

## Influence of Tailing pH on the Sorption of Copper by Sulphide Mine Tailing

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**Abstract:** A laboratory experiment was conducted to evaluate the retention of copper (Cu) by sulphide mine tailings previously treated with lime (calcium carbonate) and submerged with water over 10 years. Sub-samples of air-dried mine tailings (pH<sub>tailing</sub> range: 2.56 to 7.60) were equilibrated with 30 mL of 0.01 M CaCl<sub>2</sub> containing 100 mg Cu L<sup>-1</sup>, as CuSO<sub>4</sub>·5H<sub>2</sub>O, for seven days at room temperature. Afterwards, they were centrifuged and filtered. The filtrates were analyzed for Cu, by atomic absorption spectrophotometer, and pH (pH<sub>equilibrium</sub>). The amount of Cu retained by mine tailing solids was calculated based on the difference between the initial and equilibrium Cu concentrations. The sorption experiment was replicated two times. After the sorption step, extractable acid-soluble Cu in tailing samples was assessed by extraction with Mehlich-3 solution. Results indicated a significant positive effect of lime application rate on Cu sorption. The sorption coefficient was positively correlated ( $p < 0.001$ ) with both pH<sub>equilibrium</sub> and pH<sub>tailing</sub>. In general, desorption showed that the Cu sorption was not rigidly bound under acidic conditions. The percentage of Cu released in the tailings without lime was much more than that released in the limed tailings. A positive linear relationship was found between the amounts of Cu desorbed and the amounts of Cu previously adsorbed. Copper in mine tailings may leach into water, especially under acidic conditions. The results highlight the importance of maintaining neutral pH conditions in sulphide mine tailings in order to protect surface water from the hazards of soluble anthropogenic Cu.

**Keywords:** Acid mine drainage, Desorption, Liming

### 1. Introduction

Acid mine drainage (AMD), also called acid rock drainage (ARD) is a worldwide environmental problem facing the mining industry (Marcoux and Grenier, 1990). Despite the fact that it is a natural occurrence resulting from the exposure of sulphide minerals to atmospheric agents such as air and water, AMD can cause considerable damage to the environment. Acid mine drainage can contain elevated concentration of leachable trace metals (Lapakko, 2002).

The lixiviation of copper (Cu) from strongly acidic sulphide mine tailings in arid and temperate regions represents an environmental risk because of the potential adverse effects it may pose to ground and surface water around mines. However, bonding of Cu to mine tailings can limit transfer to surrounding water. Liming is known to be effective in enhancing Cu sorption by adsorption and precipitation, and consequently reducing Cu mobility in Cu-polluted soils (Singh and Oste, 2001). Rodriguez-Rubio *et al.* (2003) suggested that the mobility of Cu in a calcareous soil is likely to be increased when calcium carbonate (CaCO<sub>3</sub>) is removed. Thus, the sorption of anthropogenic soluble Cu by submerged-sulphide mine tailings is of great environmental concern. A laboratory sorption experiment was undertaken to assess the sorption of Cu by sulphide mine tailings that have been limed and maintained under water saturation during 10 years in order to prevent the oxidation of tailings (Samad and Yanful, 2005).

### 2. Materials and Methods

The sulphide mine tailings used originated from the Solbec site at Thetford-Mines in the province of Quebec (Canada). The original Cu-Zn-Pb ore body consisting of pyrite, chalcopyrite, sphalerite, galena and pyrrhotite, has been exploited from 1962 to 1970 producing 1.9Mt of ore. Solbec mine tailings have a 100 µm median grain-size and a rate of 20% sulphide and 2-5% heavy metal (Marcoux and Grenier, 1990). An incubation experiment was carried out 1994 in triplicate on oxidized and composite samples placed in plastic pots. The treatments consisted of three limestone levels (2, 4 and 8 g CaCO<sub>3</sub>/ 400 g of tailing, representing approximately 0.5, 1 and 2%, respectively) and a control (without lime). The pots

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were packed with 40 mm tailing depth. The lime was incorporated into 0-20 mm and 0-40 mm depth. The tailings were covered with 80 mm of deionized water and then incubated under saturated conditions at room temperature for 10 y in order to prevent their oxidation (De Coninck and Karam, 2006). After incubation, sub-samples were air-dried, ground and passed through a 2-mm sieve.

One gram of air-dried tailings ( $\text{pH}_{\text{tailing}}$  range: 2.56 to 7.60) was equilibrated with 30 mL of 0.01 M  $\text{CaCl}_2$  containing 100 mg  $\text{Cu L}^{-1}$ , as  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ , for seven days at room temperature (22 °C). The suspensions were then centrifuged at 2000 rpm for 5 minutes and the supernatant solutions were filtered through Whitman No. 42 filter papers. The pH values of the filtrates ( $\text{pH}_{\text{equilibrium}}$ ) were measured and the concentrations of soluble Cu in the filtrates were determined by atomic absorption spectrophotometer. The amount of Cu adsorbed was calculated as the difference between Cu added and Cu remaining in solution. The sorption coefficient ( $K_s$ ) was used to interpret the sorption data:  $K_s = Q/C$ , where Q is the amount of Cu adsorbed ( $\text{mg kg}^{-1}$ ), and C is Cu concentration in the equilibrium solution ( $\text{mg L}^{-1}$ ). The sorption experiment was replicated two times.

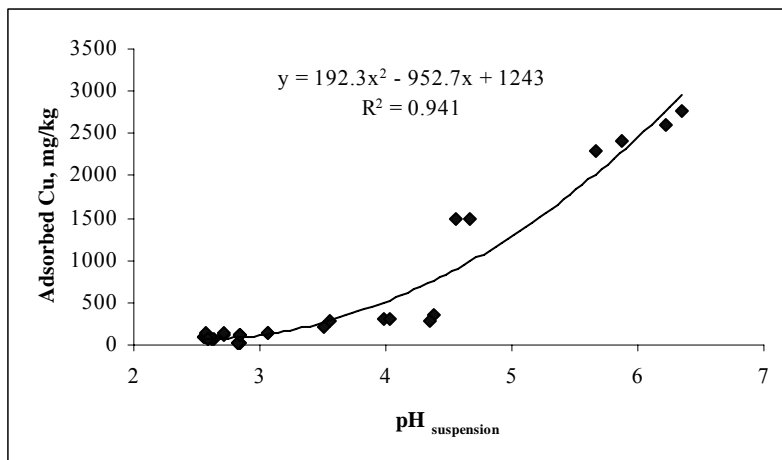
After the sorption step, extractable acid-soluble Cu in tailing samples was assessed by extraction with Mehlich-3 solution. Mehlich-3 solution (Mehlich, 1984), which is composed of 0.2 M  $\text{CH}_3\text{COOH}$ , 0.25 M  $\text{NH}_4\text{NO}_3$ , 0.015 M  $\text{NH}_4\text{F}$ , 0.013 M  $\text{HNO}_3$  and 0.001 M ethylene diamine tetraacetic acid, has been reported to extract occluded Cu binding sites, organically bound Cu fraction, and soluble, exchangeable and specifically adsorbed Cu fractions (Reed *et al.*, 1993).

### 3. Results and Discussion

Adsorbed Cu and  $K_s$  values increased with increasing lime rate (Table 1). However, the *t*-test ( $p < 0.05$ ) did not reveal significant difference between the control (no lime) and the lowest rate of lime (0.5%). The values of  $K_s$  ranged from 0.2 (without lime) to 345.0  $\text{L kg}^{-1}$  (highest lime rate). Mine tailings without lime ( $\text{pH}$  2.56) adsorbed 0.5% of added Cu whereas lime-amended tailings ( $\text{pH}$  2.72 to 7.60) can adsorb from 1.0 (lowest lime rate) to 92.0 % (highest lime rate) of added Cu. This observation suggests that the more submerged-tailing is neutral to slightly alkaline, the more it will remove anthropogenic Cu from the surface water. Residual  $\text{CaCO}_3$  present in the mine tailing matrix may act as a sorbent (Papadopoulos and Rowell, 1989), retaining Cu through ion exchange (Cavallaro and McBride, 1978).  $K_s$  values were positively correlated ( $p < 0.001$ ) with both  $\text{pH}_{\text{equilibrium}}$  ( $r = 0.800$ ) and  $\text{pH}_{\text{tailing}}$  ( $r = 0.698$ ). Similar positive correlation between Cu adsorption and pH has been reported by Jarvis (1981). This result is in agreement with literatures, where the amount of Cu adsorbed by soils, clays and sediments increased with pH (Yuan *et al.*, 2007; Zhang and Zheng, 2007; Arias, 2005; Phillips *et al.*, 2004; Hue *et al.*, 1997; Harter, 1983; Maguire *et al.*, 1981). The relationships between Cu adsorbed and both  $\text{pH}_{\text{equilibrium}}$  and  $\text{pH}_{\text{tailing}}$  are better described by a quadratic equation (Fig. 1). The differences in Cu sorption between mine tailing samples could be attributed to the  $\text{pH}_{\text{tailing}}$  induced by previous  $\text{CaCO}_3$  application. The higher content of residual lime in the tailing sample and the more sites there are for Cu sorption. Based on evidence from many experiments, Cu has very low solubility in alkaline and calcareous soils (McBride and Bouldin, 1984; Jarvis and Jones, 1980; Cavallaro and McBride, 1978). Residual  $\text{CaCO}_3$  surfaces present in sulphide mine tailings act also as nucleation sites for precipitating Cu (McBride, 2000). Thus, stabilization of sulphide mine tailings using lime would transform such waste into a matrix with metal sorption properties. Davies *et al.* (1999) who studied the efficacy of lime amendment to geochemically stabilize mine tailings, found that liming facilitates alteration of pyrite to ferrihydrite that sequestered

**Table 1. Average values of  $\text{pH}_{\text{tailing}}$ , amount of Cu adsorbed,  $K_s$ ,  $\text{pH}_{\text{suspension}}$  and amount of extractable acid-soluble Cu (desorbed Cu).**

$\text{CaCO}_3$ rate (%)	$\text{pH}_{\text{tailing}}$	Adsorbed Cu ( $\text{mg kg}^{-1}$ )	$K_s$ ( $\text{L kg}^{-1}$ )	$\text{pH}_{\text{suspension}}$	Desorbed Cu ( $\text{mg kg}^{-1}$ )
0	2.68	67.50	0.70	2.83	37.20
0.5	2.79	110.63	1.15	2.73	30.37
1.0	4.10	247.50	2.73	3.62	63.37
2.0	6.25	1653.80	103.60	4.82	1174.90



**Fig. 1. Relationship between the pH of the equilibrium solution and the amount of Cu adsorbed by limed tailings.**

weight percent concentrations of As, Cu, Pb, and Zn.

In terms of the quantities initially adsorbed, the percentage of desorbed Cu was very high for tailings without lime (96%) compared to the limed tailings (16-84%). The desorption process was also found to depend on the pH of the solution. A decrease in pH will cause desorption of the Cu initially adsorbed on the tailing. According to Van Tichelen *et al.* (2001), adsorbed Cu could easily be desorbed by protons. A positive linear relationship was found between the amounts of extractable acid-soluble Cu and the amounts of Cu previously adsorbed ( $r=0.983$ ,  $p<0.001$ ). This result indicates that under acidic conditions, adsorbed Cu is readily and largely desorbed. The environmental consequence of this observation is important. Under potential reacidification of neutralized mined lakes, much of anthropogenic Cu initially adsorbed by the tailing will be released back into the surface water.

#### 4. Conclusions

Copper sorption by limed sulphide mine tailings is highly correlated with pH. Heavily limed tailings show high Cu sorption coefficient. Consequently, sulphide mine tailings could adsorb significant quantities of Cu from contaminated water and surrounding environment, depending upon pH conditions. The results highlight the importance of maintaining neutral pH conditions in submerged sulphide mine tailings in order to protect surface water from the hazards of soluble anthropogenic Cu.

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