

FACTS AND MYTHS ON THE EFFECTIVENESS OF WATER COVERS TO SUPPRESS SULFIDE OXIDATION AND METAL LEACHING – FIELD AND LABORATORY EVIDENCE¹

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Abstract. Largely due to the low diffusivity of dissolved oxygen in water, reactive tailings are often rendered harmless upon disposal underwater. However, both field observations and results of simulated weathering studies in the laboratory have shown that as long as a water cover remains oxygenated, sulfides exposed at the tailings/water interface are susceptible to oxidation. The two primary factors that determine whether or not net acid generation is to occur are the alkalinity balance in the water cover and the rate of deposition of a more efficient oxygen scavenger like organic matter to further isolate the submerged tailings. Even if net acid generation may not materialize, metal leaching can still occur as a result of galvanic interaction. Moreover, because of the changing redox conditions, many potentially deleterious trace elements with multiple oxidation states like arsenic and antimony are subject to remobilization from mine wastes disposed underwater. Thus, the choice of a proper management alternative for the long-term disposal of reactive mine wastes must duly consider the composition of the mine wastes as well as the environmental settings of the site after mine closure.

Additional Key Words: alkalinity balance, oxygen scavenger, galvanic interaction, base metals, arsenic and antimony.

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Introduction

Since the mid-1980s, a considerable amount of research has been conducted to investigate subaqueous disposal as an effective means to manage reactive mine waste, especially under the auspices of Canada's Mine Environment Neutral Drainage (MEND) Program (Tremblay and Hogan, 2001). Although it is generally accepted that water covers can inhibit sulfide oxidation and metal leaching, there is still controversy on whether or not submerged sulfidic tailings are completely inert under field conditions (Pedersen et al., 1991; Vigneault et al., 2001). Similarly, contrasting results on the extent of metal leaching from submerged tailings have often been obtained in laboratory simulation experiments, which occasionally seem to contradict field observations (MEND, 1998, Appendix C). Moreover, most of the previous studies assumed a direct link between metal leaching and the occurrence of acid drainage. Recent research has shown that metal leaching can occur, for example through galvanic interaction, under a near-neutral to slightly alkaline, oxygenated water cover (Kwong et al., 2003). To help eliminate the persistent confusion in the community at large about the effectiveness of water covers to suppress sulfide oxidation and metal leaching, it is useful to elucidate the pertinent processes involved and identify the key parameters controlling the reactivity of submerged mine wastes.

This paper is divided into two parts. Part I presents a laboratory column experiment specially designed to investigate the geochemical behavior of reactive tailings under a water cover. Part II reviews related field and laboratory observations documented in the literature. The primary purpose of the exercise is to clarify the facts and myths surrounding the effectiveness of water covers to suppress sulfide oxidation and metal leaching. In so doing, key parameters controlling the reactivity of the submerged mine waste and its impact on the overlying water is elucidated. Conclusions are then given with regard to the type of mine waste that can be safely disposed of under water and the environmental conditions required for ensuring their long-term stability.

Part I. Laboratory Water Cover Experiment

Experimental Design and Setup

To evaluate subaqueous disposal as a method of controlling oxidation of sulfide minerals, fresh sulfidic tailings were sampled from the Louvicourt Mine located in northern Quebec, Canada, and used to set up four series of triplicate cylindrical lysimeters (columns). Each series simulated a different scenario of subaqueous tailings disposal (Blanchette et al., 2000). For this paper, only the results obtained from the two series of columns evaluating the effect of two different water depths (0.3 and 1.0 m, respectively) on the weathering of the submerged tailings are presented. The columns, measuring 30 cm inner diameter and 2.2 m high, were made of clear, 1.25 cm-thick polyvinyl chloride and equipped with side sampling ports at various heights (Fig. 1). The tailings were loaded as a slurry. The high solids content of the slurry (~70%) resulted in efficient and uniform settling. Each of the columns for studying the impacts of water depth contained approximately 140 kg of tailings with a settled height of 1 m. The tailings were fine-grained (80% finer than 50 μm) and characterized by high total sulfur (17.2%) and iron (19.8%). Pyrite was the dominant sulfide present although pyrrhotite, chalcopyrite, sphalerite, arsenopyrite and galena also occurred in trace amounts. Ankerite and magnesium-rich siderite were the prominent carbonates while the silicate minerals identified included quartz, mica, chlorite and feldspars. With a net neutralization potential of $-466 \text{ kg CaCO}_3/\text{tonne}$, the tailings were classified as highly acid-generating. The trace element contents were 64 mg/kg As, 92 mg/kg Cu, 65 mg/kg Pb and 330 mg/kg Zn.



Figure 1. Close-up view of the cylindrical lysimeters showing the arrangement of sampling ports.

The column study consisted of two phases. Phase I, which lasted for 200 days, focused on evaluating oxygen diffusion and ionic fluxes under conditions of a circulated water cover. In the first 100 days, the water cover in each column was circulated but not aerated. In the second 100 days, aeration of the water cover was also introduced. Phase II, which lasted for 13 months, incorporated precipitation, runoff and drawdown events at rates comparable to those observed in the field. These events were simulated by adding water to and draining it from the top of the overlying water column, or draining it from the bottom port of the columns at fixed rates, while maintaining the designed water depth above the tailings. At the start-up of the experiment, locally available natural water from the Ottawa River was used as the water cover, replacing the process water which provided a temporary cover during the transport of the tailings to the laboratory. The changes in water chemistry during both phases of the experiment were monitored by regular sampling at two depths in the overlying water and five depths below the water-tailings interface. Both Phases I and II commenced with a new batch of natural water as water cover such that only the porewater in each column retained remnant effects of the previous stage of testing.

Results and Interpretation

Throughout the Phase I of the experiment, the pH in the overlying water of both sets of columns remained near-neutral, comparable to that of the Ottawa River water. The 0.3 m water covers, however, showed a considerably higher average conductivity and dissolved sulfate, calcium, magnesium and zinc concentrations than the 1.0 m water covers. These parameters typically increased with time in the water cover but decreased with time in the porewaters below the water-tailings interface. The temporal variation in profiles of these parameters is exemplified by Fig. 2 for mean dissolved sulfate (i.e. average of three columns in each set). The occurrence of a steep concentration gradient in dissolved sulfate at shallow depth below the water-sediment interface indicates that, in addition to sulfide oxidation, part of the sulfate release to the overlying water was due to diffusion from the tailings porewater. The changing profiles of mean dissolved oxygen with time during Phase I for both sets of columns are shown in Fig. 3. Before the initiation of aeration on Day 100, the dissolved oxygen concentrations in the water covers decreased rapidly with time. Upon aeration, the dissolved oxygen

concentrations in the 0.3 m water covers quickly rebounded to near saturation but those in the 1.0 m water covers increased significantly but remained under saturation.

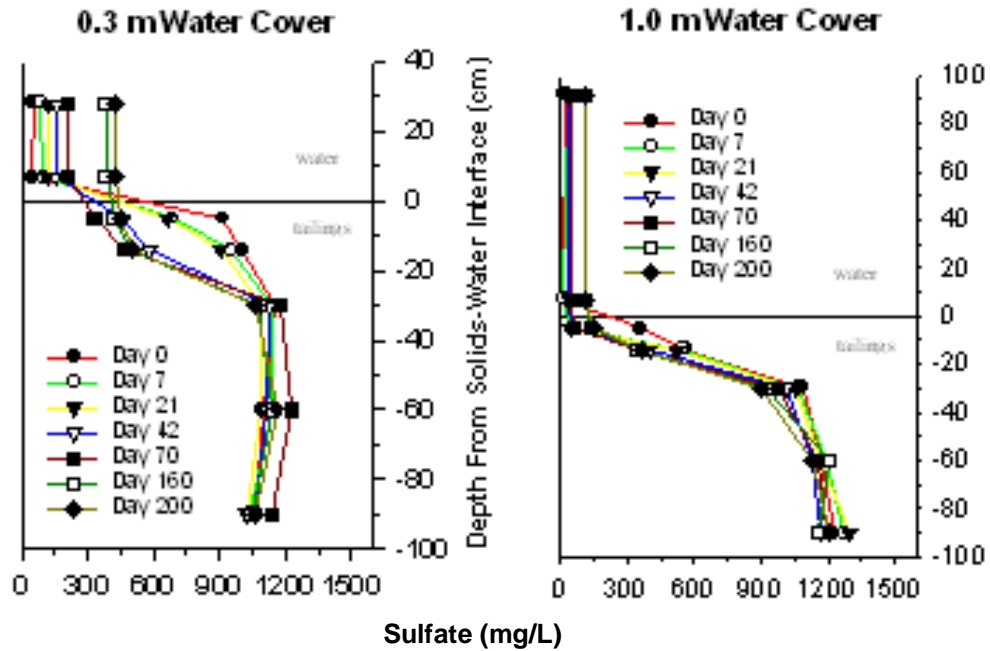


Figure 2. Temporal variation in mean sulfate profiles during Phase I of experiment.

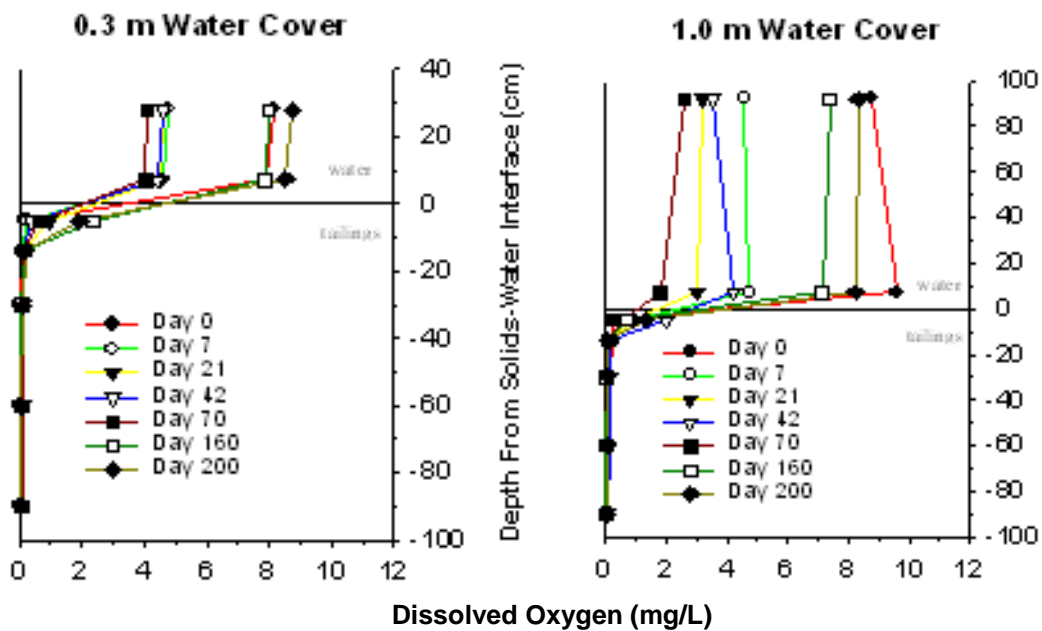


Figure 3. Temporal change in profiles of mean dissolved oxygen during Phase I of study.

Through the course of Phase II of the experiment, where water cover circulation and aeration were applied to the columns in conjunction with runoff and drawdown events, the 0.3 m water covers remained close to full saturation in dissolved oxygen while the 1.0 m water covers were slightly under-saturated. The average pH in the 0.3 m water covers dropped below 7 after about 200 days and to about 5 on Day 353 (Fig. 4), accompanied by significant increases in concentrations of dissolved sulfate, calcium, copper, magnesium, manganese and zinc. In contrast, the average pH in the 1.0 m water covers increased slightly from about 7 to 8, roughly in agreement with the seasonal change in pH of the Ottawa River water. This gave rise to only a slight increase in the concentrations of dissolved sulfate, calcium and magnesium. The solution pH of samples collected at the bottom port of the columns are also shown in Fig. 4. The lower pH values compared to those of the tailings porewater at shallower depths are indicative of possible sulfide oxidation or iron oxide precipitation occurring near the bottom sampling port.

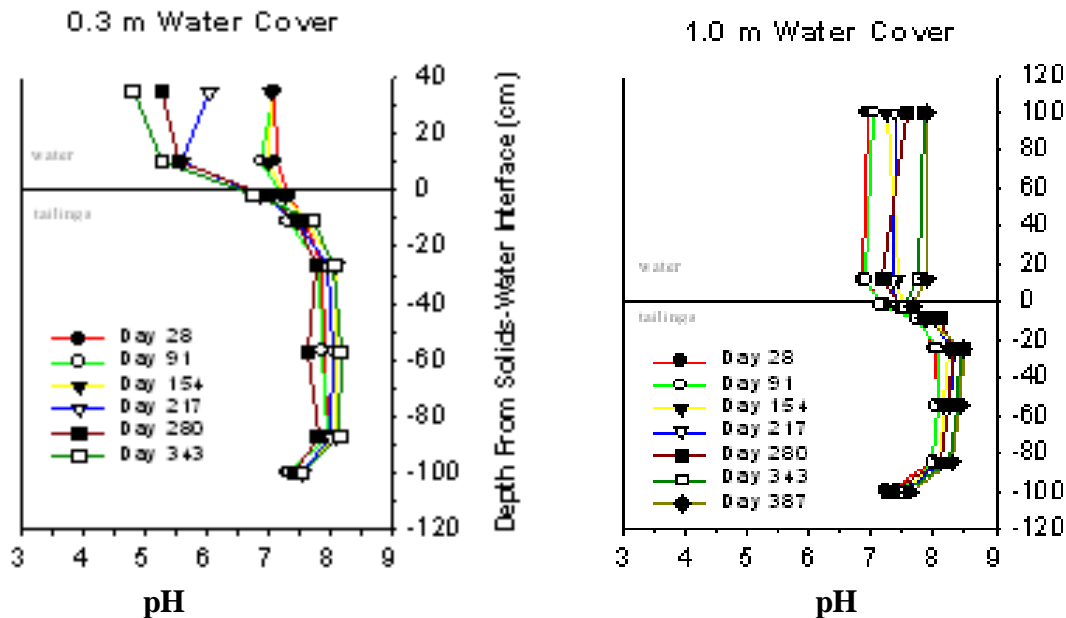


Figure 4. Temporal changes in mean pH profile during Phase II of the water cover study.

The increase in pH in the overlying water and tailings porewater of the columns with a 1.0 m water covers is also associated with an increase in total alkalinity (Fig. 5). The average total alkalinity in the tailings porewater peaks at about 9 cm below the water tailings interface. This

could have resulted from the downward migration of additional alkalinity generated by oxidation of dissolved organics (in the Ottawa River water) at the interface. Alternatively, sulfide oxidation at the interface could have led to minor dissolution of carbonates with the resultant bicarbonate ions flushed downward by the drawdown events.

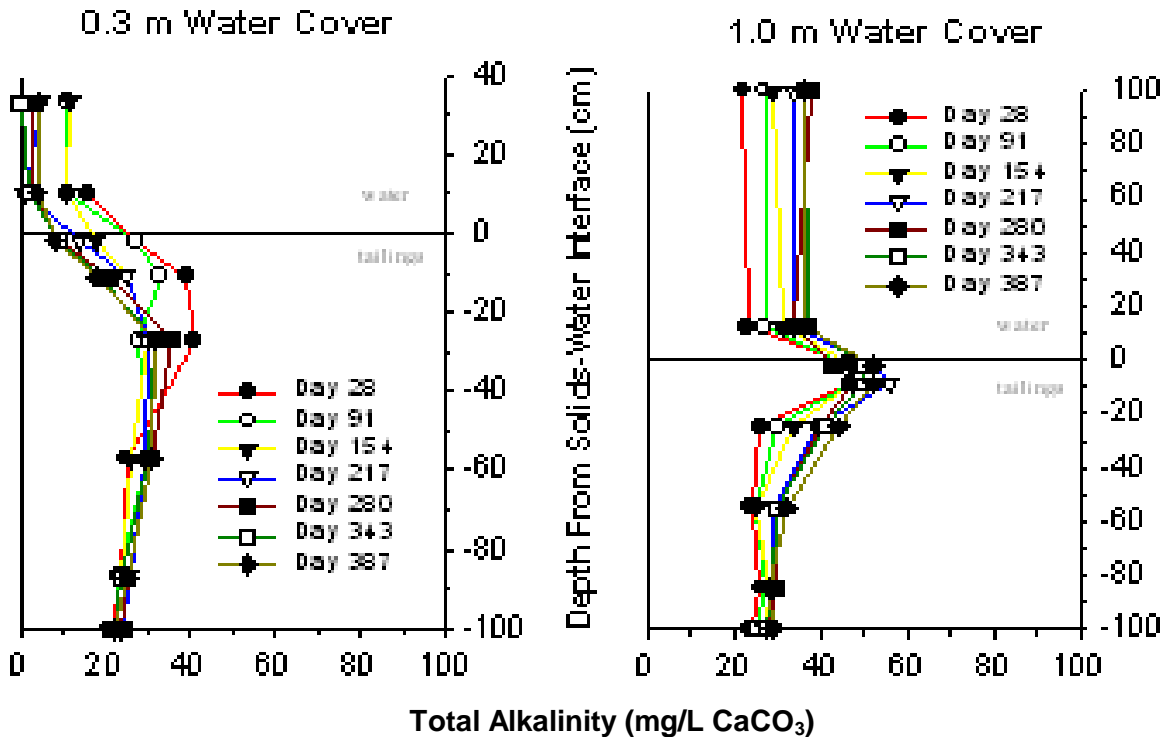


Figure 5. Temporal changes in mean total alkalinity during Phase II of water cover study.

As the volume of overlying water in the two series of columns differs by factor of 3.3, efflux loading to the water covers is a more direct measure of impact than concentrations. The mean cumulative efflux loadings of selected parameters to the overlying water in each series of columns are shown in Table 1. The efflux loading of a conservative element like calcium to the overlying water of each series of the columns are comparable in both phases of the experiment, reflecting that diffusion from the tailings porewater was the dominant cause of the efflux. The lower efflux in Phase II compared to that of Phase I is largely due to the incorporation of precipitation and drawdown events in the Phase II of the experiment.

Table 1. Cumulative efflux loading of selected parameters to the water covers.

Parameter	Time	0.3 m Cover	1.0 m Cover
Phase I			
SO ₄ (g)	Day 100	4.85	4.57
SO ₄ (g)	Day 200	8.86	7.51
Zn (mg)	Day 100	2.23	0.00
Zn (mg)	Day 200	7.13	2.26
Al (mg)	Day 200	-3.05	-3.05
Ca (g)	Day 200	1.83	2.07
Cu (mg)	Day 200	-0.35	-0.57
Phase II			
SO ₄ (g)	Day 217	3.49	1.16
Zn (mg)	Day 217	10.8	1.77
Al (mg)	Day 217	0.04	-0.59
Ca (g)	Day 217	0.64	0.55
Cu (mg)	Day 217	0.34	-0.50

Although the sulfate effluxes were comparable in both sets of columns early in Phase I of the experiment, they started to deviate after the introduction of aeration with a higher efflux loading noted in the 0.3 m covers. At the end of Phase II, the average cumulative efflux loading of sulfate to the 0.3 m water covers was triple that to the 1.0 m covers. The difference in efflux sulfate loadings in the two set of columns clearly demonstrates that in addition to possible diffusion from the tailings porewaters, sulfides at the water-tailings interface were oxidizing to generate additional sulfate and that the reaction occurred at a faster rate under the shallower water cover. As a result of sulfide oxidation, the overlying water in all the three columns with a 0.3 m water cover eventually turned acidic after about 200 days in Phase II. (Fig. 4). The 1.0 m water covers, however, did not turn acidic. This is largely due to the alkalinity content of the Ottawa River water, which is about 25 mg/L CaCO₃. With a volume more than triple that of the 0.3 m water covers, the 1.0 m water covers had sufficient alkalinity capacity to neutralize the

effect of acid generation by sulfide oxidation at the water tailings interface. Oxidation of dissolved organics in the Ottawa River water could have also contributed additional alkalinity to the water covers.

The occurrence of sulfide oxidation is also supported in both sets of columns by the positive efflux loading of zinc, which could only be derived from sphalerite in the submerged tailings. In this case, however, the zinc release occurred very early in Phase I, even prior to the introduction of aeration (on Day 100) in the columns with a 0.3 m water cover (Table 1). The early zinc release and the observed differences in efflux loading for the two sets of columns can readily be explained in terms of galvanic sulfide oxidation, which has recently been described in detail by Kwong et al. (2003). Having a much lower electrode potential than pyrite, sphalerite in the presence of an electrolyte like water will preferentially undergo oxidative dissolution, releasing zinc into solution while the adjacent pyrite is prevented from oxidation through cathodic protection. As sphalerite is characterized by a metal to sulfur ratio of one to one, its complete oxidative dissolution to give dissolved zinc and sulfate will not lead to acid generation unless it is iron-bearing. The net effect of pyrite protected from oxidation is a delay in the occurrence of acid generation while zinc leaching continues. Although the 1.0 m water covers were only marginally less oxygenated than the 0.3 m water covers, their larger volume gave rise to a weaker electrolyte solution which in turn damped the galvanic reactions, resulting in a lower zinc leaching.

The observed copper efflux to the 0.3 m water covers during the Phase II of the experiment is also compatible with galvanic sulfide oxidation occurring at the water-tailings interface. Chalcopyrite, the primary source of copper in the submerged tailings, has an electrode potential only marginally lower than that of pyrite (Kwong et al., 2003). Oxidative dissolution of chalcopyrite adjacent to pyrite will thus proceed efficiently only under acidic conditions which enhance galvanic reactions (Kwong et al., 2003). This explains why copper leaching was observed only when the 0.3 m water covers had turned acidic and not observed at all in the 1.0 m water covers. It should be noted that the submerged tailings in both sets of columns initially serve as sinks to dissolved copper and aluminum in the Ottawa River water (which was used as the water covers). It was only after the 0.3 m water covers had turned acidic that the leaching of these elements was observed in the columns with a shallow water cover (Table 1). The

acidification presumably proceeded with the oxidative dissolution of pyrrhotite, which has an electrode potential comparable to that of sphalerite, and the slower oxidation of unprotected pyrite not in contact with any sulfide minerals characterized by a lower electrode potential.

Summary of Observations

In recapitulation, the following deductions can readily be drawn from the observations made in the experiment to compare the effectiveness of two different depths of water covers to suppress sulfide oxidation:

1. As long as the water covers remain oxygenated, sulfides exposed at the water-tailings interface are susceptible to oxidation, the rate of which is limited by the replenishment of dissolved oxygen to the reaction sites;
2. The alkalinity balance in the water cover dictates whether or not net acidification is to occur; if progressive sulfide oxidation produces acidity in excess of the alkalinity pool in the water cover, acidification is unavoidable; and,
3. While metal leaching is enhanced under acidic conditions, it can also occur by galvanic interaction to a lesser extent under near-neutral conditions.

Part II. Related Field and Laboratory Observations

Many case studies on water covers have been summarized in Volume 4 of the MEND Manual on Prevention and Control (Tremblay and Hogan, 2001). A few of the more pertinent studies and other independent works are reviewed below to further elucidate the effectiveness of water covers to suppress sulfide oxidation and metal leaching.

Observations at the Louvicourt Field Cells

In conjunction with the laboratory column work, two field test cells each measuring 21 m x 21 m x 3 m deep were constructed beside the main tailings pond for detailed monitoring at the Louvicourt Mine, Val d'Or, Quebec. The field cells were filled with 2 to 3 m of fresh tailings and covered with a 0.3 m layer of natural runoff. The results of the initial 2 years of monitoring

were documented by Vigneault et al. (2001). They are similar to the results obtained in the column study described above. Salient observations include the following:

1. The shallow water cover (0.3 m) was effective in reducing the rate of sulfide oxidation in the tailings with the oxygen consumption about 4000 times less than that of tailings samples exposed to the atmosphere in humidity-cell testing;
2. While the water cover in both field cells remained near-neutral, there was clear evidence of surface sulfide oxidation in the submerged tailings at the mm scale in terms of dissolved oxygen depletion coupled with local changes in hydronium ion and sulfate;
3. Two years after the tailings were placed under water in the field cells, there was clear evidence of cadmium and zinc mobilization from the tailings into the overlying water with concomitant changes in the partition pattern of the two metals (i.e., from refractory to more mobile fractions).

Reactivity of Sulfidic Tailings Submerged in Natural Lakes

The geochemical behavior of massive sulfide tailings submerged in two natural lakes was evaluated by Pedersen et al. (1997) using high-resolution porewater sampling. Anderson Lake in Manitoba is a typical mesotrophic to eutrophic lake in the Precambrian Shield with little outflow. It is horseshoe-shaped with a length of 6 km and a maximum depth of approximately 8 m. Between 1979 and 1994, about 9 million tonnes of mill tailings from the processing of copper-lead-zinc massive sulfide ores in an alkaline medium were deposited in the lake. The tailings consisted mainly of silt-sized pyrite, quartz and feldspar with minor amounts of pyrrhotite, galena, chalcopyrite and sphalerite. The sulfidic tailings showed no evidence of oxidation even at a shallow, turbulent site where the water column was well oxygenated throughout the summer. Instead, dissolved copper, lead and zinc derived from some acid-generating waste rock located in the north shore of the lake apparently diffused from the water column into the submerged tailings, which were anoxic at a very shallow depth below the water-tailings interface. Data collected to date indicate that the sulfate inputs and organic matter settling fluxes are sufficient to sustain microbial-mediated sulfate reduction.

Buttle Lake, measuring 35 km long x 1 km wide and 87 m deep (maximum), is a large oligotrophic water body on central Vancouver Island, British Columbia. Between 1967 and

1984, about 5.5 million tonnes of pyrite-rich, copper-, lead- and zinc-bearing tailings were submerged in the south basin of the lake below the thermocline. The tailings consisted of sand- to silt-sized silicate gangue minerals and pyrite as well as residual chalcopyrite, galena and sphalerite. The mean base metal concentrations in the tailings solids amounted to 1300 mg/kg Cu, 900 mg/kg Pb and 7000 mg/kg Zn (Pedersen et al., 1997). Tailings had not been discharged into Buttle Lake for nearly two decades but Pedersen et al. (1997) found no evidence that the sulfidic tailings were oxidizing on the lake bottom. However, limited release of zinc to the bottom water was detected, which was attributed to the remobilization of zinc adsorbed on manganese and iron oxides as part of the ongoing diagenetic metal cycling process. The source of zinc was apparently acidic runoff from the adjacent mine site and not the submerged tailings. The tailings are now being progressively covered with a veneer of natural sediments, which would help to preserve their anoxic state in perpetuity.

Laboratory Study of Pilot Plant Petaquilla Tailings under a Fresh Water Cover

As part of a feasibility study, Sahami and Riehm (1999) evaluated the subaqueous reactivity of sulfidic tailings from the Petaquilla Property, Panama, in a 10-month laboratory experiment. Pilot plant tailings placed in a rectangular plexiglass tank were covered with 20 cm of deionized/distilled water. The water cover was circulated within the tank to create laminar flow across the water-tailings interface. Monitoring results using peepers indicated no significant effluxes of dissolved cadmium, copper, nickel, lead and zinc from the submerged tailings to the overlying water. Iron and manganese were reprecipitated as oxides and oxyhydroxides at the tailings surface and could have attenuated the upward transport of the dissolved base metals through sorption reactions. Dissolved oxygen measurements using microelectrodes indicated diffusion of oxygen into the tailings, which was totally consumed by organic degradation and sulfide oxidation within 2.5 cm below the water-tailings interface.

Behavior of Reactive Tailings under a Saline Water Cover.

To compare the functionality of a saline versus a fresh water cover to suppress sulfide oxidation and metal leaching, Davé (2002) reported a 2-year experiment conducted with low- and high-sulfide tailings from two historic copper mines in Newfoundland. The experiment was

conducted in four aquarium-type lysimeters, each with well-aerated water cover about 26 cm deep overlying the tailings substrate. The combinations involved in the lysimeter setup were fresh water over low-sulfide tailings, saline water over low-sulfide tailings, fresh water over high-sulfide tailings and saline water over high-sulfide tailings. Natural seawater and lake water were used as the water covers. The low-sulfide tailings contained about 4% sand- to silt-sized granular pyrite and the high-sulfide tailings contained about 20% very fine-grained and poorly recrystallized framboidal pyrite. The granular pyrite appeared to be fresh while the framboidal pyrite invariably showed evidence of incipient alteration. Both tailings types contained accessory amounts of chalcopyrite, galena and sphalerite. At the end of the experiment, the low-sulfide tailings remained non-reactive under either water cover with negligible releases of acidity and other contaminants to the overlying water. However, both the fresh and saline water covers in the lysimeters containing the high-sulfide tailings turned acidic with elevated concentrations of dissolved copper, lead, nickel and zinc. Relative to the fresh water cover, the acidification of the saline cover was delayed by about a month because of the inherent alkalinity in seawater. The results of the experiment clearly demonstrate the importance of sulfide morphology in controlling its oxidation rate and that the alkalinity balance in the water covers dictates whether or not they will eventually turn acidic. In the field, samples of the high-sulfide tailings deposited on the seafloor (at 100 m depth) off the shore of the historic mine site invariably showed a 2 - 5 cm surface oxidation layer although the porewater was alkaline (Kwong, unpublished data).

Observations Involving Submerged Mine Wastes with Metalloids

Pedersen et al. (1997) also investigated the geochemical behavior of slightly alkaline, arsenic-rich tailings deposited in the constructed tailings pond at the Equity Silver Mine near Houston, British Columbia. The Equity Silver ore comprised of chalcopyrite and the sulfosalts tennantite and tetrahedrite accompanied by pyrite, arsenopyrite, sphalerite, galena and pyrrhotite. From 1980 to 1993, the production rates ranged from 1500 to 9000 tonnes/day and the tailings were discharged to a constructed water-filled pond 1.2 km² in area and up to 5 m deep. Porewater sampling by Pedersen et al. (1997) indicated that the tailings were releasing arsenic to the porewaters but taking up antimony from the overlying water. Dissolved oxygen data showed that while the tailings were anoxic at a depth of several cm the redox gradient did not seem to

affect the distributions of arsenic and antimony. The implications were: (1) that the porewater arsenic enrichment was due to the dissolution of some soluble secondary minerals instead of the primary sulfosalts; and, (2) that the uptake of the antimony was due to the precipitation of an unknown authigenic mineral.

In contrast, based on the ratios of dissolved cobalt and nickel to arsenic in the porewaters of submerged tailings in the historic Cobalt mining district, Ontario, Kwong et al. (2000) suggested that the dissolution of secondary minerals like erythrite could not account for the large excess of arsenic. The authors provided petrographic evidence suggesting that galvanic interaction might facilitate oxidative dissolution of primary arsenides even under water. Presumably, it was the combined effect of dissolution of secondary arsenates and oxidative dissolution of primary arsenides deposited along the water courses in the Cobalt area that gave rise to elevated dissolved arsenic concentrations well in excess of the drinking water quality criterion (Percival et al., 2004).

At the Eskay Creek Mine in northern British Columbia, fresh mine fines and production waste were disposed of in a nearby lake (Albino Lake) when the mine was started in 1995 (Murphy et al., 1999). The mine exploited a sedimentary exhalative massive sulfide deposit (SEDEX) enriched in gold and silver. The dominant sulfides were pyrite, stibnite, tetrahedrite, sphalerite, galena and minor chalcopyrite. In mid-1995, antimony concentrations in Albino Lake increased from undetectable to almost 1 mg/L. The source of antimony was found to be stibnite in the mine fines. This clearly demonstrates the plausibility of antimony leaching even under a water cover.

Discussion

Based on the observations made in the laboratory experiment presented in Part I and the review of pertinent laboratory and field investigations on the performance of subaqueous disposal presented in Part II, a few facts and myths on the effectiveness of water covers to suppress sulfide oxidation and metal leaching are examined below.

On the Reactivity of Sulfides under a Water Cover

The assumption that reactive sulfides once placed underwater will become completely non-reactive is a myth. It is true that submerged sulfide tailings often show a reduced reactivity compared to the same disposed on land. This is sometimes attributed to the low concentration of oxygen in surface water, which is 30 to 2.5×10^4 times lower than that in the atmosphere depending on the choice of concentration units (MEND, 1998). However, the presence of an aqueous phase in addition to oxygen is a prerequisite for sulfide oxidation. This is clearly evident from the observation of Taylor and Wheeler (1994) that water-derived oxygen invariably forms a dominant component of sulfate, the oxidation product of sulfides. Thus a comparison of oxygen concentration in water versus that in air is not really meaningful. A more important parameter affecting sulfide oxidation is in fact the diffusivity of oxygen in water compared to that in air. Values for oxygen diffusion coefficients in water and air are 1.5×10^{-5} and $0.178 \text{ cm}^2/\text{s}$, respectively. Sulfides are invariably formed under reducing conditions and become unstable in an oxygenated environment. In submerged sulfidic tailings, the replenishment of oxygen consumed by sulfide oxidation at the tailings surface is hampered. This in turn slows down the sulfide oxidation process. Only in the presence of a more efficient oxygen scavenger like organic matter will sulfide oxidation be completely arrested. This is probably the case at Anderson Lake and Buttle Lake (Pedersen et al., 1997). For the Louvicourt field and laboratory studies described above, the paucity or absence of deposited organic matter have given risen to unequivocal evidence of sulfide oxidation at the tailings surface. In addition, the Louvicourt column studies (Part I above) and the comparative fresh versus saline water cover investigation (Davé, 2002) clearly show that once subaqueous sulfide oxidation occurs, the alkalinity balance in the water covers will determine if net acidification will occur or not.

On Metal Leaching under a Water Cover

The expectation that subaqueous disposal will totally arrest metal leaching from reactive mine waste is obviously a myth. It is true that metal leaching can be minimized, at least for base metals, by reducing the chance of net acid generation through placement of reactive sulfides under water. Nonetheless, both the Louvicourt field cell and laboratory column studies have demonstrated the leaching of some zinc and cadmium, probably through galvanic interaction, even though net acidification may not materialize. Only under completely anoxic conditions

will the base metal sulfides become stable and base metal leaching be arrested. On the other hand, the Equity Silver, Eskay Creek and the Cobalt mining camp case studies amply demonstrate the plausibility of arsenic and antimony leaching, either through dissolution of secondary minerals or oxidation of primary sulfosalts, possibly mediated by galvanic interaction, even under reducing conditions. Both arsenic and antimony are semi-metals with multiple oxidation states. Their mobility under reducing conditions is enhanced due to the thermodynamic stability of their respective reduced species in solution.

Implications for Mine Waste Management

From the discussion above, it should be apparent that subaqueous disposal as a panacea for managing all types of reactive mine wastes is a myth. Depending on the detailed composition of the mine wastes and the environmental settings of the depository, an alternative disposal may be more advantageous than placement under water. Thus, for reactive mine wastes enriched in base metals, it may be appropriate to employ subaqueous disposal if the depository is characterized by a high settling flux of organic matter to assure the development of perpetual anoxic conditions. For mine wastes containing highly mobile trace elements like arsenic and antimony even under reducing conditions, on-land disposal with simple covers maintaining an oxic environment may be preferred. For reactive mine wastes containing both base metal sulfides and sulfosalts, one has to consider the relative seriousness of the impacts of potential acid mine drainage and trace element leaching in deciding if underwater or subaerial disposal is more suitable.

Conclusions

Based on observations made in the specially designed column experiment (Part I) and the brief review of documented studies of chemical stability of reactive mine tailings disposed under water (Part II), the following conclusions can be drawn:

1. Although water covers are effective in reducing the rate of sulfide oxidation, the process is not completely eliminated in the absence of a more efficient oxygen scavenger like decaying organic matter.

2. With the progress of sulfide oxidation under water, the alkalinity balance in the water cover determines if net acidification is to occur or not.
3. Even under near-neutral to slightly alkaline conditions, metal leaching can still occur in submerged sulfidic mine waste through galvanic interaction.
4. Potentially deleterious trace elements like arsenic and antimony with multiple oxidation states are susceptible to remobilization under water with changing redox conditions.
5. The choice of long-term disposal options managing reactive mine waste must duly consider the detailed composition of the mine wastes and the environmental settings of the depository.

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Literature Cited

- Blanchette, M.C., N.K. Davé, Y.T.J. Kwong and B. Tisch. 2000. Evaluation of man-made subaqueous disposal option as a method of controlling oxidation of sulfide minerals: Column studies. MEND Report 2.12.1e. Mining and Mineral Sciences Laboratories Report MMSL 2000-060(CR), Natural Resources Canada, Ottawa.
- Davé, N.K. 2002. Chemical assessment of underwater deposited Little Bay and Tilt Cove tailings – Laboratory lysimeter studies. Mining and Mineral Sciences Laboratories Report MMSL 02-029(CR), Natural Resources Canada, Ottawa.
- Kwong, Y.T.J., J.B. Percival and E.A. Soprovich. 2000. Arsenic mobilization and attenuation in near-neutral drainage – Implications for tailings and waste rock management for Saskatchewan uranium mines. *In:* E. Ozberk and A.J. Oliver (eds.), Uranium 2000, International Symposium on the Process Metallurgy of Uranium, Saskatoon, Saskatchewan,

- Canada September 9-15, 2000. The Canadian Institute of Mining, Metallurgy and Petroleum, Montreal, pp. 579-593.
- Kwong, Y.T.J., G.W. Swerhone and J.R. Lawrence. 2003. Galvanic sulfide oxidation as a metal-leaching mechanism and its environmental implications. *Geochemistry: Exploration, Environment, Analysis*, Vol. 3, pp. 337-343. <http://dx.doi.org/10.1144/1467-7873/03/013>
PMid:12694582
- MEND. 1998. Design Guide for the Subaqueous Disposal of Reactive Tailings in Constructed Impoundments. MEND Project 2.11.9. Canada Centre for Mineral and Energy Technology, Natural Resources Canada, Ottawa.
- Murphy, M., T. Higgs and M. Bratty. 1999. Performance of the Albino subaqueous waste disposal facility at the Eskay Creek Mine. *In: Summary Notes from the 6th Annual BC MEM/MEND 2000 Metal Leaching and Acid Rock Drainage Workshop*. Vancouver, British Columbia. 1 to 2 December. 13p.
- Pedersen, T.F., B. Mueller, B. and C.A. Pelletier. 1991. On the reactivity of submerged mine tailings in fjord and lake in British Columbia. *In: J.W. Gadsby and A.J. Malick (eds.), Acid Mine Drainage: Designing for Closure*. BiTech Publishers, Vancouver, pp. 281-293.
- Pedersen, T. F., J.J. McNee, D. A. Flatter, B. Mueller, A. Sahami and C.A. Pelletier. 1997. Geochemistry of submerged tailings in Buttle Lake and the Equity Silver tailings pond, British Columbia and Anderson Lake, Manitoba: What have we learnt? *In: Proceedings of the 4th International conference on Acid Rock Drainage*, Vancouver, BC, 31 May to 6 June. Vol. 3, pp. 989-1006.
- Percival, J.B., Y.T.J. Kwong, C.G. Dumaresq and F.A. Michel. 2004. Transport and attenuation of arsenic, cobalt and nickel in an alkaline environment (Cobalt, Ontario). Geological Survey of Canada Open File 1680. <http://dx.doi.org/10.4095/214977>.
- Sahami, A.R. and D. Riehm. 1999. An assessment of the subaqueous reactivity of sulfide-rich tailings from the Petaquilla Property, Panama. *CIM Bulletin*. Vol. 92, pp. 77-88.
- Taylor, B.E. and M.C. Wheeler. 1994. Sulfur and oxygen isotope geochemistry of acid mine drainage in the western United States – Field and experimental studies revisited. *In: C.N. Alpers and D.W. Blowes (eds.), Environmental Geochemistry of Sulfide Oxidation*. ACS Symposium Series 550, American Chemical Society, Washington, DC. pp. 481-514.

Tremblay, G.A. and C.M. Hogan, Co-Eds. 2001. MEND Manual Volume 4 – Prevention and Control. MEND 5.4.2d. Canada Centre for Mineral and Energy Technology, Natural Resources Canada, Ottawa.

Vigneault, B., P.G.C. Campbell, A. Tessier and R. De Vitre. 2001. Geochemical changes in sulfidic mine tailings stored under a shallow water cover. Wat. Res. Vol. 35, pp. 1066-1076.
[http://dx.doi.org/10.1016/S0043-1354\(00\)00331-6](http://dx.doi.org/10.1016/S0043-1354(00)00331-6).