COPPER ACCUMULATION IN CONSTRUCTED WETLANDS AT BELL COPPER:
DO COPPER SPECIES INDICATE THEIR POTENTIAL FOR LONG-TERM TREATMENT OF ARD?

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Two experimental wetlands constructed at Bell Copper removed copper from low strength (1-2 ppm, pH 6-8) and high strength (40-50 ppm, pH 3) mine drainage. These peat-based systems will saturate rapidly if copper accumulates mainly in an organically bound phase, but not if it accumulates as sulphides (reacting with bacterially-generated hydrogen sulphide). Therefore, the species of copper present in the wetlands were determined to assess the long-term potential of these wetlands for treatment of mine drainage.

Mineralogical analyses confirmed the presence of copper sulphides in peat samples from the wetlands. Sequential leaching of these samples showed that copper was mainly distributed among organically bound, exchangeable, and oxide-bound phases. A smaller proportion was present as sulphides.

Copper from the high strength mine drainage was completely (>99%) removed by the wetlands for 6-8 weeks after its introduction, but started appearing in their effluent thereafter. Since the sequential leach analysis indicated that the peat binding-capacity for copper was still undersaturated after that time, it is concluded that insufficient retention was being provided by the wetlands.

In 1989, Noranda Minerals sponsored the establishment, operation and monitoring of two wetlands ("large" and "small" ponds) at the Bell Copper Mine to test their effectiveness in treating mine drainage. Copper-containing mine drainage was initially fed into the ponds in 1991, and flowed continually from April 1992 until the test was terminated in October 1993. The wetlands have been monitored for influent and effluent composition (using the mine and commercial laboratories), vegetation (R.U. Kistritz Consultants), sediment chemistry and microbiology (Microbial Technologies), and process engineering aspects (Gormely Process Engineering). Together, these investigations have characterized their performance and have identified processes responsible for improving water quality.

One of the project objectives was to determine whether the wetlands could provide long-term treatment for copper. This would only be possible if copper was removed over a long time period and remained biologically unavailable in wetland sediments. The wetland sediments consist of peat, which has a limited binding-capacity for metals. One would expect treatment to fail when that binding-capacity is exceeded. However, both sulphate-reducing bacteria (SRBs) and sulphide have been detected in the ponds during the study (Gormely et al., in press). Since copper is known to form highly insoluble compounds with sulphide, it is also possible that it was retained in the wetlands as insoluble sulphides. Unlike the metal binding-capacity of peat, sulphide production by SRBs will not be limited as long as sulphate is present in the treated mine drainage and wetland plants provide organic substrate for growth. In addition, copper sulphides are highly insoluble and will not remobilize under the reduced conditions present in the peat. Therefore, long-term removal of copper might be expected if copper was predominantly retained in wetland sediments as sulphides.

The present study sought to identify and quantify the forms of copper present in the wetland peat. Initially, a mineralogical examination was conducted to determine whether copper sulphides could be detected. Subsequently, an analytical sequential leach was conducted to quantify the various phases of copper present in the peat.

METHODS

Study site

Bell Copper Mine, a former open pit copper mine, is located on Newman Peninsula, Babine Lake, approximately 65 km northeast of Smithers, BC. Two membrane-lined wetlands with surface areas of 300 m^2 (large pond) and 75 m^2 (small pond) were constructed and planted in 1990 with floated peat mats (approximately 45 cm thick) obtained from nearby Newman lake. By 1991, both ponds were fully covered with vegetation, primarily the beaked sedge *Carex rostrata*. Cattails *(Typha latifolia)* were also present in the small pond. Copper-containing feed was introduced to the ponds from an adjacent sump, which was replenished weekly with mine drainage obtained from collection ponds at the mine site. Water from the sump was pumped through metered pumps and heat-traced pipes, allowing for year-round operation of the system.

Sampling

Influent and effluent water from the ponds were collected regularly for water quality analysis. Although both filtered (0.45 μm) and unfiltered samples were collected, the results reported in this study are for unfiltered samples only. The differences in copper concentration between filtered and unfiltered samples were negligible (unpublished observation).

Peat samples were collected in October 1993 from the large and small ponds, approximately 10 meters from their respective inlet and outlet. Samples were also collected from Newman lake, the reference site for the study. Samples were collected in sterile plastic bags 10-15 cm below the surface, within the anaerobic zone of the peat. They were stored anaerobically at 4° C until processing for mineralogical examination or leaching.

Mineralogical Examination

Mineralogical examination methods used to determine the presence of sulphides in peat included optical and electron microscopy; secondary and backseat»ered electron imagery (SEI, BEI); energy dispersive spectrometry (EDS); and wavelength dispersive spectrometry (WDS). Unfortunately, copper- and sulphur-bearing grains were not sufficiently abundant to use powder x-ray diffraction (XRD) for unequivocal identification of minerals species.

Peat subsamples were freeze dried in preparation for examination using scanning electron microscopy (SEM) techniques. Initially, samples of dried peat were carbon coated under vacuum and studied using BEI. Sulphides, if present, appear as very bright grains. A number of bright grains were identified and qualitatively analyzed for element composition using EDS. Several grains containing copper and sulphur or copper, sulphur, and iron were thus identified.

Qualitative WDS on polished grain surfaces was used to establish the absence of oxygen in the grains and hence that they were sulphides. New subsamples were dried, embedded in epoxy, ground, and polished in preparation for examination. Bright !grains identified under the optical microscope were analyzed using both EDS and WDS techniques to determine their elemental composition qualitatively.

Sequential Leaching

The procedures published by Hall and co-workers (Hall et al. 1993) for sequential leaching of sediments were modified because of the nature of peat from the experimental wetlands (e.g., it floats, it is anaerobic, etc.). Test conditions were validated empirically by running trial leaches on duplicate peat samples wherever modifications were made. A system with several glass columns was constructed to allow simultaneous extraction of several peat samples by leach solution (Figure 1).
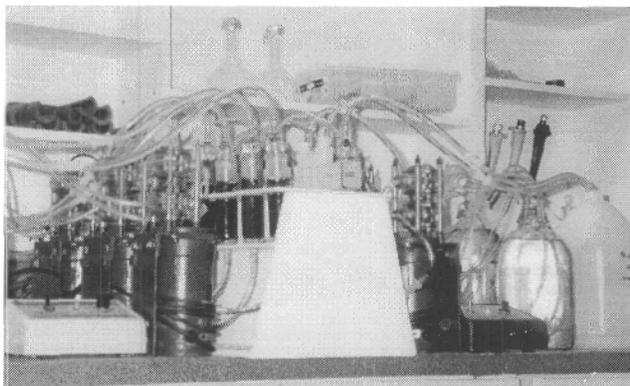

Figure 1. Column assembly used for sequential leaching of peat samples. Leach solution in glass bottles (on the right) was pumped through the bottom of glass columns and was collected in plastic bottles (far right).

Fifty grams (wet weight) of peat composited from five individual samples were loaded into the columns and washed with nitrogen-sparged distilled water previously reduced with iron filings. Subsequently, a series of leaches was carried out using the reagents and conditions presented in Table 1.

Table 1. General scheme for analytical sequential leach of peat samples

EXTRACTANT	PROCEDURE	PHASE DISSOLVED
0.1 M $Na_5O_{10}P_3$, 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 NH_2OH/HCl in 0.25% HOAc	4 hour leach @ 85° C	Crystalline Fe oxides
0.1 M NaCN, pH 10	Overnight leach in shaken flasks @ 25° C	Cyanide-sensitive sulphides
$KClO_3/HCl$; ± 4 M HNO_3	2 leaches @ 90° C; 1st without, 2nd with HNO_3	Cyanide-resistant sulphides
$HF-HClO_4-HNO_3-HCl$	Total digest	Silicates, residual crystalline fraction

The first three leaches were carried out under anoxic conditions (e.g., reagents made up in nitrogen-sparged distilled water) to preserve oxygen sensitive compounds. In addition, samples were washed with nitrogen-sparged distilled water between each extraction. The crystalline iron oxide leach step was carried out at 85° C (rather than 90° C, as described by Hall et al., 1993) because this was the highest temperature practically attainable in our system. Finally, a cyanide leach step was introduced to distin-

guish chalcopyrite from other copper sulphides (Lower and Booth, 1965), since prior examination with the SEM had tentatively identified both copper sulphide species in peat samples.

RESULTS

Copper removal by experimental wetlands

Until July 1993, the experimental wetlands at Bell received mine drainage with approximately 1 ppm copper (pH 6-8). Another source of mine drainage with 40-45 ppm copper (pH of 3) was developed at that time and fed into the ponds. The wetlands removed substantial amounts of copper from both low strength and high strength feed, as shown in Figures 2A and 2B.
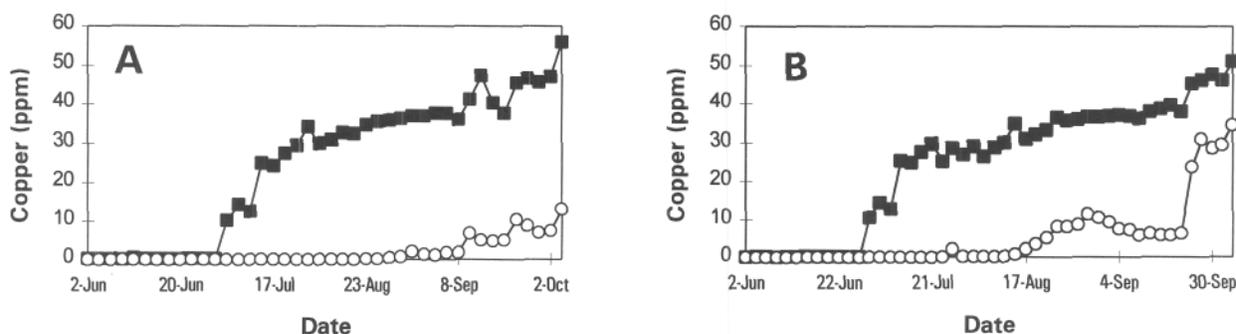

Figure 2. Copper concentration in wetland influent (•) and effluent (°). A. Small pond. B. Large pond.

The data show that the ponds removed 99% of influent copper from the low strength feed and 50-80% of influent copper from the high strength feed. Since previous analyses indicated that much of this copper remains in the peat, a study of the forms retained was initiated.

Mineralogy

Although SRBs and dissolved sulphides had been measured, and blackened, sulphur-smelling peat samples could be recovered from both ponds, we; wished to determine directly whether copper sulphides had formed. A mineralogical examination of carbon-coated samples tentatively identified both copper sulphides and copper-iron sulphides (Figure 3).
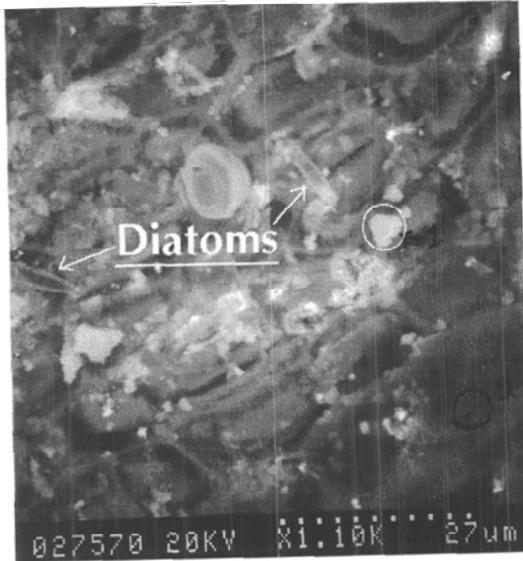
Figure 3. Photomicrograph of a sulphide grain (circled) on a carbon coated peat surface. Two algae (diatoms) are also indicated. Scale (27 μm) is on bottom right.
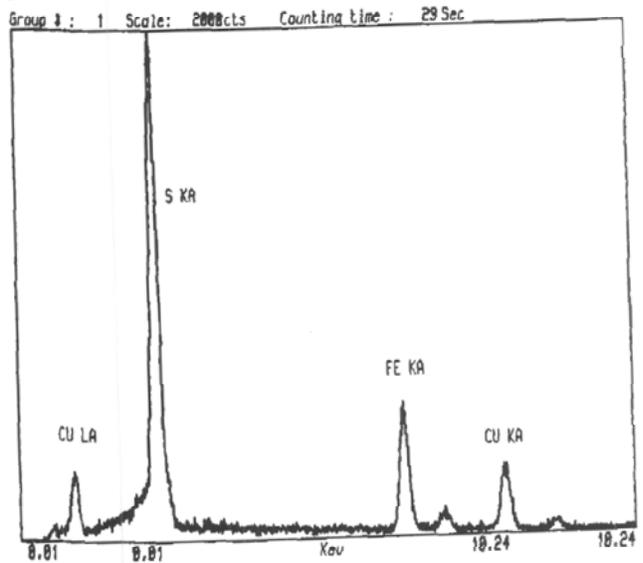
Figure 4. EDS analysis for elemental composition of a sulphide grain. Peaks for copper (CU), sulphur (S), and iron (FE) are labelled.

EBI analysis of the grain circled in Figure 3 suggested that it was a copper sulphide, possibly chalcocite. However, the presence of oxygen could not be ruled out with this sample. Therefore, additional peat samples were embedded in epoxy and prepared for EDS and WDS analysis. These analyses confirmed the absence of oxygen in all the grains examined. In addition to grains containing copper and sulphur, several grains were found that contained copper, iron and sulphur (e.g., Figure 4). Their metallic appearance under the optical microscope strongly suggested that they were chalcopyrite.

The copper sulphides identified in peat samples *by* the above methods could not be quantified. Therefore, an analytical sequential leach was carried out to quantify their relative abundance.

Sequential Leach Analysis

Samples collected from the experimental wetlands and from Newman lake were subjected to a sequential leach analysis to identify and quantify the different forms copper present in the peat. The results of this analysis are presented in Table 2.

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

PHASE[1]	Sample #	Mass[2] Cu (mg)	PHASE	Sample #	Mass Cu (mg)
1. Organic	Large Inlet	8.32	4. Cyanide	Large Inlet	0.70
	Large Outlet	0.18	extractable	Large Outlet	0.34
	Small Inlet	3.76	sulphides	Small Inlet	1.07
	Small Outlet	0.28		Small Outlet	0.55
	Newman lake	0.01		Newman lake	0.10
2. Exchangeable	Large Inlet	2.72	5. Cyanide-	Large Inlet	0.04
	Large Outlet	1.02	resistant	Large Outlet	0.08
	Small Inlet	3.12	sulphides	Small Inlet	0.12
	Small Outlet	1.16		Small Outlet	0.06
	Newman lake	0.00		Newman lake	0.00
3. Crystalline iron oxide	Large Inlet	2.07	6. Residual	Large Inlet	0.01
	Large Outlet	0.71		Large Outlet	0.01
	Small Inlet	1.96		Small Inlet	0.02
	Small Outlet	1.46		Small Outlet	0.02
	Newman lake	0.02		Newman lake	0.00

[1]Each phase corresponds to an extraction step, as described in Methods.
[2]Each value is averaged from duplicates, and is the amount of copper extracted from 50 g (wet) of peat.

The data in Table 2 show that most of the copper was present in peat sampled near the inlet of both ponds, predominantly in the organic, exchangeable: and iron oxide phases. Given the organic nature of peat, it is likely that much of the copper in the exchangeable phase is actually organically complexed. It is worth noting that the peat sampled near the inlet of the large pond had much more copper bound in the organic phase than in any other sample. By comparison, the binding-capacity for copper in the other peat samples must have been undersaturated.

Copper was also retained as sulphides, but proportionally less than in the other phases. The only exception was for the peat from Newman lake, in which the copper was mostly recovered in the cyanide-extractable sulphide phase.

Some copper was also present in the cyanide-resistant phase. This is presumed to be chalcopyrite, a finding consistent with the mineralogical analysis. Copper present in the residual phase was negligible, and it could represent material left behind from an incomplete extraction of earlier phases.

DISCUSSION

There is now a substantial literature documenting the effectiveness of wetlands in removing metals from mine drainage (Hammer, 1989; Cooper and Findlater, 1990). Several published reports on both natural wetlands (e.g., Dollhopf et al. 1988; Dave, 1993) and constructed wetlands (Wildeman et al. 1990; Hedin et al., in preparation) implicate SRBs in the metal removal process. This process is important because microbial production of sulphide will continue indefinitely as long as sulphate is present in the mine drainage and plant growth, which supplies an organic substrate for the bacteria, is supported.

Although the wetlands at Bell are unlike the more commonly used reed and cattail dominated wetlands, they still removed copper effectively from mine drainage (Figures 2 A,B). Much of the copper retained in the wetlands is associated with the peat substrate;, as opposed to the plants living in them.

The results of the sequential leach analysis presented in Table 2 show that most of this copper is organically-complexed, and only a comparatively small proportion is retained as sulphides. These results would suggest that the wetlands will not remove copper for a sustained period because the copper binding-capacity of peat should be exceeded fairly rapidly. However, this conclusion is complicated because conditions within the peat undoubtedly changed after the high strength feed was added. It is possible that much of the copper introduced before then was retained as sulphides, and that it was retained predominantly as organic complexes thereafter. Two arguments support this view. First, the lower pH of the high strength feed favours the formation of hydrogen sulphide at the expense of ionized sulphide, as shown in equation 1:

$$H_2S_g \leftrightarrow H_2S_{aq} \leftrightarrow HS^- + H^+ \quad \text{Eq. 1}$$

Since copper reacts with the ionized form of sulphide, it can be expected that a lower pH will result in less copper sulphide being formed. This effect is compounded by an observed decrease in SRB populations, and hence sulphide production, following the introduction of the high strength feed (unpublished observation). However, the study could not determine whether the microbial populations were adapting to the lower influent pH.

The sequential leach analysis indicated that the peat from the wetlands had a substantial capacity for binding copper. The fact that copper began to appear in effluent from the wetlands when the high strength feed was added, despite the incomplete saturation of the peat binding-capacity, indicates that insufficient retention was being provided. A higher retention time might have been required because of the higher copper concentration, the lower pH, or a combination of these factors.

It is worth noting that most of the copper in the peat sampled in Newman lake, the reference site for this study, was present as cyanide-extractable sulphide. It could be argued that this copper was deposited as dust from the mine site. Given that Bell is a chalcopyrite orebody, the copper deposited as dust should be chalcopyrite. However, no cyanide-resistant copper was recovered from the peat from Newman lake, ruling out this possibility. Since both SRBs and dissolved sulphide had been detected at this site (unpublished observation), it is likely that these copper sulphides were formed *in situ.* This finding suggests that copper retained in experimental wetlands might eventually form sulphide minerals, even if it was first retained in an organically bound phase.

The identification of chalcopyrite in the peat from the experimental wetlands is interesting from a mineralogical point of view. It is possible that this chalcopyrite was introduced from outside the ponds rather than being generated within the peat. For example, it might have been present in the feed added to the wetlands and have been filtered out by the peat. However, the data in Table 2 rule out this possible explanation: there is no consistent pattern of accumulation near the pond inlets, where chalcopyrite would have accumulated if it had been filtered out. Chalcopyrite might also have been deposited as airborne dust, and although the peat samples were collected from 10-20 cm below the surface, we cannot rule out this possibility entirely. Finally, it is possible that it was formed *in situ.* This is contrary to the common belief that chalcopyrite cannot be formed in the short time and under the conditions present in the constructed wetlands. However, Giblin (1988) demonstrated that pyrite formation in salt marshes can be extremely rapid, and described microbially-facilitated processes by which it can be formed. If these ideas are correct, it is possible that similar processes are taking place in the Bell wetlands as well. These processes should be studied in more detail because a better understanding may lead to improved wetland treatment of mine drainage.

In summary, both the mineralogical analysis and the sequential leach analysis have shown that copper sulphides are formed in wetlands treating copper-containing mine drainage. Copper was also present in peat in an organically-bound form. It is probable: that copper from low strength mine drainage (1-2 ppm, pH 6-8) was mainly removed as a sulphide, \vhereas that removed from high strength mine drainage (40-50 ppm, pH 3) was largely organically bound. These results suggest that peat-based wetlands may not be effective in treating pH 3 mine drainage, but that treatment of mine drainage with a higher pH may be sustained for a long time.

ACKNOWLEDGMENTS

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