

SURFICIAL LIME SLURRY APPLICATION TO EXPOSED TAILINGS DURING WET CLOSURE¹

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Abstract: The wet closure of exposed tailings is a remediation technology that has been used to reduce or eliminate the toxicity and mobility of heavy metal contaminants. For constructed wet closure cells, the application of this technology is easily accomplished and chemical amendments can be readily added, as needed, to control pH and dissolved metal concentrations. As part of the Warm Springs Ponds site remediation, exposed shoreline tailings located on the southern perimeter of Pond 2 in the Active Area of the Warm Springs Ponds Operable Unit of the Silver Bow Creek/Butte Area NPL Site (Anaconda, MT), were to be wet closed. During the flooding of these tailings, Pond 2 discharge was required to meet Interim Water Quality Standards and the impact of this remediation action on aquatic life was to be minimized. To address this problem, a series of soil column studies were undertaken to evaluate the suitability of direct surficial lime additions to exposed tailings. Results of these studies indicated that lime slurry application rate of 8.96 Mg ha⁻¹ (4.0 ton/acre) would be optimal in reducing metal release into the overlying water column. Monitoring of dissolved metal concentration in Pond 2 discharge during the Pond raise showed slightly higher dissolved Cu concentrations (0.055 - 0.105 mg/L) than predicted from column studies (0.050 mg/L). Complexation of dissolved Cu with organic exudates originating from a corresponding algal bloom in Pond 2 was believed responsible for the difference. Surficial lime application to exposed tailings prior to wet closure was effective in reducing metals release from tailings into the overlying water.

Additional Key Words: Copper, Complexation Potential, Wet Closures, Algae, Exposed Tailings.

Introduction

The Warm Springs Ponds (WSP) is a large settling pond facility that was historically used to treat Silver Bow stream inflows for suspended loads originating from upstream mining and ore processing operations. The Anaconda Copper Company made the first attempt at controlling the sediment load carried into the Clark Fork River from Silver Bow Creek during the period 1918 - 1920 by building a 6.06 m (20 foot) high tailings dam on Silver Bow Creek near the town of Warm Springs, MT, effectively creating Pond 1 (Figure 1). The need for increased detention time within the Pond system

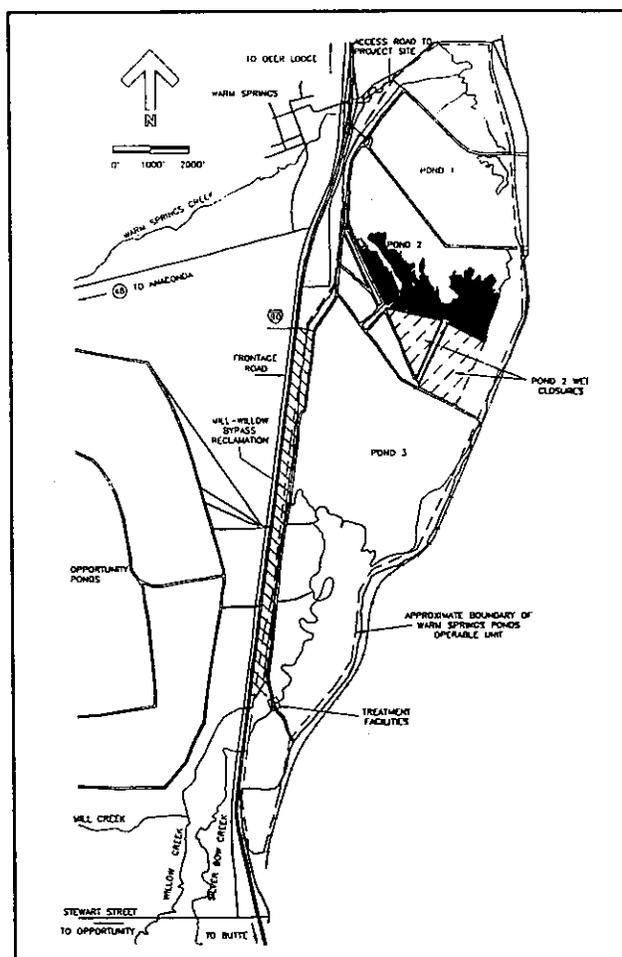


Figure 1. Site location and map for Pond 2 wet-closure study, Warm Springs Ponds. Shaded area represents exposed tailings that were wet closed.

¹Paper presented at the 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, Wyoming, June 5-8, 1995.

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necessitated the construction of additional upstream dams resulting in the formation of Pond 2 during the 1920's and Pond 3 during the period 1956 - 1959.

In 1990, an Interim Record of Decision was issued by the U.S. EPA (U.S. EPA, 1990) which outlined the preferred alternatives for remediation within the active areas of the pond system (Ponds 2 and 3). Among the selected alternatives was the wet closure of exposed tailing impoundment areas within the ponds. It is estimated that approximately 14,527,400 m³ (19,000,000 CY) of tailings, pond bottom sediments and associated soils, are contained within the Warm Springs Ponds Operable Unit.

The exposed surface tailings containing high concentrations of readily soluble copper and zinc salts were located along the Pond 2 southern shoreline and occupied approximately 16.4 ha (40.5 acres). These tailings were to be wet closed, permanently covered with water by raising the Pond 2 water level, as part of the remedial action proposed for the site. The flooding of these tailings posed several problems which included the feasibility of surficial lime application to highly compressible tailings; possible adverse impact on aquatic life in the Pond and the Clark Fork River due to dissolved metal concentrations; and the need to meet Interim Water Quality Discharge Standards during the initial Pond raise.

To address these problems, soil column studies were undertaken to evaluate the suitability of direct surficial lime slurry application to the exposed tailings and to determine the optimal lime application rate. Supplemental field studies were undertaken to evaluate the implementation of this proposed remediation and to understand the interaction of various chemical - physical - biological processes associated with the flooding process. These studies included copper metal fractionation of Total Suspended Solids (TSS) collected at the inflow and discharge stations of Pond 2 in order to determine Cu distribution among solids and the interaction of algal activity on the copper complexation potential within Pond 2.

Materials and Methods

Soil column samples were collected within the main Pond 2 area from the exposed tailings located near the southern portion of the Pond 2 (Figure 1). Intact soil columns were collected by driving 20.32 cm diameter x 91.44 cm length of PVC piping into exposed tailings to a depth of 30.48 cm. The lower edges of the soil column were leveled with the bottom edge of the piping using a stainless steel spatula and capped with a PVC end-plate. Paired soil columns were collected at nine sampling locations for a total of 27 soil columns. Nine of the soil columns were filled with 14.8 liters of Pond 3 water collected near the Pond 3 east outlet tower. Pond 3 water was added slowly down the side of the PVC column using a plastic tubing in order to minimize resuspension of the tailings. Prior to the addition of Pond 3 water to the soil columns, an aliquot of Pond 3 water was collected and analyzed for the parameters listed below. These columns were monitored for pH every 15 minutes for the first 4 hours and then at increasing time intervals for a 12 hour study period, during which time water samples were collected and analyzed for selected ions. Solution pH, however, was measured for a 48 hour period. Cations analyzed included total and dissolved Cu, Zn, Fe, Ca, Mg, Na, and K, and were determined using ICP. Anions analyzed included Cl, orthophosphate, sulfate and nitrate and were determined using colorimetric methods of analysis on a Alpkem Autoanalyzer. In addition, alkalinity was also determined for the supernatants.

A second set of nine soil columns were flooded as described above and the water was allowed to equilibrate 5 minutes (0.083 hours), after which time the solution pH was measured. The solution pH was adjusted to 9.3 by the addition of lime slurry using technical grade Ca(OH)₂ (hydrated lime). The selection of the pH 9.3 supernatant value corresponded to the optimal operating pH for the pond treatment facility. Lime was added to 100 ml of column water, stirred for one minute, and added to the water column as a slurry. The water column/lime slurry mixture was stirred for 30 seconds using a paddle to insure uniform mixing. After two hours, the pH of the water column was measured and additional lime slurry was added to bring the pH up to 9.3. Solution pH was measured at two hour time intervals for a period of 12 hours and then approximately every 24 hours, for a total period of 10 days. On days 3 and 10, additional lime

was added as needed to adjust the solution pH to 9.3. The sum of all these lime additions was considered to be the total lime requirement for the flooded tailings.

The remaining soil columns received a surficial lime slurry addition prior to flooding with 14.8 l of Pond 3 water. A surficial lime slurry application rate of 8.96 Mg ha⁻¹ (7.276 g of Ca(OH)₂ /100 ml Pond 3 water/per column) was used, as determined in the previous study. After surface application, the slurry was allowed to equilibrate one hour, at which time the soil column was flooded with Pond 3 water. The sampling scheme for ions and pH was similar to that used for the no lime treatment. Additional water samples were collected at 24 hour intervals for the study period day 3 - 13. These samples were analyzed for both dissolved and total recoverable Cu.

During the actual flooding of Pond 2, composite water samples were collected weekly from Ponds 2 and 3 discharge and analyzed for Chl *a* and the Total Suspended Solids (TSS) were sequentially extracted (fractionated) to determine the Cu partitioning between various suspended solid phases (Tessier, 1979).

Results and Discussion

Soil column flooding with Pond 3 water resulted in the rapid release of Cu, Zn and Fe into the water column due to the dissolution of surface salts (Figure 2a). Maximum dissolved metal concentrations were observed during the first four hours of flooding and occurred at time = 0.083 hr for Fe; time = 1.75 hr for Cu and time = 4.0 hr for Zn. After an initial increase in Fe concentration, dissolved Fe concentration decreased rapidly for study times > 0.083 hr and continued to decrease during the study period. The water columns were observed to be oversaturated with respect to amorphous Fe(OH)₃ and hematite (Table 1). Based on reaction kinetics and mineral solubility, amorphous Fe(OH)₃ was initially precipitated and controlled Fe³⁺ activity during the course of these studies. The transformation of Fe(OH)₃ to hematite (Fe₂O₃) is a relatively slow process and would not be expected to be a factor controlling Fe³⁺ activity during this study. Both dissolved Cu and Zn concentrations were observed to decrease with time. These decreases, however, were relatively small compared to the quantity of dissolved metals that were initially released. Dissolved metals concentration for Cu and Zn were reduced by only 2 - 3 mg/L (Figure 2b). Removal of dissolved Cu from solution, for study times < 1.75 hr, was attributable to the oversaturation of the water column with respect to Cu minerals such as Cu(OH)₂, and tenorite (CuO) (Table 1.) and the coprecipitation/-adsorption of Cu by amorphous Fe(OH)₃ (Leckie, et al. 1980). For reaction times > 1.75 hours, precipitation of Cu minerals is unlikely due to relatively low solution pH resulting in the solution undersaturation. However, scavenging of Cu by freshly formed amorphous Fe(OH)₃ was possible since the water column was saturated with respect to Fe(OH)₃ throughout the study. The scavenging efficiency of amorphous Fe(OH)₃ was reduced due to lower solution pH (Kinniburgh et al.(1976). The flooded soil columns were not saturated with respect to common Zn solid phases (Table 1). Some Zn removal from solution was possible due to adsorption onto amorphous Fe(OH)₃ (Kinniburgh and Jackson, 1982). Zinc retention via this process would probable be minimal due to the selective adsorption of Cu over Zn by Fe(OH)₃.

During the initial flooding of the soil columns, several competing chemical reactions occurred simultaneously while solution pH of the overlying water decreased rapidly (Figure 2d). Based on SI calculations using MINTEQA2 (Allison et al. 1990), a series of precipitation, dissolution, equilibration processes were occurring simultaneously involving the formation/dissolution of various copper hydroxides/oxides (Cu(OH)₂+CuO), copper carbonate minerals (CuCO₃-Cu(OH)₂) and the competitive adsorption of Cu by amorphous Fe(OH)₃. Furthermore these processes were complicated by possible exchange reactions between Cu and Zn on the surfaces of freshly formed colloidal material such as amorphous Fe(OH)₃ and between Ca and (Cu, Zn) on soil solids (Bolt, 1982). Dissolution processes were accelerated by the rapid decrease in solution pH. The rapid increase in sulfate concentration from 81.5 (Pond 3 background) to 310 mg/L was observed and was attributed to the dissolution of sulfate salts (Figure 2c). A gradual increase in SO₄ concentration was observed during the study period, reaching a maximum of 400 mg/L after 12 hours.

Table 1. Saturation indexes for selected copper, iron, and zinc minerals.

Time (hr.)	Copper					
	Tenorite (CuO)		Cu(OH) ₂		Malachite	
	No Lime	Lime	No Lime	Lime	No Lime	Lime
0	-0.909	-0.909	-1.889	-1.889	-3.688	-3.688
0.083	1.52	-5.394	0.541	-6.374	2.451	-13.942
1.75	-1.798	-2.354	-2.779	-3.112	-2.936	-14.224
4	-0.822	-0.502	-1.802	-1.482	-2.563	-18.446

Time (hr.)	Iron Minerals					
	Amorphous Fe(OH) ₃		Hematite		Calcite	
	No Lime	Lime	No Lime	Lime	No Lime	Lime
0	2.524	2.524	10.868	10.868	0.812	0.812
0.083	5.315	3.053	16.45	2.856	0.692	1.022
1.75	3.014	3.221	11.847	7.889	-0.137	0.582
4	2.88	3.404	11.581	12.637	-3.489	0.095

Time (hr.)	Zinc Minerals			
	ZnO		Zn(OH) ₂	
	No Lime	Lime	No Lime	Lime
0	-0.962	-0.962	-2.102	-2.102
0.083	-0.446	-5.51	-1.586	-6.65
1.75	-4.674	-1.332	-5.814	-2.121
4	-3.539	-0.343	-4.679	-1.802

Based on the lime requirements for a 10 day study period involving flooded soil columns, a regression equation was developed to predict the amount of lime (Ca(OH)₂) required to maintain a solution pH of 9.0 - 9.3. This expression, $y = 36.24x + 0.928$ $R^2 = 0.83$ was developed, where y = lime requirement in tons/acre, x = sum of total recoverable copper concentration measured during the study period. Based on this relationship an average quantity of lime slurry was surface applied to another series of soil columns at a rate of 8.96 Mg ha⁻¹ (7.276 g/column). Soil columns that received surficial lime application exhibited a slight increase in pH from 9.3 to 9.7 during the initial flooding (Figure 2d). The solution pH of the water columns decreased gradually during the study period from 9.7 to 8.0. Surficial lime additions resulted in a significant increase in dissolved sulfate concentration with time (Figure 2c) from 81.5 mg/L to 887 mg/L after 12 hours. The increase in sulfate concentration above 310 mg/L was attributed

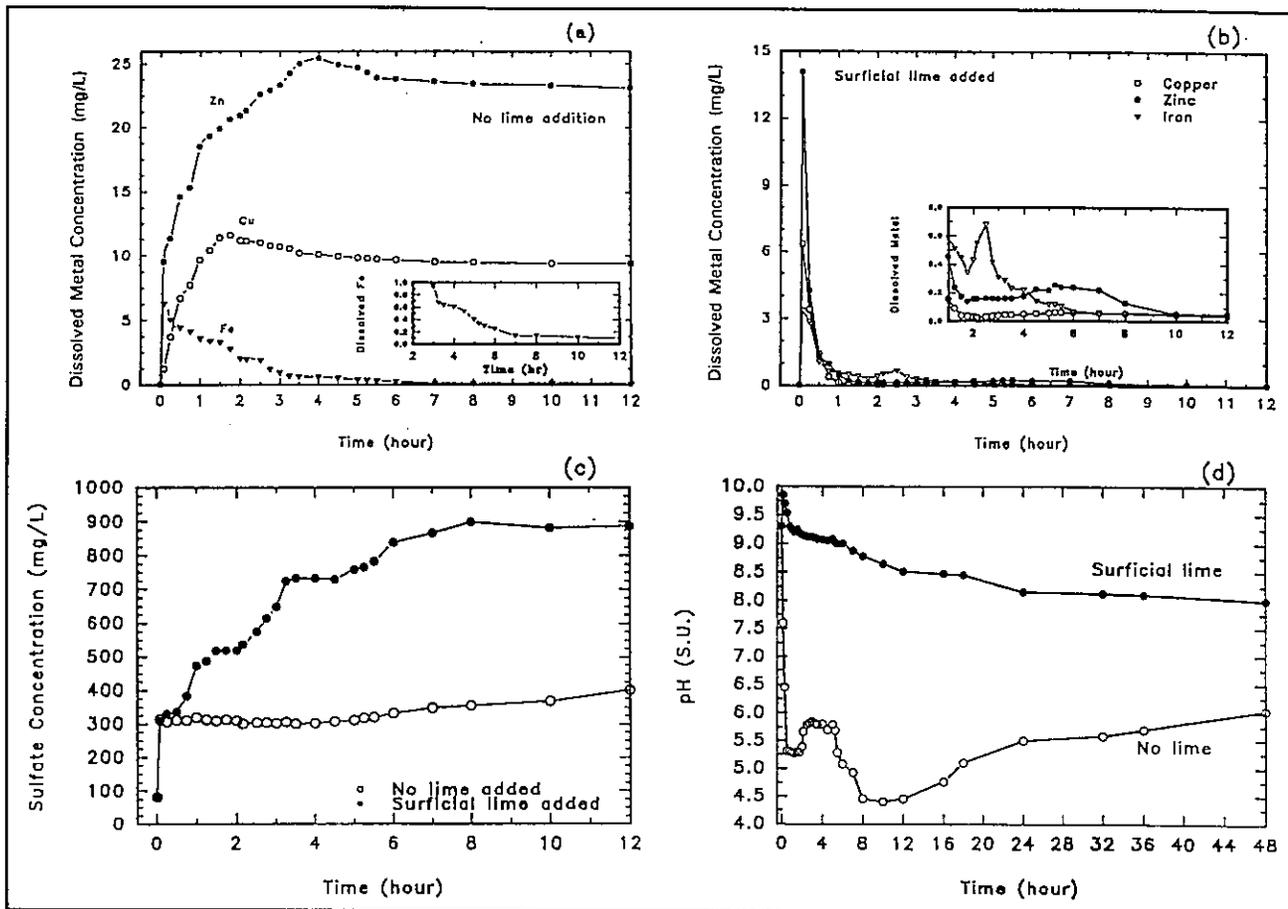


Figure 2. a) Metal release with time for flooded tailings, no lime addition. b) Metal release with time from flooded tailings, surficial lime addition. c) Effect of surficial lime additions on sulfate release. d) Solution pH with time for lime and no lime treatments.

to anion exchange process between OH^- and exchangeable SO_4 present on soil solids (Rajan, 1979) and has been observed previously in both laboratory and field studies (Chao, 1964; Parfitt and Smart, 1978). The step like release of sulfate into solution suggests that diffusion may be a limiting process in the release of sulfate into the water column.

The effect of surficial lime application prior to column flooding can be seen in Figure 2b. The initial concentration of dissolved Fe, Cu and Zn present in solution was substantially lower compared to the unlimed treatment. At time = 0.083 hr, the water columns were saturated with respect to amorphous $\text{Fe}(\text{OH})_3$, various copper and zinc hydroxides/oxides (Table 1). Dissolved metals concentrations were observed to decrease rapidly for time > 0.083 hr, with a minor fluctuations being observed in the dissolved Zn concentration (see inset Figure 2b). Calculated saturation indexes for the flooded soil columns indicated that the solutions were saturated with respect to amorphous $\text{Fe}(\text{OH})_3$ and hematite and undersaturated with respect to Cu and Zn hydroxides and oxides. At low dissolved metal concentrations, the activity of dissolved Cu and Zn have been shown to be controlled by amorphous $\text{Fe}(\text{OH})_3$ /hematite and various colloidal components present in fresh water (Sigg, 1987). From Figure 3, it can be seen that the flooded soils which received surficial lime application appear to have equilibrated at approximately 0.050 mg/L dissolved Cu with minor fluctuations being observed. Dissolved copper concentration within the flooded columns at the end of the study period were in compliance with the Tier I Daily Standards established by EPA for Pond 2 discharge (U. S. EPA, 1991).

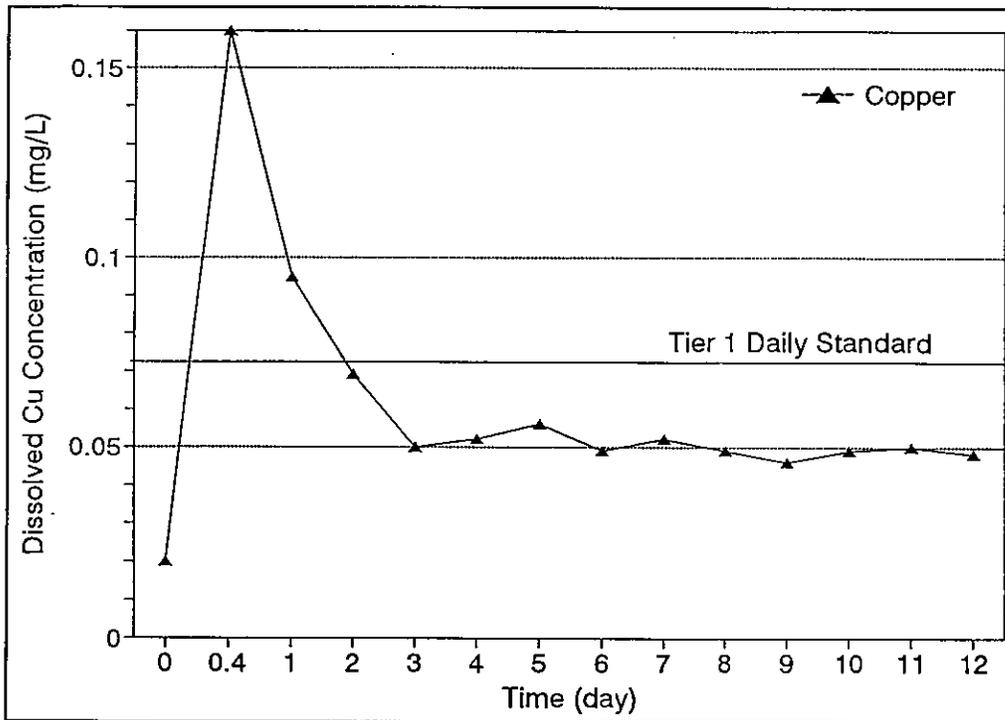


Figure 3. Copper concentration with time for exposed tailings receiving surficial lime slurry treatment.

operating during this period. Limnologically Pond 2 was undergoing ice-off and thermal turnover, which was subsequently followed by a large spring algal bloom (Williamson and Evans, 1994; Evans and Williamson, 1994). Biological activity due primarily to the algal bloom is believed responsible for a shift in equilibria between various Cu fractions associated with the Total Suspended Solids (TSS) component. TSS samples collected at the Pond 3 and 2 discharge stations indicate a large shift in Cu associated with the

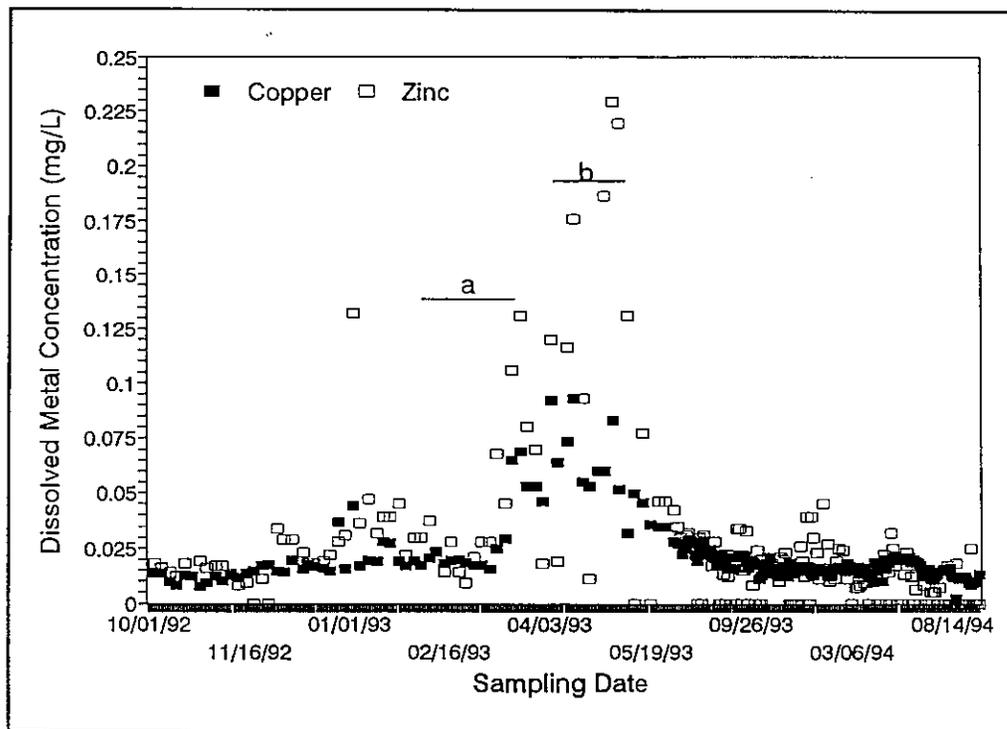


Figure 4. Dissolved metal concentration in Pond 2 discharge. a) Period of Pond 2 raise. b) Period of Pond 2 bypass, no discharge Pond 2.

A comparison of the dissolved Cu concentration from the long term flooded column study (Figure 3) with field measurements made at the Pond 2 discharge after the lime slurry addition (8.96 ton ha^{-1}) and during the raise of Pond 2 elevation (Figure 4), indicated higher than predicted dissolved Cu concentrations in the range $0.055 - 0.105 \text{ mg/L}$. Several additional environmental factors were

operating during this period. Limnologically Pond 2 was undergoing ice-off and thermal turnover, which was subsequently followed by a large spring algal bloom (Williamson and Evans, 1994; Evans and Williamson, 1994). Biological activity due primarily to the algal bloom is believed responsible for a shift in equilibria between various Cu fractions associated with the Total Suspended Solids (TSS) component. TSS samples collected at the Pond 3 and 2 discharge stations indicate a large shift in Cu associated with the exchangeable and carbonate fractions of the TSS (Figure 5). During the peak of the algal bloom, March 17 - April 20, 1993, it can be seen that more Cu was associated with the readily available biological fractions, the exchangeable and carbonate fractions, in Pond 2 compared to Pond 3, than with the iron oxide and organic matter fractions. This shift is important in that Cu associated with these solid fractions can potentially be compl-

exed either directly to algal cell walls or by organic exudates associated with algal biological activity. Dissolved Cu complexed with organic exudates are not readily precipitated as oxides or hydroxides. Consequently these Cu complexes could pass through the Pond treatment system, resulting in Cu exceedances in the allowable discharge. To determine the Cu complexation potential for both the Pond 2 and

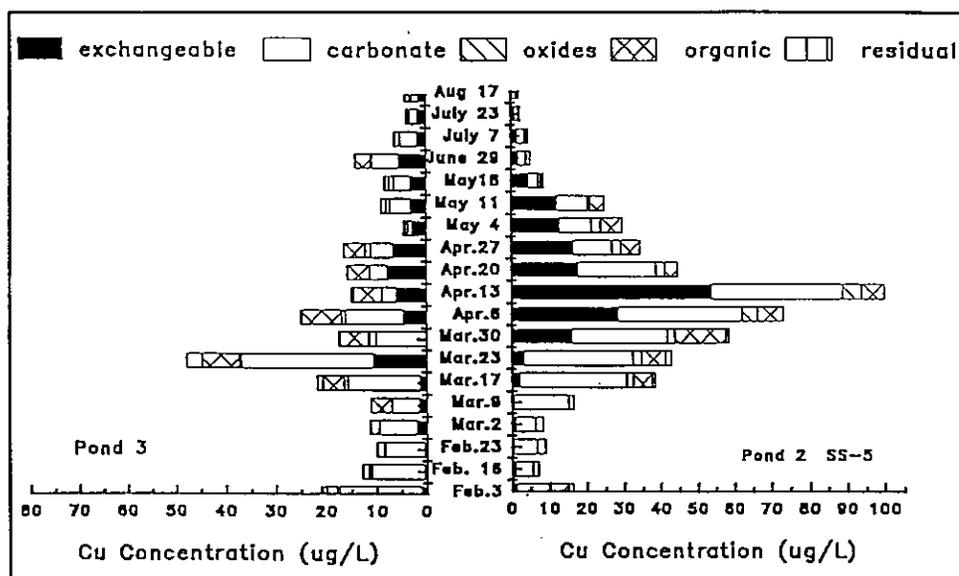


Figure 5. Sequential extraction of copper from filterable solids collected at the discharge of Ponds 2 and 3.

Pond 3 discharge water during the algal bloom water samples were collected and a complexation titration was conducted. The results of this titration are shown in Figure 6. Increases in measured solution current corresponded to the saturation of the complexing agent with Cu and the measurement of free Cu in solution. The complexation potential was estimated for Pond 2 to be 0.047 mg/L, which was in good agreement with the difference observed between that predicted from the column studies and that observed in Pond 2 discharge. The Cu complexation potential in Pond 2 would be expected to vary seasonally and be a function of algal concentration (Williamson and Evans, 1994; McKnight and Morel, 1979).

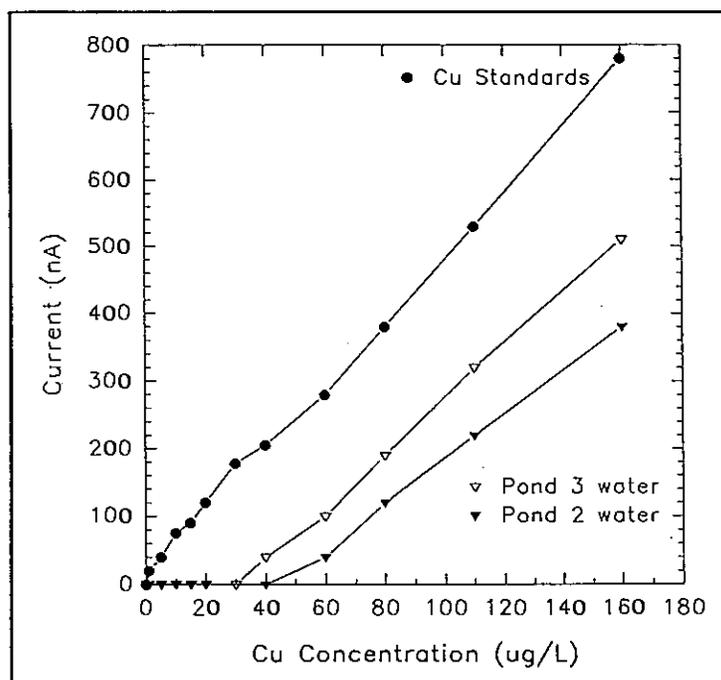


Figure 6. Complexation titration for Pond 2 and Pond 3 water. Deviation from the x-axis indicates saturation of Cu complexing agents.

Conclusions

1. Surficial lime slurry application was effective in reducing metal releases from exposed tailings that were flooded. The effectiveness of this technology is dependent upon preliminary lime requirement studies to determine optimal lime application rates.
2. Sequential copper extraction of particulate matter in Pond 2 water samples indicated that considerable copper was associated with the exchangeable and carbonate fractions of the Total Suspended Solids (TSS). This suggests that copper adsorption by calcium carbonate may be occurring within the Pond system and should be examined further.
3. Complexation of dissolved copper by organic complexing agents associated with algal activity can effectively increase copper concentration associated with the dissolved fraction. To minimize copper release from lime treated tailings during wet closure, flooding should be undertaken during periods of reduced algal activity.

Acknowledgements

The author wishes to thank Tyna Silva for her assistance in manuscript preparation.

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