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CHLORINE-ASSISTED LEACHING OF KEY LAKE URANIUM ORE

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CHLORINE-ASSISTED LEACHING OF KEY LAKE URANIUM ORE

by

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ABSTRACT

Bench-scale chlorine-assisted leach tests were conducted on the Key Lake uranium ore. Leach tests conducted at 80°C on a slurry containing 50% solids during 10 hours of agitation gave the maximum extraction of uranium - 96% and radium-226 - 91%. Chlorine was added at 23.0 Kg Cl_2/tonne of ore to maintain the leach slurry pH in the range of 1.5-1.0. To obtain residue almost free of radionuclides, hydrochloric acid leaches were conducted on the first stage leach residues. The second stage leach residue still was found to contain uranium - 0.0076% and radium-226 - 200 pCi/g of solids.

INTRODUCTION

The Key Lake uranium ore deposit is located at the southern rim of the Athabasca Basin in Northern Saskatchewan. The first orebody (Gartner) was discovered in 1975 and the second orebody (Deilmann) in 1976. The mineralogy of both ores is similar, and the principal uranium minerals are pitchblende, sooty pitchblende and coffinite. Uranium minerals are often accompanied by sulphide, arsenide and arsenosulphide of nickel. Minor amounts of pyrite, sphalerite and chalcopyrite are also present in the orebody. Although massive ore is often free of gangue minerals, orebodies generally contain quartz, chlorite, calcite, kaolinite, siderite, sericite and epidote. The grade of the ore varies from 2.5-3.0% uranium (1,2).

The Key Lake project, scheduled to start in late 1983, is a joint venture of SMDC - Saskatchewan Mining Development Corporation, UEM - Uranerz Exploration and Mining Limited, and Eldor - Eldor Resources Limited. However, Key Lake Mining Corporation (KLMC) is the project operator (2).

The Sherritt Gordon Mines Limited, Fort Saskatchewan, Alberta, has developed a two-stage countercurrent sulphuric acid leach process for the Key Lake uranium ore. The second stage leaching is conducted under oxygen pressure (600 kPa) in autoclaves at 60°C with 50% solids in the leach slurry. This process is able to extract approximately 99% uranium. However, almost all of radium-226 remains undissolved and reports to the tailing disposal site, which is specially designed to prevent any future leakage of radium in the open environment (2). Nevertheless, simple mechanical fortification cannot ensure a long-term safeguard against radium leakage into the open environment.

Present-day environmental guidelines and non-extractability of radium by sulphuric acid leaching of uranium ore, prompted CANMET* to examine alternate processes for the treatment of uranium ore. Such alternate processes should be economically viabile and environmentally acceptable. To this end chlorine-assisted leaching was considered.

When chlorine comes in contact with water it readily establishes the following equilibriums:

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$$Cl_2 + H_2O \rightleftharpoons HCl + HOCl \qquad (1)$$

The resulting solution not only becomes strongly acidic due to HCl but also contains a strong oxidant, HOCl[3]. Therefore, a reagent of this nature is expected to be fully effective in solubilizing uranium, thorium and radium. In effect, chlorine-assisted leaching might be capable of producing tailings almost free of radium.

Aqueous chlorine-leaching of ores is not a novel technique. In fact, reports are available in the literature of the application of aqueous chlorine leaching of sulphide ores (4,5,6). However, no report is available in the literature on the aqueous chlorine leaching of uranium ore.

The application of chlorine in mineral processing was restricted due to its high cost and corrosiveness. However, the availability of cheaper chlorine relative to the reagents required for the conventional processing of uranium ore (e.g. H_2SO_4, Na_2CO_3-$NaHCO_3$, $NaClO_3$ or MnO_2) and of improved corrosion resistant materials for equipment fabrication are all favourable factors (6) in adopting the process of chlorine-assisted leaching of uranium ores.

This report describes the results of laboratory-scale chlorine-assisted leaching of the Key Lake uranium ore.

GENERAL PROCEDURE

Key Lake Mining Corporation supplied the uranium ore. Table 1 shows the important elemental analysis of the ore. The ore was already ground to 55% minus 200 mesh. An aqueous slurry of the ore having a solid-liquid ratio of 1:1 was placed in a reaction kettle equipped with a mechanical stirrer, a condenser, a temperature control probe, a chlorine gas inlet tube and a thermometer. The reaction kettle was placed in a heating mantle. The heating and chlorine gas bubbling through the leach slurry were started almost simultaneously while the slurry was stirring continuously.

Chlorine gas was bubbled at the rate of 41 mL min^{-1} through the ore slurry until the pH reached 1.0 to 0.8 while the EMF (S.H.E.) varied from 500-575 mV. At the end of leaching, the leach slurry was filtered and the residue was washed thoroughly; twice with hot (~ 50°C) water acidified with

NH 2 vol % HCl and finally once with distilled water at ordinary temperature. All the washings were conducted with an approximate solid to liquid ratio of 1:1. Dried residue and the combined filtrates were analyzed.

Table 1 - Important constituents of the Key Lake uranium ore

Elements	Concentration (wt %)	Elements	Concentration (wt %)
U	1.50	Ca	0.37
Th	0.002	Ti	0.54
Ra^{226}	5220 pCi/g	C	0.36
Fe	3.04	CO_2	0.57
S	0.78	As	1.23
Si	26.0	Co	0.05
Al	7.68	Ni	2.06
Mg	2.17	Cu	0.04

Second stage leaching was conducted on first stage leach residue with hydrochloric acid (44.0 Kg/tonne) in the presence of sodium chlorate (2.0 Kg/tonne) at 65°C during 6 hours of retention time. The solid to liquid ratio of the second stage leaches was 1:1. The leach slurry was filtered at the end of leaching and the residue was washed in a similar manner as that applied in the first stage leach residue.

Unless otherwise specified radium analysis indicates radium-226 isotope only.

RESULTS AND DISCUSSION

Temperature effect

To determine the optimum temperature for the extraction of uranium and radium, leach tests were conducted at 25, 40, 60, 70, 80 and 90°C, respectively, with 6, 10 and 18 hours of retention time. Figures 1 and 2 show the plots of uranium and radium extractions against the leach temperatures.

Figure 1 is obviously indicative that per cent of uranium extraction increased with temperature but apparently retention time had very little effect above 10 hours. Maximum uranium extraction (96%) occurred at 80°C and remained unchanged even at 90°C. Although some uncommon mineralizations such as gersderffite (NiAsS), millerite (NiS), niccolite (NaAsS), bravoite ($FeNiS_2$) and chalcopyrite ($CuFeS_2$) are present in the Key Lake uranium ore (7), they essentially have no significant effect on the uranium extraction by an acid chloride system (8). Hence it is concluded that 80°C is the optimum leach temperature for the chlorine-assisted leaching of the Key Lake uranium ore.

Figure 2 shows that the per cent of radium extractions increases significantly with temperatures up to 90°C. Retention time has also the similar effect. It is further observed that the maximum radium extraction (91%) occurred at 90°C irrespective of retention time; but approximately 91% radium extraction also occurred at 80°C during 10 hours of leaching.

Generally in the absence of any interfering effect, radium extraction closely relates to the uranium extraction (9). Since the highest per cent of uranium extraction occurred at 80°C, therefore ideally, the highest per cent of radium extraction should also occur at 80°C; however, in this case it appeared at 90°C (Fig. 2).

<u>Retention time effect</u>

A series of leach tests were conducted at 70°C on leach slurries containing 50% solids with varying retention time. Figure 3 shows the plots of uranium and radium extractions against the retention time. This figure clearly indicates that the highest per cent of uranium extraction (92%) occurred after 10 hours of residence time although 87% extraction took place only after 4 hours of leaching. Similarly, the maximum radium extraction (85%) appeared after 10 hours of leaching. However, a further increase in the retention time has no effect on the maximum extractions of either uranium or radium. Therefore, these experimental data lead to the conclusion that 10 hours leaching would be the suitable retention time for the maximum uranium and radium extraction.

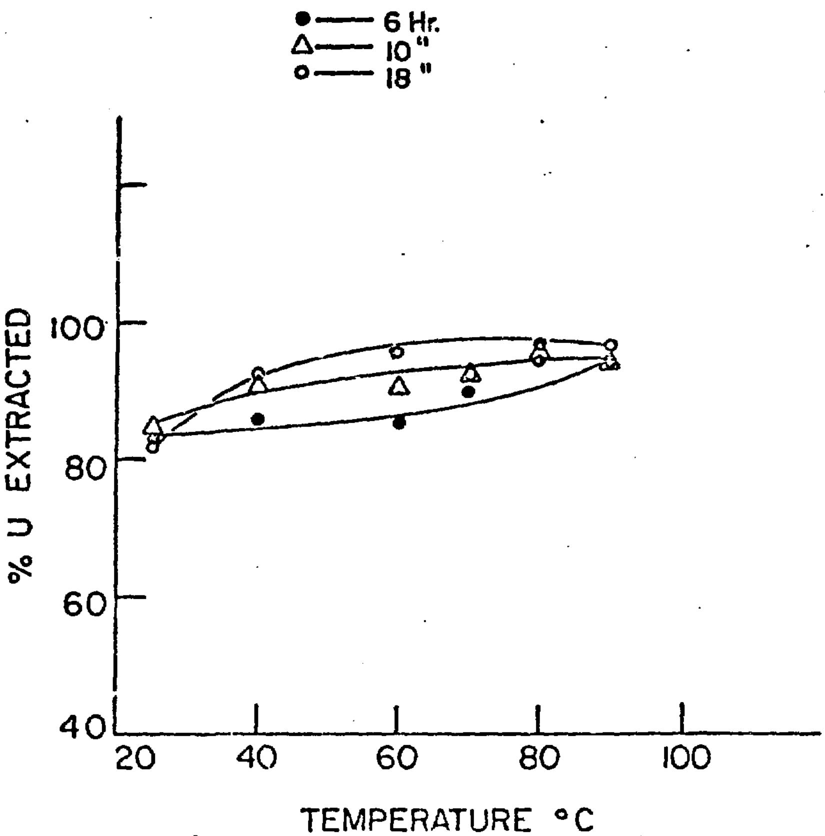

Fig. 1 - Uranium extraction as a function of temperature

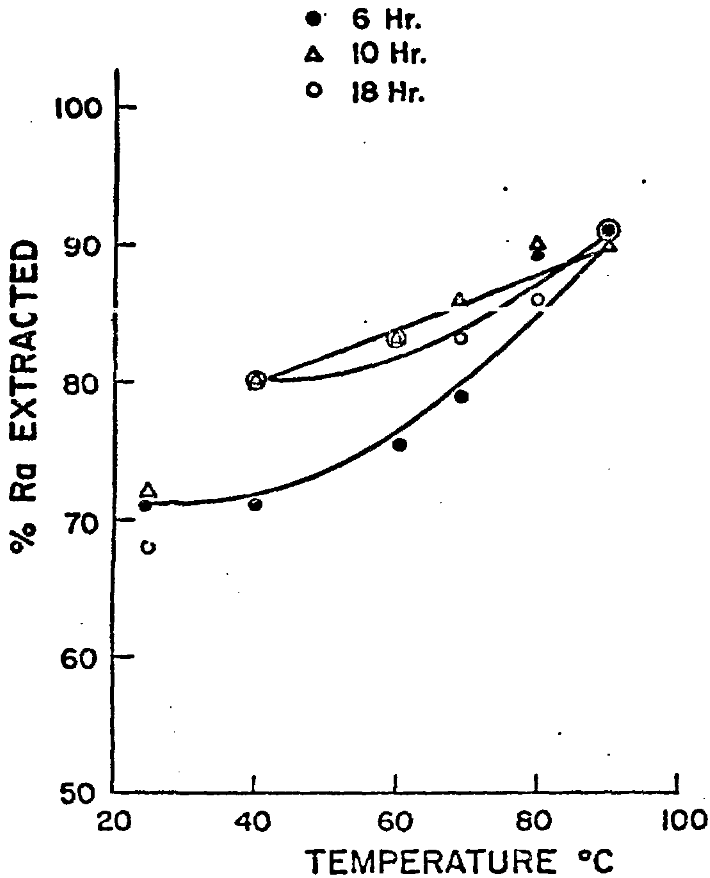

Fig. 2 - Radium extraction as a function of temperature

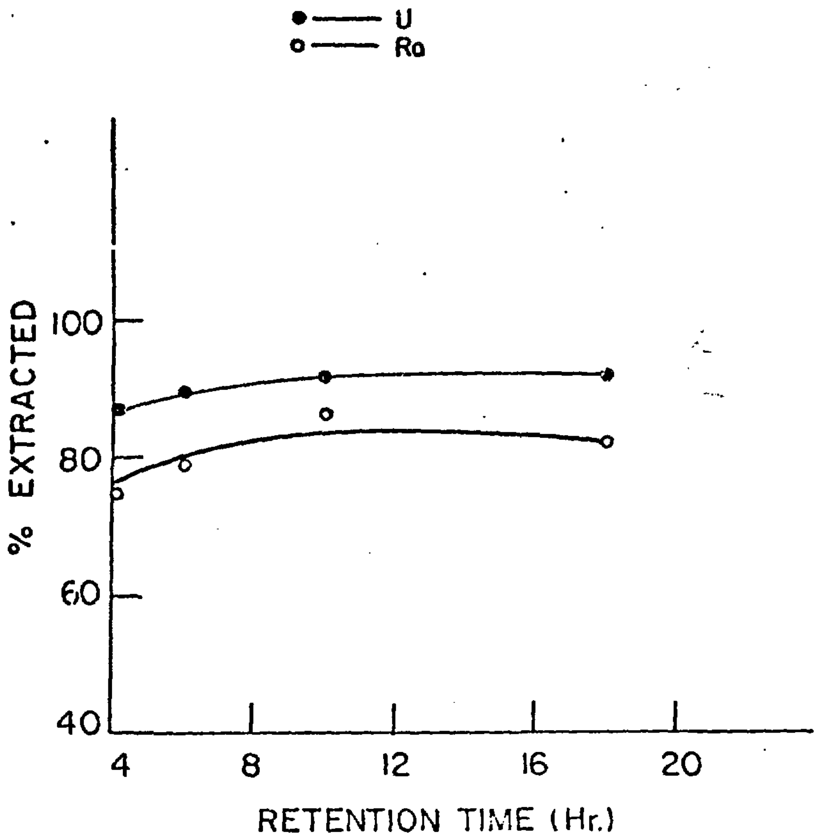

Fig. 3 - Retention time effect on U and Ra extraction

Pulp density effect

A set of leach tests were conducted on slurries containing 30, 40, 50 and 60% solids at 50°C during 18 hours of agitation. Figure 4 shows the results of uranium and radium extractions. This figure indicates that the highest per cents of uranium and radium extraction; 98% and 92% respectively, occurred from leach slurry containing 30% solids; however, the latter remained constant up to the pulp density of 50% solids. Furthermore, 97% uranium extraction occurred from leach slurry containing 50% solids and it decreased with the increase of pulp density. In view of the process economy it is concluded that 50% solids in the leach slurry would be the suitable pulp density for the chlorine-assisted leaching of the Key Lake uranium ore.

Chlorine-assisted leaching of the Key Lake uranium ore is fully effective to solubilize uranium, radium and other heavy metals present in the ore. Table 2 shows the important components of the leach liquor. Besides uranium the leach liquor also contains a considerable amount of nickel. Leach liquor of this nature might warrant the isolation and purification of nickel.

Table 2 - Some important components in the chlorine-assisted leach liquor (g/L) at optimum conditions*

U	Ra (pCi/L)	Total SO_4	Ni	As	Ca	Al	Mg	Fe
12.8	$4.2x10^6$	2.0	14.0	10.0	2.8	2.0	1.20	7.2

*Optimum Condition: 80°C, 10 hrs and 50% solids in the pulp

Furthermore, Table 3 shows the grade of the chlorine-assisted leach residues obtained at optimum conditions. These data firmly indicate that the chlorine-assisted leaching is indeed effective to extract 96% of uranium but not to obtain 100% extraction of radium. These are the accepted extraction targets for uranium and radium (9). However, the uranium grade (0.06%) of the residue warrants further leaching. Furthermore, Sherritt Gordon Mining Limited (2) contained 99% uranium extraction from the Key Lake ore by two stage sulphuric acid leach process (atmospheric pressure leaching in the first stage and autoclave leaching in the second stage). Therefore, second stage leaching was conducted with hydrochloric acid (44.0 kg/tonne) on the

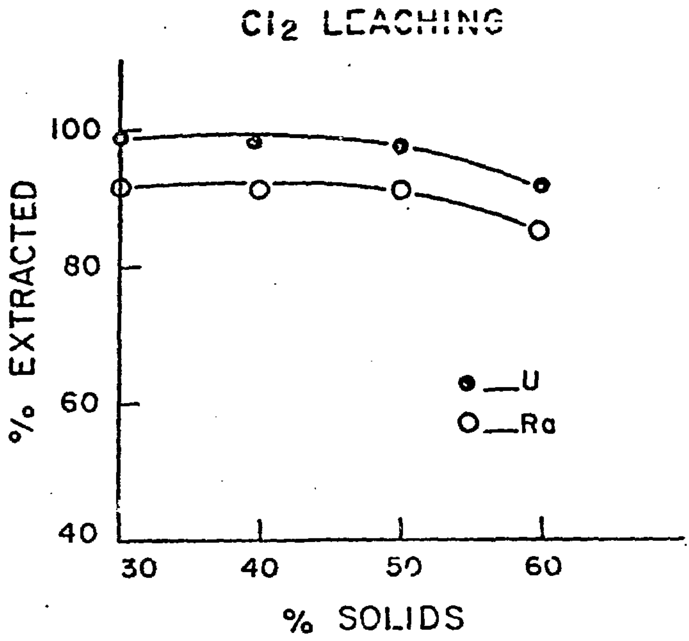

Fig. 4 – U and Ra extraction as a function of pulp density

Table 3 - Leach parameters and the residue grade

Temp. (°C)	Time (hr)	Chlorine input (Kg/tonne)	Pulp density (% solids)	% U		Ra pCi/g		% Ni		% As	
				Feed	Residue	Feed	Residue	Feed	Residue	Feed	Residue
80	10	23	50	1.50	0.06	5220	950	2.06	0.67	1.23	0.210

Table 4 - Second stage HCl leach residue grade

Temp. (°C)	Time (hr)	HCl input (kg/tonne)	Pulp density (% solids)	% U		Ra pCi/g	
				Feed	Residue	Feed	Residue
65	6	44.0	50	0.06	0.0076	950	200

first-stage leach residues. Table 4 shows the grade of the second stage leach residues.

Undoubtedly the second stage leaching improved the grade of the residue and provided | 99% overall extraction of uranium. However, this second stage leaching failed to produce residue almost free of radionuclides (9). At this point with this amount of data it might be stated that either multistage acid chloride leaching or chloride salt washing of the leach residue might be effective to yield residue almost free of radionuclides.

SUMMARY AND RECOMMENDATION

Optimum leach conditions of 80°C, for 10 hours at a pulp density of 50% solids were obtained from the experimental data for the chlorine-assisted leaching of the Key Lake uranium ore. To maintain pH of the leach slurry in the range of 1.5-1.0 chlorine requirement was found to be 23.0 kg/tonne of ore. The chlorine-assisted leaching extracted 96% uranium and 91% radium. However, the leach residue was not free of radionuclide. Therefore, hydrochloric acid leaching were conducted on the first stage leach residues.

The second stage hydrochloric acid leaching reduced the uranium and radium contents of the first stage leach residues but failed to produce residues almost free of radionuclides. As a result it is recommended that multi-stage (3 or 4) acid chloride leaching or the chloride salt washing of the first stage leach residues might be effective to produce tailings free of radium.

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