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October 1981

Project: ERP-4.4.0.2.02
Uranium extraction alternative

17pp

ENERGY RESEARCH PROGRAM
MINERAL SCIENCES LABORATORIES
DIVISION REPORT ERP/MSL 81-128(TR)

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BY

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ABSTRACT

Hydrochloric acid leaching was conducted on the radioactive mineral concentrate separated from the Agnew Lake uranium ore. Leach tests conducted at the optimum conditions (75°C; 36 hours; 66.0 Kg HCl/tonne; solid:liquid = 1:1) resulted in the extraction of 87% uranium and 84% radium. The radionuclide level of the residue was U-0.016%, Th-0.24% and Ra-65 pCi/g solids. However to obtain a residue almost free of radium (i.e, Ra level at the detection limit: 4-6 pCi/g solids), the first stage leach residue was further treated with hydrochloric acid. The radium level in the best second stage leach residue was also above the target level. Therefore, multistage (3 or 4) hydrochloric acid and/or neutral chloride leaching is recommended to obtain tailings almost free of radionuclide.

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INTRODUCTION

Agnew Lake Mines Limited is a wholly owned subsidiary of Kerr Addison Mine Limited and is located in Espanola, approximately 50 km west of Sudbury, Ontario.

The principal uranium bearing mineral of the Agnew Lake ore is uranothorite which occurs in quartz sericitic conglomerates. In addition to uranothorite, some brannerite, monazite, zircon, pyrite, and pyrrhotite are present in the conglomerate[1]. Generally Agnew Lake ores contain more thorium than uranium[2] and have a ThO_2/U_3O_8 ratio of 3:1. The uranium grade varies from 0.027-0.060%.

Mining operations at the Agnew Lake Mines Limited have stopped since early 1980. However, uranium production is continuing with broken ore left in the mine stopes being treated by flood leaching and crushed ore being heap leached on the surface. This operation is expected to continue for only a limited time.

Since Agnew Lake ore is a low grade uranium ore (average uranium grade ~0.040%), conventional milling and acid leaching of this type of ore were not considered to be economically viable. However, concentration of the uranium bearing minerals followed by acid leaching might have economic viability for such a low-grade ore.

Raicevic et al[3] of MSL, CANMET, separated the radioactive minerals and the sulphides from the bulk of the ore by applying combination of flotation, gravity separation and high intensity magnetic separation techniques. Approximately 96% of the sulphide minerals (mainly pyrite) were concentrated in a fraction representing only 3.5 wt % of the ore. The radioactive mineral concentrate which represents 28-44 wt % of the ore contained 97% uranium, 95% thorium and 94% radium respectively. As a result, the uranium grade of the radioactive concentrate improved considerably and was 2-3 lb per tonne of the concentrate whereas the flotation tailings contained uranium 0.004%, thorium 0.015% and radium 24-34 pCi/g. Tailings of this nature might be suitable for mine backfill or for surface disposal.

In view of the current environmental regulations and public concern over the issue of radiocludes present in uranium mine mill wastes, CANMET has ongoing research programs to develop an alternate process for the radioactive ores. Such an alternate process should be economically viable and environmentally acceptable[4]. Environmental acceptability of the process could be substantially improved by complete removal of harmful radionuclides from the effluents.

To fulfil these objectives hydrochloric acid leaching of uranium ore or its preconcentrate is a logical choice. A number of reports of laboratory-scale hydrochloric acid leaching of uranium ores are available in the literature[5,6,7,8], but no such report is available for the preconcentrates of uranium ore.

Although hydrochloric acid is as effective as sulphuric acid in solubilizing uranium; plant-scale application in the treatment of uranium ore has not been developed. This is largely due to the high cost and corrosiveness of hydrochloric acid. However, with the availability of hydrochloric acid at a cost comparable with the cost of reagents required for sulphuric acid leaching process and improved corrosion resistant materials for equipment fabrication, hydrochloric acid leaching processes look more promising.

This report describes the results of laboratory-scale hydrochloric acid leaching of a preconcentrate (uranium concentrate) of the Agnew Lake uranium ore.

GENERAL PROCEDURE

Agnew Lake Mines Limited of Espanola, Ontario supplied the uranium ore and the Mineral Processing Laboratory of CANMET separated and concentrated the uranium minerals and the sulphides (mainly pyrite) by flotation, gravity concentration and high intensity magnetic separation processes. Table 1 shows the analyses of the uranium concentrates.

Typically 200.0 g of the uranium concentrate of minus 75 μ (200 mesh) particle size was placed in a 500 ml capacity reaction kettle. The reaction kettle was equipped with a mechanical stirrer, a thermometer, a condenser and a temperature control probe, and placed in a heating mantle. Water and concentrated hydrochloric acid (37 wt %) were added in proportion to maintain the desired pulp density and the acid concentration. Since sodium chlorate is the most commonly used oxidant in the conventional acid leaching process of uranium ore; it was added (2.50 kg $NaClO_3$/tonne) in portions to maintain EMF of the leach slurry in the range of 450 to 550 mV (S.H.E.).

Table 1 - Analyses of the uranium concentrate

Elements	Wt %	Elements	Wt %
uranium	0.124	aluminium	8.08
thorium	0.60	potassium	3.94
radium	415 pCi/g	magnesium	1.26
silicon	27.30	phosphorus	0.60
iron	5.70	calcium	1.08
sulphur	0.30	rare earths	2.15

At the end of leaching, the leach slurry was filtered and the residue was washed twice with hot (~50°C) acidic (2 V % HCl) water and once with distilled water at room temperature. All the washings were conducted at approximately 1:1 ratio of solid to liquid. The dried residues and the combined filtrates were analyzed.

Unless otherwise specified radium analyses always indicate radium (226) isotope.

RESULT AND DISCUSSION

Temperature Effect

A set of leach tests was conducted at 25, 40, 60, 75 and 90°C respectively on leach slurries containing 50% solids with 44.0 kg HCl/tonne of solids and with 24 hours retention time. Figure 1 shows the plots of uranium, thorium and radium extraction against the leach temperature.

The curves of Figure 1 are clearly indicative that the per cent of uranium and radium extractions increased with the increase in leach temperature but only up to 75°C. The highest per cent (82%) of radium extraction occurred at 75°C and decreased with further increase of temperature. Uranium extraction which reached its maximum (84%) at 60°C remained unchanged up to 75°C, and decreased with further increase in leach temperature. In fact at 90°C which is the highest temperature in this set of leach tests, the lowest per cent (73%) of uranium extraction occurred. In contrast, thorium extraction decreased steadily from its highest per cent extraction (77%) at

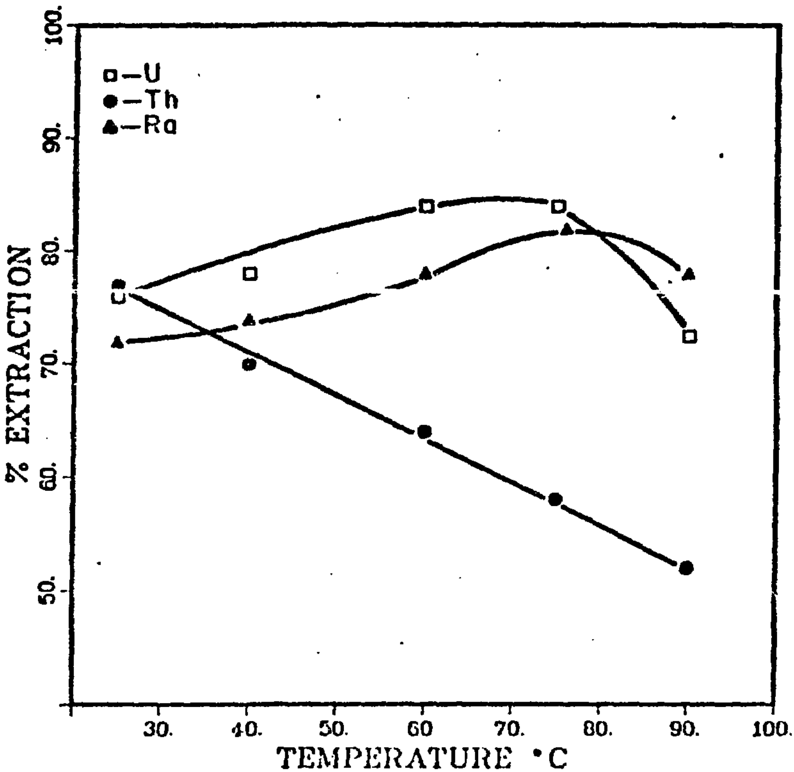

Fig. 1 - Temperature effect on U, Th and Ra extractions 50% solids, 44.0 kg HCl/tonne solids. 24 hr retention.

25°C to 52% extraction at 90°C. The explanation for such a behaviour of thorium has not been determined in the present investigations; however some comments on the adverse effect of temperature on thorium extraction has been incorporated in the latter part of the discussion.

As has been recognized, the economics of uranium ore processing depends on the maximum recovery of uranium whereas its environmental quality depends to a great extent on the efficient removal of radium from the effluents. Therefore 75°C would be the optimum leach temperature for the uranium concentrate of Agnew Lake ore.

Retention Time Effect

Figure 2 shows the results of uranium, thorium and radium extractions at various times but a constant pulp density (50% solids), temperature (75°C) and acid concentration (44.0 kg HCl/tonne). Figure 2 indicates that as the retention time was increased the per cent of uranium and radium extractions increased and their maximum extractions; uranium-87% and radium-82%, appeared after 36 hours of leaching. Further extension of the retention time to 48 hours had no effect on uranium extraction but had an adverse effect on radium extraction.

Furthermore, Figure 2 indicates that the rate of increase of thorium extraction is low; only 4% increase took place during the initial 20 hours of leaching (i.e. 54-58% from 4-24 hours of retention time). Its highest per cent extraction (58%) occurred after 24 hours of leaching; however, it decreased to 52% during the next 12 hours of leaching (i.e. after 36 hours of retention time) and remained constant up to 48 hours of leaching. Thorium extraction remained essentially within the range of 52-58% throughout 4-28 hours of retention time.

Since the maximum uranium and radium extractions were obtained after 36 hours of leaching, 36 hours retention time is considered to be the optimum leach time for the uranium concentrate of Agnew Lake ore.

Acid Concentration Effect

A set of leach tests was conducted with varying concentration of hydrochloric acid at constant temperature (75°C), retention time (24 hr.) and

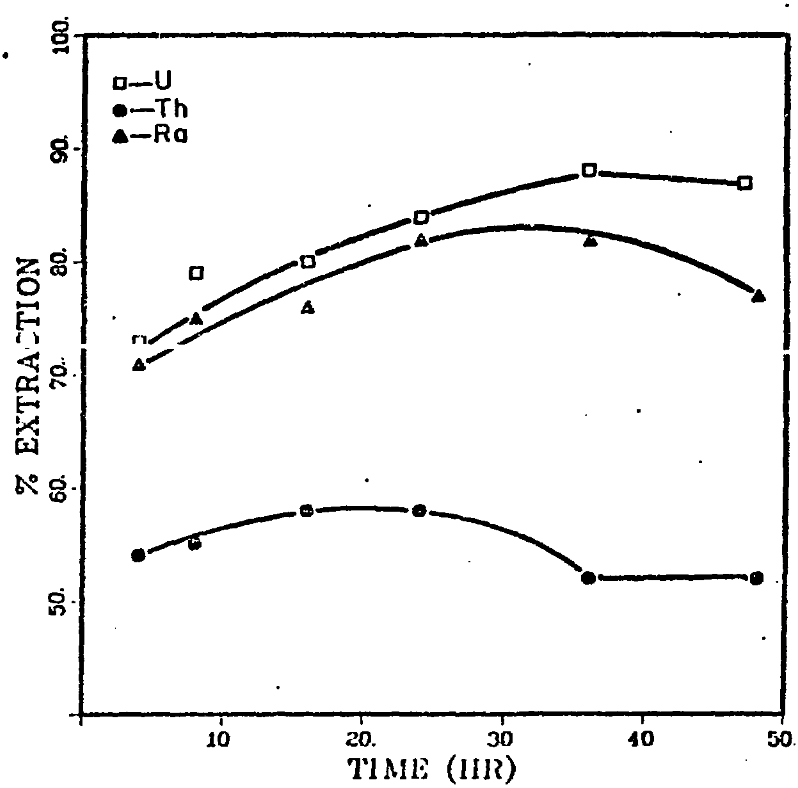

Fig. 2 - Retention time effect on U, Th and Ra extractions 50% solids, 44.0 kg HCl/tonne solids, 75°C

pulp density (50% solids). Figure 3 shows the plots of uranium, thorium and radium extractions against the concentrations of hydrochloric acid.

Figure 3 indicates that uranium and radium extractions increased with the increase by acid concentration up to the concentration of 66.0 kg HCL/tonne of the concentrate. The highest per cent of uranium extraction (90%) was obtained from the leach test conducted with 66.0 kg HCl/tonne. However, further increase in the acid concentration had a detrimental effect on uranium extraction. The maximum radium extraction (84%) was obtained from leach test conducted with 44.0 kg HCl/tonne. This maximum radium extraction remained unaffected up to the concentration of 66.0 kg HCl/tonne. Further increase in acid concentration has little effect on the radium extraction.

Interestingly, Figure 3 further indicates that the per cent of thorium extraction increased steadily with the increase of acid concentration. In fact the highest per cent of thorium extraction (85%) occurred in the leach test conducted with 132 kg HCl/tonne which was the highest concentration of hydrochloric acid applied in this series of tests.

Finally these results indicate that 66.0 kg HCl/tonne would be the optimum acid concentration required for uranium and radium extraction the uranium concentrate of the Agnew Lake ore.

Effect of Pulp Density

To study the effect of pulp density a series o ach tests were conducted on slurries containing 30, 40, 50, 60 and 70% solids at constant temperature (75°C), retention time (24 hr.) and acid concentration (44.0 kg HCl/tonne). Figure 4 shows the plot of uranium thorium and radium extractions against the per cent of solids.

It is obvious in Figure 4 that the per cent extraction of uranium and radium is not affected by variation of pulp density. In fact, on the average the per cent of uranium and radium extractions remained at 84% and 82% respectively at all the pulp densities. However, thorium behaved differently; per cent of thorium extraction increased from 34% at 30% solids to 58% at 50% solids; but it decreased with further increase in pulp density. Therefore, 50% solids in the leach slurry would be the optimum pulp density.

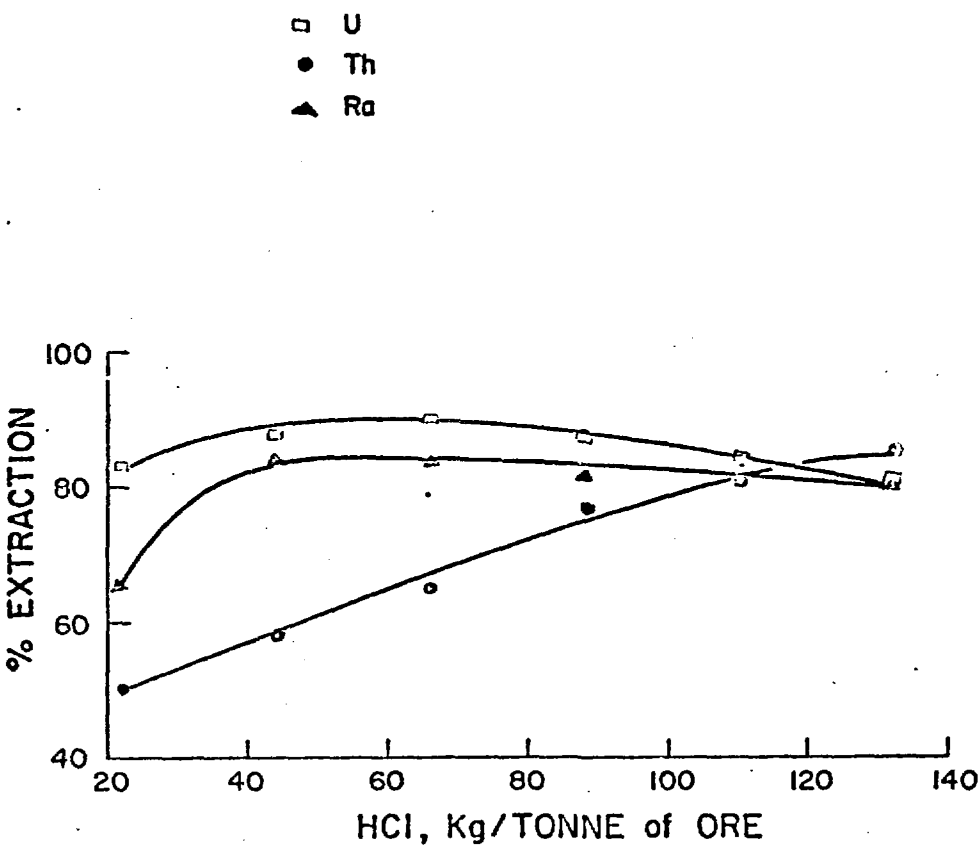

Fig. 3 - Acid concentration effect on U, Th and Ra extractions 50% solids, 75°C, 24 hours.

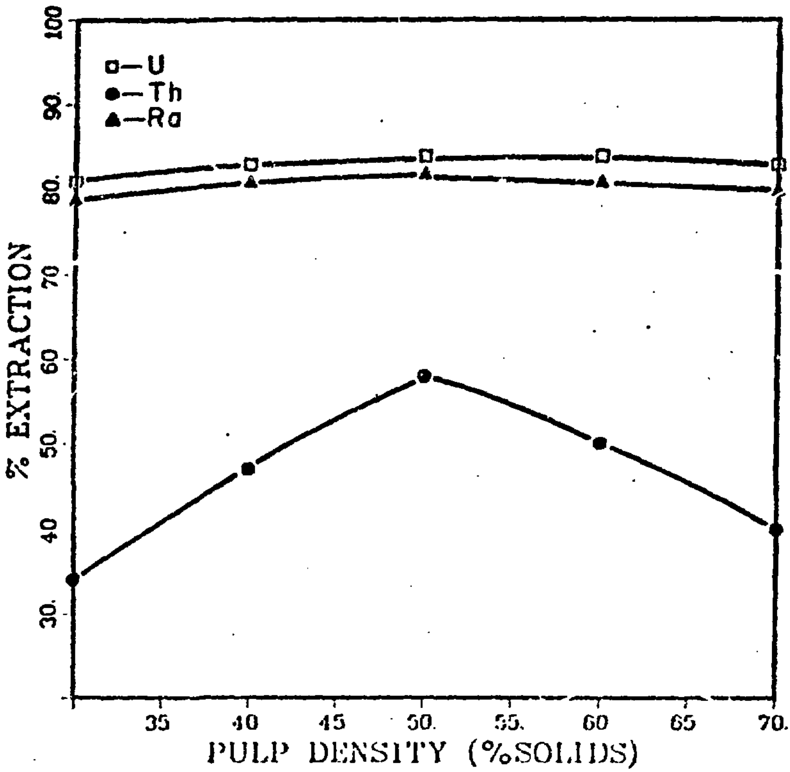

Fig. 4 - Pulp density effect on U, Th and Ra extraction 44.0 kg HCl/tonne solids, 75°C, 24 hours

Comments on Thorium Extraction

The foregoing leach results indicate that thorium extraction decreases with an increase of leach temperature (Fig. 1) but increases with the concentration of hydrochloric acid (Fig. 3). Furthermore, thorium extraction is not substantially affected by retention time (Fig. 2), however, slurry densities above 50% solids are detrimental to thorium extraction. Similar effects of temperature and hydrochloric acid concentration were also observed when Agnew Lake uranium ore was leached with hydrochloric acid[9]. Therefore, temperature and the acid concentration are directly responsible for thorium solubilization. However, at present with this type of investigation it is impossible to give an adequate explanation for the effect of temperature and acid concentration on thorium extraction. Nevertheless the following comments could be stated from chemical properties of thorium salts.

The principle radioactive minerals of the Agnew lake uranium ore are uranothorite, and monazite[1]. Monazite is a phosphatic mineral. Other phosphatic minerals such as opatite, torbernite, autunite are likely to be present in the ore matrix. Therefore during acid leaching of this ore or its preconcentrate, phosphate anion (PO_4^{-3}) is liberated from the phosphate minerals and this phosphate anion most likely forms thorium phosphates. Generally thorium phosphates are less soluble than uranyl phosphates in an aqueous system[10,11].

The increase in thorium extraction with the increase of hydrochloric acid concentration could be due to the following reaction:

$$Th_3(PO_4)_4 + 12\ HCl \rightleftharpoons 3ThCl_4 + 4H_3PO_4$$

The direction of reaction in excess hydrochloric acid will be more towards the right side of the equilibrium. As a result more thorium tetrachloride will be formed. This is highly soluble in an aqueous system. Generally concentrated acid and high temperature (120-150°C) are required to solubilize monazite[10] therefore the higher per cent of thorium extraction with the higher concentration of acid could be due to solubilization of a monazite type mineral.

Second Stage Leaching

Table 2 shows the first stage optimum leach conditions and the grade of the leach residue. These results clearly indicate that the residues contain considerable amounts of radionuclides; and hence tailings of this nature are not free of environmental concern. However, residues containing U-0.0012%, Th-0.012% and Ra-20 pCi/g were obtained by single stage hydrochloric acid leaching of Agnew Lake uranium ore[9]. Residue of this nature might be acceptable for surface disposal.

In view of the present-day environmental concern over the radionuclides present in the uranium mill waste, the first stage hydrochloric acid leach residue of the preconcentrate was further treated with hydrochloric acid to reduce the radionuclide level. Table 3 shows the grade of the residues after 6, 10 and 18 hours of leaching with 44.0 kg HCl/tonne at 75°C on leach slurries containing 50% solids.

The data of Table 3 indicate that uranium extraction from the first stage leach residue improved with the extention of leach time and the best residue with respect to uranium and radium grades (U-0.01%) and (Ra-70 pCi/g) was obtained after 18 hours of continuous leaching. However, the best thorium grade (0.17%) of the second stage leach residue was obtained after 10 hours of leaching. The results of Table 3 also indicate that the best residue (i.e. with lowest content of radionuclides) still contains sufficient radionuclides and could raise environmental concern in the event of surface disposal.

Summary and Recommendations

Leach tests conducted at 75°C on a slurry containing 50% solids with 66.0 kg HCl/tonne of concentrate during 36 hours of retention time provided the highest per cent of uranium (87%) and radium (84%) extractions. Residues obtained from these leach tests were found to obtain uranium-0.016%, thorium-0.24% and radium-85 pCi/g.

As a result second stage hydrochloric acid leachings were conducted on the first stage leach residues to obtain residue almost free of radium*. The radionuclides content of the second stage leach residue was also fairly high (Ra-70 pCi/g, Table 3).

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* To reduce Ra level of the solids down to detection limit: 4-6 pCi/g solids; an opinion of the MSL spectroscopist.

Table 2 - Optimum leach conditions and residue grade

Temp. (°C)	Time (hr)	HCl kg/tonne	Pulp density (% solids)	U Wt %		Th Wt %		Ra (pCi/g)	
				Feed grade	Residue grade	Feed grade	Residue grade	Feed grade	Residue grade
75	35	66	50	0.124	0.016	0.60	0.24	415	85

Table 3 - Second stage HCl leach results*

Retention time (hr)	U grade (wt %) Feed+	U grade (wt %) Residue	Th grade (wt %) Feed+	Th grade (wt %) Residue	Ra grade pCi/g Feed+	Ra grade pCi/g Residue
6	0.020	0.018	0.32	0.26	145	100
10	0.020	0.014	0.32	0.17	145	80
18	0.020	0.010	0.32	0.17	145	70

* Leach conditions were not optimized; but maintained at HCl (44.0 kg/tonne $NaClO_3$ (3.0 kg/tonne), 75°C, 50% solids.

\+ Feed for the second stage leach tests was actually a mixture of several first stage leach residues.

The second stage leach results indicate that the overall uranium extraction is approximately 92% from the uranium concentrate. To improve the uranium extraction to 96% or above severe leach conditions (e.g. high acidity, temperature and/or retention time) might be required. Furthermore, flotation reagents, xanthates and organic oils, might have formed a protective coating around the mineral particles. To improve uranium, thorium and radium extractions this organic coating should be removed and this might be achieved by pretreating the uranium concentrate (i.e. by washing with organic solvents or heating up to approximately 500°C). This type of investigation will be conducted in our future program.

Lastly, to obtain tailings almost free of radionuclides stagewise leaching (3 or 4 times) of the uranium concentrate might be necessary.

ACKNOWLEDGEMENTS

One of the authors B. Ipekoglue gratefully acknowledges the financial support of IAEA, Vienna, Austria. Thanks are also due to the staff of Chemical Laboratories for the chemical analyses.

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