

COPPER REMOVAL FROM MINE DRAINAGE BY AN EXPERIMENTAL WETLAND AT BELL COPPER MINE, SMITHERS, B.C.

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Experimental wetlands removed copper in low strength (0.3-1.0 ppm, pH 7-8) and high strength (35-50 ppm, pH 3.5) mine drainage at the former Bell copper mine. Copper removal from the low strength mine drainage exceeded 98%, even during winter operation. Removal efficiency for the high strength mine drainage was initially similar, but it gradually deteriorated. Copper removal was a function of retention time, better removal being observed with a greater retention time.

Some metal was taken by plants in the experimental wetlands. However, copper was predominantly retained in the wetland peat, or sediments, building up to levels of nearly 1.0% after three years. Copper accumulated in the inlet section of the ponds approximately twice more than in the outlet section.

Sulphide, produced by sulphide-reducing bacteria (SRB), was detected in the peat interstitial water. However, while mineralogical analyses indicated the presence of copper sulphides in the peat, sequential leaching of this substrate showed that copper was mainly distributed among organically-bound and oxide-bound phases, with a smaller proportion present as sulphides. The available data suggest that copper was retained as sulphides when low strength mine drainage was applied to the wetlands, but that the low pH of the high strength mine drainage prevented their formation.

Key Words: acid mine drainage, wetland treatment systems, cold climate, sulphate-reducing bacteria, sequential leach analysis, copper geochemistry.

Introduction

A growing literature has demonstrated the effectiveness of wetlands in removing metals from mine drainage (1,2). Treatment of acidic drainage from Eastern coal mines has been shown to occur primarily through the oxidation and hydrolysis of dissolved iron and manganese (3). Reports on natural wetlands (4, 5, 6) and constructed wetlands (7,8) also implicate SRB-generated hydrogen sulphide in the metal removal process. Considering the characteristics of drainage from base metal mines, the latter process may be more important for treatment than the former.

To ascertain the effectiveness of wetlands in treating drainage from base metal mines, Noranda Minerals Inc. sponsored the development, operation and monitoring of two experimental wetlands ("large" and "small" wetlands) at the former Bell Copper Mine. The test program had two main objectives: a) to determine the level of treatment achievable at a Northern mine on a year-round basis, and b) to establish process-based design parameters for construction of wetlands at Canadian mines. From 1991 to 1993, the experimental wetlands have been monitored for influent and effluent composition, vegetation, sediment chemistry and microbiology, and process engineering aspects. Together, these investigations have characterized their performance and have identified processes responsible for improving water quality. Key findings from these investigations are presented herein.

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Methods

Study site and description of the experimental wetlands

Bell Copper mine is a former open pit mine located on Newman Peninsula, Babine Lake, approximately 65 km northeast of Smithers, B.C. (Figure 1). Two membrane-lined ponds with nominal surface areas of 300 m² (large pond) and 75 m² (small pond) were prepared in 1990. They were fertilized with manure and planted with floated peat mats (approximately 45 cm thick) obtained from a nearby donor site on the property (Newman Lake). The peat mats were dominated by the sedges *Carex aquatilis* and *C. laeviculmis*, species common in the area. Significant numbers of cattails (*Typha latifolia*) were also planted into the small wetland. By 1991, both wetlands were fully covered with vegetation.



Figure 1. Location of the study site, the former Bell Copper mine.

Characteristics of the treated mine drainage

Water from two different sources on the property was used in the study: a low strength (0.3-1.0 ppm copper, pH 6-8) and a high strength (35-50 ppm copper, pH 3.5) seep. Levels of other metals were negligible, except for sub-ppm concentrations of iron and zinc (9). Sulphate concentrations in both sources of water were greater than 2000 ppm. Influent and effluent composition were monitored bi-weekly throughout the project by measuring pH, conductivity, sulphate, total and dissolved copper, and iron.

Water was introduced to the wetlands from an adjacent open sump, which was replenished weekly from the abovementioned sources. The water was pumped through metered pumps at nominal flows of 8L/min. and 2L/min. for the large and small pond, respectively. The actual retention times measured for the wetlands (using bromide as a conservative tracer) were 12 and 22.5 days for the large and small pond, respectively.

Wetland sampling

Yearly measurements of plant community structure were done from permanent study plots. The donor site was sampled concurrently to provide reference (control) measurements and plant material. Above- and belowground plant material was also collected from these sites for metal analyses.

In situ measurements of pore water pH and redox potential were made 2-3 times a year from a total of 25 sites⁴. Dissolved sulphide concentrations in pore water at these site were measured concurrently by withdrawing water samples and assaying immediately using the methylene blue method. Peat sediment samples were also collected for microbial and chemical analyses. Samples were transported and stored anaerobically at 4° C until processed. Chemical analyses for metals were

⁴ These were located approximately 10 meters from the inlet and outlet sections of each pond (5 sites each, 20 sites altogether), and in Newman Lake (5 sites). They are referred in the text as the inlet and outlet sections of the ponds, and the reference site.

performed on a nitric acid/hydrogen peroxide digest of the peat. Enumeration of SRB was done as described in Battersby (10).

Sequential Leaching Analysis

Peat (composited from five individual samples for each pond section) sampled in October 1993 was analyzed for the distribution of copper in different phases, using the procedures for geochemical analysis of sediments published by Hall and co-workers (11). These procedures were slightly modified to account for the nature of peat in the wetlands (e.g., it is buoyant, anaerobic), as described by Sobolewski (12). The steps used in the sequential leach and the presumed copper phases corresponding to each step are summarized in Table 1.

Table 1. List of reagents and conditions used during a quantitative sequential leach of wetland peat samples.

EXTRACTANT	PROCEDURE	PHASE DISSOLVED
0.1 M $\text{Na}_5\text{O}_{10}\text{P}_3$, pH 10	4 hour leach @ 25° C	Soluble organic complexes
1 M NaOAc/HOAc, pH 5	16 hour leach @ 25° C	Adsorbed and exchangeable metals, carbonates
1 M $\text{NH}_2\text{OH}/\text{HCl}$ in 0.25% HOAc	4 hour leach @ 85° C	Amorphous and crystalline iron oxides
0.1 M NaCN, pH 10	Overnight leach in shaken flasks @ 25° C	Cyanide-sensitive sulphides
KClO_3/HCl ; \pm 4 M HNO_3	2 leaches @ 90° C; 1 st without, 2 nd with HNO_3	Cyanide-resistant sulphides
$\text{HF}-\text{HClO}_4-\text{HNO}_3-\text{HCl}$	Total digest	Silicates, residual crystalline fraction

Results

Copper removal by experimental wetlands

From April 1992 until the end of June 1993, the experimental wetlands received mine drainage with 0.3-1.0 ppm copper and a pH varying from 7-8. Copper removal exceeded 98% for both wetlands, even during the winter of 1992/93 (Figures 2A, B). The effluent pH was slightly lowered by the wetlands, ranging from 7.1-7.5 (data not shown). Figure 2 also shows that removal effectiveness was unaffected by occasional spikes in copper concentrations of up to 10 ppm.

Starting on June 28, 1993, high strength mine drainage (35-50 ppm copper) was introduced into the wetlands. For the first 6 weeks, copper was effectively removed by the wetlands (Figures 2C, D). However, removal effectiveness gradually deteriorated until, by October 1993, copper removal reached ca. 40% for the large wetland, and ca. 80% in the small wetland. At that time, plant dieback was evident in both ponds, but it was undistinguishable from that at Newman Lake, the study reference site.

The period of efficient copper removal (following addition of the high strength feed) corresponds to a time when effluent pH in both ponds remained above 6.5. Copper began to appear in pond effluents when the pH decreased below 5.0. The decrease in pH for the large pond was faster than for the small pond: by August 26, it had reached 4.7 for the large pond vs 5.1 for the small pond. At that time, copper concentrations in their effluents were approximately 8 ppm and 0.5 ppm, respectively. Their pH was still more than one pH unit more than that of the added feed, indicating that the wetlands had some buffering capacity for at least 3 months after introduction of the high strength feed.

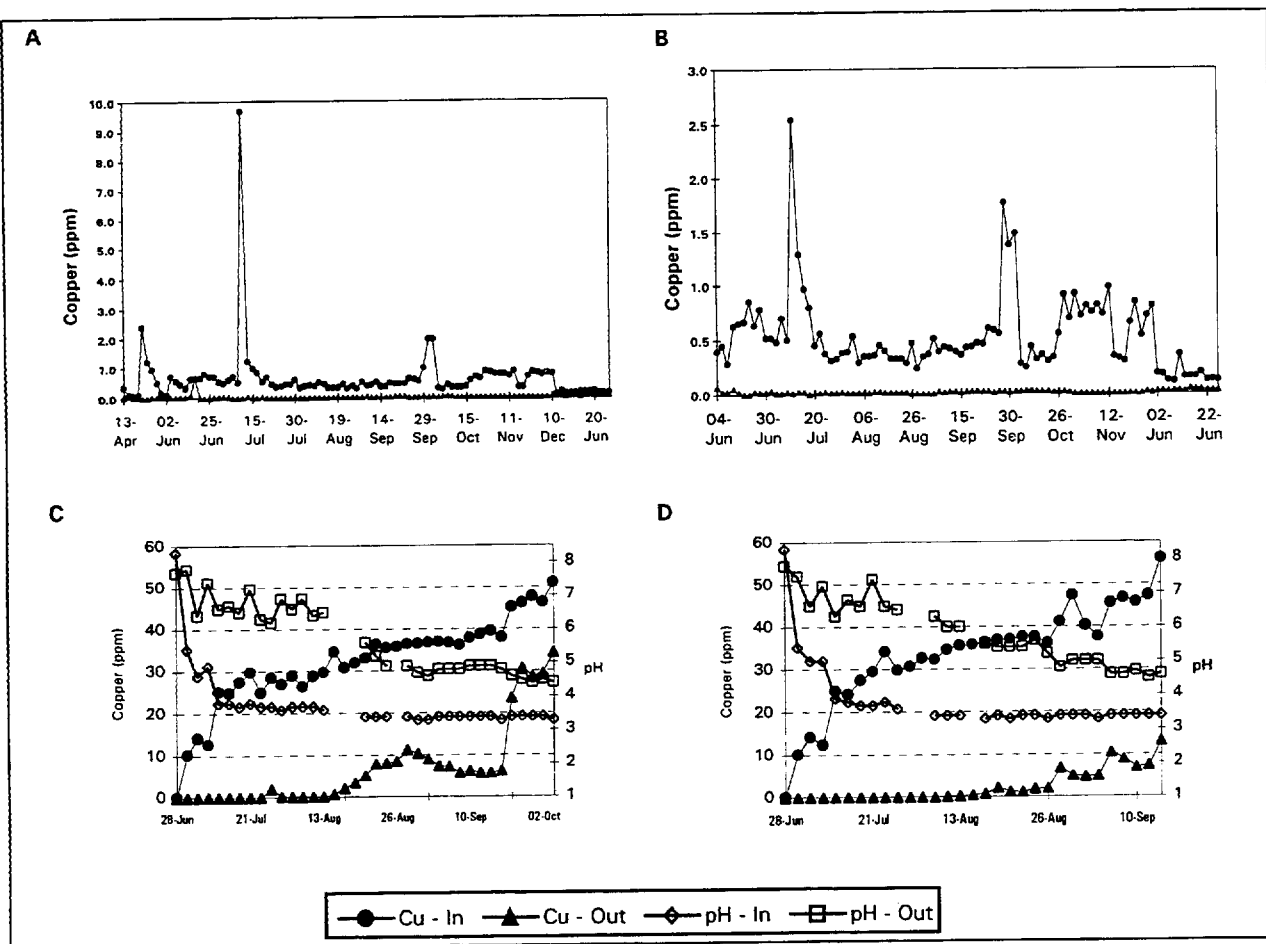


Figure 2. Copper concentrations and pH of influent and effluent for the large (A, C) and small pond (B, D). Refer to legend above for symbols. These variables were measured continuously from April 13, 1992 to Oct 3, 1993 and are shown separately for the low strength (A, B) and high strength feed (C, D). Note different scales used in A and B.

Fate of copper within the wetlands

Mean copper concentrations in aboveground plant tissues were highest in sedge vegetation of the large pond (Figure 3). These copper levels were significantly above those measured in the control vegetation. Copper levels in cat-tail leaves (small pond) were much below those of sedge leaves. From 1991 to 1993, increased tissue copper levels were evident only in the vegetation of the large pond. Although an analysis of belowground plant tissue was also attempted, it was impossible to separate live tissue from dead and to determine whether the elevated copper levels that were measured resulted from uptake or sorption onto dead material.

Analysis of pond sediments (peat sampled deep and away from plants)

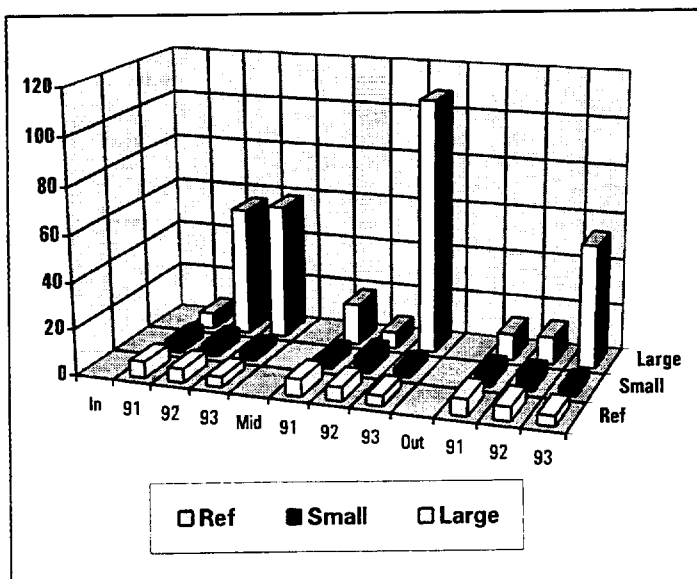


Figure 3. Copper concentrations in plant leaves from inlet, middle, and outlet sections of ponds, and from reference site, expressed in mg/dry kg (ppm).

showed that copper accumulated mainly there (Figure 4: contrast scale with that of Figure 3). More accumulated in the inlet half of both ponds was greater than in the outlet half, reaching 8000 ppm in the small pond inlet section.

Analysis of wetland peat during treatment

Soon after the mine drainage was introduced into the ponds, blackened, sulphur-smelling pockets of peat could be observed. This suggested that SRBs might have been active within the ponds. This was confirmed by enumeration of SRBs in peat: their numbers ranged from 10^3 cell/dry gram at the end of the fall to 10^9 cell/dry gram during the summer. Sulphide concentrations in the peat pore water reflected these numbers, averaging 0.1 ppm during the fall months and 1 ppm during the summer. The redox potential of sediment pore water also reflected their activity. It ranged from -100 mV in the fall to -300 mV in the summer.

Sequential leach analysis

A sequential leach analysis was carried out to determine the mass of copper associated with different phases in peat samples from the experimental wetlands and from Newman Lake. A prior mineralogical examination had identified copper sulphides in peat samples collected from the experimental wetlands, but their levels could not be quantified.

A greater mass of the copper was present in peat sampled near the inlet section of both ponds compared with the outlet sections (Table 2). This copper was mainly in the organic and exchangeable phases. Given the organic nature of peat, and given that the peat was acidic at the time of sampling, it is likely that much of the copper recovered in the exchangeable phase was actually organically complexed, rather than as a carbonate.

Surprisingly, 17% and 25% of the total mass of copper in the large and small ponds was recovered in the iron oxide phase, respectively (Figure 5). The peat in both ponds has remained anaerobic since 1991, suggesting that iron oxides might have been absent⁵. However, the observation of ferrite-like minerals during a prior mineralogical examination suggests that crystalline iron oxides were still present in the wetland peat.

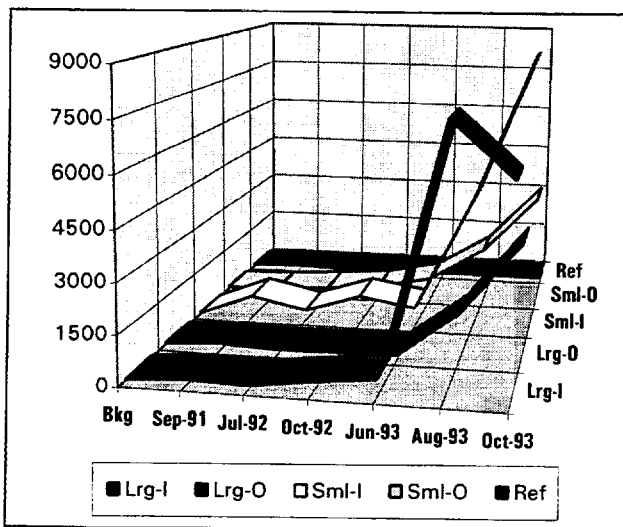


Figure 4. Copper concentrations in peat from inlet and outlet sections of ponds, and from reference site, in mg/dry kg (ppm).

⁵ An "iron flush" was noted after mine drainage was first introduced into the ponds in 1991, supporting this idea.

Table 2. Mass of copper extracted in each phase from wetland peat samples.

Sample Source	Organic ¹	Exchangeable	Iron oxides	CN-extractable sulphides	CN-resistant sulphides	Residual
Large Inlet	8.32 ²	2.72	2.07	0.70	0.04	0.01
Large Outlet	0.18	1.02	0.71	0.34	0.08	0.01
Small Inlet	3.76	3.12	1.96	1.07	0.12	0.02
Small Outlet	0.28	1.16	1.46	0.55	0.06	0.02
Newman Lake	0.01	0.00	0.02	0.10	0.00	0.00

¹Each phase corresponds to an extraction step, as described in Table 1.

²Each value is averaged from duplicates, and is the amount of copper (in mg) extracted from 50 wet g of peat. Copper concentrations in duplicate samples were typically within 30% of each other.

Copper sulphides were also present in the peat, but in lower proportions than in the other phases. The only exception was for the peat from Newman Lake, where nearly 90% of the copper was recovered in the cyanide-extractable phase.

Some copper was recovered in the cyanide-resistant phase, a finding consistent with the presumptive identification of chalcopyrite in peat sampled from these sections (12). Copper sulphides were present in greater proportion in the outlet sections of the ponds than in their inlet sections (Figure 5). However, they were more abundant, on a mass basis, in their inlet sections (Table 2).

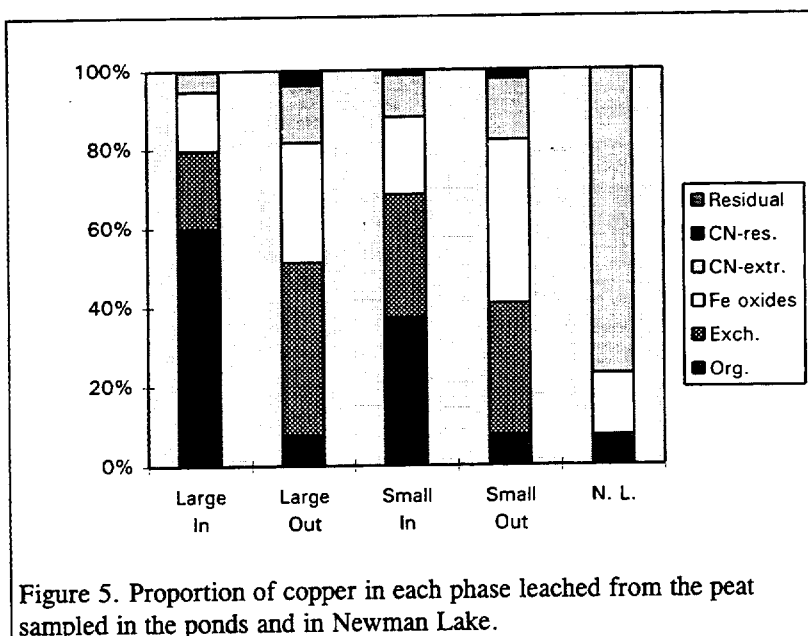


Figure 5. Proportion of copper in each phase leached from the peat sampled in the ponds and in Newman Lake.

Virtually no copper was recovered in the residual phase. This is consistent with the non-mineral nature of the peat substrate. Indirectly, this finding confirms that extraction of earlier phases were exhaustive.

Discussion

One project objective was to assess the long-term potential of the wetlands for treating mine drainage in a cold climate. The present study shows that low strength mine drainage can effectively be treated on a year-round basis at mines in Northern locations (Figure 2A,B). The continued removal of copper when the experimental wetlands were fully covered with ice underscores this fact. Although low flows were maintained in this study, there is no reason to believe that wetland treatment systems cannot be designed for higher flows.

Treatment of high strength feed by the experimental wetlands was ineffective, indicating that some limit in the type of water that can be treated was exceeded (Figure 2C,D). This limitation could be due to the low pH, the high acidity, or the high copper concentration of the high strength feed. Figure 2 shows that the effluent pH started to decrease soon after the high strength feed was added, whereas copper retention was not diminished until much later. This suggests that the decrease in treatment performance was due to low pH (or high acidity, or both) rather than because of high copper concentrations.

The effluent pH decreased much more gradually than the influent pH when the high strength feed was added (Figure 2C,D). Although dissolution of carbonates in the wetlands might account for this, it seems unlikely to have been responsible for the prolonged buffering that was observed. Sulfate-reducing bacteria (SRB) are known to produce bicarbonate (13), and their activity might account for this buffering capacity. Such a function of SRB has often been proposed (5, 7, 14, 15).

By August 1993, the buffering capacity of the ponds began to be eroded. According to the above argument, this would reflect a reduction in overall SRB activity. Consistent with this, reduced SRB populations were measured at that time (data not shown)⁶. The production of bicarbonate by SRB helps to maintain their environment at a pH of 7.0-7.5, which is optimal for growth and activity (13). It is likely that this capacity to maintain optimal conditions was gradually overwhelmed by addition of the high strength feed. Once this capacity was exceeded, SRB metabolic activity and growth started to decrease, resulting in even less buffering capacity. This reduced buffering capacity resulted in a lower pH, in further reduction of SRB activity, and so on until the microbial population collapsed (or adapted to a new, more acidic environment). During this process, less sulphide would have been produced and less copper sulphide would have been formed (if it was formed at all).

As noted earlier, differences in the buffering capacity of the two experimental wetlands were observed. While the ponds differed in their plant composition, the difference in their retention times (12 days vs 22.5 days for the large and small pond, respectively) was probably a more significant factor. If the above idea that buffering capacity is due to SRB activity is correct, a higher retention time would allow SRB to better resist the reduction of pore water pH by acidic mine drainage. The above result is consistent with, and reflects the existence of a relationship between the acidity of the mine drainage, retention time, and the production of alkalinity by SRB.

Another difference between the two ponds is that sedges in the large pond accumulated significant amounts of copper, whereas cat-tails sampled in the small pond did not. Given that these plants were sampled in late August 1993, it is also possible that the lower pH in the large pond, as compared with the small pond, accounts for this difference.

There were consistent differences in the copper concentrations in peat between the inlet and outlet sections of both ponds. Copper was predominantly in the organic phase in the inlet sections, contrasting its much lower distribution in this phase of the outlet section samples (Figure 5). The present data provide no basis for explaining this difference. However, this suggests that the organic phase of the outlet section of the ponds was undersaturated with respect to copper. The more equal distribution of copper in the iron oxide phase suggests that they were saturated with respect to copper, or that the hydraulic retention time was insufficient to allow these interactions to go to completion.

The above results allow for an assessment of the viability of these types of wetlands in treating mine drainage over long time periods. Long-term treatment will be only possible if copper is continually removed and retained by the wetlands. Removal processes that quickly become saturated, such as sorption to fixed sites, are unlikely to achieve this objective (16). While others have demonstrated that peat-based wetland treatment systems can remove metals from mine drainage through this process (17, 18), their binding-capacity is limited by the initial mass of organic matter plus that which is added by plant growth. In these systems, improvement in water quality will cease when this capacity is exceeded (15). Formation of sulphides in wetlands would provide for long-term removal of metals, since metal sulphides will remain in their sediments as long as they are not re-oxidized. Unlike sorption to fixed sites, sulphide production will proceed as long as sulphate is present in the influent water and wetland plants provide organic substrate for growth of SRB.

⁶ SRB populations in peat were measured in August and in October 1993. Whether they were adapting to the lower influent pH could not be determined.

The results from the sequential leach analysis indicate that only a comparatively small amount of copper was retained as sulphides. This suggests that the wetlands will not remove copper for a long time. However, this conclusion is clouded by the fact that approximately 90% of the copper extracted during the sequential leach originated from the high strength feed, the remaining 10% originating from the low strength feed. Conditions within the peat undoubtedly changed after addition of the high strength feed, and it is possible that copper was retained mostly as sulphides before its addition, but that it was retained mostly as organic complexes afterward. Two arguments support this view.

Firstly, addition of high strength mine drainage lowered the pH in the peat, favouring the formation of hydrogen sulphide at the expense of ionized sulphide, as shown below:



A pH reduction of approximately 1 unit was measured in the effluent shortly after addition of the high strength feed, resulting in a decrease in ionized sulphide. Further reduction in sulphide levels probably resulted from an observed decrease in SRB populations. Since copper reacts with the ionized form of sulphide, the combination of these two effects might have resulted in substantially less copper sulphide being formed.

Secondly, the copper in the peat from Newman Lake, the reference site for this study, was mostly recovered in the cyanide-extractable phase⁷. If copper predominantly forms stable organic complexes in peat-based wetlands, a significant amount should have been recovered in the organic and/or exchangeable phases. This result indicates that, even if copper had sorbed onto organic matter (as is probable), most of the copper entering the lake was eventually retained as copper sulphides⁸. The fact that Newman Lake is not known to have been exposed to low pH mine drainage, but more likely to neutral mine drainage, suggests that the copper added in the low strength feed was probably similarly retained as sulphides in the experimental wetlands.

Taken together, these arguments suggest that wetlands may effectively treat mine drainage in a Northern climate, as long as the pH (or acidity) of the mine drainage is not too low. Pretreatment by anoxic limestone trenches may permit enhance treatment effectiveness (or stability) for the more acidic mine drainage. The design of these treatment systems should balance loadings of acidity with the production of bicarbonate by SRB within the wetland. Given the low flows that were tested in this study, our conclusions about treatment effectiveness are limited in their application to small seeps at mine properties, not to systems with large flows. Further studies with other wetlands, both natural and constructed, should help to identify the limitation of these systems.

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⁷ It could be argued that the copper recovered in peat from Newman Lake originated as dust from the mine site. However, Bell is a chalcopyrite orebody, and the copper deposited as dust should be chalcopyrite, which resists extraction by cyanide. Since, no cyanide-resistant copper was recovered from the peat from Newman Lake, this possibility can be ruled out.

⁸ Both SRB and dissolved sulphide have been detected in the peat from Newman Lake, and its pH is comparable with that from the experimental wetlands prior to addition of the high strength mine drainage (Gormely *et al.* 1994).

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