

# METAL RELEASE CHARACTERISTICS OF TAILINGS IN A MARINE ENVIRONMENT – A LABORATORY STUDY<sup>1</sup>

Pamela L. Drake, Robert H. Lambeth, and Anthony J. Paulson<sup>2</sup>

**Abstract:** Very little is known about the postdepositional behavior of submerged tailings. To better understand the metal release characteristics of submerged tailings, researchers at the U.S. Bureau of Mines simulated the effects of submarine tailings disposal using depyritized tailings from a mesothermal vein deposit. In an investigation of the long-term effects after deposition, these tailings were placed in aquariums and covered with seawater under oxic and anoxic conditions. Long-term dissolution of tailings was monitored by sampling the water above the tailings to detect the products of geochemical reactions that may affect toxicity. Copper, cadmium, lead, and zinc concentrations were less than the marine aquatic criteria. The concentration of lead and zinc were highest within the seawater control, suggesting adsorption was removing these metals from the overlying water column. Manganese was released in limited amounts under anoxic conditions. After approximately 100 days under oxic conditions, manganese concentrations were less than 10 µg/L due to precipitation of manganese minerals.

**Additional Key Words:** Subaqueous Disposal; Tailings Disposal; Aqueous Geochemistry; Trace Metals.

## Introduction

Tailings produced as a waste product of ore beneficiation by flotation are most commonly disposed of in a surface impoundment near the mine-mill complex. Depending on ore mineralogy and site geography, this disposal method can result in a variety of environmental hazards. The tailings can become a source of dust containing significant amounts of metals and easily eroded tailings can produce siltation problems in nearby lakes and streams. A significant amount of land surface is utilized as a long-term waste repository that many believe is "visual pollution." Perhaps the most serious potential environmental problem, however, is the production of acid rock drainage (ARD). ARD is produced when tailings that contain an appreciable amount of sulfide minerals and have a limited buffer capacity are exposed to air and moisture. The sulfide minerals oxidize with the aid of bacterial catalysts to form sulfuric acid, which in turn solubilizes many toxic metals (Nordstrom, 1982). This effluent can escape the impoundment and become a serious environmental problem.

An alternative method of waste disposal applicable to coastal mines is direct discharge into the marine environment. The environmental problems associated with surface disposal of tailings are thus eliminated. Dust cannot form, fresh water lakes and streams cannot be contaminated with silt, and land is not used as a repository. ARD will not develop in a marine environment because the dominant bacterial catalyst, *Thiobacillus ferrooxidans*, requires large quantities of oxygen and carbon dioxide. In addition, seawater has a large buffer capacity for neutralizing acidic oxidation products.

This method of tailings disposal has been used at several locations throughout the world and the results have been mixed. The most extensively studied site is the marine tailings disposal facility at the Island Copper Mine (ICM) on the north end of Vancouver Island near Port Hardy, BC. At this site, 310 million tonnes of tailings from a porphyry copper mine have been discharged into Rupert Inlet between 1971 and 1992 (Poling and Ellis, 1993, p. 3-1). The most serious environmental problems observed to date are burial of native marine fauna and sporadic resuspension of tailings near a sill in the inlet. No metal

---

<sup>1</sup>Paper presented at the 1995 National Meeting of the American Society for Surface Mining and Reclamation, Gillette, Wyoming, June 5-8, 1995.

<sup>2</sup>Pamela L. Drake, Research Chemist, Robert H. Lambeth, Mining Engineer, Anthony J. Paulson, Hydrologist, Spokane Research Center, U.S. Bureau of Mines, Spokane, WA 99207.

dissolution appears to have occurred within the submerged tailings; however, anomalous metal concentrations have been noted near a shoreline mine waste dump. Benthos recolonization does occur, although it exhibits a population mix different than that on the native sediment (Ellis and Hoover, 1990, p. 441).

Perhaps the most frequently cited location for illustrating significant negative impacts of marine tailings disposal is the Black Angel Mine near the Affarlikassaa fiord, West Greenland. Water from the inlet contains highly elevated concentrations of lead (200  $\mu\text{g}/\text{kg}$ ), zinc (422  $\mu\text{g}/\text{kg}$ ), and cadmium (2.5  $\mu\text{g}/\text{kg}$ ) (Asmund, 1992, p. 589). Again, there are multiple sources of metal contamination—waste rock along the beach, dust, and tailings deposited directly into the fiord. The deposit at ICM is silica-dominated, whereas the Black Angel deposit is carbonate-hosted, and some researchers believe the contamination may be attributable to the relatively soluble carbonate mineral in the deposit (Asmund et al., 1988, p. 3).

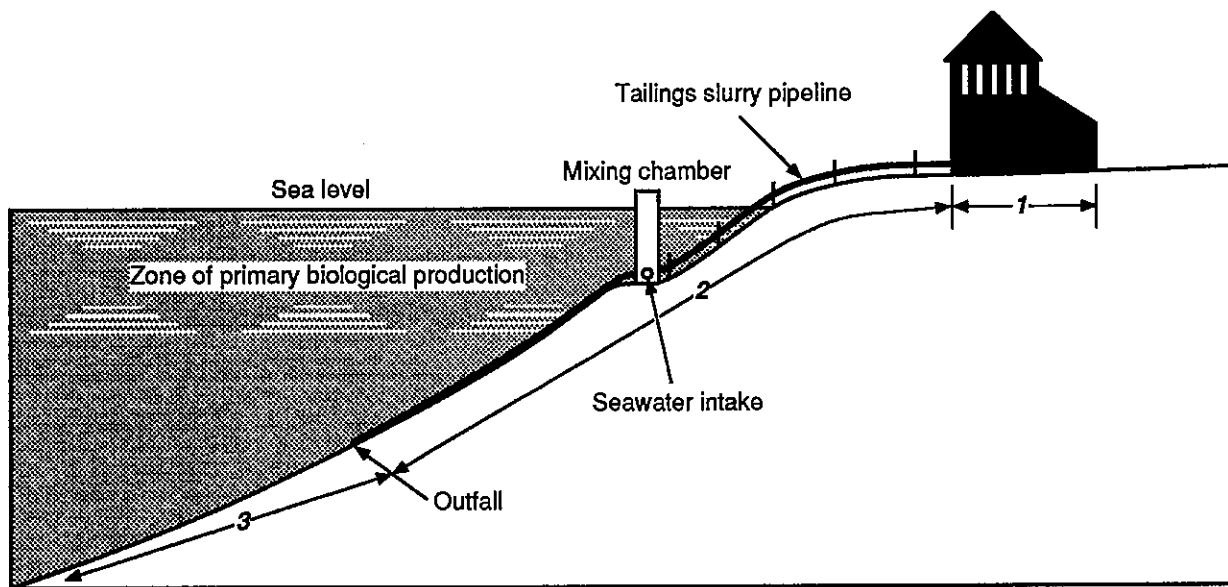
As a consequence of the Clean Water Act and 40CFR440, Subpart J, discharge of mill tailings containing "process waters" into "natural waters" of the United States is prohibited. The regulations actually prohibit the discharge of process *wastewater* into natural waters, not the solid portion. Since the tailings would contain process wastewater, they fall under this prohibition. Examination of case histories (Poling and Ellis, 1993; Ellis et al., 1994) illustrates that the environmental feasibility of submarine disposal of mine tailings is very site specific and that a comprehensive prohibition may not be wise either environmentally or economically.

Many factors control the dissolution of heavy-metal minerals in seawater, including deposit mineralogy, particle size distribution, redox state, physiography at the disposal site, biological activity, and the kind of process used in the mill. Researchers at the Spokane Research Center (SRC) of the U.S. Bureau of Mines (USBM) initiated a project in which the environmental feasibility of submarine disposal of various types of tailings was examined. The information gained can be utilized by regulatory agencies and Congress to help formulate language within the environmental laws currently controlling mine waste disposal in waters of the United States. Because any future regulations that permit submarine waste disposal would require environmental safeguards, a decision was made to first examine ore deposits that would most likely produce benign, nonreactive tailings.

### Research Approach

During a typical submarine tailings disposal operation, mill tailings are not discharged directly into seawater. Instead, the tailings are discharged from mill thickeners into a mixing tank, as illustrated in Figure 1. A natural siphon is established so that seawater flows into the mixing tank at a calibrated rate that will ensure that the discharge plume is not buoyant. A specific density is needed to guarantee the plume will flow downslope after being discharged below the photic zone and will not accumulate at the outfall. A minimum residence time within the mixing tank is needed to allow de-aeration of the mill effluent, which will prevent secondary flotation of sulfide minerals after they are discharged.

The effluent is subjected to three distinct environments in which chemical changes, such as dissolution or precipitation, could occur. The first is during beneficiation. Minerals are subject to possible oxidation and dissolution in an aerated, neutral-to-alkaline environment where ionic strengths are moderate and where the minerals may form complexes with reagents. The second is after entry into the mixing tank, within the final discharge line, and at the outfall where the composition of the liquid fraction changes significantly and the ionic strength is much higher. The increased ionic strength tends to shift mineral equilibrium toward dissolution, but this is often countered by precipitation of dissolved metals as secondary minerals or by sorption onto finely ground gangue minerals or other secondary minerals, such as iron oxyhydroxide. These are rapid reactions since the residence time within the mixing chamber and discharge pipeline is relatively short. The third environment is after final deposition on the ocean floor. Reactions here are long term and kinetically much slower. The ionic strength is slightly higher than that within the discharge system. Deposition sites may be oxidizing (which tends to induce dissolution) or reducing (which tends to fix contaminant metals).



**Figure 1.** Modern submarine tailings disposal system. Numbers signify the zone for the laboratory simulations.

Three laboratory simulation experiments were designed to simulate a submarine disposal system.

1. To simulate the beneficiation environment, an ore sample was processed by a bench-scale flotation cell, and the liquid and solid fractions of the effluent were sampled and characterized.
  2. To simulate short-term reactions within a discharge system, tailings samples were combined with seawater, placed on a rotating wheel, and subjected to a series of timed mixing experiments.
  3. Long-term post-deposition reactions were simulated within aquariums in the laboratory.
- Only simulations (1) and (3) will be discussed at length in this paper. Simulation (2) will be addressed in a USBM publication in process.<sup>3</sup>

The site selected was a quartz-dominated, mesothermal, auriferous vein deposit along the southeast Alaska coast. Gold in the system is associated with pyrite. The process proposed was to subject the ore to ball-mill grinding followed by nonselective froth flotation of sulfide minerals. Gold would then be extracted from the pyrite concentrates by cyanidation. Residual cyanide would then be neutralized. Normal disposal procedures called for mixing the treated concentrates with the inert gangue tailings prior to disposal. However, to maintain the theme of "benign, nonreactive tailings," USBM personnel elected to use only depyritized tailings. This is a reasonable concept, because at deposits with a relatively low sulfide mineral content, the sulfide minerals can be removed and stored separately from the gangue.

The ore sample was crushed to minus-2.54 cm at the prospect site in Alaska prior to being shipped to Spokane, WA, for beneficiation at N.A. Degerstrom Laboratories. Water for processing was obtained from the prospect site. The sample was crushed to minus-0.64 cm with a roll crusher, then further reduced in a ball mill to 100% passing through an ASTM 100-mesh (0.0149-cm opening) screen. This feed was allowed 20 min residence time in an agitated flotation cell containing methylisobutylcarbonol as a frothing agent and potassium amyl xanthate as a flotation reagent. Only the depressed gangue was used for the laboratory simulations. The sulfide mineral concentrate was returned to the mine for metallurgical testing.

---

<sup>3</sup>The results of these experiments are currently in the process of being published in a USBM publication by Drake, Paulson, and Lambeth.

## Effluent Characterization

### -Simulation 1-

To determine tailings mineralogy, the solid portion of the effluent was examined by consulting mineralogist James Canwell in Spokane, WA, using optical methods, and by X-ray diffraction and X-ray fluorescence methods at the USBM's Reno Research Center. The results are shown in Table 1. A solid sample was also analyzed for total metal content in a low-pressure microwave aqua regia digest at SRC and the resultant solution was analyzed by inductively coupled argon plasma spectrometry (ICP). These results are shown in Table 2. This solution will dissolve all minerals except silicate minerals.

**Table 1. Mineral composition of tailings.**

Minerals	Weight percent
Quartz [SiO <sub>2</sub> ] . . . . .	75
Ankerite [(Ca,Fe)CO <sub>3</sub> ] . . . . .	10
Biotite/chlorite [K(Mg,Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub> /Mg <sub>3</sub> Al <sub>2</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>8</sub> ] . .	5
Albite [NaAlSi <sub>3</sub> O <sub>8</sub> ] . . . . .	5
Pyrite [FeS <sub>2</sub> ] . . . . .	<1
Magnetite [Fe <sub>3</sub> O <sub>4</sub> ] . . . . .	<1
Ilmenite [FeTiO <sub>3</sub> ] . . . . .	<1
Hornblende [NaCa <sub>2</sub> (Mg,Fe,Al) <sub>5</sub> (Si,Al) <sub>8</sub> O <sub>22</sub> (OH) <sub>2</sub> ] . . . . .	<1
Apatite [Ca(PO <sub>4</sub> ) <sub>3</sub> (F,Cl,OH)] . . . . .	<1
Garnet [(Fe,Mg,Mn,Ca) <sub>3</sub> (Al,Fe) <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> ] . . . . .	<1
Zircon [ZrSiO <sub>4</sub> ] . . . . .	<1

**Table 2. Analysis of tailings using aqua regia digestion.**

Element	Amount, mg/kg
Cd . . . . .	51
Ca . . . . .	35,000
Cu . . . . .	160
Fe . . . . .	7,800
Mg . . . . .	3,100
Mn . . . . .	700
Pb . . . . .	ND
S . . . . .	500
Zn . . . . .	80

During the processing of the ore sample at Degerstrom Laboratories, filtered samples of the liquid fraction of the tailings effluent were taken with an acrylic Millipore<sup>4</sup> vacuum filtering assembly using a 0.45- $\mu$ m pore size polytetrafluoroethylene (PTFE) filter. The apparatus and filters were first washed with 4-molar nitric acid and thoroughly rinsed with deionized water. The samples were transferred to similarly cleaned polypropylene bottles and preserved with nitric acid. The samples were analyzed with an ICP-mass

<sup>4</sup>Reference to specific equipment or trade names does not imply endorsement by the U.S. Bureau of Mines.

spectrometer at Eastern Washington University, Cheney, WA. Sulfate analysis was performed at SRC using a Dionex ion chromatograph. Dissolved oxygen concentrations, pH measurements, Eh measurements, and alkalinity titrations were performed at the processing site. The analyses are shown in Table 3. The samples were not obtained and processed under "clean lab" conditions, and it is likely that these concentrations—although extremely low—are caused by sample contamination. Actual values may be somewhat less.

**Table 3. Analysis of filtered liquid effluent sample by ICP-MS from tailings samples.**

Constituent	Concentration, $\mu\text{g/L}$	Project discharge standards (where applicable)
Element		
Al . . . . .	140	
As . . . . .	2	36
Ca . . . . .	30,000	
Cd . . . . .	<1	9.3
Cr . . . . .	2	50
Cu . . . . .	6	2.9
Fe . . . . .	340	
K . . . . .	40,000	
Mg . . . . .	6,300	
Mn . . . . .	60	100
Na . . . . .	24,000	
Ni . . . . .	4	8.3
P . . . . .	100	
Pb . . . . .	2	5.6
Se . . . . .	1	10
Si . . . . .	6,200	
Zn . . . . .	15	58
Other:		
SO <sub>4</sub> <sup>2-</sup> , mg/L . . . . .	90	
HCO <sub>3</sub> , mg/L . . . . .	88	
pH . . . . .	8.35	
Eh, v . . . . .	0.19	
DO, mg/L . . . . .	7	

DO = Dissolved oxygen.

## Results and Discussion

Calcium, magnesium, bicarbonate, manganese, iron, and nonferrous base metals in solution were probably derived from dissolution of ankerite and other carbonate minerals during the milling process. If one assumes that all sulfur is in sulfide form as pyrite and that the dominant source of dissolved calcium, iron, magnesium, and manganese is normalized as ankerite, these results may be interpreted as indicating that the dominant source of leachable metals is ankerite with an approximate composition of (Ca<sub>0.76</sub>, Fe<sub>0.11</sub>, Mg<sub>0.11</sub>, Mn<sub>0.02</sub>)CO<sub>3</sub> after correction for iron associated with pyrite. Carbonate minerals, such as calcite and ankerite, usually contain other metals, such as copper, cadmium, lead, and zinc, as cation replacements within the crystal lattice and are thus a potential source for these metals (Mason and Barry, 1968, p. 331;

Hurlbut, 1971, p. 318). Aluminum and silicon sources are quartz, chlorite, and feldspar. Phosphorus probably originated from apatite dissolution and the sulfate formed during oxidation of pyrite. Potassium and sodium are components of the flotation reagent potassium amyl xanthate.

The computer model WATEQ4F (Ball and Nordstrom, 1991; Truesdell and Jones, 1974; Plummer et al., 1976) was used to characterize the effluent. WATEQ4F is a specific-ion-association model that assumes equilibrium conditions and uses pH, oxidation potential, dissolved oxygen, temperature, and concentrations of dissolved constituents to calculate the species distribution of ions in solution. The calculation routines then identify possible minerals from an internal database that can equilibrate with the solution and determine the saturation index (SI) of each mineral. SI is a logarithmic ratio that indicates the tendency of a mineral to precipitate or dissolve. A positive value indicates oversaturation, so the mineral will tend to precipitate. A negative number indicates undersaturation, so the mineral will tend to dissolve. A value of zero indicates equilibrium, but because of uncertainties of constants in the thermodynamic database, Nordstrom recommends that for most minerals values between  $-1.000$  and  $+1.000$  approximate equilibrium. Such minerals, depending on their stability in a given geochemical environment, can, therefore, be either a source or a sink for ions in solution.

SI is defined as  $SI = \log_{10}(IAP/K_{sp})$  where IAP = total appropriate ion activity products and  $K_{sp}$  = solubility product constant. The SI's of appropriate ion source and sink minerals for the effluent solution are listed in Table 4. For all simulations, the classical  $H_2O/O_2$  relationship was used to speciate redox active phases.

**Table 4. Saturation indices of ion mineral source and sink phases determined from WATEQ4F for filtered effluent sample.**

Phase	Saturation index
Ion source mineral phases:	
Albite . . . . .	-0.98
Calcite . . . . .	0.23
Chlorite 14A . . . . .	-7.6
Chlorite 7A . . . . .	-11.0
Magnesite [MgCO <sub>3</sub> ] . . . . .	-2.8
Quartz . . . . .	0.40
Rhodochrosite (c) [MnCO <sub>3</sub> ] . . . . .	-0.17
Siderite (c) [FeCO <sub>3</sub> ] . . . . .	-1.7
Ion sink mineral phases:	
Allophane (a) [(Al(OH) <sub>3</sub> ) <sub>1-x</sub> (SiO <sub>2</sub> ) <sub>x</sub> ] . . . . .	-0.28
SiO <sub>2</sub> (a) . . . . .	-0.91

(a) = amorphous; (c) = crystalline

Ion source minerals are those found in the tailings. Three of the ion source mineral phases listed in Table 4 (quartz, chlorite, and albite) were identified by mineralogical examination. These minerals will dissolve at low temperature and pressure surface conditions, but cannot precipitate. The other most probable ion source minerals are carbonate minerals. The WATEQ4F database does not contain ankerite, the dominant carbonate gangue mineral, because ankerite is a solid solution mineral that would have a variable stability constant. However, all end member carbonate mineral species (calcite, magnesite, rhodochrosite, and siderite) were equilibrated or undersaturated. This indicates carbonate minerals exhibit a slight tendency to dissolve and are potential source minerals for ions in solution. Silicate minerals within the tailings sample (albite, chlorite, and quartz) are also equilibrated to undersaturated and will tend to dissolve and release

sodium, magnesium, and silicon. However, their dissolution rates are quite slow. The minerals found in low quantities (<1 weight percent) were not applicable to this WATEQ4F simulation or are insignificant ion sources in comparison to the other gangue minerals.

Ion sink minerals are those secondary minerals which, if oversaturated or equilibrated and are stable in this geochemical environment, would tend to remove ions from solution by precipitation or sorption. The SI's of all potential secondary mineral precipitates containing copper, lead, zinc, cadmium, manganese, and other dissolved base metals as major components are highly undersaturated and would not tend to precipitate. These are not tabulated. However, potential metal sorbant phases [allophane (a) and SiO<sub>2</sub> (a)] were equilibrated and are listed in Table 4.

The preceding information indicates that although minerals tend to dissolve, aqueous phase metals tend to be far below saturation concentrations. There are three probable explanations: (1) metals are adsorbing on gangue minerals such as quartz or on sorbant precipitates such as SiO<sub>2</sub> (a), (2) concentrations of available metals within the tailings are low relative to the large liquid-to-solid ratio used during processing, resulting in significant dilution, or (3) equilibrium was not achieved, because of the short residence time during processing. The fact that many source minerals are approaching equilibrium indicates that the latter may not be true. There is not enough information to determine if dilution during processing is a major cause of low metal concentrations. The authors, therefore, cannot state whether sorption is the dominant control of metal concentration in the liquid effluent during the processing of the ore.

### Postdepositional Simulation

-Simulation 3-

#### **Sampling and Analytical Methods**

Long-term dissolution studies were designed to simulate post-depositional behavior of submerged tailings and their potential to supply dissolved heavy metals to the water column. The depositional environments for possible submarine disposal projects could range from very deep anoxic fiords to highly oxygenated open canals. Oxidic and anoxic environments were simulated by bubbling air and nitrogen, respectively, into overlying seawater. Approximately 2.5 L of well-mixed tailings were poured into 18-L aquariums and allowed to settle for 4 h. The remaining process water was then siphoned, and 5 L of seawater from the site was added to each aquarium. A control aquarium, with oxygenated seawater only, was also maintained. Since the amount of light on the ocean floor is minimal, all aquariums were stored under black plastic to minimize any chemical reactions caused by room lighting.

Each aquarium was equipped with a clear acrylic cover that had two ports for the gas lines, a port for the sampling tube, and a small port for venting. Teflon fluorinated ethylene polypropylene (FEP) tubing was used for the gas lines and the sampling tube. Plastic air diffusers were installed on the ends of the gas lines to enhance the amount of bubbling. Within the overlying seawater, the FEP sampling tube in each aquarium was fixed at 6 cm above the tailings surface to ensure uniform sampling. The acrylic covers were sealed to the aquariums with silicone sealant to minimize evaporation. Also, to aid in evaporation control, the gases were first bubbled through deionized water and then into the aquariums.

Air-Tite syringes, Swinnex filter holders, 30-mL bottles, and 0.4- $\mu$ m Nuclepore polycarbonate filters were soaked in 4-M, trace-metal-grade nitric acid baths. Before use, all labware was rinsed with deionized water. The gaskets in the Swinnex filter holders were soaked in 0.1-M hydrochloric acid overnight and rinsed with deionized water. The sample collection procedure consisted of withdrawing approximately 20 mL of the overlying seawater by connecting the syringe to the sampling tube mounted on each aquarium. The sample was filtered into a 30-mL bottle and preserved with 100  $\mu$ L of concentrated trace-metal-grade nitric acid to a pH of less than 2.

This sampling procedure was modified when random contamination problems were observed. All acid cleaning and rinsing were subsequently done in a laminar flow hood. The syringe and bottle were soaked in 4-M, trace-metal-grade nitric acid baths in the laminar flow hood, rinsed with 1% nitric acid, and rinsed again with ultrapure water. The syringe was sealed in a Ziplock plastic bag until used. After withdrawing the sample from the aquarium, the syringe was returned to the laminar flow hood in the plastic bag, and the sample was filtered and preserved. Instead of the Swinnex filter holder and gasket, a Syrifil-FN syringe-tip disposable filter with a 0.45- $\mu\text{m}$  PTFE membrane and a polypropylene backing was used. The procedure for cleaning the Syrifil filter was to first wet the filter with methanol, then push approximately 10 mL of 4-M trace-metal-grade nitric acid through the filter, and rinse the filter again with 20 mL of ultrapure water.

A 1.5-mL sample was withdrawn from each aquarium for pH measurements. To obtain the dissolved oxygen measurements, an oxygen probe was submerged directly into each aquarium. The temperature in the laboratory ranged from 20° to 27° C.

Sampling frequency was gradually decreased over time starting with daily samples for the first 13 days; three times per week for 2 weeks; two times per week for 4 weeks; once per week for 8 weeks; and finally once a month for 6 months.

Development of the analytical method was difficult because of the complex seawater matrix and trace-level concentrations of metals within the samples. The metal determinations were done by direct-injection graphite furnace atomic absorption spectrophotometry using a Perkin-Elmer model ZL5100 spectrophotometer. The samples were diluted by 5 with ultrapure water and analyzed. The detection limits for copper, cadmium, and lead using this method were too high at 10, 10, and 50  $\mu\text{g/L}$ , respectively.

To reduce the seawater matrix problem and lower the detection limit, a Co-APDC extraction (Boyle and Edmond, 1975) was used to determine copper, cadmium, and lead. All operations were performed in a laminar flow hood. The sample, approximately 15 mL, was weighed into an acid-cleaned Teflon centrifuge tube. Two-hundred-fifty microliters of 3.3-mM cobalt chloride and 250  $\mu\text{L}$  of 2% Banco APDC solution were added to each tube. After 1-1/2 hours, the sample was vacuum filtered through an acid-cleaned, 0.4- $\mu\text{m}$  Nuclepore membrane and the precipitate was rinsed with ultrapure water. The membrane was transferred to an acid-cleaned Teflon vial. On the day of analysis, 0.5 mL of 8-M ultrapure nitric acid and 0.5 mL of ultrapure water were added to the vial. After the precipitate dissolved, the solution was transferred to a sample cup and analyzed. To calculate the concentration factor, the 1-mL volume added to the vial is used along with the net weight of the sample and the density of seawater. In addition to the sample, a processing blank of 1% nitric acid and Standard Water Reference Materials (CASS-2 and SLRS-2) were extracted.

The detection limits for the Co-APDC extraction method were calculated as three times the standard deviation of the processing blanks. The average detection limits for the Co-APDC extraction method were 0.1  $\mu\text{g/L}$  for copper, 0.004  $\mu\text{g/L}$  for cadmium, and 0.1  $\mu\text{g/L}$  for lead. The certified CASS-2 values for copper and cadmium are 0.675 and 0.019  $\mu\text{g/L}$ , respectively, where the observed CASS-2 value was 0.593  $\mu\text{g/L}$  for copper and 0.018  $\mu\text{g/L}$  for cadmium. The certified SLRS-2 value for lead is 0.129  $\mu\text{g/L}$  and the observed SLRS-2 value was 0.112  $\mu\text{g/L}$ . To analyze for manganese and zinc, the samples were diluted with deionized water and analyzed by direct injection. The detection limit was 10  $\mu\text{g/L}$  for manganese and 1  $\mu\text{g/L}$  for zinc.

## Results and Discussion

The results of the analysis of filtered seawater samples from aquarium simulations are shown in Table 5 and Figures 2 and 3. Again, the computer model WATEQ4F was used to identify the saturation indices of the available minerals and determine the species of ions in solution. The data from Table 5 were used for input. Concentrations of cadmium, copper, lead, zinc, manganese, and sulfate were determined



at SRC by the previously described procedures. Bicarbonate was determined by titration at SRC; pH and dissolved oxygen measurements were obtained directly from the simulation at SRC. All other concentrations were obtained from Hem, 1989, p. 7.

**Table 5. Analysis of filtered seawater samples from aquarium simulations at 275 days.**

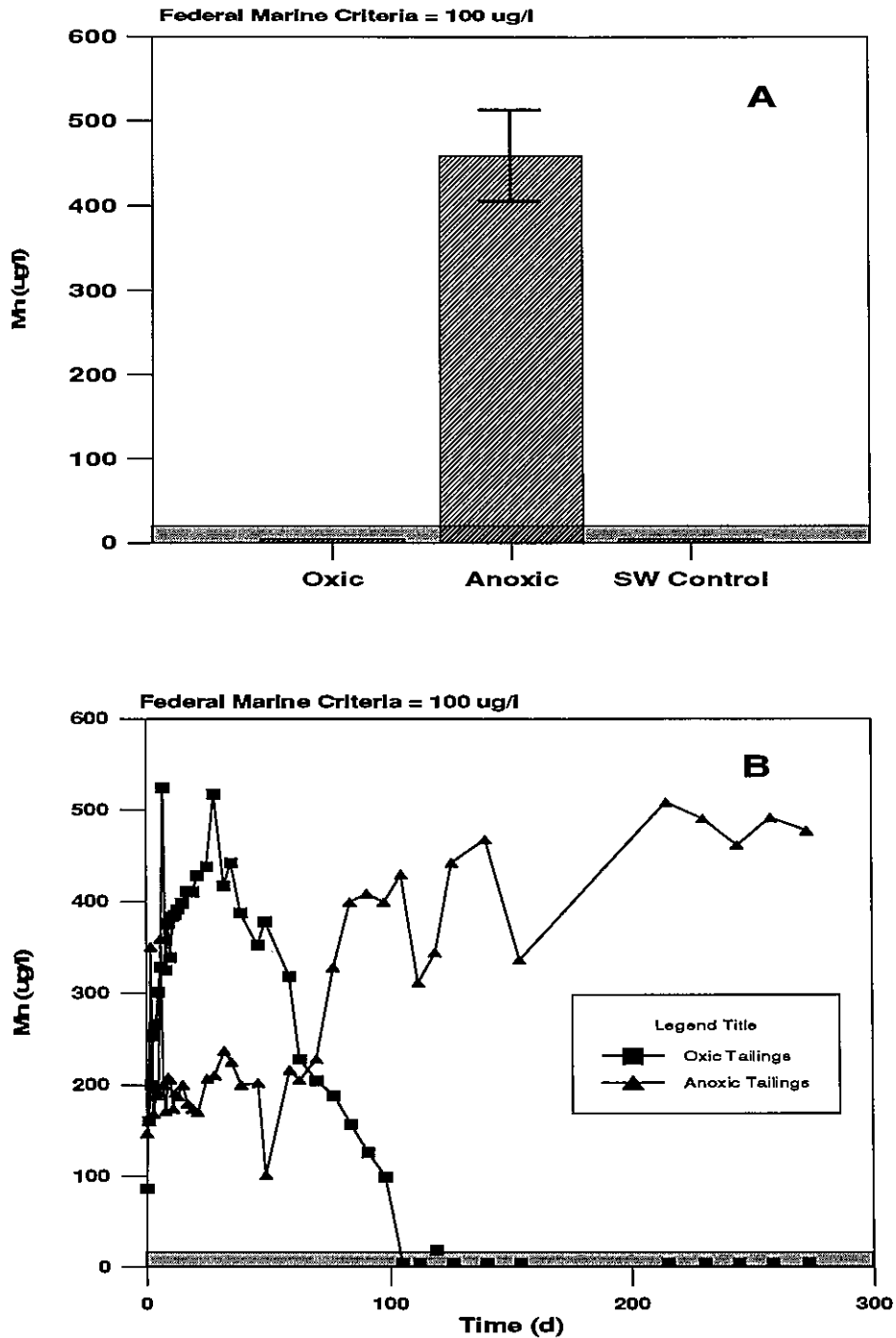
Constituent	Detection limit	Control aquarium	Marine criteria	Oxic aquarium	Anoxic aquarium
Element, $\mu\text{g/L}$ :					
Al . . . . .				1	1
Ca . . . . .				410,000	410,000
Cd . . . . .	0.004	0.02	2.9	0.029	<0.004
Cu . . . . .	0.07	0.37	9.3	0.62	<0.07
Fe . . . . .				3	3
K . . . . .				390,000	390,000
Pb . . . . .	0.05	1.6	5.6	<0.05	<0.05
Mg . . . . .				1,400,000	1,400,000
Mn . . . . .	10	<10	100	<10	450
Na . . . . .				10,000,000	10,000,000
P . . . . .				140	140
Si . . . . .				3,000	3,000
Zn . . . . .	1	8	58	<1	<1
Other:					
SO <sub>4</sub> <sup>2-</sup> , mg/L . . . .				2,700	2,700
HCO <sub>3</sub> <sup>3</sup> , mg/L . . . .				130	130
F, mg/L . . . . .				1.3	8.8
Cl, mg/L . . . . .				19,000	19,000
pH . . . . .				8.1	8.8
DO, mg/L . . . . .				5.5	0.1

DO = Dissolved oxygen.

Note: Concentrations of manganese exceed marine criteria in the anoxic simulations.

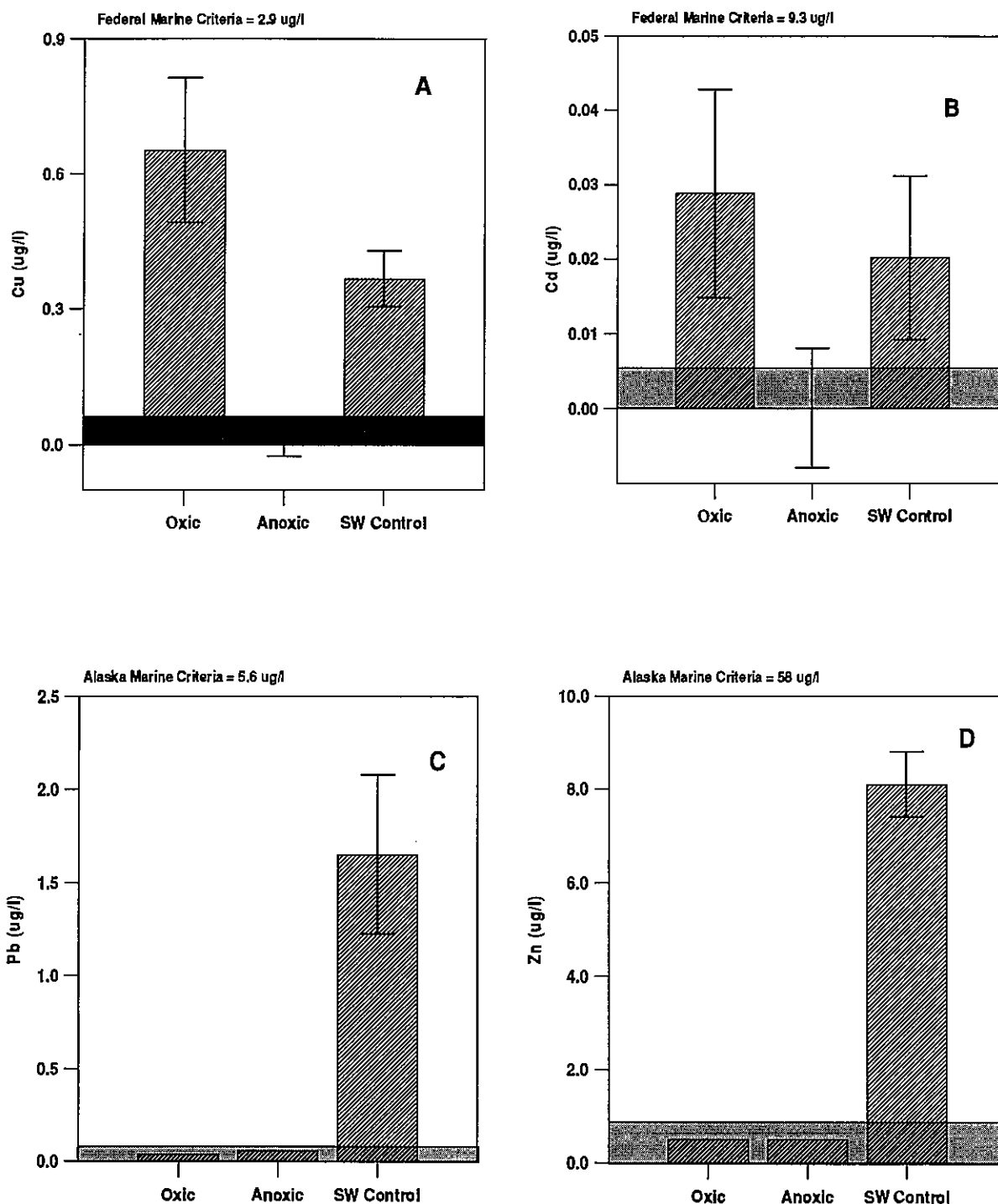
The dominant mineral within these tailings is quartz at 75%. It is equilibrated, but the dissolution reaction kinetics are slow. The other major constituent of the gangue is ankerite (10%). Carbonate minerals such as ankerite tend to carry significant amounts of other heavy metals as replacements within the crystal lattice. As such, they become potential sources for dissolved heavy metals when they are undersaturated. By examining the SI for carbonate end member minerals listed in Table 6, one can determine whether carbonate family minerals are soluble in the aquariums.

Calcite, magnesite, and rhodochrosite (c) were equilibrated in the oxic aquariums. In the anoxic aquariums, calcite and magnesite were slightly oversaturated, whereas rhodochrosite was equilibrated. Siderite was highly undersaturated in both simulations. These carbonate minerals were, in general, equilibrated-to-undersaturated in both the oxic and anoxic aquariums, and one would expect metals to be released into the overlying water. Albite was undersaturated in both simulations, but as with quartz, the dissolution reactions are very slow. Chlorite was oversaturated in both oxic and anoxic environments and will not tend to dissolve. Sulfide minerals such as pyrite will contain lattice substitutions of other metals, such as cadmium, copper, lead, and zinc. The trace amount of pyrite in the tailings could be a source of



**Figure 3.** Manganese concentrations in simulated postdepositional environments. Shaded regions at the bottom are detection limits. *A*, Manganese; *B*, concentration of manganese versus time.

Secondary cadmium, copper, lead, and zinc precipitate minerals within the WATEQ4F database were undersaturated in the anoxic aquariums. With the exception of rhodochrosite (d), secondary minerals that tend to coprecipitate or adsorb other metals, such as SiO<sub>2</sub> (a), were also undersaturated in the anoxic aquariums. Therefore, direct precipitation and sorption to secondary minerals did not control metal concentrations. Since these tailings are 75% quartz and finely ground quartz is a strong sorbent, the metal ions may have been adsorbed onto the surface of quartz particles and thus removed from the water column. Chlorite, a phyllosilicate, will act in a similar manner.



**Figure 2.** Metal concentrations in simulated postdepositional environments. Shaded regions at the bottom are detection limits. A, Copper; B, cadmium; C, lead; D, zinc.

these metals in the oxic simulations. However, the redox-driven reaction kinetics are extremely slow at near-neutral pH. This reaction will not occur in the anoxic simulations. Sulfide minerals are not included in Table 6 because SI's cannot be determined with WATEQ4F without  $HS^{-1}$  determinations.

After the tailings had been submerged for 275 days, the concentrations of copper, cadmium, lead, and zinc in the anoxic aquariums were all below detection limits. Given that carbonate source minerals tended to dissolve in both the oxic and anoxic aquariums, explanations of the lack of metals within the water column of the anoxic aquariums are precipitation and sorption of the metals from the water column.

**Table 6. Saturation indices of ion mineral source and sink phases determined with WATEQ4F for oxic and anoxic aquariums.**

Phase	Oxic	Anoxic
Source phases:		
Albite . . . . .	-1.6	-1.7
Calcite . . . . .	0.50	1.0
Chlorite 14A . . . . .	4.5	10
Chlorite 7A . . . . .	1.1	6.6
Magnesite . . . . .	0.79	1.3
Quartz . . . . .	0.12	0.081
Rhodochrosite (c) . . . . .	0.010	0.40
Siderite (c) . . . . .	-12	-13
Sink Phases:		
Birnessite [MnO <sub>2</sub> ] . . . . .	5.6	NA
Bixbyite [Mn <sub>2</sub> O <sub>3</sub> ] . . . . .	6.6	NA
Hausmannite [Mn <sub>3</sub> O <sub>4</sub> ] . . . . .	4.2	NA
Manganite [MnOOH] . . . . .	3.6	NA
Mn <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> . . . . .	NA	-15
MnCl <sub>2</sub> ·4H <sub>2</sub> O . . . . .	NA	-9.5
MnSO <sub>4</sub> . . . . .	NA	-11
Nsutite [MnO <sub>2</sub> ] . . . . .	6.6	NA
Pyrochroite [Mn(OH) <sub>2</sub> ] . . . . .	NA	-3.6
Pyrolusite [MnO <sub>2</sub> ] . . . . .	6.9	NA
Rhodochrosite (d) . . . . .	-1.7	-0.33
SiO <sub>2</sub> (a) . . . . .	-1.2	-1.2

NA = Not applicable in given environment.

(a) = amorphous

(c) = crystalline

(d) = disordered

The authors believe that adsorption onto silicate minerals, coupled with possible coprecipitation with disordered rhodochrosite, may control cadmium, copper, lead, and zinc concentrations in the anoxic aquariums. An example of a possible adsorption phenomena was observed during a seawater mixing experiment (see footnote 3). Fifteen minutes after mixing was initiated, zinc concentrations went from 2.6  $\mu\text{g/L}$  to below the detection limit of 1  $\mu\text{g/L}$ . In three out of the four mixing experiments, the lead concentration went from 1.8  $\mu\text{g/L}$  to below the detection limit of 0.07  $\mu\text{g/L}$ . The aquarium studies show similar results, with the lead and zinc concentrations being less than the detection limits in both the oxic and anoxic aquariums. Asmund (1992, p. 591) noted post-depositional adsorption of lead from the water column from a marine tailings deposit at the Black Angel Mine. At Mandy Lake in Manitoba, Canada, dissolved zinc in natural water was being consumed by tailings deposited in the lake (Pederson and others, 1991, p. 201).

In a reducing environment, manganese will tend to remain in the water column. This is evident from a comparison of manganese concentrations in the anoxic aquariums versus oxic aquariums (Fig. 3). The most common reduced-phase secondary manganese minerals, Mn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>, MnCl<sub>2</sub>·4H<sub>2</sub>O, and MnSO<sub>4</sub> (as shown in Table 6), were highly undersaturated in the anoxic aquariums. The manganese concentration from

day 215 forward appears to have plateaued. Disordered rhodochrosite, another key secondary manganese mineral, is equilibrated and is probably the dominant control of manganese concentrations, or at least maintains it at a maximum concentration of 450  $\mu\text{g/L}$ .

In the oxic aquariums, concentrations of lead and zinc remained below their respective detection limits while concentrations of cadmium and copper, although still quite low, were slightly higher than in the anoxic aquariums. Again, all secondary sink phases for these metals were undersaturated. This indicates probable concentration control by sorption. Adsorption by silicate minerals coupled with coprecipitation with manganese minerals will probably maintain metal concentrations well below normal saturation limits.

In an oxidizing environment, manganese will tend to precipitate from solution. After 35 days, a black precipitate began to form on the tailings surface in the oxic aquariums. The formation of this precipitate corresponded to a decline in the concentration of manganese from the water column (Fig. 3B). The appearance of a black precipitate, which is probably a mixture of oxidized manganese minerals, may correspond with the development of an active culture of manganese oxidizing bacteria. The importance of bacterial catalysis of oxidation and precipitation of manganese and other metals has been identified by numerous researchers (Hem, 1989, p. 88; Stumm, 1987, p. 458). Saturation indices calculated by WATEQ4F indicated that at the detection limit of 10  $\mu\text{g/L}$ , the most common manganese precipitates, birnessite, bixbyite, hausmannite, manganite, and pyrolusite (shown in Table 6) were highly oversaturated in the water column. One would, therefore, expect the true concentrations of manganese to be very near zero, at which point the SI's would probably be equilibrated. Prior to the formation of the black precipitate, when the concentration of manganese was measurable, the SI's (WATEQ4F runs not shown here) for the manganese minerals were even higher.

WATEQ4F calculations did not identify any clear differences between the species distribution of the two simulations, and therefore, an explanation is not provided as to why the copper and cadmium concentrations in the oxic aquariums were slightly higher than the anoxic aquariums. However, the copper and cadmium concentrations were only slightly above the detection limits and, as the error bars indicate, concentrations in the oxic aquariums may not be different from the control.

### Conclusions

Static aquarium simulations indicated that even without an exchange of water, which would occur in the mixing zone, concentrations of copper, cadmium, lead, and zinc were all well below their respective marine aquatic criteria. Concentrations of lead and zinc were higher in the seawater control aquarium than in the aquariums with the tailings. This suggests that the tailings may actually adsorb some metals from the seawater column, which was noted by Asmund (1992, p. 591). Manganese appeared to be released from the tailings, but in an oxic system, this element oxidizes and secondary manganese minerals precipitate to yield dissolved manganese concentrations well below marine criteria. In the anoxic laboratory simulations, manganese concentrations were above marine criteria, as would be expected in any anoxic environment.

### References

- Asmund, G. 1992. Pollution from the marine tailings disposal at Maarmorilik, West Greenland. *In* R. Singhal, A. Mehrotra, K. Fytas, and J. Collins (eds.), *Environmental Issues and Management of Waste in Energy and Mineral Production*. Proceedings: Second International Conference, Calgary, AL, Sept. 1-4, 1992, p. 587-594.
- Asmund, G., M. Hansen, and P. Johansen. 1988. Environmental impact of marine tailings disposal at the Lead-Zinc Mine at Maarmorilik, West Greenland. *In* Proceedings: International Congress on the Control of Environmental Problems from Metal Mines, Røros, Norway, June 20-24, 1988, 11 p.

- Ball, J.W., and D.K. Nordstrom. 1991. User's Manual for WATEQ4F, with revised thermodynamic data base and test cases for calculating speciation of major, trace, and redox elements in natural water. U.S. Geol. Surv. OFR 91-183, 188 p.
- Boyle, E.A., and J.M. Edmond. 1975. Determination of trace metals in aqueous solution by APDC chelate coprecipitation. In T.R.P. Gibbs (ed.), Analytical Methods in Oceanography. Amer. Chem. Soc., Adv. Chem. Ser. 148, p. 44-55.
- Ellis, D.V., and P.M. Hoover. 1990. Benthos recolonizing mine tailings. *Marine Min.*, 9:441-457.
- Ellis, D., G. Poling, and C. Pelletier. 1994. Case studies of submarine tailings disposal. Vol. 2: Further case histories and screening criteria. USBM OFR 37-94, 152 p.
- Hem, J.D. 1989. Study and interpretation of the chemical characteristics of natural water. U.S. Geol. Surv. Water-Supply Paper 2254, 263 p.
- Hurlbut, C. 1971. Dana's Manual of Mineralogy, 18th ed. John Wiley & Sons, 579 p.
- Mason, B., and L.G. Berry. 1968. Elements of Mineralogy. W.H. Freeman, 550 p.
- Nordstrom, D.K. 1982. Aqueous pyrite oxidation and the subsequent formation of secondary iron minerals. In J.A. Kittrick, D.S. Fanning, and R.L. Hossner (eds.), Acid Sulfate Weathering. Soil Soc. Amer. Publ. 10, p. 37-56.
- Pederson, T., B. Mueller, J. McNee, and C. Pelletier. 1991. Diagenetic reactivity of mine tailings in mesotrophic lakes in Manitoba and British Columbia. In Proceedings of the Second International Conference on the Abatement of Acidic Drainage, Montreal, PQ, Sept. 16-18, 1991, 4:201-226.
- Plummer, L.N., B.F. Jones, and A.H. Truesdell. 1976. WATEQF—A FORTRAN IV version of WATEQ, A computer program for calculating chemical equilibrium of natural waters. U.S. Geol. Surv. Water Res. Invest. Report 76-13, 61 p.
- Poling, G., and D. Ellis, eds. 1993. Case studies of submarine tailings disposal. Vol. 1: North American examples. USBM OFR 89-93, 206 p.
- Stumm, W., ed. 1987. Aquatic Surface Chemistry. John Wiley & Sons, 520 p.
- Truesdell, A.E., and B.F. Jones. 1974. WATEQ—A computer program for calculating chemical equilibrium of natural waters. U.S. Geol. Surv. J. Res., 2:233-248.