm Fe	ppm U
Eluate	A	1000 ml, light green	245	14	ND
	B	500 ml, light blue green	690	345	ND
	C	500 ml, light blue	1000	665	ND
	D	500 ml, light blue	965	1430	ND
	E	300 ml, brown	181	5128	ND

			ppm Cu	ppm Fe	ppm U
Eluate	1	40 ml, dark yellow	4	10675	ND
	2	40 ml, lightly colored	ND	321	10
	3	40 ml, very light yellow	ND	ND	165
	4	40 ml, yellow	ND	ND	4125
	5	30 ml. yellow	ND	ND	2450
	6	40 ml, colorless	ND	ND	80
	7	40 ml, colorless	ND	ND	2
	8	40 ml, colorless	ND	ND	ND
	9	40 ml, colorless	ND	ND	ND

Eluate fractions A through D in Table V and A through E in Table VI results from loading of the column with two (2) liters and 2.8 liters of liquid waste, respectively. The subsequent eluate fraction identified with numbers correspond to elution of the column with the eluants enumerated at the start of each Table.

Note :

ND - detection limit from 0 to 0.2 ppm

DISCUSSION OF RESULTS
AND CONCLUSIONS

Table I shows that a good leaching efficiency can be obtained with the use of 1.66 kg/ton oxidant at 50°C. Doubling the amount of oxidant (2.35 kg/ton) at 34°C (without heating) likewise gives fairly good leaching results and this method is therefore suggested for economic reasons. Some experiments (LE-1, LE-7 and LE-15) yielded erratic results due to stirrer malfunction. Acid consumption and redox readings in all cases were satisfactory, except LE-23 and LE-25 which consumed more acid due probably to erroneous pH-meter readings.

For preconcentrate containing 300 to 400 ppm U_3O_8 (Tables II and III), leaching conditions with negligible amount of oxidant even at high temperatures (59°C and 66°C) gave poor efficiency. Trials LE-1 to LE-3 and LE-4 in Table II gave poor leaching results, due to the low temperature used (no heating) and the small amount of oxidant used, respectively. Similar results can be observed in Table III except for LE-13 where good dissolution is achieved. All other experiments using 4-5 kg/ton oxidant at a temperature of 47°C-53°C gave high efficiency.

Trials LE-1 to LE-4 (Table IV) illustrate that leaching without oxidant, even if the temperature is increased (50°C), is not effective. Addition of minute quantities (0.288 kg/ton) of oxidant (LE-5 and LE-6) could not improve the results.

It can be deduced that with minimal amount of oxidant (1.6 to 3 kg NaClO_3 per ton of ore), elevated temperature (at least 47°C) is required to obtain high efficiency. With five (5) kg. oxidant per ton of ore, good leaching can be achieved even without heating.

The preliminary test which utilized the resins available to us (Dowex 1 x 8) in the recovery of 10 to 60 ppm uranium gave very encouraging results (Tables V and VI). The method consist of passing the liquid waste through the anion-exchange resin and the sequential elution of interfering copper and iron which are both present in great amounts. Copper, iron and uranium can be eluted with $0.005\text{N H}_2\text{SO}_4$, $1\text{N H}_2\text{SO}_4$ and $4\text{N H}_2\text{SO}_4$ respectively. Elution of uranium with $2\text{N H}_2\text{SO}_4$ and $3\text{N H}_2\text{SO}_4$ did not give acceptable results due to tailing in the elution curve of uranium.

The objectives of the experiments on the treatment of liquid waste were attained - that of saving and concentrating low amounts of uranium and reducing to a great extent the amount of uranium left in the waste solution. It is, however, suggested that the economics or financial aspect of the technique be included in further studies.

A C K N O W L E D G E M E N T

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