

**SUBAQUEOUS DISPOSAL
OF REACTIVE MINE
WASTES: AN OVERVIEW**

MEND Project 2.11.1a

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Executive Summary

Finding an environmentally safe, yet economical, method of disposing of reactive mine wastes is a challenge facing both the mining industry and government. When such materials contain sulphides, the conventional practice of land-based disposal has often resulted in the generation of acidic water and the concomitant leaching of trace metals from the mine wastes. Acid production in tailings and waste rock is a result of the oxidation of sulphide minerals (principally iron pyrite). Acid generation results in various, often severe, impacts on water chemistry and biological resources. The environmental implications are considerable, particularly since the problem can persist after active mining has ceased.

One method for controlling acid generation which is receiving increasing attention is the practice of depositing reactive mine wastes underwater. While the Metal Mining Liquid Effluent Regulations, authorized under the federal *Fisheries Act*, currently prohibit lake disposal of mine tailings, an exemption can be issued through a federal cabinet Order-in-Council. An argument for subaqueous disposal is based on the premise that acid generation is suppressed in submerged mine wastes that are essentially unexposed to oxygen and bacterial action. This suggestion is predicated on knowledge of the biogeochemical nature of lacustrine sediments, and appears to be supported by observations made in specific field studies. Hence, it is consistent to suggest that sulphide-rich mine wastes may be disposed of underwater without significant release of metals to the overlying waters. In some circumstances, however, a number of factors can act individually or in concert to promulgate release of metals, with the associated potential for environmental degradation. Nevertheless, with sufficient knowledge of post-depositional chemical reactivity of the specific tailings and adherence to disposal criteria, these factors can be mitigated to various extents and impacts on water quality and indigenous biota minimized.

While this conventional wisdom supporting subaqueous disposal may be correct, only a limited number of reviews and even fewer field studies have been undertaken that add significant insight. Consequently, the efficacy of underwater disposal remains largely unproven.

Responding to the clear need for establishing effective methods to mitigate acid mine drainage, and recognizing the considerable promise subaqueous disposal holds in this regard, the British Columbia Acid Mine Drainage Task Force issued a call for proposals to complete a literature review on underwater disposal of reactive mine wastes. The study was to focus on the state-of-the-art in theoretical knowledge and case studies of British Columbia mines disposing of wastes in a freshwater environment. Consideration was to be given to potential impacts on freshwater biological systems, including both physical and chemical effects of mine waste disposal. As a consequence, Rescan Environmental Services Ltd. was retained to undertake the literature review on the *Subaqueous Disposal of Reactive Mine Wastes*.

This study was completed based on a comprehensive review of all aspects of subaqueous disposal of reactive mine wastes in a freshwater environment, both theoretical and applied. While emphasis was placed on the British Columbia experience with underwater disposal practices, as mandated in the RFP, attention was also given to other parts of Canada and the United States. During the review, numerous and varied sources of literature were consulted through both desk and computer-aided search methods. Sources of information included, among others, literature on acid mine drainage mechanisms and chemistry, aquatic chemistry, geochemistry, hydrogeochemistry, biochemistry, microbiology, limnology and aquatic biology/ecology. Whenever possible, relevant case study data were obtained which often addressed one or more of the above areas to various degrees of detail. Although the scope of this report is confined to freshwater (i.e. lake disposal), the literature review includes documentation on land-based tailings and leach dumps or heaps insofar as they contained data relevant to subaqueous disposal. Similarly, results from marine disposal operations are only included where such work illustrates principles which are applicable universally to aquatic

systems. The results of this literature review are summarized below. Section 7.0 provides a comprehensive bibliography of information on both the theory and practice of subaqueous disposal.

Of all the conclusions drawn from this study, perhaps the most salient is that AMD poses serious disadvantages for land-based disposal of reactive mine wastes and that the underwater disposal of such wastes holds considerable promise for suppressing acid generation. Nevertheless, the potential long-term impacts associated with subaqueous disposal remain poorly understood.

Various factors, sometimes acting synergistically, determine the potential for mine wastes deposited underwater to generate acid and, consequently, the potential for biological impacts. These factors include, among others, the natural chemistry of the receiving environment, physicochemical conditions which may help limit concentrations of dissolved metals, hydrochemical conditions that may increase heavy metal solubility and the composition of the mine wastes being deposited. Of the range of predictive tests available to evaluate potential for acid generation (Section 2.3), the kinetic shake flask test appears somewhat suitable for subaqueous storage of reactive mine wastes.

The complex processes of bioavailability of metals in lake-bottom sediments and bioaccumulation in the freshwater food chain are not well understood, particularly with regard to reactive mine waste disposal. To help improve the level of understanding, lake studies should be conducted whereby post-depositional reactivity of submerged wastes is evaluated to determine if benthic effluxes of selected metals, i.e. Cu, Pb, Zn, Cd, Mn, Fe, As, and Hg are present and to what extent they are obviated by the gradual deposition of a veneer of natural sediments. Apart from potential impact, other biological effects of underwater disposal include turbidity, sedimentation on lake bottoms and toxicity to aquatic organisms.

Following a review of the literature relating to acid mine drainage, subaqueous disposal, and its potential biological implications, numerous case studies documenting existing occurrences of subaqueous disposal in a freshwater environment were reviewed. The cases analyzed within British Columbia include Buttle Lake, Benson Lake, Babine Lake, Bearskin Lake (proposed), Brucejack Lake (proposed), Kootenay Lake, Pinchi Lake, Summit Lake, Equity Silver Mines Ltd. (flooded open-pit), Endako Mine (flooded open-pit), Cinola Gold Project (proposed) and Phoenix Mine. Other Canadian and U.S. cases examined include Garrow Lake, Northwest Territories; Mandy Lake, Anderson Lake, and Fox Lake, Manitoba; and Reserve Mining Co. Ltd., Silver Bay, Minnesota. Generally it was concluded that although the case studies reviewed represented a diversity of environments, the results yielded were somewhat inconclusive. Data were generally superficial, only remotely relevant, reflect questionable sampling practices, and were not gathered with a view toward better understanding the long-term impacts associated with the subaqueous disposal of reactive mine wastes.

Based on the results of the literature review, it is recommended that field studies be undertaken to evaluate the post-depositional reactivity of sulphide-bearing mine wastes and to conduct more detailed, site-specific investigations of potential biological impacts in the freshwater receiving environment. Studies should include a detailed evaluation of the ore and tailings mineralogy, particle size distributions, predicted settling behaviour of mine wastes, and leaching behaviour or reactivity of the wastes once exposed to freshwater. It is considered critical that geochemical and limnological field investigations be completed in concert to both increase our knowledge of the factors which control metal release or uptake by tailings and the potential associated, direct or indirect, impacts that might accrue to the biological community.

The geochemical studies recommended require analyzing interstitial waters collected from suites of cores raised from submerged tailings deposits in a number of lakes including Buttle Lake, Benson Lake and/or Kootenay Lake, British Columbia; Mandy Lake, Fox Lake, and/or Anderson Lake, Manitoba. Such studies should embrace a variety of deposits including unperturbed sediments and tailings with contrasting mineralogies, and should include assessment

of alteration effects and connate water and/or groundwater chemistry in contrast to tailings disposed on-land. The studies should include locations no longer receiving mine wastes and active depositional regimes. It is highly recommended that the geochemical investigations include chemical analyses of selected major and minor element concentrations in the solid phases from which the pore waters are extracted, mineralogical characterization, and measurements of organic carbon concentrations.

Comparative mineralogic studies of both facies should be undertaken to contrast the extent and nature of mineral alteration where tailings of the same composition have been discharged both underwater and on-land (e.g., Buttle and Benson Lakes). Such comparisons have the potential to provide a particularly enlightening suite of examples of the relative diagenetic behaviour of tailings exposed to the atmosphere versus those submerged in a freshwater environment.

In association with the geochemical analyses described above, limnological and biological investigations must be completed to link the complex process of metals release from submerged wastes to their potential uptake by aquatic organisms and bioaccumulation in the food chain. The purpose of these studies will be to describe the lake(s) considered in terms of features that can assist in predicting the impacts of mine wastes deposited in similar lakes. Lake morphology and hydrology, physical and chemical limnology and biological characteristics should all be measured to allow investigators to calculate lake turnover and residence time, determine circulation and mixing features, and evaluate the potential for wastes to be mobilized and the rate at which contaminants would be dispersed from the mine waste deposit. A better understanding of metal transfer between sediments and the aquatic food chain would also be achieved.

Site-specific experiments on lacustrine biota should be designed to establish the impacts of heavy metals on both infauna and epifauna. Metal levels within the tissues of these organisms may reflect metal uptake rates and the potential for bioaccumulation in the food chain. It is also advised that one or two suitable fish species (i.e. those characterized by low mobility, long life-spans, and/or higher trophic level feeding) be chosen for tissue metals analysis due to the high interest in fish by both regulatory agencies and the general public.

Finally, based on a combination of theory as documented in this literature review, and empirical field study data, it is recommended that a decision model be developed to evaluate the suitability of future underwater waste disposal strategies. Initial attempts at this have been confounded by the insufficient and/or unreliable data describing conditions at existing subaqueous disposal sites.

The type of decision model proposed would incorporate physical, chemical, geochemical, biochemical, limnological and biological conditions, identified in theory and refined through field investigation, in a critical path framework to evaluate the environmental implications associated with strategies for the subaqueous disposal of mine wastes. It would provide a pragmatic method for screening disposal alternatives by both industry and government regulators, based on a fatal flaw approach that would identify key potential problem areas for given proposed discharge strategies. The decision model would be developed based on theoretical and case study information collected through this review, coupled with empirical data gathered through field studies such as those outlined above, and would assist both industry in effectively choosing methods of reactive mine waste disposal and government charged with the responsibility for ensuring wastes are disposed of in an environmentally acceptable manner.

Acknowledgements

We would like to acknowledge the British Columbia Acid Mine Drainage Task Force for their cooperation and support throughout this project. We would specifically like to acknowledge the following individuals from the Task Force Technical Committee who provided valuable comments during the draft review: Mr. J.D. Robertson, P.Eng. - Chairman; and Mr. K.D. Ferguson, P.Eng. Mr. M. Filion of CANMET and Mr. W. Fraser of Hudson Bay Mining and Smelting Co. Limited also provided thoughtful insights to the final version of this report.

The *Subaqueous Disposal of Reactive Mine Wastes* report was completed as a multidisciplinary exercise through the efforts of those individuals listed below. Their technical and editorial input have directly resulted in the successful completion of this document.

- **MR. C.A. PELLETIER, B.Sc. (CHEMISTRY)**

As Project Manager, Mr. Pelletier oversaw the project and reviewed the final document. His considerable experience with environmental issues relating to the mining industry, especially in subaqueous disposal of mine wastes, has been an invaluable source of information throughout the project. He provided guidance to the team of scientists accumulating the information for the compilation of this literature review.

- **DR. T.F. PEDERSEN, B.Sc. (GEOLOGY), Ph.D. (MARINE GEOCHEMISTRY)**

Dr. Pedersen's extensive experience in the field of sediment geochemistry (he is Associate Professor, Department of Oceanography, UBC), particularly his research on the chemical reactivity of submerged mine tailing deposits. His specific research on tailings deposits in Buttle Lake, Rupert Inlet and Alice Arm, B.C., was of particular importance.

- **DR. G.W. POLING, B.Sc. (MINING AND METALLURGICAL ENGINEERING), Ph.D. (MINERAL PROCESSING)**

Dr. Poling is one of Canada's leading experts in the environmental management of mining operations with special emphasis on tailings disposal, waste solids handling and acid drainage control. He is Professor and Head of Mining and Mineral Process Engineering, UBC. His environmental work for the Island Copper mine significantly added to the knowledge base of this work.

- **DR. D.V. ELLIS, B.Sc. (ZOOLOGY), M.Sc. (BIOLOGY), Ph.D. (MARINE BIOLOGY)**

Dr. Ellis's 30 years of experience in aquatic biology and environmental sciences, in particular that related to the impact of underwater tailings disposal in the aquatic environment, provided a significant source of knowledge in the documentation of limnological and biological components of the study. Complementing his wealth of practical experience with subaqueous tailings disposal, Dr. Ellis has written extensively on the subject, including *Mine Tailings Disposal* (Ann Arbor Science Press, 1982).

- **DR. D.W. DUNCAN, B.S.A. (HONS.), Ph.D. (MICROBIOLOGY)**

Dr. Duncan has been working in the field of microbiological oxidation of sulphide minerals since 1962. His work has included research to prevent the unwanted oxidation of waste which generates acid mine drainage, and has included the first practical procedure to estimate the acid generating potential of sulphide bearing materials. Dr. Duncan's specific involvement in the assessment of the potential for AMD from mine tailings in Buttle Lake was also of considerable help. He contributed to the limnological and biological components of this study.

- **DR. T.G. NORTHCOTE, B.A., Ph.D. (FRESHWATER ECOLOGY/LIMNOLOGY)**

Dr. Northcote is Professor, Forest Sciences and Zoology at UBC, and specializes in limnology and the ecology of freshwater habitats. He has worked extensively in lake ecosystems investigating the relationship of fish ecology and behaviour, and has extensive experience with mining-related activities and their associated effects on the freshwater environment. Dr. Northcote provided his extensive knowledge in freshwater biological and limnological systems.

Other members of the Rescan team who contributed to the documentation of *Subaqueous Disposal of Reactive Mine Wastes* include:

- Mr. K.P.M. Dushnisky, B.Sc. Hons. (Ecology) M.Sc. (Resource Management)
- Mr. S.T. Robinson, M.A.Sc. (Environmental Engineering)
- Mr. S.R. Bilevicius, M.A.Sc. (Environmental Engineering)
- Mr. R.S. Kinasevich, M.Sc. (Mineral Technology)

Without the dedication and support of the individuals noted above, the successful completion of this document would not have been possible.

Introduction

The safe and economic disposal of waste rock and tailings is a continuing source of difficulty plaguing both the mining industry and governments. When these mine waste materials contain sulphides, the conventional practice of on-land containment has resulted in the generation of highly acidic water and the concomitant leaching of trace metals. This has far reaching and serious environmental implications and supports more recent initiatives toward subaqueous disposal, especially since the problem may continue long after mining operations have ceased. To investigate the problem of acid mine drainage, several industry-government task forces have been established including the national Mine Environment Neutral Drainage (MEND) program and the British Columbia Acid Mine Drainage Task Force. These committees are playing an increasingly important role in supporting research, including this literature review on the *Subaqueous Disposal of Reactive Mine Wastes*, to encourage the establishment of environmentally safe methods for mitigating acid mine drainage.

1.1 Purpose of Study

Subaqueous disposal of mine waste rock and tailings relies on the premise that submerged mine wastes, minimally exposed to oxygen and bacterial processes, will be suppressed from generating acid. While this premise may be correct, it remains largely unproven. A limited number of reviews of the short and long-term environmental implications of the disposal of mine wastes to the aquatic environment have been undertaken and only a few of the field studies have addressed such issues. Although basically an unproven method of mitigation, there is an ever-increasing number of mines being developed which are proposing to adopt subaqueous disposal as a means of combating potential acid generation problems. A thorough review of the history of existing subaqueous disposal practices is, therefore, needed in order to provide a foundation for making informed and confident judgements on the suitability of aquatic discharge strategies in the future.

Responding to the need for economic and effective approaches to resolve the problem of acid mine drainage, the British Columbia Acid Mine Drainage Task Force issued a call for proposals to review the British Columbia experience with subaqueous disposal of reactive mine wastes in a freshwater environment. Briefly, the terms of reference for the study were as follows:

- The consultant was to investigate the effectiveness of disposing of waste rock and tailings underwater to discourage acid generation, and to assess the potential impacts of this disposal method on the freshwater environment.
- Based on a review of relevant literature, including project specific data gathered from British Columbia mines utilizing subaqueous disposal, the consultant was to evaluate the biological impacts of mine waste disposal in a freshwater environment, considering both the physical and chemical effects of subaqueous deposition.

Following a review of the proposals submitted, the British Columbia Acid Mine Drainage Task Force commissioned Rescan Environmental Services Ltd. in November 1988 to complete the review contained herein.

1.2 Study Scope and Methodology

This study was completed based on a comprehensive literature review of all aspects of subaqueous disposal of reactive mine wastes in a freshwater environment. Though emphasis was placed on the British Columbia experience as mandated in the RFP, consideration was also given to mines utilizing subaqueous disposal practices in other parts of Canada and the United States. Numerous sources of information were consulted during the review through both desk and computer-aided search methods. The types of literature investigated included, among others, information on acid mine drainage mechanisms, aquatic chemistry, geochemistry,

hydrogeochemistry, biochemistry, microbiology, limnology, and aquatic ecology. While the scope of this review is limited to freshwater environments, land-based tailings, leach dumps/heaps, and submarine disposal systems were also considered insofar as they provided data relevant to freshwater disposal.

This review, although contemporary and considered to be timely, is certainly not the first to address the disposal of mine wastes. Other reviews, studies and reports, some with quite comprehensive literature reviews, have appeared over the past two decades. In fact, a 1970 report entitled *The Disposal of Mining and Milling Wastes with Particular Reference to Underwater Disposal* was somewhat similar in scope to the one submitted here. The fundamental difference between past efforts and this attempt to address subaqueous disposal is that this report evaluates the state-of-the-art in underwater disposal theory, coupled with data gathered from mines utilizing the practice, both to advance the current level of understanding and recommend practical strategies for future field studies to improve our knowledge of the long-term behaviour and impacts of extant and abandoned submerged tailings deposits.

This report is comprised of two parts: a theoretical literature review and an overview of selected case studies. The theory component first describes fundamentals of acid mine drainage that have plagued land-based tailings disposal, then examines the practice of subaqueous deposition with emphasis on physical, chemical, geochemical, microbiological and macrobiological implications for the freshwater environment. The literature review supporting this theoretical section is extensive and provides a comprehensive database for those interested in reactive mine waste disposal.

The case studies selected were chosen based on a number of criteria including data accessibility and method of subaqueous disposal (flooded tailings ponds, pits, underground workings). Along with the British Columbia experience with freshwater subaqueous disposal, Rescan also reviewed mines in other parts of Canada and the U.S. The sites examined within British Columbia include Buttle Lake, Babine Lake, Benson Lake, Brucejack Lake (proposed), Bearskin Lake (proposed), Kootenay Lake, Pinchi Lake, Summit Lake, Equity Silver Mines Ltd. (flooded open-pit), Endako Mine (flooded open-pit), City Resources (Canada) Limited - Queen Charlotte Islands and Phoenix Mine. Outside British Columbia, the sites investigated include Garrow Lake, Northwest Territories; Mandy Lake, Anderson Lake and Fox Lake, Manitoba. Also reviewed was Reserve Mining Co. Ltd., Silver Bay on Lake Superior, Minnesota.

Based on a review of theoretical considerations and the results of the case study analysis, conclusions are drawn and recommendations are made for future field investigations to increase our understanding of the long-term behaviour and impacts of subaqueous mine waste disposal through the collection and analysis of empirical data. This improved understanding will permit more confident review and evaluation of future subaqueous disposal strategies.

1.3 Overview of Literature Search

A comprehensive search was made for literature dealing with the subaqueous disposal of reactive mine wastes, and included consideration of hydrogeochemistry, microbiology, biochemistry, biology and limnology. The bibliography compiled in Section 7.0 represent a substantial collection of scientific and technical knowledge on underwater tailings disposal.

Although the scope of this report focusses on subaqueous tailings disposal, the literature search located and incorporated documentation on land tailings disposal and leach dumps, if these were found to contain useful information.

The literature review incorporated on-line computer database searches using a variety of index systems, in addition to an extensive effort to locate information in journals and technical textbooks. Lists of keywords and authors were compiled from an overview of key publications. Database systems used include the comprehensive CAN/OLE and DIALOG

systems, and the QL System. Recognized scientific and engineering index systems that were searched include:

- **NTIS** (1964 - present) - listing U.S. Government Publications, although not a complete listing of U.S. Environmental Protection Agency documents;
- **Pollution Abstracts** (1970 - present) - a leading source of literature on environmental quality, solid wastes and water pollution;
- **Chem Abstracts** (1967 - present) - citations of all research into chemistry and its applications;
- **Engineering Index - COMPENDEX** (1970 - present) - abstracted information from world-wide engineering and technical literature including over 4,500 journals, government reports and books;
- **Enviroline** (1971 - present) - covers environmental information and indexes over 5,000 international publications, including geology, biology and chemistry;
- **Aquaref-WATDOC** (1970 - present) - Canadian water resources references encompassing scientific and technical literature;
- **Mintec/Minproc - CANMET** (1968 - present) - Canadian Mining and Mineral Processing index.

Subsequent to computer database searches, publications were retrieved from the following collections:

- University of British Columbia Library;
- Geological Survey of Canada Library;
- Environment Protection Service (Environment Canada) Library, Pacific Region.
- Fisheries and Oceans Library;
- Inland Waters Directorate (Environment Canada);
- Vancouver Public Library, Sciences and Technology Division;
- University of Waterloo Groundwater Research Library;
- Rescan Environmental Services Library, and the personal libraries of associates who have contributed to the study.

1.4 Discussion of Literature on Subaqueous Mine Waste Disposal

Much has been observed, investigated and written on acid mine drainage and its control, acid generation within terrestrial tailings impoundments and waste dumps, and oxidation-reduction reactions involving discarded iron and other residual metallic sulphide minerals (pyrite, pyrrhotite, arsenopyrite, chalcopyrite, and residual zinc and lead sulphides). Only a small portion of the literature attempts to address underwater disposal in the freshwater environment. Few reports contain data or observations from existing operations which are sufficient for general evaluation of freshwater disposal. Pertinent references strongly suggest that optimum conditions for subaqueous disposal are not fully understood and that more analyses will be required to permit developing guidelines for its use.

Some of the more pertinent references include:

- Bohn et al., 1981 •
- Daley et al., 1981 •
- Halbert et al., 1982 •

- Hamilton and Fraser, 1978 •
- Hawley, 1975 •
- IMPC, 1982 •
- Kennedy and Hawthorne, 1987 •
- Knapp, 1981 •

In addition, the content or themes of several biologically oriented overviews or articles suggest caution about underwater tailings disposal. Some references of this type that require special attention are:

- Allan, 1986 •
- Campbell et al., 1988 •
- Daley et al., 1981 •
- Evans and Lasenby, 1988 •
- Forstner and Wittmann, 1983 •
- Hamilton, 1976 •
- Harvey, 1976 •
- Jackson 1978, 1980, 1988 •
- Malo, 1977 •

There is a substantial body of literature on marine disposal, but judicious consideration is required when this information is applied to freshwater subaqueous disposal. Little information has been located on flooded pits and mine shafts (Gallinger, 1988). In British Columbia there are several depleted and closed-down workings which now exist as abandoned or decommissioned open pits.

Chapter 2

Acid mine drainage (AMD) is the hydrogeologic expression of a host of complex oxidation reactions of sulphide minerals. In general, whenever sulphide minerals such as pyrite, FeS_2 , marcasite, FeS_2 , or pyrrhotite, $\text{Fe}_{1-x}\text{S}_x$, are exposed to water and to oxygen, the production of hydrous ferrous sulphate will result. Ground waters percolating through or flushing around or saturating these minerals will dissolve the ferrous salts and acid. The ferrous iron will subsequently be oxidized to ferric ions or ferric oxyhydroxides either chemically or biochemically. A buildup of ferric ion will usually mean that this species will far exceed oxygen as the dominant oxidizing agent of exposed sulphide minerals. As the reactions progress, the rate of oxidation of the sulphides continues to increase as more ferric ion is generated and this in turn oxidizes more iron sulphide to release more ferrous and eventually more ferric ions. In this sense the oxidation of the sulphides can become auto-catalytic.

Percolation or flushing of surrounding ground waters, which picks up the reaction products of sulphide oxidation, will normally contain some alkalinity, such as CaCO_3 , which can react to neutralize the acid. Thus the eventual drainage might be neutral in pH with elevated sulphate concentrations. Whether or not the percolating or flushing waters will eventually emerge as "acid drainage", therefore, will depend not only on the balances of acid-producing sulphides and acid-consuming rocks (such as CaCO_3) but also on the *rates* of acid production versus alkaline production.

Drainage conditions can change dramatically over long periods of time. Should carbonate be consumed, production of neutralizing alkalinity would cease while acid production continued. A neutral drainage could then rapidly convert to a strongly acid one. It should not be surprising, therefore, that predictive technology of AMD is necessarily complex.

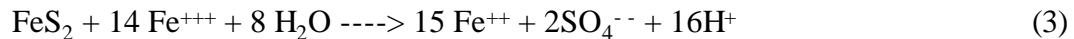
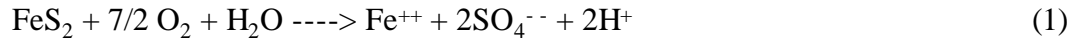
2.1 AMD Generation/Consumption

Thermodynamically, sulphides are only stable in reducing aqueous environments. One of the best ways to depict the various domains of thermodynamic stability is to use an E_h versus pH diagram. Cloke (1966) concisely outlines methods for construction of E_h -pH diagrams. Figure 2-1 shows such a "Pourbaix Diagram" for the Fe-S- H_2O system

under standard conditions of temperature (298°C) and pressure (1 atmosphere) for 10^{-6} activity of dissolved iron species (Garrels and Christ, 1965).

Figure 2-1 indicates that oxidizing conditions (higher E_h) are required to dissolve pyrite to yield Fe^{++} or eventually Fe^{+++} species. A Pourbaix diagram for the S- H_2O system is shown in Figure 2-2 which also indicates the need for oxidizing conditions to form $SO_4^{=}$ ions.

Commonly accepted reactions describing the natural oxidation of pyrite are as follows (Singer and Stumm, 1969):



Singer and Stumm (1969) reported that oxidation of Fe^{++} (reaction (2) above) was rate limiting and very slow under sterile conditions. Bacteria, which are ubiquitous in these systems, are capable of catalyzing this iron oxidation and hence propagate the leaching cycles. Oxygen remains a critical reactant by serving to regenerate the ferric ion. Oxygen is also critical to the growth of bacteria such as *Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans* which participate in the sulphide oxidation. These microorganisms normally depend also on dissolved CO_2 as their source of carbon and require nitrogen and phosphorus for chemosynthesis and growth. Hence aeration of water is crucial to the formation of AMD by oxidation of sulphide minerals.

Although some authors attempt to describe acid formation as either a chemical or electrochemical reaction mechanism, Figure 2-1 indicates that almost every reaction in the Fe-S- H_2O system involves electron transfer or change in oxidation state or electrochemistry. On the Eh vs. pH diagrams, only vertical lines separating domains or "fields of stability" involve no electron transfer. Since essentially all lines, except the equilibrium between Fe^{3+} and Fe_2O_3 are either horizontal or sloping, all reactions depicted in Figure 2-1 are electrochemical in nature.

The prospect of driving the oxidation of sulphides by galvanic coupling between contacting mineral phases of differing potentials is unlikely to be significant except in

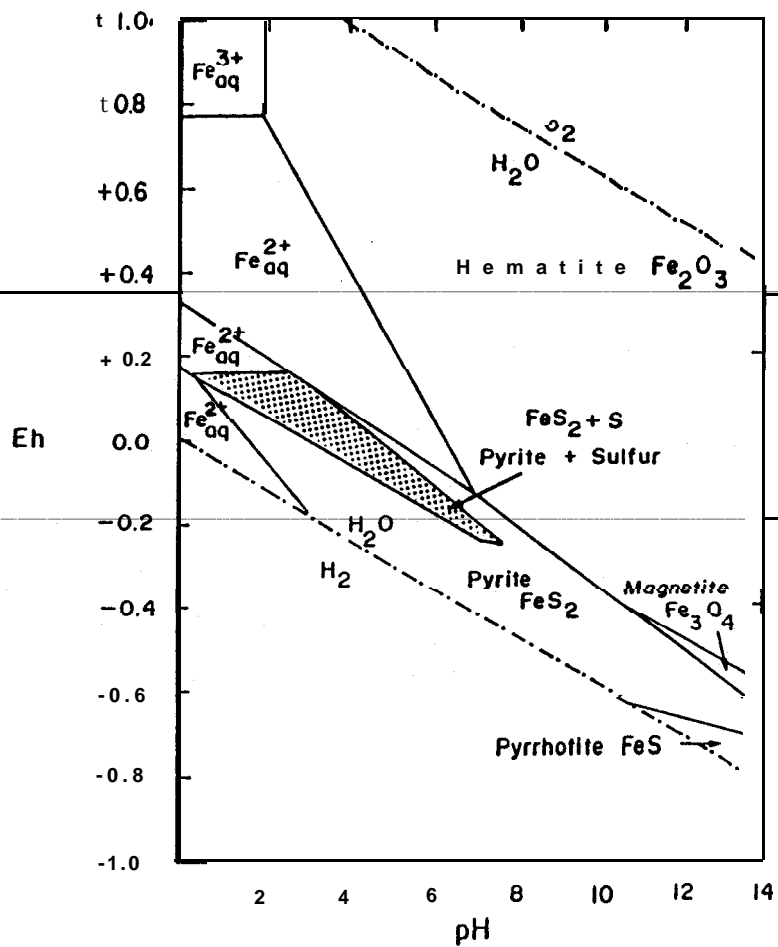


Figure 2-1 Pourbaix d&gram for the Fe-S-H₂O system at 298°K and 1 atm total pressure. Total dissolved sulfur species = 10⁻¹ M. (After Garrels and Christ, 1965.)

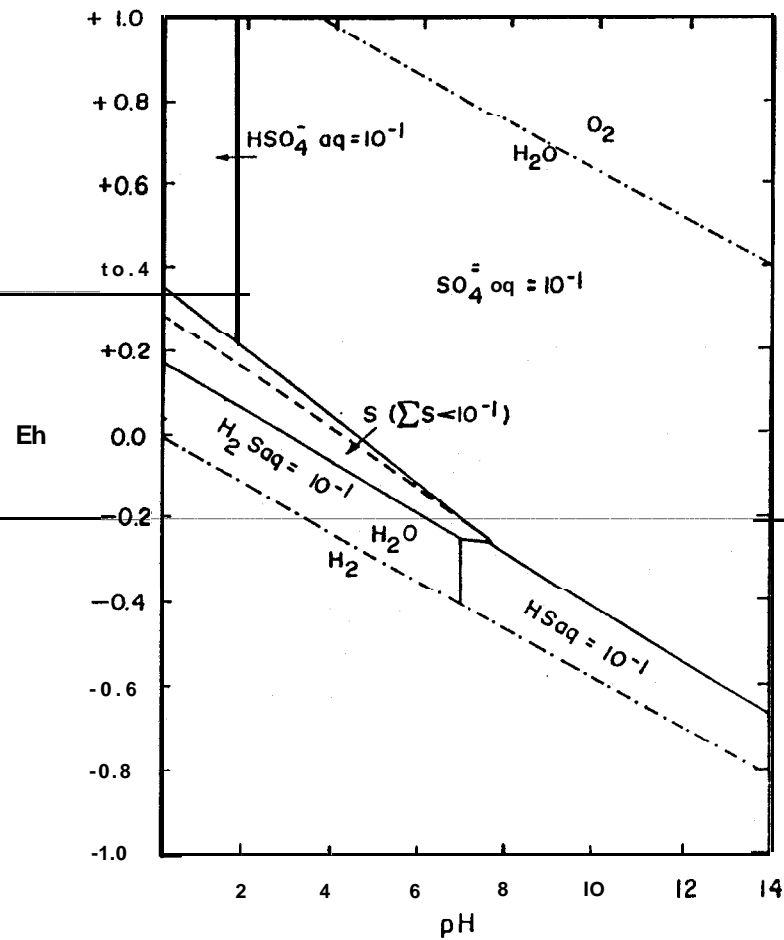
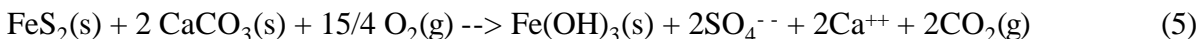


Figure 2-2 Pourbah diagram for the S-H₂O system at 298°K and 1 atm total pressure. Total dissolved sulfur species = 10⁻¹ M. (After Garrels and Christ, 1965.)

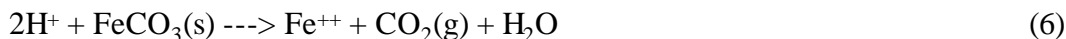
relatively massive sulphide deposits. In any case transportation of oxidant rather than electron-transfer reactions generally controls the rate of acid generation as explained further in Section 2.2.

Acid-consuming reactions can involve direct reaction of acid with carbonate minerals such as calcite or dolomite, i.e.:



or reaction of acid with dissolved carbonate-bicarbonate species in the percolation or flushing of surrounding waters. Factors affecting carbonate solubility include pH, partial pressure of CO_2 , the surface area of the exposed carbonate mineral and the nature of the carbonate mineral. Equation (5) predicts that 3.12 grams of calcite would neutralize the acid generated from the oxidation of 1 gram of pyrite. By analogy 2.87 grams of dolomite ($\text{Ca Mg}(\text{CO}_3)_2$) would neutralize the acid from 1 gram of pyrite. Note that according to equation (5), two moles of dissolved SO_4^{2-} might persist indicating that acid has been produced by the oxidation of pyrite. If calcite is present in the rocks, the SO_4^{2-} concentration might be limited to ~ 400 ppm since above this concentration gypsum would be precipitated.

There is evidence that some carbonate minerals, such as siderite, FeCO_3 , would have little or no neutralizing action on acidic waters:



Subsequent oxidation of Fe^{++} to Fe^{+++} and precipitation of $\text{Fe}(\text{OH})_3(\text{s})$ again releases H^+ ions (see equations (2) and (4)); hence no net H^+ ions would be consumed. Thus, distinguishing the nature of the carbonate mineral present can be important.

Weathering of silicates also consumes acid but such reactions are generally too slow to be considered effective alkalinity producers for the prevention of AMD. Olivine is one exception; neutralization of concentrated acids can take as little as two hours using crushed olivine (Pietersen et al., 1988).

2.2 Rates of Acid and Alkalinity Production

Although the chemistry, biochemistry and electrochemistry of acid generation processes are certainly important, the physics of acid/alkalinity generation processes are usually pre-eminent. The kinetics of acid formation can sometimes be limited by the rate of transportation of oxidant (either O_2 or Fe^{+++}) to the sulphide surface. There is also strong evidence that for above-ground mine wastes, the concentration of acidity is a function of the length of time between periodic flushing of the rock (Caruccio and Geidel, 1984). Figures 2-3 and 2-4 show results of simulated weathering studies on pyrite-containing coal and shale. Figure 2-3 shows that increasing the interval between flushing did not produce a decrease in cumulative acidity; instead the cumulative acidity remained relatively constant. Figure 2-4 shows that reducing the frequency of flushings simply increased the concentration of acidity in each flush. These results indicate that oxidation of the pyrite continued unabated during periods of relative dryness or flushing.

On the other hand, with contained limestone, the higher the frequency of flushing the greater was the cumulative alkalinity produced (see Figure 2-5). Figure 2-6 shows that the concentration of alkalinity produced in these simulated weathering tests was independent of flushing frequency.

This suggests strongly that alkalinity produced by dissolution of CaCO_3 in water rapidly attained an equilibrium governed by solubility considerations. The kinetics of acid and alkalinity production in waste rock above ground and subject to alternate drying and flushing sequences can thus differ dramatically and be highly time dependent.

In contrast to the above, **storage of reactive wastes under water** produces dramatically different reaction conditions. With atmospheric oxygen as the ultimate crucial oxidant in the acid-producing reactions, underwater disposal can drastically curtail reaction rates. Firstly, the concentration of dissolved oxygen in water can attain a maximum of $8.6 \times 10^{-6} \text{ g/cm}^3$ at 1 atmosphere air pressure; far lower than the oxygen concentration in air. Secondly, the diffusion constant for oxygen in water ($\sim 2 \times 10^{-6} \text{ cm}^2/\text{sec}$) is nearly five orders of magnitude less than the diffusion constant for oxygen in air (0.178). Thus less than a metre of relatively stagnant water will reduce the oxidation rate of submerged pyrite effectively to zero. Natural levels of alkalinity in the water body can serve to neutralize a small amount of emergent acidity.

Current theory and limited field data thus support the proposition that storage of fresh but reactive sulphide waste rock or tailings underwater should prevent the generation of acid. Oxygen serves as a critical reactant for the electrochemical oxidation of S^{2-} to S^{+6} (in SO_4^{2-}) and for maintaining an aerobic bacterial colony to catalyze oxidation of Fe^{++}

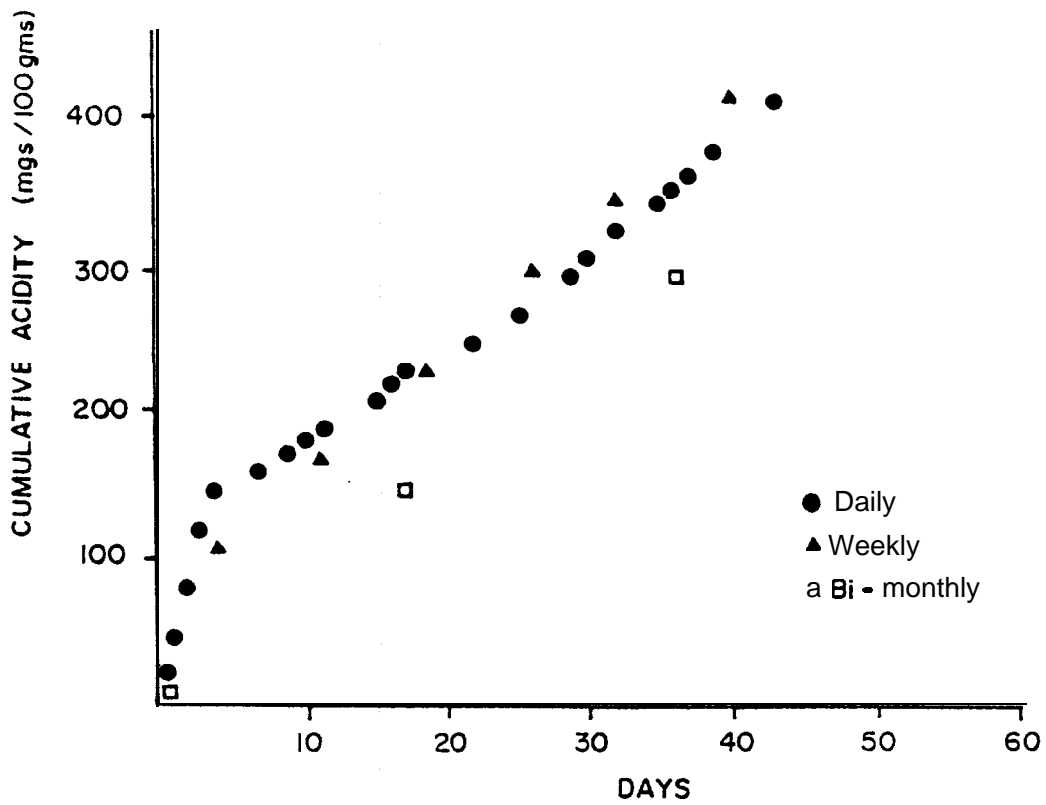


Figure 2-3 The cumulative acidity for an acid producing coal sample for various leaching Intervals. After Caruccio, F.T. and Geidel, G. (1984)

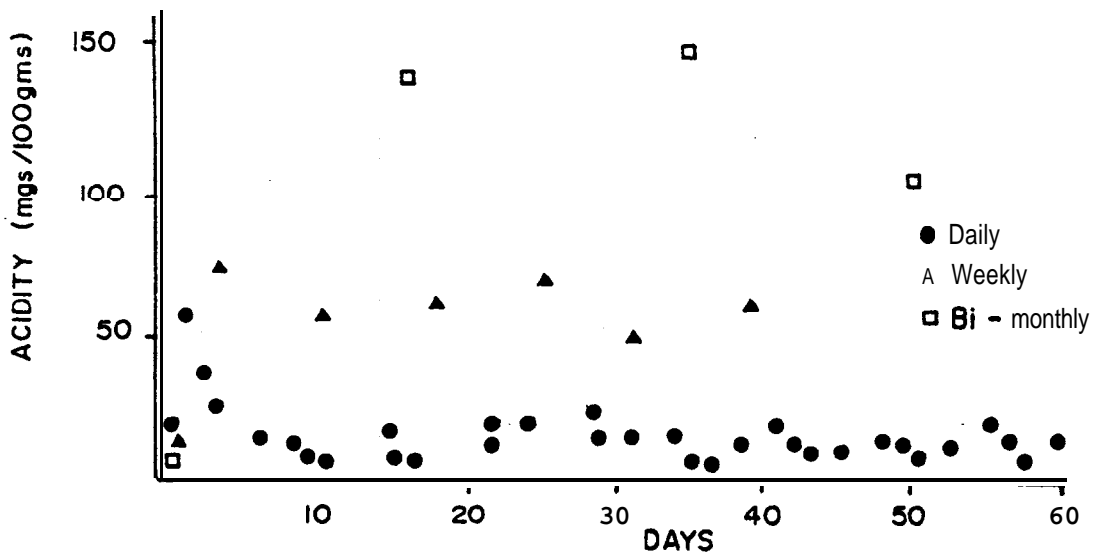


Figure 2-4 The daily acidity values for an acid producing coal sample for various leaching intervals. After Caruccio, F.T. and Geldel, G. (1984)

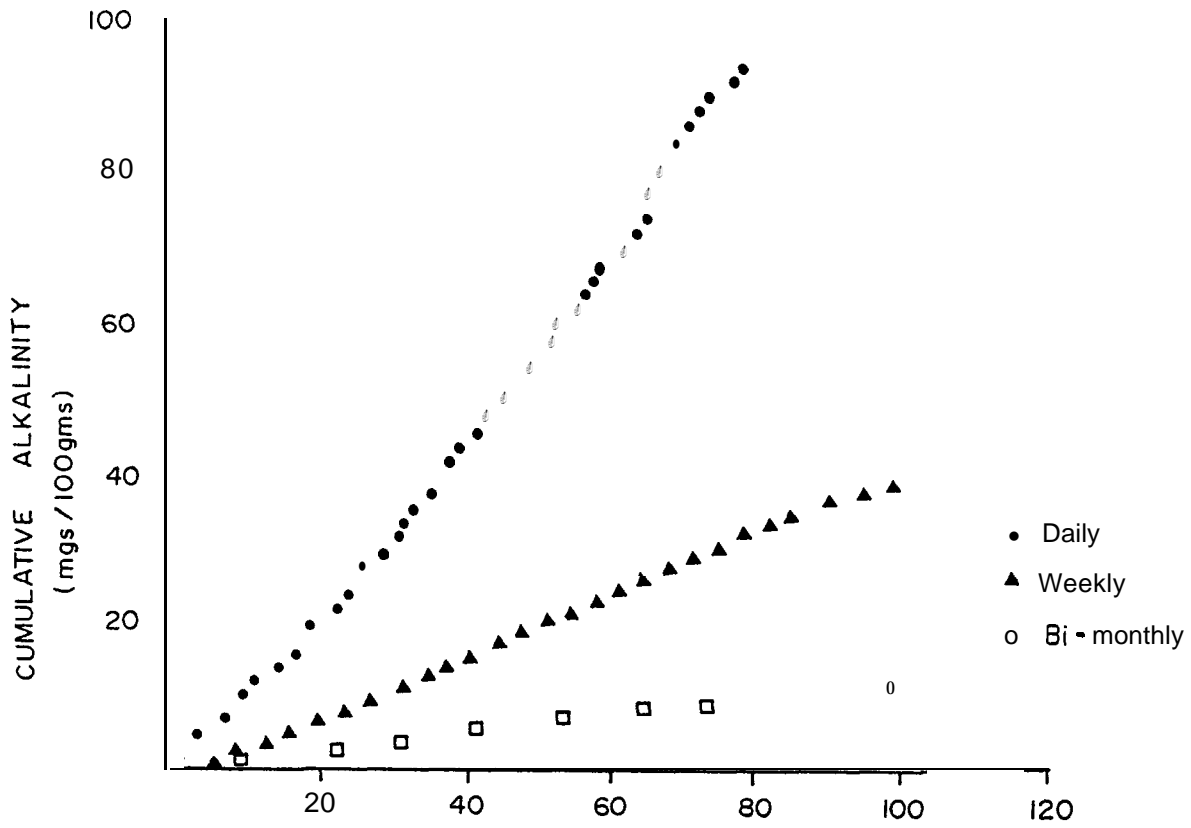


Figure 2-5 The cumulative **alkalinity** for a limestone sample for various leaching intervals. After **Caruccio, F.T.** and **Geldel, G.** (1984)

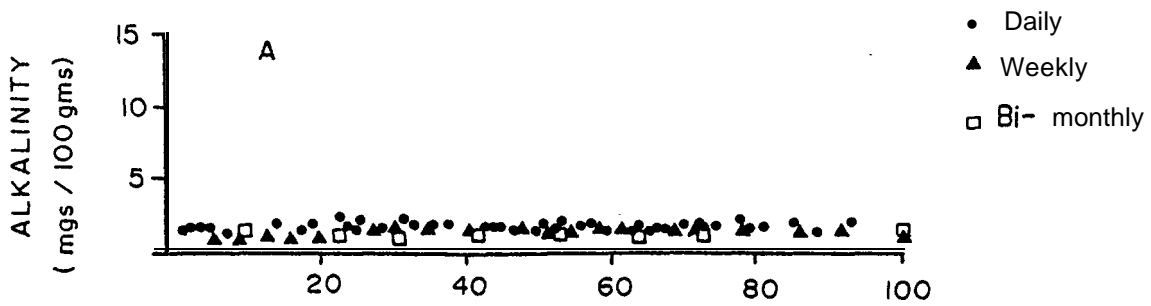


Figure 2-6 The daily **alkalinity** values for a limestone sample for various leaching intervals. After **Caruccio, F.T.** and **Geldel, G.** (1984)

to Fe^{+++} . This does not, however, suggest that all sulphide wastes can be safely stored underwater. Should the sulphides be heavily pre-oxidized, then their oxidation products might be rapidly hydrolyzed to form acids if disposed of underwater. Once the soluble oxidation products have been dissolved (and hopefully neutralized) oxidative leaching of residual sulphide should be curtailed as would fresh sulphides.

2.3 Acid Mine Drainage - Prediction

Predicting the quality of ground water draining from a mine waste dump or derived from the supernatant water above a mine waste sediment depends critically on an assessment of the potential of the waste to produce acidity versus the potential to produce alkalinity. If a macro environment is closed or isolated, analyses of total acid production potential versus total alkalinity potential of a waste material should indicate whether the system will remain neutral or become acidic over a geologically long period of time. So called static methods of acid/base accounting might then have merit at least as screening tests to determine whether more expensive kinetic tests are warranted.

In most disposal systems water and dissolved gases will percolate or flow in and out of the micro-environments generating acidity and/or alkalinity. The rates at which sulphides produce acidity and calcareous components produce alkalinity are not equal. Thus the kinetics of acid/alkaline release become important. Several predictive kinetic tests have been developed to attempt to accelerate weathering reactions and enable direct determination of aqueous effluent or supernatant qualities.

2.3.1 Static - Whole Rock Acid/Base Accounting

Simplicity, rapidity and low cost makes static-whole rock determinations of acid production potential versus alkaline production potential popular predictive methods. There are several published procedures for determining these characteristics of waste materials:

2.3.1.1 B.C. Research Initial Test

This test uses direct sulphuric acid titration of -400 mesh ground material to an end point of $\text{pH} = 3.5$ and room temperature to determine the acid consumption for neutralization potential. Acid production potential is calculated by analyzing the sample for total sulphur content and assuming that all of this would eventually be converted to S^{+6} in H_2SO_4 . Both acid production potential (AP) and acid consumption or neutralization potential (NP) are expressed as equivalents of kg CaCO_3 per tonne of sample. If $\text{AP} > \text{NP}$ then the waste rock or tailing is said possibly to generate AMD (Duncan and Bruynesteyn, 1979).

In some samples, use of total sulphur rather than only sulphide sulphur analyses can dramatically overestimate acid production potential. Thus the estimate can be very conservative.

2.3.1.2 Acid/Base Accounting

This test is somewhat similar to the above procedure but uses a hot excess HCl reaction followed by NaOH titration of excess HCl to an end point of $\text{pH} 7.0$ to determine "neutralization potential" (NP). AP is determined as above by total sulphur analyses. If $\text{NP} - \text{AP}$ is less than $-5 \text{ kg CaCO}_3/\text{tonne}$ then the waste is considered potentially acid producing (Sobek et al., 1978).

This procedure can overestimate AP for the same reasons as above. The hot acid titration can also overestimate NP by virtue of measuring and equating non-neutralizing carbonates such as siderite with effective alkaline producers such as limestone or dolomite.

2.3.1.3 Alkaline Production Potential: Sulphur Ratio

Alkaline production potential (APP) is determined by measuring the HCl consumed in two hours of room temperature reaction (with ~23 µm sample) after titrating excess acid added with NaOH to an end point of pH 5.0. APP is calculated as mgs CaCO₃ per 500 g sample. AP is determined again by total sulphur analyses and expressed as a percent. Wastes of low APP:S ratio are suspected of being producers of AMD (Caruccio et al., 1981).

Comparisons of the APP:S ratio with kinetic weathering charts are claimed to qualify these ratios as having a predictive capacity. Without such comparisons, the results are suspect.

2.3.1.4 Net Acid Production Test

This method, developed at Coastech Research, uses hydrogen peroxide addition to oxidize sulphides in one hour. Acids generated by this oxidation are either consumed by alkaline constituents or excess acid is titrated to pH 7 using NaOH. Excess Net AP is then expressed as kg CaCO₃ equivalent per tonne. A positive Net AP is believed to indicate the potential for AMD (Albright, 1987; Lutwick, 1987).

The test accuracy for tailings and waste rock has been confirmed by field comparison.

2.3.1.5 Other Static Tests

A so-called Hydrogen Peroxide Test (Finkelman and Giffin, 1986) uses hydrogen peroxide oxidation to determine the amount of pyrite or reactive sulphide in a sample. The rate of change of pH is compared to a standard curve developed using pyrite-seeded standards.

Preliminary results appear to be too inaccurate to be of real use.

A Manometric Carbonate Pressure Analysis (Evanglon et al., 1985) is used to characterize the nature of alkaline-producing carbonate in a sample. Carbonate contents can be characterized as calcite, dolomite or siderite to assist in evaluating the effectiveness of alkalinity production in a sample.

Results to date are inconclusive in establishing the reliability of this technique.

2.3.2 Kinetic - Accelerated Weathering Tests

Leaching and simulated weathering tests are used to develop kinetic data aimed at characterizing drainage from waste rock or tailing disposal schemes. There are at least six different published kinetic tests.

2.3.2.1 B.C. Research Confirmation Test

This is a biologically-inoculated oxidation test designed to determine whether sulphide oxidizing bacteria can generate more acid than can be consumed by an equal quantity of the sample. The pulp is first acidified to pH 2.0-2.4 and then inoculated with *Thiobacillus ferrooxidans* culture adapted to grow on pyritic ore. Oxidation initially proceeds until a stable pH is reached, then an equivalent weight to the original sample is added in two increments after 24 and 48 hours. If the pH is less than 3.5, 24 hours after each addition, the sample is considered to be an acid producer (Duncan and Bruynesteyn, 1979).

This test has correctly predicted many field results. The initial acidification of the sample is believed, however, to make some results unrealistic.

2.3.2.2 Humidity Cell Test

The humidity cell models the processes of geochemical weathering wherein a bed of crushed rock or tailing sample is subjected to three days of dry air, then three days of moist air then one day of leaching in water. Leachates are analyzed for a range of parameters such as pH, redox,

acidity, alkalinity, sulphate, conductivity and dissolved metals. This test generally takes 8-10 weeks to complete (Sobek et al., 1978).

The humidity cell has correctly predicted field results on tailings and on waste rock samples. The test seems well suited to waste rock dumps alternately subjected to infiltration, drying and flushing sequences. Improvements to the original Sobek type humidity cell are currently being evaluated.

2.3.2.3 *Shake Flask Tests*

Tailings or waste rock are ground to $-50\ \mu\text{m}$, washed with sulphuric acid to remove residual alkalinity, and then subjected to leaching in an inoculated, incubated shake flask test extending up to three months. The objective is to determine the rate of pyritic sulphur oxidation by measuring sulphate production in the leachate versus time. In the original procedure employed by Halbert et al. (1983) a triple factor x two level factorial design procedure was used to determine the effect of temperature, initial pH and pyrite oxidizing bacteria on sulphate generation. In addition to pH and sulphate analyses, dissolved metals were also determined on the leachates produced. Low initial pH (pH = 3.0) and higher incubation temperatures (21°C) resulted in accelerated sulphate generation rates.

The shake flask tests have correctly predicted field behaviour of tailing samples, but have not been entirely successful in predicting field behaviour of waste rock.

Based on the constant leaching action of the shake flask test it should not perhaps be surprising that this test seems accurate in predicting the field behaviour of tailings, which are often saturated or of low oxygen permeability. The test does not appear to perform well for waste rock dumps which would be subjected to alternate infiltration, wetting and drying followed by flushing events.

2.3.2.4 *Soxhlet Extraction Tests*

A special Soxhlet extraction apparatus is used to simulate an accelerated geochemical weathering using either acetic acid or distilled water as extractant. The Singleton-Lavkulich procedure uses an extraction temperature of 68°C and both acetic acid and distilled water, while the modified Sullivan-Sobek procedure uses 27°C and only distilled water (Singleton and Lavkulich, 1978; Sullivan and Sobek, 1982).

Soxhlet extractions using water have correctly identified acid generating behaviours in tailings samples and in waste rock samples. The acetic acid extraction procedure appears to be unrealistic in evaluating AMD behaviours.

2.3.2.5 *Columns/Lysimeters*

Column/lysimeter studies have been conducted by CANMET (Ritcey and Silver, 1982). In this testwork, samples were placed in columns or boxes and periodically leached with water. A simulated rain cycle plus timed intervals of light and darkness were used to accelerate weathering times ~ nine-fold. Such tests sometimes last two to three months.

Preliminary results from the CANMET lysimeter tests appear to parallel field experience closely. Fifty kilogram samples were used, and the tests simulated eight years of natural leaching.

2.4 Summary

In the absence of oxygen, the bacterially-mediated acid-generating oxidation of sulphide minerals is strongly inhibited. Under conditions of low turbulence, a relatively thin layer of water appears to be sufficient to lower the oxidation rate of submerged pyrite substantially. Diagenetic factors which can promote or inhibit oxidation in sediments are discussed in the following chapter.

Although many different methods exist to predict acid mine drainage, only a few seem to be accurate for a broad range of tailings and waste rock from metalliferous mines in Canada. Due to their low cost, simplicity and rapid results, static, whole rock acid/base accounting procedures will probably persist for preliminary screening purposes. The available evidence indicates that acid production potentials should be based on sulphide sulphur analyses rather than total sulphur. There is also evidence to suggest that cold acid titrations are preferable, as they exclude carbonates such as siderite (FeCO_3).

Certain kinetic tests, although time consuming and expensive, do appear capable of accurately predicting AMD. Alternating wetting, drying and flushing cycles, such as humidity cells or lysimeters appear to be the preferable method for evaluation of AMD potential in unsaturated waste rock stored on land. Shake flask tests appear more suited for evaluating the acid-generating potential of tailings or waste rock stored under water.

Chapter 3

Natural lacustrine sediments characteristically exhibit a chemical zonation with depth which reflects the integrated influence of physical, microbiological and inorganic chemical phenomena. Factors as diverse as the reactivity and rate of accumulation of organic matter, the concentration of oxygen in bottom water, input to the sediments of detrital oxyhydroxide phases, and the presence or absence of benthic fauna all play major roles in governing the distribution of a number of dissolved constituents in interstitial water and the distribution of specific authigenic phases at various sub-bottom depths. All these factors will, to varying extents, also affect the diagenetic behaviour of submerged mine tailings. In the following section, therefore, such diagenetic elements will be described individually as they pertain to natural sediments, and their collective theoretical influence on the reactivity of submerged sulphide-bearing materials will be discussed.

3.1 Biogeochemical Zonation - Theory

Bacterial oxidation of reactive organic matter in lacustrine sediments proceeds via a series of overlapping, enzyme-mediated electron-transfer reactions in which the thermodynamically-unstable reduced carbon compounds serve as electron donors and various oxidants act as terminal electron acceptors as degradation proceeds. Heterotrophs act simply as catalysts during such degradation; they are unable to carry out reactions which are not thermodynamically possible (Fenchel and Blackburn, 1979).

During oxidation, organic matter will donate electrons to orbitals of lowest available energy level, as this produces the greatest free energy gain per unit of organic material oxidized. The reaction sequence (Table 3-1) thus proceeds in an order which is determined by net free energy yield, with aerobic oxidation, the highest-yield reaction, preceding (in thermodynamic order) denitrification, manganese and iron oxyhydroxide reduction, sulphate reduction, and methanogenesis (CO₂ reduction) (Froelich et al., 1979).

In sedimentary systems which are receiving a constant input of reactive (i.e. degradable) organic detritus, a steady-state zonation will be established with depth if the bacterial demand for oxidants exceeds the rate of supply by diffusion or advection. In such cases,

Oxidation Reactions of Sedimentary Organic Matter

1. Aerobic oxidation:	$G^\circ = -475$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 138 \text{ O}_2 = 106 \text{ CO}_2 + 16 \text{ HNO}_3 + \text{H}_3\text{PO}_4 + 122 \text{ H}_2\text{O}$		
2. Nitrate reduction (denitrification):	$G^\circ = -448$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 84.8 \text{ HNO}_3 = 106 \text{ CO}_2 + 42.4 \text{ N}_2 + 16 \text{ NH}_3 + \text{H}_3\text{PO}_4$ + 148.4 H_2O		
3. Manganese oxide reduction:	$G^\circ = -349$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 236 \text{ MnO}_2 + 472 \text{ H}^+ = 236 \text{ Mn}^{2+} + 106 \text{ CO}_2 + 8 \text{ N}_2$ + H_3PO_4 + 366 H_2O		
4. Iron oxyhydroxide reduction:	$G^\circ = -114$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 424 \text{ FeOOH} + 848 \text{ H}^+ = 424 \text{ Fe}^{2+} + 106 \text{ CO}_2 + 16 \text{ NH}_3$ + H_3PO_4 + 742 H_2O		
5. Sulphate reduction:	$G^\circ = -77$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) + 53 \text{ SO}_4^{2-} = 106 \text{ CO}_2 + 16 \text{ NH}_3 + 53 \text{ S}^{2-} + \text{H}_3\text{PO}_4 + 106 \text{ H}_2\text{O}$		
6. Methanogenesis (fermentation):	$G^\circ = -70$	kJ/mol
$(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4) = 53 \text{ CO}_2 + 53 \text{ CH}_4 + 16 \text{ NH}_3 + \text{H}_3\text{PO}_4$		

Listed in order of the free energy yields shown, compiled from Froelich et al. (1979), Bender and Heggie (1984) and Kadko et al. (1987). The free energy yields are presented as kJ per mole of CH_2O oxidized, and the organic matter stoichiometry chosen is equivalent to the Redfield ratio for marine plankton (Redfield, 1958).

O₂ will be depleted at some depth below the sediment-water interface. As the oxygen concentration decreases to low (but not yet zero) levels, nitrate reduction will commence. The other oxidants listed in Table 3-1 will subsequently be reduced in the order shown should there continue to be a deficiency of oxidant supply relative to demand.

In sediments in mesotrophic or eutrophic lakes, the organic carbon content is usually sufficient to establish anoxic conditions at depths ranging from a few millimetres to one decimetre. The resulting chemical zonation is therefore characterized by a steadily decreasing redox potential with depth, and the release to interstitial solution (pore water) of a number of reaction products (Table 3-1, Figure 3-1). Because the depth to the oxic-anoxic boundary is determined by relative rates of supply and consumption of oxidants, the zonation shown in Figure 3-1 can be thought of as a "biogeochemical rubber band" which is stretched when oxidant demand decreases relative to supply, and compressed when the opposite conditions occur. Thus, in the absence of secondary dissolution/ precipitation reactions, and because the oxidant reaction sequence is based on thermodynamics, the relative distribution of dissolved species in pore water is constant from site to site; only the depth scale changes based on the intensity of diagenesis (Bender and Heggie, 1984). Note that the zones defined in Figure 3-1 overlap in all cases to some extent. In theory, thermodynamic considerations prohibit such overlaps but they occur for two main reasons in the natural environment. First, kinetic effects (such as rates of abiologic oxidation of diffusing reduced species) tend to smear the thermodynamic boundaries, and second, organic matter is in general not distributed homogeneously in sediments, which can give rise, for example, to reducing microenvironments in the aerobic oxidation zone.

Aerobic oxidation involves a single enzyme-mediated transfer of four electrons as O₂ is reduced directly to water; thus oxygen is considered to be a strong oxidant in aqueous systems (Stumm and Morgan, 1981). It is typical of aerobes that they carry out, within each cell, a complete oxidation to CO₂ of the organic compounds that they assimilate (Jorgensen, 1983). Due to their oxygen consumption, the oxic zone constitutes only a rather thin layer in most cases. In terms of the amount of carbon oxidized, however, oxygen is the principal oxidant in most lacustrine sediments (Fenchel and Blackburn, 1979). Oxygen is consumed not only by the mineralization of organic matter but also by the oxidation of Fe²⁺, Mn²⁺ and other reduced substances, including sulphide species and methane, which diffuse up into the oxic zone (Gobeil et al., 1987).

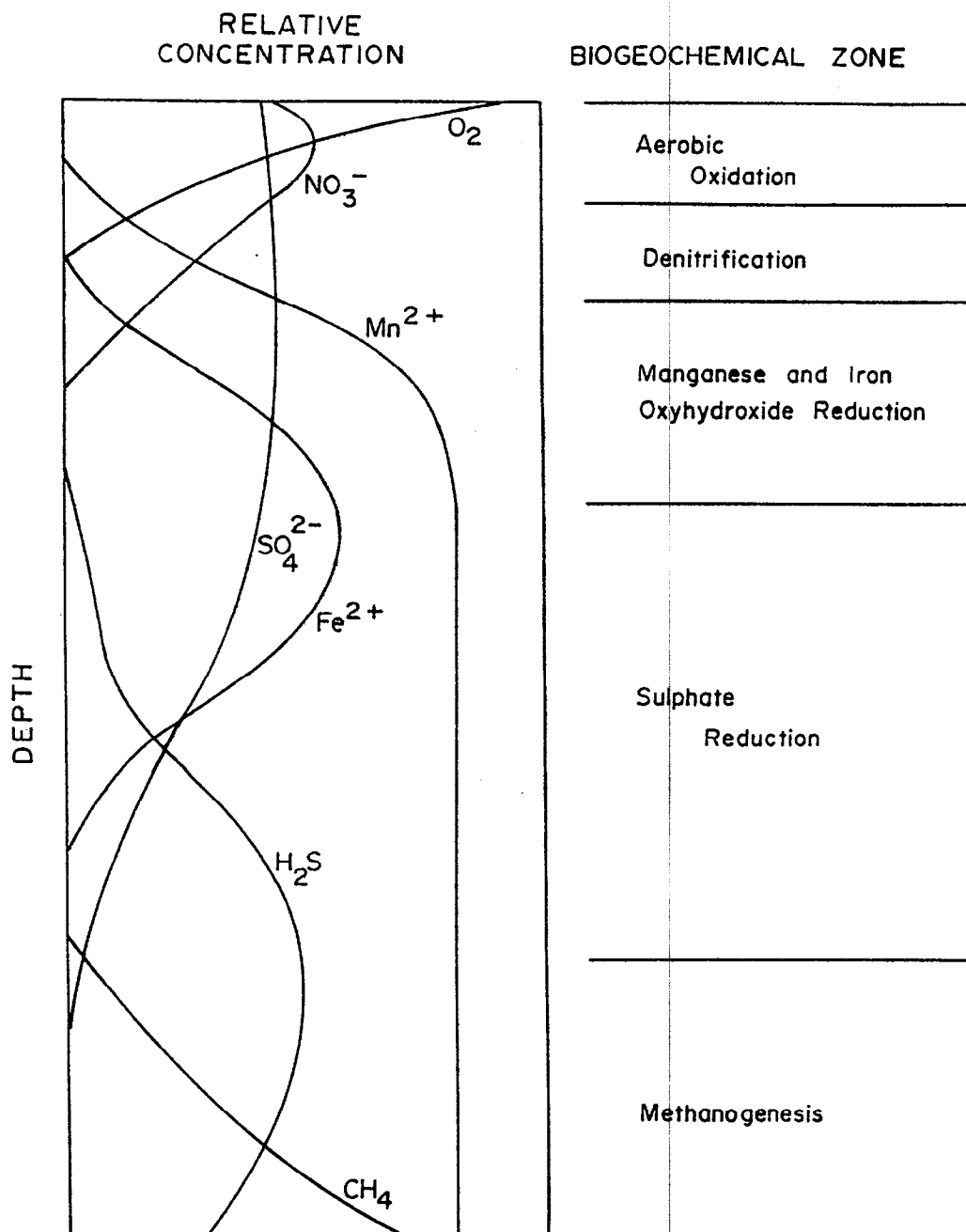


Figure 3-1 Schematic distribution of biogeochemically important species in interstitial waters in sediments showing the zonation typically observed in marine and lacustrine sediments. This distribution will stretch or compress in response to changing physical, chemical and biological conditions as discussed in the text.

Nitrate and the intermediate species nitrite, thermodynamically the first of the secondary oxidants, are produced during nitrification in the aerobic zone and consumed by denitrification as O_2 becomes essentially depleted (Smith et al., 1983). The nitrate maximum sometimes observed at shallow depths in sediments reflects oxidation of upward-diffusing NH_4^+ ; first to NO_2^- by *Nitrosomonas* spp. and then to NO_3^- by *Nitrobacter* spp., in addition to the release to solution by aerobes of oxidized organic N. Nitrate (and, for that matter, nitrite) will diffuse downward from the maximum to be reduced by denitrifying bacteria below the oxic zone. Despite the relatively large free energy yield associated with reduction of NO_3^- (Table 3-1), nitrate respiration as a fraction of the total respiration in sediments is quantitatively minor which reflects the low NO_3^- concentration characteristic of bottom and pore waters (Sorensen and Jorgensen, 1987).

The utilization by bacteria of the next-favoured electron acceptors, Mn and Fe oxides, results in the dissolution of the solid phases and the release to pore water of dissolved Mn^{2+} and Fe^{2+} . In practice, manganese oxide reduction commences slightly before complete depletion of NO_3^- , as shown in Figure 3-1. Fe^{2+} typically appears in pore water at a slightly greater depth than manganese, which reflects the different free energy yields (Table 3-1) upon reduction of the oxides and the slower kinetics of oxidation of Mn^{2+} (Jacobs et al., 1985; Pedersen et al., 1986). Because the reduction of MnO_2 commences in practice almost as soon as O_2 has been depleted, the depth at which Mn^{2+} first appears in pore water is a reasonably precise indicator of the sub-bottom oxic-anoxic boundary.

Sulphate-reducing bacteria will consume SO_4^{2-} below the zone of iron oxyhydroxide reduction, yielding H_2S (which occurs mostly as dissolved HS^- at the neutral or slightly acid pH of most lacustrine pore waters). In sulphate-bearing lake waters, such as the saline lakes of the B.C. interior (e.g. Hall and Northcote, 1986), sulphate reduction probably accounts for a considerable portion of the total amount of organic material oxidized in the sediments. In other meromictic lakes, such as those where post-glacial isostatic rebound trapped seawater behind newly-emerged sills (e.g. Powell and Sakinaw lakes in B.C. (see Sanderson et al., 1986), Garrow Lake on Little Cornwallis Island (Ouellet and Page, 1988; Bohn et al., 1981; Kuit and Gowans, 1981; Kuit, 1982) and a number of lakes along the Norwegian coast (Strom, 1957)), the reduction of sulphate at depth in the stratified water columns generates large concentrations of H_2S . Ferric iron (as $FeOOH$, for example) can be reduced by upward-diffusing sulphide species either chemically or via bacterial catalysis. Evolved Fe^{2+} will be rapidly precipitated in the presence of dissolved sulphide as FeS or FeS_2 , as discussed below. Such authigenesis is responsible for the decrease of both sulphide and dissolved iron in the sulphate-reduction zone in the Figure 3-1 schematic.

Reduction of carbon dioxide with concomitant production of methane proceeds once sulphate has been depleted. In marine or sulphate-rich lacustrine sediments, the inventory of SO_4^{2-} relative to the pool of degradable organic matter is large and the sulphate reduction zone often thick. These phenomena, coupled with the fact that sulphate-reducing bacteria are capable of oxidizing most types of organic matter (except the most refractory compounds), usually preclude the onset of methanogenesis in sulphate-replete deposits (Jorgensen, 1982).

However, most fresh waters are relatively depleted in SO_4^{2-} ; a condition which commonly fosters methane production at depth in lacustrine sediments rich in labile organic matter.

Studies of the hydrogen ion activity in anoxic lacustrine pore waters in lakes of normal (i.e. non-alkaline) hardness indicate that the pH falls typically in the relatively neutral range 6.0 to 7.5 (Emerson, 1976; Carignan and Nriagu, 1985), even in cases where the overlying lake water may be acid (pH's as low as 4.5, Carignan and Nriagu, 1985). The near neutrality of the interstitial waters reflects buffering in the anaerobic zone by production of HCO_3^- (alkalinity, via such reactions as sulphate reduction, iron oxyhydroxide reduction, and FeS precipitation, which can be expressed collectively (Carignan and Nriagu, 1985) as $4\text{Fe}(\text{OH})_3(\text{s}) + 4\text{SO}_4^{2-}(\text{aq}) + 9\text{CH}_2\text{O} = 4\text{FeS}(\text{s}) + \text{CO}_2 + 8\text{HCO}_3^- + 11 \text{H}_2\text{O}$), and NH_4^+ (via hydrolysis of ammonia, NH_3). Stumm and Morgan (1981) and Morel (1983) note that other reactions, such as the weathering of silicates, as well as the ion exchange of H^+ for other adsorbed cations, may contribute to the buffering capacity of pore waters. Aerobic diagenesis in the oxic zone can sustain lower pH levels as a consequence of CO_2 production, but because this stratum is usually thin in most lake sediments, the mean pH in lacustrine pore waters can be considered to be more neutral.

3.2 Factors Affecting the Biogeochemical Rubber Band

The intensity of sedimentary diagenesis is a function of two key variables, the availability of oxidants, which is controlled both by physical and chemical factors, and the demand for oxidants that accrues from the presence of labile organic substrate, which in turn is controlled by the relative input of inorganic and organic phases and the composition or "quality" of the organic compounds.

The depth to the oxic-anoxic interface in lacustrine deposits is controlled in part by the rate at which oxygen can diffuse into the sediments (see Section 3.4.3) to replace that consumed by bacteria and by oxidation of upward-diffusing reduced species. An increase in the O_2 concentration in bottom water which will enhance the downward diffusive flux of oxygen, will promulgate a deepening of the sedimentary redoxcline, all other factors being equal.

The depth to the redoxcline also reflects the content of labile organic matter, which in turn is controlled by the relative input fluxes of particulate organic and lithogenic materials. The flux of inorganic detritus plays two opposing roles in this regard. First, such material acts as a diluent, reducing the percentage of organic carbon in the sediments, thereby reducing the bacterial oxygen demand per unit volume. Second, a large input flux increases the linear sedimentation or burial rate of the organic fraction, which more quickly removes a specific horizon from diffusive communication with the overlying water, the source of most of the oxidant pool. It should be noted that the concentration of dissolved oxygen in natural waters is low, rarely exceeding $400 \mu\text{mol L}^{-1}$. Therefore, in rapidly-accumulating deposits, the small quantity of oxygen in the interstitial water (which is also being quickly buried) is rapidly exhausted. Because the consumed oxygen cannot be replaced by diffusion acting over a steadily increasing distance, a high sedimentation rate promotes the establishment of anoxic conditions at a relatively shallow depth.

The composition of sedimentary organic matter provides another major influence on the rate of oxidant consumption during diagenesis. Detritus from vascular plants, particularly cellulose

(polysaccharides) and lignins (phenolic polymers), is particularly resistant to bacterial degradation because of the high degree of crosslinking between structural units (Emerson and Hedges, 1988). A low oxidant demand is associated with the deposition of such materials. In contrast, carbohydrates and nitrogenous materials derived from relatively protein-rich detritus such as planktonic matter are much more readily degraded by microbes. Thus, input of algal remains to sediments will foster a higher oxidant demand and shallower oxic-anoxic boundary than settled or buried woody debris. It follows that highly productive rather than oligotrophic lakes will tend to be floored by sediments which are anoxic at shallow depths, even given a higher input of relatively refractory vascular plant debris to the latter.

Bioturbation, the mixing of sediments by burrowing animals, can increase significantly the depth of penetration of oxygen, both by advection as animals circulate bottom water through their burrows, and by facilitating diffusion throughout the mixed zone and particularly at its base. Three principal factors determine the extent of burrowing activity: the organic matter content (i.e. the amount of food for the burrowers), the oxygen content in bottom water, and the depth at which H_2S accumulates in pore water. As discussed earlier, these three variables are closely related, and must be considered in concert rather than in isolation. H_2S is toxic to animals and its presence limits their activity. Thus, an ecological conflict exists: H_2S , which is deleterious to bioturbators, is generated at relatively shallow depths in organic-rich sediments, but the high organic content of the same deposits tends to support an active infaunal community.

Bioturbation is being recognized increasingly as a very important influence on fluxes across the sediment-water interface in both marine and lacustrine environments (e.g. Kadko and Heath, 1984). In the absence of microstructure, and under steady-state conditions, the cycling of redox-sensitive elements can be greatly enhanced by bioturbation (Westerlund et al., 1986), although fluxes due to molecular diffusion are the most important transport mechanism in the upper few centimetres in cases where concentration gradients are steep. Advection associated with bioturbation is more important as a transport mechanism for sediments below this zone (Emerson et al., 1984).

Bioturbation can alter concentration gradients in pore waters by increasing the effective surface area of sediment particles exposed to adsorption-desorption and precipitation-dissolution reactions (Kadko et al., 1987). Bioturbators which probe the upper reaches of the suboxic or anoxic zones in sediments can promote the oxidation of authigenic sulphides, which fosters release of metals to interstitial solution, in effect creating a new dissolved metal source at depth (Emerson et al., 1984).

Assessment of diagenesis in bioturbated sediments is further complicated by:

- differing reaction rates around burrows resulting from concentration gradients induced by adding a third dimension to diffusion;
- temporal variability in burrow location;
- burrow size variations; and
- physical discontinuities associated with burrow structures (Aller, 1983).

In summary, the presence of an active infauna in sediments tends to thicken the aerobic zone and promote enhanced fluxes of some dissolved constituents in both directions across the sediment-water interface.

It has been demonstrated in a number of studies that rates of diagenesis and consequent stretching or compression of the biogeochemical rubber band vary seasonally in lacustrine and marine sediments in temperate and northern latitudes (see, for example, Jorgensen, 1977; Holdren and Armstrong, 1980; Sholkovitz and Copland, 1982; and Klump and Martens,

1981). A number of factors control such variations. First, dissolved oxygen contents in bottom water reflect the influence of stratification, which has a strong seasonal character in most lakes. Second, primary productivity varies seasonally, typically being highest during the well-illuminated spring and summer months; the settling flux of organic matter directly and almost immediately reflects such variability. Third, seasonal warming of sediments and overlying water promotes increased rates of bacterial metabolism, which amplify the benthic oxidant demand. The net effect of these influences is to compress the biogeochemical zonation (i.e. intensify diagenesis) during the late spring/summer period. Associated steepening of concentration gradients promotes larger benthic fluxes of most constituents involved in near-surface diagenetic reactions.

3.3 Diagenetic Consequences

3.3.1 Role of Oxyhydroxide Phases

Poorly ordered, often amorphous, iron and manganese oxides and hydroxides are ubiquitous constituents in lacustrine sediments, frequently occurring in concentrations ranging from about 1 to >10 wt. % (e.g. Hamilton-Taylor, 1979; Farmer et al., 1980; Carignan and Nriagu, 1985; Cornwell, 1986). These phases are important diagenetically because of their participation in redox reactions as discussed above, and because their surfaces provide sites for the removal of trace metals from natural waters. Kadko et al. (1987) note that sedimentary iron and manganese oxides are quantitatively very important scavengers of trace metals because of their high specific surface areas, high negative surface charge, and high cation adsorption capacity over the pH range of most natural waters. A number of studies have addressed the specific adsorption of trace metals on Mn and Fe oxyhydroxides (e.g. Balistrieri and Murray, 1982, 1984, 1986), and it is clear from this work that the distributions in sediments of a range of trace metals including Cu, Ni, Zn, Cd, Pb and Mo are strongly influenced by the behaviour of the oxide phases. In many cases, sedimentary concentration profiles of trace metals which decrease with depth parallel those of the major oxides (e.g. Cornwell, 1986). Such distributions do not necessarily reflect recent anthropogenic influences but may instead be a reflection of a natural diagenetically-produced oxide-trace metal association.

Iron and manganese oxides are characteristically recycled during early diagenesis in sediments (see for example Pedersen et al., 1986, and Carignan and Nriagu, 1985). Reductive dissolution below the aerobic zone releases Mn^{2+} and Fe^{2+} to pore water, which supports an upward diffusive flux of both ions. Oxides reprecipitate when the dissolved species encounter O_2 in the aerobic zone, producing a stratum relatively enriched in manganese and iron. Under steady-state conditions, this layer is subsequently buried and the cycle is repeated. This recycling procedure usually maintains solid-phase Mn and Fe enrichments near the sediment-water interface (Figure 3-2). The thickness of this oxide-rich zone is, to a first approximation, inversely proportional to the intensity of diagenesis in a given sediment column, and can therefore be used as a rough indicator of the comparable diagenetic status of sediments from different locations.

3.3.2 Authigenic Sulphides

Under anoxic conditions, hydrous oxides and oxyhydroxides are replaced by sulphides as the dominant solid authigenic phases (see Section 3.4.1). The log solubility product (i.e. pK_{sp}) ranges from about 25 (ZnS) to about 53 (HgS), which implies that a large proportion of trace metals dissolved in anoxic, sulphide-bearing pore waters should precipitate and be fixed in the sediments as solid sulphide phases (Framson and Leckie, 1978).

Dissolved iron precipitates readily as metastable FeS in the presence of H₂S. This monosulphide phase is common in sediments, and because it is known to form solid solutions (Framson and Leckie, 1978), it is suspected that other metals are coprecipitated by FeS (Gobeil et al., 1987). The solid phase activity of a trace metal in

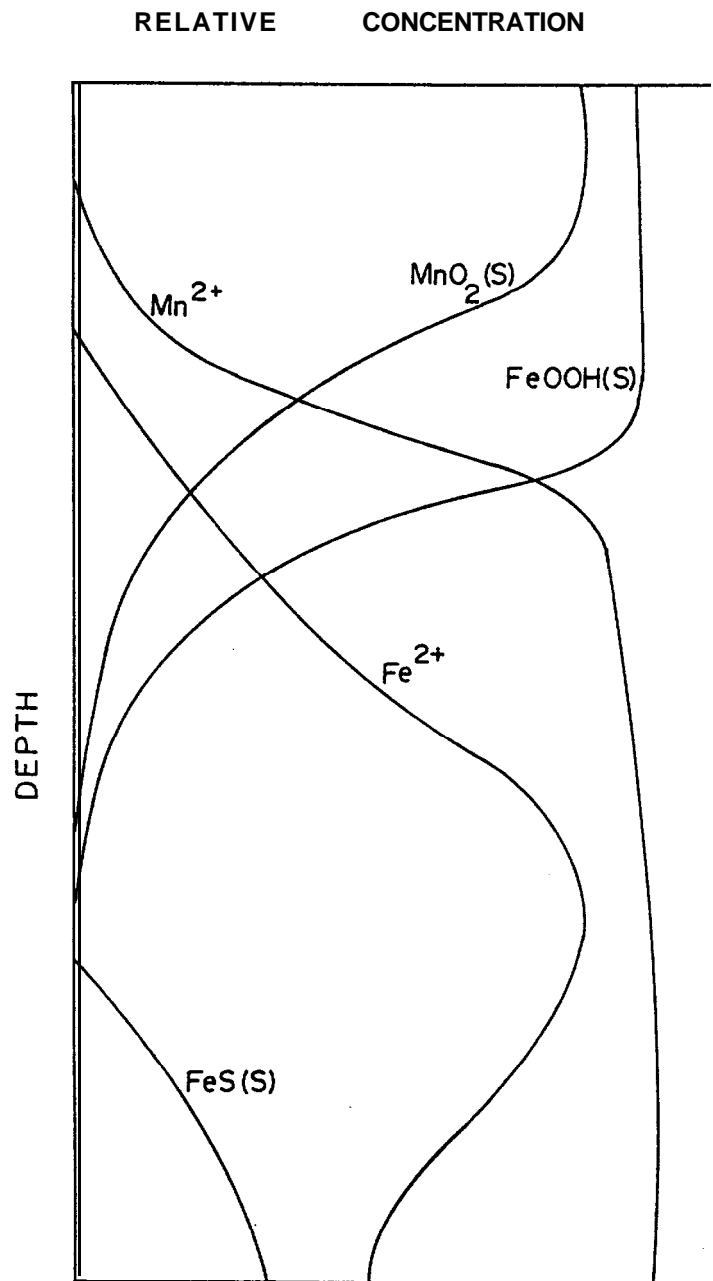
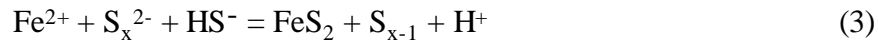
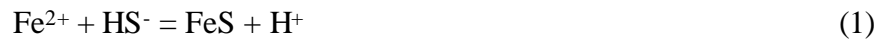


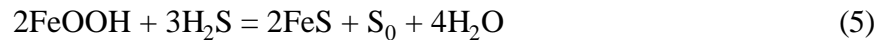
Figure 3-2 Schematic distribution with depth of manganese and iron species in interstitial water and solid sediments. Steady state is assumed. The near-surface oxyhydroxide enrichments reflect input of detrital oxides to the sediment surface, continuous dissolution at depth, upward diffusion of dissolved species and reprecipitation in the aerobic zone.

a solid solution is a function of both its solid phase activity coefficient and its mole fraction (Jacobs and Emerson, 1982), and is usually <1. This decreased solid-phase activity is especially important in governing the solubility of the minor component of the solid solution. Stumm and Morgan (1981) note that the observed occurrence of metals in sediments formed from solutions that appear to be formally unsaturated (ignoring solid solution formation) with respect to the impurity can often be explained by solid solution formation. However, Jacobs et al. (1985) used carefully measured field data as a basis for suggesting that chemical equilibrium with an impure FeS phase is not the major process controlling the dissolved trace metal concentration in sulphidic waters; instead they invoked the formation of pure, specific metal sulphide phases as the probable leading control.

Pyrite forms in anoxic sediments following the reaction of FeS with elemental sulphur (Berner, 1964, and Rickard, 1969; equations (1) and (2)), or of ferrous iron with elemental sulphur or polysulphide ions in the presence of dissolved sulphide species (Rickard, 1975, and Howarth, 1979; equations (3) and (4)), viz:



Davies-Colley et al. (1985) note that free sulphides and polysulphides can react more directly through bacterially catalyzed reactions with Fe and Mn oxides to produce poorly ordered, black, fine-grained monosulphides via



The monosulphide phase may then react with elemental sulphur to form FeS₂ as in (2) above. Hence, sulphides that diffuse into the oxide reduction zone may be oxidized by FeOOH (or MnO₂) to form S⁰ and pyrite. Because of its ability to coprecipitate trace metals, pyrite is thought to be a significant sink for metals in anoxic sediments (Dyrssen, 1985).

3.3.3 Benthic Fluxes

As noted earlier, oxygen is the primary oxidant in lacustrine systems, in part because sulphate occurs only in small concentrations in fresh waters, unlike the case in seawater. Dissolved O₂ in bottom water will diffuse into sediments along the gradient of decreasing concentration established by consumption at or below the sediment-water interface. The quantity of oxygen (or other oxidants) which can diffuse per unit time to a given depth below the interface (J_z, in μmol cm² sec⁻¹) is governed by the steepness of the concentration gradient, dC/dZ (in μmol cm⁻⁴), sediment porosity (ϕ, dimension-less), tortuosity (a measure of the tortuous path length followed by a diffusing molecule, determined by measuring the electrical resistivity of wet sediments and described by a dimensionless variable, F, the formation factor (Manheim, 1970)), and the molecular diffusion coefficient D_{j(T,P)}⁰ which varies as a function of temperature and pressure and is given in units of cm² sec⁻¹. These variables collectively form Fick's First Law of diffusion, viz:

$$J_z = -(D_{j(T,P)}^0/F)\phi(dC/dZ)$$

In practice, estimation of the concentration gradient is complicated by the presence of a thin, essentially stagnant layer immediately above the interface (the diffusive boundary layer) in which eddy diffusivity is zero and solutes move only via molecular diffusion. This zone is typically a fraction of a millimetre to several millimetres thick (Boudreau and Guinasso, 1982). The difficulty inherent in estimating this thickness accurately limits the precision of all flux calculations where concentration gradients are very steep, such as in sediments where anoxic conditions prevail within several millimetres of the interface.

Although oxidants will, in general, diffuse into sediments, other constituents, including aqueous species regenerated from organic nitrogen and phosphorus and dissolved metals, will diffuse upward if concentrations in shallow pore water are higher than in overlying bottom water. Such benthic effluxes are quantitatively important in the cycling of nutrients in many lakes (Holdren and Armstrong, 1980). Dissolved metals appear to diffuse readily into lacustrine sediments where anoxic conditions occur at shallow depths (e.g. Carignan and Nriagu, 1985). This phenomenon can be explained by the precipitation of mineral phases such as ZnS, NiS and CuS within the upper 1-2 cm of the sediments. Such downward fluxes and precipitation reactions are believed to account for a substantial portion (on the order of 50%) of the accumulation of Ni and Cu in the sediments of polluted shield lakes near Sudbury, Ontario (Carignan and Nriagu, 1985) and of Zn in an acid lake in southeastern Quebec (Carignan, 1985). In contrast, dissolved metals concentrations in pore waters immediately below the sediment-water interface of unpolluted coastal marine sediments are typically higher than in the overlying bottom waters. In these cases, the sediments act as a source rather than a sink for metals (e.g. Pedersen, 1985; Westerlund et al., 1986), and reflect the release to solution of organically-bound metals as organic matter near or at the interface is aerobically degraded. Diffusion from a near-surface maximum characteristically occurs in both upward and downward directions; the latter reflecting low dissolved metals concentrations in the sulphidic zone at depth.

Sundby et al. (1986) and Westerlund et al. (1986) carried out a series of experiments on benthic fluxes of metals which illuminate particularly well the role of oxygen in governing diagenetic release near the sediment-water interface. Although the experiments were performed on shallow (6 m), organic-rich, marine sediments, the results are fully applicable to lakes. These authors used stirred benthic chambers in which the pH was kept constant by the addition of NaOH and the oxygen content was either kept constant by the addition of O₂ via a capillary or was allowed to be depleted by benthic respiration. Under oxygenated conditions, which probably extended to only a few millimetres depth, Cd, Cu, Zn and Ni were released to the overlying water while Co, Mn and Fe were taken up. When the O₂ concentration in the water was allowed to fall to zero, dissolved Cd, Cu, Zn and Ni concentrations in the chamber fell significantly, indicating uptake by the sediment, and Co, Mn and Fe were released from the sediment surface. Three main reactions appeared to be responsible for the observed behaviour. First, oxidative degradation of organic matter at the interface releases associated trace metals to solution (probably much of the Cd, Co, Cu, Zn and Ni). Second, in the oxygenated chamber, the high concentrations of Mn²⁺ and Fe²⁺ initially present were oxidized to form particulate oxyhydroxides whose occurrence was apparently restricted to the top millimetre of the sediments. The precipitation behaviour in this experiment of both of these elements but particularly iron is consistent with the rapid kinetics of oxidation at neutral pH (Stumm and Morgan, 1981). Cobalt is readily scavenged from solution by FeOOH, which explains its observed covariance with Fe²⁺. Although the other metals would also be scavenged by the oxyhydroxides, their lack of depletion in the chamber water while oxygen was present probably reflected the dominance of addition from the presumed degrading organic source. Third, the

decrease of the trace metals concentration when oxygen became depleted was ascribed to their precipitation at very shallow depths as discrete sulphide phases. The concurrent release of Mn, Fe and Co was attributed to reductive dissolution of oxyhydroxides as the redox potential in the upper millimetre or so of the sediments fell. These observations conform with the behaviour predicted by the biogeochemical zonation theory discussed earlier, and demonstrate quite clearly that the presence or absence of oxygen is a fundamental determinant of the behaviour and distribution of dissolved metal species in aqueous systems.

3.4 Application to Submerged Sulphide-Bearing Mine Waste Deposits

The theoretical framework of early diagenesis as it pertains to the behaviour of metals in natural sediments, described on the preceding pages, is equally applicable to submerged mine tailings deposits. In this section we consider the role that diagenesis should play in governing the mobility of metals in sulphide-bearing lacustrine tailings and mine wastes.

3.4.1 The Oxidation Problem: Theory

As noted earlier, sulphide minerals are invariably only very sparsely soluble, and under anoxic conditions, they can be considered to be stable phases. In the presence of molecular oxygen, however, this stability is greatly reduced, to the extent that some sulphide minerals (e.g. FeS) are readily chemically (i.e. abiotically) oxidized. Such reactions yield a range of alteration products which are typically amorphous oxyhydroxide phases, carbonates and sulphates with solubilities considerably higher than those of their precursor sulphides. Solubility products for selected monosulphide minerals in freshwater (ionic strength, I, of zero) are listed for reference in Table 3-2 along with equilibrium solubility constants for oxides and hydroxides, carbonates and hydroxide carbonates. Note that it is not possible to compare the solubility constants of sulphides with the other phases directly, given the differing reaction stoichiometries. It is more instructive to compare the concentration of the free ions of the dissolved metals in solutions which are in equilibrium with the solid phases of interest, as in Figure 3-3. Note that at a pH of 6, and ignoring the formation of hydroxo metal complexes, the concentrations of Cd^{2+} , Zn^{2+} and Cu^{2+} are quite high, while that of dissolved Fe^{3+} is extremely low; this observation reinforces the fact that iron oxide phases are extremely insoluble in natural oxygenated waters, in contrast to

Constants for Selected Solubility Equilibria

Sulphides		log K, 25°C, I = 0
$\text{MnS(s)} = \text{Mn}^{2+} + \text{S}^{2-}$		-13.5
$\text{FeS(s)} = \text{Fe}^{2+} + \text{S}^{2-}$		-18.1
$\text{ZnS(s)} = \text{Zn}^{2+} + \text{S}^{2-}$		-24.7
$\text{CdS(s)} = \text{Cd}^{2+} + \text{S}^{2-}$		-27.0
$\text{CuS(s)} = \text{Cu}^{2+} + \text{S}^{2-}$		-36.1
$\text{PbS(s)} = \text{Pb}^{2+} + \text{S}^{2-}$		-27.5
$\text{HgS(s)} = \text{Hg}^{2+} + \text{S}^{2-}$		-52.7
Oxides	and	Hydroxides
$\hat{\text{A}}\text{-FeOOH(s)} + 3 \text{H}^+ = \text{Fe}^{3+} + 2 \text{H}_2\text{O}$		*K _{s0} = 0.5
(am) $\text{FeOOH(s)} + 3 \text{H}^+ = \text{Fe}^{3+} + 2 \text{H}_2\text{O}$		*K _{s0} = 2.5
$\text{ZnO} + 2 \text{H}^+ = \text{Zn}^{2+} + 2 \text{H}_2\text{O}$		*K _{s0} = 11.14
(am) $\text{Zn(OH)}_2 + 2 \text{H}^+ = \text{Zn}^{2+} + 2 \text{H}_2\text{O}$		*K _{s0} = 12.45
$\text{CuO(s)} + 2 \text{H}^+ = \text{Cu}^{2+} + \text{H}_2\text{O}$		*K _{s0} = 7.65
Carbonates	and	Hydroxide
		Carbonates
$\text{Zn(OH)}_{1.2}(\text{CO}_3)_{0.4}(\text{s}) + 2 \text{H}^+ = \text{Zn}^{2+} + 1.6 \text{H}_2\text{O} + 0.4 \text{CO}_2(\text{g})$		*K _{ps0} = 9.8
$\text{ZnCO}_3(\text{s}) + 2 \text{H}^+ = \text{Zn}^{2+} + \text{H}_2\text{O} + \text{CO}_2(\text{g})$		*K _{ps0} = 7.95
$\text{Cu(OH)(CO}_3)_{0.5}(\text{s}) + 2 \text{H}^+ = \text{Cu}^{2+} + 3/2 \text{H}_2\text{O} + 1/2 \text{CO}_2(\text{g})$		*K _{ps0} = 6.49
$\text{PbCO}_3(\text{s}) = \text{Pb}^{2+} + \text{CO}_3^{2-}$		K _{s0} = -13.1
$\text{CdCO}_3(\text{s}) + 2 \text{H}^+ = \text{Cd}^{2+} + \text{H}_2\text{O} + \text{CO}_2$		*K _{ps0} = 6.44
$\text{MnCO}_3(\text{s}) = \text{Mn}^{2+} + \text{CO}_3^{2-}$		K _{s0} = -10.4

Source: Stumm and Morgan (1981). Asterisked constants represent the original terminology in the tables of constants published by L.G. Sillen and A.G. Martell, *Stability Constants of Metal-Ion Complexes*, Special Publications, Nos. 17 and 25, Chemical Society, London, 1964 and 1971.

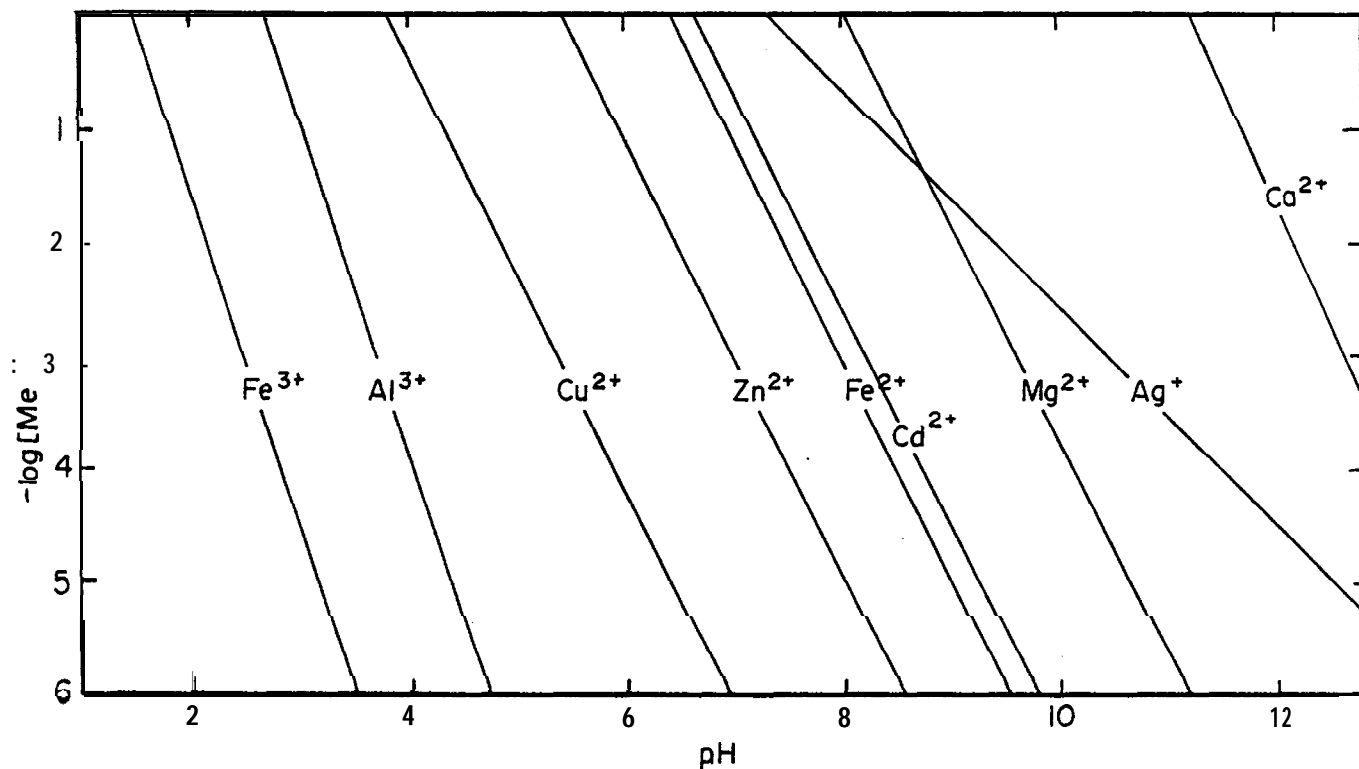


Figure 3-3 Solubility of selected oxides and hydroxides plotted as free metal ion concentration in equilibrium with solid oxides or hydroxides vs. pH. Note that the plot is based on $I = 0$ and that the occurrence of hydroxo metal complexes has not been taken into account After Stumm and Morgan (1981).

most other metal oxides. As pH decreases, solubility of all the solid oxyhydroxide phases increases; a drop of one pH unit promotes a rise of roughly two orders of magnitude in the concentration of dissolved metals. Similar considerations apply to metal carbonate equilibria in non-alkaline solution, and the solubility of hydroxide-carbonates, such as hydrozincite (Figure 3-4).

A simple comparison illustrates the solubility contrast between sulphides and their oxidation products. Consider, for example, ZnS and hydrozincite ($\text{Zn}_5(\text{OH})_6(\text{CO}_3)_2$). Ignoring complex formation, and using solubility constants from Stumm and Morgan (1981) and the specific conditions $\text{pH} = 6$, $I = 10^{-2.4}$, $T = 25^\circ\text{C}$, total dissolved $\text{CO}_2 = 10^{-3.5}$ M and $P = 1$ atm., then $[\text{Zn}^{2+}]$ in equilibrium with hydrozincite will be approximately 10^{-6} M. In a similar but anoxic solution, with $[\text{total H}_2\text{S}] = 10^{-6}$ M (a lower concentration than is typically encountered in anoxic pore waters), a pK_{sp} for sphalerite of 11.4 (based on an equation of the form $([\text{Zn}^{2+}][\text{HS}^-])/[\text{H}^+]$, as formulated by Jacobs et al., 1985), the concentration of Zn^{2+} in equilibrium with ZnS will be about 10^{-12} M, some six orders of magnitude less than that for hydrozincite. Clearly, the presence of sulphide in solution will establish extremely low dissolved metal concentrations in most cases; unfortunately, much higher metal levels will characterize oxygenated waters in contact with sulphide oxidation products.

3.4.2 The Oxidation Problem: Practice

In general, oxidation in natural sediments is inhibited where rapid accumulation is accompanied by a high organic matter content. As noted above, because the concentration of dissolved O_2 in water is rather low, the available oxygen in pore waters will be rapidly depleted given a respiring bacterial community and a linear sedimentation rate high enough to remove newly deposited sediments reasonably quickly from diffusive communication with overlying bottom water. Thus, the combination of a high organic load and rapid sedimentation will ensure the establishment of anoxic conditions at shallow depths and prevent the oxidation of deposited or authigenic sulphide minerals.

One other major factor which bears on the potential for oxidation of tailings is grain size. Because it is desirable to limit the surface area of sulphide particles exposed to oxygen during and after deposition in lakes, a mean particle size as large as possible is preferred; however, this must be balanced by metallurgical feasibility.

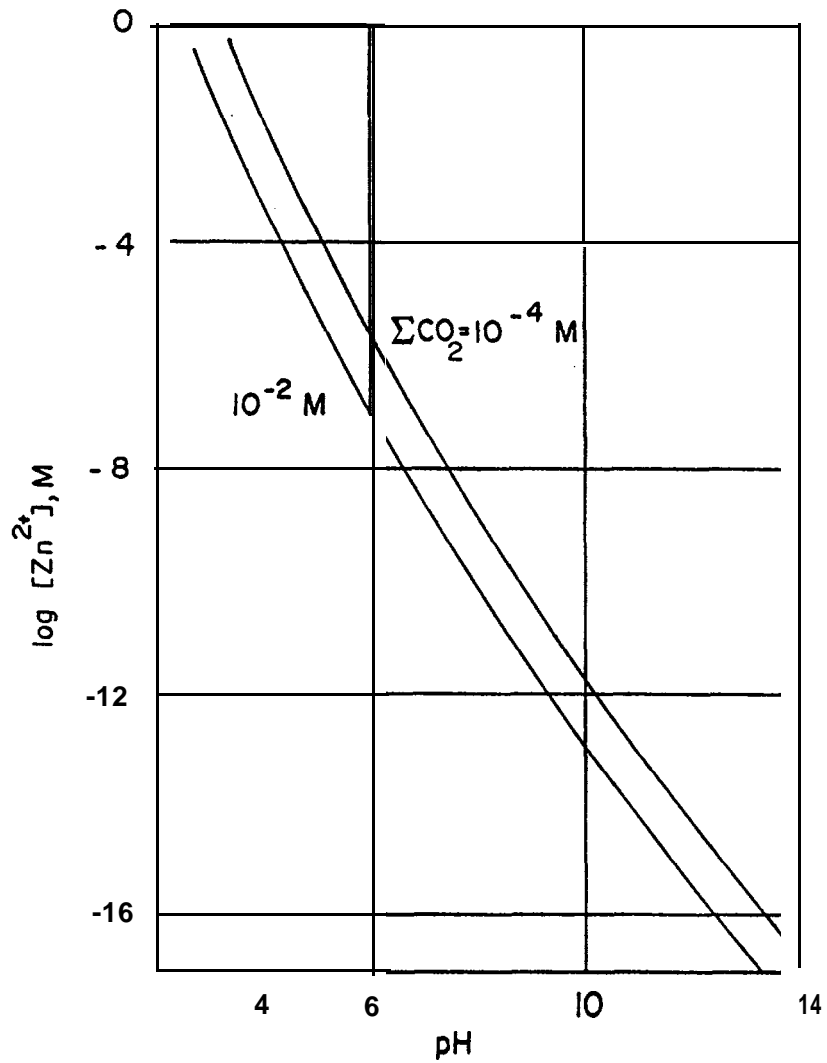


Figure 34 The concentration of Zn^{2+} in equilibrium with hydrozincite vs. pH (25XC, $I = 4 \times 10^{-3}$, $pK^{SO} = 67$). Note that hydrozincite is not stable over the entire pH range shown, and that hydroxo Zn complexes have been ignored in the calculation of the curves (after Stumm and Morgan, 1981). After Stumm and Morgan (1981).

Oxidation of submerged tailings and mine wastes and release of contained metals would be entirely prevented if such materials could be deposited in lakes or fjords which contained anoxic bottom water; such environments are relatively rare, however. In oxygenated basins, it is clear that rapid vertical accumulation of tailings or waste rock is preferable to lateral dispersion given the need to limit the flux of oxygen into the deposits. Similarly, the admixture of organic matter, derived either from codeposition of natural organic detritus, or by purposeful addition, will promote desired rapid oxygen consumption.

Most lakes are floored by sediments which are naturally anoxic at shallow depths. Thus, following cessation of tailings or waste rock discharge, it is a reasonable expectation that the deposits will be covered by an accumulating veneer of natural sediments which will act as a permanent protective barrier to oxidation. The time that elapses between the cessation of discharge and the development of an oxic-anoxic boundary in the accumulating cover layer will depend on the local character of sediment deposition in the recipient basin.

3.4.3 Speciation of Metals in Natural Waters

Speciation refers to the distribution of a trace element over the suite of complexing inorganic and organic ligands present in natural waters. Understanding impacts on biota requires consideration of this phenomenon given the relatively recent recognition that it is not the total amount of a metal pollutant in aquatic systems that is most important but rather the concentration of biologically available species of the metal (e.g. Sunda and Guillard, 1976; Lewis and Cave, 1982).

Significant ligands for trace metals in aerobic waters include OH^- , Cl^- , CO_3^{2-} , HCO_3^- , SO_4^{2-} , organic molecules and macromolecules, surface sites, and to a lesser extent, phosphorus and silicate species and NO_3^- (Bourg, 1988). Reduced or intermediate sulphur species are additionally important in anaerobic environments. In freshwaters, in which the concentration of inorganic ligands is quite low, the complexing capacity varies quite widely, largely as a function of the concentration of dissolved organic matter and the presence of particulate phases. Complexed metals can exist in true solution, in association with colloids, or adsorbed onto particle surfaces (Figure 3-5).

The complexing capacity of sediments is relatively high because of the enriched content of dissolved organic carbon compounds (largely humic and fulvic acids) in pore waters

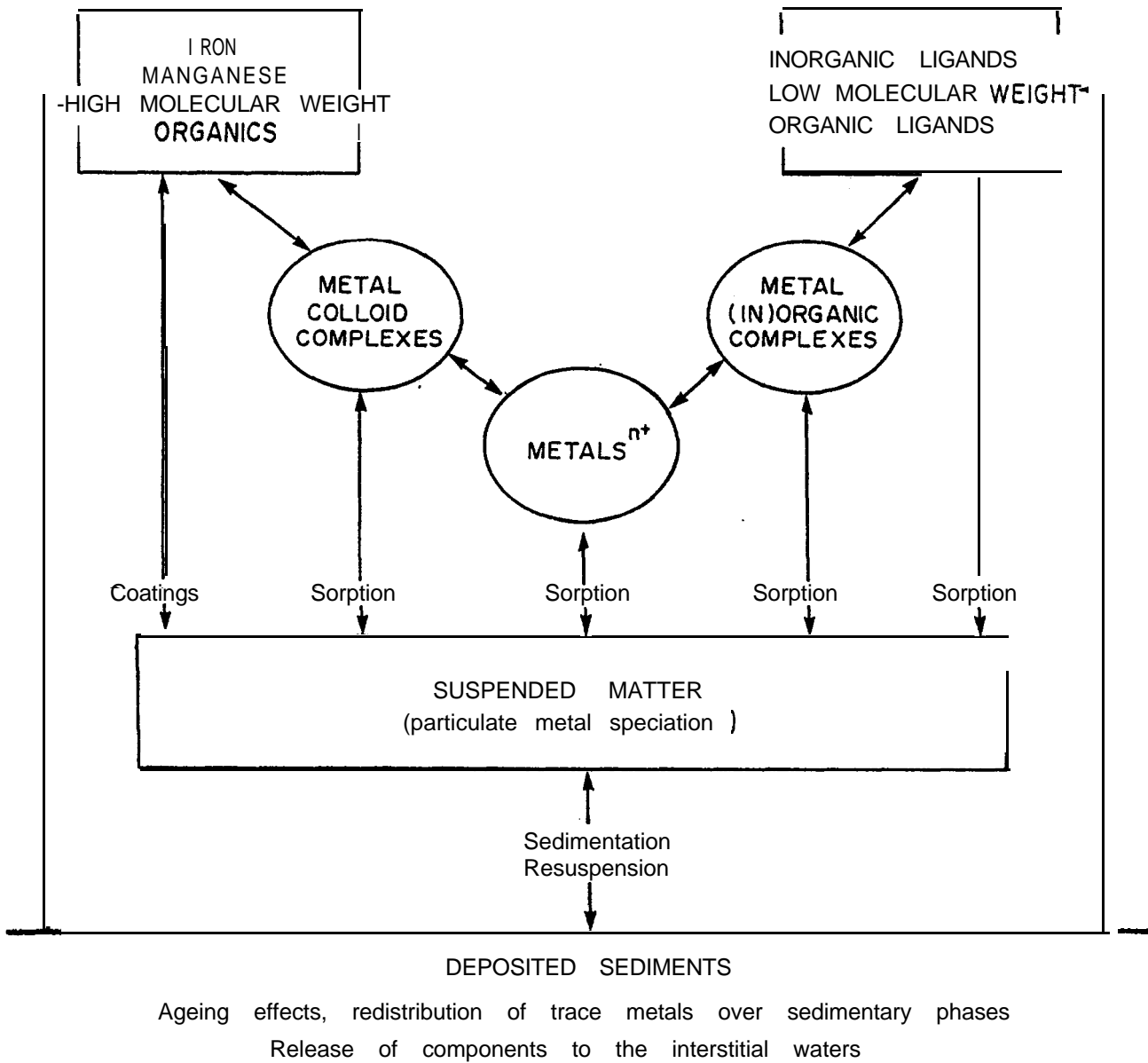


Figure 3-5 Summary of **major processes** and **mechanisms** in the **interactions between dissolved** and **solid metals species in surface waters.**

Source: **Salomons** and **Forstner** (1984).

and the presence of abundant particle surfaces. Stumm and Morgan (1981), Solomons and Forstner (1984), and Bourg (1988) describe speciation models for metals in natural waters which take into account the relative affinities of ligands in solution and on surfaces. One example is shown in Table 3-3. Note in this model that for metals such as Cu, there is considerable contrast between the complexing ability of citrate (high) and glutamate (low), and a widely different degree of complexation of citrate of Cu compared to Ag. Note also that complexes of metals with inorganic ligands are in general quantitatively unimportant in the fresh water model because the major cations occur in low concentrations; only CO_3^{2-} plays a significant role (Table 3-3). The addition of a relatively strongly-complexing organic ligand such as citrate reduces the proportion of Cu complexed by CO_3^{2-} by a factor of 500 ($10^{-9.7}$ M versus 10^{-7} M). Clearly, speciation in interstitial and lacustrine waters will be a complex function of the concentration and type of inorganic and organic ligands and particulate matter present, pH, total metal concentration, the redox state, and the flow rate of solution through the aquatic system (Bourg, 1988). This complexity has been addressed in previous and extant computer models (e.g. Mantoura et al., 1978; Turner et al., 1981), and in laboratory studies of metal partitioning in freshwater sediments (Tessier et al., 1979, 1982; Rapin et al., 1986). The empirical studies have highlighted the inherent variability that is characteristic of metal speciation and partitioning in natural sediments. It is not yet clear, however, to what extent the results of these predictive and empirical studies can be applied in assessments of impacts of pollutant metals on biota; much work remains to be done in this area.

Table 3-3

Equilibrium Model: Effect of Complex Formation on Distribution of Metals in Aerobic Waters

Fresh Water Inorganic fresh water, pH = 7.0, 25 ° C, free ligands: pSO ₄ 3.4; pHCO ₃ 3.1; pCO ₃ 6.1; pCl 3.3					Inorganic fresh water plus 7 x 10 ⁻⁶ mol litre ⁻¹ of each of the indicated organic ligands corresponding to 2.3 mg litre ⁻¹ of soluble organic carbon ^b . Inorganic ligands remain unchanged.								
M	M _T ^c	Free M	Major Species	% Free Ion	Free M	Major Inorganic Species	Free Ligand	Organic Complexes ^{d,e}					
								Acetate 5.16	Citrate 6.91	Tartrate 5.34	Glycinate 5.16	Glutamate 5.16	Phthalate 5.30
Ca	2.7	2.72	CaHCO ₃ , 4.6	95	2.72	CaHCO ₃ , 4.6		7.0	5.2	5.6	9.1	8.6	5.7
Mg	3.7	3.72	MgSO ₄ , 5.1	95	3.72	MgSO ₄ , 5.1		8.0	7.0	7.1	8.0	9.1	-
Fe(III)	Satd.	17.70	Fe(OH) ₂ , 8.7	V.low	17.73	Fe(OH) ₂ , 8.7		19.0	7.2	-	15.1	-	-
Mn(II)	7.0	7.04	MnSO ₄ , 8.5	91	7.04	MnSO ₄ , 8.5		11.3	9.7	-	11.5	11.1	-
Cu(II)	7.0	7.46	CuCO ₃ , 7.2	35	9.93	CuCO ₃ , 9.7		13.1	7.0	11.3	9.4	9.4	11.4
Zn(II)	6.7	6.72	ZnSO ₄ , 8.2	95	6.72	ZnSO ₄ , 8.2		10.3	10.5	8.9	9.6	8.6	9.1
Cd(II)	7.7	7.73	CdSO ₄ , 9.2	93	7.76	CdSO ₄ , 9.2		11.5	9.2	9.6	11.5	10.3	9.7
Pb(II)	7.0	8.02	PbCO ₃ , 7.1	9.5	8.04	PbCO ₃ , 7.1		11.0	8.9	8.8	10.1	-	9.2
Ag(I)	9.0	9.19	AgCl, 9.5	65	9.19	AgCl, 9.5		13.8	17.5	-	13.3	-	-
							% ^f	1.5	98.2	35.2	0.3	0.4	29.0

^a All concentrations are given as - log (mol litre⁻¹). Charges of species are omitted.

^b Organic matter of approximately composition C₁₃H₁₇O₁₂N.

^c Total concentration of metal species. The concentrations of heavy metals given are higher than those typically found in unpolluted seawater or fresh water. The relative effects of complex formation as trace elements are independent of the total concentration of these elements; waters are in equilibrium with Fe(OH)₃(s).

^d The concentrations refer to the sum of all complexes, for example, CuCit, CuHCit, CuCit₂.

^e A dash means that no stability constants are available for such complexes.

^f Percentage of each ligand bound to metal ions.

After Stumm and Morgan (1981).

Chapter 4

The preceding sections described contemporary understanding of the acid mine drainage process and how subaqueous disposal might be used as a means of mitigating the problems associated with it. This section discusses the potential biological impacts of subaqueous disposal of reactive mine wastes in a freshwater environment. Impact on macrobiota is addressed with respect to species specific effects of turbidity and sedimentation on various biological parameters, toxicity, and the potential for bioaccumulation and biomagnification. In addition, the implications of limnology to site selection are considered.

It is important to note that the biological impact of disposing mine wastes into freshwater varies with the study organism, the physical and chemical nature of the waste, and the limnological characteristics of the receiving waters. In addition, the biota of these waters are not always the passive victims of deposited materials. Some organisms re-work the sediments thereby altering the physical and chemical nature of the microhabitat and its suitability for other life forms. These considerations are also incorporated in the following discussion.

4.1 Microbiology

A search of the literature indicates that there is very little published material on the microbiology of mining wastes following subaqueous deposition. In addition there is little ecological information on the two groups of micro-organisms of primary interest in such situations: the sulphide oxidizers and the sulphate reducers.

Karavaiko (1978) in his review of the microflora of land micro-environments, reports that various authors have found that many and diverse micro-organisms are present in the products of rock degradation. Many require a source of carbon for growth (the heterotrophs) while the autotrophic organisms obtain their energy for growth by the oxidation of reduced forms on nitrogen, sulphur and iron.

Ore deposits, being a source of both reduced sulphur and iron compounds, are an excellent ecological niche for members of the genus *Thiobacillus* as well as similar types of micro-organisms such as those cited by Karavaiko which can oxidize Sb^{+3} , Co^{+3} , and As^{+3} .

4.1.1 Sulphide Oxidizers

The most important organism relative to microbiological alteration of sulphide bearing materials is *Thiobacillus ferrooxidans*. This organism, which was discovered in the acidic drainage from coal mines in Pennsylvania in 1947 (Colmer and Hinkle, 1947; Colmer et al., 1950; Temple and Colmer, 1951), is characterized as an autotrophic, motile, aerobic, gram negative rod. It usually measures 0.5 by 1.5-2.0 microns and is capable of oxidizing ferrous iron, thiosulphate, sulphur and metallic sulphides (McGoran et al., 1969) to obtain energy for growth while using oxygen as the final electron acceptor. It uses carbon dioxide as its sole source of carbon and requires an environment with an acidic pH.

The literature refers to two other organisms, *Ferrobacillus ferrooxidans* (Leathen et al., 1956) and *Ferrobacillus sulfooxidans* (Kinsel, 1960), which have the same characteristics, but most researchers consider them all to be the same organism (Hutchinson et al., 1966).

In this report, reference to *T. ferrooxidans* includes all the acidophilic thiobacilli capable of oxidizing metallic sulphides and ferrous iron.

Other thiobacilli are frequently cited as being associated with the microbiological leaching environment but they cannot oxidize ferrous iron. *Thiobacillus thiooxidans* has very similar characteristics to *T. ferrooxidans* but it cannot oxidize iron nor can it oxidize metallic sulphides with the exception of sodium sulphide (Unz and Lundgren, 1961).

T. ferrooxidans has minimal requirements for growth. It obtains energy from the oxidation of reduced sulphur and iron compounds. It requires CO₂ as a carbon source, NH₄⁺ for the formation of cellular proteins, phosphate for the formation of adenosine triphosphate (ATP), other trace nutrients for various cellular components, and oxygen as the ultimate electron acceptor. Oxygen and the various inorganic nutrients are normally present in ample supply in the environment associated with terrestrial ore bodies. Ammonia nitrogen may be limiting, although there is a preliminary report in the literature that suggests the organism may be able to fix atmospheric nitrogen (Mackintosh, 1971).

T. thiooxidans has very similar characteristics except that suggests it only utilizes sulphur or thiosulphate as its energy source. It cannot oxidize the metallic sulphides or iron found in ore bodies (Unz and Lundgren, 1961).

Both *T. ferrooxidans* and *T. thiooxidans* are extremely acid tolerant; pH values of less than 1 have been generated frequently in culture laboratory studies at B.C. Research. The upper limit for sulphide oxidation by *T. ferrooxidans* is around pH 4, whereas sulphur oxidation has been found to occur at pH 5 (McGoran et al., 1969). The upper limit for sulphur oxidation by *T. thiooxidans* is around pH 7. The upper limit for the oxidation of ferrous iron by the former organism is difficult to determine since the auto-oxidation of this iron is extremely rapid above pH 3.5. In general, the most favourable pH range for growth is 2-3.

In spite of its acidophilic nature and the low pH range for oxidation of its two main energy sources, it is known that *T. ferrooxidans* will survive for extended periods of time at a pH of 8. Studies showed that the organism survived for 24 hours at pH 9, but no viable organisms were found after 48 hours at that pH.

Most strains of *T. ferrooxidans* have an optimum temperature in the range 28-37°C. In B.C. Research studies it would not survive at 45°C. The rate of activity of the organism drops off as the temperature decreases below 28°C. Oxidation rates are very slow below 5°C.

As mentioned above, oxygen is the ultimate electron acceptor and the reduced oxygen combines with the oxidized sulphur to yield sulphate. Two moles of oxygen are required for every mole of sulphide oxidized, thus the rapid oxidation of sulphides requires significant oxygen.

The other gas required by the bacteria is carbon dioxide. For all intents and purposes this is the organism's sole source of carbon. It can assimilate other sources of carbon but it is unclear if it is truly capable of growth using carbon compounds as an energy source. Normally, the availability of carbon dioxide will not be a growth limiting factor.

T. ferrooxidans is not inhibited by high concentrations of most heavy metals. In studies at B.C. Research, concentrations as high as 62 g/L copper, 120 g/L zinc, 26 g/L nickel and 20 g/L arsenic have been tolerated. Two metals that have been shown to be toxic are molybdenum (100 mg/L) and uranium (1100 mg/L). In both cases, the toxicity appears to be due to the fact that these metals occur as cations at the acidic pH values preferred by the organism. Other anions toxic to *T. ferrooxidans* are chloride and nitrate. Anions, with the exception of sulphate, are generally found to be inhibitory.

As shown by the above brief summary, *T. ferrooxidans* occupies a rather unique ecological niche. This niche is relatively easy for the organism to develop and maintain in the terrestrial environment. Even in alkaline host rock, the organism can attach itself to an exposed sulphide surface (as long as it is moist), obtain the oxygen it needs and initiate oxidation in that micro environment. The acid generated maintains the desired conditions and then gradually neutralizes the surrounding alkaline rock thereby expanding the size of the desirable environment. As more sulphide is exposed to the acid environment, the process accelerates.

In the subaqueous environment represented by a lake bottom or a sea bed, however, it is much more difficult, if not impossible, for the bacteria to establish a micro-environment. The amount of oxygen available is severely reduced. On land, air containing 20% oxygen is normally in contact with the thin film of moisture in which the bacteria are located. Under water, oxygen availability is inhibited by the limited solubility of O₂, the depth of the water column and by competing oxidative processes. Oxygen transfer thus becomes a rate-limiting step.

In addition, in the subaqueous environment the micro environment is not isolated but is constantly subject to dilution by the mass of the surrounding water. Even if there were no active currents which would cause rapid dilution, the diffusion of acid out of the micro-environment would be more rapid than the diffusion of oxygen into the environment given the very high diffusion coefficient for protons. As stated above, it takes two moles of oxygen (ignoring any oxygen required for iron oxidation) to produce one mole of sulphuric acid (which is equivalent to two moles of hydrogen ions). It is unlikely, therefore, that the concentration of hydrogen ions will ever accumulate to a level that causes a drop in pH sufficient to accelerate microbiological activity.

Another inhibitory factor in seawater is chloride ion toxicity. Laboratory studies at B.C. Research have shown that normal bacterial leaching of metals occurred when the medium contained 10% seawater, reduced leaching occurred at 25% seawater, but no leaching was evident at 50% and 100% seawater. Based on these results, it was concluded that the normal terrestrial strains of *T. ferrooxidans* are unlikely to oxidize sulphide minerals when the salinity exceeds 13 ppt.

To the best of our knowledge, strains of *T. ferrooxidans* have not been isolated from seawater. Marine thiobacilli have been isolated, however, (Tilton et al., 1967) and they are considered to be distinctly different from non-terrestrial types. In addition, several of the strains isolated were capable of oxidizing H₂S (Adair and Gunderson, 1969).

4.1.2 Sulphate Reducers

The other group of micro-organisms associated with subaqueous disposal of mining wastes that have a potential influence on the environment are the sulphate reducing bacteria. These organisms are responsible for dissimilatory microbial sulphate reduction, a process in which sulphate is used as the electron acceptor in the oxidation of organic matter. This reduces sulphur from the +6 oxidation state to sulphide (-2 oxidation state). Although the *Desulfovibrio*

are the most commonly studied organisms of this type, *Desulfotomaculum* also have this capability (Miller and Hughes, 1968).

Desulfovibrio are small, gram negative, curved rods which are strict anaerobes. They are motile by means of a single polar flagellum and grow in both fresh and seawater at natural pH values.

The interaction of *Desulfovibrio* with mining wastes is based on its ability to generate sulphide ions which interact with metals to form insoluble sulphides. It requires significant quantities of organic matter to drive its metabolism; however this component is normally lacking in mining wastes. Another key factor is the need for an anaerobic environment. It is unlikely, therefore that both *T. ferrooxidans* (an aerobe) and *Desulfovibrio desulphuricans* (an anaerobe) will be active at the same time. The environment will favour one or the other.

4.2 Macrobiological Effects

The possibilities and problems of aquatic disposal of mining wastes have received considerable attention in Canada for a number of years. Indeed, in the mid-1970's there was a flurry of publications dealing with environmental and biological implications of such practices. Clark (1974) made a comprehensive review of the effects of effluents from metal mines on aquatic ecosystems in Canada and provided toxicity information on some 47 components of mining wastes on the biota of receiving waters, including plankton, benthos and fish. Effects of specific toxicants such as arsenic, cadmium and copper also were given special attention at that time (Penrose, 1974; Ray and Coffin, 1977; Black et al., 1976). Harvey (1976) noted in his report on aquatic environmental quality in Canada, that despite the many problems with tailings ponds, on-land disposal was preferred over direct dumping of mine wastes into the aquatic environment. As an example, Harvey (1976) cited the long-term disposal of tailings from one mine on Lake Superior (Reserve Mining Co.) which introduced more than five times the solids entering the lake naturally through shore erosion and rivers input.

Macrobiological effects, separated for editorial convenience (but not functional significance) from microbiological effects, may be placed into four major categories: turbidity, sedimentation, toxicity, and contamination. Each is discussed in turn.

Impacts related to turbidity include the biological effects of reduced water transparency on primary and secondary production as well as effects on respiration, feeding and other behaviour of water column organisms in both "standing" (lakes, reservoirs, ponds) and flowing waters. Sedimentation effects embrace phenomena associated with settling and smothering of benthic organisms on lake and river bottoms. The discussion on toxicity will include a wide range of lethal, sub-lethal and behavioural effects of trace metals or acid-generating materials on freshwater biota. Under the heading contamination, the uptake and bioaccumulation of trace metals will be considered, as well as their biomagnification; especially by inclusion of metals in short, direct food web linkages.

Finally, because the effects of aquatic disposal of mining wastes can vary so greatly depending on the type and conditions of receiving waters, it will be necessary to comment briefly on some significant interactions in this area.

4.2.1 Turbidity Effects

Many inland waters of Canada were subjected to much higher levels of turbidity during late phases of deglaciation than occur today, so the biota have had a long evolutionary history with turbidity in this area. Despite this, the possibilities for adaptation are not great. Hence long-term changes in turbidity usually result in major changes in species composition and abundance. Effects on primary producers are expressed mainly, but not entirely, through reduction in light penetration by high turbidity; in lakes (Wetzel, 1983), and also in rivers such as the Fraser (Northcote et al., 1975; Northcote and Larkin, 1988). In addition to particle concentrations, particle shape can have important consequences; in particular the scouring action of suspended

particles on periphyton (attached algae) in streams and rivers can be greater if the particles are derived from crushed rock in mining operations rather than from natural alluvial sediments. Furthermore, the respiratory and filter-feeding structures of many planktonic as well as benthic invertebrates are hampered by high suspended sediment levels in lakes and streams.

The acute and chronic effects on fish of long-term exposure to suspended sediment are well documented (Wallen, 1951; Hebert and Merkins, 1961; Vinyard and O'Brien, 1976; Noggle, 1978; Sigler, 1981; Gardner, 1981; Crouse et al., 1981; McLeay et al., 1987; Servizi and Martens, 1987). Even relatively brief exposure (minutes to hours) to suspended sediment levels over a few hundred mg·L⁻¹ can cause significant mortality in some salmonid fishes, and longer exposure (several days) at levels in the range of a few thousand mg·L⁻¹ can produce obvious gill damage and severe mortalities (often >50%) in rainbow trout. Moderate increases in turbidity often cause an increase in ventilation and oxygen consumption rates in fish (Horkel and Pearson, 1976) and though there may be no severe mortality as a result, there are energy costs involved. Turbidity effects that are negative to some species (e.g. salmonids), may be positive to others, such as cyprinids (Gradall and Swenson, 1982). Some species such as the arctic grayling can survive well given high suspended sediment levels, but may show signs of stress in other physiological and behavioural interactions (McLeay et al., 1983; 1984). Similar effects have been reported for yearling coho salmon and steelhead trout (Redding et al., 1987). Exposure to short-term (1 hour) pulses of suspended sediment can result in territorial breakdown, reduced feeding ability, and increased gill-flaring ("cough" response) in stream-dwelling young coho salmon (Berg and Northcote, 1985). Indirect effects of suspended sediment on fish, especially salmonids, include reductions in growth rate and delays in migration.

4.2.2 Sedimentation Effects

The blanketing of lake or stream bottoms by sediment, if continuous, inhibits colonization and production of periphyton and would likely have similar effects on macrophytes. The food supply (benthic algae) to many forms of benthic invertebrates may thus be reduced by smothering, and the habitat for epifaunal forms which utilize spaces between rocks or other bottom materials may also be degraded. Infaunal groups such as aquatic earthworms may not be affected however. Stretches of sand or other fine sediment deposited in streams may impede or block upstream movement and hence colonization of stream insects (Luedtke and Brusven, 1976).

Perhaps some of the most serious detriments of sedimentation on salmonid fishes are effects on egg and alevin developing in stream or lake gravels, and on fry emerging from these rearing habitats. Changes in survival are directly related to the amount of fine particle size materials (< ~1-3 mm) which are included in the spawning gravel. Relatively small changes in the amount of fine materials can have large effects on survival. For example, levels of about 5% by volume in spawning gravel have little effect on survival of pink salmon eggs, but levels of 10% can reduce it by up to 50%. Emergence of salmonid late-alevins or fry from rearing gravels may be greatly inhibited by sedimentation and mortality at that stage can be severe.

Sedimentation can also have indirect effects on fish, mainly by alteration and reduction in cover which thereby increases their predation risk (see for example Alexander and Hansen, 1983).

4.2.3 Toxicity Effects

As noted previously, there are nearly 50 components in mining wastes which can have toxic effects on biota in receiving waters (Clark, 1974). Only some of the more important and common of these are reviewed here with their acute and chronic effects on survival as well as their sub-lethal, physiological and behavioural manifestations. To facilitate later location of the information available, the components covered will follow the sequence: acid mine waters and aluminum (by themselves or together), arsenic, cadmium, chromium, copper, cyanide, iron, lead, mercury, nickel, tin, zinc, and mixtures (organized under the biotic groups: phytoplankton, periphyton, macrophytes, zooplankton, zoobenthos and fish). No attempt was made to cover

effects on higher vertebrates. Laboratory, lake and stream (or river) results are included. For details on many components, Chapter 3 of the Canadian Water Quality Guidelines (CCREM, 1987) should be consulted.

4.2.3.1 Phytoplankton

Lower phytoplankton cell density, production, and species diversity were recorded in two northern Ontario lakes affected by acid mine wastes, compared to an unaffected one (Johnson et al., 1970), but possible interactions with aluminum were not measured. Aluminum can have direct toxic effects on phytoplankton in concentrations as low as 135 $\mu\text{g}\cdot\text{L}^{-1}$ (Bohm-Tuchy, 1959), but in acidic waters may act through phosphorus limitation as Nalewajko and Paul (1985) have shown in Ontario Precambrian Shield lakes where significant decreases in photosynthesis were demonstrated at an aluminum concentration of 50 $\mu\text{g}\cdot\text{L}^{-1}$.

Arsenic, in the presence of high nutrient (N, P) concentrations, did not inhibit high algal biomass in the tube experiments of Brunskill et al. (1980). Within the ambient concentrations used (< 160 $\mu\text{g}\cdot\text{L}^{-1}$), Conway (1978) found no detrimental effects on growth or on micronutrient utilization for the planktonic diatom *Asterionella formosa*. Furthermore, Planas and Lamarche (1983) found no effect of arsenic on phytoplankton communities developed under various nutrient conditions. Interestingly, Baker et al. (1983) reported that arsenic methylation occurred in mixed green algal phytoplankton cultures, suggesting an additional source for the formation and cycling of organo-arsenic compounds in freshwater ecosystems. Vocke et al. (1980) noted arsenic toxicity at levels ranging upwards from 48 $\mu\text{g}\cdot\text{L}^{-1}$ for *Scenedesmus obliquus*.

Cadmium is rapidly sorbed by the common planktonic diatoms *Asterionella formosa* and *Fragilaria crotonensis*, actively by the former but passively by the latter (Conway and Williams, 1979). As concentrations were increased in the 2-9 $\mu\text{g}\cdot\text{L}^{-1}$ range, the growth rate of the former decreased (Conway, 1978; Conway and Williams, 1979) but was unchanged in the latter.

Although copper has long been known to be toxic to phytoplankton at very low concentrations, for example in the 10-10 to 10-12 M range (Stumm and Morgan, 1981), there are suggestions that secretions of complexing ligands by some algae can ameliorate such toxicity (Van den Berg et al., 1979). For the blue-green phytoplankter *Aphanizomenon flosaquae*, Wurtsbaugh and Home (1982) have shown a linear inhibition of N and C fixation as well as pigment accumulation between 10 and 30 $\mu\text{g}\cdot\text{L}^{-1}$ Cu.

Zinc concentrations in the 10-20 $\mu\text{mol}\cdot\text{L}^{-1}$ affect growth of *Chlamydomonas variabilis* with important interactions with phosphorus and pH (Bates et al., 1983, 1985; Harrison et al., 1986).

Synergistic effects of metal mixtures on phytoplankton are now starting to be examined (Wong et al., 1982).

4.2.3.2 Macrophytes

Aluminum concentrations of 2.5 $\text{mg}\cdot\text{L}^{-1}$ brought about a 50% reduction in root growth of Eurasian milfoil (*Myriophyllum spicatum*) at a pH near neutrality (Stanley, 1974).

The Northwest Miramichi River system of New Brunswick has been affected by copper-zinc mining pollution since the early 1960's (Besch and Roberts-Pichette, 1970). After an eight year period, mine water discharges seriously reduced or eliminated the riparian vascular flora. Submerged macrophytes were the most sensitive group with the horsetail *Equisetum arvense* the least sensitive species.

Revegetation of 32 year old tailings in Mandy Lake (Hamilton and Fraser, 1978), rich in sulphides, took place by sedges (*Carex* spp.), riverweed (*Podostemum ceratophyllum*) and spike rushes (*Eleocharis* spp.), whereas macrophyte species in areas away from the tailings were more diverse; mainly cattails (*Typha latifolia*), yellow pond lily (*Nuphar variegatum*),

water smartweed (*Polygonum amphibium*), bullrushes (*Scirpus* spp.) and pondweeds (*Potamogeton* spp.).

4.2.3.3 Zooplankton

Toxic effects of aluminum, in combination with acid waters, often appear at concentrations below 1 mg·L⁻¹ (Biesinger and Christensen, 1972; Shephard, 1983; Havas and Likens, 1985; Arts and Sprules, 1987; see also CCREM, 1987). Although estuarine zooplankton are resistant to relatively high arsenate concentrations (up to 100 µg·L⁻¹), indirect effects may be much more severe (Sanders, 1986).

Cadmium appears to be especially toxic to zooplankton with levels as low as 10-8.5 M showing effects on *Daphnia* (Stumm and Morgan, 1981). Population decline and reproductive depression have been reported in the 0.2 to 4 µg·L⁻¹ range (Marshall, 1978; Marshall and Mellinger, 1980; Marshall et al., 1981) but the effects were decreased at low pH (Lawrence and Holoka, 1987).

During molt, *Daphnia pulex* has a significantly higher mortality when exposed to chromium at 0.56 mg·L⁻¹ (Lee and Buikema, 1979).

Toxicity of copper for *Daphnia magna* put the adult 3-week LC₅₀ at 0.044 mg·L⁻¹ and a 50% reproductive impairment at 0.035 mg·L⁻¹ (Biesinger and Christensen, 1972), but both are increased to 0.26 mg·L⁻¹ when 2 mg·L⁻¹ of the chelator NTA is added (Biesinger et al., 1974). Winner and Farrel (1976) give chronic toxicity values of copper for four species of *Daphnia*.

Synergism of toxicity in multimetal mixtures has been known for some time in freshwater organisms (Anderson and Weber, 1975) and has been clearly demonstrated in freshwater copepods, primarily *Cyclops* spp. (Borgmann, 1980).

4.2.3.4 Zoobenthos

Significant (37%) mortality of chironomid larvae (*Tanytarsus dissimilis*, second and third instars) occurred at aluminum concentrations of 0.8 mg·L⁻¹ at pH 6.8 (Lamb and Bailey, 1981). Effects of cadmium were reported for lakes (Andersson and Borg, 1988) and streams (Stephenson and Mackie, 1988). Toxic effects of copper in relation to pH have been examined for two species of amphipods by de March (1979, 1983). Earlier studies on copper effects include those of Arthur and Leonard (1970) and Peterson (1978). Clements et al. (1988) have recently shown that experimental stream results of copper and zinc toxicity compare well with field results.

Lead concentrations as low as 19 µg·L⁻¹ provided significant increases in snail (*Lymnaea palustris*) mortality but not growth rate (Borgmann et al., 1978). Mercury exposure reduced artificial stream biomass and diversity (Sigmon et al., 1977). Other effects of heavy metals on stream survival and community structure of insects are given by Hall et al. (1988), Winner et al. (1980) and Burton and Allan (1986); see also Havas and Hutchinson (1982) and Waterhouse and Farrell (1985). Acute toxicities to amphipods of binary mixtures of metals are considered by de March (1988).

4.2.3.5 Fish

More general aspects of the toxic effects of mine wastes on freshwater fish have been reviewed from the eastern to western regions of Canada (Elson et al., 1973; Elson, 1974; Somers and Harvey, 1984; Alderdice and McLean, 1982). A variety of physiological and behavioural effects have been suggested, including altered chemoreception (Hara, 1972, 1981; Brown et al., 1982), spermatogenesis (Cochran, 1987), bone development (Hamilton and Reash, 1988),

fecundity (Reash and Berra, 1986), temperature selection (Peterson, 1976), vertical positioning (Scherer, 1976), and susceptibility to bacterial infection (Pippy and Hare, 1969). Sensitive indicators of metal pollution using fish have been suggested (Roch et al., 1982) as have the interactions between genetic and environmental factors in the development of resistance to such pollution by fish (Swarts et al., 1978).

Explanations for the decline or disappearance of some species of salmonids from headwater lakes and streams now include complex interactions between acidity, low calcium and toxic aluminum concentrations, as illustrated for brook trout (Cleveland et al., 1986; Siddens et al., 1986; Mount et al., 1988a, b). Changes in gill structure also are involved (Tietge et al., 1988). Similar or complimentary investigations are being conducted on other salmonids such as rainbow trout (Neville, 1985) and lake trout (Gun and Noakes, 1987).

Early work on toxicity of arsenic to fish was conducted by Alderdice and Brett (1957). Acute toxicity of arsenic for several freshwater fishes is in the 10-15 mg·L⁻¹ range (CCREM, 1987) but chronic toxicities are reported at much lower levels.

Acute toxicity levels for cadmium are in the 1-3 µg·L⁻¹ range for rainbow trout, with slightly lower chronic toxicity values. Both are inversely dependent on water hardness (CCREM, 1987). Possibly because rainbow trout are the piscine equivalent of the laboratory rat, a large body of detailed physiological work has been done on this species with respect to cadmium (and other heavy metal) toxicity (see for example Chapman, 1978a; Roch and Maly, 1979; Pärt and Svanberg, 1981; Majewski and Giles, 1981; Giles 1984; Lowe-Jinde and Nümi, 1986; Reid and McDonald, 1988; Giles, 1988). Nevertheless there have been numerous studies on cadmium toxicity in other salmonids such as brook trout (Benoit et al., 1976; Sangalang and Freeman, 1979; Hamilton et al., 1987a, b), Atlantic salmon (Peterson et al., 1983; 1985), and chinook salmon (Finlayson and Verrue, 1982). Effects on catostomids, i.e. suckers, (Duncan and Klaverkamp, 1983; Borgmann and Ralph, 1986) and cyprinids have not been overlooked (Pickering and Galt, 1972; Sullivan et al., 1978; McCarty et al., 1978; Houston and Keen, 1984; Andros and Garton, 1980).

In addition to the few references on chromium toxicity reported by CCREM (1987), the study by Adelman et al. (1976) on two species of cyprinids should be noted.

Acute and chronic toxicity of copper seem to be reasonably well established for rainbow trout (Harrison, 1975; Giles and Klaverkamp, 1981; CCREM, 1987) and other studies on this species have considered effects on olfaction (Hara et al., 1976), bioenergetics (Lett et al., 1976), hematocrit (Waiwood, 1980), acclimation (Dixon and Sprague, 1981; Laurén and McDonald, 1987a, b), avoidance (Giattina et al., 1982), and growth and survival (Seim et al., 1984). Nearly as well studied are lethal and sublethal effects of copper on Atlantic salmon (Sprague, 1964a; Sprague and Ramsay, 1965; Sprague, 1965; Sprague et al., 1965; Zitko et al., 1973) as well as its effects in this species on avoidance (Sprague, 1964b) and on migration (Saunders and Sprague, 1967; Sutterlin and Gray, 1973). Similar studies on other salmonids include those on brook trout (McKim et al., 1970; McKim and Benoit, 1971; Drummond et al., 1973), coho salmon (Waldichuk, 1976) and on sockeye salmon (Davis and Shand, 1978). Copper effects on non-salmonids have been examined in striped bass (Bohammer, 1985), white suckers (Munkittrick and Dixon, 1988), cyprinids (Mount and Stephan, 1969; Kleerkoper et al., 1972, 1973; Tsai and McKee, 1980) and in an ictalurid, i.e. catfish (Brungs et al., 1973).

For cyanide, acute and chronic toxicities as well as several other effects and interactions are covered in the literature cited by CCREM (1987). The studies by Broderius et al. (1977), Kimball et al. (1978), Leduc (1978), Kovacs and Leduc (1982a, b) provide useful examples.

In addition to the few studies on iron toxicity reported by CCREM (1987), those of Brenner et al. (1976) on the common shiner and of Smith and Sykora (1976) on brook trout and coho salmon should be consulted.

Long-term effects of lead exposure have been described for brook trout (Holcombe et al., 1976; see also Dorfman and Whitworth, 1969) as well as its chronic and sublethal effects on rainbow trout (Hodson et al., 1980; Sippel et al., 1983; see also Hodson et al., 1982). Blood characteristics of several fishes have been used as an indicator of harmful exposures to lead (Hodson, 1976a; Hodson et al., 1977, 1978; Schmitt et al., 1984).

Acute toxicity levels for forms of mercury have been reported for rainbow trout fry and fingerlings (Wobeser, 1975; see also CCREM, 1987). Mercury is said to block taste responses in Atlantic salmon parr (Sutterlin and Sutterlin, 1970).

Many of the studies on copper toxicity reported previously, especially those on brook trout and Atlantic salmon, also provided information on zinc toxicity. Additional work on zinc includes that by Sprague (1968) and Hodson (1976b) for rainbow trout, effects on Atlantic salmon (Hodson and Sprague, 1975; Zitko and Carson, 1977) and on brook trout (Holcombe et al., 1979) and sockeye salmon (Chapman, 1978b; Boyce and Yamada, 1977). Zinc is also known to affect the immunity of fish to viral and bacterial infection (Sarot and Perlmutter, 1976) as well as their growth, sexual maturity and reproduction (Pierson, 1981).

Efforts to demonstrate genetic selection for zinc tolerance in laboratory (flagfish) and wild (common shiner) populations of fish were not successful (Rahel, 1981).

4.2.4 Contamination Effects

There is an enormous volume of literature on the uptake, bioaccumulation and biomagnification of many metallic components originating from mine wastes discharged into freshwaters, as well as from natural inflows. The study by Wagemann et al. (1978) provides an example for arsenic, giving concentrations in the sediment, water and biota compartments. Allen (1986) reviews the bioavailability and bioaccumulation of toxic metals in the biota of several large Canadian lakes and rivers. Examples of lead, mercury, nickel and tin accumulation in phytoplankton are given, respectively, by Denny and Welsh (1979), Rudd and Turner (1983), Watras et al. (1985) and Wong et al. (1984).

Metal contamination in aquatic macrophytes has been studied by Franzin and McFarlane (1980), Marshall et al. (1983), Campbell et al. (1985), and Andersson and Borg (1988).

Accumulation levels of several metals in zooplankton are reported by Denny and Welsh (1979), Watras et al. (1985), Bodaly et al. (1987) and Jackson (1988).

For the benthic community, bioaccumulation data for several trace metals may be found in the publications of Smith et al. (1975), Bindra and Hall (MS 1978), Rudd et al. (1980), Tessier et al. (1984), Evans and Lasenby (1983), Van Duyn-Henderson and Lasenby (1986), Jackson (1988) and Evans et al. (1988).

For fish, correlations between sediment concentration of several metals and that in fish from several Ontario lakes have been reported (Johnson, 1987). Cadmium uptake by fish has been observed in several systems (Atchison et al., 1977; Ramamoorthy and Blumhagen, 1984; Andersson and Borg, 1988). Accumulation of chromium by fish (Buhler et al., 1977) and of copper (Duthie and Carter, 1970) has been recorded. One of the most intensively studied trace elements in respect to uptake by fish has been mercury (Gillespie and Scott, 1972; Uthe et al., 1973; Scott, 1974; Reinert et al., 1974; Laarman et al., 1976; McKim et al., 1976; Scherer et al., 1976; Hartman, 1978; Huckabee et al., 1978; Phillips and Buhler, 1978; McFarlane and Franzin, 1980; Rudd et al., 1980; Rodgers and Beamish, 1981, 1983; MacCrimmon et al., 1983; Walczak et al., 1986; Hecky et al., 1987; Bodaly et al., 1987).

Zinc uptake by fish has been studied by Hodson (1975), Atchison et al. (1977), Ramamoorthy and Blumhagen (1984), and Spry et al. (1988).

4.2.5 Receiving Water Conditions

The physical, chemical and biological condition of waters proposed or being used for subaqueous disposal of mining wastes will have major implications on the suitability of such systems for that purpose. Perhaps the first major consideration is whether or not the waters are "standing" or moving, i.e. is the proposed site a lake, pond, reservoir or is it a stream or river. Responses of these two major categories to subaqueous disposal can be profoundly different.

The second major consideration is the question of scale; largely revolving around morphometric features of the receiving system. The size of the receiving water in relation to the quantity of input is critical. In the case of lakes or reservoirs, the surface area to volume relationships are important but so are other morphometric features such as fetch, shoreline development, average basin slope, and maximum depth. In a small lake, a high tailings input and sedimentation rate can have severe impacts on biota and recreational use (Osborne, 1976). For rivers, another set of morphometric parameters must be used including, for example, width, cross-sectional area, bank slope and maximum depth. The basin (lakes) or channel (rivers) morphometry will, in part, set the discharge characteristics, which will have major bearing on site suitability. Short-term, seasonal as well as annual variation in retention time (or its converse; flushing rate) must be considered for lakes and reservoirs, as must discharge hydrographs for rivers.

In lakes and reservoirs the existence, extent and timing of seasonal stratification and mixing patterns must be known as these features will profoundly influence disposal considerations. It must be known therefore whether or not the lake is holomictic or meromictic, dimictic or polymictic, and the depths, temperatures and other related features of the stratifications must also be known. For rivers, the mixing patterns are different but there may well be marked cross-sectional and "side" differences to be considered. Because rivers flow, does not necessarily mean that mixing is instantaneous or spatially localized. Pollutant inflows into large rivers often impart a "one-sidedness" in characteristics for kilometres downstream.

There are also many chemical parameters to consider. The non-mixing (monimolimnetic) waters of meromictic lakes often are markedly different in chemical characteristics compared to the overlying mixed (mixolimnetic) waters. There can be major differences, therefore, in dissolved gases, minerals, alkalinity, conductivity and salinity, between upper and lower layers. These differences can have major influence on the turbidity, sedimentation, toxicity and contamination effects considered previously. Even in holomictic lakes there can be great seasonal differences in the extent, depth and effectiveness of mixing and thereby in the chemical conditions noted above.

Biotic interactions, whether at depth in the sediments, at the mud-water interface, in the water column itself, or at the water-air interface, can be of great importance in effecting metal toxicity and contamination. The benthic infauna can effect major changes in mineral sedimentation, stratification and availability within bottom deposits. Some benthic invertebrates such as mysids (a type of freshwater shrimp) and chaoborids spend daylight hours as benthic feeders and rise each night up to near-surface waters. Through feeding, vertical migration and predatory interactions, they can act as concentrators and transporters of materials between bottom and water column compartments of lakes. For example, certain heavy metals (zinc, lead and cadmium) are transported via the vertical migration of Kootenay Lake mysids, which are consumed by kokanee salmon (Evans and Lasenby, 1983; Van Duyn-Henderson and Lasenby, 1986). A vertical migration of 30-40 m is not uncommon. Such metal uptake by fish suggests only a very short food chain linkage to man. It seems clear that the community structure and food web structure of lake and river ecosystems also may play major roles in their functional processes, concentration or cycling of elements and thus in problems of toxicity and contamination.

Chapter 5

5.1 Introduction

A number of case studies which either have or are currently utilizing freshwater subaqueous disposal are outlined in Tables 5-1 and 5-2 and described below. The sites chosen represent a range of ore types and receiving environments. Not all mines utilizing subaqueous disposal practices have data available which are adequate for understanding the impacts of tailings input, although considerable monitoring data may exist. We have endeavored to include as much detail as possible on the sites listed in Tables 5-1 and 5-2; however, as will become evident, in many cases only limited information is available. Lake disposal at Brucejack, B.C. (Newhawk Gold Mine's Sulphurets Property) is being considered for startup in 1989. Bearskin Lake at the Golden Bear Project (Noramco/Chevron) was initially considered for lake disposal but was subsequently rejected. Some information on these two projects is also included below.

5.1.1 British Columbia Mine Sites

5.1.1.1 Babine Lake (Granisle Mines)

Noranda Minerals Inc. acquired the Granisle Mine and its operating and ancillary surface facilities from Zapata-Granby Mining in the late 1970's. The mine is currently operating along with Bell Copper, and together the two mines form Noranda's Babine Division. Granisle is a copper-mineralized porphyry deposit comprised of a central bornite-chalcopyrite zone grading outwardly to chalcopyrite; a pyrite halo surrounds the copper-rich zone.

The Granisle Copper mine-mill operation is on McDonald Island in Babine Lake, with tailings ponds occupying the area between McDonald Island and Sterrett Island to the south. The mine-milling complex has a closed tailings system with discharge to the sectioned-off area of the lake and water recycled from the tailings pond for reuse in the mill. The lake is monitored in the area just off the No. 2 dam fronting east on the lake (between McDonald and Sterrett Island) and the settling dam, fronting west. A lake station, about 1 km offshore is monitored as a control.

Selected Case Studies, Lake Disposal of Mine Wastes

Lake/Mining Company or Property	Ore Type
British Columbia	
Babine	Lake
• Granisle Mines (Noranda Inc.)	Cu
Bearskin	Lake
• Noramco/Chevron Minerals Ltd. (Golden Bear Operating Co.)	Au
Benson	Lake
• Cominco's Coast Copper Mine	Cu
Brucejack	Lake
• Newhawk Gold Mines Ltd.	Au
Buttle	Lake
• Westmin Resources (Western Mines) Ltd.	Cu/Pb/Zn
Kootenay	Lake
• Cominco's Bluebell Mine at Riondel (east bank)	Pb/Zn
• Dragoon Resources at Ainsworth (west bank) ¹	Pb/Zn/Ag
Pinchi	Lake
• Cominco	Hg
Summit	Lake
• Scottie Gold Mines Ltd.	Au
St. Mary's	River/Kootenay
• Sullivan Mine - Cominco Ltd.	-
Canada	
Fox Lake, Manitoba	Cu/Ni in massive sulphides Mine
• Farley & Sherridon	
Garrow Lake, Little Cornwallis Island, N.W.T.	Pb/Zn
• Polaris Mine/Cominco Ltd.	
Mandy Lake, Manitoba	Cu/Ag/Au & S
• Mandy Mine/Hudson Bay M	
Anderson Lake, Manitoba	Cu/Zn/Pb & S
• Hudson Bay M	
International	
Silver Bay (Lake Superior, Minnesota, U.S.A.)	Fe Taconite (siliceous)
• Reserve Mining Co.	

1. Formerly David Minerals.

Selected Case Studies, Flooded Pits and Shafts

Mining Company				Ore Type	
Endako Mines Division, Placer-Dome Inc. (flooded pit)				Mo	Lake
• Fraser					
Equity Silver Mines Ltd. (flooded Southern Tail pit)				Ag	
• Houston					
Phoenix Mine (decommissioned open pit)				Cu	
• Greenwood					
Cinola	Gold,	City	Resources	(Canada)	Limited*
• Queen Charlotte Islands				Au	

*Note: Projects in conceptual stages.

Water quality monitoring data for 1976 are shown in Table 5-3. Analyses for samples taken off the face of the two dams correspond closely to those for the control station in the lake. Lake water was only moderately alkaline, with relatively low dissolved solids and low suspended solids. All metal values were low, as was sulphate, and cyanide was not detected. Overall data indicate water of high quality. The pH range for samples taken adjacent to the dams was above similar values for the control station; however values were still within the biological range. Increases in copper levels (over background) were evident in samples taken at the dam faces, but again values were still low.

The Bell Copper tailings pond is in complete recycle with mill operations and ditches collect seepage from the various dams for return to the pond. The company monitors water quality parameters at three locations in Babine Lake, immediately offshore of the two major tailings dams, fronting in the lake and in Rum Bay, and a third location some distance north, offshore from the concentrator. Surface, bottom and mid-depth waters are monitored.

Typical analyses are shown in Table 5-4. Analytical values indicate a moderately alkaline lake, of high clarity, with minimal dissolved solids and particularly low sulphate values. Monitoring for metals, both total and dissolved, has indicated low levels below the detection limits of the analytical methods. Arsenic and cyanide levels also were low. In fact, analytical values for individual parameters were virtually identical for all

Water Quality Characteristics of Babine Lake
in the Environs of Granisle Copper Operations

	East of No. 2 Dam		West of Settling Dam		WNW of Settling Dam (3/4 mile)	
	Avg.	Range	Avg.	Range	Avg.	Range
Total solids	96	66-170	83	58-120	77	58-140
Suspended Solids	9	1-36	4	1-15	3	1-11
pH	7.5	7.0-8.5	7.7	7.1-8.3	7.4	7.2-7.6
Copper	0.023	0.005-0.050	0.014	0.005-0.030	0.008	0.004-0.014
Zinc	0.016	0.001-0.025	0.008	0.001-0.015	0.006	0.001-0.010
Iron	0.010	0.005-0.050	0.006	0.005-0.011	0.007	0.005-0.012
Total cyanide	<0.2	-	<0.02	-	<0.02	-
Sulphate	6	5.8-6.2	4	3.3-6	6	3-8.3

Note: Units for all values shown are in mg/L except pH.

Water Quality Characteristics of Babine Lake in the Immediate Environs of the Bell Copper Mine-Milling Operation

	Location									
	No. 1 Dam			West of Concentrator			Rum Bay (No. 3 Dam)			
	Surface	Middle	Bottom	Surface	Middle	Bottom	Surface	Middle	Bottom	
pH	7.7	7.7	7.6	7.7	7.7	7.7	7.7	7.6	7.6	
Dissolved solids (mg/L)	60	68	47	70	66	70	55	65	62	
Suspended solids (mg/L)	1	1	1	1	3	1	<1	<1	<1	
Turbidity (JTU)	4.0	3.9	3.7	4.0	4.0	3.7	4.1	3.7	3.5	
Oil and grease (mg/L)	2.4	2.1	1.8	2.7	1.8	3.2	2.6	3.2	2.2	
Sulfate (mg/L)	3	2	3	3	3	3	3	3	3	
Cu* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Zn* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Pb* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cd* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ni* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As* (mg/L)	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02
Ag* (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
CN _T (mg/L)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

*Note: Value indicated represents results for both total and dissolved metals.

three sites and for each of the three depths at each site. Overall results do not indicate any impact on lake water quality.

5.1.1.2 Bearskin Lake, Noramco/Chevron Minerals Ltd.

North American Metals Corp. and Chevron Minerals Ltd. are joint venture partners of the Golden Bear gold project near Telegraph Creek. It is scheduled for production start-up in the third quarter of 1989 and will use combined open pit and underground mining. The 360 tonnes per day mill will use dry grinding, fluidized bed roasting and carbon-in-pulp cyanide leaching for gold recovery.

The original concept was for lake disposal of tailings, via a barge, into Bearskin Lake, although perhaps not year round (Stage I Environmental Impact Assessment, Vols. 1, 3, July 1987). Modelling and computer simulations indicated that Hg and Pb would periodically exceed water quality guidelines. When Hg and Pb metal levels exceeded allowable limits, the tailings would be sent to on-land disposal sites, which would also be used during early operation.

The objectives for the maximum concentration of metals in the lake are:

- Hg - 0.1 µg/L
- Pb - 5 µg/L (published provincial objective set in other watersheds)
2 µg/L (federal guideline)

At the time of this report, the tailings disposal concept had changed to eliminate any lake disposal of tailings.

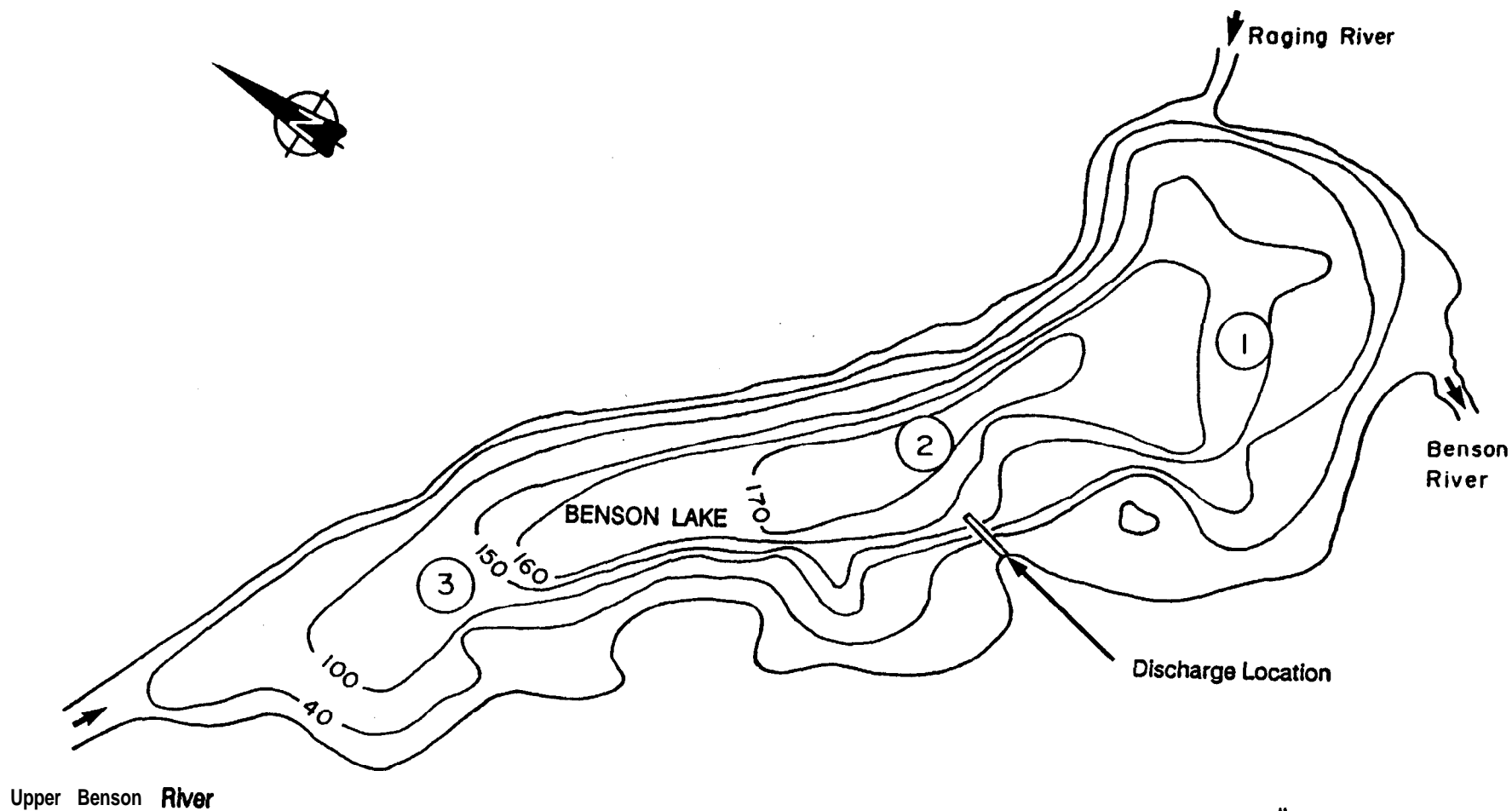
5.1.1.3 Benson Lake (Coast Copper Co./Cominco)

Cominco's Coast Copper mine, located near Port Hardy, B.C., exploited two underground deposits - Benson Lake and Coast Copper. The mine operated from August 1962 to January 1973 when it closed down because of unfavourable economics. The tonnage mined over the operating interval totalled 3.6 million tons.

Although rated at 750 tpd, the mill often processed 850 tpd. Copper concentrate was produced from high grade ore (mean grade 2.02% Cu). In March 1963, a magnetite recovery plant began operation to produce iron concentrate (64-65% Fe) from iron plant feed assaying 29% Fe. The iron plant shut down in September 1970 because sulphur content in the concentrates exceeded specifications.

The mill discharged tailings under permit into Benson Lake. Terrain constraints precluded land disposal into a conventional impoundment. Figure 5-1 shows Benson Lake bathymetry, Secchi disc stations and the initial tailings discharge location. A typical mineralogical composition of the tailings is listed in Table 5-5. From Table 5-5, the sulphur content of the tailings is estimated to be approximately 1%.

According to reports by DOE/Fisheries Service and Environment Canada/EPSPR, excessive turbidity was an immediate and lingering problem throughout the mine's operation (Benson Lake Monitoring Data (pH, Clarity/Secchi, turbidity), 1961-68). The tailings contained a slow-settling colloidal fraction that the Cominco and government reports did not identify.



A pprox Scale 1" = 1100 ft.

(All readings in feet)

March 16, 1970

② Cominco Secchi disc stations

Figure 5-1 Benson Lake Showing Contours, Secchi Disc Stations, and Discharge Location (Kussat et al., 1972)

Estimated Minerals Composition for Coast Copper Mine Tailings¹

Mineral	Estimated Percentage in the Tailings
Garnet	32.00
Epidote	27.00
Calcite	3.00
Feldspar.....	4.00
Diopside.....	0.50
Actinolite	0.50
Chlorite.....	0.50
Quartz	0.30
Sericite.....	0.30
Magnetite.....	28.80
Chalcopyrite11
Bornite.....	.10
Pyrrhotite	1.00
Pyrite.....	1.00
Unidentified.....	.89
Total.....	100.00

¹1960 Cominco internal memo.

Cominco attempted unsuccessfully to mitigate the problem through the use of flocculants. At the request of the Fisheries Service, Cominco twice moved the tailings outfall to deeper areas of the lake. A summary of these efforts is listed below¹:

Tailings Outfall Location	Dates	Ore Treated Short Tons	Lake Depth m	Downpipe Length m
Initial	Aug./62 - Sept./64	550,000	42.7	30.5
First move; 305m down lake	Sept./64 - Nov./70 plus	1,800,000	45	30.5 raft
Second move; a further 305m down lake	Nov./70 - Jan./73 (mine closed)	900,000	48.8	45

¹1967 Cominco internal memo.

Despite these measures, the turbidity problem remained, particularly during the winter months when the lake was isothermal. Extensive limnologic surveys were carried out in 1970 and 1971 in an attempt to understand the interplay between temperature stratification and turbidity in the water column. Temperature profiles collected at Stations 1, 2, and 3 in July 1970 (Figures 5-2, 5-3 and 5-4) indicated typical summer stratification with the thermocline occurring between about 7.5 and 20 m depth. Subsequent surveys outlined isothermal conditions on March 16, 1971 and again on September 9, 1971, indicating in the latter case an early fall turnover. On these dates, suspended tailings solids were found to be present throughout water column to a depth of 50 m at Station 2, and this finding was confirmed at two additional stations. An EPS report (Hallam et al., 1974) suggested that the seasonal thermocline acted as a density barrier and prevented the colloidal tailings in the hypolimnion from entering the upper epilimnion.

Subsequent homogenization of the lake water during the fall turnover promoted dispersion of colloidal tailings throughout the water column (Kussat et al., 1972). Turbidity in the lake during the winter was also influenced by the input of sediments from inflowing streams. There are no turbidity data prior to commencement of discharge in 1962 although Secchi disc readings were taken during the preceding winter.

Few physical or water quality data other than Secchi disc, temperature and pH measurements were collected during the limnologic surveys, and baseline studies prior to the mine's start-up do not exist since none were required at the time of the mine's 1962 inception. However, some dissolved metals data are available. Measurements reported by Kussat et al. (1972) suggested that the zinc level in the soft waters of Benson lake was high (Table 5-6).

Table 5-6

Mean Concentrations of Some Heavy Metals in Trout and Water from Benson and Maynard Lakes¹

Specimen	Metals	Benson Lake (ppm)		Maynard Lake (ppm)
		Water	Fish	Fish
<i>Salmo clarki</i> (cutthroat trout)	Hg	<0.00005	0.1	0.1
	Cu	<0.005	0.2	0.3
	Zn	0.06	6.5	8.5
	Pb	<0.01	0.1	0.1
	Cd		0.1	0.1

¹ Fish samples taken March 16, 1971; water sample taken February 2, 1971; heavy metal analyses by Cominco's Trail laboratory. Data from Kussat et al., 1972.

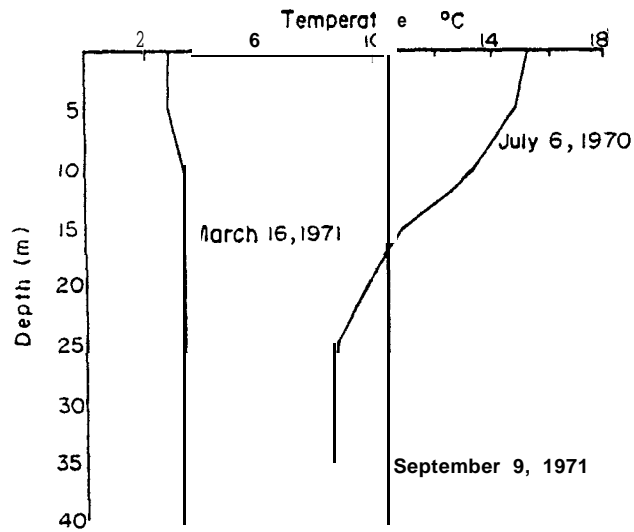


Figure 5-2 Benson Lake Thermal Stratification, Station 1 (Kussat et al., 1972)

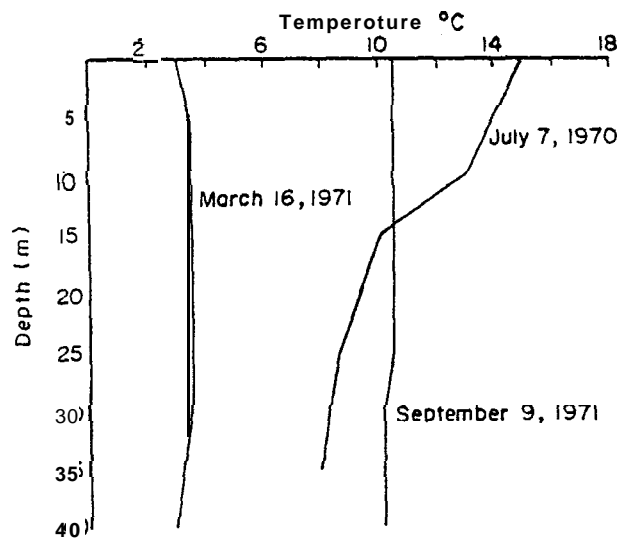


Figure 5-3 Benson Lake Thermal Stratification, Station 2 (Kussat et al., 1972)

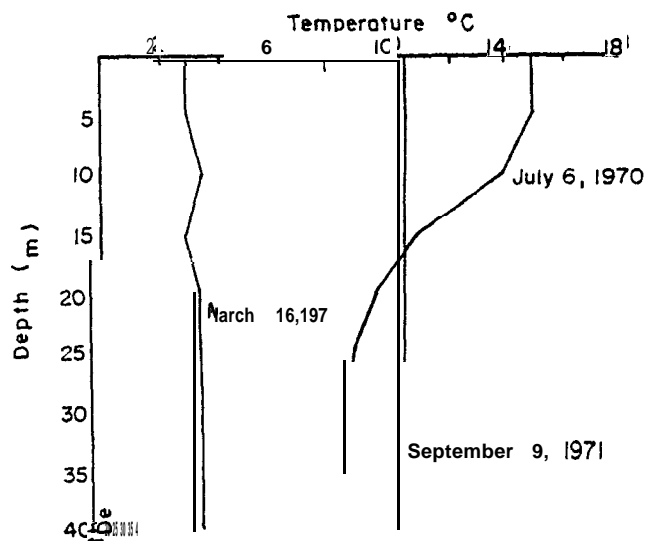


Figure 5-4 Benson Lake Thermal Stratification, Station 3 (Kussat et al., 1972)

Biological investigations were initiated in February 1967 in an attempt to document benthic fauna and determine the substrate composition in the deeper waters of Benson Lake. At that time, tailings were found to cover the entire lake bottom and there were no benthic organisms. Turbid waters were observed in the lower Benson River together with a shallow deposit of tailings fines and coexisting benthic organisms.

No significant difference was observed in heavy metal content between cutthroat trout (*Salmo clarki*) samples collected in 1971 from Benson and Maynard Lakes (Table 5-6), despite the fact that the latter, a dammed lake immediately upstream of Benson Lake, was not influenced by mining activity (although its watershed has been logged extensively). The small sample size, however, (two trout per lake) rendered the comparative results inconclusive. The coincidence of the high zinc levels in both fish tissue and the soft water in Benson Lake, coupled with recognition that soft waters enhance metal toxicity to aquatic organisms and previous observations of high zinc levels in Benson River water, led to a recommendation for increased monitoring. In November 1973, after the fall turnover and some ten months after closure of the mine, EPS conducted a survey of Benson Lake to determine physical and chemical characteristics, and to assess impacts to the biota (Hallam et al./EPS, 1974). A marked reduction in turbidity was noted, although total metal concentrations in lake water and fish tissue were unchanged between 1971 and 1973. No significant bioaccumulation in the food chain of heavy metals contained in the tailings appeared to be occurring.

5.1.1.4 Brucejack Lake (Newhawk Gold Mines Ltd.)

The Sulphurets property is a joint venture between Newhawk Gold Mines Ltd. (NPL) and Granduc Mines Ltd., both of Vancouver. The property is located 56 km northwest of Stewart in northwestern B.C.

Brucejack Lake is located in the southeastern corner of the claims area at an elevation of 1376 m. The lake is on a high plateau above the timberline and is ice-bound most of the year. The total surface area of the lake is 81 ha with a length of 1300 m and an average width of 623 m. The lake is 88 m deep at its deepest point, located close to the centre of the lake. The total storage volume of the lake is approximately 29 million m³.

Underground mining is planned at a production rate of 318 tonnes/day. Precious metal recovery will be accomplished utilizing gravity concentration followed by flotation of a silver-rich sulphide concentrate.

As tailings and waste rock were found to be potentially acid generating and because of a limited amount of suitable land, tailings and waste rock will be disposed of underwater in Brucejack Lake. The tailings, together with mine water, will be deposited using a submerged outfall located at depth (65 m) in the eastern basin of Brucejack Lake.

Tailings solids are expected to settle on the lake bottom at a maximum slope of 2% in the deepest areas of the lake. Total tailings production from existing reserves is expected to be 550,000 t with 50% of the tailings solids being used for backfill in the mine. The first site to be used consists of a small embayment adjacent to Brucejack Creek which will be flooded following the installation of a hydroelectric intake dam on Brucejack Creek. The second site selected consists of a small bay located in the northwest corner of Brucejack Lake. Dumping in this area will be restricted to a 5 month maximum open water period. An average 97 m³/hr combined tailings fines and mine water will be gravity fed at approximately 6.9% solids to the submerged tailings outfall.

Results from extensive laboratory testing of tailings supernatant and solids components, including particle size distribution, metal analyses of tailings fractions and settling velocities were used as input parameters to a one-dimensional finite difference model of Brucejack Lake for purposes of predicting the effects of deep lake tailings disposal. The model used available estimates of minimum lake inflows, non-settleable particulates and associated metal levels, together with conservative estimates of relevant dispersive processes.

The suspended sediment model was run for a simulation period of 8 years to encompass the estimated life of the mine, and predicted a generally increasing sediment concentration leaving Brucejack Lake through the first five years or so of operating the tailings disposal system. After this, the average annual concentrations levelled off suggesting an equilibrium had been reached.

On an annual basis, the modelled sediment concentrations exhibited two distinct phases. The first occurred at the autumn turnover when the sediment concentrations increased markedly. The concentrations then remained approximately constant over the winter and spring during the period of low inflow. The second phase occurred when high summer runoff diluted the outflow concentrations to near background levels. The outflow concentrations then increased marginally up to the autumn turnover event.

During the final year of simulation the peak suspended sediment concentration was modelled at 13 mg/L, or roughly half the MMLER guidelines value of 25 mg/L. The particulate concentrations of eight metals (As, Cu, Fe, Pb, Hg, Mo, Ag and Zn) were also predicted using the model. Table 5-7 lists the peak concentrations and flow-weighted average annual concentrations leaving the lake during the final year of simulation.

The behaviour of the particulate metal concentrations followed similar time distribution curves to the suspended sediment concentrations. The difference in outflow concentrations between the summer and winter periods is dependent on the relative metal concentrations of the creek inflows and the tailings discharge.

The modelling of lake tailings disposal demonstrated that outflows from Brucejack Lake will meet both federal and provincial effluent quality criteria on a consistent basis. On the basis of combined worst case scenarios for discharge quality and available dilution in the receiving environment, only total particulate iron, lead, silver and copper would be above the Canadian Council of Resource and Environment Ministers (CCREM) recommended guidelines for protection of freshwater aquatic life in Sulphurets Creek.

5.1.1.5 Buttle Lake (Westmin Resources Ltd.)

The discharge of mill tailings into Buttle Lake from Westmin's Myra Falls mine in B.C.'s Strathcona Provincial Park represents a recent mining operation which has used subaqueous lacustrine tailings disposal. The lake is the domestic water source for the town of Campbell River, which is roughly 93 km from the mine. Pedersen and Losher (1988) reported on prior studies of chemical behaviour of Buttle Lake tailings; their review has been supplemented below by recent information published by the B.C. Ministry of Environment and Parks (Deniseger et al., 1988).

Buttle Lake is a large (30 km long by 1.5 km wide) lake which occupies a U-shaped valley in an area of high relief on Vancouver Island. The south basin of the lake reaches a maximum depth of 87 m, and during 1967 to 1984 received tailings via a slightly submerged outfall. A relatively shallow sill 5 km north of the discharge site effectively limits physical dispersion of the deposited material. By 1984 when tailings disposal ceased, nearly 5.5 million tons of mill tailings had been deposited into the lake. Tailings are currently being disposed on land.

Table 5-7

**Simulated Metal Concentrations at Outlet of Brucejack Lake
After 8 Years of Operating the Tailings Disposal System**

Metal	Peak Concentration (µg/L)			Flow-weighted Average Annual Conc. (µg/L)			Provincial Objectives (µg/L)	MMLER (µg/L)
	Particulate	Dissolved	Total	Particulate	Dissolved	Total		
Arsenic	3.0	2.6	5.6	2.8	2.5	5.3	100 - 1000	500 - 1000
Copper	4.4	1.1	5.5	3.2	1.1	4.3	50 - 300	300 - 600
Iron	630	36	670	550	35	590	300 - 1000	-
Lead	13	0.64	14	9.0	0.61	9.6	50 - 200	200 - 400
Mercury	0.013	0.10	0.11	0.010	0.084	0.094	0 - 5	-
Molybdenum	0.14	1.5	1.6	0.10	1.4	1.5	500 - 5000	-
Silver	2.0	0.13	2.1	1.4	0.12	1.5	50 - 500	-
Zinc	7.7	5.8	14	5.6	5.6	11	200 - 1000	500 - 1000

Westmin's operations at Myra Falls includes the HW, Lynx, Myra and Price mines, which contain recoverable quantities of copper, lead, zinc, gold, silver, and cadmium. Open pit and underground mining of the Lynx deposit began in 1966 with milling commencing at the 750 tpd Lynx mill. Since that time, mill capacity has been increased several times to the current 4400 tpd. The mill process uses conventional crushing and grinding followed by selective differential flotation where separate copper, lead and zinc concentrates are produced.

After concentrator startup in December 1966, tailings were discharged to a small nearby pond; however, Westmin obtained a permit in 1967 to discharge tailings to the bottom of Buttle Lake. Cyclones removed the sand-sized material in the underflow for use as backfill in the underground mine. Under gravity, cyclone slime overflow, at 7 to 10% solids, passed through seven vertical drop boxes to a tailing raft several hundred feet off shore, and were discharged via a submerged outfall that extended below the thermocline. Flocculant was used to assist solids to settle to the lake bottom, which was about 35-50 metres deep at the discharge point.

The tailings originated from the zinc circuit after milling of the high grade copper-lead-zinc ore and consisted of sand-sized and silt-sized silicate gangue minerals and residual copper, iron, lead and zinc sulphides. Heavy metal concentrations in the tailings solids ranged widely but averaged 7000, 1300 and 900 mg/kg for Zn, Cu and Pb respectively.

Lime (CaO) was the only reagent used in significant quantity; approximately 1.0 kg/t ore was added to the tailings to raise the pH in the milling circuits and to enhance coagulation in the thickening tanks (Eccles, 1977). During the initial six years of operation, with ore from the Lynx Mine, dissolution of heavy metals in the milling circuit was minimal due to the high pH and extremely low solubility of metal sulphides. In June 1970, the mill began limited production of lead ore (galena), and in early 1973, this was increased when high-lead ore from Myra Falls came on-line. Because production of a copper concentrate with a low lead content was required, cyanide was used in the continuous copper-lead separation circuit. This resulted in substantially increased levels of cyanide and dissolved copper in the effluent (at high pH, copper complexes with cyanide). Consequently, Westmin introduced alkaline chlorination to destroy residual cyanide and to precipitate dissolved copper in the tailings. Table 5-8 compares effluent before and after chlorination.

Table 5-8

Comparison of Tailings Entering Buttle Lake Before and After Commencing Treatment

	Maximum Permit Levels	Jan.-June 1973 No Chlorination Plant	July-Dec. 1973 Chlorination Plant in Full Operation
Total Solids	138,800 mg/L	*	70,500 mg/L
pH	6.0 to 10.0	7.7	9.74
Dissolved Copper	0.3 mg/L	2.85 mg/L	0.09 mg/L
Dissolved Lead	0.1 mg/L	0.17 mg/L	0.08 mg/L
Dissolved Zinc	5.0 mg/L	3.27 mg/L	0.43 mg/L
Dissolved Sulphate	1000 mg/L	*	380 mg/L
Total Cyanide	0.5 mg/L	4.72 mg/L	0.18 mg/L
Total Chlorine	-	-	0.1 mg/L

*Not recorded.

Source: SENES/Knapp, 1981 (unpublished).

Some water quality and sediment chemistry data for Buttle Lake are available. Pedersen (1983) discussed the distribution of dissolved Zn, Cd, Cu, Mn and Fe in pore waters extracted by centrifugation under nitrogen from four cores collected from both tailings and natural sediments in the south basin of Buttle Lake (Table 5-9). Concurrent with this investigation, dissolved Zn and Cu levels in the overlying lake water were very high and it was speculated that remobilization of metals from the deposited tailings was the cause. It was later realized that high metal concentrations in Buttle Lake were due to inflow from Myra Creek, which was draining a waste rock dump containing sulphide-rich wastes. Metal concentrations in the creek water averaged 600 µg/L Zn, 40 µg/L Cu and 1.4 µg/L Cd, in July 1981 (B.C. Research, cited in Pedersen 1983).

Although the sediment cores exhibited pore water metal concentrations which ranged widely, it is clear from the data in Table 5-9 that diagenetic remobilization of metals was not substantial; in fact, metal concentrations in the tailings pore waters were much lower than in the overlying lake water. In the interstitial waters of natural sediments

Dissolved Interstitial Metal Concentrations in Buttle Lake Cores, Measured by Graphite Furnace AAS (Data from Pedersen 1983)

Core	Sample Depth (cm)	Dissolved Metal Concentration (µg/L)				
		Zn	Cd	Cu	Mn	Fe
B1	0-3	35	<0.5	15.6	170	24
	3-6	20	<0.5	8.0,8.3	130	18
	6-10	27	<0.5	13.4,13.1	140	16
	10-14	31,31	<0.5	3.4	170	72
	14-19	34	<0.5	2.2	210	34
	25-30	36,37	<0.5	5.0	550,560	23
	35-40	26	<0.5	0.5	114	13
	45-50	23	<0.5	1.9	90	29
B2	0-3	34	<0.5	5.6	650	42
	3-6	34,34	<0.5	6.3	800	62
	6-10	13	<0.5	4.2	630	30
	10-14	19	<0.5	5.9	370,350	15
	20-25	23	<0.5	0.7,0.9	650	36
	35-40	26	<0.5	6.2	350	13
	55-60	29	<0.5	6.5	290,300	15
	78-83	30	<0.5	4.4	280	39
B3	0-3	33,31	2.7,2.1	13.2,13.1	3190,3120	42
	3-6	6.4	<0.5	2.0	2740	32
	6-10	78,79	<0.5	2.0	2240	23
	10-14	35	<0.5	4.7	2390	38
	20-25	28	<0.5	1.1	1610	58
	30-35	5.8	<0.5	<0.5	580	481
	45-50	42	<0.5	0.5	520	111
	60-65	<3.0	<0.5	<0.5	7400,7330	1550
B4	0-6	22,20	<0.5	<0.5	12100	8700
	5-10	21	<0.5	<0.5	26900	13900
	10-15	7.4	<0.5	<0.5	24900,25000	9300
	30-35	<3.0	<0.5	<0.5	44800	12900
Lake bottom water 54m		170 depth,	1	11 near	-	- B2
Lake bottom water 87m		230 depth,	0.4	15 near	-	- B4

Source: Pedersen and Losher, 1988.

(core B4) the Zn concentration decreased rather sharply with depth, indicating that the metal was being incorporated into an authigenic precipitate.

Pedersen (1983) concluded that several factors controlled these distributions. First, oxidation of the tailings on the lake bottom was not occurring, presumably because the rate of discharge was sufficient to bury the deposits continuously and quickly, thus minimizing the time of exposure to dissolved oxygen in the bottom water. Because Zn and Cu oxyhydroxides are much more soluble than their sulphide counterparts, oxidation of the detrital sulphides in the tailings would release metals to interstitial solution. An example of this phenomenon is shown in Table 5-10. Water which was allowed to accumulate by dewatering on the tops of two of the Buttle Lake cores showed significantly higher Zn and Cu concentrations after the tailings had been exposed to air for 8-11 h. The absence of any similar increase in dissolved Zn, Cu or Cd concentrations with depth in the tailings cores (Table 5-9) confirmed that the tailings were relatively unreactive on the lake bottom. There was no evidence that progressive oxidation with concomitant metal release was occurring.

Table

5-10

Zn, Cd and Cu Concentrations in Supernatant Water Immediately After Core Collection (A) and After 8-11 h of Partial Exposure of the Tailings on the Top of the Cores to Air (B)

Core	Dissolved Metal Concentration (µg/L)			
	Zn	Cd	Cu	
B1	(A)	22,20,20	<0.5,<0.5	0.8
	(B)	56,56	1.0,1.0	14.6,14.8
B2	(A)	44	<0.5	5.2
	(B)	117	<0.5	12.0,13.9

Source: Pedersen and Losher, 1988.

Secondly, the absence of detectable dissolved Zn or Cu in the natural sediments underlying the tailings in core B3 and the decreasing Zn gradient in core B4 indicated that these metals were diffusing into the natural sediments from the overlying metal-rich lake water and were being removed from solution, presumably by incorporation into authigenic sulphide minerals. Support for this contention is given by the associated increase of dissolved Mn and to a lesser extent, Fe (Table 5-9). Because manganese and iron oxyhydroxides serve as preferred electron acceptors after oxygen and nitrate have been depleted (Chapter 3), their presence at high concentrations in solution in the uppermost sample in core B4 is evidence that anoxic conditions are established at shallow depths in the natural sediments. Iron sulphide precipitation in this facies is of course limited by the scarcity of reducible sulphate, but is nevertheless indicated by the decreased Fe concentration at depth in B4 relative to the steadily increasing dissolved Mn level.

The Buttle Lake study demonstrated clearly the tailings were not diagenetically reactive while deposition was proceeding at a high rate. In this type of example, the key factor which mitigates against release of metals is the high sedimentation rate, which places a strong limit on the amount of oxygen which can diffuse into the tailings from bottom water to support oxidation of detrital sulphide minerals. As the data in Table 5-10 demonstrate, oxidation with associated metal release can occur quite rapidly in the presence of high oxygen concentrations. Therefore, metal remobilization from the lacustrine tailings could occur in the period following cessation of discharge but preceding burial by subsequent natural sedimentation. In the south basin of Buttle

Lake, the natural sedimentation rate measured at a representative site using ^{210}Pb data is about 2 mm/yr (Table 5-11). In the same core the solid-phase Mn concentration decreases sharply between 0 and 3 cm depth (Table 5-11), indicating solubilization at depths below 1 cm. This distribution is consistent with the pore water data in core B4. Assuming that the data from both cores are representative of the natural sediments in the basin in general, then it can be suggested logically that the tailings would become covered with a veneer of natural sediments, anoxic at a shallow depth, within 15 to 20 years following the cessation of discharge. At that point the metal-rich deposit would, in effect, become chemically sealed with respect to upward diffusion of metals from the previously oxidized, but now buried tailings.

Deniseger et al. (1988) have recently reviewed the effects of increased heavy metal levels in Butte Lake water on indigenous biota during the subaqueous discharge phase of the mine operations, and have discussed the recovery of the biota during the period 1983-1986. This three-year study period mostly postdates collection and treatment of the leachate from the waste rock dump near Myra Creek (which commenced in 1983) and cessation of lacustrine discharge in July, 1984. An abbreviated summary of their report is presented below.

²¹⁰Pb (supported and unsupported) and Zn Concentrations in Sediments from Core B8

Depth in Core (cm)	²¹⁰ Pb (dpm/g)	Zn (µg/g)	Mn (µg/g)
0-1	12.7 ± 3.3	3800	10400
1-2		4100	4410
2-3	9.8 ± 2.7	740	-
3-4		184	2170
4-5	5.6 ± 3.3	142	-
5-8		128	2100
8-11	4.7 ± 2.7	-	-
11-15		135	2030
15-20	0.0 ± 4.6	-	-
30-35	0.0 ± 4.0	-	-

Source: Pedersen and Losher, 1988.

Metal levels in the lake reached approximately steady-state maximum concentrations in 1981. At that time, elevated levels of hepatic metallothionein measured in rainbow trout livers in Buttle Lake and in lakes immediately downstream were shown to correlate well with mean dissolved zinc levels in the individual basins (Roch et al. 1982; Roch and McCarter, 1984). Zinc concentrations as high as 440 µg L⁻¹ were measured in the south basin of the lake during that period.

Major changes were observed in the zoo- and phytoplankton populations as metal loadings increased, including decreasing numbers of cladocerans and calanoid copepods, and an altered phytoplankton species composition. By the early 1980's, zooplankton species such as *Leptodora kindtii*, *Holopedium gibberellum*, *Polyphemus pediculus* and *Daphnia* spp. were essentially absent. By the late summer of 1985, when metal levels had fallen by a factor of roughly 4-5 from their peak in 1981, these species had reappeared. By 1986, species composition and diversity were similar to those sampled in 1966-67 (Whately, 1969, cited in Deniseger et al., 1988). This improvement is commensurate with falling metal levels in the lake, although it should be noted that contrary to expectations, dissolved metal concentrations have yet to decline to their pre-mine levels.

Similar changes were noted in the phytoplankton community. The dominant association of *Rhizosolenia/Asterionella/Tabellaria/Ceratium/Peridinium* seen in 1966-67 was significantly different by 1980 (Deniseger et al., 1988). *Rhizosolenia eriensis*, for example, essentially disappeared from the south basin waters where metal concentrations were highest. This species remained scarce until late 1983. Massive blooms of *R. eriensis* persisted from mid-1984 to mid-1985, possibly in response to an observed increase in the NP ratio which may have accrued from increased discharge to the lake of explosives residues, sewage and eroded soil as the mine expanded in the mid-1980's. In addition, *R. eriensis* appears to be more tolerant to metals than other species, and the 1984-85 bloom may have reflected a transitory competitive advantage while metal concentrations were falling but were still relatively high (Deniseger et al., 1988).

Decreasing hepatic metallothionein levels in fish and increasing diversity of plankton demonstrate that biological stress has been significantly reduced in Buttle Lake. However, Deniseger et al. (1988) note that Cu and Cd levels in fish livers remain relatively high. Although injection of dissolved metals into the lake from Myra Creek has been much reduced since 1983,

concentrations in creek water, and thus the lake, have not yet reached background levels. The phytoplankton community will apparently require further improvements in water quality before the species composition can return to its pre-mine state.

5.1.1.6 Kootenay Lake (Cominco's Bluebell Mine) Riondel (Pb, Zn, Ag)

The Bluebell mine at Riondel on Kootenay Lake's east shore was for many years a major high-grade lead-zinc operation which also produced significant silver, cadmium, copper and gold. Tailings containing up to 10% zinc, in addition to arsenic (in arsenopyrite, FeAsS) were discharged directly into the lake. Although no acid generation testwork on the mine wastes was available, it is expected that these wastes were acid generating since the ore was a massive sulphide deposit. During the 1930's the Bluebell mine had several different owners, but Cominco operated the mine during its maximum production period from 1952 until it closed in 1972 (Kuit, 1989; Environment Canada/IWD: Daley et al., 1981; Douglas, 1984). In the 1960's, Cominco, and recently others have sampled deposited tailings and conducted bathymetric surveys to evaluate the feasibility of further metal recovery. Most of the tailings are likely dispersed over a wide area of the lake bottom, however, because the slopes are steep.

Small scale mining activity began in the Kootenay Lake area in 1890 (Environment Canada/IWD: Daley et al. 1981). Almost all mines and concentrators around Kootenay Lake disposed of their waste rock, mill tailings and mine drainage water (sometimes softened with polyphosphates) directly into the lake. In the Ainsworth and Riondel areas, tailings and waste rock containing iron and arsenic minerals from lead and zinc ores were also dumped into the lake.

At the Bluebell mine, Cominco mined 4.8 million tons of ore during the 20 year operating period. Waste rock was dumped into the lake to build a breakwater used to shelter a marina. Barges carrying concentrate from Riondel to Proctor also routinely dumped concentrate into the lake when they were cleaned and swept. In addition, four rail cars carrying high grade Pb and Zn concentrates from a Cominco barge spilled their cargo into the bay near Riondel in the mid 1960's.

Because of the history of metal mining activity adjacent to Kootenay Lake, several studies in the late 1970's attempted to gather data to assess the impact of waste dumping on sediment geochemistry and the distribution of metals within lake waters (Daley et al., 1981; Chamberlain and Pharo, 1981). Some key findings from the 1979-80 Kootenay Lake study are outlined below.

Overall metal concentrations in lake water were found to be low and reflected background concentrations. Concentrations of certain metals were slightly higher near the centre of the lake, possibly due to wastes from the Pilot Bay smelter.

Sediment core profiles showed strong enrichments of Pb, Zn, Ag, Cd and As in surface layers, directly indicating the presence of mine wastes in the lake. Comparative data shown in Table 5-12 illustrate the magnitude of the enrichments relative to other lakes.

Metal concentrations in the flesh of fish from the lake were also low. These observations are also consistent with the results of leaching experiments performed on the enriched surface sediments which suggested that, despite the high concentrations, the metals were not readily bioavailable. However, Pharo (1989) admitted that the design of the extraction test procedure did not provide firm conclusions regarding potential accumulation of heavy metals in the food chain. Evans and Lasenby (1983) and Vanduynd-Henderson and Lasenby (1986), in contrast, suggested that there may indeed be some transfer of metals from sediments into the food chain (Lasenby, 1989). It appears that further work is warranted in order to confirm or refute this suggestion.

Table 5-16

Description of Bore Hole Five (BH5), Sherridon Tailings, Beneath Fox Lake¹

Sample	Length (inches)	Depth (feet)	Grain Size	Comments	Extent of Sulphide Oxidation	Authigenic Minerals
BH5-1	0-6	(0)	Sand	Pine needles, plant remains:	35-40%	
5-2	6-12		Sand	Loose	20-25%	Jarosite,
5-3	12-16		Sand	Loose	15-20%	Goethite,
5-4	16-20		Sand	Loose	10%	Gypsum
BH5-5	20-26		Sand	Compacted, dense	30-35%	
5-6	26-32		Sand	Compacted, dense	15-20%	Goethite,
5-7	32-38		Sand	Compacted, dense	25%	Jarosite,
5-8	38-42.5		Sand	Compacted, dense	25-35%	Gypsum
BH5-9	42.5-48.5		Sand	Compacted, dense	25-30%	
5-10	48.5-54.5		Sand	Compacted, dense	30%	Goethite,
5-11	54.5-60.5		Fine sand	Compacted, dense	25%	Jarosite,
5-12	60.5-66.5		Fine sand	Compacted, dense	25%	Gypsum
BH5-13	66.5-72.5		Sand, silt	Laminated interlayered sand and	sand 15-20%	
5-14	72.5-78.5		Sand, silt	silt; appreciable sphalerite, trace chalcopyrite	silt < 10%	Gypsum
5-15	78.5-84.5		Sand, fine sand	Compacted, dense	15-20%	Jarosite,
5-16	84.5-90.5		Fine sand	Compacted, dense		Goethite
BH5-17	90.5-96.5		Silt, fine sand	Compacted, dense		
5-18	96.5-111.5		Silt	Compacted, dense	< 5-10%	Anhydrite*
5-19	111.5-116.5		Silt	Compacted, dense		(trace Jarosite,
5-20	116.5-121.5		Silt	Compacted, dense		Goethite)
BH5-21	121.5-126.5	(21)	Silt, mud	Lake bottom sediment, no sulphide	N.A.	
5-22	-	21-26	Silt, mud	Lake bottom sediment, no sulphide	N.A.	Gypsum

Crude layering is common in most samples. The first 21 feet of drilling through slurried tailings yielded 126.5 inches of compacted core. LENGTH refers to the length of core sample; DEPTH refers to the actual extent of drilling. The extent of oxidation of the sulphide minerals, pyrite and pyrrhotite with sporadic sphalerite and rare chalcopyrite, is visually estimated. Authigenic minerals are listed in approximately order of abundance.

*Anhydrite is reported from Cu-Zn mines in the Lynn Lake area, and may not be an authigenic phase.

¹From Kennedy and Hawthorne 1987.

5.1.1.7 Kootenay Lake (Dragoon Resources Ltd., formerly David Minerals) Ainsworth (Pb, Zn, Ag, Au)

David Minerals, an underground operation with a 135 tpd flotation mill, deposited untreated tailings with a pH of 9.1 directly into Kootenay Lake. Although little information has been located, it is known that liquid effluent quality guidelines were not being met in 1982.

5.1.1.8 Pinchi Lake (Cominco Ltd.)

Cominco's Pinchi Lake mercury mine, located 15 miles from Fort St. James, has undergone two periods of operation; the first during World War II, and subsequently from 1964 to 1972.

Mineral processing included a roasting step to form a calcine that was discharged into the lake; tailings were impounded. Since the mine opened before there were environmental regulations, no pre-operational baseline or background data exists.

Although no studies were done on the calcine, mercury has a low sublimation temperature (583°C) and roasting of mercury ores is known to be quite efficient. Consequently, it is unlikely that substantial quantities of mercury remained in the calcine that went into the lake. Additional information on the handling and disposal of mine waste was not located.

Due to depressed mercury prices, operations were suspended in 1975. Cominco still holds the property and there is on-going water quality work on downstream receiving waters to monitor existing mine and mill waters for mercury (Kuit, 1989; Canadian Mines Handbook, 1988-89).

5.1.1.9 St. Mary's River/Kootenay River (Sullivan Mine - Cominco Ltd.)

A survey of the St. Mary's River - Kootenay River system was conducted during 1965 and 1966 to evaluate the impact of wastes from Cominco's Kimberley Mine and fertilizer plant on fish and other aquatic organisms. Large quantities of iron and acid wastes were being discharged directly from the mine operations into upper Mark Creek, and the Marysville fertilizer plant routinely released gypsum into lower Mark Creek, and ultimately the St. Mary's River. In addition, the Sullivan concentrator-impoundment wastes flowed into Cow Creek, which emptied into the St. Mary's River (Cominco Amendments to Pollution Control Permit PE-189, November 23, 1982). Deleterious effects of these effluents on the biota were suspected but had not been extensively researched. The results of the Sinclair survey are summarized below (Sinclair, 1966).

Although the water quality of the St. Mary's River was excellent above Mark Creek, extremely toxic conditions existed in the St. Mary's River at a station below Mark Creek. Fish exposed to these conditions died within 48 hours. Similarly, there was an absence of benthic fauna in Mark Creek below the Sullivan operations, and in the St. Mary's River below Mark Creek when the benthic fauna upstream of contamination sources was abundant and healthy. Bottom fauna were extremely sparse as far as 15 km downstream of the confluence of Mark Creek with the St. Mary's River and it appeared that mine effluents had killed fish food organisms and greatly reduced native populations of cutthroat and rainbow trout, mountain whitefish and Dolly Varden char. Even 40 km downstream from the Cominco plant in the Kootenay River, the important food organisms were significantly diminished although the large dilution flows in the Kootenay had reduced toxicity.

Water and sediment sampling indicated high quantities of gypsum and other foreign materials in the St. Mary's River, with gypsum deposits 10-14 cm deep in the river bottom at Wycliffe. High concentrations of lead, zinc, and fluorides, all extremely toxic to fish, were also noted, along with significant turbidity and discoloration.

5.1.1.10 Summit Lake (Scottie Gold Mines Ltd.)

Summit Lake is a 180 tonne per day underground gold mine. The mine and mill are located at Summit Lake, approximately 32 km north of Stewart, B.C.

The lake is an ice-dammed glacial body of water lying at the head of Salmon Glacier at an elevation of approximately 823 m. The entire volume of the lake has discharged under Salmon Glacier into Salmon River numerous times. As the ice dam has retreated and thinned, the lake discharge has become an annual fall event.

The tailings pond was constructed below the historical high-water table, hence it is inundated with lake water during the latter stages of the fill cycle (May-August). At other times of the year, the tailings remain in a saturated state since the groundwater is essentially at the surface.

The tailings were demonstrated to be acid generating, which reflected the high pyrite and pyrrhotite composition of the ore. The sulphide content of the tailings was not determined, however, tests on the waste rock showed the rock to be acid consuming. All waste rock was utilized for fill and road construction.

Typical deposited tailings characteristics are shown in Table 5-13 for three locations. No recent water quality data were found; however 1979 water quality are presented in Table 5-14.

Table 5-13

Deposited Tailings Characteristics in Summit Lake

		Location		
		Near spigot	30 m below break	60 m below break
Aluminum	Al	23600	19100	24600
Arsenic	As	1620	3000	637
Barium	Ba	19.5	18.7	30.2
Beryllium	Be	<0.2	<0.2	<0.2
Calcium	Ca	35300	31300	64200
Cadmium	Cd	22.1	51.6	20.9
Cobalt	Co	205	354	135
Chromium	Cr	17.9	13.3	22.3
Copper	Cu	691	1100	908
Iron	Fe	163000	244000	152000
Mercury	Hg	<0.008	<0.008	<0.008
Magnesium	Mg	18100	14700	18200
Manganese	Mn	1590	1430	1720
Molybdenum	Mo	8.6	<0.8	34.8
Sodium	Na	60	70	120
Nickel	Ni	<3	7	<3
Phosphorus	P	1080	1090	1190
Lead	Pb	750	1340	759
Silicon	Si	890	780	1850
Tin	Sn	<2	<2	<2
Strontium	Sr	44	41.7	84
Titanium	Ti	1670	1350	1530
Vanadium	V	167	153	179
Zinc	Zn	1750	2960	1710

Note: All values expressed in ug/g.

The mine and surface streams were of relatively good quality; Summit Lake was typical of a glacial lake with high turbidity and solids.

Water Quality at Scottie Gold, 1979

	Mine Water	Creek Water at Summit Lake Camp	Summit Lake
pH	7.90	6.45	7.10
Conductivity (micromhos/cm)	223.	16.4	56.6
Turbidity (JTU)	2.8	2.1	380.
Total Suspended Solids (mg/L)	12.2	0.6	35.2
Dissolved Sulphates SO ₄ (mg/L)	44.0	6.0	10.0
Dissolved Iron Fe (mg/L)	<0.030	<0.030	0.047
Dissolved Cadmium Cd (mg/L)	<0.001	<0.001	<0.001
Dissolved Copper Cu (mg/L)	<0.001	<0.001	<0.001
Dissolved Lead Pb (mg/L)	<0.001	<0.001	<0.001
Dissolved Zinc Zn (mg/L)	0.002	0.004	0.002
Dissolved Antimony Sb (mg/L)	0.024	<0.003	<0.003
Dissolved Arsenic As (mg/L)	0.009	<0.001	<0.001
Dissolved Cobalt Co (mg/L)	<0.005	<0.005	<0.005
Total Mercury Hg (mg/L)	<0.0002	<0.0002	<0.0002

5.1.2 Other Canadian Mine Sites

5.1.2.1 Fox Lake (Farley and Sherridon Mines, Sherritt Gordon Mines Ltd.)

Sherritt Gordon Mines Ltd. intermittently operated the Fox Lake copper-zinc- gold-silver mine from 1930 to 1952. On average, 3,000 tpd were milled during this period. Although it is known that both on-land and subaqueous tailings disposal into Fox Lake were used, subaqueous disposal is thought to have been practiced only during the last few years of operation (1949 to 1952). Information on the quantity and mineral composition of the tailings is also scarce. Kennedy and Hawthorne (1987) studied the high sulphide tailings which were disposed on-land and those which were submerged, and attempted to compare the identity and character of the authigenic minerals, the extent of sulphide mineral oxidation and the identity and composition of altered and unaltered silicate minerals.

Little is known about the tailings sampling procedures and techniques which were used for this study; apparently, field notes were not taken. From the Farley and Sherridon tailings disposed on-land, five samples, including hardpan and material which was poorly consolidated and thoroughly oxidized, were selected and examined. Of the submerged tailings, 22 samples from a single borehole (BH5) were recovered from the tailings submerged in Fox Lake. Both tailings samples were screened into their >200 and -200 mesh fractions. A magnetic component was also recovered from selected sand fractions. Unfortunately, no pore water samples were recovered from the submerged tailings.

Cold mount epoxy impregnation was used to prepare the samples as polished thin sections. Samples were subsequently analyzed using optical and electron probe analysis of minerals within the thin sections and optical examination under transmitted and reflected light microscopy. Powder X-ray diffraction (XRD) was also used to examine the different size fractions of the oxidized land tailings samples, as well as those of the submerged tailings samples. Where XRD was not successful due to sample size, a Gandolfi camera was used to obtain powder diffraction patterns.

Tables 5-15 and 5-16 illustrate the general mineralogy and texture of both the oxidized land-disposed tailings and the submerged deposits in Fox Lake. Silicate minerals comprised 65-75% of both the land and underwater tailings. Phlogopite and biotite mica were predominant in the underwater tailings. The land tailings contained quartz (25-30%), albite (plagioclase) and potassium feldspars, and small amounts of magnesium-rich chlorite, hornblende, biotite, phlogopite and muscovite.

In the land-disposed tailings, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), jarosite [$\text{K Fe}_3(\text{SO}_4)_2\text{OH}_6$], goethite (FeOOH) and analcite, $\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$ are the principal authigenic minerals present in the hardpan. Authigenic minerals are those derived from the oxidation of sulphides and percolation of acid-bearing solutions. Goethite and jarosite are the main cementing ingredients. Hardpans in land tailings are an indication of incomplete oxidation of relict sulphides (pyrite and pyrrhotite); thoroughly oxidized tailings contain no sulphides, due to their dissolution into percolating porewaters, and as a result are poorly cemented.

On-land tailings rarely contained the mica-type minerals biotite and phlogopite. This is attributed to the oxidation of sulphide minerals and associated generation of sulphuric acid, which reacts with the mica-type minerals, altering them to finely interlayered clay

Table 5-12

Background (A) and Maximum (B) Element Concentration (ppm) and the Ratios of B/A (= F, a Sediment Enrichment Factor) in a Core from Kootenay Lake Compared with Other Lakes

Element (ppm)	Lake Constance ¹			Lake Michigan ¹			Lake Monona ¹			Lake Erie ¹			Lake Erie Western Basin ²			Kootenay Lake Core F ³		
	A	B	F	A	B	F	A	B	F	A	B	F	A	B	F	A	B	F
Cu	30	34	1	44	75	1.5	22	268	12	18	58	4	6	75	12	48	206	4
Pb	19	52	3	40	145	3.5	14	124	9							28	2400	86
Zn	124	380	3	129	317	2.5	15	92	6	7	42	6	20	225	11	157	1880	12
Ag																0.1	4.4	44
Fe(%)													1.0	2.3	2.3	4.62	6.15	1.3
Mn																1637	8350	5
Ni	55	50	1	54	44	1	34	50	1.5	40	95	2.5	25	82	3.2	44	50	1.1
Co													6	12	1.9	18	22	1.2
Cr	50	153	3	77	85	1	7	49	7	13	60	4.5	11	125	11	19	30	1.6
Cd	0.21	0.68	3				2.5	4.6	2	0.14	2.4	17	0.9	3.5	4	0.3	9.1	30
As				11	22	2	2	51	25	0.6	3.2	5.5	0.2	0.	13	18	600	33
Ti(%)	0.2	0.8	4	0.04	0.2	5	0.24	1.12	5	0.04	0.48	12	0.05	2.0	39			

¹Forstner (1977).

²Allan and Brunskill (1977).

³This study.

Source: from Daley et al. (1981).

Table 5-15
Description of On-Land Tailings from Sherridon¹

On-Land Tailings, Oxidized Samples				
	Description	Colour	Sulphide Minerals	Authigenic Sulphate and Oxide Minerals
TP12-46	Hardpan: well cemented	Deep reddish brown	<8% Pyrite > Pyrrhotite	Goethite > Jarosite > Gypsum
TP7-28	Hardpan: well cemented	Laminated: light brown and yellowish brown	<5% Pyrite > Pyrrhotite	Goethite > Jarosite > Gypsum (trace Lepidocrocite)
BH7-S2	Hardpan: moderately to well cemented, along margin of more oxidized material	Reddish brown (also with more oxidized, yellowish brown material)	<15% Pyrite > Pyrrhotite	Jarosite > Goethite > Gypsum (trace) (Sulphides > Authigenic minerals)
TP-BH2	Poorly cemented, friable	Bright, yellowish brown to orange brown	None	Lepidocrocite > Jarosite > Gypsum

Note the indication of the relative proportion of sulphides and authigenic minerals and that all authigenic minerals are hydrated. Sample No. BH7-S2 also contains analcite, $\text{Na}(\text{AlSi}_2\text{O}_6) \cdot \text{H}_2\text{O}$, which is probably authigenic.

¹From Kennedy and Hawthorne 1987.

minerals, including chlorite. Kennedy and Hawthorn (1987) suggest that the micas act as sulphuric acid buffers, liberating Fe^{3+} and K^{+} ions and promoting the formation of goethite and jarosite.

In contrast, submerged tailings exhibit abundant biotite and phlogopite, indicating far less acid-induced alteration due to sulphide oxidation. Oxidation of sulphides is advanced in the sandy-textured tailings near the sediment surface, and has consumed an estimated 20-35% of the pyrite and pyrrhotite. Although this is a lesser degree of oxidation than that of the land tailings, such reactivity was unanticipated in view of the generally high water quality in Fox Lake. The degree of sulphide oxidation correlated directly with grain size; only minor oxidation was noted in the silty, less porous fraction. Sulphide grains often displayed prominent oxidized coatings of cryptocrystalline goethite.

Goethite, jarosite and gypsum are ubiquitous authigenic minerals in the submerged deposits. Kennedy and Hawthorn (1987) note that phlogopite, Mg-biotite and muscovite have reacted extensively with the acid generated during sulphide oxidation. Pertinent reactions indicating the formation of the principal alteration products are shown in Table 5-17. Heavily altered phlogopite and biotite are replaced by very fine-grained aggregates of chlorite, montmorillonite, quartz, illite and kaolinite, with interstitial jarosite. Virtually all the mica grains have been altered to some degree, which is manifest by potassium depletions.

Kennedy and Hawthorn (1987) suggest that the observed mineral distributions, which clearly indicate extensive oxidation, reflect the percolation of oxygenated lake water through the sandy tailings after deposition. However, it is not known if oxidation is still proceeding. It is also not clear whether or not the tailings were initially stored on land and subsequently submerged or originally deposited directly in the lake. Kennedy and Hawthorn make the interesting observation that the large volume increase associated with the formation of hydrated ferric oxides and jarosite from the oxidation of sulphides must eventually restrict permeability. They speculate that these reactions have the potential to seal the deposits with time and eventually inhibit continued oxidation.

5.1.2.2 Garrow Lake (Polaris Mine, Cominco)

The Polaris Pb/Zn mine on Little Cornwallis Island, N.W.T., commenced discharging tailings into proximal Garrow Lake when the mine opened in 1981. The lake is

Mineral Reactions Associated with the Oxidation of Sulphide Minerals in Reactive Mine Tailings

OXIDATION	OF	SULPHIDE	MINERALS		
(1) Pyrite:	$\text{FeS}_2 + 3 \cdot 5\text{O}_2 + \text{H}_2\text{O}$	---->	FeSO_4	+	H_2SO_4
(2) Pyrrhotite:	$\text{Fe}_7\text{S}_8 + 15 \cdot 5\text{O}_2 + \text{H}_2\text{O}$	---->	7FeSO_4	+	H_2SO_4
(3)	$4\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{O}_2$	---->	$2\text{Fe}_2(\text{SO}_4)_3$	+	$2\text{H}_2\text{O}$
(4)	$\text{Fe}_2(\text{SO}_4)_3 + 4\text{H}_2\text{O}$	---->	$2\text{FeO}(\text{OH})$ (goethite	or	$3\text{H}_2\text{SO}_4$ lepidocrocite)
REACTION	OF	SULPHURIC	ACID	WITH	SILICATE
(5) Mg-Biotite	---->	Jarosite	+	Mg-Chlorite	+ quartz
	$4[\text{K}_2\text{Mg}_{3.5}\text{Fe}_{1.5}\text{Al}_{0.5}(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH})_4]$	$+ 12[\text{H}_2\text{O}]$	$+ [\text{O}_2]$	---->	
	$2[\text{Mg}_7\text{Fe}_2\text{Al}_{2.5}(\text{Si}_{5.5}\text{Al}_{2.5}\text{O}_{20})(\text{OH})_{14}]$	$+ 13[\text{SiO}_2]$	$+ 2[\text{KFe}_3(\text{SO}_4)_2\text{OH}_6]$	$+ 3\text{K}_2\text{O}^*$	
(6) Muscovite	---->	Jarosite	+	Kaolinite	
	$2[\text{K}_2\text{Al}_4(\text{Si}_6\text{Al}_2\text{O}_{20})(\text{OH})_4]$	$+ 12[\text{FeSO}_4]$	$+ 20[\text{H}_2\text{O}]$	$= 5[\text{O}_2]$	---->
	$3[\text{Al}_4(\text{Si}_4\text{O}_{10})(\text{OH})_8]$	$+$	$4[\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6]$		

*K is taken up by other mineral reactions, or goes into solution.

Source: Kennedy and Hawthorne (1987).

approximately 3 km long by 2 km wide with a depth of 46 m, and its surface is only 7 m above sea level. Runoff enters the lake from a relatively small watershed. Surrounding elevated terrain shelters it somewhat from the prevailing winds. Limnological studies in the 1970's established that Garrow Lake is meromictic, with a slightly brackish aerobic zone overlying anoxic H₂S-bearing brine.

The lake is stratified into three distinct hydrological regimes (Bohn et al., 1981; Kuit and Gowans, 1982). The brackish surface layer (epilimnion) extends to a depth of 13 m and is subject to inflows and surface mixing. The transition zone (metalimnion) from 13 to 20 m depth exhibits decreasing dissolved oxygen, increasing salinity, and is influenced only to a limited degree by wind-induced mixing. Permanently stagnant, highly-saline bottom water, reaching about 9‰ S, extends beneath the transition zone (the hypolimnion) to a depth of 46 m. Characteristic temperature and salinity profiles are presented in Figure 5-5, and distributions of selected chemical parameters are shown in Figure 5-6.

The ore at Polaris consists of sphalerite and galena in a matrix of marcasite, calcite and dolomite. The tailings are therefore enriched in Pb and Zn and contain high concentrations of FeS₂. Due to the nature of the ore (i.e. massive sulphide deposit) it is expected that the tailings are acid generating; however, the exact sulphide content was not determined.

It was originally anticipated that the relatively high dissolved sulphide concentrations in the bottom water would render the lake an ideal repository for sulphide-bearing tailings, and that the release of Pb and Zn to solution would be negligible, providing the tailings were deposited in the anoxic hypolimnion. However, complications arose during testing of simulated discharges. First, in order to minimize pluming and areal dispersion of the tailings, and avoid contamination of the oxic epilimnion and consequent harm to the indigenous biota, the behaviour of discharges having different densities was examined. Tests which simulated the direct discharge of concentrator tailings at 32% solids pulp density predicted that substantial pluming and dispersion would occur. In addition, and unexpectedly, this particular mixture consumed copious quantities of H₂S from the receiving solution, which permitted the dissolution of Pb and Zn sulphides (Kuit and Gowans, 1982). Apparently, the consumption reflected the adsorption of HS⁻ onto the surfaces of iron-bearing minerals. The extent of sulphide depletion was shown to be inversely proportional to relative particle size and proportional to the total iron content. As Kuit and Gowans (1982) note, these phenomena demonstrate that minimizing dispersion is a critical factor in limiting the the post-depositional reactivity of tailings solids.

Following further tests, thickener underflow at 60% solids pulp density was chosen as the optimum mixture for discharge to the lake. Pluming of this slurry was minimal and sulphide adsorption was negligible, being restricted to a thin layer on the surface of the settled deposits.

In actual practice, the tailings discharge points are located well below the halocline in Garrow Lake. Pulp density of the tailings during 1982-83 was maintained at an average 55% solids. Weekly monitoring of the water column for the initial 18 months of operation showed little or no change in water quality in the epilimnion; metal concentrations remained well below maximum values stipulated by the discharge

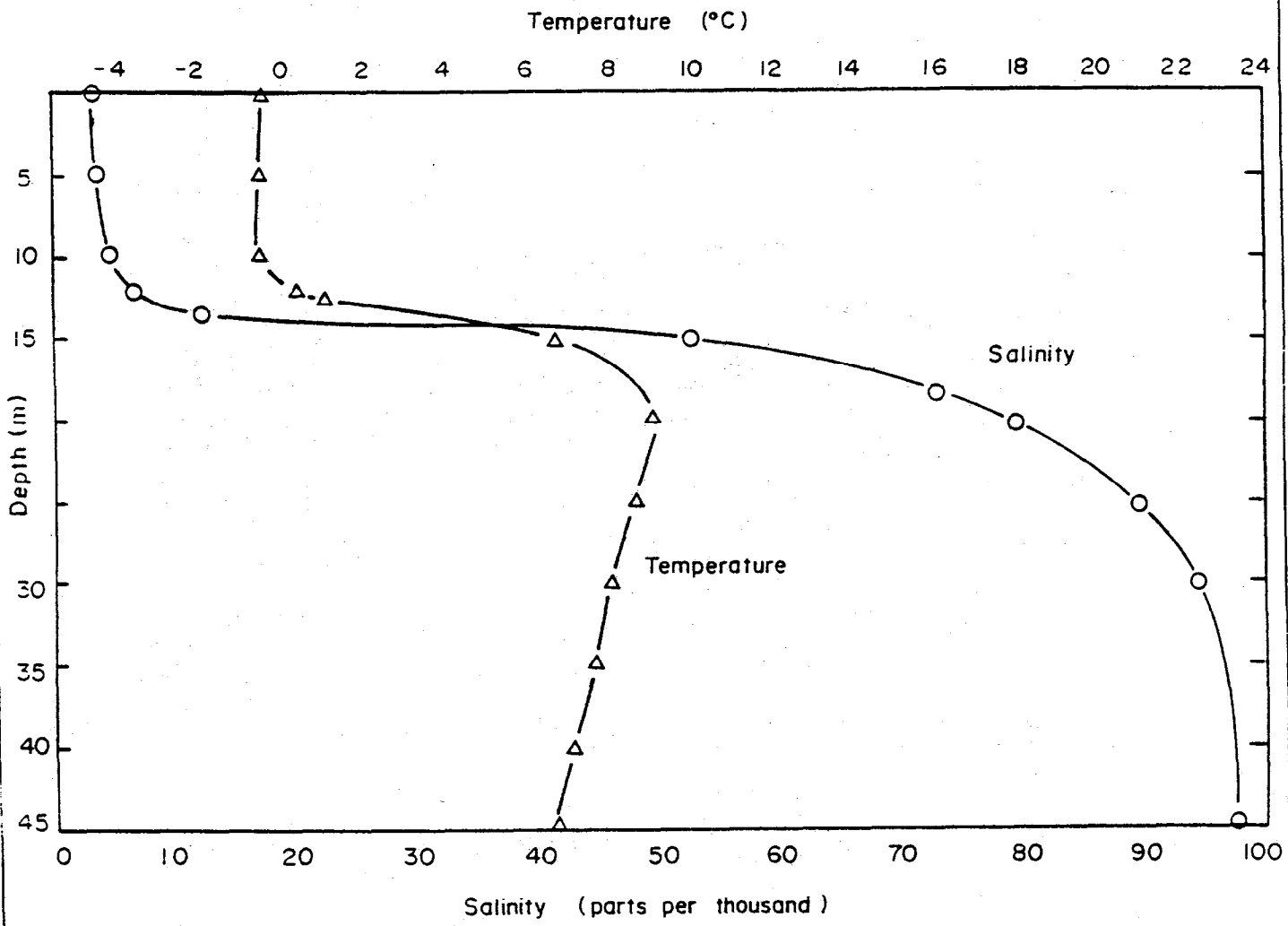


Figure 5-5 Garrow Lake - Salinity and Temperature Profiles (Kuit and Gowans, 1982)

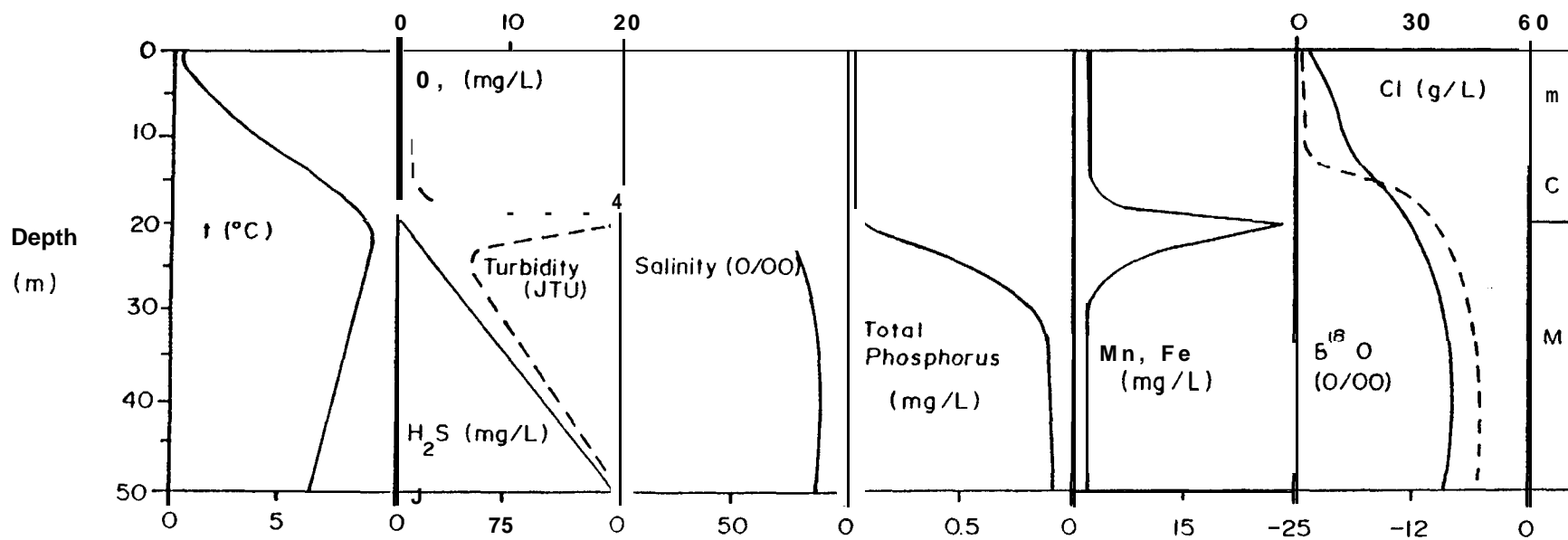


Figure 5-6 Typical Physicochemical Stratification of Garrow Lake by Water Depth (Ouellet and Page, 1966)

license, as shown in Table 5-18. Continuing monitoring indicates that surface water quality in the lake has not been compromised by its use as a receptacle for tailings (W.J. Kuit, 1989, pers. comm.).

Table 5-18

Garrow Lake Surface Water Quality, 1982

Parameter	License Maximum, mg/L	Actual, mg/L
Total Cu	.07	<.008
Total Pb	.02	.01
Total Zn	0.15	<.02
Total CN	1.0	<0.1

Source: Kuit and Gowans (1982).

5.1.2.3 Mandy Lake at Mandy Mine Hudson Bay Mining and Smelting Ltd., Flin Flon, Manitoba

Mandy Mine was located near Flin Flon, Manitoba. The ore vein averaged over 20% copper as solid chalcopyrite and contained significant precious metals in lower grade sulphides. From April 1943 to December 1944, the mine deposited tailings into Mandy Lake, a shallow water body next to the property (Hamilton and Fraser, 1978).

Hudson Bay Mining and Smelting Ltd. (HBMS) conducted two sampling programs in 1975 and 1976. Investigation of predominantly pyrite tailings which were submerged in shallow water (0.3 - 1 m deep) for 32 years was carried-out to determine the extent of oxidation. The original chemical and mineralogical composition of the tailings is not well known, but pyrite was the predominant iron sulphide mineral and the ore likely had a sulphur content of 15-17%. Levels of zinc and copper are thought to have been appreciable.

Tailings samples (four underwater, two onshore) and water samples (four taken above the submerged tailings samples, two taken in Mandy Lake inlet and outlet streams) were analyzed. Results were compared to analyses of land-disposed Cuprus Mine tailings, located 11 km southeast of Flin Flon, because these also were high in sulphides and had been exposed for the same length of time. Tables 5-19 and 5-20 summarize and compare the analytical data (Hamilton and Fraser, 1978). Reactivity generally correlates with the intensity of exposure to oxygen. Tailings with some degree of water cover were found to have oxidized to a lesser degree as indicated by the iron oxide content (Table 5-19) and the leaching behaviour (Table 5-20).

Table 5-19

Composition of Tailings from Mandy Mine and Cuprus Mine

Constituent (%)	Mandy Mine		Cuprus Mine
	Underwater	Shore	Top Profile

Total Iron	17.4	19.8	24.5
Iron as Fe ₂ O ₃	0.8	2.9	15.8
Total sulphur	15.5	15.8	6.6
Sulphide sulphur	15.4	15.5	2.7
Sulphate sulphur	0.03	0.30	3.9
Alumina (Al ₂ O ₃)	8.4	6.7	2.9
Silica (SiO ₂)	35.7	37.7	27.7
Copper	0.91	2.70	0.19
Zinc	4.70	1.60	0.18
Lead	0.13	0.12	0.08
Cadmium	0.01	<0.01	<0.01
Calcium	1.04	0.51	2.87
Magnesium	1.75	1.03	0.54

Source: Hamilton and Fraser (1978).

Table

5-20

Soluble Constituents in a 1:5 Distilled Water Leach of Tailings from Mandy and Cuprus Mine

Constituent (mg/kg tailings)	Mandy Mine		Cuprus Mine
	Underwater	Shore	Top Profile
Iron	0.9	84.3	8,530
Copper	0.25	6.23	797
Zinc	15.5	44	218
Lead	0.35	1.05	1.27
Cadmium	0.05	0.28	0.57
Calcium	145	2,590	2,360
Magnesium	18	121	577
Sulphate	240	7,340	35,400
pH	6.9	4.9	2.5
Conductivity (mmho/cm)	0.4	2.45	7.20

Source: Hamilton and Fraser (1978).

Comparison of the quality of inlet and outlet waters to and from the lake (Table 5-21) suggests that the submerged tailings had no significant influence on the dissolved metal inventories during the 1975-76 study. Furthermore, animal species were present universally throughout the non-affected and tailings-affected areas; no distinction was evident between the two.

Table

5-21

Quality of Inlet and Outlet Water at Mandy Lake

Parameter	Sample Source		
	Inlet	Outlet	Above Tailings

pH	7.5	7.7	7.7
Conductivity (mmho/cm)	0.20	0.39	0.26
Copper (mg/L)	0.01	0.02	0.01
Zinc (mg/L)	0.14	0.13	0.20
Lead (mg/L)	0.01	0.01	0.01
Cadmium (mg/L)	0.01	0.01	0.01
Iron (mg/L)	0.11	0.23	0.05
Calcium (mg/L)	22.0	22.5	21.0
Magnesium (mg/L)	5.3	5.5	5.6
Sulphate (mg/L)	28.8	21.7	-

Source: Hamilton and Fraser (1978).

Vegetation was well established on the water-covered deposit in the mid-1970's but was absent on the subaerial tailings. Hamilton and Fraser (1978) noted that a layer of decaying organic material up to 2.5 cm thick covered 90-95 % of the surface area of the submerged deposit. Presumably, such layers enhance oxygen consumption and further reduce the possibility of oxidation of sulphides. This is consistent with studies by Jackson (1978) on Schist Lake, also near Flin Flon, where deliberate stimulation of algal blooms through nutrient enrichment in a small lake serving as a disposal site for toxic metal wastes caused metals to be trapped and immobilized in the bottom sediments as sulphides or metal-organic complexes. Fertilization with sewage or other sources of available nutrients results in algal blooms which have been found to concentrate metals, transporting these metals to the lake bottom when the algae die-off and sink. Reducing conditions caused by putrefaction of algal organic matter tends to further immobilize metals in the organic bottom muds. Moore and Sutherland (1981) similarly found that heavy metal releases into Great Bear Lake, Northwest Territories, had become bound in the organic sediments, resulting in little impact on metal concentrations in the overlying water and in fish flesh.

In summary, few, if any, detrimental effects on water quality were observed in Mandy Lake some three decades after deposition of the tailings, and the submerged sulphide-rich material appeared to be essentially unreactive. In contrast, the land-based tailings were heavily altered and had apparently undergone severe oxidation, presumably with concomitant acid production. There are, unfortunately, no data available which would permit evaluation of the impact on the lake of the submerged tailings in the immediate and short terms following emplacement. However, HBMS is planning to submit a proposal that Mandy Lake be considered as a target for field tests under CANMET's Mine Environmental Neutral Drainage (MEND) program (Musial, 1989).

5.1.2.4 Anderson Lake (Hudson Bay Mining and Smelting Ltd.)

Hudson Bay Mining and Smelting's Snow Lake mill, rated at 3450 m/tpd, receives various copper-lead-zinc ores from seven Snow Lake area underground mines (Fraser, 1989; Canadian Mines Handbook, 1988-89), and discharges tailings to proximal, and shallow, Anderson Lake. During the last decade, about 0.75 million tons of tailings have been deposited in the lake annually.

Disposal locations on the lake are varied seasonally, with the more shallow depths (3 m) being selected in summer and greater depths (average 6 m) used in winter. Discharge is through a 30 cm floating Sclair pipe which can be moved to distribute the tailings from two discharge points in order to keep a water cover of 0.6 m. Lake bottom contours are measured yearly as part of planning the seasonal discharge.

There are no detailed mineralogic or compositional analyses of the tailings, which vary with the composite ore feed from the different mines. Pyrite and pyrrhotite are the primary sulphide gangue minerals in the Anderson Lake chlorite schist host rock. Sulphur content is 20-25%.

A pre-operational environmental assessment was carried out and impacted receiving waters undergo further assessment every three years. Periodic water quality monitoring is done for metals, pH and suspended solids; federal effluent guidelines are reportedly being met (Fraser, 1989).

Anderson Lake is marshy and eutrophic, floored with a soft organic ooze, and historically has contained very few fish. Tailings initially deposited into the lake maintained a 25-30° angle of repose, and did not readily disperse due to the very quiescent lake conditions and the short drop from the discharge outfall. Initially, some mine waste and tailings built up above the lake surface and had to be moved in order to keep the deposits submerged.

5.1.3 International Mines

5.1.3.1 Silver Bay, Minnesota, on Lake Superior (Reserve Mining Co.)

A brief summary of the Reserve Mining Company case study is included here to demonstrate that chemical behaviour is not the only aspect of lacustrine tailings discharge which has important implications to environmental quality.

Following a 1950's technical breakthrough that led to the economic processing of low grade, siliceous and abrasive magnetic taconite iron ores, the Reserve Mining Co. of Silver Bay, Minnesota started beneficiating iron ore at a plant northeast of Duluth on Lake Superior. The company was permitted to discharge a large quantity of tailings directly into Lake Superior and built a concentrator that would process 88,500 tpd of crude feed (grading 24-25% iron) and produce 59,000 tpd of tailings. The tailings were composed of about 50% quartz, 43% other silicate minerals (including cummingtonite, an asbestiform mineral), and 7% magnetite (Oxberry et al., 1978).

Although its effectiveness had not been proven, lake tailings disposal was initially accomplished by allowing the tailings to flow as a density current downslope to an offshore trough which ranged in depth from 200 to 300 m. Studies were initiated at the same time to predict the properties of the tailings suspension in lake water, and to predict settling behaviour (Engineering and Mining Journal 1972, 1976). When the discharge entered the lake, coarser particles quickly settled to form a delta (Temple, 1980), and the fines flowed in density currents down the delta face to form prodelta deposits. However, a portion of the fine-particle suspension was later found to escape the density current and under certain conditions fine particles became widely dispersed. Eventually, tailings settled over more than 2500 km² of the lake floor. The tailings were found to affect organisms in direct toxicity tests and to have inhibited algal photosynthesis (Shaumburg, 1976). Although the tailings released soluble components when exposed to lake water, no heavy metal releases were reported.

In 1969, the tailings were determined to be polluting Lake Superior waters, and the Reserve Mining Co. was charged by the U.S. government. What began as a water pollution abatement case became, after the discovery of asbestos-type fibers in Lake Superior, a public health impact issue concerning asbestiform particles discharged into the air and water (Durham and Pang, 1976). Eventually, in 1978, Reserve was forced to use on-land tailings disposal, at an estimated cost of U.S. \$250 million.

5.1.4 Flooded Pits and Shafts

5.1.4.1 Endako Mines Division (Placer-Dome Inc.)

There are two open pits at Endako's molybdenum operation near Fraser Lake in north-central British Columbia; the initial Endako pit, which was closed in June 1982 due to depressed molybdenum prices, and the Denak pit. The Endako pit was allowed to flood in 1982.

Some recent water quality monitoring data from the Endako pit were provided by B.C. MOEP (Roberts, 1989) and are given in Table 5-22:

Table

5-22

Water Quality in Endako Pit

Constituent	Analysis			
	(mg/L)			
SO ₄ ⁻²	Ranges			886-425
Cu	0.001,	0.002,	0.003,	0.01
CN-	n.d.			
Mo	15			

Discharge from the Denak pit to an intermittent creek that flows to the Endako River or via a settling pond to Watkins Creek and thence to Francois Lake contains about 15 mg/L Mo, about 500-fold higher than the B.C. Water Quality Criterion for wildlife (0.05 mg/L). Concentrations as high as 86 mg/L (J.B. Brodie, unpublished report, 1986) have been measured. Such high concentrations in the effluent from both the Denak and Endako pits are of current concern to the Waste Management Branch, and have serious implications for the eventual abandonment of the mine, particularly in view of the probability that the pits will be purposely or passively flooded once the mine closes.

Studies are underway which will address the impact to date of effluent discharges on receiving waters, soils, vegetation, and wildlife in the mine vicinity. At the time of writing, no results from these investigations are available. Mitigation of the release of Mo to pit waters will need to be considered as part of any abandonment plan, as discussed in Chapter 6.

5.1.4.2 Equity Silver Mines Ltd. (Placer-Dome Inc.)

Equity Silver Mines Ltd. (ESML) is located near Houston, B.C. in the Bulkley River drainage system. Acidic drainage containing dissolved Cu, Zn and Fe at the mine's 50 million tonne waste rock dump results from oxidation of pyrite, and was first noted just one year following the mine's opening in 1981. The acid drainage flowed into the Bulkley River and threatened to degrade valuable fish habitat and drinking water.

ESML subsequently initiated a reclamation and revegetation program, and constructed a series of collection ditches which direct acid mine drainage (AMD) to an on-site treatment plant. Approximately 800,000 m³/yr of acid drainage is mixed with lime to raise the pH to 8.5, which fosters the precipitation of metal hydroxides, and the solution is then discharged to a settling pond where a high proportion of the previously-dissolved metal inventory settles out as a calcium sulphate/metal hydroxide sludge. The resulting clear supernatant is discharged to the environment; according to ESML's Decommissioning and Closure Plan (1988), such discharges are carefully monitored and regulated to ensure minimal impact, and they comply with established water quality guidelines. Representative water quality data are shown in Table 5-23 (Gallinger, 1988). The metal-rich sludge from the settling ponds is currently mixed with tailings in a ratio of 1:10 and added to the regular tailings ponds.

Several alternatives currently exist for long-term pit abandonment, AMD treatment and associated sludge disposal. The Main Zone and Waterline open pits will be allowed to fill and form a lake. The tailings pond will become a shallow lake, submerged to a

A.M.D. Treatment Statistics
 ESML's Water Quality Data (Gallinger, 1988)

	Values in mg/L					
	pH	Acidity	SO ₄	Cu(d)	Zn(d)	Fe(d)
Raw A.M.D.	2.35	10,000	8,500	120	80	800
Treated	7.80	NIL	1,600	0.01	0.04	0.03
Permitted	6.5-8.5			0.05	0.2	0.3

maximum depth of 1-2 m; submergence is expected to lessen susceptibility of tailings to oxidation.

The Southern Tail pit has already been flooded, following partial backfilling with 2.5 million cubic metres of waste rock; acid generation under the water in the pit is expected to be obviated. Ongoing mitigation of the waste-dump AMD will produce approximately 80,000 m³ (1% solids) of sediment sludge annually, which may be deposited in an existing diversion pond basin (20 year minimum capacity) or in the Main Pit (on the order of 200 year capacity). The latter option has the benefit of long lifetime, but it may be incompatible with the current plan to flood the Main Zone Pit following abandonment. Concern for the potential generation of AMD from the exposed pit walls during the six-year filling time is expressed in ESML's Closure Plan (1988). Should a low pH result (and possibly persist), the potential for dissolution of hydroxide precipitates in the sludge exists. Should this become the case, then the anticipated establishment of aquatic life in the flooded pit will be compromised. Provision will be made to route Main Zone overflow to the AMD treatment system should it become necessary to treat acidic overflow water from the newly-created lake. Such a circumstance will require alternate arrangements for the disposal of the sludge to be made, possibly in proximal landfills. However, indications from other sites, such as in Mandy Lake (Section 5.1.2.3), imply that eventual submergence of sulphides in the pit walls should inhibit oxidation and concomitant acid production. Such a result would obviously be beneficial, and would limit the period of concern to the six-year filling time.

Other mine operators, for example, HBMS (Typliski and Labarre, 1980) have successfully used lime neutralization to clarify mine waste effluents and recover metals, for a net economic return. Presumably this is not an economically viable option for ESML, as it is unremarked in the Decommissioning and Closure Plan (1988).

5.1.4.3 Phoenix Copper Mine (formerly with Granby Mining Co.) Decommissioned Open-pit

Kalmet (1989) reports that the Phoenix open pit, abandoned in the late 1970's, is flooded and contains very clear water. Since the host rock is limestone, the acid generating potential is low. The most recent water samples were collected from the pit in 1984 (Jarman, 1989) and were analyzed for metals and nutrients (Table 5-24). At that time, the water contained concentrations of nitrate which exceeded drinking water guidelines, low concentrations of lead and relatively high levels of Cu, Mo and Fe. The source of the metals is not clear.

Following cessation of mining, the tailings impoundment was breached by cutting a channel into the dam to permit the draining of ponded water. This drainage is diverted via a perimeter ditch

to Twin Creek, the water quality of which is monitored (Kalmet, 1989; Jarman, 1989). Data collected during the course of monitoring downstream receiving waters between 1973 and 1984 indicate that copper and sulphate concentrations decreased significantly during that 11 year period (Table 5-25). Reclamation of the tailings impoundment is now complete.

5.1.4.4 City Resources (Canada) Limited (formerly Consolidated Cinola Mines Ltd.)
• Queen Charlotte Islands, B.C.

The Cinola Gold Project is a proposed open pit mine for the production of approximately 6.4 million tonnes of ore and waste rock per year. Approximately 68% of the mine wastes are potentially acid producing.

Acid generating waste rock will be separated into two groups for separate disposal. One quarter of the acid generating waste rock will be permanently submerged in the tailings impoundment while the remaining three quarters of the potentially acid generating rock will be stored in a stockpile and backfilled to the open pit upon completion of mining. The pit will subsequently be filled with water thus inundating the backfilled rock.

Table

5-24

1984
Phoenix Flooded/Decommissioned Open Pit

Water

Quality

Data

Constituent	Analyses
Nitrate	12.14 mg/litre ¹
Dissolved	Metals
Cu	0.019 mg/litre
Mo	0.08 mg/litre
Pb	0.002 mg/litre
Iron	0.12 mg/litre
Al	0.44 mg/litre
Dissolved Oxygen (field)	9.6 mg/litre
Sp. Cond.	1540
pH - field	7.52 ²
pH - lab	7.92
Turbidity	Low

¹Exceeds drinking water standard.
²Estimated 3 day delay between field and lab analysis.

Table

5-25

Sulphate Ion and Dissolved Copper Concentrations in Providence Lake¹

Constituent, mg/litre	Year
SO ₄ ⁻² - 516	1975 ¹
- 71.2	1984
Dissolved Cu - 0.012	1973
- 0.001	1984

¹1975: plant operating; last year tailings pond effluent discharged to Providence Lake.

Environmental monitoring for water and groundwater quality, and acid generation will be conducted throughout the construction, operation and reclamation phases of the project.

5.2 Summary

The case studies which have been reviewed in this chapter demonstrate that some data are available which usefully document some processes of concern to subaqueous disposal; however, such illustrative studies are very few in number. The majority of examples which have been described in the open and grey literature are often of limited utility because they adopt too narrow a focus. For example, few conclusions about diagenetic processes underwater can be drawn from comparative mineralogic studies in the absence of interstitial water data. However, the studies which have been reviewed imply that, in general, oxidation of submerged tailings may be inhibited even in very shallow waters, as suggested by the Mandy Lake example. Similarly, no evidence for oxidation and associated metal release was found in Buttle Lake, where sulphide-rich tailings are overlain by an oxygenated and much deeper water column.

During the course of preparation of this chapter, no substantive evidence was uncovered to support the notion that significant acid generation can occur under water. This does not mean, however, that submergence categorically excludes oxidation; the available information is too discrete and limited to permit such a generalization to be drawn at this point, as is noted in the following chapter.

Chapter 6

The literature review presented in this report was conducted as a multidisciplinary exercise to evaluate the current understanding of both acid generation and subaqueous disposal practices and to establish a foundation for proceeding with further studies. The additional studies, when completed, would provide site-specific information to fill gaps in existing data and improve our understanding of the long-term behaviour of active and abandoned submerged mine waste deposits. Only then can a set of criteria for environmentally safe methods of underwater disposal of reactive mine wastes be established to permit confident decision-making on the suitability of aquatic discharge strategies.

Much information was collected and reviewed in our study, a good deal of which is summarized in the preceding sections. Based on the combination of theoretical and case study data, a series of conclusions and recommendations follow which provide a synopsis of the state-of-the-art in subaqueous disposal and demonstrate where further field investigation should be completed to improve the level of understanding of the physical, chemical and biological implications of storing reactive mine wastes underwater.

6.1 Conclusions

Based on the theoretical review of AMD and case study investigations, the following conclusions have been drawn. They consider both technical and non-technical issues, and provide a foundation for the subsequent discussion of recommended further studies. Individual conclusions are not mentioned in order of importance.

- AMD is a serious disadvantage for land-based tailing disposal, particularly in wetter climates characterizing certain areas of British Columbia. The typical oxidation-reduction (redox) reactions and galvanic interaction of commonly occurring waste sulphide minerals (pyrite, pyrrhotite) that occur in the presence of oxygen, moisture and *Thiobacillus ferrooxidans* (catalyst) can result in the generation of highly acidic water and concomitant leaching of trace metals from mine wastes. By minimizing exposure to oxygen by storing reactive wastes underwater, subaqueous disposal practices hold considerable promise for

suppressing acid generation. Further study is required however to understand more fully the conditions under which underwater disposal will be successful.

- Tests to evaluate acid mine drainage and/or acid-generating potential of land-based mine wastes appear to have very limited or marginal predictive ability for wastes submerged underwater (unless the body of water is very well oxygenated). Of the range of tests available, the kinetic shake flask test, which gives an indication of the degree to which metals can enter the water column when tailings are disposed into a lake, appears somewhat suitable for underwater storage of reactive mine wastes as it best simulates actual field conditions and has been shown to be accurate in its predictions.

- Any databases which contain chemical and/or physical data for lakes currently exist in a form too incipient to be of significant use for evaluating candidate lakes as mine waste repositories. This reflects the relatively recent concern about the long term impacts of subaqueous disposal.

- Critical areas in the biological arena still remain that require more detailed investigation, particularly the complex processes of bioavailability of metals in lake-bottom sediments and bioaccumulation in the freshwater food chain. Lake studies have not adequately evaluated post-depositional reactivity of submerged sulphide-bearing tailings to determine if benthic effluxes of heavy metals are present.

- Macrobiological impacts must be examined under each of four categories: turbidity, sedimentation, toxicity to freshwater biota and contamination of the food web. Each category can represent significant macrobiological impacts; the primary impacts of which are outlined as follows. Turbidity affects water transparency and hence primary and secondary production as well as respiration, feeding and other behaviour of water column organisms. Sedimentation results in the smothering of eggs and benthic organisms. Toxicity includes a wide range of lethal, sub-lethal and behavioural impacts of trace metals or acid-generating materials on freshwater biota. Contamination effects consider the bioaccumulation of trace metals through the food chain.

- Various factors representing a wide array of processes, chemical reactions, and site-specific conditions interact, perhaps synergistically, in determining whether or not mine wastes deposited underwater have the potential for introducing substances toxic to biological systems. Several factors worth considering include the following:

- the natural chemistry or chemical properties of the receiving environment;
- physicochemical conditions which may aid in reducing concentrations of dissolved metal species through conversion into authigenic phases, i.e. precipitation;
- size of the water body and its capacity to tolerate a given amount of effluent;
- hydrochemical conditions that may increase heavy metal solubility;
- the existence and frequency of flushing cycles in a lake;
- the composition and pH of the mine wastes which can reflect a range of metal recovery treatment processes - anywhere from state-of-the-art selective flotation to those that have undergone some alteration, for example, through cyanidation or other hydrometallurgical or roasting pre-treatment; and
- the existence and the types of aquatic life that inhabit the lake and their migratory and feeding habits. Through certain mechanisms, biota have the potential for transporting metals in the sediments or water column into the food web.

- The case studies reviewed, although considered representative, yield inconclusive results. Data are generally sparse or superficial, only somewhat relevant, reflect limited sampling, and/or have little predictive capacity to permit improving our understanding of

long-term phenomena associated with subaqueous disposal. The data collected are usually for short-term environmental impact assessments and not for detecting biogeochemical processes or longer term trends. Water quality data are common but very little sediment mineralogy is available and virtually no pore water chemistry.

- Regular, comprehensive monitoring of water chemistry in flooded open-pits is sparse at present. Such information, if available in significant quantity and quality, could provide a database to assist in future predictions of the chemical evaluation of drainage from abandoned pits.

6.2 Recommendations for Field Investigations

The preceding chapters demonstrate that the subaqueous disposal of reactive mine wastes appears to be a highly promising alternative to land-based disposal, but that critical gaps exist in the data which prevent establishing a set of criteria for effectively evaluating alternative disposal strategies. Clearly, further field studies need to be designed to evaluate post-depositional reactivity of submerged sulphide-bearing mine wastes to determine if benthic effluxes of selected metals exist and to what extent they are mitigated by the gradual deposition of a natural sediment layer. Included must be more detailed, site-specific investigations of impacts on the biological community native to the receiving environment.

Although discussed individually below, it is most important that the geochemical and biological components be conducted for each site investigation. This suggestion reflects the necessity of increasing our knowledge of the factors which control metal release or uptake by tailings and waste rock and the associated direct or indirect impacts on aquatic organisms. It is only then that a complete understanding of the long-term nature of submerged mine wastes and their potential biological impacts can be fully appreciated.

6.2.1 Geochemical Investigations

It is recommended that in future work, detailed studies be carried out on the distribution of dissolved metals and metabolites in interstitial waters collected from suites of cores raised from submerged tailings deposits in a number of lakes. Previous work has demonstrated the utility of this approach in assessing the post-depositional reactivity of tailings deposits in such environments (e.g. Pedersen, 1983).

For comparative purposes, such studies should embrace a variety of deposits, including unperturbed sediments and tailings which have contrasting mineralogies, and should include assessment of alteration effects, and connate water and/or groundwater chemistry in companion subaerial tailings deposits on land. In both types of deposits, the work should include locations which are no longer receiving mine waste, as well as active depositional regimes. It is strongly recommended that these investigations include chemical analyses of selected major and minor element concentrations in the solid phases from which the pore waters are extracted, mineralogical characterization, and measurements of the organic carbon concentration.

Where tailings or waste materials of the same composition have been discharged both underwater and on land (as for example at Buttle and Benson Lakes), comparative mineralogic studies of both facies should be carried out by X-ray diffraction to contrast the extent and nature of alteration of minerals under on-land and submerged conditions. The degree of such alteration is expected to be minor in the submerged deposits, but this requires confirmation. Such comparisons with waste materials on land, which are frequently heavily altered, have the potential to provide a particularly illustrative suite of examples of the relative chemical diagenetic behaviour of tailings and waste rock exposed to the atmosphere versus those under water.

To extract interstitial waters properly, considerable precautions must be taken to collect undisturbed cores and to avoid oxidation and contamination of the samples. Such work is, therefore, time and labour intensive and recognition of this requirement should be made in future budget deliberations. Interpretation of the pore water chemistry will require collection of

supporting limnological information, including dissolved oxygen and other hydrographic measurements.

Such studies, if carried out in sufficient detail, promise to deliver increased understanding of processes governing the post-depositional release (or lack of release) of dissolved metals to waters in the host basins, as well as permit calculations of the metal effluxes or influxes from impacted lake floors.

Given the several stages of chemical evolution which are expected to characterize the history of a submerged deposit, it is suggested that the recommended studies incorporate the following components:

- pore water work on a suite of representative cores should be performed one or two years after the mines have commenced discharging in order to assess the fluxes of metals out of or into the deposits. The purpose of this effort is to monitor the post-depositional chemical behaviour of the deposits during the active depositional stage. Ideally, characterization of the ambient chemistry of interstitial waters should also be carried out in lake basins chosen for sub-aqueous discharge *before* such disposal begins. Such pre-operational work would permit definition of metal releases for sediments which are known to occur in some pristine lakes as a consequence of natural geochemical cycles. For example, tailings discharge to Brucejack Lake in northern B.C. is planned to commence in 1990; it is recommended that a survey of the distribution of certain dissolved metals in Brucejack Lake sedimentary pore waters should be made before tailings deposition commences. Such baseline data would prove to be invaluable to subsequent comparisons with the chemistry of pore waters in the tailings;
- the same sampling strategy should be employed at two later stages:
 1. within 12 months of cessation of discharge, in order to assess the potential effects of oxidation following the abrupt change in the nature and rate of sedimentation; and
 2. two to six years after cessation of discharge, to permit evaluation of the potential "sealing" effect which is expected to be provided by the accumulation of natural sediments on the surface of the waste deposit.

Potential targets in British Columbia for the required detailed work include Buttle Lake, Benson Lake, and Kootenay Lake (especially the location where the 1960's spill of high-grade lead-zinc concentrates occurred, where significant potential exists for galvanic interaction between dissimilar sulphides in contact with each other, or in proximity to the Bluebell Mine at Riondel). Outside British Columbia, Mandy Lake, Fox Lake or Anderson Lake are suggested as suitable targets for study, given their shallow depths, relatively small size, and the high sulphide contents in the submerged tailings.

In addition to the foregoing, there are several British Columbia coastal marine environments containing mine tailings that could be investigated, ideally by using the same strategy outlined above. This information could supplement that collected at the freshwater lakes outlined above and aid in drawing conclusions as to the environmental impacts of subaqueous disposal of mine wastes. Topics which require investigation include: the nature and extent of remobilization of selected heavy metals from sediments, chemical speciation and toxicity of different species, and the mechanisms and extent of metal uptake by organisms. Sites in which such studies could most effectively be carried out include:

- Rupert Inlet (Island Copper) - mine still active. Studies of early diagenesis during the active depositional stage have been carried out previously (Pedersen, 1984, 1985).
- Howe Sound (which hosts tailings derived from the former Britannia Mine) - investigation of pore water is currently underway by members of the Department of Oceanography, U.B.C. Release of tailings to the fjord ceased in 1974.

- Alice Arm (Kitsault/Amax Canada) - tailings deposition ceased November, 1982. Work on arsenic speciation in interstitial waters has been carried out at Royal Roads Military College (Esquimalt), on Mo and metabolite chemistry by Losher (1985), and on Cu, Cd, Zn and Pb distributions by J.A.J. Thompson (Ocean Chemistry, Institute of Ocean Sciences; unpublished data).
- Anyox - site of B.C.'s (Canada's) first copper smelter; the local bay is thought to contain mine, mill and smelter wastes.

With the exception of the Alice Arm, Rupert Inlet, Buttle Lake and Howe Sound deposits, we suspect that very little monitoring or sampling (apart from water quality in the overlying water columns) has been done at the great majority of abandoned sites of submerged wastes. In many cases, it is clear that the "window of opportunity" has passed in which it may have been possible to assess the initial post-abandonment behaviour of waste materials in a number of water bodies. Such behaviour could then have been compared with subsequent studies which would have permitted a long-term chemical history to be derived. It will be possible however to assemble such diagenetic histories for locations in which deposition is underway or has recently ceased, in particular deposits such as those in Buttle Lake and to a lesser extent Benson Lake.

6.2.2 Limnological and Biological Investigations

Limnological and biological studies must be completed in association with geochemical investigations to link the complex process of metals release from submerged mine wastes to their uptake by aquatic organisms and bioaccumulation in the food chain.

The purpose of the limnology/biology program will be to describe the lake in terms of features that can be used to predict the impact of mine wastes deposited in similar lakes. These measurements will allow investigators to calculate lake turnover and residence time (flushing rate), determine circulation and mixing features, and evaluate the potential for the waste material to be mobilized by meteorological or hydrological events and the rate at which contaminants from the deposit would be dispersed. In addition, the measurements will fill existing data gaps on metal transfer from sediments up through the aquatic food chain, a process which is currently poorly understood with respect to submerged mine wastes.

Dissolved oxygen, pH, and redox potential are parameters which will influence the reactivity of the sediments. Our assumption is that if the sediments and interstitial waters are anoxic, then the solubility of metals will be minimized by the presence of hydrogen sulfide. The research program would, ideally, investigate this hypothesis for at least two, quite different lake types:

1. low productivity, high oxygen lakes which are high in alkalinity; and
2. highly productive lakes which are anoxic or suboxic for at least a portion of the year.

Research conducted by one member of our study team suggests that tailings high in calcium (e.g. lime-bearing tailings) may significantly reduce phosphate regeneration from the sediments which, in turn, may influence primary production rates in the lake. This study would evaluate the sediment and water chemistry data collected to test this hypothesis.

It is suggested that site-specific experiments on lacustrine biota be designed to establish the impacts of heavy metals on both the infauna and epifauna. Organisms which reside in the sediments (infauna) can have a significant influence on the degree of mixing that occurs, which in turn may influence the mobilization of metals. Metal levels within the tissues of the infauna and epifauna may reflect metal uptake rates and the potential for transfer to, and bioaccumulation in other organisms. The mobility of fish may make interpretation of metal levels in their tissues difficult to correlate to mine waste disposal, particularly if historical or pre-discharge information is not available. Because of the high interest in fish by both regulatory agencies and the public, however, selection of one or two suitable species (e.g. based on low mobility, longer life-spans, or higher trophic level feeders) is considered appropriate.

Based on a combination of theory and empirical case study data, initial attempts were made at developing a decision model with which to evaluate the suitability of future underwater waste disposal strategies. These efforts were confounded, however, by the insufficient and/or unreliable data that exist which document conditions at existing subaqueous disposal sites. This barrier to developing a systematic and comprehensive method for evaluating discharge options reinforces the need for the research initiatives outlined above. Such research will directly assist in the development of a decision model that will incorporate both physical theory and empirical, geochemical, limnological and biological data in a critical path framework for evaluating the environmental efficacy of subaqueous disposal of reactive mine wastes.

Examples of physical parameters to be included in the model include the extent and profile of the mine waste deposit, lake bathymetry (particularly near the disposal area), turnover patterns and flushing rates. Dissolved oxygen and pH, particularly near the sediment/water interface, which along with analysis of dissolved metals and salts in the lake water, represent some of the chemical parameters which must be considered. Sediment chemistry, interstitial water chemistry, organic carbon content of sediments, metal partitioning and speciation in sediments, the presence of oxidized minerals and evidence of potassium scavenging in the sediments are all pertinent considerations. Biological/limnological parameters, as described earlier, must include lake productivity, degree of bioturbation in sediments, and metal levels in representative infauna, epifauna and fish species.

The decision model will incorporate the parameters of concern to subaqueous disposal identified above and those refined through field study. Once developed, the model will have a very practical application for both industry and government in the screening of disposal alternatives based on a pragmatic fatal flaw approach that identifies key potential problem areas with proposed discharge strategies. Overall, benefits from developing and applying the decision model will accrue to industry in terms of effectively choosing methods to dispose of reactive mine wastes and to government charged with the responsibility of ensuring wastes are disposed of in a manner consistent with the protection of the natural environment.

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GLOSSARY OF TERMS

Advection:	Within-lake unidirectional motion that transports matter in lake systems; identity of transported substance unchanged.
Allochthonous:	Sedimentary rocks whose constituents have been transported and deposited some distance from their origin. Rock masses transported via tectonic forces.
Allogenic:	Minerals brought into the lake by surface water, shore erosion, glacial transport, aeolean processes (cf. endogenic).
Anthropogenic:	Originated or caused by man.
Authigenesis:	Process by which minerals form in a sedimentary rock after its deposition, i.e. formed where found (q.v. diagenesis).
Autochthonous:	Sedimentary rocks formed in place; bedrock masses that remain in place in mountain belts.
Autotrophic:	Pertaining to organisms able to manufacture their own food from inorganic substances.
Benthic/Benthonic:	Relating to, or occurring at the bottom of a body of water and/or in ocean depths.
Benthos:	Aquatic organisms that live on or in the bottom of a body of water.
Bioturbation:	Burrowing activity/mechanical disturbance caused by benthic organisms or fauna; stirring of sediments by the activity of burrowing benthonic organisms.
Daphnia:	An important invertebrate freshwater crustacean, and one of the most sensitive to heavy metals.

Diagenesis:	Sum total of processes (physical, chemical and/or biological) bringing about changes in sediment or sedimentary rock after its deposition in water (q.v. authigenesis).
Endogenic:	Minerals originating from processes occurring within the water column.
Epifauna:	Organisms that inhabit the water column, remote from sediments.
Epilimnion:	Upper zone of lake waters, generally well-mixed by surface currents and wave action, and can be significantly warmer than poorly-mixed deeper waters, i.e. hypolimnion.
Euphausiids:	An order of shrimp-like crustacean organisms, commonly luminescent.
Euphotic:	Relates to or constitutes the upper layers of a body of water penetrated by sufficient light to permit growth of green plants.
Exuviae:	Cast-off skin, shell or covering, as in molting organisms, animals.
Floodplain Lake:	Lake subject to periodic silt influxes and nutrient-laden river water either by inundation or sometimes by connections to river channels; receive highly variable amounts of river water.
Halocline:	Water layer in which there is a large change in salinity with depth.
FTU:	Formazin Turbidity Units.
Hemipelagic:	Refers to organic-rich fine-grained sediments found on continental margins or the transitional zone between a continental shelf and the deep sea.
Heterotrophic:	Requiring preformed organic compounds of nitrogen and carbon for food; unable to manufacture food from inorganic compounds.
Hypolimnion:	Poorly-mixed deeper waters of a lake.
Infauna:	Organisms that inhabit/reside in sediments.

Instars:	Discrete stages of growth or development
JTU:	Jackson Turbidity Units.
Lacustrine:	Of, or pertaining to, or formed or growing in, or inhabiting lakes.
Lakes:	<p>Dimictic: A lake which circulates vertically twice a year.</p> <p>Dystrophic: Lake decaying to extinction.</p> <p>Eutrophic: Rich in dissolved nutrients (phosphate and nitrate); often shallow and seasonally deficient in oxygen; denotes degree to which lake has aged.</p> <p>Holomictic: The whole lake volume undergoes, at sometime, complete mixing - usually taken to be approximately annually.</p> <p>Meromictic: Part of the lake undergoes mixing; bottom never mixes. Water mixing is incomplete; non-circulating bottom waters are isolated from circulating upper waters, i.e. a permanently stratified lake.</p> <p>Mesotrophic: Having a moderate amount of dissolved nutrients.</p> <p>Oligotrophic: Deficient in plant nutrients; has abundant dissolved oxygen with no marked stratification; i.e. sparse productivity and sterile substrate.</p> <p>Polymictic: Periodic, irregular, complete mixing, i.e. tropical lakes.</p>
Lysimeter:	A device for measuring the percolation of water through soils and for determining the soluble constituents removed in the drainage.

Macrobenthos:	See Benthos; bottom organisms of larger size that cause or contribute to bioturbation, q.v. microbenthos.
Mesocosm:	Intermediate to microcosm and macrocosm.
Metabolites:	Compounds elaborated by the biological activity of organisms and/or products of metabolism, i.e. NH_4^+ and PO_4^{3-} . Chemical products from biotransformation of xenobiotica.
Mixolimnetic:	Mixing strata of water.
Monimolimnetic:	Non-mixing.
Morphology:	Structure or form of something. Basic physical features of lake, i.e. depth, area, volume, perimeter, shoreline development.
Mysids:	A type of freshwater shrimp.
NTU:	Nephelometric Turbidity Units.
Pelagic:	Pertaining to the open sea.
Phytoplankton:	Microscopic plant forms of plankton.
Redoxcline:	Oxic-anoxic interface.
Suspended Solids:	Particulate matter in suspension, usually referring to particles of $>0.4 \mu\text{m}$ diameter.
Taconite:	A flint-like sedimentary rock, hard enough to cut glass; a merchantable or non-merchantable ferruginous chert or ferruginous slate comprising compact, siliceous rock containing very finely disseminated iron oxide.
Thermocline:	A transition zone or mixing layer in a thermally stratified body of water that separates an upper, warmer, lighter, oxygen-rich zone from a lower, colder, denser zone which may be oxygen-poor.
Trophic:	Relating to nutrition or nutritional.

Upland Lake:	Isolated from river water; usually clear water bodies with stable, well-vegetated banks, and bottoms that slope gently from shore. Bottom substrates typically organic muck, but shallow areas can be hard sandy material overlain by smooth gravel and cobbles. Emergent and submergent rooted vegetation is common. Lakes are deepest in regions of pronounced relief; may have bottom areas with abrupt and considerable depth variations.
Vadose water:	Subsurface water above the zone of saturation in the zone of aeration.
Vadose Zone:	Region/area with groundwater suspended or in circulation above the water table.
Zoobenthos:	Benthic fauna that lives on or in the lake bottom.
Zooplankton:	Animal forms of plankton.