

Arsenic Rich Waste Rock Disposal under Subaqueous and Anoxic Conditions

Michael J. Rinker¹, R.V. Nicholson^{1,2}, Don Lush¹ and Nan H. Lee³

¹Beak International Inc., 14 Abacus Rd. Brampton, ON Canada. L6T 5B7

²University of Waterloo, Waterloo, ON Canada N2L 3G1

³Cogema Resources, 45th Street West, Saskatoon, SK Canada S7K 3X5

Abstract. Waste rock from the Cigar Lake project in Northern Saskatchewan, Canada, was evaluated for in-pit disposal under subaqueous and anoxic conditions. Column tests were conducted to assess arsenic release rates and sequential leach tests were conducted to form the basis of a mass balance approach for predicting arsenic concentrations over time. The arsenic concentration in pore water was a function of the pore water residence time and this suggests a new paradigm for interpretation of column tests under subaqueous conditions. The relatively ‘steady state’ concentration of arsenic in pore water correlated well with the ‘leachable’ fraction of arsenic in the solids. The relationship provided a tool to assess the risk of arsenic leaching in wastes using solids assays.

Introduction

The Cigar Lake Project is currently the world’s largest undeveloped uranium project with an estimated reserve sufficient to sustain mining for up to 40 years. Over the life of the Cigar Lake Project, approximately 1.32 million cubic metres of waste rock will require environmentally appropriate management. One effective way to manage this waste rock is to place it in an environment similar to that from which it was extracted. That is, surrounded by water and isolated from atmospheric conditions, such as at the bottom of a flooded open pit. Arsenic was the primary constituent of concern in Cigar Lake waste rock. Radionuclides, including uranium, were at relatively low concentrations and comparable to background levels.

Waste rock studies were conducted in 2000 to estimate pore water concentrations in waste rock under anaerobic and subaqueous conditions and to quantify the

leachable mass fractions of arsenic from solids with a wide range of values for arsenic content (mass balance approach).

Column studies were conducted to refine estimates of chemical constituent concentrations in pore water associated with waste rock and to assess the relative effect of cement, that may be incidentally added to the waste rock during mining on leaching behaviour of the waste rock. The pore water concentration will be used to estimate constituent loadings to groundwater moving through the waste rock and eventually discharging to the environment (surface water bodies) down gradient to the open pit. Sequential leach tests were used to compare the leaching efficiencies of selected solutions to extract "leachable" constituents, in order to estimate the leachable fraction that could contribute to the pore water concentrations when waste rock is submerged in water. The tests were designed to provide some insight into the geochemical mechanism controlling arsenic release and to develop a kinetic and mass balance approach to predict constituent loadings to groundwater passing through the waste rock in the post closure period.

Methods

Tests were conducted on altered and unaltered graphitic metapelite drill core samples (1 year old) and fresh drill core samples (1 month old) from Cigar Lake. The samples had a range of arsenic concentrations that bracketed the expected values for waste rock that will be disposed in the Sue C pit.

Samples of waste rock from a three year-old stockpile at Cigar Lake were also tested to compare and contrast the results from weathered samples in the stockpile to those with the relatively fresh drill core samples. Waste rock samples were obtained from the stockpile by coring eight holes (114 mm diameter) using a sonic drill.

Column tests were conducted on Cigar Lake waste rock to refine estimates of arsenic concentration in pore water and to assess the relative effect of cement contained in the waste rock on leaching constituents from the waste rock. The conditions for column tests conducted for this study included the following:

- 20 kg of waste rock per column;
- column filled with water and sealed to minimize ingress of oxygen;
- no water column over the waste rock;
- porewater volume of 5 L; and
- sample volumes of 150 mL were removed bi-weekly for chemical analysis, resulting in a pore water residence time of approximately 1.5 years for each column.

The results from these column tests were carried out in 2000 compared to results from previous waste rock investigations that were conducted in 1994 (CLMC, 1995) to evaluate water quality associated with submerged waste rock, and to determine representative concentrations of arsenic and other constituents in pore water that would be used for the assessment of waste rock disposal options. The test conditions for these previous tests included the following:

- 1.5 to 4 kg of waste rock per column;
- columns filled with water and sealed to prevent ingress of oxygen;
- each column included a volume of water overlying the rock that was also sampled in some cases; and
- 1 litre of water was removed (and replaced) weekly for analysis resulting in pore water residence times that ranged from a few days to 1.5 weeks.

Sequential leaching tests were conducted on waste rock samples. Sequential leaching refers to a method of repeated washing of the same solid sample with a fresh leach solution for a selected number of cycles and solution types. All sequential leach tests had water to solids ratio of 20:1 (1 L of water to 50 g of solids). Several leach solutions were tested initially to assess the most effective condition to leach arsenic. The leaching solutions that were investigated included de-ionized water, de-ionized water with pH adjusted to 5 with acetic acid, de-ionized water with pH adjusted to 5 with phosphoric acid, de-ionized water with pH adjusted to 10 with NaOH, and de-ionized water with hydroxylamine-hydrochloride (HAH; 0.01 M) with a pH of 4.5.

Waste rock samples were placed in a plastic vessel and solution was added. The vessel was agitated for a specified period of time (typically 24 hr and 48 hr intervals) and sample aliquots were removed from the leaching solutions and submitted for chemical analysis. A fresh leach solution was added to the vessel and the procedure was repeated. The total leachable amount of any constituent was interpreted as the sum of the constituent leached in all sequential steps performed on the sample.

Samples evaluated in this study include drill core (1 month to 1 year old) and samples collected from a three year old stockpile produced during test mining and development.

Results

Column Tests

Solids

The elemental composition of selected constituents in waste rock in the column tests is provided in Table 1. The results show that the waste rock samples tested in 1994 are very similar to samples tested for this study. Arsenic values found in the waste rock are relatively high compared to the average crustal abundance of 1 to 13 mg/kg (Taylor and McLennan, 1985), and is the primary constituent of concern for Cigar Lake waste rock. The sulphide-sulphur values were greater than

2% and suggest that there is a relatively high risk to acidic drainage and metal leaching if the waste rock is disposed of on land indefinitely.

Table 1. Concentration of selected constituents in waste rock used for column tests.

Constituent	1994 Column Test	2000 Column Test
Sulphide (%)	2.5	2.1
Arsenic (mg/kg)	460	444
Uranium (mg/kg)	14.5	18
Nickel (mg/kg)	280	181

Pore Water Concentrations

Two column tests were conducted for this study carried out in 2000. Both columns contained Cigar Lake waste rock, and one column contained rock with cement added (0.75 weight percent). The concentrations of sulphate and arsenic and pH in pore water as a function of time are shown in Fig. 1. An attempt was made to place waste rock of similar arsenic concentration and mineralogy in each column but it is possible that there was variation between the columns.

In general, the results show that marginally higher pH values were observed in pore water associated with waste rock that contained cement (mean pH value 7.7) relative to values observed in pore water associated with waste rock that did not contain cement (mean pH value 7.2).

Sulphate concentrations exhibited increasing trends over the first two weeks, followed by marginally decreasing values thereafter. The maximum sulphate concentrations were 640 mg/L for the test with cement, and 850 mg/L for the test without cement. Arsenic concentrations increased to values of 40 to 55 mg/L over the first 6 to 15 weeks of testing followed by more slowly rising values thereafter. The mean, relatively steady-state, arsenic concentrations in pore water were 53 mg/L for the test with cement and 65 mg/L for the test that did not contain cement.

Selected results for the 1994 column test results are provided in Fig. 1. In general, the results show that sulphate was rinsed from the waste rock over the first few weeks of testing, and relatively low steady-state concentrations were observed thereafter. In contrast, arsenic concentrations exhibited initial increases with relatively steady-state values over time. The maximum observed arsenic concentration in leachate was 4 mg/L. The pH values were relatively constant for the duration of the tests with a mean value of 7.5.

The trends observed for sulphate and the maximum values observed for arsenic in the tests conducted in 2000 are significantly different than those observed in the 1994 tests. Because the waste rock samples were similar in both the 1994 and the current tests, it is likely that the experimental methodology accounted for the difference. The differences in experimental methods and limiting assumptions are discussed below.

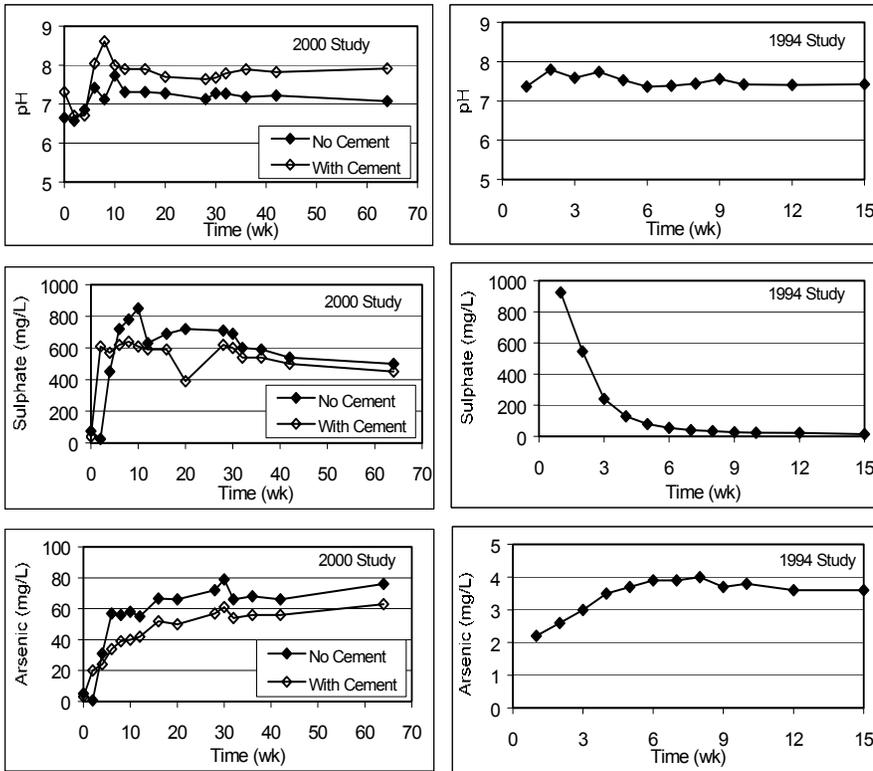


Fig. 1. Selected results for column tests conducted in 2000 (this study) and in 1994 (previous study).

The trends observed for sulphate and the maximum values observed for arsenic in the tests conducted in 2000 are significantly different than those observed in the 1994 tests. Because the waste rock samples were similar in both the 1994 and the current tests, it is likely that the experimental methodology accounted for the difference. The differences in experimental methods and limiting assumptions are discussed below.

Sequential Leaching of Drill Core Material

Preliminary leach tests were conducted to refine the methodology used to determine the leachable inventory of arsenic in waste rock samples. The solution pH effects were evaluated by pH adjustment to values of 5 and 10 with acetic acid and sodium hydroxide respectively. Reductive dissolution was investigated using hydroxylamine hydrochloric acid (HAH), and sorption was investigated using

phosphoric acid at pH 5 (~300 mg/L PO₄). Leaching with de-ionized water was also assessed.

The solution with a pH of 10 and the weak phosphoric acid solution were the most effective at leaching arsenic. There was no indication that dissolving ferric iron solids with HAH affected the quantity of arsenic leached from the solids. However, the response of arsenic leaching in other solutions was consistent with sorption of arsenic onto solids such as clays. This was further supported by the lower or depressed arsenic concentrations observed in the acetic acid (pH 5) solutions, and the higher concentrations associated with the pH 10 solutions. Because of the indication that sorption appeared to be important, a solution containing phosphate was considered to be adequate to quantitatively extract the total leachable arsenic.

For the purpose of determining the leachable inventory of arsenic in the Cigar Lake waste rock, the rock samples were subjected to 2 rinses with de-ionized water (to determine the water leachable fraction) followed by 2 rinses with phosphoric acid (to determine the total leachable fraction) with solution:solids ratios of 20:1.

Leaching Drill Core

Six leach tests were conducted on Cigar Lake core samples. The results of the leach tests are presented in Table 2 that presents the equivalent mass of arsenic leached per mass (%) of arsenic in the solids. These results show that the percentage of arsenic leached by water from the solids ranged from about 9% to about 17% of the arsenic inventory for core samples. The additional phosphate solution resulted in the cumulative quantity of leachable arsenic that approached 30%.

Leaching of Stockpile C Samples

Sequential leach tests were also conducted on samples collected from Stockpile C at the Cigar Lake mine site. These tests were conducted to determine the soluble arsenic inventory in material that had been stored on surface for several years and exposed to oxidation. A total of 15 samples from eight drill holes were tested.

The leach test results are presented as the equivalent mass of arsenic leached per mass (%) of solids in Table 2. These results account for the total quantity of arsenic leached from the solids after four sequential extractions. The quantity of arsenic leached with water ranged from 1% to 24% of the arsenic inventory in the samples. The additional phosphate solution resulted in a cumulative quantity of leachable arsenic that was identical to that observed for the drill core material (28%).

Table 2. Water and total leachable fractions of arsenic in Cigar Lake waste rock..

Sample	Water Leachable		Total Leachable	
	Range (%)	Mean (%)	Range (%)	Mean (%)
Core Samples (n=6)	9 to 17	12.4	27 to 29	28
Stockpile Samples (n=15)	1 to 24	7.4	12 to 67	28

Discussion

Pore Water Concentration

The arsenic concentrations in pore water that were observed in the 1994 tests were significantly different from those observed in the column test in this study. This difference primarily reflects the relatively short pore water resident time (1.5 weeks) for the 1994 tests compared to longer resident times in this study (1.5 years). The short resident time is acceptable for constituents that dissolve to “equilibrium” or that leach readily in each new pore volume (e.g., sulphate). However, it is not necessarily applicable for arsenic because insufficient time between sampling events prevented arsenic from dissolving to “equilibrium” concentrations which may be expected if the water remained in contact with the waste rock for several decades in a typical disposal scenario, for example.

The results of this study suggest that the submerged waste rock tests may require residence times of several months to exhibit concentrations that would be representative of those observed after disposal. If the residence times in the previous experiments were longer, pore water concentrations would have been higher than those observed. The concentrations that could occur with longer residence times can be calculated by summing the total arsenic released from the waste rock (collected as sampled during the test) and then dividing by the volume of resident pore water.

The results for all tests conducted over the past 8 years on Cigar Lake waste rock under saturated conditions are summarized in Table 3 showing the solids arsenic content, the maximum observed leachate arsenic concentrations, and recalculated arsenic concentrations that could occur if the residence times were longer. The solids arsenic content of samples ranged from 20 to more than 708 µg/g, and maximum observed arsenic concentrations ranged from 0.1 to 70 mg/L.

The observed or recalculated concentrations of arsenic in pore water were compared to the amount of arsenic in the solids (i.e., waste rock arsenic content). This correlation between solids content and pore water concentrations is shown in Fig. 2. Testing of samples with a range of arsenic concentrations provided a relationship between solids chemistry and pore water chemistry and a means to predict pore water concentrations for submerged waste rock that will be disposed at the Sue C open pit. The waste rock to will be hauled and disposed of in the Sue C pit has estimated arsenic content of 175 $\mu\text{g/g}$. The source term concentration (initial pore water concentration) for the Cigar Lake waste rock was predicted to be 17.5 mg/L using this relationship. Table 3. Summary of test programs conducted on Cigar Lake Project waste rock under saturated conditions.

Table 3. Summary of test programs conducted on Cigar Lake Project waste rock under saturated conditions.

Test Program	Solids As Content ($\mu\text{g/g}$)	Maximum Observed Leachate As Conc. (mg/L)	Recalculated Pore Water As Conc. (mg/L)
CW-93-7B ¹	24	0.1	1.1
CW-93-8B ¹	20	0.5	5.2
CW-93-9B ¹	708	11.0	60
CW-93-10B ¹	686	11.4	75
CW-94-13S1 ²	460	4.0	38
CW-94-13S2 ²	460	3.5	35
CW-94-13S3 ²	460	7.2	45
CW-94-13S4 ²	460	9.1	55
Bulk Leach Test ³	51	4.0	7
CW-00-14C1 ⁴	444	55	55 ⁵
CW-00-14C2 ⁴	444	70	70 ⁵

¹ 1993 test program conducted on graphitic metapelite from Cigar Lake (CLMC, 1995).

² 1994 test program conducted on graphitic metapelite from Cigar Lake (CLMC, 1995).

³ Bulk leach test conducted on a blend of rock types from Cigar Lake (CLMC, 1995).

⁴ Tests conducted for this study.

⁵ Pore water concentrations were not calculated for these tests because the solids dissolved to near equilibrium concentrations during the course of testing.

Influence Of Waste Exposure Time Prior To Submergence

During this and previous studies, the degree of weathering or exposure to the atmosphere and moisture was considered to influence the concentration of arsenic in the pore water. Previous hypothesis suggested that longer weathering periods prior to testing resulted in higher concentrations in pore water. This study, however, exhibited results that suggested that more weathered samples resulted in lower concentrations of arsenic in pore water as shown in Table 2. This trend is evident in the distribution of sequential leach results on the fresh core and weathered stockpile samples as shown in Fig.3 reflecting the average "water leachable" values shown in Table 2.

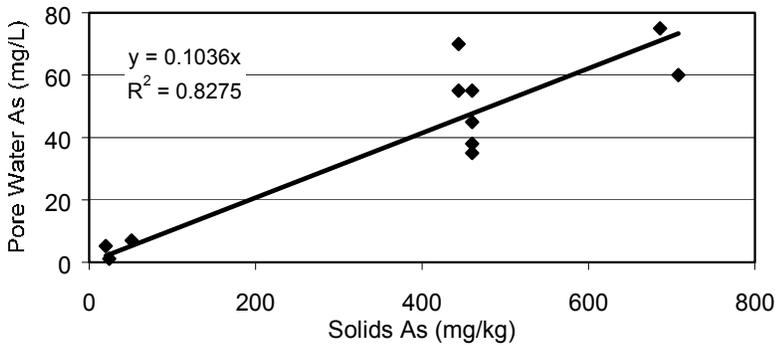


Fig. 2. Recalculated or observed arsenic concentrations in pore water as a function of arsenic content in the solids

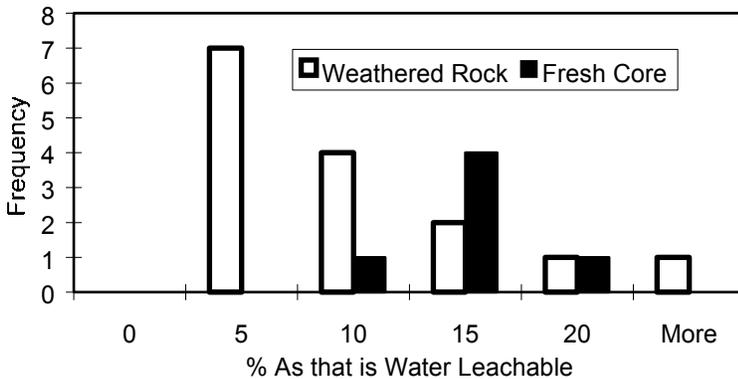


Fig. 3. Distribution of sequential leach test results.

Leachable Inventory and Implications for Management

The behaviour of arsenic during sequential leaching suggests that there is a readily soluble fraction, as well as a fraction that is more strongly sorbed on the solids. While leachable sulphate represented a small fraction of the total sulphur inventory (less than 1%), water leachable arsenic represented 7.4% of the total arsenic, on average, in the stockpile samples and 12.4% of the total arsenic, on average, in the core samples. The contrast in behaviour between arsenic and sulphur in the rock suggests that the controls on reactions that transform the primary solids in the rock to soluble forms are significantly different for these two elements. This may

imply that the kinetics of the reactions are significantly different, or that the arsenic transformation process is not completely controlled by oxidation processes.

A significant amount of the transformation reaction for arsenic occurs rapidly after the rock is disturbed, and the amount of leachable arsenic appears to decrease with time. The primary arsenic must transform to a more leachable form when disturbed and cannot be in a leachable form *in situ*; there is no evidence of high levels of arsenic in local groundwater and arsenic would likely have leached from the rock over the geologic history of the deposit. It is well known that arsenic occurs in several mineral phases in the rock associated with uranium mineralization in Saskatchewan. The different rates of transformation would be consistent with the depletion of a very reactive phase or phases, and slower reaction rates associated with the arsenic in the other remaining phases. For example, the rate of arsenopyrite (FeAsS) oxidation is known to be similar to that of pyrite (FeS_2) and could not explain the rapid transformation that resulted in the high proportions of leachable arsenic observed in this study. The rate of oxidation of the gersdorffite ($[\text{Ni},\text{Co}]\text{AsS}$), however, is not known but this finely disseminated infilling mineral may exhibit very high rates of oxidation after disturbance and could be responsible for the high values for leachable arsenic.

The rapid release of arsenic initially upon excavation and exposure together with the subsequent slower rate or restabilization of arsenic after months of further exposure suggest that waste rock can be stored on surface for several years without substantially increasing the amount of leachable arsenic in the rock. There may be no appreciable benefit from immediate submergence of the waste rock, and the results of this test program suggest that waste rock can be stored on surface during mine operation and hauled in campaigns without significant negative geochemical consequences.

References

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- Taylor, S.R. McLennan S.M. 1985 The Continental Crust: Its Composition and Evolution. Blackwell Scientific Publ., Oxford, England, 312 pp.