WATER COVERS FOR THE DECOMMISSIONING
OF SULFIDIC MINE TAILINGS IMPOUNDMENTS[1]

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Abstract: Covering sulfidic mine tailings with water effectively reduces oxygen influx to the tailings and the resulting acid generation. However, metals present in porewater solutions or in soluble mineral phases may still be released from the flooded tailings impoundment. Several laboratory leach tests are performed to evaluate metal release rates and times.

Results from 20-day laboratory tests where fresh, unoxidized sulfide tailings are leached under controlled hydraulic and chemical conditions show limited metal releases even as pH changes occur in the leach water. Metal release times are generally of short duration. Monitoring of tailings seepage and surface waters is recommended for detecting sudden metal releases which could occur from natural pH variations.

Results from a 3-month column experiment where oxidized tailings are covered by 1 m of water showed that transfer of zinc, sulfate, and iron from the tailings to the water column could occur. This transfer could be controlled by the addition of a protective sand layer over the tailings. Results for this case suggest that removal of zinc by treatment of surface and seepage water is still required for a long period after implementation of the water cover.

The construction costs for artificial hydraulic containment structures to obtain an adequate water storage over the tailings are always high. It is therefore necessary, before deciding to commit to these costs, to evaluate treatment and maintenance requirements using laboratory and field testing, such as described herein.

Introduction

Water covers have been proposed at several Canadian mine sites as a long term decommissioning measure for sulfide tailings impoundments. Covering the tailings with water reduces oxygen influx to the tailings and the resulting acid generation. The main advantage of water covers is that implementation costs are less dependent on surface area than other oxygen barriers such as soils, which require more transport and handling. As the most abundant and available oxygen barrier, water can sometimes be controlled to cover large surfaces with relatively little effort. However, the benefits of implementing a water cover are highly site-dependent. Some of the influencing factors are the geochemical history of the tailings, the degree and quality of natural or manmade containment in place at the time of decommissioning, and the physical and hydrogeological setting of the tailings disposal area.

This paper presents results from laboratory simulations of tailings disposal scenarios and provides details on some of the acting principles and processes occurring in water-covered tailings systems. Factors that can influence decision making at the time of decommissioning are discussed.
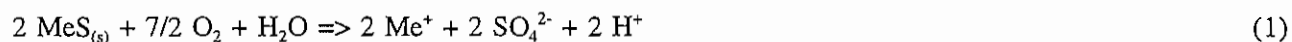

Chemical Evolution of Unsaturated Tailings

Sulfide oxidation results from the exposure of mined rock to geochemical conditions that are different from those in which it originated and is described by the following reaction:

$$2 \; MeS_{(s)} + 7/2 \; O_2 + H_2O => 2 \; Me^+ + 2 \; SO_4^{2-} + 2 \; H^+ \tag{1}$$

where Me represents a metal such as iron, lead, zinc, or nickel. Tailings oxidation models (for example Senes 1991) suggest that, in most cases, the oxidation of unsaturated tailings slows down with time, as sulfide minerals become depleted near the tailings surface and oxygen transport paths to fresh sulfide particles become longer. This was verified during controlled oxidation experiments in 1-m columns presented earlier by Yanful and Payant (1993). Figure 1 shows acid fluxes decreasing by approximately 37% in a period of approximately 600 days as the downward movement of the oxidation front reached a depth of approximately 40 cm below surface. This decrease in acid production would be slower under field conditions because oxidation rates in colder temperatures are slower. After many years, the downward progression of the oxidation front should reach the water table; at that point, acid production should cease.
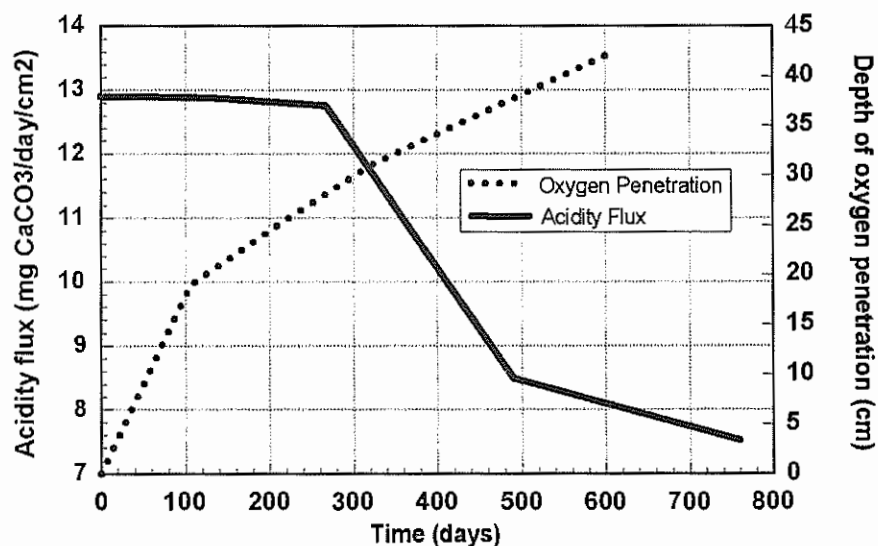

Figure 1. **Acidity flux and oxygen penetration in laboratory column**

Metal release from tailings is also influenced by the precipitation and dissolution of minerals below the oxidation front. The net resulting acid generation is therefore a complex function of the overall chemical composition of the tailings solids, as described, for example, by Dubrovsky et al. (1984) and Blowes et al. (1990). Table 1 lists some of the minerals that commonly constitute fresh, unoxidized, tailings solids (primary minerals) produced from the mining of Canadian sulfide base-metal ore bodies, and minerals that have been found to appear as a result of reactions occurring after tailings deposition (secondary minerals). As the mineralogy of tailings deposits evolves toward equilibrium with atmospheric geochemical conditions, sulfide minerals are replaced by secondary minerals which eventually form a major proportion of metallic constituents. The evolution rate is a function of factors such as the sulfide mineral type and abundance, tailings grain size, and temperature.

The placement of a water cover induces changes in geochemical conditions which will promote reactions other than those generally described above. The importance of these reactions depends on the length of time during which the tailings were exposed to atmospheric conditions. If tailings exposure to atmospheric conditions is not long enough to allow the formation of a significant quantity of secondary minerals, reactions with primary minerals will dominate effluent quality from the flooded tailings. These conditions were observed in previous laboratory studies described in Ritcey (1986) and in field studies by Rescan (1990). Morin (1993) recently reviewed the theory of sulfide oxidation rates under water.

Table 1. Minerals commonly found in Canadian base metal mine tailings.

Primary minerals		Secondary minerals	
Name	Formula	Name	Formula
Pyrite	FeS_2	Ferrihydrite	$Fe(OH)_3$
Chalcopyrite	$CuFeS_2$	Goethite	$FeOOH$
Pyrrhotite	$Fe_{(1-x)}S$	Lepidocrocite	$FeOOH$
Sphalerite	ZnS	Jarosite	$KFe_3(SO_4)_2(OH)_6$
Galena	PbS	Melanterite	$FeSO_4.7H_2O$
Arsenopyrite	$FeAsS$	Gypsum	$CaSO_4.2H_2O$
Chalcocite	Cu_2S	Anglesite	$PbSO_4$
Covellite	CuS	Gibbsite	$Al(OH)_3$
Magnetite	Fe_3O_4		
Calcite	$CaCO_3$		
Dolomite	$MgCa(CO_3)_2$		
Siderite	$FeCO_3$		

On the other hand, if the tailings are exposed long enough to allow the formation of significant quantities of secondary minerals, the geochemistry of the effluent may be dominated by reactions with these minerals. In general, the dissolution of sulfate and hydroxide minerals occurs more readily in aqueous solutions than that of sulfides and silicates (Stumm and Morgan 1981). The following sections give two examples where laboratory simulations of water cover conditions have been done.

Flooding of Fresh Tailings

In this case example, highly acid-generating tailings, typically containing 45% pyrite and less than 1% of other sulfide minerals, are produced from the milling of polymetallic ore. It is planned to deposit the tailings in an engineered disposal cell and to maintain the tailings in saturated conditions throughout the active life of the impoundment. The tailings will be deposited in a slurry at a pH above 10. After closure, a 1-m water cover will be permanently maintained over the tailings.

Variations in the chemistry of water above the tailings are expected, as atmospheric water will replace the mill water in the impoundment. Typical rain water for the region shows a pH near 5, and it is therefore expected that chemical conditions in the water-covered tailings system will become less alkaline, and that pH will decrease to

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values closer to the rain water pH. In addition, there is the risk that some tailings may be exposed for longer times, allowing some oxidation, which could further decrease the pH.

Standard shake flask tests conducted at a pH of 4.8 (EPA procedure 1311) suggested the possible release of zinc and manganese from the tailings. These tests give only a rough estimate of possible metal releases from the tailings, because of the large water-solid ratio (approx 100:1) and the large amount of energy applied to the flask (18-hr shake). Other tests, such as humidity cell tests, are not applicable because they allow air to freely contact the sample, a condition that should not occur under water-cover conditions.
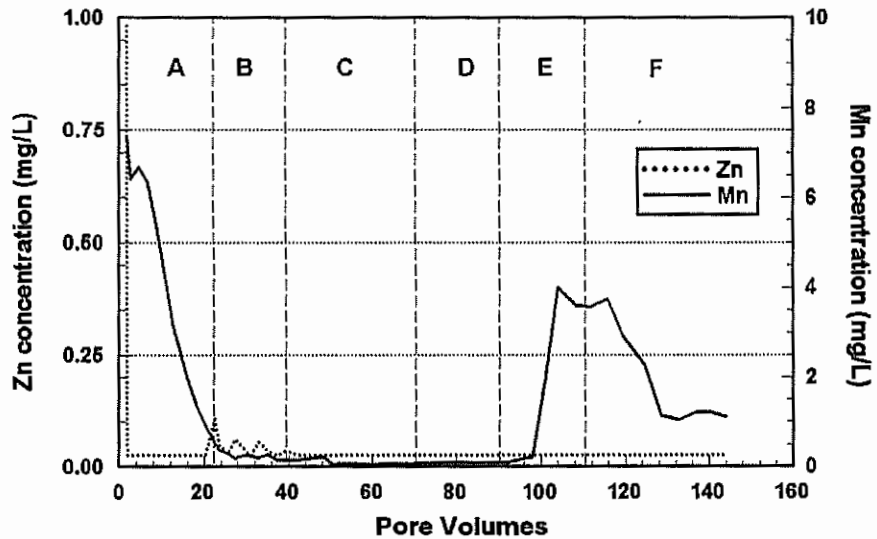
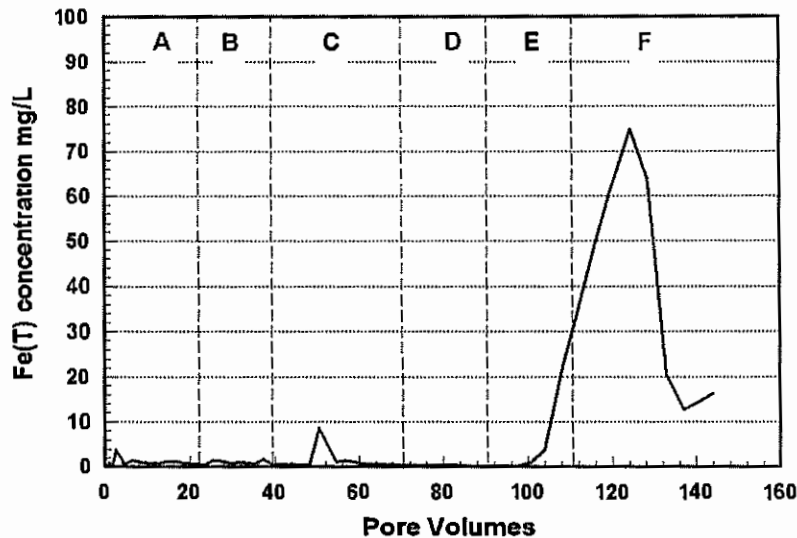| inflow	A	B	C	D	E	F
pH	10	7	5	5	5	3
Fe (mg/L)	0	0	0	0	100	0

Figure 2. Metal concentrations in column effluent

To more realistically assess the possibility of metal leaching from the tailings, a column test was initiated. The test involved the percolation of water through a 15 cm long by 10 cm diameter tailings sample. Saturated conditions were maintained in the sample throughout the test, and water was percolated from a reservoir placed at a height of 50 cm above the sample (hydraulic gradient equal to 5). Possible pH fluctuations were reproduced in the test by modifying the distilled water influent pH between 10 and 5 using NaOH or HCl addition. Figure 2 shows concentrations of some of the metals dissolved in the column effluent plotted with respect to the number of pore volumes that passed through the sample. After respectively 21 pore volumes of influent at pH 10, 18 at pH 7, and 49 at pH 5, no zinc release was measured in the effluent. Manganese release occurred during the initial flushing of 21 pore volumes at pH 10, then decreased. Toward the end of the test period (at 88 pore volumes), 21 pore volumes of a 100 mg/L ferrous iron (Fe^{2+}) solution were introduced in the inflow as iron sulfate. As the solution passed through the sample, a rise in manganese concentrations up to 5 mg/L was produced.

The conclusion of the preliminary column test is that leaching of zinc and other metals from the minerals contained in the tailings would not occur under normal conditions in which the tailings would be deposited. Some release of manganese could occur as an association with the mobilization of iron. Possible chemical mechanisms for manganese release are dissolution of manganese carbonates due to changes in redox conditions, and replacement of manganese by iron in hydroxide mineral structures.

The changes in pH and iron concentration in the influent water correspond to chemical variations that could probably occur in the field. However, the simulated flow rates, which are governed by the hydraulic conductivity of the sample and the hydraulic gradient, could be quite different under field conditions. While the measured laboratory hydraulic conductivity of 6×10^{-6} cm/s could resemble field conditions, the hydraulic gradient in the field could likely be as much as 50 to 100 times lower than the one simulated in the laboratory. Pore water could therefore flush the tailings at a rate which could be 50 to 100 times slower than in the laboratory column. The flushing of 88 pore volumes across the tailings sample could thus correspond to 176 yr of actual conditions. However, this last affirmation is not exactly true because the effect of flow rate on the resulting water chemistry depends on the availability of source minerals and on the rate of transfer of metals into the pore water. It is likely that the rate of metal transfer to the pore water is very slow, and that metal concentrations in the tailings pore water become higher as the residence time of water in the tailings pores increases.

Flooding of Oxidized Tailings

In this case, tailings from the milling of polymetallic sulfide ore containing 33% pyrite, 1.5% sphalerite, and 1% of other sulfide gangue minerals have been deposited in a small lake. Additional containment was provided by dams constructed of cycloned tailings spilled over waste rock "starter dams"—a construction technique typically used at most Canadian mineral processing sites prior to the mid-1970's. These dams offered only physical support to the tailings mass, allowing the tailings to drain freely and to develop an unsaturated zone. Oxidation and geochemical evolution occurred during a period of approximately 20 yr, as generally described in the first section of this paper.

As a consequence of tailings oxidation, seepage from the tailings exhibited the high levels of dissolved metals and sulfate and low pH typical of acid mine drainage. Decommissioning work at the site included interception of all seepage and removal of metals by lime treatment. Decommissioning plans are to treat water and store treatment sludges on site. A water cover is being considered as an option to reduce future tailings oxidation, to reduce future water and sludge management, and to generally decrease postclosure operational requirements.

A description of the laboratory model used to simulate the water-covered tailings was presented earlier in St-Arnaud and Yanful (1993). The model consisted of 2-m-high by 30-cm-diameter plexiglass columns. The bottom 1-m section was filled with 60 cm of unoxidized and 35 cm of oxidized tailings. The top 1-m column section was filled with clean water. Sampling ports allowed the pore water in the tailings and water above the tailings to be sampled with time.

In the first stage of the laboratory simulation, the water column was maintained stagnant over the tailings. Figure 3 shows that zinc concentrations reached 20 mg/L in the water column after 152 days. Iron concentrations were controlled by the rapid and sustained formation of hydrous ferric oxide precipitates at the surface of the tailings. These precipitates are commonly formed as ferrous iron dissolved in the pore water seeps to surface; the iron is then oxidized to ferric and rapidly hydrolyzes to form the reddish solid. The chemical reaction describing the hydrolysis of ferric iron is

$$Fe^{3+} + 3H_2O = Fe(OH)_3(s) + 3\ H^+. \tag{2}$$

Dissolved iron levels can be so high that the reaction, by producing hydrogen ions, may significantly contribute to water acidification. Acidification of the water cover is undesirable because additional water treatment would be required if release to the environment became necessary and because leaching of the tailings solids could be increased if acidic water would seep into the tailings. Measured pH in the laboratory column was near 4.

It was demonstrated that upward diffusion of ferrous iron present in the pore water prior to flooding of the tailings can account for only part of the iron release to the water column. Another apparent mechanism affecting metal
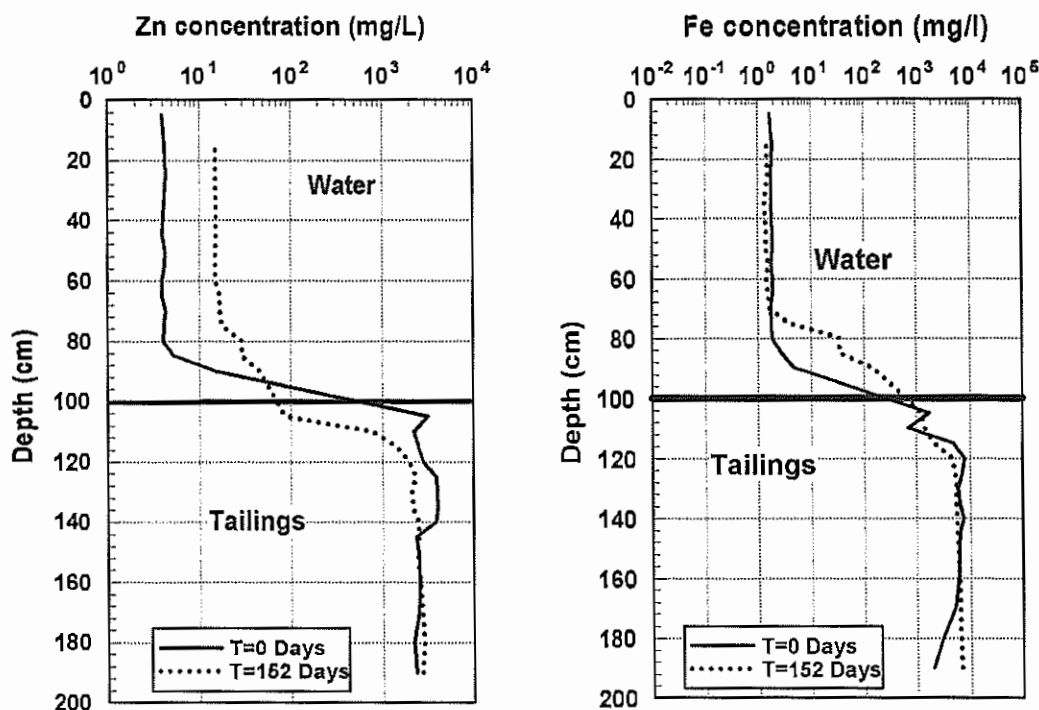

Figure 3. Zinc and iron concentration profiles in laboratory columns

transfer is the dissolution of iron sulfate and hydroxide secondary minerals present in the oxidized part of the column, followed by advection due to the consolidation effect created by the change in volume induced by the dissolution. In addition to the release of iron, the dissolution of secondary mineral phases induces the release of other metals, which are commonly adsorbed or coprecipitated on amorphous hydroxide phases. The chemical kinetics of metal sorption on amorphous metal hydroxides were described by Gadde and Laitinen (1974) and Kinniburg et

al. (1976). More recent reports by Music and Ristic (1992) and Morel and Hering (1993) state that, in general, heavy metal retention by amorphous minerals is highly reversible and pH-dependent. Blowes and Jambor (1990) found that sorption and coprecipitation with hydroxide and sulfate minerals was a major removal mechanism for zinc in oxidized tailings. It is likely that metal transfer will last for a long period of time, as the relative proportion of secondary minerals available for dissolution could be important. The metal transfer should decrease with time, however, and should cease after the dissolution of soluble minerals is complete. The composition and proportion of secondary mineral phases in the oxidized tailings are presently being evaluated.

As secondary mineral dissolution and the associated metal releases occur in the oxidized tailings, the subsequent migration and reformation of iron hydroxides at the surface of the tailings is also associated with heavy metal sorption. In the water-covered tailings system, sorption of metals by the observed iron hydroxide coating would effectively intercept upward-moving dissolved metals, thereby reducing loading to the water cover. However, because of the reversible nature of the sorption, the metals could remain available for release if, for example, pH changes occur in the water. As reported in St-Arnaud and Yanful (1993), iron hydroxide precipitate was visible on the field wherever ponding occurred on the tailings. Analysis of the precipitate revealed the presence of 0.2% of zinc in the sample, and zinc mobility was confirmed by shake flask tests. Since downward infiltration of water into the tailings which occurs in the field probably counteracts upward metal transfer by diffusion, dissolution followed by consolidation is probably the only mechanism that could be responsible for the metal transfers observed in the field.

To modify the mobility of metals from the tailings to the water body, additional laboratory columns were installed as described above, with the addition of a 10-cm layer of sand on top of the tailings. The results, plotted on figure 4, show that zinc and iron concentrations decreased to values lower than 0.02 mg/L in the water column during the 4-month (122-day) test period. It appears that the transfer of zinc and iron is limited significantly by the sand protective layer because iron hydroxide precipitated rapidly at the sand-tailings interface, filling the sand pore spaces and limiting further transfer of metals. The benefit of the sand is to offer a stable physical support for hydroxide gels, which, once in place, can become an effective barrier to upwardly moving metals. The same benefit could also be obtained by using other granular materials, such as clean, coarse tailings.

Further chemical monitoring under conditions where the water column is allowed to infiltrate through the tailings is ongoing in order to measure the duration of metal transfers into downward-moving pore waters.

Discussion

The laboratory simulations of tailings disposal scenarios presented above demonstrate that (1) tailings oxidation in unsaturated conditions slows down with time, (2) if the tailings are placed under water while still fresh (unoxidized), metal releases should be very low compared to uncovered tailings, (3) metal releases from water-covered oxidized tailings could be significant and could last for long time periods; they should however decrease with time; (4) upward metal release from water-covered oxidized tailings may be controlled by a layer of clean, granular material such as sand.

The environmental benefits of placing a water cover over sulfide tailings before they can oxidize were discussed. Economic benefits are also possible if the chemistry of the water-covered tailings system can be controlled so there is no requirement for extensive water treatment.

In the case where oxidized sulfide tailings are to be decommissioned, water capture and treatment are often necessary, leading to significant labor, capital, and operation costs. The physical limit to unsaturated tailings oxidation suggests that operation costs should slowly decrease with time even when the tailings remain uncovered. In addition, operation costs for a lime neutralization plant and sludge disposal become less significant when distributed over long time periods because economic evaluations normally discount future cash flows (positive or negative) at a rate equal to the average cost of capital, which in turn is related to the opportunity to use capital to generate revenues. Consequently, the real cost of operating treatment facilities decreases with time, and, depending

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on the economic situation, costs to be incurred 15 or 20 yr in the future may become quite small when discounted to present values. Of course, the real costs may be greatly increased by legislative requirements for the advanced payment of financial assurances to cover future operation costs for decommissioned sites.

Placing a water cover over oxidized tailings may require immediate investments for the upgrade of dams to obtain an adequate water storage over the tailings and for the emplacement of protective layers on the tailings surface for
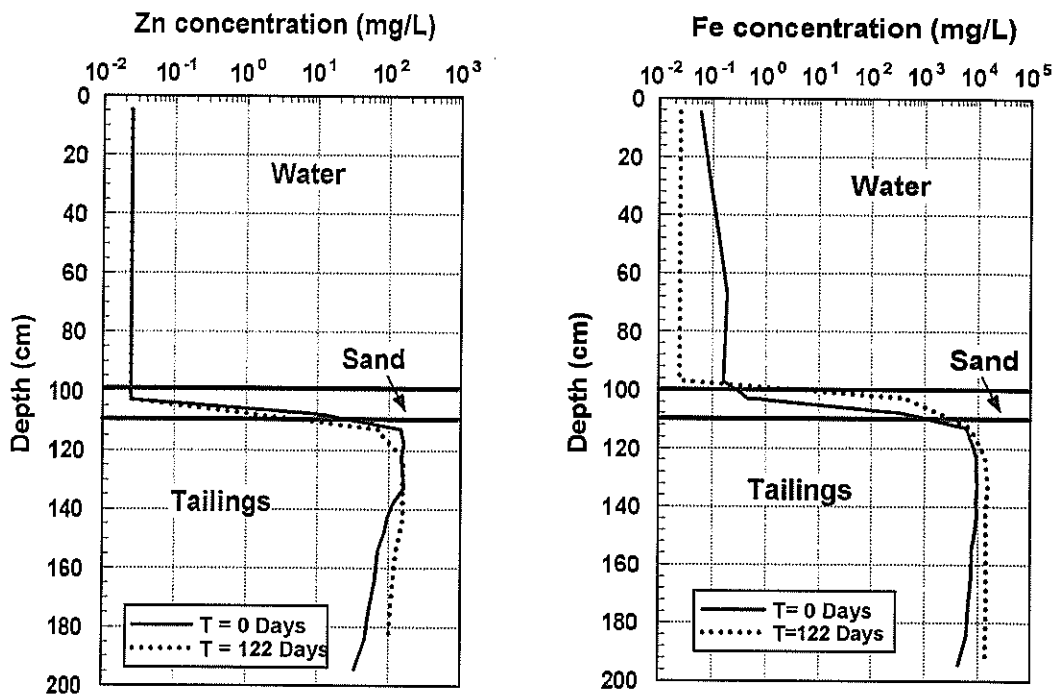

Figure 4. **Zinc and iron profiles in laboratory column with sand layer**

physical stability and to limit metal transfer. For the water cover to be environmentally and economically acceptable, reduction in metal releases would have to occur within 15 to 20 yr after implementation. The evaluation of treatment and maintenance requirements using laboratory and field testing such as described in this paper is therefore necessary before decision making on final decommissioning can be done.

Acknowledgements

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