Molybdenum Treatment at Brenda Mines

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ABSTRACT

Brenda Mines, located 22 km Northwest of Peachland in British Columbia, Canada was an open pit copper-molybdenum mine which closed in 1990 after 20 years of operation. The primary concern in Brenda's tailings and waste rock drainage is molybdenum at a concentration of approximately 3 mg/L. The mine drainage is alkaline and contains little or none of the typically problematic heavy metals. Given that the waters downstream are used for municipal water supply and some irrigation, a discharge limit of 0.25 mg/L molybdenum was imposed with specific water quality guidelines in the receiving creek. A review of all existing and potential molybdenum removal methods was undertaken prior to mine closure. The chosen process is a two-step iron co-precipitation with clarification and sand filtration at a slightly acidic pH. A 4,000 usgpm (912 m^3/h) treatment plant was constructed and commissioned in 1998, at a cost of $10.5M. The successful removal of molybdenum from the drainage water is explained with details on some design innovations and operational challenges encountered during plant start-up. Investigated sludge disposal options are discussed although the long term disposal scenario has not yet been finalised.

INTRODUCTION

The Brenda copper molybdenum mine site is situated in the southern interior British Columbia, approximately 22 km from the municipality of Peachland. The mine was brought into production in 1970 and was officially closed in June 1990, due to a depleted ore reserve. Noranda Inc. assumed 100% ownership of Brenda in 1996.

Site reclamation activities began in 1988. This included aerial seeding and fertilisation, and irrigation of newly planted areas. From closure in 1990 to 1998, all precipitation from the affected site area was collected and stored in the open pit or tailings pond. Options were evaluated for disposal of this water. Also required were studies of drainage patterns, seismic stability of the dams, aquatic species, plants, forage crops and trees.

Two committees provided guidance during the evaluation: a Technical Committee of government representatives and a Public Surveillance Committee with local residents. A detailed closure plan was in place by 1993 and an amended Ministry of Environment permit to discharge was issued first in 1997 and then with further requirements in 1998 and 1999. Between 1990 and 1997, $38 million were spent on site closure and reclamation activities. The treatment plant was constructed and commissioned in 1998.

Closure Facts:
• Closure and reclamation expenditures
(1990 - 1997) $38 million

Water Treatment Plant
• Construction costs $10.5 million
• Annual operating costs $1.5 million (estimated)

Tailings Pond
• Water Surface   87 hectares
• Depth   3 to 4 meters

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Open Pit
- Diameter   914 meters
- Volume of water   40 million cubic meters

Authorised Discharge

Discharge of treated water will occur between October and June. The maximum authorised rate of discharge is 6,000,000 cubic meters per calendar year, and the anticipated average annual rate of discharge is approximately 3,100,000 cubic meters per year. These numbers are based on the maximum and typical amounts of rain and snow runoff on the site. Discharge is not to exceed the following concentrations at point of discharge from the plant:

dissolved copper	0.03 mg/L
total iron	0.30 mg/L
dissolved manganese	0.10 mg/L
dissolved molybdenum	0.25 mg/L
dissolved zinc	0.20 mg/L
total dissolved solids	950 mg/L
total nitrogen	3.0 mg/L
pH	6.5 - 8.5 units
total phosphate	0.10 mg/L
dissolved sodium	100 mg/L
dissolved sulphates	500 mg/L
total suspended solids	15 mg/L

As the downstream waters are used as a municipal water supply for Peachland, BC, Brenda also has some in-stream concentration limits. They must not exceed an average monthly concentration of 0.03 mg/L Mo dissolved with a maximum concentration of 0.06 mg/L single sample at the municipal intake. As the drinking water guidelines for BC are of 0.25 mg/L Mo, these limits are considerably lower than what is considered potentially harmful for human consumption.

EVALUATED OPTIONS FOR TREATMENT

Every technology identified, whether only theoretical or applied, was evaluated to treat and release the site drainage waters. Molybdenum treatment was not widely applied and no existing process was known for treatment of similar concentrations and flowrates. Iron co-precipitation/adsorption, ion exchange, reverse osmosis, electrodialysis, solvent extraction, sulphide precipitation, biological sulphate reduction, and biosorption were all investigated. The most promising technologies were brought to laboratory-scale evaluations, then pilot-scale testing.

Studies were also carried out to investigate the use of aquatic communities for bioaccumulating the Mo in-situ. The establishment of a thriving aquatic ecosystem and a significant plant cover in the tailings was accomplished within 3 years (St-Germain et al. 1997). Although a significant improvement was measured in some cases, natural bioaccumulation was not sufficient to produce an acceptable effluent.

The only process which showed consistent results and economic feasibility was iron co-precipitation. An iron co-precipitation process was originally developed for removal of molybdenum and antimony at Battle Mountain Golden Giant in the early eighties. The Brenda flowsheet is based on this work. Many laboratory tests and pilot programs were initiated to define the operating process parameters such as ferric concentration and pH. One of the bench-scale campaigns were performed at Noranda Inc., Technology Centre (NTC) in 1996.

NTC Molybdenum Removal Tests

Twenty seven bench tests were performed in the fall of 1996. Iron addition rates ranged from 5 to 100 mg/L. Treatment pH ranged from 4 to 6, with subsequent neutralisation up to pH 7 in certain tests. As some of the process equipment was to be constructed of steel, and steel corrosion rates increase exponentially below pH 4, no tests were conducted below that threshold. According to previous tests, the Mo removal was just as efficient at pH values between 3.5 and 4.0.

As Brenda Mines' Mo limit was 0.25 mg/L, a 0.15 mg/L maximum concentration was a defined as a successful test in the laboratory. The raw water contained approximately 2.7 mg/L Mo. The testing method involved adding the required mass of ferric sulphate to the raw water, stirring for 3 minutes, then controlling the pH to the desired setpoint with sulphuric acid. After three minutes, the solids were allowed to decant and

a sample was taken to evaluate the Mo removal efficiency. Some tests were conducted without acidification and others combined the two steps into one. Figure 1 summarises the laboratory evaluation results.

To obtain a minimum of 0.15 mg/L, 15 mg of Fe per litre was required. This could be accomplished with pH values of up to 5.5. With higher concentrations of Fe, lower concentrations of Mo resulted, until about 25 mg/L. At and above 25 mg/L Fe addition, the detection limit of 0.05 was attained at pH values of up to 5.0. Between pH 5.0 and 5.5, the Mo concentration remained in the range of 0.05 to 0.15 mg/L. It should also be noted that Fe addition rates of 50 mg/L or more caused the pH to decrease below 4.0, undesirable due to steel corrosion rates as previously mentioned. Such high concentrations of Fe would therefore require pH adjustment with an alkali as opposed to an acid.
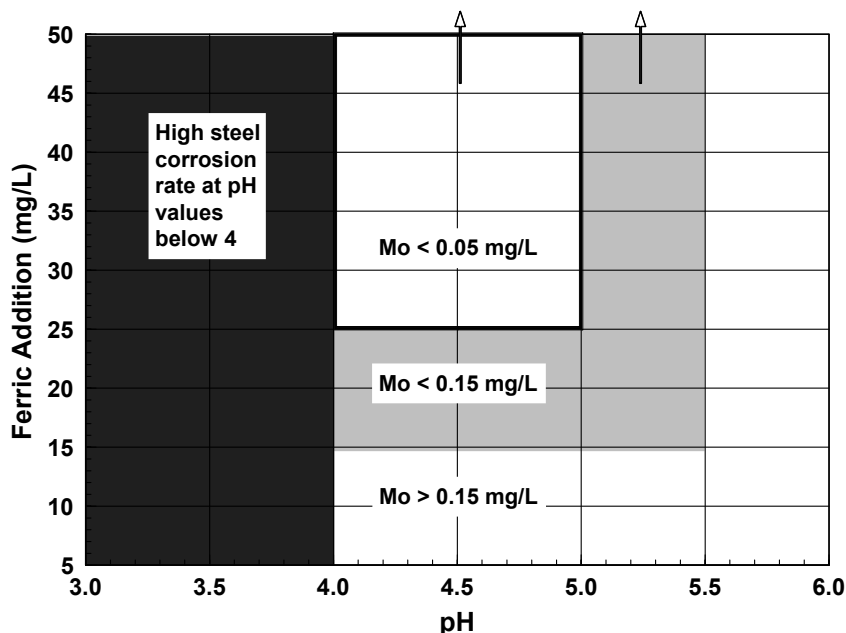

**Figure 1 Iron addition and pH range for molybdenum removal.**

The bench scale results suggest that to treat 2.7 mg/L, a minimum of 15 mg/L Fe are needed and the pH must be lower than 5.5. If 25 mg/L Fe is added, the resulting Mo concentration was below the detection limit of 0.05 mg/L. This suggests a mass ratio (mg Fe/mg Mo) of approximately 5.5 would meet 0.15 mg/L Mo in the effluent. To decrease the final Mo concentration to its' minimum, a mass ratio of 9 or 10 would be required.

Following precipitation of ferric hydroxides, caustic was used in a number of tests to increase the pH. When the sludge pH was increased, the Mo invariably re-mobilised. This suggests that the Mo is only loosely attached to the precipitates, as is often the case with adsorption. Molybdenum chemistry is not very well known and some solid complexes may form (Cotton and Wilkinson, 1967), but these may be slower processes not necessarily occurring in the treatment plant. The treatment process is generally referred to as co-precipitation though this may not be the case.

TREATMENT PROCESS DESCRIPTION
The Brenda Water Treatment Plant (WTP) uses the best available technology for Mo removal from a wastewater stream. This is a ferric co-precipitation process with two stages of pH adjustment and three levels of polishing for removal of suspended solids. The process is shown in Figure 2. The raw water is pumped into the first reactor, where a ferric sulphate solution is added. In the second reactor, sulphuric acid is used to control pH near 4.5, the optimum for stabilisation of Mo on ferric hydroxide precipitates. A reactor-clarifier is then used for contacting the fresh precipitates with a flocculant for improved settling of these solids. Sand filtration virtually eliminates all solids from the treated water stream. The filtered water is essentially free of Mo, but must be neutralised to meet the minimum pH requirement of 6.5. A polishing pond (not shown) follows the final pH adjustment to allow settling of any precipitates resulting from the alkali addition.

Apart from the raw water feed, all flows in the process are by gravity. The two process reactors are elevated in order to cascade down to the clarifier. Polymer addition is done in-line just following the overflow from Reactor 2. The clarifier itself was built on the side of a small hill in order to keep it well above the sand filters. The flow to and out of the polishing pond is also by gravity.
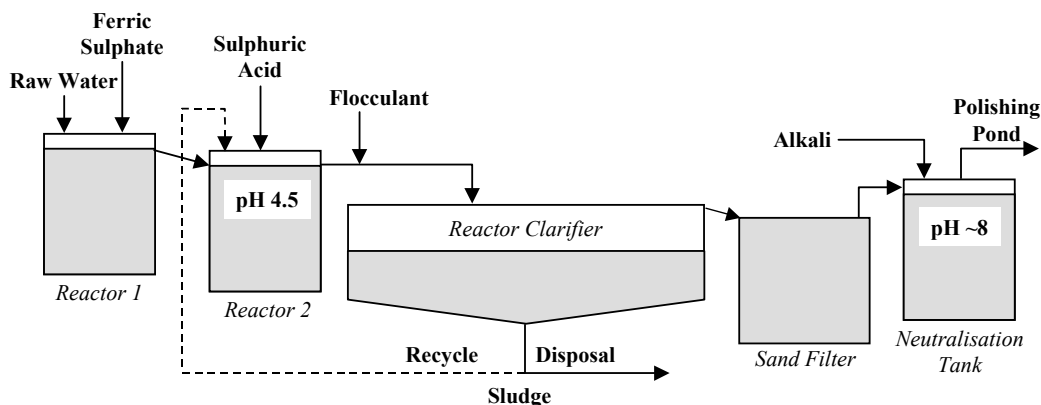
Figure 2 Brenda water treatment process flowsheet.

The Brenda WTP is highly automated. It is controlled by a programmable logic controller (PLC), which maintains the desired pH and reagent addition throughout the plant. Most important is an alarming system which can stop the plant should a risk of discharging a non-compliant effluent occur. During day shifts, when operators are on-site, an alarm must be acknowledged by an operator, and corrected quickly. At night, all alarms are communicated to the designated operator via a call-out system. The computer automatically calls the operator in charge, who can then communicate to the plant electronically and verify the problem. The operators have full access to the plant and can change setpoints or pumps remotely from their home.

Raw Water

The raw water is fed to the WTP either from the tailings pond or the open pit. Both water bodies contain Mo at concentrations of about 3 mg/L. The tailings is now a thriving ecosystem with a wide variety of plant species and insects. The pit contains simply collected water and no significant biota. The pH of both water sources is slightly alkaline, varying essentially from about 7.8 to 8.3. All the affected precipitation as rainfall and snowmelt is collected in these ponds at a rate of about 3.1 million cubic metres per year.

The Mo issues mainly from waste rock piles located around the periphery of the pit. The rock drainage is mostly collected by gravity into the pit, with a smaller fraction of this reporting to the tailings. Extensive water management works have minimised the amount of precipitation affected by Mo mobilisation. This serves to ensure a constant flow of clean water downstream while minimising the volume of water to be treated. The downstream flow is important for irrigation and municipal water supply, particularly during periods of drought.

Process Reactors

Both reactors have a residence time of approximately 3 minutes at full flowrate. This retention is sufficient for precipitation of ferric hydroxides and adsorption of molybdenum. The pH is measured in both reactors but controlled only in Reactor 2. The Reactor 1 pH is used simply as an indicator of process performance as the ferric hydroxide precipitation will decrease the pH to about 5.5 at a Fe:Mo ratio of 10:1. When the ferric addition ratio is decreased to 9:1, the pH is closer to 5.9. A significant change in ferric sulphate addition rate will therefore be shown by the pH and will cause a process alarm which must be acknowledged and corrected by an operator.

The iron is already precipitated as it overflows to the second reactor but the Mo is not entirely removed from solution. The pH is decreased to 4.5 or 5.0 in the second reactor by controlled addition of sulphuric acid. At this point, the Mo is removed from solution and included in the solids fraction. A sludge recycle can also be added to Reactor 2 to help solids settling. The recycle was used only sporadically in the first year of operation, in an attempt to improve the clarifier overflow quality. It did not appear to make any difference in process performance, whether positive or negative.

Sand Filtration

The sand filters consist of two banks each with three cells. These are dual-media filtration beds with anthracite filtration followed by sand. The anthracite captures the larger particles and allows for longer operation without plugging or agglomeration of the finer sand media. The media is cleaned by backwashing as explained in the following paragraph.

Each sand filter bank has a reservoir of filtered water maintained over top for backwashing. The backwash can be triggered in one of three ways: 1) manually, 2) on back-pressure, and 3) on a time-delay. Whenever a backwash is triggered, the sequence starts at the first cell and backwashes all three cells of that bank. The backwash, containing mostly ferric hydroxides with some adsorbed Mo, flows by gravity down to the tailings pond. A "backwash sludge pond" captures most of the solids and allows settling before the water reaches the pond. This is essentially treated water returned to the raw water. A capture sump to recycle the backwash may be implemented in the future.

Neutralisation Tank

Following the overflow from the sand filtration banks, the clarified effluent is essentially free of Mo, but the pH is too low for direct discharge. Also, some residual iron may still be dissolved in the water. For these reasons, the pH is increased by alkali addition in a small Neutralisation Reactor. At start-up, caustic (NaOH) was used for neutralisation. Caustic had been proposed as lime is known, in some cases, to cause precipitates which can result in high suspended solids.

Polishing Pond

The polishing pond was designed for a residence time of approximately 6 days prior to release. It is used to equilibrate the plant effluent and allow for settling of any precipitates which may form due to the final neutralisation. In the bottom of the polishing pond is a drain pipe which can be used to divert the effluent if ever the water within the pond did not meet the required discharge limits. This pipe can also be used to partially drain the pond, thereby removing accumulated solids. Draining the pond can also be useful for maintenance or verification purposes.

At the pond overflow, a flume-house was installed to measure the discharge flowrate. The pH and turbidity are measured continuously. All measured parameters are communicated back to the WTP and included in the PLC input. This allows for historical data logging, trending, and most importantly alarming. Problems with flows or pH will be known almost instantly by the operator.

PLANT START-UP

At plant start-up in the fall of 1998, the pre-determined optimal parameters were used to ensure proper Mo treatment. The Fe addition was set to a mass ratio of 10 and the pH in Reactor 2 was set to 4.5. This put the process in a range defined to minimise the final Mo concentration, not the reagent consumption.

At start-up of the WTP, the Mo concentration limit was easily met but iron was a little more difficult. Apparently, a small fraction of the iron added as ferric was partially reducing to ferrous iron in the process. With approximately 30 mg/L added, and a 0.3 mg/L limit, only 1% of ferric iron reduction was sufficient to cause difficulty in meeting the final effluent discharge criteria.

The caustic addition in the neutralisation tank was used to bring the pH up to 9.0 in an attempt to precipitate the iron. Unfortunately, even though the iron did precipitate, it did not settle in the polishing pond. The particles formed from 0.3 or 0.4 mg/L iron were very small and did do not agglomerate well. The precipitates were simply making it through the polishing pond and reported as total iron in the overflow.

Lime was then attempted to partially replace the caustic solution. The result was that the Ca from the lime, which is a natural coagulant, affected the surface chemistry of the fresh precipitates and enhanced the agglomeration and settling. With lime used as the alkali, the iron limit can be met consistently. Iron concentrations in the final effluent have been in the order of 0.15 mg/L since the change to lime.

The feared suspended solids problem with lime did not occur because the precipitates likely to form at some other plants are not as likely to form here. There are two precipitates which can form when using lime: gypsum ($CaSO_4 \cdot 2H_2O$) and calcium carbonate ($CaCO_3$). In practice, gypsum will form when the sulphate concentrations are above 2,000 mg/L. This is a very slow precipitation reaction and gypsum formation is low even in some super-saturated solutions. At Brenda, where the sulphate concentrations do not exceed 350 mg/L, significant gypsum formation is not likely to occur.

Calcium carbonate formation occurs readily at alkaline pH, when the Ca and carbonate concentrations are sufficiently high. During a sampling campaign in May 1999, the Ca concentration from the pit water was near 80 mg/L while the treated plant effluent contained just over 90 mg/L. The tailings pond water is known to have up to 120 mg/L Ca concentrations. At high pH, some calcium carbonate precipitation is possible at these concentrations. In Brenda's case, by the time the effluent reaches the polishing pond overflow, the pH is

usually below 8 and very little carbonate precipitation is expected a that pH. Even with lime addition, the total suspended solids of the final effluent was in the order of 1 mg/L, well below the limit of 15 mg/L.

After more than one full operating season, it is clear that the Brenda water treatment plant is very successful. Iron concentrations are well under control with the use of lime, and the molybdenum concentrations have been consistently below 0.05 mg/L, five times lower than the regulated limit. All other regulated parameters have also been easily met.

SLUDGE DISPOSAL

Sludge samples were collected at the beginning of 1999 and sent to Noranda Inc. Technology Centre for investigation. The sludge was found to contain approximately 44% iron and 5% molybdenum. Minor components of the sludge solids include some inorganic carbon, organic carbon, and sulphur. Other components were at concentrations of less than 0.5%, including Al, Si and Ca, at concentrations of 0.1 to 0.3%. The regulated metals, Cu, Mn and Zn, were all at concentrations of less than 0.005% in the sludge.

Disposal Options and Test Results

The preferred option for sludge was the recovery of Mo, but no facility was identified to accept a high water content, high iron content sludge with 5% molybdenum. Sending the sludge to a disposal site was also considered but this required high costs and included the risk of transporting a watery sludge on public roads. The preferred option was therefore to find a means of stabilising the sludge and storing it on-site where risks could be minimised. The slightest chance of Mo re-mobilisation will be contained and treated by keeping the sludge within the collected watershed of Brenda Mines.

Tests were conducted to evaluate several disposal options for Brenda Mines WTP sludge. It was found that the Mo remained stable when the sludge was disposed under normal atmospheric conditions. Freeze-thaw testing showed that the sludge density could be significantly increased without affecting the chemistry of the sludge. De-ionised water at a slightly acidic pH was used to simulate precipitation on samples of sludge in small columns. The pH of this water was similar to that of expected local precipitation. After 10 weeks, the samples were centrifuged to collect the porewater and measure the dissolved metal concentrations. Iron concentrations remained below 1 mg/L and molybdenum was below the detection limit (0.05 mg/L) for duplicate tests.

Encapsulation also maintained the stability of the sludge. The idea behind encapsulation was the possible disposal of sludge-filled membranes in the open pit. Unfortunately, tearing of the membranes would re-mobilise the Mo due to the high pH of the pit water. Encapsulation and burial was considered as an alternative, but the ground water also has a pH at or above neutral. The risk of re-mobilisation should a membrane fail led to the elimination of this option.

Fixation using cement was found to mobilise the Mo due to the high pH of such binders, leading to the immediate elimination of this option.

Storage under reducing conditions using an organic cover was also tested. The idea behind this option was that by storing the sludge under reducing conditions, it was hoped that sulphate reduction would form sulphides and Mo could re-precipitate as a molybdenite (MoS_2). Unfortunately, reducing conditions caused the ferric iron to reduce to ferrous iron and dissolved the sludge prior to formation of sulphides. By dissolving the ferric hydroxide sludge, the Mo was mobilised. This option is therefore not viable, as a risk of actively mobilising the Mo exists.

The most promising scenario is ponding over a sand bed to allow drainage of interstitial waters. Since both freeze-thaw and subaerial deposition maintained the Mo stability, this is considered a safe long term disposal scenario. The porewater collected from sludge exposed to these conditions did not contain any measurable concentrations of Mo. This suggests that drainage water filtered through a sand bed would meet discharge criteria for Mo. This option has the additional advantage of further densifying the sludge through 1) drainage, 2) evaporation, and 3) freeze-thaw. Densification reduces storage volume in the long term thereby minimising the footprint and the long-term risk of re-mobilisation (Aubé and Zinck, 1999).

CONCLUSIONS

The Brenda water treatment plant has successfully treated molybdenum from site drainage since start-up in October 1998. Among the lessons learned since start-up are:

1 - Iron co-precipitation combined with sand filtration can consistently bring molybdenum concentrations to less than 0.05 mg/L.

2 - Low concentrations of iron (<0.5 mg/L) in the plant effluent can be treated with lime prior to polishing in a large pond. If caustic is used alone for neutralisation of the effluent waters, settling of the minuscule precipitates may be difficult. The calcium from lime apparently acts as a coagulant to enhance the settling properties of iron hydroxides.

3 - The sludge formed from the process is essentially stable when exposed to atmospheric conditions, such as in a pond with a sand bed for enhanced draining.

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