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LEACHING OF URANIUM FROM ELLIOT LAKE ORE IN THE PRESENCE OF BACTERIA

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Leaching of uranium from Elliot Lake ore in the presence of bacteria

Testing by the Departments of Mines and Technical Surveys and of Agriculture showed that mine water and stope ore from Denison Mines contained bacteria belonging to the Ferrobacillus-Thiobacillus *group. Percolation leach tests showed that the bacteria promote the production of an acid-oxidizing solution effective in leaching, whereas in the absence of bacteria no leaching of the uranium occurred.*

By V. F. HARRISON*, W. A. GOW** and K. C. IVARSON***

IN THE EARLY 1960's the operators of mines in the Elliot Lake, Ontario uranium field observed that the mine waters had become acid and contained appreciable concentrations of uranium and ferric iron in solution. This led to the subsequent current practice at Denison Mines Limited, Rio Algom Mines Limited and Stanrock Uranium Mines Limited of recovering economic quantities of uranium by washing the broken ore on the floors of completed stopes with mine water, thus picking up soluble uranium that can be recovered on surface in the conventional ore treatment plant. Because of the low cost and ease with which uranium could be recovered by this method, it was obviously of interest to determine the mechanism and controlling factors involved with a view to improving the rate of uranium dissolution.

A study of the known facts indicated that the sulphuric acid and iron in the solution result from the oxidation of the pyrite and pyrrhotite, which make up 5-6 per cent of the Elliot Lake ores. On the other hand, the high ferric/ferrous ratio found in the solution suggests an oxidation reaction more intense than simple air oxidation. Since a similar rapid oxidation of sulphide minerals in coal mines and copper operations in the U.S. [1] [2] [3] had been traced to the presence of bacteria identified as *Thiobacillus ferrooxidans*, it was thought that bacterial action might be contributing to the oxidizing reactions observed at Elliot Lake. Consequently, a test program was undertaken by the Extraction Metallurgy Division of the Mines Branch to investigate this possibility.

This paper discusses the program's first phase, which was done in cooperation with the Soil Research Institute of the Department of Agriculture, and which was aimed at determining if the dissolution of uranium from the underground workings is due to the presence of identifiable bacteria. The procedures used are described and the results of both the bacteriological studies and the bench scale leaching tests on ore are discussed.

Procedure

Two samples of mine water and one of dry minus 10 mesh ore from a stope floor were obtained from Denison Mines Limited for the bacteriological study. One of the mine water samples was taken from a pool in a stope (Sample A), while the other was taken from a stream flowing out of a stope (Sample B). Some stope ore was added at the mine to the water samples to provide nutrients for any bacteria that might be present. Chemical analyses of the two solutions are given in Table I. The ore sample from the stope had mineralogical and petrological characteristics [4] typical of the Elliot Lake ore deposits, and analysed 0.14 per cent U_3O_8 of which about one-half was oxidized to the hexavalent form.

Table I — Mine water analysis

Sample	pH	Chemical Analyses, g/l					
		U_3O_8	Total Fe	Fe^{++}	P	NO_3^-	NH_3
A — from pool in stope.....	2.20	1.70	1.91	0.06	<0.01	<0.01	<0.01
B — flowing from stope.....	2.38	0.86	0.28	<0.01	<0.01	<0.01	<0.01

To promote the development of any bacteria present in the mine water, 25 ml of mine water (Sample A) was added to a sterilized flask containing 8 litres of a sterile aqueous solution of the composition shown in Table VI. This solution, referred to as 9K medium, was made up according to specifications suggested by Silverman and Lundgren [5], who found it to be a suitable nutrient for the bacteria that were most likely to be present in the mine water. The mixture of mine water and 9K medium was aerated vigorously through a stone frit for 5 days during which time the temperature was controlled at 28°C. by means of a water bath. After 5 days the solution was passed through a Servall continuous centrifuge operating at 20,000 rpm to concentrate any bacteria present. The concentrate was diluted with 500 ml of distilled water and stirred mechanically for 15 minutes at 4°C and allowed to settle overnight in a refrigerator also at 4°C. After settling, the solution was separated from any solids that settled to the bottom of the container by de-

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cantation, and then centrifuged as described above. The concentrate from the centrifuge was stored at 4°C. To prevent heat generated in the centrifuge affecting bacteria that might be present, the centrifuging was done in a cold room held at 4°C.

TABLE II — Composition of 9K medium

Constituent	g/l
$FeSO_4 \cdot 7H_2O$	44.2
$(NH_4)_2SO_4$	3.0
K_2HPO_4	0.5
KCl	0.1
$MgSO_4 \cdot 7H_2O$	0.5
$Ca(NO_3)_2 \cdot 4H_2O$	0.02
H_2SO_4	0.5
pH	2.6

To determine if bacteria were present in the centrifuge concentrate, glass slides of samples of the concentrate were prepared as outlined in standard text books for viewing under the microscope. In this procedure, one drop of the centrifuge concentrate was mixed with 10 ml of distilled water and shaken. Using a piece of stainless steel wire with a small loop at one end, a sample of the diluted solution was transferred to a glass slide, stained with nigrosine dye, and air dried.

Another method used for cultivating any bacteria present in either the mine water or stope ore involved the use of a silica gel medium prepared in Petri dishes by combining silicic acid and 9K medium [6]. The preparation was hardened in an autoclave at 121°C and 15 atmospheres pressure for 15 minutes. About a tenth of a gram of mine ore or three drops of mine water was placed on the surface of the gel, after which the Petri dish was covered and allowed to stand at room temperature for 2 weeks. A small amount of gel containing bacterial colonies was diluted with 10 ml of distilled water and glass slides were prepared as described above.

The equipment used for the leaching tests on the ore is shown in Fig. 1. When using this apparatus 400 g of sized ore was placed in the glass column and 600 ml of leaching solution was added to the solution reservoir. The leaching solution was air-lifted to the top of the column from where it percolated through the ore and back to the reservoir.

Samples of freshly-broken, unoxidized mine ore were leached in this work. The analyses of sized fractions of this ore are given in Table III. The leaching solutions used were Quirke Lake water or barren solution from the

TABLE III — Analysis of sized, unoxidized, mine ore

Fraction	Chemical Analyses, %			
	U_3O_8	Secondary* U_3O_8	Fe	S
−1" + 3/8	0.14	0.019	4.91	5.87
−3/8" + 4m	0.11	0.017	4.90	3.68
−4 + 6m	0.12	0.021	4.82	3.59
−6 + 8m	0.14	0.018	4.84	3.35

*Percentage of U_3O_8 that dissolved in hot Na_2CO_3 solution. This indicates the amount of U^{+6} present in the leach feed.

ion exchange operations at the Denison property. In most tests a bacterial culture, prepared from the mine water, was added. In one test, bacterial action was stopped by adding mercuric chloride to the leach liquor to kill any bacteria present. In most tests ammonium sulphate and potassium orthophosphate were added to the leach liquor to serve as nutrients for the bacteria. The leaching tests were run for periods of several weeks, the progress of uranium and iron leaching being followed by periodic sampling and analysis of the recirculating leach solutions.

Results

Both mine water Samples A and B of the compositions shown in Table I, and the sample of ore taken from a worked-out stope floor were examined for the presence of bacteria. Sample A mine water was tested by the method outlined in the section on procedure in which 25 ml of the mine water was aerated with 8 litres of 9K medium for five days at 28°C. On centrifuging the mixture on completion of the aeration step, 75 ml of a milky suspension was recovered. Analysis of the relatively clear decant from the centrifuge showed that, where the solution had contained 8.9 g Fe^{++}/1 at the beginning of aeration, it now contained 7.0 g Fe^{+++}/1 and less than 0.01 g Fe^{++}/1. It was observed that some iron had precipitated out of the solution during aeration, which would account for the 1.9 g/1 loss of iron from the solution. Since the aeration was done at pH 2.6, it would not be expected that the ferrous iron would be completely oxidized in as short a period as 5 days by air oxidation, which is very slow in acid solution [7].

When samples of the milky suspension obtained by centrifuging were examined under the microscope at 1240 magnifications, numerous colourless cells one micron long and one quarter micron in diameter were observed (Fig. 2). The evidence in the photomicrograph and the ability of the organisms to oxidize ferrous iron in an acid medium suggested they belong to the *Ferrobacillus-Thiobacillus* group of bacteria.

Mine water from Sample B and the dry stope ore were examined for the presence of bacteria by the agar-gel technique. After a period of 2 weeks tan-coloured colonies were observed on the surface of the gels. Under the microscope the colonies were found to contain bacteria similar to those seen in the previous experiment. In specimens made from gel where stope ore was tested the

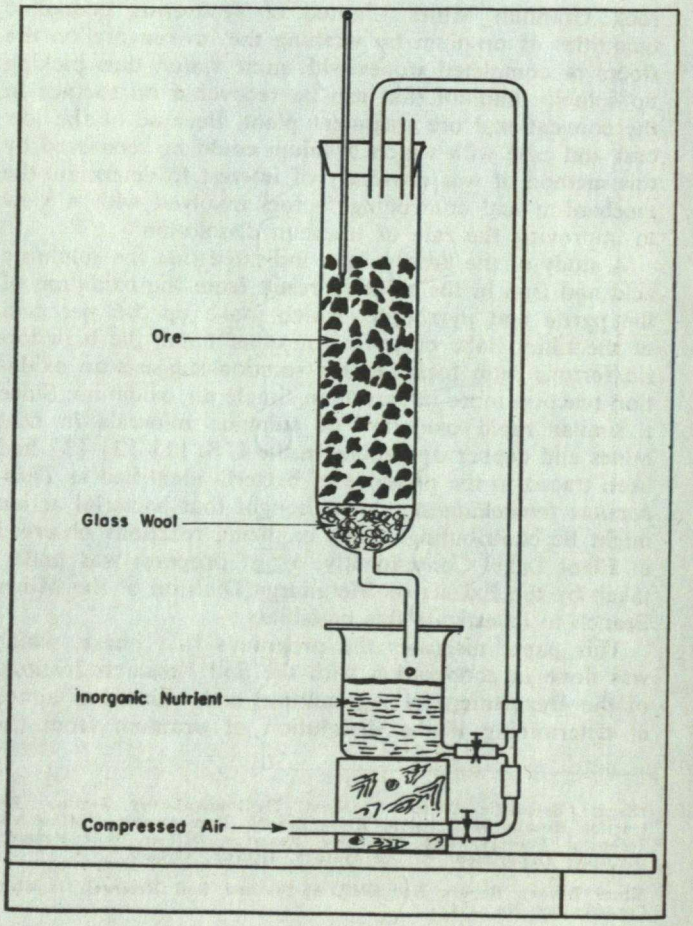

Fig. 1. Percolation leaching apparatus.

bacteria were seen to be arranged in clusters around ore particles (Fig. 3).

Since the bacteriological study had shown that bacteria were present in the mine waters and stope ore, the next step was to determine if the bacteria were necessary to promote the leaching of uranium. To investigate this, tests were done using the percolation apparatus shown in Fig. 1 in which fresh unoxidized minus 4 plus 6 mesh mine ore was leached with Quirke Lake water for several weeks at room temperature (28°C). In one test 10 ml of culture produced in the bacteriological study was added to the leaching solution, while in another test about 0.1 g mercuric chloride was added to kill any bacteria present in the ore or leaching solution. In the test where bacteria were used, 3 g/l of ammonoum sulphate and 0.5 g/l potassium orthophosphate were added as nutrient for the bacteria. In both tests sulphuric acid was added to adjust the pH to 2.5 initially. The leach feed contained 0.12 per cent U_3O_8 of which about 15 per cent was oxidized while the Quirke Lake water analysed 0.00001 g/l U_3O_8, <0.01 g/l Fe, <0.001 g/l P, 0.004 g/l NH_3, 0.006 g/l NO_3 and pH 6.2.

The results of these tests, shown in Fig. 4, provide conclusive evidence that the presence of bacteria found in the mine water is necessary for uranium leaching to occur at an appreciable rate. In the test in which bacteria were present, 17.5 per cent of the uranium was extracted in 5 weeks increasing to 53.5 per cent in 11 weeks, while in the test in which the bacteria were killed with mercuric chloride only 1 per cent of the uranium was extracted in 11 weeks. It was also observed that, where bacteria were present, the amount of iron in solution increased to 1.38 g/l, almost all in the ferric state.

To explore further the leaching of uranium from the Elliot Lake ores in the presence of bacteria, several additional percolation leach tests were done using unoxidized ore crushed to varius sizes (Table III). In three of the tests the leaching solution was Quirke Lake water, adjusted to pH 2.5 with sulphuric acid, to which 3.0 g $(NH_4)_2SO_4$/l and 0.5 g K_2HPO_4/l were added. In a fourth test the leaching medium was barren solution from the Denison Mines Limited ion exchange plant. This solution analysed 0.004 g U_3O_8/l, 1.16 g Fe/l, 0.73 g Fe^{++}/l, 0.004 g P/l, 0.15 g NH_3/l, 0.70 g NO_3/l and pH 2.2. Since this solution contained a considerable amount of nitrogen, the ammonium sulphate added as nutrient for the bacteria in the tests using the Quirke Lake water was omitted, although the potassium orthophosphate was added as in the other tests. In all of these four tests, 10 ml of bacterial culture was added at the beginning of the test.

The results of these tests are given in Fig. 5. It can be seen that the uranium extractions obtained in the two coarser fractions ($-1+\frac{3}{8}$ inch and $-\frac{3}{8}$ inch + 4 mesh) in 11 weeks were similar at about 15 per cent. On the other hand, the results obtained in the $-6+8$ mesh ore showed a uranium extraction of 55 per cent in the same leaching period with the curve still rising. These results indicate that the uranium extraction rate is very slow at particle sizes greater than 4 mesh.

In the test using ion exchange barren solution, the uranium extraction obtained in 11 weeks was similar to

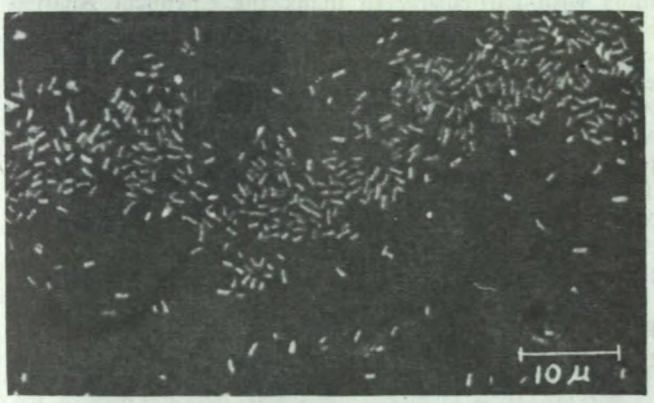

Fig. 2. Bacteria from Denison mine water, negatively stained with nigrosine, 918X.

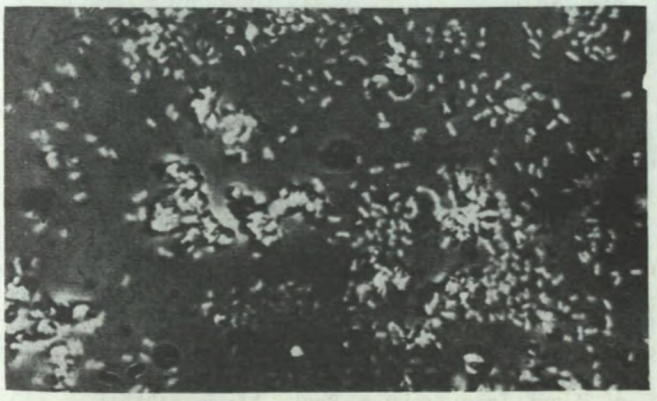

Fig. 3. Bacteria from Denison stope ore, negatively stained with nigrosine 918X.

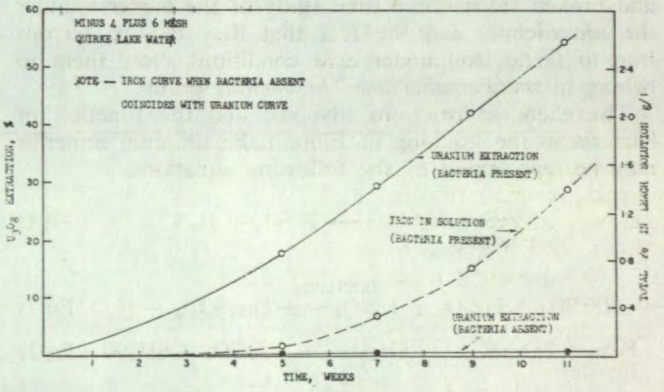

Fig. 4. Effect of bacteria on uranium and iron leaching.

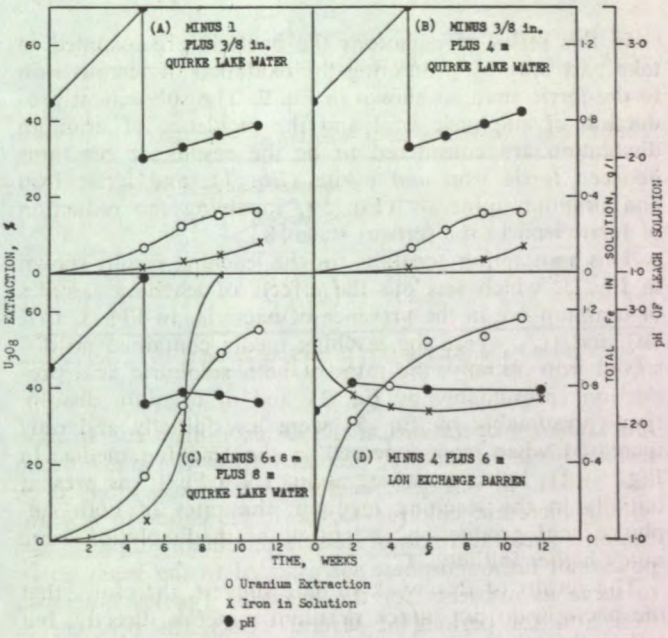

Fig. 5. Effect of ore size and solution composition on uranium and iron leaching.

that obtained using Quirke Lake water (Fig. 5 (d)). However, the rate of extraction was much higher initially when the ion exchange barren was used, the extraction in 4 weeks being 40 per cent compared to only 17.5 per cent in 5 weeks when Kirke Lake water was used.

In the tests using Quirke Lake water (Fig. 5 (a), (b) and (c)) the pH increased slowly over the first 5 weeks of leaching from an initial value of 2.5 to about 3.5. Because of this the pH was adjusted with sulphuric acid to a value of about 2.0 at the fifth week. After pH adjustment, the pH of the solution in the tests on the coarser fractions gradually increased to about 2.3, while in the test on the finest size the solution pH remained relatively constant. In the test using ion exchange barren as leach solution, pH adjustment was not necessary. These results suggest that there is a relationship between the rate of acid production and the amount of soluble iron in solution since only in Test 5 (d), where an appreciable amount of soluble iron was present initially, was pH adjustment unnecessary. The results given in Figure 5 also indicate a relationship between the rate of uranium extraction and the concentration of iron in solution.

Discussion

The test work reported in this paper has demonstrated that bacteria are present in the Elliot Lake mine waters and broken stope ore. Visual study of the bacteria under the microscope, and the fact that they oxidize ferrous iron to ferric iron under acid conditions show them to belong to the *Ferrobacillus-Thiobacillus* group.

The chemical reactions involved and the function of bacteria in the leaching of Elliot Lake uranium minerals may be represented by the following equations:

$$\underset{\text{(pyrrhotite)}}{FeS} + H_2SO_4 \longrightarrow FeSO_4 + H_2S \qquad \text{(Eq 1)}$$

$$2FeSO_4 + H_2SO_4 + 1/2\ O_2 \xrightarrow{\text{(bacteria)}} Fe_2(SO_4)_3 + H_2O \qquad \text{(Eq 2)}$$

$$\underset{\text{(pyrite)}}{FeS_2} + 7Fe_2(SO_4)_3 + 8H_2O \longrightarrow 15FeSO_4 + 8H_2SO_4 \qquad \text{(Eq 3)}$$

$$\underset{\text{(pyrite)}}{2FeS_2} + 7O_2 + 2H_2O \longrightarrow 2FeSO_4 + 2H_2SO_4 \qquad \text{(Eq 4)}$$

$$Fe_2(SO_4)_3 + UO_2 \longrightarrow UO_2SO_4 + 2FeSO_4 \qquad \text{(Eq 5)}$$

In this series of equations the bacteria are assumed to take part only by promoting the oxidation of ferrous iron to the ferric state, as shown in Eq. 2. The subsequent production of sulphuric acid and the incidence of uranium dissolution are considered to be the results of reactions between ferric iron and pyrite (Eq. 3), and ferric iron and uranium minerals (Eq. 5), involving the reduction of ferric iron to the ferrous state [8].

This assumption accounts for the leaching results shown in Fig. 5, which sets out the effects of leaching samples of uranium ore in the presence of bacteria. In Fig. 5, (a), (b) and (c), where the leaching media contained no dissolved iron initially, the rates of both sulphuric acid production (presumably by Eq. 3) and of uranium dissolution (presumably by Eq. 5) were low initially and only increased when iron appeared in the leaching media. In Fig. 5 (d), however, where about 1.9 g Fe/l was present initially in the leaching medium, the rates of both sulphuric acid production and of uranium dissolution were much higher initially.

The results of this work to date suggest, therefore, that the bacteria do not attack uranium minerals directly, but rather that they set up chemical conditions suitable for the dissolution of uranium.

The possibility exists that the oxidation of pyrite to form sulphuric acid by Eq. 4 is also promoted by bacterial action. This has not been established for the materials used in this study, but is under investigation by one of us (K.C.I.).

The work of Kennecott Copper Corporation in the U.S. and of the British Columbia Research Council in Vancouver, Canada, has demonstrated the ability of *Thiobacillus ferrooxidans* to accelerate the leaching of copper sulphides by producing ferric sulphate and sulphuric acid from pyrite [3], [9]. Based on the present work, the role of bacteria in the leaching of the Elliot Lake uranium ores appears to be similar to the role played by bacteria in the leaching of copper ores as found by these other investigators.

Conclusions

Microorganisms of the *Ferrobacillus-Thiobacillus* group, obtained from the Denison mine water and stope ore samples, are able to grow in an aqueous solution containing sulphuric acid, iron and uranium. It was observed that their presence in the test solutions results in the formation of ferric iron that ultimately leaches the uranium from unoxidized ore. Based on the limited number of tests performed in this investigation, the extraction rate for uranium appears to increase with diminishing ore size. Our work has also shown that a complete assessment of the possible applications of leaching with the help of bacteria will require a detailed study of the effect of pH, ore size, bacteria nutrient requirement, and iron concentration in solution.

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