

## **GEOCHEMICAL CHARACTERIZATION OF MOLYBDENUM LEACHING FROM ROCK AND TAILINGS AT THE BRENDA MINESITE, BRITISH COLUMBIA**

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### **ABSTRACT**

The Brenda copper-molybdenum minesite is located near Peachland, British Columbia, and operated from 1967 to 1990. Since 1990, the site has been closed and reclaimed.

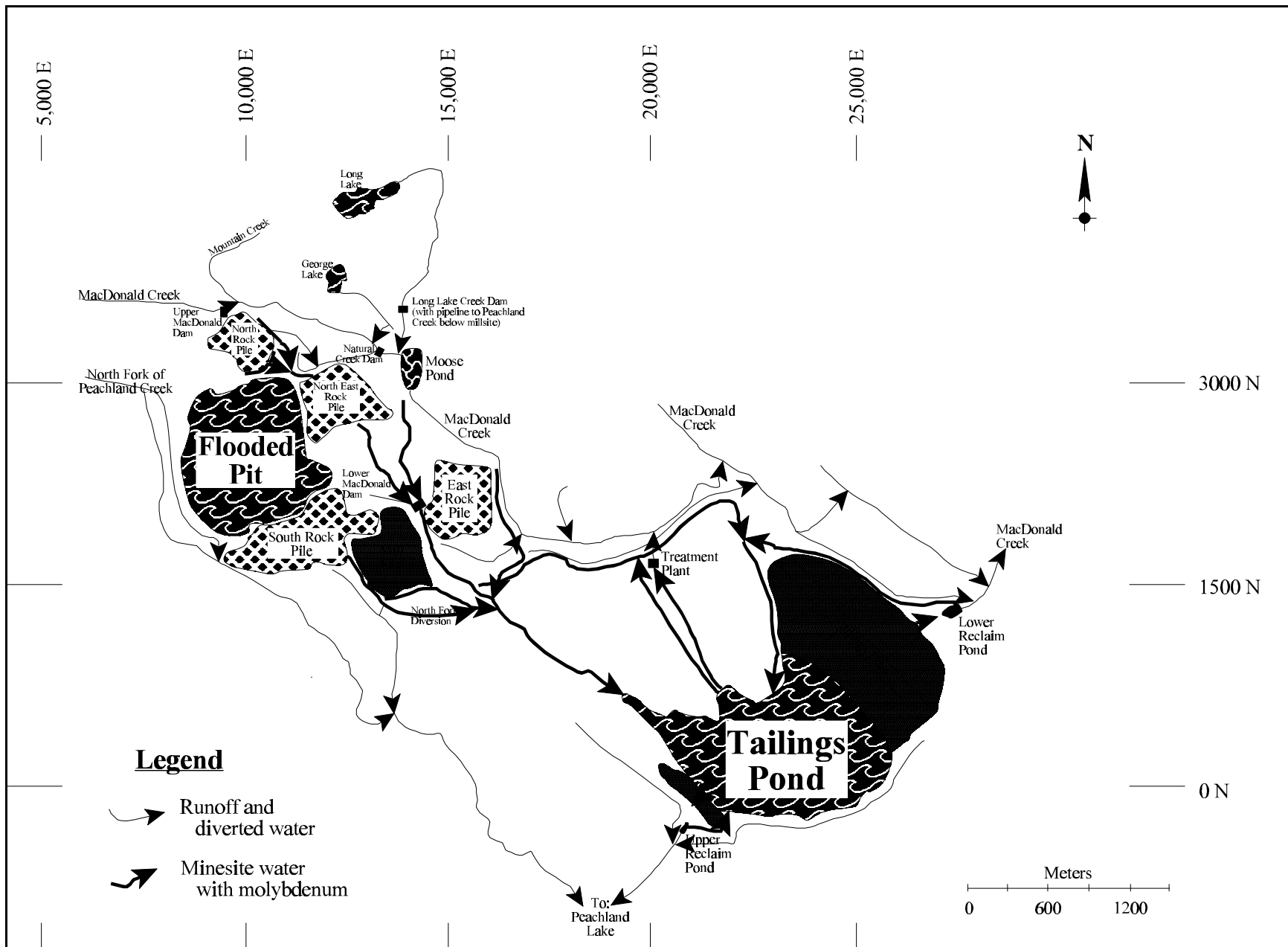
In 1998, a detailed review and interpretation of all water chemistry on and around the Brenda minesite, involving more than 7,000 analyses since 1970, identified various physical and geochemical control mechanisms on metal concentrations at the minesite. However, the geochemical control on aqueous molybdenum concentrations was not clear, but appeared to be kinetic in nature with factors like time, flow rate, and location having significant effects. This led to additional geochemical testwork, including (1) static tests, like total metals and whole-rock analyses, (2) kinetic tests, including Sobek humidity cells and recirculating leach columns, and (3) geochemical modelling based on recently published thermodynamic data for molybdenum that was added to the U.S. EPA's MINTEQA2 model.

The static tests showed a large range in solid-phase molybdenum levels, reflecting the presence of nearly barren waste rock to low-grade ore in Brenda's rock piles. Observations based on the cells and columns include (1) the rate of leaching is highly variable among samples and through time, and (2) the apparent maximum "equilibrium" concentration is also variable among samples. Geochemical modelling showed that powellite ( $\text{CaMoO}_4$ ) is closest to mineral saturation and solubility control on aqueous molybdenum, with wulfenite ( $\text{PbMoO}_4$ ) and other molybdenum minerals playing a much lesser role. However, no molybdenum mineral in the database explained properly the results of the kinetic tests or the monitoring data. Therefore, the control mechanism for molybdenum at Brenda remains unknown. Nevertheless, the recirculating columns showed there is such a control that creates local maximum concentrations that vary by sample, but these are altered by kinetic processes like time and flow rate under on-site conditions.

### **INTRODUCTION**

The Brenda minesite (Figure 1) is located near Peachland, British Columbia, and operated from 1967 to 1990 (SRK, 1993). Since 1990, the minesite has been closed and reclaimed. Chemical monitoring of waters above, draining through, and downstream of the site has been ongoing since July, 1970.

In 1998, a detailed review and interpretation of past water chemistry at the Brenda minesite, involving more than 7,000 analyses and tens of thousands of values, revealed the geochemical processes controlling the leaching of several metals from waste rock and tailings (Morin and Hutt, 1998). This in turn allowed predictions of future concentrations and options for lowering current levels. However, the geochemical processes controlling molybdenum leaching were not so obvious, but appeared to be kinetic



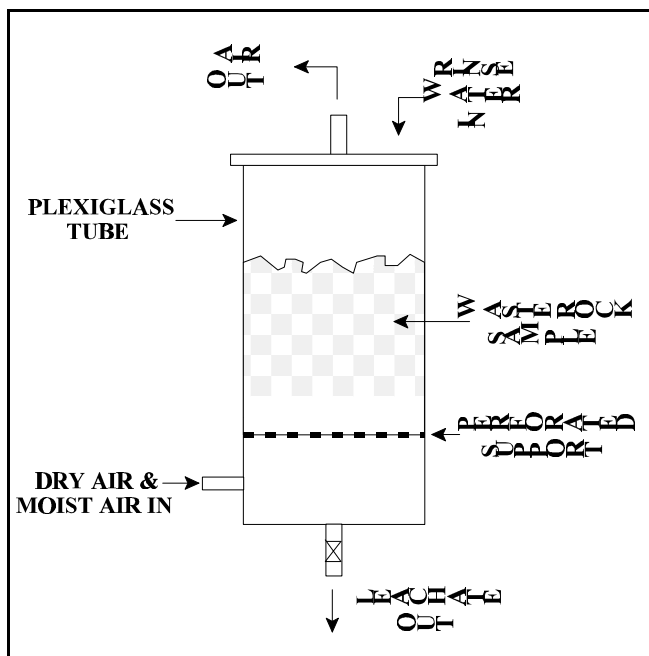
**FIGURE 1. General Layout and Water Movement in and around the Brenda Minesite (adapted from maps by/for Brenda Mines).**

in nature so that factors like time, flow rate, and location significantly influenced concentrations. As a result, additional geochemical work was conducted in 1998 and 1999. This work was also conducted to ensure Brenda's geochemical database was consistent with the three documents released by the Ministry of Energy and Mines and of Environment, Lands and Parks on metal leaching in 1998 (Province of British Columbia, 1998a).

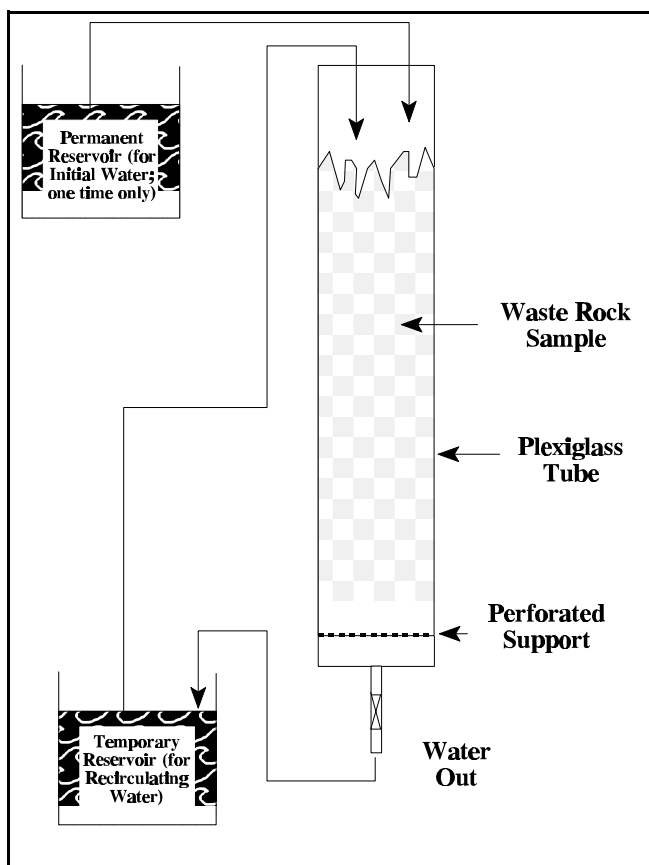
The additional work carried out in 1998 and 1999 included (1) static tests, like total metals and whole-rock analyses, (2) kinetic tests, including Sobek humidity cells (Figure 2) and leach columns (Figure 3), and (3) geochemical modelling based on recently published thermodynamic data for molybdenum that was then added to the U.S. EPA's MINTEQA2 model (Allison et al., 1990). This work provided a better understanding of molybdenum leaching from rock and tailings at Brenda.

### GENERAL GEOLOGY AND MINERALOGY OF THE BRENDA MINESITE

Brenda rock can be divided into two, similar rock units, a quartz diorite and a porphyritic diorite (Soregaroli and Whitford, 1976; Province of British Columbia, 1998b). Both units contain roughly 10-30% quartz, 10-20% potassium feldspar, 45-60% plagioclase ( $An_{34}-An_{48}$ ), 1-15% biotite, 2-30% hornblende,



**FIGURE 2. Schematic Diagram of a Humidity Cell (adapted from Morin and Hutt, 1997).**



**FIGURE 3. Schematic Diagram of a Brenda Column.**

with minor magnetite, sphene, and apatite. The dominant sulphide minerals are chalcopyrite and molybdenite, with minor pyrite. The ratio of chalcopyrite to pyrite is 10:1 and pyrite is generally less than 0.05%. Observed secondary minerals at Brenda include limonite, malachite, azurite, hematite, ferrimolybdate, powellite ( $\text{CaMoO}_4$ ), and tenorite. Because of the overwhelming abundance of neutralizing minerals and the relative scarcity of pyrite and other acid-generating sulphide minerals, no acid rock drainage has been detected at Brenda and none is expected. The average pH in the historical database is 8.05 with a standard deviation of 0.49.

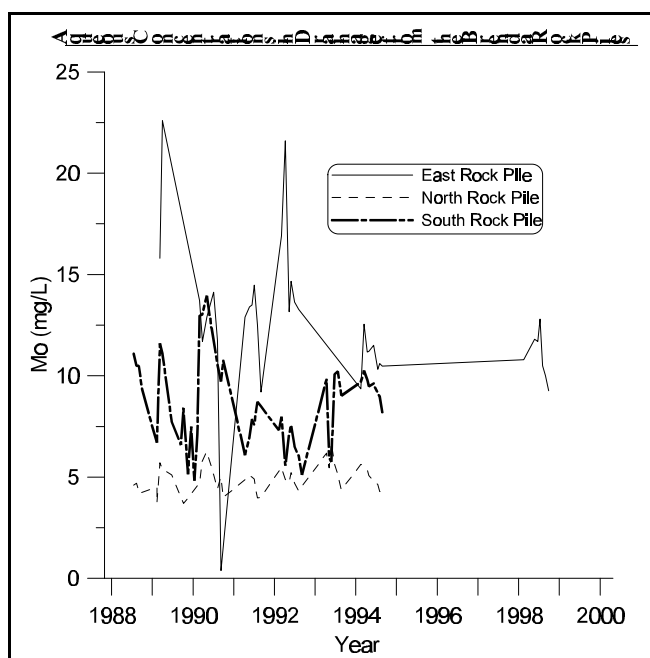
### TOTAL-METAL CONTENTS OF BRENDA ROCK AND TAILINGS

A total of 35 samples of rock were collected from test pits and as surface grab samples from the various rock piles around the site (Figure 1). The samples were submitted for total-metal analyses after triple-acid digestion. These samples contained a range of 5 to 576 ppm Mo, which exists as a sulphide ( $\text{MoS}_2$ ) and in various secondary forms like powellite ( $\text{CaMoO}_4$ ) as mentioned in the previous section.

For tailings, a total of seven samples were collected from test pits and as surface grab samples from various locations around the tailings impoundment (Figure 1). Like the rock, these tailings samples were submitted for total-metal analyses after triple-acid digestion. The results spanned a range from 12 to 81 ppm.

### HISTORICAL AQUEOUS MOLYBDENUM CONCENTRATIONS ON THE MINESITE

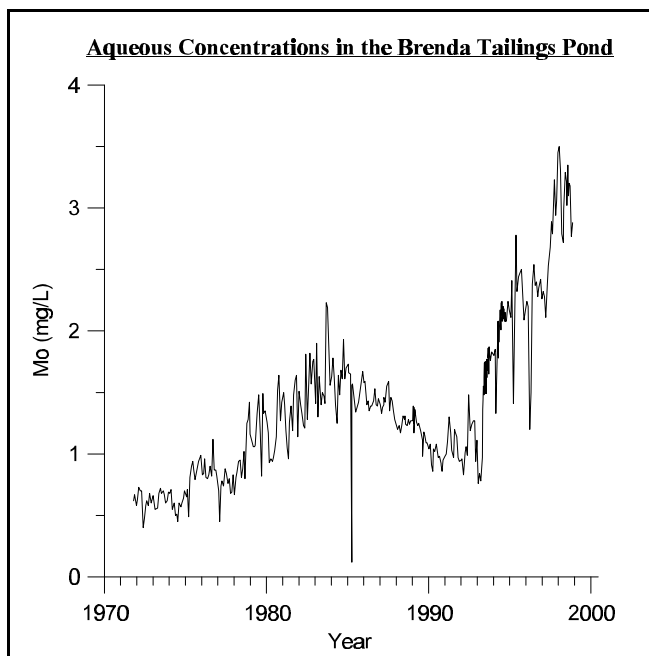
Although the solid-phase levels of molybdenum in rock and tailings are relatively low, the molybdenum can leach by the oxidation of its sulphide form and the redissolution of its secondary forms. Historical monitoring of aqueous concentrations from the rock piles showed that molybdenum was typically around 4-5 mg/L from the North Pile, 7-12 mg/L from the South Pile, and 10-20 mg/L from the East Pile (Figure 4). Long-term monitoring of the tailings pond shows concentrations generally increasing through the years to roughly 3 mg/L in



**FIGURE 4. Temporal Trend of Aqueous Molybdenum Concentrations in Drainage from the Brenda Rock Piles.**

1998 (Figure 5), which is partly due to the drainage of rock-pile water into the tailings pond.

One obvious question from the historical monitoring is whether concentrations in the tailings pond could continue to increase with time. Also, there could be a concern if aqueous concentrations from the rock piles increased much higher. The answers to these and other related questions were the focus of this study.



**FIGURE 5. Temporal Trend of Aqueous Molybdenum Concentrations in the Brenda Tailings Pond.**

### BRENDA KINETIC TESTS

As explained above, there were two types of kinetic tests operated on Brenda rock and tailings: repetitive-flush Sobek humidity cells (Figure 2) for a total of three rock cells and three tailings cells, and recirculating leach columns (Figure 3) for a total of two rock columns and two tailings columns (one tailings column was stopped shortly after starting because the flowrate was too low). The initial solid-phase levels of molybdenum were higher in the rock samples compared to the tailings (Table 1). The cells are designed to provide kinetic rates of molybdenum leaching through time during high-dilution events, whereas the columns provide the maximum attainable levels of aqueous molybdenum and the time to attain them.

<b>TABLE 1</b>			
<b>Description of Kinetic-Test Samples</b>			
Location	Sample	Cell or Column?	Initial Solid-Phase Mo (ppm)
East Rock Pile	E1-1F	both	515
Northeast Rock Pile	NE2-1F	both	256
South Rock Pile	S1-1F	cell only	197
Tailings	T3	cell only	49
Tailings	T5	cell only	81
Tailings	T6	both	36

The results of the humidity cells show typical trends where accumulated soluble molybdenum, probably as a secondary mineral, is initially rinsed from the cells through time, so aqueous concentrations fall with time until kinetic rates are obtained (Figures 6 and 7). For Brenda, long-term kinetic rates are expected to represent the oxidation rate of molybdenite ( $\text{MoS}_2$ ). While the typical decreasing rate through time is apparent, the cell containing rock from the Northeast pile actually shows increasing levels in later weeks (Figure 6), apparently representing the acceleration of molybdenite oxidation. In any case, the leaching from the three rock samples has not yet stabilized at near-steady values, while the leaching from the three tailings samples has generally stabilized.

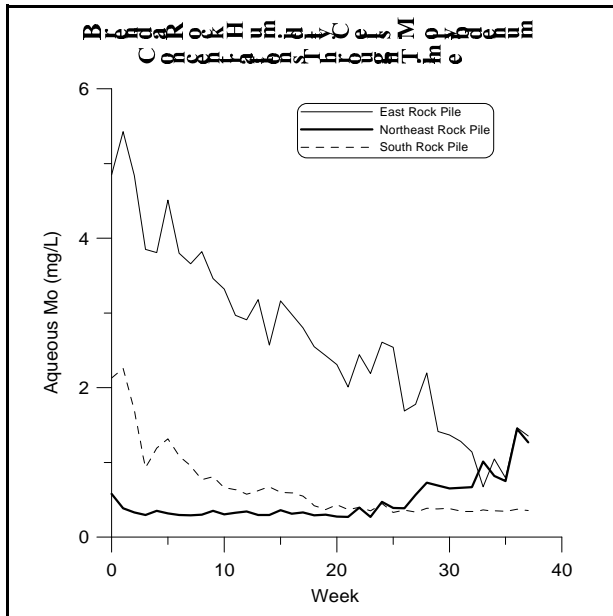
When the current cell concentrations are converted to kinetic leaching rates, the most recent five-week-average rates for the tailings span 0.064-0.16 mg of molybdenum/kg of tailings/week (mg/kg/wk), whereas the unstable last-five-week-average rates for rock span 0.17-0.49 mg/kg/wk. These kinetic rates show a general correlation with initial solid-phase molybdenum (Figure 8).

The results of the recirculating columns were plotted against the number of pore volumes during the test (Figure 9). One pore volume represents the amount of pore space in the sample, and this was estimated for the columns based on approximate specific gravity (3.0) and weight of the sample (500 g). Approximately 10 pore volumes passed through the columns each month.

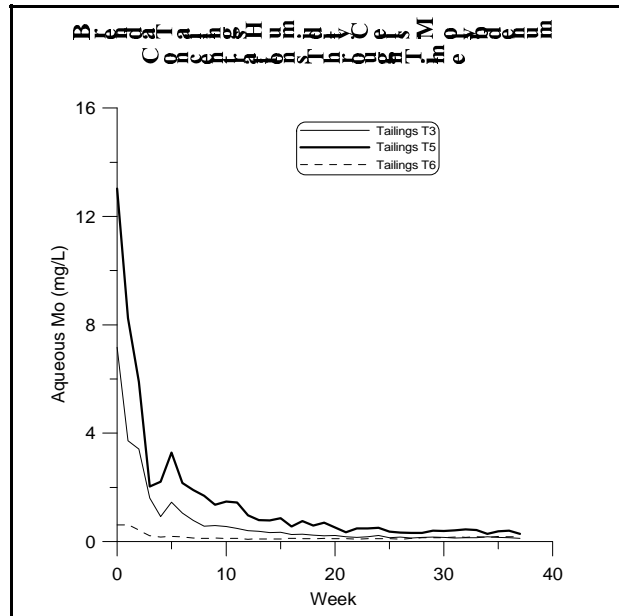
The results show that both rock columns had reached relatively stable concentrations within 30 pore volumes, although the tailings column required more than 40 pore volumes (Figure 9). The average maximum concentrations for the East, Northeast, and tailings samples were 11.5, 0.884, and 0.555 mg/L, respectively. Another important observation is that rock and tailings can produce stable, maximum concentrations within a relatively short period of time (months) and after relatively few pore volumes.

As explained above, the columns quickly reached their maximum concentrations, probably due to the fast release of accumulated, soluble molybdenum as noted in the initial weeks of the cells (Figures 6 and 7). However, even in the absence of accumulated soluble molybdenum, the kinetic production rates from the humidity cells indicate the 0.5 kg of sample in each column could release 0.13-0.98 mg Mo into the recirculating water (approximately 1 L) each month. This alone would raise aqueous concentrations to those seen in the columns within a year if water is continuously recirculated.

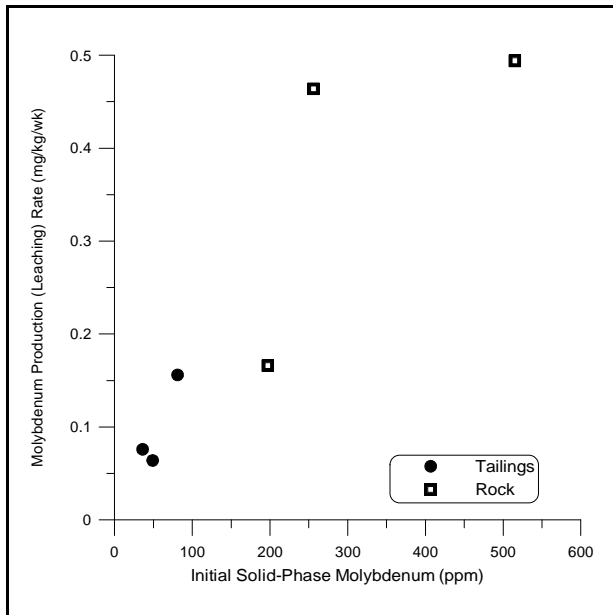
Another interesting point is that the similar maximum concentrations produced by the Northeast rock and the tailings, and the much higher maximum concentration from the East rock cannot be explained



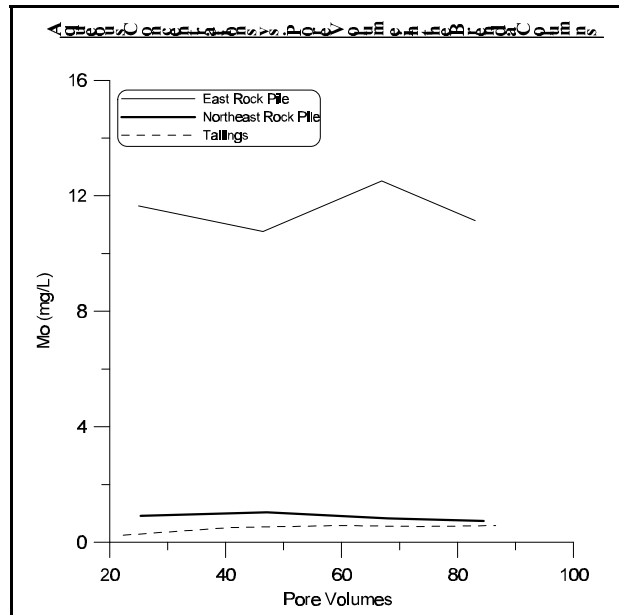
**FIGURE 6. Trend of Aqueous Molybdenum Concentrations from the Brenda Humidity Cells Containing Rock.**



**FIGURE 7. Trend of Aqueous Molybdenum Concentrations from the Brenda Humidity Cells Containing Tailings.**



**FIGURE 8. Scatterplot of Initial Solid-Phase Molybdenum and Production Rates from the Brenda Humidity Cells.**



**FIGURE 9. Molybdenum Concentrations in the Recirculating Columns vs. Pore Volume.**

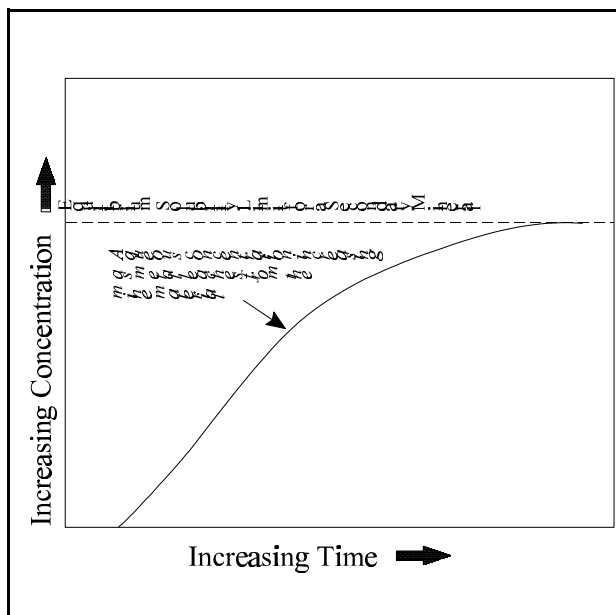
by the initial amount of molybdenum in the samples (Table 1), because the two rock samples differ by only a factor of two, and the tailings sample differs from the similar-leaching Northeast rock by a factor of seven. As a result, there is some major influence on molybdenum concentrations other than initial amount of molybdenum and material type. This is also shown by the tailings column producing less than 0.6 mg/L, whereas the tailings pond currently contains around 3 mg/L (Figure 5). This control is discussed in the following section.

## **GEOCHEMICAL CONTROLS ON MOLYBDENUM LEACHING AT BRENDA**

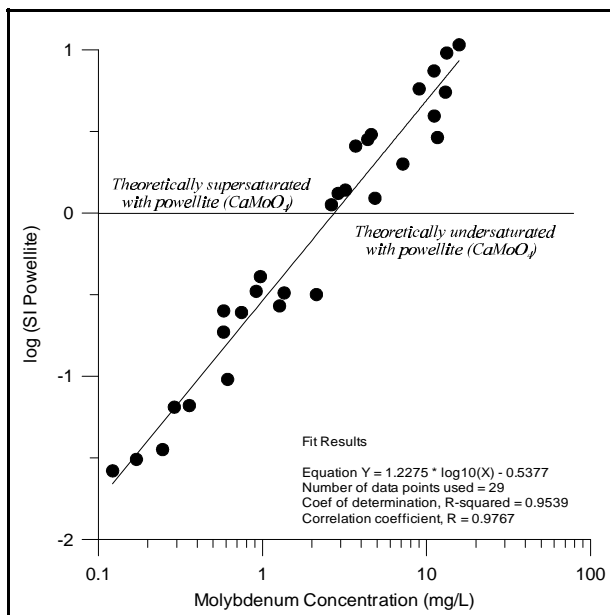
The kinetic tests discussed above indicate the rock and tailings typically retain some soluble molybdenum, likely as a secondary mineral. If this mineral could be identified and aqueous molybdenum were controlled by its rapid precipitation and dissolution, then aqueous concentrations would not be strongly influenced by other factors like flow rates and residence times (Figure 10). In other words, aqueous concentrations would be relatively constant and predictable under such “equilibrium” conditions. The recirculating columns (Figure 9) show that there is some control that establishes a maximum concentration in a relatively short period of time at Brenda, although the kinetic tests and the decades of field monitoring fail to reveal a constant maximum level through time or at one location (Morin and Hutt, 1998).

Geochemical “speciation” computer programs calculate the theoretical concentrations of aqueous complexes and then compare aqueous concentrations to known solubilities of various minerals. If concentrations from several samples are close to the solubility limit of a particular mineral, a reasonable conclusion is that the solubility of this mineral is the primary control on aqueous concentrations. The comparison of a water sample to a mineral’s solubility is often expressed as a Saturation Index (SI), where the  $\log_{10}(\text{SI}) = 0$  means the water sample is exactly at the mineral’s solubility limit. A  $\log(\text{SI})$  value  $< 0$  means the water is undersaturated with respect to the mineral and can dissolve more of it if present. Conversely, a  $\log_{10}(\text{SI}) > 0$  indicates the water is supersaturated and the mineral should precipitate from the water. In reality, the solubilities of many minerals are variable from minesite to minesite (Morin and Hutt, 1997). As a result, a perfect match to  $\log(\text{SI})=0$  is rarely attained, and empirical site-specific solubility values such as  $\log(\text{SI})=-0.25$  or  $\log(\text{SI})=+0.80$  can sometimes be determined using on-site monitoring data (resembling Figure 10), although this did not work for molybdenum at Brenda.

A well known speciation program, freely available from the U.S. EPA, is MINTEQA2 (Allison et al., 1990). Like most programs, MINTEQA2 does not contain molybdenum because of the general lack of a consistent thermodynamic database, but does allow the addition of metals if such data becomes available.



**FIGURE 10. Schematic Diagram of Aqueous Concentrations Limited by the Equilibrium Solubility of a Secondary Mineral.**



**FIGURE 11. Scatterplot of Log10 (Saturation Index of Powellite) and Corresponding Molybdenum Concentrations in Selected On-Site Monitoring Data and Kinetic Tests.**

In 1999, Meima and Comans (1999) presented a molybdenum database that included various aqueous complexes and various molybdenum minerals like powellite ( $\text{CaMoO}_4$ ), wulfenite ( $\text{PbMoO}_4$ ),  $\text{CuMoO}_4$ , and  $\text{ZnMoO}_4$ . This database was added to MINTEQA2, then selected samples from the on-site monitoring database and from the kinetic tests were entered into the program.

The only molybdenum mineral close to equilibrium was powellite. However, relatively large  $\log(\text{SI Powellite})$  values, above and below the theoretical  $\text{SI}=0$  line, were obtained. Moreover, a comparison of  $\log(\text{SI Powellite})$  to aqueous molybdenum showed a good correlation (Figure 11), meaning that powellite was not controlling molybdenum concentrations as depicted in Figure 10. In fact, the correlation in Figure 11 is similar to one expected for simple dilution. However, the slope in Figure 11 is somewhat greater than 1.0, indicating the  $\log(\text{SI})$  value is decreasing proportionally faster than molybdenum, because of a decrease in calcium concentrations (not shown).

## CONCLUSION

As a result, a reliable and consistent geochemical control on aqueous molybdenum at Brenda has not

been identified, although the recirculating columns show there is some limiting mechanism that varies with sample. The on-site monitoring also shows that concentrations can vary widely with location and time. Therefore, the primary conclusion remains that molybdenum at Brenda is controlled primarily by kinetic factors, like time and flow rate, but there is some as-yet unidentified process that limits maximum concentrations on a local scale.

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