THE POTENTIAL EFFECTS OF ALKALINE MILL EFFLUENT ON TAILINGS MANAGEMENT FACILITY WATER QUALITY AND IMPLICATIONS FOR CLOSURE

S. Nowicki, BSc.1
S. Jensen, PEng2

1Staff Geochemistry Consultant, SRK Consulting, Vancouver, Canada.
2Senior Environmental Engineering Consultant, SRK Consulting, Vancouver, Canada.

ABSTRACT
Lime is commonly used as a depressant for flotation of non-ferrous ore such as molybdenum and copper. Addition of lime during the flotation process increases the alkalinity and pH of mill effluent, consequently reducing dissolved concentrations of some metals such as cadmium, copper, manganese, nickel, lead, and zinc by metal hydroxide precipitation and co-precipitation. This process is also the basis of lime treatment, which is the most common type of treatment for mine-influenced water. Bench scale tests showed that lime addition in the mill circuit can reduce concentrations of cadmium in tailings slurry and supernatant. The tests indicate that co-precipitation and adsorption interactions are critically important in this system. This is further supported by water quality data from an operating mine site. Neglecting to account for metal hydroxide formation, co-precipitation, and adsorption interactions enabled by cycling water through the mill can cause model predictions for the operations period to overestimate dissolved concentrations of some constituents in tailings management facilities (TMFs). Similarly, using operations phase TMF water quality to inform post-closure predictions could result in underestimation of dissolved concentrations since improvements in TMF water quality due to the mill process are unlikely to persist after closure.

KEY WORDS
tailings management facility, water quality, post-closure mine water quality, water treatment, acid generation, mine closure, mineral processing, flotation, tailings

INTRODUCTION
Most base metal, precious metal, coal, uranium, and diamond mines excavate large quantities of geologic materials, the drainage from which often has concentrations of metals and other elements exceeding permissible effluent standards (Price 2009). Predicting the chemistry of this drainage enables proactive mitigation measures and environmentally sound, cost-effective management of mine water. Successful mine water quality predictions must account for all relevant mine components. Tailings management facilities (TMFs) are particularly important because, in addition to storing tailings and mill effluent, they are often used to consolidate
drainage from other mine components such as waste rock dumps and open pits (Figure 1). Often water from the TMF is reclaimed as process water for the mill.

Figure 1 Typical role of a tailings management facility in relation to other mine components.

In flotation circuits for non-ferrous ores such as molybdenum and copper, lime is commonly used as a depressant (settling aid) to separate the valuable minerals from the gangue. Lime addition increases alkalinity and pH, consequently reducing concentrations of pH sensitive multivalent metals ions such as cadmium, copper, manganese, nickel, lead, and zinc through hydroxide precipitation and co-precipitation. This effect is well-known and is the basis of lime treatment, commonly used for mine-influenced water. In addition to precipitation and co-precipitation of hydroxides, adsorption onto mineral surfaces may also reduce dissolved concentrations of some constituents in mill effluent.

This paper discusses bench scale laboratory tests as well as a mine-site case study that indicate how lime addition in the mill flotation circuit substantially impacts TMF water quality. The chosen examples demonstrate the importance of considering the mill process when predicting TMF water quality. Neglecting to account for the effect of cycling TMF water through the mill can cause model predictions for the operations period to overestimate dissolved concentrations of constituents in the TMF. However, the improvement in TMF water quality is unlikely to persist after closure. Inflow to the TMF from various site components will continue and, without continuous cycling of water through the mill, operations phase water quality will not be
maintained. The change in water quality will be strongly dependent on the characteristics of the inflow as well as the long term geochemical stability of constituents within the TMF.

**COMPARING HIGH DENSITY SLUDGE AND MINERAL FLOTATION PROCESSES**

The solubility of many metal ions that are present in acidic, mine-influenced waters (e.g. cadmium, copper, iron, nickel, lead, and zinc) is a function of pH. These ions precipitate out of solution when pH increases in various optimum ranges (US EPA 1983). Figure 2 shows how solubility of these common metals varies with changing pH. Dissolved cadmium concentrations, for example, decrease as pH increases from 8 towards 11.

![Figure 2 Solubility of common metal ions as a function of solution pH (Hoffland 2012).](image)

These relationships between pH and solubility of various metal ions are very useful for water treatment applications. Based on consideration of effectiveness, cost, and ease of operation, the most common treatment method for mine waters is addition of lime to increase pH and concurrently decrease dissolved concentrations of a broad spectrum of metals by hydroxide precipitation (Lou et al. 1992; Tunay and Kabdasli 1994). A broad spectrum of metals can be removed because co-precipitation can result in residual metal solubilities lower than what could be achieved by precipitating each metal individually at its optimum pH (US EPA 1980).

There are five basic steps in lime addition treatment, as outlined in the EPA Design Manual for Neutralization of Acid Mine Drainage (1983):
1) Equalization – large holding basins are used to equalize flow and quality of influent to the treatment system with the objective of simplifying controls and operator attendance.

2) Neutralization – lime is mixed into the water to raise the pH.

3) Aeration – ferrous iron (Fe^{2+}) is oxidized to ferric iron (Fe^{3+}), which is the less soluble form. Minimum solubility for Fe^{2+} is between pH 9 and 12 whereas Fe^{3+} begins to precipitate as iron hydroxide around pH 4 with minimum solubility around pH 8. The key reactions are:

\[
\begin{align*}
Fe^{2+} + \frac{1}{2}O_2 + H^+ & \leftrightarrow Fe^{3+} + \frac{1}{2}H_2O \\
Fe^{3+} + 3H_2O & \leftrightarrow Fe(OH)_3 + 3H^+
\end{align*}
\]

4) Sedimentation – holding basins are used to settle out precipitated metal hydroxides and other suspended particles.

5) Sludge recirculation and disposal – a proportion of the treatment sludge is recirculated and the remainder is disposed of in various different ways depending on the site.

The recirculation of sludge from Step 5 is a variation on conventional lime treatment that was developed in 1970 and is referred to as the High Density Sludge (HDS) process. Recirculating the sludge achieves better reactivity of lime and produces smaller volumes of sludge with higher solid metal hydroxide content. This is because the recirculated solids act as nucleation sites for precipitation reactions. Continuous recirculation creates increasingly large metal hydroxide particles. The ideal ratio of sludge recirculated to disposed is between 20:1 and 30:1 (US EPA 1983). The recirculated sludge is returned to the reactor where the lime is added (Figure 3).

Figure 3 High Density Sludge (HDS) lime addition treatment process.
There are several functional similarities between the HDS process and the mineral flotation process that is used to extract valuable non-ferrous minerals from ore. Lime can be added to mill process water as a modifier. It has the obvious effect of increasing pH and can be useful for dispersion and depression of certain gangue minerals including pyrite. Of course, as in the HDS process, addition of lime in the flotation circuit also causes precipitation of multivalent metal ions as hydroxides (SME 2007).

The third step of the HDS process, aeration, also occurs in the mineral flotation process – the ore slurry is vigorously agitated after lime addition when pH is elevated. The primary solids separation step in both processes is gravity settling. Although sludge is not recirculated in the same way in the mineral flotation process, the mineral solids present in the ore slurry may act as nucleation sites for metal precipitation; essentially serving the same purpose as the recirculated sludge in the HDS process.

**BENCHMARK TESTING**

Bench scale laboratory tests from the Kitsault molybdenum project in British Columbia provide an example of how lime addition in the mill flotation circuit can substantially impact mill effluent water quality. The tests were conducted on tailings slurry and supernatant samples obtained from Kitsault’s metallurgical pilot plant. The purpose of the testing was to establish (1) how effectively lime addition in the mill flotation circuit removes dissolved metals, and (2) whether use of sulphide reagent to further reduce dissolved concentrations by precipitating metal sulphides is necessary as an additional treatment step to meet effluent water quality standards. The focus of the bench-scale testing was dissolved cadmium concentrations, which are required to be very low in order to meet water quality standards downstream of the TMF.

**Testing Methodology**

The testing program consisted of four sequential steps with an aliquot sampled at each step to follow the behavior of cadmium:

1) A total of 17 samples (7 slurry and 10 supernatant) were spiked with approximately 2 µg/L of dissolved cadmium. After approximately 2 hours, measurements of cadmium concentration in each sample were taken.

2) Hydrated lime (Ca\([\text{OH}_2]\)) was added to a selection of samples to reach target pHs of 9.5 or 10.5, and sodium hydrosulphide (NaHS) was added to a selection of samples (as detailed in Table 1). The samples were left to settle for approximately 2 hours and a measurement of cadmium concentration in the overlying water was taken.

3) All of the samples were passed through a 0.45 µm filter (the cut-off size for dissolved metals), which targets cadmium hydroxide (Cd\([\text{OH}_2]\)) particles, and a measurement of cadmium concentration in the filtered water was taken.
4) Finally, all of the samples were passed through a 0.1 µm filter (captures some colloidal-sized solids), which targets cadmium sulphide (CdS) particles, and a measurement of cadmium concentration in the filtered water was taken.

The pH of each sample was measured before and after cadmium was added, and after hydrated lime and/or sodium hydrosulphide was added (Table 1).

Table 1 pH Measurements from Kitsault In-Plant Water Treatment Testing.

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<th>Test No.</th>
<th>Feed Type</th>
<th>Cadmium Addition</th>
<th>Hydrated Lime Addition</th>
<th>Sodium Hydrosulphide Addition</th>
<th>pH before</th>
<th>pH after</th>
<th>Target pH</th>
<th>Ca(OH)₂ Added (mL)</th>
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Cadmium Hydroxide Formation Results

Generally, in oxic freshwater systems with circumneutral pH, cadmium occurs predominantly as dissolved cadmium (Cd²⁺) cations. At high pH, cadmium hydroxide forms and cadmium cation concentrations decrease (McGreer et al. 2012). The simple precipitation reaction for cadmium hydroxide is:

$$\text{Cd}^{2+} + 2\text{OH}^- \rightarrow \text{Cd(OH)}_2(s)$$

and the minimum solubility of Cd(OH)₂ occurs around pH 10.5 (Patterson et al. 1977; Luo et al. 1992). After passing through the 0.45 µm filter, the two samples with the highest final pHs (sample Slurry 3 had pH 10.7 and sample Supernatant 10 had pH 10.5) had the lowest concentrations of cadmium (both 0.03 µg/L) (Figure 4). The other 15 samples did not reach pHs above 10, but cadmium concentrations decreased in most of them between step 1 and step 3.
As shown in Figure 5, there were two main differences between the slurry and supernatant samples:

1) The majority of dissolved cadmium in the slurry samples was removed from solution in step 1, prior to addition of lime and/or sodium hydrosulphide. The pH values of the samples were between 7.0 and 8.1 and the cadmium concentrations ranged from 0.09 to 0.17 µg/L. These values are low compared to the supernatant samples which ranged from 1.8 to 3.5 µg/L. Dissolved cadmium concentrations are known to decrease as a result of co-precipitation and/or adsorption onto mineral surfaces (Hem 1985; McGreer et al. 2012), which are readily available in tailings slurry.

2) For the supernatant, the final cadmium concentrations in the samples that had lime added to them were approximately an order of magnitude lower than in the samples that did not. For the slurry samples, lime addition had less of an effect on cadmium concentrations. This may be due in part to the slurry samples having notably lower cadmium concentrations than the supernatant samples after step 1. Dissolved cadmium did decrease in three of the four slurry samples in steps 2 and 3 (Figure 5). The exception was sample 2, which had higher concentrations after step 3 than after step 1 – likely due to experimental error or analytical inaccuracy, which is common when concentrations are close (within a factor of 10) to the analytical detection limit (in this case 0.01 µg/L).
Cadmium Sulphide Formation

In addition to hydrated lime, sodium hydrosulphide (NaHS) was added to some of the samples in an attempt to precipitate cadmium as cadmium sulphide (CdS), which is many orders of magnitude less soluble than cadmium hydroxide (Cd(OH)₂) over a broad range of pH. Adding sulphide reagent re-solubilizes metal hydroxides by reducing dissolved metal concentrations below the equilibrium level predicted by hydroxide solubility, essentially converting metal hydroxides to metal sulphides. Metal sulphides generally form by discrete precipitation (rather than nucleation – precipitating onto already existing particles) as small particle fines and hydrated colloidal particles (US EPA 1980). Consequently, cadmium sulphides are more effectively removed by a 0.1 µm filter as opposed to a 0.45 µm filter.

For the supernatant samples that had sodium hydrosulphide added, cadmium concentrations were lower after 0.1 µm filtration, indicating that sulphide precipitation contributed substantially to removal of cadmium from solution. In the slurry samples, however, the effect of sulphide addition on dissolved cadmium concentrations was less clear. In the two slurry samples that had lime and sodium hydrosulphide added, cadmium actually increased after the sample was passed through the finer filter – likely because of analytical inaccuracy. In the two slurry samples that had only sodium hydrosulphide added, cadmium concentrations decreased overall between steps 1 and 4 but once again displayed variability indicative of analytical inaccuracy.

Figure 5 Line-plot showing slurry and supernatant sample concentrations throughout testing.
MINE SITE CASE STUDY

This case study uses water quality data from a copper mine to exemplify the effect of cycling TMF water through the mill. The primary mineral in the ore that is processed at the mine is chalcopyrite (CuFeS₂). The ore is crushed and ground before it enters the mill flotation circuit. After the first round of flotation, copper concentrate is reground and floated again to produce a final copper concentrate. All tailings and tailings supernatant are discharged into a TMF. Water from the TMF is reclaimed as process water for the mill or discharged to the environment provided that it meets discharge criteria.

The main constituent of concern for water quality at this site is copper, which occurs predominantly as cupric cations (Cu²⁺) in oxygenated waters. At above neutral pH in waters that contain dissolved carbon dioxide (CO₂) species, formation of copper hydroxides (Cu[OH]₂) and copper carbonates (CuCO₃) can decrease concentrations of Cu²⁺ to around 0.01 mg/L or less. Additionally, dissolved copper concentrations can be further reduced by co-precipitation and / or adsorption interactions (Hem 1985).

On the site, approximately 2.0 million m³ of water was allowed to accumulate in an open pit. Dissolved copper concentration in the pit water were generally above 0.01 mg/L and as high as 0.05 mg/L. In just over 4 months the accumulated water was pumped into the TMF, which contained approximately 1.8 million m³ of free water at the beginning of the 4 month period. Historically, copper concentrations in the TMF were generally between 0.001 and 0.01 mg/L.

A simple mixing model was developed to calculate the concentrations of dissolved constituents in the TMF after mixing with water from the open pit. The model assumed that the inflowing pit water was perfectly mixed with the existing free water in the TMF. Loss of free water and associated loads from the TMF, both to the underlying tailings and to the receiving environment, was taken into account. Figure 6 shows the results of the mixing model for dissolved copper and strontium along with actual measured concentrations in the TMF.

Predicted strontium concentrations were similar to actual measured strontium concentrations. Strontium was chosen because it is a conservative constituent that isn’t altered in the mill flotation circuit. It is generally unreactive and stable in dissolved form (Sr²⁺) when it occurs at low concentrations (below 10 mg/L) as it does in both the pit and TMF water (HEM 1985). At the start of the pumping period, strontium concentrations were just below 3 mg/L in the pit water and almost 5 mg/L in the TMF, accordingly the model predicted that over the pumping period concentrations in the TMF would gradually decrease to around 3.7 mg/L. The modelled concentrations closely approximated the actual concentrations measured in the TMF during the entire pumping period.

Dissolved copper concentrations were modelled in the same way that strontium was, but the actual copper concentrations measured in the TMF during the pumping period were substantially lower than what the model predicted (Figure 6). The model predicted that concentrations would
increase to just around 0.012 mg/L by the end of the 4 month pumping period, but actual concentrations remained below 0.002 mg/L.

Figure 6 Modelled and actual dissolved copper and strontium concentrations in the TMF.
When the pit water mixed with the water in the TMF, dissolved copper was removed from solution. This was not a result of simple pH-controlled copper hydroxide or copper carbonate precipitation. The optimal pH for precipitating copper out of solution is around 8 (Hoffland 2012). In the pit water, pH levels were consistently between 7.5 and 8, and the difference in pH between the pit and TMF was not substantial enough to explain the persistence of low copper concentrations in the TMF (Figure 8).

As was the case for dissolved cadmium in the slurry samples from the Kitsault bench scale testing, a likely explanation for the persistence of low copper in the TMF is co-precipitation and/or adsorption onto mineral surfaces within the tailings slurry. This process is made possible by cycling the TMF water through the mill. Additionally, the solids in the tailings slurry may have facilitated precipitation of copper and other metal hydroxides by acting as nucleation sites, as is the case with recycled sludge in HDS treatment processes.

Copper and strontium were chosen to demonstrate two different effects that a milling process may have on reclaim water – *i.e.* near-complete removal and “no effect”. The effect is not as clear for other dissolved constituents. There are other factors that affect constituent loadings and concentrations in TMF water such as ore characteristics, seasonal conditions, and operational/process changes on the mine site.
CONCLUSION

The Kitsault bench scale laboratory tests and the mine site case study discussed in this paper demonstrate that lime addition in mill flotation circuits reduces dissolved concentrations of multivalent cations, like cadmium and copper, by hydroxide precipitation and co-precipitation. It was also shown that the solids within the tailings slurry have an important role, acting as nucleation sites for precipitation and providing surfaces for adsorption.

Caution should be applied when using operational water quality data to infer post-closure water quality in a TMF. Improvement in water quality that may result from precipitation, co-precipitation, and adsorption processes facilitated by cycling TMF water through the mill, may not persist after closure even if the pH regime is not expected to change. The change in water quality will be strongly dependent on the characteristics of the inflow as well as the long term geochemical stability of constituents within the TMF. Conversely, water quality predictions for the operations phase of a mine that do not account for the effect of mill effluent may be overly conservative.

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