CHEMISTRY OF THE DRAINAGE FROM A WASTE DUMP
AT BHP-UTAH MINES LTD, ISLAND COPPER MINE

By

MICHAEL GUOQING LI

B.Eng., Wuhan University of Iron and Steel Technology, China, 1982

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We accept this thesis as conforming
to the required standard

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Department of **MINING AND MINERAL PROCESS ENGINEERING**

The University of British Columbia
Vancouver, Canada

Date **DECEMBER 31, 1991**
ABSTRACT

This thesis examines the chemistry of the drainage around the North Dump at BHP-Utah Mines Ltd., Island Copper Mine. It also presents the calculations of the pathway of water from precipitation and the acid generation and consumption of some areas on the North Dump.

Information used in this study includes mine site fresh water quality monitoring records, acid-base accounting results of the North Dump drilling samples, flow rate measurements of drainage streams around the North Dump and of pit dewatering, physical parameters of the North Dump, surface topographical maps, meteorological records, etc.

It has been found that a typical contaminated drainage has a total ionic strength of 0.0426 and that the activity coefficients of the dissolved species in consideration depart markedly from unity. Most dissolved species are found to be under-saturated with respect to their most insoluble compounds, although over-saturation also exists. Levels of dissolved species are controlled by their rates of release and the frequency and amount of precipitation.

Redox reactions and solubility control are investigated. Chemical reactions involving minerals present in the waste rock are considered in view of their effects on acid generation or consumption and on release rates of dissolved species. Eh-pH diagrams and solubility diagrams are constructed at conditions specific to the drainage under study.
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<td>AAS - Atomic Absorption Spectrometry (A.A.S.)</td>
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<td>EDD - East Drainage Ditch</td>
<td>ACP - Acid Consuming Potential</td>
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<td>EDL - East Drainage Lake</td>
<td>AMD - Acid Mine Drainage</td>
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<td>EMO - Eastern Most Outslope</td>
<td>APP - Acid Producing Potential</td>
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SPECIAL NOTES

The data collected in this study are up-to-date to January, 1989. The first draft of this thesis was completed in December, 1989. Therefore, the conclusions and statements made in this thesis are only up-to-date to January, 1989, although the thesis is dated October, 1991.

Both the Metric and the Imperial systems of measures are used in this thesis, since the original data exist in both systems. Whenever a calculation involved figures in both systems, the figures in the Imperial system were converted to those in the Metric system, and the result was presented in the Metric system. Special attention is required to distinguish between the Metric ton, spelled as tonne (tonnes), and the Imperial ton, spelled as ton (tons).

References are identified in the text with the author's name followed by the year of publication. References without named authors are identified with the title of the publication.
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I am very grateful to BHP-Utah Mines Ltd., Island Copper Mine and the Department of Mining and Mineral Process Engineering at the University of British Columbia for their financial support.
1.0 INTRODUCTION

Acid rock drainage or ARD, sometimes referred to as acid mine drainage, or AMD, is a serious problem facing today's mining industry. ARD results from the exposure by mining of some reactive sulfide minerals, primarily pyrite, to air and water. Prior to mining, sulfide minerals are usually in a state of slow oxidation or no oxidation at all under burial conditions. Mining activities bring a large quantity of sulfides into direct contact with abundant oxygen in air and water from precipitation, resulting in a remarkable increase in the surface area of sulfides. Oxidation accelerates considerably and ARD results. ARD generation is inevitably catalyzed by bacteria except at extreme conditions such as freezing.

Unfortunately, sometimes ARD is unavoidable because sulfides occur with many minerals of mining interests and many metals exist and are mined as sulfides. Sources of ARD in a mine include open pit walls, waste dumps, access roads, stock piles, tailings facilities, and underground workings.

ARD gives rise to two kinds of problems: productional and environmental. ARD corrodes mining equipment and, when cleared by pumping from underground workings or from open pits during production, also corrodes pumps and pipes, thus increasing the operational cost.
The environmental damage that ARD causes is serious. The low pH in ARD helps dissolve metals such as Ca, Mg, Hg, Zn, Cd, Pb and non-metal elements such as As, P, and S from rock. Some of these elements are toxic or accumulatively toxic to animals and men. ARD is thus often an aqueous mixture characteristic of high total dissolved solids, high acidity, and low pH values. If ARD infiltrates into ground water, the quality of the ground water will deteriorate and become unsuitable for drinking and other purposes. If ARD is released untreated to natural waters, it can kill aquatic lives, overthrow ecological balances, and menace human beings through the food chain.

While ARD adds a little cost to the production, its environmental implications concern not only mining companies but also governments and the public. The treatment of ARD in order to conform to environmental standards could easily turn a profitable mining operation into a money-losing business. The probability of ARD production and remediation should be well examined during the planning stage of a new mine. The aftermath of an irresponsibly (or improperly) abandoned mine that produces ARD could be even more costly and often becomes a financial burden of local governments, as illustrated by the Rum Jungle Rehabilitation Project in Australia (Northern Territory Department of Mines and Energy, 1986) and the Mount Washington Acid Mine Drainage Abatement Program in British Columbia (Steffen Robertson and Kirsten et. al., 1987). For these reasons and for the purpose of environmental protection, both the Canadian and the U.S. governments have issued stringent standards for mining and milling effluent to be released to biota-containing waters. These standards usually specify the minimum allowable pH and maximum allowable levels of total suspended solids and a few dissolved metals. The British Columbia...
New Mine Development Review Process prescribes the examination of ARD issue to be a 
pre-requisite in the application of a new mine.

In light of the seriousness of the ARD problem, studies of various aspects of ARD prospered 
in the last three decades and are widely dispersed in the literature. These studies include, 
among others, prediction and modelling of ARD in acid-generating environments, laboratory 
simulation of the acid generation process, the bacterium *Thiobacillus ferrooxidans*, various 
remedial methods, and different preventive techniques. However, studies of the solution 
chemistry specific to ARD are relatively scarce. This thesis examines from a 
thermodynamic point of view the solution chemistry of the drainage emanating from the 
North Dump at BHP-Utah Mines Ltd., Island Copper Mine located on the northern end of 
Vancouver Island.

The present thesis evolves from a research project entitled "Acid Mine Drainage Study of 
the North Dump" undertaken jointly by the Department of Mining and Mineral Processing 
Engineering at the University of British Columbia and BHP-Utah Mines Ltd., Island 
Copper Mine (Acid Mine Drainage Study of the North Dump, 1991). The objectives of the 
Island Copper Mine project were to:

- determine how widespread and significant acid generation is in the Old North 
  Dump, the North Dump and the Eastern Most Outslope regions of the North Dump;
help develop both short and long-term procedures to mitigate or abate acid
generations from these waste dumps, and help develop plans for abandonment of the
above mentioned waste dumps.

Data collected in the Island Copper Mine project are used in this thesis. The objectives of
the present thesis are to:

- investigate the mechanism controlling the levels of dissolved species in the drainage
  by means of equilibrium chemistry and examine the interactions among different
dissolved species in the drainage;

- study the solubilization of metal species from waste rock and the removal of metal
  species from the drainage solution;

- infer the status of the dump with respect to oxidation and acid generation and help
  develop conceptual mitigation measures;

- calculate the acid generation life and the acid consumption life of the EMO and the
  Caps and evaluate the water balance of two self-enclosed areas;

- explore the role played by bacteria.
2.0 LITERATURE REVIEW

Acid mine drainage probably has as long a history as the mining industry itself. However, it was not until 1919 that the involvement of bacteria in acid mine drainage formation was recognized when Parr and Powell reported that the coal inoculated with unsterilized ferrous sulfate solution produced higher sulfate concentration than did the sterilized one.

In 1947, the bacteria *Thiobacillus ferrooxidans* were first isolated by Colmer and Hinkle (Colmer and Hinkle, 1947). At this time, *Thiobacillus ferrooxidans* were merely considered to oxidize iron by precipitating Fe(OH)$_3$. Since then, the study of acid mine drainage has flourished. The following sections give an account of some aspects of acid mine drainage studies related to this thesis.

2.1 Acid Generation Mechanisms

In 1970, Singer and Stumm showed that natural oxygenation was too slow to account for the rapid acid generation in acidic mine environments, therefore they proposed that
*Thiobacillus ferrooxidans* catalyzed the pyrite oxidation by converting ferrous iron to ferric iron, which in turn acted as an oxidant to pyrite (Singer and Stumm, 1970).

Kleinmann and Crerar demonstrated that *Thiobacillus ferrooxidans* can survive at pH values as high as 6.0 and at a pH slightly above 4.0 can reproduce at a relatively rapid rate, given the condition of minimum water flow (Kleinmann and Crerar, 1979). They inferred that *Thiobacillus ferrooxidans* directly oxidized pyrite, created a semi-isolated micro-environment, and spread once the local pH was lowered to roughly 4.0. They concluded that at such conditions the precursor *Metallogenium*, which was believed to mediate the acid formation process by bringing pH from 4.5 to 3.5 (Walsh and Mitchell, 1972), was not necessary.

A pH of 2.0 is not unusual in acid mine drainage. The lowest recorded pH is 0.5 (Rawat, 1983). The initial acidification process in acid mine drainage formation may proceed abiotically or with the help of bacteria. Abiotic acidification is possible but very unlikely to bring pH to below 4.0 because of its relatively slow reaction rate, its slowdown by decreases in pH and the lowering of acidity by frequent washing effect of rainfalls. One scenario where abiotic oxidation could bring pH to below 4.0 would be a case where precipitation were very little so that the acidity could accumulate, where the temperature were so low that it virtually prevented bacteria growth by freezing. The acid mine drainage formation at Faro in Yukon, Canada may have taken this route due to its geographical location.
Bacterially enhanced initial acidification is by far the most common mechanism in acid mine drainage environments. This bacteria-catalyzed acidification process can be expressed by the following three-stage reaction mechanism (Kleinmann and Crerar, 1979; Kleinmann, Crerar and Pacelli, 1981):

\[
\begin{align*}
FeS_2 + 7/2 \, O_2 + H_2O & \rightarrow Fe^{++} + 2 \, SO_4^{2-} + 2 \, H^+ \quad (1) \\
\text{(abiotic or by } \text{T.f.}) \\
Fe^{++} + 5/2 \, H_2O + 1/4 \, O_2 & \rightarrow Fe(OH)_3(s) + 2 \, H^+ \quad (2) \\
\text{(abiotic)}
\end{align*}
\]

Stage one: Abiotic Oxidation  
Mechanism: Reaction (1) proceeds both abiotically and by direct bacterial oxidation. Reaction (2) proceeds abiotically, slows down when pH falls.  
Chemistry: pH above approximately 4.5, high sulfate, low iron, little or no acidity.

\[
\begin{align*}
FeS_2 + 7/2 \, O_2 + H_2O & \rightarrow Fe^{++} + 2 \, SO_4^{2-} + 2 \, H^+ \quad (1) \\
\text{(by } \text{T.f.} \text{ or abiotic)} \\
Fe^{++} + 5/2 \, H_2O + 1/4 \, O_2 & \rightarrow Fe(OH)_3(s) + 2 \, H^+ \quad (2) \\
\text{(by } \text{T.f.})
\end{align*}
\]

Stage two: Bacterially Catalyzed Oxidation  
Mechanism: Reaction (1) proceeds by direct bacterial oxidation as well as abiotically. Reaction (2) proceeds at a rate determined by the activity of \textit{T. ferrooxidans}.  
Chemistry: Approximate pH 2.5-4.5, high sulfate, increasing acidity and total iron, low ferric/ferrous ratio.
Stage three: Bacterially Catalyzed Cycle

Mechanism: Reaction (3) proceeds at a rate totally determined by the activity of \textit{T. ferrooxidans}. Reaction (4) proceeds at a rate primarily determined by the rate of reaction (3).

Chemistry: pH below approximately 2.5; high sulfate, acidity, total iron and ferric/ferrous ratio.

The three stages are defined by the role that bacteria, presumably \textit{Thiobacillus ferrooxidans}, play. In the first stage, the fine-grained pyrite is oxidized by atmospheric oxygen and/or by \textit{Thiobacillus ferrooxidans} with the production of sulfate ions and acidity. If the pH is high enough the oxidation and hydrolysis of iron proceed. \textit{Thiobacillus ferrooxidans} are important in the continuation of the process, because they accelerate the decline of pH. Each rainfall interrupts the previous acidity accumulation, increasing the pH value. Without the involvement of bacteria, the pH would be likely to stay at a value near neutrality if rainfalls are frequent enough. At this stage, it is possible to stabilize the pH at a neutral value by neutralization. As long as available alkalinity exceeds acidity, the only downstream effect is an increase in SO$_4$$^{2-}$. 

\begin{align*}
2 \text{Fe}^{2+} + \frac{1}{2} \text{O}_2 + 2 \text{H}^+ & \rightarrow 2 \text{Fe}^{3+} + \text{H}_2\text{O} \quad (3) \\
(\text{by T.f.}) \\
\text{FeS}_2 + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} & \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (4) \\
(\text{abiotic})
\end{align*}
If acidity exceeds alkalinity, the pH begins to fall continuously until it reaches 3.0. At this point, the abiotic oxidation of Fe\(^{++}\) considerably slows down, since the reaction rate is a second order function of OH\(^-\) concentration. As the abiotic reaction (2) tends to cease, *Thiobacillus ferrooxidans* take over the role to oxidize Fe\(^{++}\). Although the overall stoichiometry remains the same, the turnover of reaction (2) from abiotic to biological symbols the onset of stage two. Again, the pH of the system could be stabilized with physical means such as sealing from oxygen, neutralization, etc., if conditions favour such treatments (low permeability, low surface pyrite exposure, etc.). It is difficult to bring the system back to stage one without appealing to bactericides.

If no preventive measures are taken at this point, the pH of the pyritic system will further decrease. As pH drops below 3.0, the increasing solubility of Fe\(^{3+}\) results in a great increase in Fe\(^{3+}/Fe^{++}\) ratio, whereby reactions (3) and (4) are turned on, stage three begins.

Once the pH reaches 2.5, which provides an optimal bacteria multiplication environment, an oxidation cycle of pyrite to SO\(_4^{2-}\) and Fe\(^{++}\) by Fe\(^{3+}\) and of Fe\(^{++}\) to Fe\(^{3+}\) by bacteria commences and gives rise to a great amount of acid production.

Kleinmann’s three stage acidification model was based on laboratory studies of simulated coal mine environments. With the difference between coal mine environments and metal mine environments in mind, one can apply the model to a metal mine environment to achieve insight into the acid generation mechanism.
However, laboratory simulations are idealized and simplified versions of real field conditions. Many natural (random) variations can not be simulated in a laboratory setup. While the general framework of Kleinmann's acidification model may remain valid at real field conditions, details will vary from one case to another. It is also possible that the real conditions are so far removed from the conditions Kleinmann simulated that the three stage model fails completely.

Some researchers have studied or observed acid drainage generation in field conditions. Rawat and Singh reviewed some of the literature on acid mine drainage (Rawat and Singh, 1983) and concluded that in coal mines: (1) organic sulfur is structurally bound and is insignificant in contributing to acid mine drainage; (2) pyrite is the major source of acid mine drainage; (3) framboidal (raspberry-like) pyrite is the most reactive form to produce acid mine drainage; and (4) bacteria are important and *Thiobacillus ferrooxidans* enhance the rate of pyrite oxidation.

From a different perspective, a group of Australian researchers investigated the microenvironment and the transport of oxygen to reaction spots within waste rock dumps undergoing pyrite oxidation (Bennett, et. al. 1987, 1988; Harries, Hendy and Ritchie, 1987; Harries and Ritchie, 1981, 1983, 1985, 1986, 1987). They studied the relationships among oxidation rates, temperature profiles, heat transfer, gas transport, and bacterial population densities in different regions and depths of two waste dumps. What they have achieved is summarized below:

- The rate of oxidation of pyrite materials depends on the rate of supply of oxygen.
Oxygen is transported into the dump in gas phase by diffusion, convection and advection. The extent to which one process dominates reflects the proximity of the edge of the dump and the variability of the gas transport properties of different parts of the dump. The differences in gas transport properties reflect in turn the differences in the types of material excavated from the pit, differences in the weathering properties of the excavated material, and the way in which the dumps were constructed.

Convection is the major transport mechanism of oxygen into those regions deep within the dumps where there is a high rate of pyrite oxidation and therefore a high temperature. The oxygen appears to be transported horizontally from the sides of the dumps, and then vertically through the hot oxidizing regions. This transport mechanism can penetrate into the dump up to 70 meters from the edge.

Diffusion is the dominant process away from the edges of the dump and is very slow.

Advection caused by atmospheric pressure variations occurs preferentially along high permeability paths in some locations.

High carbon dioxide and low oxygen levels were found within the dump which could be attributed to slow exchange rates between pore spaces and atmosphere, to oxygen consumption by pyrite oxidation, and to the release of carbon dioxide by dolomite weathering.
The wet/dry seasonal variations of the measured physico-chemical parameters (temperature profiles and pore gas concentrations) were insignificant, indicating that there was little variation in pyritic oxidation rate.

Temperature profiles can be used in a heat transfer mathematic model to find heat generation (i.e. intense oxidation) sources.

There were no measurable changes in bacterial population to correspond changes in the intensities of oxidation.

Acidification process is only one of the many processes involved in the acidic drainage generation. For an acidic seepage to occur from a waste dump, the following processes are also involved: the infiltration of precipitation into the dump, transport of free acidity by the infiltrating water, on-the-route neutralization of the migrating acidic water by acid-consuming materials, leaching of mineral constituents by the migrating acidic water, chemical interactions between different species in the migrating solution (such as precipitation of insoluble salts), and all the effects caused by the fluctuation of ground water table and movement of ground water if these are applicable, i.e., if there is a ground water table present within the dump. The quality of the drainage and ground water that leave the dump is determined by all of the above processes.

Comprehensive studies on the migration of acidity and dissolved species by flushing rain water and ground water in a waste dump environment are lacking. The geochemistry of the weathering of various minerals and of the neutralization of acidity in water paths
within a dump is poorly understood. It is understood, however, the percolation of rain water through waste dumps tends to follow some established channels. Probably only a fraction of the acidity generated within a dump is flushed out by rain water due to channelling. For a coal refuse dump, approximately 75% of the water intake during a rain storm is flushed through within 24 hours; 25% is retained in the dump for a much longer time (Dugan, 1987). A general discussion of various processes involved in acid mine drainage formation can be found in Steffen Robertson and Kirsten (B.C.), et. al., 1989.

The extent to which pyritic oxidation is accelerated by bacteria has been reported to vary widely, from several times to several thousands of times. This reflects the influence of environmental conditions on the effectiveness with which bacteria catalyze acid generation processes, as well as differences in research methodology.

While many researchers believe that the bacteria *Thiobacillus ferrooxidans* play a dominant role in accelerating pyrite oxidation, others disagree (Muyzer et. al., 1987). Using a special technique they developed, called combined immunofluorescence-DNA-fluorescence staining technique which readily differentiates *Thiobacillus ferrooxidans* from other bacteria species, Muyzer and his fellow workers demonstrated that *Thiobacillus ferrooxidans* were not able to multiply due to the competition of other bacteria in an unsterilized pyritic coal slurry inoculated with both a pure culture of *Thiobacillus ferrooxidans* and a mixed culture containing a variety of bacteria species. *Thiobacillus ferrooxidans* were only able to grow significantly when competing bacteria were absent, i.e., on a sterilized coal slurry inoculated with pure *Thiobacillus ferrooxidans* only. In addition, the total iron leached from pyrite by pure *Thiobacillus ferrooxidans* only was much less than that by mixed cultures. Muyzer
suggested that many "pure cultures" used by previous investigators were probably contaminated with other bacteria species, thus leaching effects caused by a mixed population of a variety of bacteria may have been incorrectly attributed to *Thiobacillus ferrooxidans*.

Muyzer's argument was also supported by other experiments. Harrison examined 23 strains of *Thiobacillus ferrooxidans* culture in 1982 and found that one quarter were contaminated with heterotrophic bacteria (Harrison, 1982). Lobos et. al. isolated *Acidiphilium organovorum* from a culture of *Thiobacillus ferrooxidans* which had been grown autotrophically on FeSO₄-basal salts medium for several years (Lobos et. al., 1986). As is understood now, real pure culture of *Thiobacillus ferrooxidans* is difficult to obtain and several species, both autotrophic and heterotrophic, or even mixotrophic are quite resistant to traditional purification techniques.

Muyzer's experiment probably represents one extreme while assuming complete domination of *Thiobacillus ferrooxidans* the other. The real bacterial population composition probably lies somewhere between these extremes and varies from place to place according to environmental conditions. Evaluation of bacterial population composition in a typical metal mine acidic waste rock environment is a rather difficult task and yet to be carried out.

In a more general sense, the B.C. AMD Task Force Draft Technical Guide Volume I (Steffen Robertson and Kirsten et. al., 1989) describes the major chemical factors which determine the rate of acid generation in the absence of significant bacterial enhancement as follows:

a) pH,
b) Temperature,
c) Oxygen content of the pore gas phase if saturation is less than 100%,
d) Oxygen concentration in the water phase,
e) Degree of saturation of dumps (or tailings) with water,
f) Chemical activity of Fe$^{3+}$,
g) Surface area of exposed metal sulfides,
h) Chemical activation energy required to initiate acid generation.

Strictly speaking, these factors determine the rate of sulfide oxidation rather than acid generation. Acid generation involves, in addition to oxidation, the neutralization of acidity by acid-consuming materials and hydrolysis of dissolved species in the solution phase. Therefore, the rate of acid generation from a dump is determined by the rate of oxidation as well as the rate at which acidity is consumed by neutralization or generated by hydrolysis. For example, if an originally acidic solution from sulfide oxidation contains high concentration of Fe$^{3+}$ and Al$^{3+}$, upon neutralization in a different region of the dump through which the water is percolating, Fe$^{3+}$ and Al$^{3+}$ will be precipitated as Fe(OH)$_3$ (ferric hydroxide) and Al(OH)$_3$ (gibbsite) by hydrolysis, contributing acidity to the solution:

$$\text{Fe}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3(\text{s}) + 3 \text{H}^+$$

$$\text{Al}^{3+} + 3 \text{H}_2\text{O} \rightleftharpoons \text{Al(OH)}_3(\text{s}) + 3 \text{H}^+$$

Among the listed factors that determine the rate of sulfide oxidation, factor d), oxygen concentration in the water phase, only operates when some part of the dump or tailings is
immersed in a water table. If a dump is completely above water table, factor d) has negligible effect on the rate of oxidation.

Factor f), the chemical activity of Fe$^{3+}$, or more straightly the concentration or activity of dissolved Fe$^{3+}$, rarely amounts to such an extent that it has a significant effect in the rate of oxidation in nature, if bacterial involvement is negligible.

Factor g), the surface area of exposed metal sulfide can be broken down to a few sub-factors: the size distribution of sulfide materials, the interlocking of sulfides with inert minerals, the dissemination of sulfide minerals, and the forms of existence of sulfide minerals (euhedral, amorphous, aggregative, etc.). Some of these may not have an immediate effect on the initial total surface area of sulfide minerals (which depends largely on the rock size distribution and exposure of sulfide on broken rock surfaces), they will determine the total surface area of exposed sulfides when rocks disintegrate through weathering.

Activation energy of a chemical reaction refers to the energy barrier that the reactants must overcome in order to be transformed into products. It measures the ease with which the chemical reaction can proceed. Since the initial acidification process is a quite complicated one which involves many possible reaction mechanisms rather than a simple chemical reaction, the activation energy (in a strict chemical sense) of a dump or tailings system is not defined. If factor h), chemical activation energy required to initiate acid generation (oxidation), is used in a broader sense to represent the ease with which the initial acidification process proceeds, it should cover the following factors (see above discussion of Kleinmann’s three-stage model of acidification): the total annual precipitation, the
frequency of precipitation, the total sulfide sulfur and its total exposed surface area, the kinds of metal sulfides present, the form of existence of sulfides, the availability of acid consuming materials and their properties, etc. It can be seen that some of these factors are already represented in the listed factors.

There is a very important factor that affects the rate of oxidation in a waste dump or tailings but that is not listed: the time that has past since the initial deposition. This affects the rate of oxidation in two ways: First, time is required for the acidity to build up. When acidity builds up, bacterial oxidation accelerates. This was demonstrated at Island Copper Mine by the fact that the EMO, the Old North Dump and the North West Dump all took a few years to acidify. Second, as time passes rocks are weathered, disintegrated to expose more sulfide minerals.

It is believed that bacteria are indigenous to sulfide waste environments. In most cases, bacteria will become involved sooner or later, even though their role in the early stage is insignificant. If bacteria are involved significantly to accelerate the oxidation process, the following factors, listed in the B.C. AMD Draft Technical Guide, also act to determine the overall rate of oxidation in addition to the factors that determine the abiotic oxidation listed previously.

a) Biological activation energy,
b) Population density of bacteria,
c) Rate of population growth,
d) Nitrate concentration,
e) Ammonia concentration,

f) Phosphorus concentration,

g) Carbon dioxide content,

h) Concentrations of any bacterial inhibitors.

Among these factors, d), e) and f) reflect the nutrient requirements of the autotrophic bacteria. Although the growth of bacteria require other nutrients (such as some metal elements that are used in special enzymes), the amounts needed are so small that they very rarely become limiting factors of growth. We can add the following factors to the above list to make it more complete:

i) Interaction of autotrophic bacteria with heterotrophic bacteria, molds and fungi, for example, the competition for growth-limiting nutrients,

j) The bacterial composition of the microflora.

Finally, the total acidity and pollutants carried away by seepage and ground water depend on, in addition to the factors mentioned above which determine the chemical and biological oxidation rate, the following factors:

a) The neutralization capacity of the waste materials,

b) The tortuosity of the waste dump or tailings,

c) The types and mineral composition of the waste rock,

d) The solution chemistry of the percolating water.
2.2  *Thiobacillus ferrooxidans*

Due to the involvement of *Thiobacillus ferrooxidans* in acid mine drainage formation and their utilization in bioleaching of valuable metals from low-grade ores, *Thiobacillus ferrooxidans* have been extensively studied. Their morphology, metabolism and culturing techniques are quite adequately established. Some of their genetic nucleotide sequences have been decoded. Many strains of different characteristics have been isolated. This section briefly summarizes what we currently know about this bacteria (Blancarte-Zurita et. al., 1986; Blancarte-Zurita, 1988; Clum, et. al., 1985; Collis, 1969; Cooper et. al. 1987; Gloxhuber, 1980; Hendy, 1987; Kleinmann and Crerar, 1979; Kleinmann, Crerar and Pacelli, 1981; Lobos et. al., 1986; Rawat et. al., 1983; Steffen Robertson and Kirsten et. al., 1989).

*Thiobacillus ferrooxidans* are rod-shaped (bacillus means "rod"), gram-negative, non-spore forming, aerobic (oxygen-dependent), motile bacteria. They measure 1.2-3.2 micrometers in length and 0.5-1.25 micrometers in diameter. They are acidophilic bacteria. They grow optimally in the pH range 1.5-4.0 and can survive in the pH range 0.5-7.0.

*Thiobacillus ferrooxidans* are mesophilic (medium temperature-loving) bacteria. They multiply most readily in the temperature range 20-35°C and can survive 15-40°C. However, strains that are able to grow at a temperature as low as 6°C has been reported (Ferroni, 1986). Harries et. al. reported a thermophilic bacteria species which was isolated from a waste dump undergoing intense oxidation (Harries, Hendy and Ritchie, 1987). The bacteria
had a optimum growth rate at pH 1.4 between 50-55°C and was able to oxidize iron. Whether the bacteria were *Thiobacillus ferrooxidans* was unclear.

*Thiobacillus ferrooxidans* derive energy for metabolism from the oxidation of sulfide to sulfate and of ferrous iron to ferric iron (hence *Thio-* meaning "sulfur" and *ferrooxidans* meaning "oxidizing iron"). They are also called chemoautotrophic (meaning "feed on inorganic carbon and derive energy from chemical reactions"), lithoautotrophic (meaning "derive energy from rock"), or chemolithotrophic. When the above mechanisms are not available, they are also able to oxidize other reduced forms of sulfur (such as thiosulfate) to sulfate to extract energy. They have been reported to use copper as an energy source (Nielsen and Beck, 1972; Tuovinen and Kelly, 1972; Ehrlich, 1978; Tuovinen et. al., 1978; all as cited by Blancarte-Zurita, 1988).

*Thiobacillus ferrooxidans* obtain carbon by fixing atmospheric carbon via the Calvin cycle. So they are autotrophic (meaning "feed on inorganic carbon"). *Thiobacillus ferrooxidans* either extract nitrogen from an inorganic source such as ammonium salts or nitrates or from fixation of atmospheric nitrogen (Blancarte-Zurita, 1988; Pretorius et. al., 1987).

The cell composition of *Thiobacillus ferrooxidans* has been reported to be 44% protein, 26% lipid, 15% carbohydrate and 10% ash. The cell envelope consists of three zones: a cytoplasmic membrane which constitutes the inner layer of the envelope bordering the cytoplasm, a middle zone that consists of a rigid layer of peptidoglycan and the periplasmic space, and an outer layer which contains lipopolysaccharide and lipoprotein. Elemental
analysis of the dried microorganism was 47.6% carbon, 10.1% nitrogen and 7.3% hydrogen (Blancarte-Zurita, 1988).

*Thiobacillus ferrooxidans* are usually cultivated in the 9K medium established by Silverman and Lundgren in 1959, or a modification of it. Heterotrophic bacteria are supposedly eliminated by serial culturing of *Thiobacillus ferrooxidans* in an organic carbon-free media such as 9K media. Other autotrophic bacteria that oxidize reduced forms of sulfur but not ferrous iron can be eliminated by growing *Thiobacillus ferrooxidans* culture on a medium that contains ferrous iron as the only energy source.

In addition to numerous antibiotics, *Thiobacillus ferrooxidans* are inhibited by simple organic acids such as malonic acid, itaconic acid, citric acid (Tuttle et. al., 1976), benzoic acid, sorbic acid (Onysko et. al., 1984); by some surfactants such as sodium lauryl sulfate (SLS), akylbenzene sulfonate (ABS) and alpha olefin sulfonate (AOS) (Kleinmann et. al., 1982, 1983; Onysko et. al., 1984); by certain metals such as mercury (Baldi et. al., 1987), molybdenum and tellurium (Kleinmann et. al., 1983), and by chlorides.

Tuttle et. al. examined the inhibition of bacterial oxidation of iron and sulfur by a series of organic acids (Tuttle et. al., 1976). They concluded that:

- Any organic substance which has an ability to interact abiotically with ferrous iron can be an apparent inhibitor of iron oxidation;
The relative electronegativity of the inhibitor molecules appears to correlate with the inhibition effectiveness;

A portion of inhibitive activities of organic acids can be attributed to the direct inhibition of the iron-oxidizing system;

At a concentration of about $2 \cdot 4 \times 10^{-6}$ M, malonic, itaconic, dihydrowyfumaric and hydroxypyrivic acids are inhibitory to the autotrophic growth. 10-fold greater concentrations of citric, transaconitic, isocitic, alph-keto-glictaric, malic and succinic acids have similar effect;

Bacteria can accumulate organic substances which adversely affect the growth of the bacteria themselves.

Kleinmann et. al. examined in laboratory and field-tested the bactericidal effect of SLS, ABS and AOS and found that the most effective biocidal agent was SLS.

Microorganisms' tolerance to metals varies from strain to strain. It is possible to selectively cultivate stains of bacteria that are highly tolerant to certain metals (Clum et. al., 1985) for use in bioleaching.

Estimation of *Thiobacillus ferrooxidans* population density can be performed by direct methods or indirect methods. Direct methods include Most Probable Number test (MPN), direct plate count, microscopic count with staining technique, etc. Indirect methods include
measurements of cell component such as total cell carbon weight and total cell protein weight, weight of metabolic products such as ATP (adenosine triphosphate), or consumption of growth essentials such as carbon dioxide or oxygen.

Bacteria can be killed in two ways: cell disintegration and/or irreversible damage to the genome (Mason et. al., 1986). The mechanism by which surfactants inactivate or kill *Thiobacillus ferrooxidans* can be depicted as follows: Although *Thiobacillus ferrooxidans* are an acidophilic chemoautotroph, their internal pH is approximately neutral. This is attained through the cellular control of the semi-permeability of the cell wall as well as the cytoplasmic membrane. Anionic surfactants, which alter the semi-permeability of the cytoplasmic membrane, result in the seepage of H⁺ into the cell. The change in internal pH inactivates the pH-sensitive enzymes in the cell, which in turn causes a slowdown of the Fe⁺⁺ oxidation catalyzed by the enzymes, thus induces bacteriostatic effects. High concentrations of surfactants kill the bacteria by permanently damaging the enzymes and by disintegrating the membrane material and the cell walls.

*Thiobacillus ferrooxidans* are very adhesive to solids such as rock particles (Bagdigan, 1986). Most of the bacteria population are probably resident on the solid surfaces rather than in liquid phase in a pyritic coal slurry. It is very difficult to detach the microorganisms from solid surfaces even with the help of such physical means as vigorous shaking and ultrasonic washing.
2.3 Literature on Island Copper Mine

There is abundant literature on the Island Copper Mine. Young described the exploration and geology of the Island Copper Mine property (Young and Rugg, 1971). Evans et. al. documented the establishment of the monitoring program for the underwater discharge of tailings into Rupert Inlet (Evans et. al., 1972, 1979). Drinkwater examined the patterns of tidal mixing in Rupert and Holberg Inlets and their environmental implications (Drinkwater, 1973). Hay carried out a comprehensive study of the underwater transport of tailings, the formation and evolution of submarine channels and the turbidity currents in Rupert Inlet using acoustic sensing technique (Hay, 1981). Waldichuk et. al. gave a critical review of the environmental significance of the underwater tailings disposal at Island Copper (Waldichuk and Buchanan, 1980). A comprehensive list of pre-1980 literature entries can be found in Waldichuk et. al., 1980.

However, the above literature is mostly concentrated on various aspects of the underwater disposal of tailings at Island Copper Mine, since the acid mine drainage problem was not realized until 1985. The acid mine drainage problem was addressed in the report by BHP-Utah and Rescan, 1988, which presented the study of the South Wall Pushback Project and related environmental issues.
3.0 RESEARCH SITE

3.1 General Description

Island Copper Mine, owned and operated by BHP-Utah Mines Ltd., is one of Canada's largest open pit, low-grade copper mining operations. It is located on the north shore of Rupert Inlet, about 16 kilometres south of Port Hardy at the north end of Vancouver Island (Figure 1). The revenue-producing metals are copper, molybdenum, gold, silver and rhenium.

The operation at Island Copper Mine consists of open pit mining by truck and shovel method in conjunction with the use of an in-pit crushing/conveying system, and milling in its concentrator by a conventional grinding/flotation circuit.

At Island Copper Mine, waste rock is disposed of in waste dumps at various locations near the pit, both on land and into the sea. As of January, 1989, four waste dumps have been developed on land since the commencement of operation: the North Dump ($84.2 \times 10^6$ tons), the North West Dump ($1.1 \times 10^6$ tons), the West Dump ($6.6 \times 10^6$ tons) and the South Dump ($6.6 \times 10^6$ tons). The majority of the waste rock ($510 \times 10^6$ tons) has been placed on the Beach Dump along the north shoreline of, and extending into Rupert Inlet.
Although assessment of acid mine drainage problems has today become an integral part of the environmental assessment required by government regulatory agencies, the AMD problem was not widely recognized at the time of design and construction of the Island Copper Mine. In fact, the waste rock at ICM was all expected to be non-acid generating. Little detailed consideration was given to the aspect of AMD prevention and handling during the early stage of waste deposition.

The generation of AMD was not fully appreciated at Island Copper until 1982. Then the west pit wall, after being exposed by mining activity and left undisturbed, showed acidification with pH values as low as 3.5; and visible yellow stains (Fe(OH)$_3$) started stringing out on the wall. In December 1985, the seeps from the Old Marginal Dump at the north western corner of the North Dump - the oldest land dump - began to show a significantly elevated level of zinc, indicating the oxidation of waste material in the dump. Concurrent with the increasing interest in AMD by industry and academia, the advance of our understanding of acid generation process in nature and the development of acid drainage at several metal mines in B.C., and prompted by the indications of potential acid production problems, Island Copper expanded its monitoring program of land dump drainage with a purpose of pin-pointing acid-generating spots. This resulted in the finding of a few active areas, the most serious of which was the Eastern Most Outslope, followed by the Old North Dump.
3.2 Geology

The Island Copper deposit is underlain by a thick section of Bonanza Volcanic Formation, which strikes about N60°-70°W and dips 30°-40° to the south. The principal ore control is a dyke-like quartz-feldspar porphyry intrusion, Jurassic in age, which has invaded the Triassic Bonanza tuffs. The porphyry dyke is reversed-U shaped, strikes N70°W over 6,000 feet, dips 50°NNE, and is usually 400-500 feet thick, although its maximum thickness reaches 900 feet. Ore is concentrated along both the foot wall and the hanging wall of the dyke structure, but occasionally occurs in some places entirely across the dyke.

The weakly mineralized porphyry dyke separates the ore body into two limbs, which are connected on the east and open on the west. The ore zone averages about 1,100 feet in thickness from the hanging wall to the foot wall boundaries, and extends approximately 3,000 feet along the dyke, with the north limb extending 1,000 feet further west than the south limb.

Copper and molybdenum mineralization occurs in all rock types but is found primarily in the fractured and silicified andesite as fillings and smears. About one half of the ore grade mineralization is found in the biotite and transition zone andesite, and the remainder in the crackle zone, the rotational breccia and the dyke.

The mineralization in the deposit consists of pyrite, magnetite, chalcopyrite, some bornite and molybdenite in order of decreasing percentages. Pyrite is found in all types of rocks present in finely disseminated forms and also as thin and randomly oriented seams. The
pyrite content of the ore body generally varies from two to five percent but there are local concentrations, primarily fracture-controlled, of 15 to 20 percent.

Alterations of several types have affected the volcanic host rocks. In order of decreasing intensity they are: 1) silicification 2) argillization 3) saussuritization and 4) biotitization. In addition, some potassium feldspar has been introduced and carbonate, talc, chlorite and pyrophyllite have been developed in varying amount. Silicification is generally pervasive through the mineralized zone but is most intense in the brecciated volcanics along the dyke margins. The clay alteration is quite closely associated with the silicification and is most evident in the fault zones. Saussuritic alteration is quite pervasive and may be largely deuteritic. The potassium feldspar alteration is closely associated with silicification and is particularly intense near the porphyry-dyke contacts. Some carbonate is present in fractures. Talc and chlorite are the common alteration products of the mafic elements in the andesite and are probably of both deuteritic and hydrothermal origins.

The Island Copper deposit is in general covered with a glacial till layer with a depth ranging from a few feet to as deep as 250 feet.

3.3 The North/Old North Dump

The North Dump is the largest of the four dumps developed on land at the Island Copper Mine (Figure 2). The initial deposition of waste on the North dump began in April, 1971 and the dump was completed in August, 1985. During the fifteen years, 84.2 million tons of waste rock and till were disposed of in an area of 140 hectares.
Figure 2  Location of the North Dump at Island Copper Mine
Several regions of the North Dump possess their own common characteristics and were designated by different names. They are the Caps, the Eastern Most Outslope (EMO), the Old Marginal Dump and the Old North Dump (Figure 3). The physical parameters of these regions are given in Table 1.

<table>
<thead>
<tr>
<th>Physical Parameters of Designated Regions on North Dump†</th>
<th>North Dump</th>
<th>The Caps</th>
<th>EMO</th>
<th>Old Marginal</th>
<th>P.N.D.E. C.E.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Mass (million tonnes)</td>
<td>76.4</td>
<td>9.12</td>
<td>4.67</td>
<td>1.28</td>
<td>62.6</td>
</tr>
<tr>
<td>% of Till</td>
<td>36.5</td>
<td>0.0</td>
<td>2.42</td>
<td>65.4</td>
<td>44.4</td>
</tr>
<tr>
<td>Area (Ha.)</td>
<td>140.0</td>
<td>40.0</td>
<td>15.2</td>
<td>N/A</td>
<td>84.8</td>
</tr>
<tr>
<td>Total Volume (x10^6 m³)</td>
<td>38.9</td>
<td>4.7</td>
<td>2.5</td>
<td>0.65**</td>
<td>31.6</td>
</tr>
<tr>
<td>Average Bulk Density (kg/m³)</td>
<td>1965</td>
<td>1928</td>
<td>1840</td>
<td>&gt;1981</td>
<td>1981</td>
</tr>
<tr>
<td>Average Porosity (%)</td>
<td>21.0</td>
<td>27.3</td>
<td>30.3</td>
<td>&lt;19.0</td>
<td>19.0</td>
</tr>
</tbody>
</table>

† Figures in this table are taken from *Acid Mine Drainage Study of the North Dump - Final Report*, University of British Columbia, Department of Mining and Mineral Process Engineering, 1991.

* The Part of the North Dump Excluding the Caps and EMO.

** Calculated using a bulk density of 1981 kg/m³.
Figure 3  Regions of North Dump and Locations of Drill Holes

NOTE: Coordinate scale follows that of ICM
Figures are in feet
3.4 Hydrology

The North Dump area at ICM is located mainly within the historic End Creek watershed. A small part of the North Dump intrudes Stephens Creek watershed on the northwest and another small part lies within the historic Trey Creek watershed. Figure 4 is a pre-mining surface topographical map, on which surface water courses and watershed boundaries are drawn according to the topography. The current pit boundary, the Beach Dump and the North Dump are superimposed on the map to illustrate their locations relative to the historic watersheds. Before mining, rain water received by what is now the North Dump area reported to three locations: 1) the East Twin Lake, which was connected to the West Twin Lake, which fed to the Bay Lake, which was the headwaters of Stephens Creek; 2) End Creek, which collected the majority of the water from the area and reported to Rupert Inlet; and 3) Trey Creek and other small streams which also flowed into Rupert Inlet.

The development of the North Dump has significantly altered the surface hydrology of the area in two ways: The deposition of waste materials has redistributed the rain water and the drainage management has completely changed the natural water courses. The rain water redistribution by the existence of waste materials depends on several factors, such as the topography of the waste dump, the porosity distribution of the dump, presence of compacted layers and the size of the rain storm.
The drainage management system has evolved over the past years. At the time of writing (1990), all drainage running off or flowing through the North Dump, except that lost to ground water and a small subterranean flow which leaks some drainage from NDD to the Twin Lakes, is collected by a ditch system around the dump, treated by mixing with the pit dewatering water and released to Rupert Inlet through the Beach Dump. This ditch system consists of NDD, TED, TCR, EMO, EDL and EDD (Figure 5).

NDD, which flows into TED, intercepts the flow emanating from the north western part of the North Dump and previously reporting to Twin Lakes. TED intercepts the Old End Creek and other subterranean flows and surface runoffs within the End Creek watershed. All the old water courses within the North Dump area have been redirected to the treatment pond on the Beach Dump. It is also noted that the part of the End Creek watershed to the north of the North Dump contributes some water to the North Dump, mostly as subterranean flows through the North Dump.

3.5 Land Dump Monitoring

The Island Copper Mine Environmental Department has operated a comprehensive fresh water monitoring program since the pre-operational phase of the mine. The monitoring scheme generally satisfied our research requirements. Some modifications to the monitoring scheme were made corresponding to the research needs. During the past years, ICM regularly sampled the streams listed in Table 2 for water quality analysis. Locations of the sampling stations are shown in Figure 5.
Figure 5  ICM North Dump Drainage Collection Ditch System and Fresh Water Sampling Stations
Table 2  Island Copper Regular Fresh Water Sampling Stations

<table>
<thead>
<tr>
<th>Station Code</th>
<th>Station Name</th>
<th>Sampling Frequency</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDD</td>
<td>North Drainage Ditch</td>
<td>Monthly</td>
</tr>
<tr>
<td>TED</td>
<td>Ten Eighty Ditch</td>
<td>Monthly</td>
</tr>
<tr>
<td>EDD</td>
<td>East Drainage Ditch</td>
<td>Monthly</td>
</tr>
<tr>
<td>PDW</td>
<td>Pit Dewatering</td>
<td>Monthly</td>
</tr>
<tr>
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<td>Bay (Francis) Lake</td>
<td>Monthly</td>
</tr>
<tr>
<td>TLD</td>
<td>Twin Lakes Discharge</td>
<td>Monthly</td>
</tr>
<tr>
<td>SCR</td>
<td>Stephens Creek</td>
<td>Monthly</td>
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<td>JLD</td>
<td>Joe Lake Drainage</td>
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<td>TCR</td>
<td>Old Trey Creek</td>
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<td>PDP</td>
<td>Pit Dewatering Pond</td>
<td>Monthly</td>
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V-notched weir flowmeters have been installed on six streams that flow through the North Dump area. The six stations are: NDD, EDL, EMO, EDD, TED, TCR. Instantaneous flow rates are read on the flowmeters. Flow rate data are however sparse up to the time of writing because of the short time of data accumulation and irregularly-scheduled measurements. Two in situ measurements - flowrate and conductivity - were taken weekly on these streams. Frequency was increased during the wet seasons, especially during major rain storm events.
4.0 RESEARCH METHODS

4.1 Data Collection

Data collected at the research site that are relevant to this study include:

- All available water quality analyses of streams around the mine site,
- Pre-operational baseline monitoring records of fresh water streams,
- All available flowrate measurements of drainage ditches and pit dewatering,
- Acid-base accounting of land dump drill hole samples,
- Mine site and Port Hardy meteorological records,
- Mining records, including the North Dump development records, month-to-month benchwise mining operation records, truck haulage records, etc.,
- Aerial photographs of the pit and dump areas,
- Land dump drainage management history,
- Settling pond water quality,
- Various maps, including location maps, topographical (contour) maps and survey maps, all drawn to scale,
- South Wall Pushback project study report.
4.2 Drainage Sample Collection

Drainage sample collection, measurement of physical parameters and chemical analysis were performed by qualified personnel from ICM environmental laboratory. Temperature and pH were measured *in situ* at each fresh water monitoring station. A one-litre sample was then taken directly from each stream into an acid-washed polyethylene bottle. Samples were returned to the laboratory for immediate filtration through 0.45 μm membrane filters. The filtrates were stored prior to analysis in a second set of acid-washed polyethylene bottles and preserved by the addition of 7 ml of concentrated nitric acid. Separate samples were collected for the analyses of arsenic and mercury, although these were treated in the same manner.

4.3 Methods of Chemical Analysis and Physical Measurement

Total dissolved solids was measured gravimetrically. Sulfate was determined turbidimetrically. Total alkalinity was determined using a potentiometric titration. Calcium and magnesium were measured by flame atomic adsorption spectroscopy (AAS). Dissolved cadmium, copper, iron, lead, manganese, molybdenum and zinc were analyzed by flame atomic absorption spectrometry (AAS) after digestion and concentration with HNO₃:HClO₄:HF. Total and dissolved arsenic were determined by reduction to As(III) using KI:HCl and analyzed using hydride generation AAS. All analytical methods were based on those described in APHA, 1985 and were documented in detail in the ICM Environmental Department Methods Manual of 1986.
5.0 RESULTS AND DISCUSSION

5.1 Acid Generation Assessment of the North Dump

5.1.1 Acid-Base Accounting

A drilling program was conducted on the North Dump to sample the dump material. Seven wells were percussion-drilled with a Becker drill. Drill cuttings were sampled in an eight-foot interval and submitted for acid-base accounting. The locations of the drill wells are illustrated in Figure 3 and the acid-base accounting results are tabulated in Table 3.

5.1.2 Flowrate Analysis

Table 4 presents all the available flowrate data on fresh water streams. These data were measured by weirs except those of PDW which were pit dewatering pumping records. An analysis was performed on the data and the results are presented in Table 5 and Figure 6.
Table 3  Acid-Base Accounting Results of North Dump Drilling Samples

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* Sample was from 3 - 5 feet.
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6 - 14 | 64.8 | 28.5 | -36.3 | 60.9 | 55.4 | -5.5
14 - 22 | 63.2 | 18.7 | -44.5 | 62.2 | 57.7 | -4.5
22 - 30 | 35.9 | - | - | 77.3 | 57.7 | -19.6
30 - 38 | 33.1 | - | - | 68.5 | 47.9 | -20.6
38 - 46 | 45.6 | 8.0 | -37.6 | 101.9 | 26.7 | -75.2
46 - 54 | 52.5 | 19.9 | -32.6 | 97.5 | 71.2 | -27.3
54 - 62 | 65.8 | 15.9 | -49.9 | 101.5 | 58.7 | -42.8
62 - 70 | 93.4 | 71.4 | -22.0 | 72.0 | 58.7 | -13.3
70 - 78 | 87.0 | 68.3 | -18.7 | 68.4 | 70.8 | 2.4
78 - 86 | 86.4 | 79.0 | -7.4 | 43.5 | 42.4 | -1.1
86 - 94 | 62.1 | 20.5 | -41.6 | 71.2 | 50.7 | -20.5
94 - 102 | 99.5 | 64.3 | -35.2 | 70.8 | 59.1 | -11.7
102 - 110 | 74.7 | 38.6 | -36.1 | 68.1 | 16.1 | -52.0
110 - 118 | 60.6 | 24.8 | -35.8 | 66.2 | 18.7 | -47.5
118 - 126 | 85.6 | 45.9 | -39.7 | 56.1 | 16.3 | -39.8
126 - 134 | 90.4 | 88.5 | -1.9 | 50.1 | 16.1 | -34.0
134 - 142 | 99.1 | 69.4 | -29.7 | 77.3 | 17.5 | -59.8
142 - 150 | 86.3 | 71.2 | -15.1 | - | 15.4 | -
Average | 67.2 | 44.3 | -22.9 | 71.2 | 42.6 | -28.6

Notes: APP - Acid Producing Potential, kg H\textsubscript{2}SO\textsubscript{4}/tonne of Waste Material.

ACP - Acid Consuming Potential, kg CaCO\textsubscript{3}/tonne.
Note that 1 kg H\textsubscript{2}SO\textsubscript{4}/tonne = 1.02 kg CaCO\textsubscript{3}/tonne.

NNP - Net Neutralizing Potential, Unit Same as ACP.
### Table 4  
Volumetric Flow Rate Monitoring Data of Some Drainage Streams

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Table 5  Summary of Flowrate Data Analyses

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<th>EMO</th>
<th>EDL</th>
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<td>5.5</td>
<td>4.7</td>
<td>10.8</td>
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Figure 6  Contribution of Fresh Water Streams to TED
5.1.3 Water Balance Calculation

We calculated the pathway of the total precipitation in the period September 27, 1987 - September 24, 1988 on the basis of an enclosed area on the North Dump. It is assumed that all the rain water falling on this area either evaporated, or reported to TED, or percolated into the ground water system. The result is presented in Table 6. A similar pathway calculation was also performed on the rain water falling on EMO. The results appear in Table 7. Details of calculation and assumptions for Tables 6 and 7 are included in Appendix I.

The percentage of the rain water recharging the ground water in EMO, 7.3%, is much lower than that of the first calculation. This difference may be due partly to variations in environmental conditions between the two areas, and partly to assumption errors.

Table 6  Pathway of Rain Water Falling on an Enclosed Area on North Dump

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<th>Volume of Water (m³)</th>
<th>Percentage (%)</th>
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<tr>
<td>Evaporation</td>
<td>783,000</td>
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<td>To TED (as runoff and seepage)</td>
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<tr>
<td>Percolation to Ground Water</td>
<td>618,000</td>
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* Calculated based on the pit area, precipitation and dewatering data for the period Sept. 27, 1987 - Sept. 24, 1988. Details can be found in *Acid Mine Drainage Study of the North Dump - Final Report*. It is felt that this figure is probably too high.
Table 7 Pathway of Rain Water Falling on EMO

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<th>Breakdown</th>
<th>Volume of Water (m$^3$)</th>
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<tr>
<td>Evaporation</td>
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<td>To EMO Ditch (As Seeps or Runoff)</td>
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<td>To Ground</td>
<td>22,600</td>
<td>7.3</td>
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* See the footnote for Table 6.

5.1.4 Calculation of Acid Generation Life of EMO and Caps

The duration of acid generation in both EMO and the Caps has been calculated using the data presented in the above three sections. The details of calculation are documented in Appendix II. The calculation, however, is on an entirely static basis. It did not take into consideration the changes in the rate of acid production and consumption in the future. To forecast the changes in acid production rate and acid consumption rate requires a mathematical model, which was not attempted in this study. The results of the calculation can nevertheless be used in guiding the abandonment planning if caution is exercised.

It is found that the EMO contains enough acid-producing material to produce sulfuric acid at the current rate (approximately 370 tonnes H$_2$SO$_4$ / year) for 650 years. Presently, 80% of the sulfuric acid produced by the EMO is neutralized by acid-consuming materials within
the dump. The acid-consuming materials will be depleted in 300 years. If the current rate of acid release continues after that, the pH of the EMO drainage will significantly drop and perhaps will approach the lower limit of 1.5.

Based on the current rate, the Caps is estimated to be capable of producing acid for 650 years at a rate of 730 tonnes per year, of which approximately 87% is consumed within the dump. The acid-consuming material will last almost as long as the acid-producing material. Therefore, the major downstream effect during the entire acid-generating life of the Caps will be elevated levels of sulfate and some easily soluble metals.

5.2 Land Dump Drainage Monitoring Records

Tables 8 through 16 present the available water quality data of drainage streams emanating from the North Dump. These data are used in the following sections to examine the chemistry of the dump drainage at Island Copper Mine.
Table 8  North Dump Drainage (NDD) Water Quality 1980-1989

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<th>Solids (mg/l)</th>
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<th>Alkal. (mg/l)</th>
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<th>Total Mg (mg/l)</th>
<th>Cu (mg/l)</th>
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Level 11.5 |
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* Old North Dump reclaimed. 80% flow diverted into TED. ** 100% drainage diverted into TED. ** After the first major rainstorm 1987.

† ICM's permit for the release of effluent to sea water. This is included here for reference only.
Table 9  Twin Lake Discharge (TLD) Water Quality 1986-1988

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<th>Date</th>
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<th>Total Mg (mg/l)</th>
<th>Cu (µg/l)</th>
<th>Fe (µg/l)</th>
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<th>Cd (µg/l)</th>
<th>As (µg/l)</th>
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*Fresh Water 7.1* 69 4.53 7.83 1.83 5.4 248 3.6 57 4.1 32 0.85 1.3

Baseline

†ICM Permit 6.5-
Level 11.5

These are the annual averages of the year 1971 of twelve fresh water streams around the mine site. Data were collected in the pre-operational monitoring program. See BHP-Utah, ICM and Rescan, April, 1988.

† See the footnote for Table 8.
Table 10  North Dump Subterranean Flow (NDS) Water Quality 1988

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**ICM Permit 6.5-**

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**Fresh Water**

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* See the footnote for Table 8.
** See the footnote for Table 9.
Table 11 Ten Eighty Ditch (TED) Water Quality 1986-1989

| Date  | pH  | Solids | Sulph. | Alkal. | Ca | Mg | Cu | Fe | Pb | Mn | Mo | Zn | Cd | As |
|-------|-----|--------|--------|--------|----|----|----|----|----|----|----|----|----|----|----|
| Mar 86 | 8.2 | 690    | 340    | 130    | 150.0 | 17.0 | 15.0 | 36 | 2.4 | 170 | 19.0 | 170 | 1.00 | 0.4 |
| Jun 86 | 8.0 | 1100   | 550    | 190    | 220.0 | 27.0 | 18.0 | 16 | 3.6 | 77  | 22.0 | 140 | 0.50 | 0.6 |
| Sep 86 | 8.0 | 1200   | 680    | 210    | 210.0 | 36.0 | 10.0 | 12 | 1.2 | 26  | 25.0 | 49  | 0.10 | 0.5 |
| Dec 86 | 7.9 | 660    | 440    | 79     | 120.0 | 14.0 | 19.0 | 50 | 3.8 | 250 | 16.0 | 400 | 3.50 | 1.3 |
| Mar 87 | 7.8 | 820    | 370    | 120    | 150.0 | 18.0 | 22.0 | 34 | 1.2 | 260 | 16.0 | 330 | 2.10 |    |
| Jun 87 | 8.0 | 720    | 610    | 190    | 240.0 | 29.0 | 15.0 | 18 | 2.5 | 300 | 19.0 | 93  | 0.60 | 0.1 |
| Sep 87 | 8.2 | 1300   | 690    | 220    | 290.0 | 38.0 | 18.0 | 16 | 3.8 | 130 | 18.0 | 99  | 0.40 | 1.4 |
| Dec 87 | 7.9 | 1200   | 690    | 97     | 250.0 | 27.0 | 10.0 | 47 | 2.4 | 170 | 12.0 | 950 | 4.40 |    |
| Jan 88 | 8.1 | 640    | 420    | 29     | 160.0 | 17.0 | 31.0 | 32 | 1.0 | 400 | 11.0 | 870 | 5.40 |    |
| Feb 88 | 7.1 | 570    | 400    | 69     | 150.0 | 16.0 | 23.0 | 26 | 2.0 | 320 | 14.0 | 790 | 5.90 |    |
| Mar 88 | 8.1 | 590    | 380    | 87     | 140.0 | 15.0 | 16.0 | 29 | 2.0 | 280 | 13.0 | 480 | 3.60 | 0.4 |
| Apr 88 | 8.4 | 800    | 360    | 130    | 180.0 | 22.0 | 12.0 | 14 | 3.1 | 350 | 11.0 | 400 | 2.40 |    |
| May 88 | 8.6 | 900    | 480    | 160    | 180.0 | 22.0 | 10.0 | 12 | 2.5 | 380 | 13.0 | 210 | 1.50 |    |
| Jun 88 | 8.5 | 700    | 420    | 150    | 170.0 | 21.0 | 9.0  | 15 | 3.0 | 340 | 14.0 | 190 | 1.80 | 0.7 |
| Jul 88 | 8.0 | 460    | 230    | 190    | 32.0  |    | 11.0 | 16 | 1.0 | 110 | 17.0 | 29  | 0.10 |    |
| Aug 88 | 8.1 | 910    | 460    | 220    | 200.0 | 32.0 | 13.0 | 14 | 1.2 | 14  | 17.0 | 20  | 0.10 |    |
| Sep 88 | 4.5 | 840    | 600    | -59    | 190.0 | 15.0 | 280.0| 400| 1.0 | 560 | 4.0  | 900 | 5.80 |    |
| Oct 88 | 6.8 | 700    | 47     | 230.0  | 25.0  |    | 75.0 | 11 | 3.2 | 1500| 14.0 | 4000| 21.00|    |
| Nov 88 | 6.9 | 220    | 11     | 2.4    | 870   | 13.0 | 28.0 | 34 | 1.0 | 310 | 13.0 | 1100| 5.80 | 0.2 |
| Dec 88 | 7.5 | 710    | 489    | 87     | 160.0 | 17.0 | 28.0 | 54 | 1.0 | 510 | 13.0 | 1100| 5.80 |    |

**Fresh Water** 7.1 | 69 | 4.53 | 7.83 | 1.83 | 5.4 | 248 | 3.6 | 57 | 4.1 | 32 | 0.95 | 1.3 |

Baseline

**ICM**

**Perm 6.5**

**Level 11.5**

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* See the footnote for Table 9.
** See the footnote for Table 8.
Table 12  Trey Creek (TCR) Water Quality 1987-1989

<table>
<thead>
<tr>
<th>Date</th>
<th>pH</th>
<th>Diss. Solids (mg/l)</th>
<th>Total pH (mg/l)</th>
<th>Total Sulph. (mg/l)</th>
<th>Total Alkal. (mg/l)</th>
<th>Total Ca (mg/l)</th>
<th>Total Mg (mg/l)</th>
<th>Dissolved Metals (μg/l)</th>
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</thead>
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<td>1800</td>
<td>970</td>
<td>200</td>
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<td>48.0</td>
<td>15.0</td>
<td>9.3</td>
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<td>740</td>
<td>100</td>
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<td>970</td>
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<td>970</td>
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<td>1600</td>
<td>1050</td>
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<td>1560</td>
<td>1050</td>
<td>90</td>
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<td>118</td>
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<td>100</td>
<td>5.1</td>
<td>110</td>
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<td>150</td>
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<td>120</td>
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<td>1900</td>
<td>1200</td>
<td>190</td>
<td>420.0</td>
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<td>6.8</td>
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<td>1900</td>
<td>1200</td>
<td>180</td>
<td>410.0</td>
<td>150</td>
<td>6.8</td>
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| **Fresh Water** | 7.1 | 69 | 4.53 | 7.83 | 1.83 | 5.4 | 248 | 3.6 | 57 | 4.1 | 32 | 0.85 | 1.3 |
| **Baseline**    |     |    |      |      |      |    |     |    |    |    |    |     |     |
| **ICM**         |     |    |      |      |      |    |     |    |    |    |    |     |     |
| **Permit Level**| 5.5 | 50 | 50   | 500  | 10  | 100 |

* See the footnote for Table 9.  
** See the footnote for Table 8.
Table 13  Eastern Most Outslope (EMO) Water Quality 1987-1989

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<th>Date</th>
<th>pH</th>
<th>Diss. Solids</th>
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<th>Alkal. (mg/l)</th>
<th>Total Ca (mg/l)</th>
<th>Total Mg (mg/l)</th>
<th>Cu (mg/l)</th>
<th>Fe (mg/l)</th>
<th>Pb (mg/l)</th>
<th>Mn (mg/l)</th>
<th>Mo (mg/l)</th>
<th>Zn (mg/l)</th>
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<th>As (mg/l)</th>
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<td>14.00</td>
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* Fresh Water 7.1 69 4.53 7.83 1.83 5.4 248 3.6 57 4.1 32 0.85 1.3

** Baseline

# ICM Permit 6.5-

| Level 11.5 | 50 | 50 | 500 | 10 | 100 |

* See the footnote for Table 9.
** See the footnote for Table 8.
<table>
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</table>

**Fresh Water**: 7.1 | 69 | 4.53 | 7.83 | 1.83 | 5.4 | 248 | 3.6 | 57 | 4.1 | 12 | 0.05 | 1.3

**Baseline**: 6.5-

**ICH Permit 6.5-**

**Level 11.5**: 50 | 50 | 500 | 10 | 100

---

* See the footnote for Table 9.

** See the footnote for Table 8.
Table 15  East Dump Drainage (EDD) Water Quality 1981-1988

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<th>Date</th>
<th>pH</th>
<th>pH sulph.</th>
<th>pH solids</th>
<th>Ca [mg/l]</th>
<th>Mg [mg/l]</th>
<th>Cu [mg/l]</th>
<th>Fe [mg/l]</th>
<th>Po [mg/l]</th>
<th>Mn [mg/l]</th>
<th>Ho [mg/l]</th>
<th>Zn [mg/l]</th>
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** Fresh Water: 7.1 ** 69 4.53 7.81 1.83 5.4 248 3.6 57 4.1 32 0.85 1.3

Baseline

ICM

Permit 6.5

Level 11.5

* See the footnote for Table 9.

** See the footnote for Table 8.
## Table 16  East Dump Drainage (EDD) Water Quality 1988-1989

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*Fresh Water 7.1  69 4.53 7.83 1.83 5.4 248 3.6 57 4.1 32 0.85 1.3
Baseline

** See the footnote for Table 8.

See the footnote for Table 9.
5.3 Chemistry of North Dump Drainage Water

As is observed by researchers, many natural waters are not in thermodynamic equilibrium. The drainage streams at ICM may be no exception. Realizing this limitation, we can nevertheless employ equilibrium chemistry in our aid in understanding the processes in AMD generation. As has been demonstrated in many natural water studies, thermodynamics can deliver very good, sometimes excellent answers to many questions.

No one can avoid the problem of activity coefficients while dealing with electrolyte solution chemistry. What we measure with analytical tools such as AAS and ICP is the concentration. What we use in the entire kingdom of equilibrium chemistry (that is, thermodynamics) is the activity. The bridge linking these two is the activity coefficient. In very dilute solutions, such as those with a total molar ionic strength of $10^{-6}$ or less, the distinction between activity and concentration disappears. But in the case of ICM drainage, whose total ionic strength is around 0.0426 as demonstrated in the following section, activity coefficients deviate markedly from unity and therefore have to be taken into account. This is accomplished by first estimating the total ionic strength of a typical drainage and then calculating the individual ion activities using the improved Debye-Hückel formula. Today's science provides very exact but complicated empirical expressions for the calculation of activity coefficients. They were not adopted because firstly any gain in precision would be outweighed by the inaccuracy of estimated total ionic strength which all the empirical expressions are based on and secondly the extended Debye-Hückel formula does give an adequate accuracy up to a total ionic strength of 0.1.
The activity of water can be taken to be unity in all cases without incurring noticeable error. The water activity in sea water is 0.98 at an ionic strength of about 0.7. All the drainage at ICM has an ionic strength less than 0.1, therefore a water activity greater than 0.98 but less than unity.

Although working with individual ion activities in solving electrolyte aqueous solution problems is convenient, individual ion activities are not experimentally measurable. What we can measure experimentally is the mean activity coefficient. To partition the mean activity coefficient of ionic salts into individual ion activity coefficients, we need to adopt a more or less arbitrary reference point. We shall follow the convention that $\gamma_{\text{KCl}} = \gamma_{\text{Cl}} = \gamma_{\text{K}^+}$, where $\gamma$ represents the mean activity coefficient and $\gamma_i$ the individual ion activity coefficients. Under this reference frame, the individual ion activities can be calculated by the Debye-Hückel formula, which was originally developed for calculating mean activity coefficients. The constants $A$, $B$ and $\tilde{\alpha}$ can be viewed as data fitting constants although they also have physical interpretations. The Debye-Hückel formula has the form

$$-\log \gamma_i = \frac{Az_i^2 \sqrt{I}}{1 + \tilde{\alpha}_i B \sqrt{I}}$$

where $I$ is the total ionic strength and $z_i$ the charge on the ion $i$. The total ionic strength of an aqueous electrolyte solution is defined as

$$I = \sqrt[2]{\sum (m_i z_i^2)}$$
where \( m_i \) is the molality of ion \( i \) and the summation is over all ionic species. In the case of ICM drainage, we can neglect the deviation of drainage density from unity and thus use molarity in lieu of molality. Values of \( A, B \) and \( \alpha \) for various ionic species are tabulated in Garrels, 1965. The above formulae will be used in the next section to calculate the total ionic strength and activity coefficients of a typical ICM drainage.

Colloids and suspended solids may play at times important roles in the metal balance of drainage water. They are discussed in a later section very briefly because we have only data on dissolved species.

5.3.1 Mineral Constituent Mobilization and Dissolved Species Removal in General

The earth surface has been undergoing weathering for billions of years. Weathering is responsible for the formation of soil which supports the great majority of advanced lives and plants, for the earth’s surface landscape (plate tectonics also contributes to this), and for the saline nature of the ocean. Weathering can be broadly divided into physical weathering and chemical weathering. Physical weathering is the disintegration of rocks by physical means such as temperature fluctuation, the action of flowing water, wind action, frost action, abrasion and so on. One of the important effects of physical weathering is that it accelerates the rate of chemical weathering by increasing the total surface area of rocks upon which chemical weathering attacks. We will not discuss physical weathering further since this is rather irrelevant to our subject. Chemical weathering is the change of mineral composition of rocks through chemical reactions. The composition of water contained in the ocean, rivers, and lakes is largely determined by chemical weathering. Chemical
weathering is a very broad field and has attracted tremendous interest of study. We will discuss briefly the chemical weathering processes that are important in our present study - the chemical weathering processes of silicates, sulfides, oxides and carbonates.

Igneous rock makes up 95% of the outer 15 km of the earth's crust and 25% of the earth's surface. The vast majority of igneous rock-forming minerals are silicates. Silicate minerals are thermodynamically stable at the conditions of their formation: high temperature, high pressure, and low oxidizing potential. They become thermodynamically unstable when they are exposed at the earth surface, which is characterized by low temperature, low pressure, high oxidizing potential and presence of water. The stability of silicates is not much affected by the change of redox potential from the earth interior to the surface, since all the elements in silicates are already in their most stable oxidation states under earth's surface conditions. The weathering of silicates, therefore, is not a redox reaction. The thermodynamic instability is brought about by the change in temperature, pressure and chemical environments, most importantly by the contact with water. The silicate minerals weather by releasing alkaline or alkaline earth metal cations (K⁺, Na⁺, Ca++, Mg++), which are subsequently carried to the ocean, leaving behind aluminum oxides (gibbsite, bauxite), aluminosilicates (clay minerals), silicon oxides (silica, crystalline or amorphous), and others, all of which contribute to the formation of soil. The alkaline and alkaline earth metal cations are displaced by H⁺; thus the chemical weathering of silicate is usually an acid consuming process. The weathering of silicates via the above mechanism can be regarded as hydrolysis. It is important to remember that the weathering of silicates is usually very slow. Different silicates weather at different rates. It has been observed that the relative rates of weathering of silicates can be described by the reverse of Bowen's Reaction Series:
the earlier a silicate mineral appears in Bowen’s Reaction Series, the faster its weathering rate.

Sulfide minerals are generally of igneous origin. Their formation is characterized by strongly reducing conditions and usually high temperature and pressure. But high pressure and high temperature are not essential. In contrast to silicates, the instability of sulfides under earth surface conditions is caused by the change in redox conditions. The oxidation state of sulfur in primary sulfides is usually -I or -II while the only stable oxidation state of sulfur at earth’s surface is +VI. The weathering of sulfides is unexceptionally redox reactions. These redox reactions convert reduced sulfur into S(+VI) in the form of sulfate. The occurrence of sulfides in igneous rock masses is usually localized. The rate of weathering of sulfides is much greater than that of silicates. The weathering of sulfides is frequently self-enhancing, because the release of acidity from previous weathering, if not removed, tends to make the environment more oxidizing, and a more oxidizing environment spurs a faster release of acidity.

Soil is a product of rock weathering and biological activities. The type of soil formed in a particular area is dependent of five broad variables: climate (temperature and precipitation), parent rock, biological activity, topography, and the time during which the soil has been forming (Carroll, 1970). Variations in the five variables have resulted in numerous soil types, which are classified virtually according to chemical compositions.

Having said this much about weathering, we now turn our attention to see how chemical weathering is related to the investigation of acid mine drainage and water pollution. Usually, natural weathering does not result in great concentrations of toxic species in
natural streams because of the low surface area to mass ratio of undisturbed rock masses. Water pollution refers to the release of environmentally toxic species in concentrations that greatly exceed the natural levels due to man's activities. Since our goal is to find out how and why the pollutants in ICM drainage come to the present levels and what the future trend is, only the aqueous species whose concentrations greatly exceed natural levels, namely pollutants concern us. We use the phrase "mineral constituent mobilization" to describe the transfer of chemical elements, toxic or not, from minerals into solution. Mineral constituent mobilization differs from the phrase "chemical weathering" in that the latter has a broader meaning than the former. In addition to the release of mineral constituent elements to aqueous solution, chemical weathering also concerns about the transition between different minerals, formation of soil, etc., which are out of our scope of interest.

There are also some differences in the interest of study between chemical weathering and our present acid drainage study. Chemical weathering studies concern the effects of mineral breakdown or mineral transition on the water composition of river systems, on the soil formation and on new mineral formation. Our acid mine drainage study concerns about the effect of mineral breakdown or mineral transition on the release of pollutants at concentrations greatly exceeding the natural levels. Chemical weathering studies are often carried out on very large catchment basins while our study is on a very small and localized area.

Water draining waste dumps is in constant motion and the waste dumps receive intermittent renewal of fresh water from precipitation. The products of mineral breakdown are carried away from the reaction spot by flushing water. Therefore the concentrations
of pollutants in the acid mine drainage from waste dumps are affected by the rate of mineral breakdown, the removal of pollutants by various mechanisms such as precipitation, coprecipitation, adsorption to solid surfaces, etc. and the pattern of precipitation (frequency, amount, interval, etc.) in a relatively complex manner. The mechanisms of mineral breakdown that are relatively fast are more important than those that are relatively slow. We will examine the mechanisms of mineral breakdown next.

Keller pointed out in 1955 the various types of chemical reactions involved in chemical weathering. These include hydrolysis, ion exchange, oxidation, carbonation, hydration, chelation, dialysis, simple dissolution and chemical reconstruction. To this list we must add complexation. Of these reaction types, hydrolysis, oxidation, carbonation and simple dissolution are more important ones in environmental considerations of the study of acid mine drainage. They are considered in further detail in the following sections. Cation exchange and chelation are more profound near the surface zone of plant growth. These two processes contribute an insignificant amount to the total release of mineral constituents into acid mine drainage because chemical weathering takes place throughout the entire depth of the waste dump, of which the surface zone is only a very small portion. Hydration and mineral reconstruction do not release mineral constituents into solution. The contribution of dialysis is also regarded insignificant in the present study.

Natural waters draining an igneous formation contains in significant concentrations K⁺, Na⁺, Ca²⁺, Mg²⁺, H₄SiO₄ (SiO₂·2H₂O), SO₄²⁻, HCO₃⁻ and Cl⁻. The first five species in the above list come from the chemical weathering of silicate rocks. Bicarbonate ions derive from the dissolution of atmospheric CO₂ and subsequent dissociation of carbonic acid, and of carbonate minerals. Cl⁻ is primarily from precipitation. SO₄²⁻ originates from the
dissolution of gypsum and the oxidation of primary sulfides when available. Because of the igneous nature of ICM waste rocks, all these species are expected to be present in the drainage from the waste dumps at ICM.

Due to the high acidity and low pH in some of the ICM waste dumps, some metal species are mobilized into solution to significant concentrations. These are Cu, Fe, Mn, Mo, Zn, and Cd. Pb and As are not in concentrations much higher than natural levels, but are considered because firstly they are very environmentally toxic and secondly ICM has monitored them. In addition, $\text{SO}_4^{2-}$, $\text{Ca}^{2+}$, $\text{Mg}^{2+}$ are in concentrations much greater than natural levels owing to the oxidation of sulfides and the accelerated silicate mineral weathering. The concentration of $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ is probably also attributable to the destruction of calcite and dolomite by acid generated in the dump.

Table 17 presents the results of a survey of the concentrations of various species in the ICM drainage streams for the period from January, 1988 to January, 1989. The factors to convert original concentrations of various species in mg/l or $\mu$g/l to those in mol/l are listed in the table. The conversion was performed for EMO drainage. Since the concentrations of various species vary in a wide range from stream to stream and within a stream from time to time, it is unrealistic to consider the chemistry of all streams and for all variations. We choose to take EMO drainage to carry on our study of solution chemistry. The treatment of other streams is similar except the range of contaminant concentrations. The EMO drainage is chosen because firstly it is the most seriously polluted drainage and more efforts are needed in alleviating its pollution and secondly the water quality of other drainage streams may approach that of the EMO drainage in the future when the sulfide
Table 17  Range of Contaminant Concentrations January 1988 - January 1989

<table>
<thead>
<tr>
<th>Stream</th>
<th>pH</th>
<th>SO4</th>
<th>Ca</th>
<th>Mg</th>
<th>Total Ca</th>
<th>Total Mg</th>
<th>Dissolved Metals (μg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Cu</td>
</tr>
<tr>
<td>TLD</td>
<td>6.0-7.8</td>
<td>13-110</td>
<td>14-46</td>
<td>1.5-12</td>
<td>1.6-33</td>
<td>69-190</td>
<td>0.50-3.1</td>
</tr>
<tr>
<td>BLA</td>
<td>6.0-6.7</td>
<td>1.0-38</td>
<td>9.2-15</td>
<td>1.3-11</td>
<td>1.7-4.6</td>
<td>68-300</td>
<td>0.50-1.2</td>
</tr>
<tr>
<td>SCR</td>
<td>6.4-7.6</td>
<td>0.70-16</td>
<td>5.8-9.9</td>
<td>0.80-1.4</td>
<td>0.60-2.0</td>
<td>92-310</td>
<td>0.50-2.6</td>
</tr>
<tr>
<td>NDD</td>
<td>4.4-7.2</td>
<td>380-1000</td>
<td>120-210</td>
<td>13-27</td>
<td>5.4-2400</td>
<td>4.7-480</td>
<td>0.50-67</td>
</tr>
<tr>
<td>NDS</td>
<td>6.5-7.4</td>
<td>260-700</td>
<td>93-260</td>
<td>10-24</td>
<td>31-110</td>
<td>32-89</td>
<td>0.50-4.9</td>
</tr>
<tr>
<td>TED</td>
<td>4.5-8.6</td>
<td>380-700</td>
<td>140-230</td>
<td>15-32</td>
<td>9.0-280</td>
<td>11-400</td>
<td>1.0-3.2</td>
</tr>
<tr>
<td>TCR</td>
<td>7.5-8.5</td>
<td>830-1300</td>
<td>180-450</td>
<td>18-59</td>
<td>5.1-14</td>
<td>6.7-32</td>
<td>0.50-3.0</td>
</tr>
<tr>
<td>EMO</td>
<td>4.2-4.8</td>
<td>500-2200</td>
<td>370-540</td>
<td>24-82</td>
<td>290-1200</td>
<td>100-830</td>
<td>0.50-7.5</td>
</tr>
<tr>
<td>EDL</td>
<td>7.0-8.3</td>
<td>460-1000</td>
<td>120-350</td>
<td>11-27</td>
<td>8.1-65</td>
<td>8.3-37</td>
<td>0.50-2.9</td>
</tr>
<tr>
<td>EDD</td>
<td>4.6-7.8</td>
<td>650-1400</td>
<td>210-360</td>
<td>16-51</td>
<td>7.8-300</td>
<td>11-170</td>
<td>1.0-2.7</td>
</tr>
<tr>
<td>Range</td>
<td>4.2-8.6</td>
<td>0.7-2200</td>
<td>5.8-540</td>
<td>0.80-82</td>
<td>0.60-2400</td>
<td>4.7-830</td>
<td>0.50-67</td>
</tr>
<tr>
<td>ICM</td>
<td>50</td>
<td>50</td>
<td>500</td>
<td>10</td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(To convert the above figures into mol/l, multiply them by the following factors)

<table>
<thead>
<tr>
<th>Stream</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>EMO</td>
<td>1.04E-5, 2.50E-5, 4.12E-5, 1.57E-8, 1.79E-9, 1.62E-8, 1.04E-8, 1.53E-8, 8.90E-9, 1.34E-8</td>
</tr>
<tr>
<td>Typical Drainage</td>
<td>1.0E-2, 1.0E-2, 1.0E-2, 1.0E-5, 1.0E-5, 1.0E-8, 1.0E-4, 1.0E-7, 1.0E-4, 1.0E-9</td>
</tr>
</tbody>
</table>

* See the footnote for Table 8.
oxidation proceeds to more advanced stages. The ranges of concentration variations of various aqueous species in the EMO drainage are shown in mol/l in Table 17. From the EMO drainage, we construct a "typical drainage" (hereforth referred as "the typical drainage") using the orders of magnitude of the concentrations of the aqueous species in the EMO drainage. The composition of this typical drainage is shown in Table 18.

We have shown above that the ICM drainage contains in significant concentrations K⁺, Na⁺, Ca²⁺, Mg²⁺, H₄SiO₄ (SiO₂.2H₂O), SO₄²⁻, H₂CO₃, HCO₃⁻, Cl⁻, Cu, Fe, Pb, Mn, Mo, Zn, Cd, and As. For the typical drainage, we already know the concentrations in mol/l of the eight dissolved metal species (including As), SO₄²⁻, Ca²⁺, Mg²⁺, and pH. In order to calculate the total ionic strength of the typical drainage, we need to estimate the concentrations of HCO₃⁻ and Cl⁻. H₂SiO₄ and H₂CO₃ are neutral species and do not contribute to the total ionic strength. The concentrations of carbonate species in solution depend on the solution pH (see the Eh-pH diagram and concentration-pH diagram of C-O-H system presented in Section 5.3.2.2). At the pH of the typical drainage (4.5), the prevailing species is carbonic acid H₂CO₃; the concentration of bicarbonate ion HCO₃⁻ is two orders of magnitude lower than that of H₂CO₃ and the concentration of carbonate ion CO₃²⁻ is almost nil. If we assume the total concentration of carbonate species in solution to be 10⁻³ mol/l, which is a common value for natural waters draining non-carbonate rock formations with some surface vegetation (Drever, 1982), the concentration of aqueous H₂CO₃ would be 10⁻³, that of HCO₃⁻ 10⁻⁵ and that of CO₃²⁻ nearly zero. For Cl⁻, we will adopt the order of magnitude in an average precipitation, 10⁻⁶ mol/l. The rain water usually also contains nitrogen species, presumably NO₃⁻, in a concentration comparable to that of chloride ion (10⁻⁵ mol/l). Biological activities can add much more nitrogen species, such as NO₃⁻ and NH₄⁺ to the solution. This is ignored since the biological activities are only appreciable near the surface while the
Table 18  Composition of the Typical Drainage

<table>
<thead>
<tr>
<th>Species</th>
<th>pH</th>
<th>SO$_4^{2-}$</th>
<th>H$_4$SiO$_4$</th>
<th>H$_2$CO$_3$</th>
<th>HCO$_3^-$</th>
<th>Cl$^-$</th>
<th>NO$_3^-$</th>
<th>Diss.N$_2$</th>
<th>Diss.O$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/l)</td>
<td>4.5</td>
<td>10$^{-2}$</td>
<td>10$^{-3}$</td>
<td>10$^{-3}$</td>
<td>10$^{-5}$</td>
<td>10$^{-5}$</td>
<td>10$^{-5}$</td>
<td>9.5x10$^{-4}$</td>
<td>3.1x10$^{-4}$</td>
</tr>
<tr>
<td>Activity Coefficient</td>
<td>0.86</td>
<td>0.467</td>
<td>1.10</td>
<td>1.10</td>
<td>0.83</td>
<td>0.82</td>
<td>0.82</td>
<td>1.10</td>
<td>1.10</td>
</tr>
<tr>
<td>Activity</td>
<td>2.7x</td>
<td>4.67x</td>
<td>1.10x</td>
<td>1.10x</td>
<td>8.3x</td>
<td>8.2x</td>
<td>8.2x</td>
<td>1.05x</td>
<td>3.4x</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>10$^{-3}$</td>
<td>10$^{-3}$</td>
<td>10$^{-6}$</td>
<td>10$^{-6}$</td>
<td>10$^{-6}$</td>
<td>10$^{-3}$</td>
<td>10$^{-4}$</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Species</th>
<th>K$^+$</th>
<th>Na$^+$</th>
<th>Ca$^{++}$</th>
<th>Mg$^{++}$</th>
<th>Cu$^{++}$</th>
<th>Fe$^{++}$</th>
<th>Pb$^{++}$</th>
<th>Mn$^{++}$</th>
<th>HM0$_4^-$</th>
<th>Zn$^{++}$</th>
<th>Cd$^{++}$</th>
<th>H$_2$AsO$_4^-$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (mol/l)</td>
<td>10$^{-4}$</td>
<td>10$^{-4}$</td>
<td>10$^{-2}$</td>
<td>10$^{-3}$</td>
<td>10$^{-5}$</td>
<td>10$^{-5}$</td>
<td>10$^{-8}$</td>
<td>10$^{-4}$</td>
<td>10$^{-7}$</td>
<td>10$^{-4}$</td>
<td>10$^{-7}$</td>
<td>10$^{-9}$</td>
</tr>
<tr>
<td>Activity Coefficient</td>
<td>0.82</td>
<td>0.83</td>
<td>0.50</td>
<td>0.53</td>
<td>0.50</td>
<td>0.50</td>
<td>0.48</td>
<td>0.50</td>
<td>0.83</td>
<td>0.50</td>
<td>0.49</td>
<td>0.83</td>
</tr>
<tr>
<td>Activity</td>
<td>8.2x</td>
<td>8.3x</td>
<td>5.0x</td>
<td>5.3x</td>
<td>5.0x</td>
<td>5.0x</td>
<td>4.8x</td>
<td>5.0x</td>
<td>8.3x</td>
<td>5.0x</td>
<td>4.9x</td>
<td>8.3x</td>
</tr>
<tr>
<td></td>
<td>10$^{-5}$</td>
<td>10$^{-5}$</td>
<td>10$^{-3}$</td>
<td>10$^{-4}$</td>
<td>10$^{-6}$</td>
<td>10$^{-6}$</td>
<td>10$^{-9}$</td>
<td>10$^{-5}$</td>
<td>10$^{-8}$</td>
<td>10$^{-5}$</td>
<td>10$^{-8}$</td>
<td>10$^{-10}$</td>
</tr>
</tbody>
</table>

Total Ionic Strength: 0.0426
chemical weathering takes place in the entire dump. In cases where the rock contains phosphate minerals, phosphorous species may be present in significant concentrations. ICM waste rocks do not contain significant amount of phosphate minerals therefore phosphorous species need not be considered.

In Table 18, the total ionic strength is calculated from the molarities of all ionic species and the activity coefficients are calculated from the total ionic strength and the concentrations in molarity of various species using the extended Debye-Hückel formula. Activity coefficients of neutral species are calculated using the equation (Drever, 1982):

\[
\gamma = 10^{0.118}
\]

where I is the total ionic strength. Dissolved N\textsubscript{2} concentration is calculated from the solubility of N\textsubscript{2} at 25°C (23.3 cm\textsuperscript{3}/l). Dissolved O\textsubscript{2} concentration is based on measurements made at ICM.

Dissolved species are removed from solutions by a number of chemical, physical, or biochemical processes: over-saturation with respect to a highly insoluble compound, redox reactions that yield a highly insoluble compound, complexation that results in a highly insoluble compound, adsorption onto solid or colloid surfaces, and biological uptake. In the study of ICM acid mine drainage, chemical removal of dissolved species is by far the most important.

Usually, the reactions that remove ionic species from solutions are much faster than the reactions that bring these species from mineral lattice to solutions. As a general rule, reactions between dissolved species in solutions are always much faster than solid-liquid
interfacial reactions, which is in turn faster than solid-solid reactions. In a solution, all ionic or molecular particles of dissolved species take part in the chemical reaction while in a solid-liquid interfacial reaction only particles on the solid surface are involved. For reactions in solutions, non-redox reactions are usually faster than redox reactions.

5.3.2 Redox Reactions

Reduction-oxidation, or redox reactions are very common in geochemical processes and are responsible for the weathering of many minerals, including sulfides.

There are two very basic processes in the realm of chemistry: electron transfer and proton transfer. Eh measures the potential of electron loss or gain and pH measures the potential of proton loss or gain. We can speak of Eh of an aqueous solution, of a half-cell reaction, or of a redox reaction. The Eh of a half-cell reaction or a redox reaction is clearly defined in terms of the activities of the species involved in the reactions. As to pH, it always refers to aqueous solutions. The pH is clearly defined at any moment for any homogenous solution (at equilibrium or semi-equilibrium) as the negative common logarithm of the activity of free hydrogen ions.

The Eh of aqueous solutions, however, deserves some clarification. It usually refers to the potential of an inert electrode (such as a platinum electrode), which is dipped into the solution being measured, relative to the Standard Hydrogen Electrode (SHE). Before the measurement is taken, the inert electrode is usually allowed some time to reach "equilibrium" with the solution. If the solution being measured is at real equilibrium, all
possible redox pairs in the solution will define the same redox potential. Now if the platinum electrode and the measuring process itself exert a negligible influence on the equilibrium of the solution and therefore do not upset the equilibrium of the solution (which is equivalent to saying that the electric current that occurs during the measurement of the potential between the inert electrode and the reference electrode is infinitesimal and that the insertion of the inert electrode does not bring any foreign substances), and if we further assume that the inert electrode does achieve equilibrium with the solution, the potential so measured can be attributed to the solution without ambiguity. However, if the solution being measured is not at equilibrium (which, as we have mentioned earlier, is a common situation in natural waters), what is the meaning of such a measurement? Since the solution itself is not in thermodynamic equilibrium, such a measurement is called by some geochemists a "formal potential". In the solution, the concentrations of many redox species (thus the potentials between redox pairs) are constantly changing in such a way as to bring the system towards equilibrium. But some of these changes take place so slowly that they are often at disequilibrium with the potential established commonly by those fast-reacting species, which we refer to as "semi-equilibrium potential". The semi-equilibrium potential is usually determined in the early stage in the course from disequilibrium to equilibrium by a few fast-reacting redox pairs. If an inert electrode is immersed into such a system, and if the open circuit emf is measured across the inert electrode and the reference electrode, the potential obtained should be in the proximity of the semi-equilibrium potential; otherwise if the potential between the inert electrode and the reference electrode is measured using an electrometer with an external current (however small it may be) that is great enough to upset the local semi-equilibrium around the inert electrode, the potential obtained will be dominated by the fastest-reacting redox pair or pairs.
In reality, most of the Eh measurements of natural waters are probably made by the second method mentioned above; so these Eh values should reflect the potentials dominated by the fast-reacting redox pairs. The values of such measurements could be very different from those calculated from the concentrations of a particular redox pair if the solution is not in equilibrium, which is what is meant by disequilibrium after all. Nevertheless, the formal potential Eh represents the main stream redox potential of a solution. The usefulness of the formal (measured) Eh of natural water bodies is that, first, using the formal Eh as a yardstick, we can designate a water body as oxidizing water, or reducing water, or transitional water; second, knowing the Eh, we can frequently predict the redox actions that will take place if a new species is introduced, as well as the stable species in a solution. In the following discussions, we will make extensive use of Eh-pH diagrams. One more point to make about Eh-pH diagrams is that, being constructed from thermodynamic data, they represent the equilibrium information only for the species considered, subject to the accuracy of the thermodynamic data employed. They tell nothing about species not considered in their construction. Therefore, some caution has to be exercised to choose the species to be considered according to the application. For instance, when we construct an Eh-pH diagram for iron (Fe), there are two species of Fe(III) oxides to choose from, \( \text{Fe}_2\text{O}_3 \) (hematite) and \( \text{Fe(OH)}_3 \) (ferric hydroxide). We know that hematite is thermodynamically more stable than amorphous \( \text{Fe(OH)}_3 \), which can be written alternatively as hydrated ferric oxide \( \text{Fe}_2\text{O}_3\cdot3\text{H}_2\text{O} \):

\[
2\text{Fe(OH)}_3 \text{(amorphous)} \rightarrow \text{Fe}_2\text{O}_3 \text{(hematite)} + 3\text{H}_2\text{O}
\]

\[
\Delta G^* = -63.7 \text{ kJ/mol}
\]
Therefore, given enough time, ferric hydroxide will dehydrate to convert to hematite. We also know from experience that the species to form if ferric ion Fe\(^{3+}\) is precipitated from solution by raising pH is ferric hydroxide. Given the above information, we will choose Fe(OH)\(_3\) in constructing the Eh-pH diagram if the removal of metal species from polluted water by chemical treatment is to be examined, although Fe(OH)\(_3\) is only metastable and will slowly revert to Fe\(_2\)O\(_3\). On the contrary, if our interest is to investigate the geological occurrence of iron oxides in an area, we will consider Fe\(_2\)O\(_3\) in the Eh-pH diagram, since Fe(OH)\(_3\) would have had enough time to be converted to hematite in the geologic past. The effect on the Eh-pH diagram of choosing Fe(OH)\(_3\) instead of Fe\(_2\)O\(_3\) is, all other things being equal, that ferric hydroxide occupies a smaller stability field on the Pourbaix diagram. This is expected because ferric hydroxide is thermodynamically less stable than hematite. The structure of the Eh-pH diagram will remain the same as if hematite were used.

Another benefit in using Eh-pH diagrams is that when the total activities of some species change, there is usually only a slight parallel shift of the boundaries involving the species whose activities change, other boundaries are unaffected, and the general structure remains. Therefore, an Eh-pH diagram can be used effectively for solutions whose species activities are in the neighbourhood of those assumed in constructing the Eh-pH diagram. They need not be exactly the same.

Redox potentials of natural waters vary widely according to their environments. Figures 7 and 8, both taken from Garrels, 1965, demonstrate the natural variations in Eh-pH measurements and his effort to zone the Eh-pH diagram according to the origins of the waters in which the Eh and pH were measured.
Figure 7  Distribution of Eh-pH Measurements of Natural Aquous Environments
(After Garrels, 1965 with modifications)
Figure 8 Approximate Positions of Some Natural Environments as Characterized by Eh and pH. (After Garrels, 1965 with modifications)
In addition to Eh, another important concept in electrochemistry is redox buffering. A system is buffered with respect to redox processes if oxidizable and reducible compounds (or species) are present that prevent a significant change in Eh in response to additions of small amounts of strong oxidizing or reducing agents. Redox buffering is a close analogy to acid-base buffering. Just as acid-base buffering is realized by the presence in comparable concentrations of a buffering pair, such as H₂CO₃/HCO₃⁻ and CH₃COOH/CH₃COO⁻, redox buffering is facilitated by the presence of a redox buffering pair, such as O₂/H₂O, SO₄²⁻/H₂S and H₂O/H₂S, although not necessarily at comparable concentrations. Figure 9 illustrates schematically how the redox pair O₂/H₂O buffers the change in Eh. It is assumed that the water was initially in equilibrium with atmospheric oxygen, but no additional oxygen is added as the organic matter decomposes. It can be seen that as long as free dissolved oxygen is present, Eh remains high, but as soon as free oxygen is depleted, the Eh of the system drops dramatically to that buffered by the redox pair SO₄²⁻/H₂S.

Natural waters contain simultaneously many buffering pairs. The question arises in regard to which of these buffering pairs dictates the measured Eh, thus the overall redox conditions. It appears justified to say, from the view point of the foregoing discussion of semi-equilibrium in natural waters, that the dictating redox pair (or pairs) would be that (or those) whose redox reaction(s) is the fastest in the environment concerned. Many such pairs have been identified in different natural environments. Figure 10 shows some of the important natural redox buffering pairs along with their buffered Eh at pH 7.0 and 25°C. The buffered Eh of many of the natural buffering pairs changes with pH due to the involvement of H⁺ in redox reactions. This point is illustrated in Figure 11, which depicts some possible redox buffers in a ground water environment.
Figure 9 Change in pE (Eh) of a Fresh Water as a Function of the Amount of Organic Matter Decomposed. (Dissolved oxygen = 10 mg/l, dissolved SO$_4^{2-}$ = 96 mg/l, pH is assumed constant at 7.0. Reactions involving nitrogen compounds may provide a small amount of buffering between the O$_2$/H$_2$O and the SO$_4^{2-}$/H$_2$S levels, but they are ignored here. Also note the pE-Eh conversion chart at 25°C on the right.)

(After Dreyer, 1982)
Figure 10  Approximate pE (or Eh) Values at which Various Redox Reactions Occur in Water at pH 7 and 25°C. See Figure 34 for pE-Eh conversion. (After Drever, 1982.)

Figure 11  Some Possible Redox Buffers in a Groundwater System. Solid/solution boundaries are drawn for activity of solute = 10^6. See Figure 34 for pE-Eh conversion. (After Drever, 1982.)
Dreyer discussed the problem of dominant redox pairs of oxygenated (surface) water. The overall reduction of oxygen

\[ \text{O}_2 + 4\text{H}^+ + 4e^- \rightleftharpoons 2\text{H}_2\text{O} \]  
(1)

\[ \text{Eh} = \text{Eh}^0 - \frac{2.303\text{RT}}{\text{nF}} \log\left[ \frac{a^2_{\text{H}_2\text{O}}}{(a^4_{\text{H}_2\text{O}}, p_{\text{O}_2})} \right] \]

\[ = 1.229 - 0.05917\text{pH} \]  
(2)

\[ = 0.815 \text{V} \text{ (at pH 7.0)} \]

Generally does not occur as a single step, but as two separate reactions

\[ \text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons \text{H}_2\text{O}_2 \]  
(3)

\[ \text{Eh} = \text{Eh}^0 - \frac{2.303\text{RT}}{\text{nF}} \log\left[ a_{\text{H}_2\text{O}_2}/(a^2_{\text{H}_2\text{O}_2}, p_{\text{O}_2}) \right] \]

\[ = 0.682 - 0.05917\text{pH} \]  
(4)

\[ = 0.27 \text{ (V) (at pH 7.0)} \]

And

\[ \text{H}_2\text{O}_2 + 2\text{H}^+ + 2e^- \rightleftharpoons 2\text{H}_2\text{O} \]  
(5)

Breck (as cited by Dreyer) pointed out that reaction (5) was much slower than reaction (3) and hence Eh was essentially controlled by reaction (3) (in accordance with the semi-equilibrium theory we discussed earlier). The effective Eh for oxygenated water would then
be 0.27 V (at pH 7.0) as predicted by reaction (1). Stumm (also as cited by Drever) disagreed and pointed out that some natural redox systems seemed to respond as if reaction (1) determined Eh, and some as if reaction (3) controlled Eh. Drever favoured Stumm's opinion that the use of a single Eh to characterize oxygenated waters was meaningless because the various redox couples in natural waters are not in equilibrium with each other. Stumm argued that since a single Eh for all redox systems could not be defined, it is probably best to think of Eh as "high" without specifying an exact number. Since in reality most of the Eh measurements are performed with a meter that employs an electrometer, we believe that the measured Eh of natural waters is determined by the most reactive redox pair(s) (one that facilitates the largest exchange current) and is close in value to that of the semi-equilibrium.

We have plotted equations (2) and (4) on Figures 7 and 8. Equation (2) is the upper limit of water stability, and equation (4) is represented by the line labelled $O_2/H_2O_2$ in Figure 7. The vast majority of the measured Eh-pH conditions of natural oxygenated (surface) water fall between the two lines defined by equations (2) and (4). This is to say that reactions (1) and (3) actually define a boundary of occurrence of natural surface water (mine water, rain, streams, sea water, etc.) Eh-pH conditions. It seems that Breck's argument that the redox potentials of surface oxygenated water are controlled by reaction (3) is closer to reality, since the average line of the measured Eh-pH points falls closer to the line predicted by reaction (3) than to that predicted by reaction (1). Furthermore, almost no measurements of natural waters fall within the band approximately 0.2V wide below the upper limit of water stability line.
One more observation to make on Figure 7 and 8 is that the trend followed by the measurements on natural surface aerated waters parallels the line of water upper stability limit and the line defined by reaction (3). This implies that the more acidic a natural surface water, the more oxidizing it is. This explains from one particular angle why the oxidation of primary sulfides is favoured by low pH values.

Based on the foregoing discussion of the measurements of natural aqueous environments and the considerations on the ICM environmental conditions, we can now "quantify" on an empirical basis a field on the Eh-pH diagram to encompass the possible Eh-pH conditions in ICM drainage and within ICM waste dumps that are undergoing active oxidation. This area is represented by the parallelogram ABCD, as shown on Figures 7 and 8. The boundaries AB and CD are defined by equations pH=2.0 and pH=8.0, respectively. This pH range is believed to cover most of the possible pH values in the drainage and the waste dumps at ICM.

Line EF represents the line along which the Eh-pH measurements of natural waters appear most frequently. It is the same line drawn on Figure 8 by Garrels and has an empirical equation

\[ \text{Eh} = 0.863 - 0.0592 \text{pH} \]  

The lower boundary line AD is defined by the reduction of free oxygen to peroxide, reaction (3), in the form of

\[ \text{Eh} = 0.682 - 0.0592 \text{pH} \]
The use of equation (4) as the lower boundary of measured natural Eh-pH conditions is subjective, thus somewhat arbitrary, although one can justify such a choosing on the basis of Figure 7 in that this line actually does represent a lower limit for the occurrence of natural Eh-pH measurements.

The upper limit, line BC, is also chosen subjectively and can be justified on the basis of Figure 7. Line BC is chosen such that it is parallel to line EF and is the same distance above line EF as line AD is below line EF. The equation for line BC is therefore

\[ Eh = 1.044 - 0.0592 \text{ pH} \] (7)

In the sections to follow, we superimpose the defined parallelogram ABCD on some of the Eh-pH diagrams of our interests to make observations and to draw thermodynamic conclusions.

5.3.2.1 Sulfur

The Eh-pH diagrams for the system S-O-H at activities of dissolved sulfur of $10^{-2}$ and $10^{-3}$ are presented in Figures 12 and 13. The sulfate activity of the typical drainage is $4.67 \times 10^{-3}$. Sulfite, thiosulfate, and other sulfur species rarely encountered in natural waters are not considered in the construction of the Eh-pH diagrams. Note that the only difference between the two diagrams is that the solid phase of elemental sulfur field is slightly bigger in the more concentrated solution.
Figure 13  Eh-pH Diagram for Part of the System S-O-H. The assumed activity of dissolved ES=10^{-2}.
Figure 12 Eh-pH Diagram for Part of the System S-O-H. The assumed activity of dissolved ES=10^{-3}.
From Figures 12 and 13, it can be seen that in the Eh-pH conditions we can possibly encounter in ICM drainage (defined by the parallelogram ABCD), the predominant species is $SO_4^{2-}$. Sulfuric acid is a very strong diprotonic acid, its first dissociation constant is very large, therefore in the pH range 0-14, aqueous $H_2SO_4$ does not appear. In very reducing conditions close to the lower water stability limit, reduced sulfur species are stable and exist as aqueous $H_2S$ or $HS^-$, depending on pH. The sulfide ion ($S^-$) field lies to the right of that of $HS^-$ when pH is greater than 14. In anoxic environment such as the bottom of stratified lakes, sulfate can be reduced to $H_2S$ or $HS^-$. This reduction can be greatly catalyzed by sulfate-reducing bacteria. Sulfur species play a very important role in geochemistry. The stability of various sulfides and sulfates will be discussed with different metal elements.

5.3.2.2 Carbon

Figure 14 presents the Eh-pH diagram of C-O-H system with a total dissolved carbon activity of $10^{-3}$. The total activity of carbon species in the typical drainage is $1.11 \times 10^{-3}$ (Table 18).

It can be seen from Figure 14 that in the Eh-pH conditions we are likely to encounter (parallelogram ABCD), the predominant species are $H_2CO_3$ and $HCO_3^-$. Only when pH is greater than 10.3 is $CO_3^{2-}$ the predominant species. This configuration of the Eh-pH diagram of carbonate species (i.e., both $H_2CO_3$ and $HCO_3^-$ are available in the pH range of natural waters (pH 5-8) in comparable concentrations) renders $H_2CO_3$ the most important
Figure 14  Eh-pH Diagram for Part of the System C-O-H. The assumed activity of dissolved EC=10^{-3}.
weathering agent of igneous silicate minerals in the nature. Carbon dioxide (CO$_2$) from the atmosphere or from soil horizons dissolves in water that subsequently penetrates igneous formations. Part of the CO$_2$ dissolved forms carbonic acid (H$_2$CO$_3$). When igneous silicate minerals weather, they extract H$^+$ from H$_2$CO$_3$, converting H$_2$CO$_3$ to HCO$_3^-$ . The H$^+$ ions are used to displace alkaline or alkaline earth metal cations, which are released into solutions; and to combine with the residue to form new minerals such as clay minerals. In turning H$_2$CO$_3$ into HCO$_3^-$, igneous silicate minerals have neutralized part of the acidity stored in carbonic acid. The weathering of silicate minerals by carbonation is an acid-consuming process. In cases where large concentrations of free H$^+$ are present (low pH), such as the EMO drainage at ICM, silicate minerals need not extract H$^+$ from carbonic acid, they instead utilize the readily available free H$^+$ to displace K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$. In doing so, they have consumed the free H$^+$ acidity in the water.

Figure 15 is a logarithmic concentration-pH diagram for 10$^{-3}$ M (activity) carbonic acid. It shows the variations of activities of various species in the system with pH. Comparing this diagram with Figure 14, we can better understand what the predominant fields of species mean. Note that the predominant field of a species A does not mean that it is the only stable species in the solution. It only means that species A has the greatest activity of all stable species and is therefore the most stable species. In the predominant field of species A, away from the field boundaries, species A which we label the field with is in much greater activity (concentration) than all other species. Close to the boundaries, this predominance decreases until the activity of species A is equal to that of another species B on the AB boundary.
Figure 15  Logarithmic Diagram for $10^3$ M Carbonic Acid
Across the boundary is the predominant field of species B, which has the greatest activity of all species in the solution, including A. Species A still exists but not in the greatest activity. Another important point to remember about Eh-pH diagrams is that both Eh and pH are logarithms of activities (that is, $pE = -\log(a_e)$ and $pH = -\log(a_{H^+})$). Therefore, when we move along either axis, the actual changes in activity of $H^+$ or $e^-$ are an exponential function (with a base of 10) of the unit changes on the scale. The activities of dissolved species change in a similar manner, that is to say, when we move away from the A/B boundary into the predominant field of A, the activity of species B will diminish exponentially. Except for areas very close to boundaries, the activity of A is usually several orders of magnitude greater than that of all others - species A predominates its stability field.

The above points can best be illustrated by comparing Figures 14 and 15. Within the water stability field, from pH 0.0 to 6.4 is the predominant field of $H_2CO_3$. At pH 2.0, which is far away from the $H_2CO_3/HCO_3^-$ boundary, the activity of $H_2CO_3$ is $10^{-3}$, that of $HCO_3^-$ $10^{-7.3}$ (4.3 orders of magnitude less) and that of $CO_3^{2-}$ $10^{-15.7}$ (12.7 orders of magnitude less). Moving toward the $H_2CO_3/HCO_3^-$ boundary, at pH 5.0, the activity of $H_2CO_3$ is $10^{-3.02}$, that of $HCO_3^-$ $10^{-4.38}$ (1.36 orders of magnitude less) and that of $CO_3^{2-}$ $10^{-9.69}$ (6.67 orders of magnitude less). At the $H_2CO_3/HCO_3^-$ boundary, the activity of $H_2CO_3$ equals that of $HCO_3^-$ (both $0.5x10^{-3}$, or $10^{-3.3}$), the activity of $CO_3^{2-}$ is $10^{-7.2}$. From pH 6.4 to pH 10.3 is the predominant ground of $HCO_3^-$. At pH 8.3, approximately the middle of this field, the activity of $HCO_3^-$ is $10^{-3}$, the activity of $H_2CO_3$ equals that of $CO_3^{2-}$ (both $10^{-4.94}$, 1.94 orders of magnitude less). From pH 10.3 starts the stability field of $CO_3^{2-}$, in which the activity of $HCO_3^-$ is much less than that of $CO_3^{2-}$, and that of $H_2CO_3$ is nearly zero.
Figures 16 and 17 show the Eh-pH diagrams of the Ca-C-O-H-S system at two sets of activities: i) $\Sigma Ca=10^{-2.5}$, $\Sigma S=10^{3}$, $\Sigma C=10^{3}$; ii) $\Sigma Ca=10^{2}$, $\Sigma S=10^{2}$, $\Sigma C=10^{8}$. In the typical ICM drainage, the activities are $\Sigma Ca=10^{-2.3}$, $\Sigma S=10^{-2.33}$, $\Sigma C=10^{-2.96}$.

Calcium has two oxidation states: 0 and +II. The only species of Ca with an oxidation state of 0 is metal Ca, which is not stable in the stability field of water. Only Ca(+II) appears in the Eh-pH diagram of Ca.

At the first set of activities, both Ca$^{2+}$ and SO$_4^{2-}$ are under-saturated with respect to gypsum CaSO$_4\cdot2H_2O$, therefore gypsum phase does not appear in the Eh-pH diagram. At the second set of activities, the solution becomes over-saturated with respect to gypsum when pH is greater than 1.9, but at pH>7.4, gypsum is less stable than calcite, therefore gypsum occupies the field between pH 1.9 and pH 7.4.

**Solubilization of Ca** At ICM dissolved Ca$^{2+}$ derives from two sources: weathering of plagioclase and dissolution of calcite and/or dolomite. The weathering of igneous silicate minerals will be discussed in later sections. The fate of calcite depends essentially on three variables of the solution with which it is in equilibrium: pH, concentration of Ca$^{2+}$, and concentration of SO$_4^{2-}$. Larger concentrations of Ca$^{2+}$, lower SO$_4^{2-}$ levels and higher pH favour the stability of calcite. At the conditions of the typical drainage, the solution is under-saturated with respect to both calcite and gypsum, therefore calcite will dissolve and
Figure 16  Eh-pH Diagram for Part of the System Ca-C-O-H-S
Assumed activities for dissolved species are:
ECa=10^{-2.5}, ES=10^{-3}, EC=10^{-3}.  

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Figure 17 Eh-pH Diagram for Part of the System Ca-C-S-O-H. Assumed activities of dissolved species are: $ECa=10^{-2}$, $ES=10^{-2}$, $EC=10^{-3}$. 
gypsum will not form. The $\text{CO}_3^{2-}$ ions released from calcite add one $\text{H}^+$ to form $\text{HCO}_3^-$ ions, which add another $\text{H}^+$ to form $\text{H}_2\text{CO}_3$, which is the most stable species and is in equilibrium with atmospheric carbon dioxide (see Figure 14). Excessive $\text{CO}_3^{2-}$ will be eliminated from the solution through the above chain into the atmosphere as carbon dioxide. In the process, each $\text{CO}_3^{2-}$ ion consumes two $\text{H}^+$ ion to form one $\text{H}_2\text{O}$. This is what "carbonate alkalinity" refers to. One interesting point to note is that the presence of sulfate ions causes calcite to act as an acid consumer at a higher pH. For example, at fixed total activities of $\text{C}=10^{-3}$, $\text{Ca}=10^{-2}$ and $\text{S}=0$ in the solution, calcite becomes an acid consumer at $\text{pH}<7.0$, while in the presence of total activity of $\text{S}=10^{-2}$, calcite becomes an acid consumer at $\text{pH}<7.4$. The fundamental reason for this phenomenon is that the occurrence of gypsum field pushes the stability field of calcite to the right. It is obvious then that the solution must be oversaturated with respect to gypsum in order for the effect to appear.

**Removal of Dissolved $\text{Ca}^{2+}$** The Eh-pH diagrams indicate that within the pH range 4-7, which covers the majority of ICM drainage, $\text{Ca}^{2+}$ ions released either from plagioclase weathering or calcite (or dolomite) dissolution only precipitate as gypsum when the sulfate activity is greater than approximately $10^{-2}$, which corresponds to a sulfate concentration of 2056 mg/l if the activity coefficient is assumed to be 0.467 (Table 18). This concentration has not been reached in ICM drainage streams except EMO drainage, which occasionally has sulfate concentrations greater than 2000 mg/l. $\text{Ca}^{2+}$ ions are not removed as calcite below pH 7.3.
Figure 18 presents the Eh-pH diagram for part of the system Mg-O-H at activities of dissolved \( \Sigma \text{Mg}=10^{-2.3} \). The \( \Sigma \text{Mg} \) activity in the typical drainage is 10\(^{-3.28} \).

The Eh-pH diagram of Mg is very simple. Like calcium, magnesium has only one stable oxidation state in the water stability field: +II. Due to the high solubility products of magnesium carbonate (1.0\( \times \)10\(^{-5} \) versus 3.84\( \times \)10\(^{-9} \) for calcium carbonate) and magnesium sulfate (3.09\( \times \)10\(^{-5} \) versus 2.5\( \times \)10\(^{-8} \) for calcium sulfate), at a total Mg activity of 10\(^{-3} \), the presence of S species in an activity less than 10\(^{-2} \) and/or C species in an activity less than 10\(^{-2} \) will not produce new phases on the Eh-pH diagram within the pH range 0-14. They simply exist as aqueous species. The Eh-pH diagram we have presented here can actually be viewed as that of the system Mg-C-S-O-H as far as Mg species are concerned.

\( \text{Mg}^{2+} \) ions are primarily released into solution by ferromagnesian silicate mineral weathering and perhaps by dolomite dissolution.

For 10\(^{-3} \) total magnesium activity, \( \text{Mg}^{2+} \) ions are removed from solution as hydroxide when pH is greater than 9.8. 10\(^{-3} \) Mg activity corresponds to 45.85 mg/l. On the other hand, the highest concentration recorded at ICM (that of EMO) is 82 mg/l, which gives an activity of 1.79\( \times \)10\(^{-3} \). For \( \text{Mg}^{2+} \) ions at this activity to be precipitated as hydroxide, the pH of the solution at least has to be great than 9.4 (at which 10\(^{-2} \) Mg starts to precipitate, see Figure 18.). Since the pH of ICM drainage streams has never exceeded 8.6 (Table 17), we can safely conclude that all the magnesium solubilized has been carried out in drainage streams.
Figure 18  Eh-pH Diagram for Part of the System Mg-O-H. The assumed activity of dissolved EMg=10^{-2.3}. 
(excluding any adsorption onto solid and colloid surfaces). The removal of $Mg^{2+}$ as sulfates and carbonates is negligible.

5.3.2.5 Copper

Figures 19 through 21 present the Eh-pH diagrams for the systems Cu-O-H, Cu-S-O-H, and Cu-S-C-O-H. The assumed total activities are $\Sigma Cu=10^{-6}$ for the first system; $\Sigma Cu=10^{-6}$, $\Sigma S=10^{-3}$ for the second system; and $\Sigma Cu=10^{-6}$, $\Sigma S=10^{-3}$, $\Sigma C=10^{-1.3}$ for the third system. In the ICM typical drainage, $\Sigma Cu=5.0\times 10^{-6}$, $\Sigma S=4.67\times 10^{-3}$ and $\Sigma C=1.1\times 10^{-3}$. Another element that greatly affects the Eh-pH diagram of Cu-S-O-H is iron (Fe). When Fe is introduced to the Cu-S-O-H system, the Eh-pH diagram becomes extremely complicated, such as those in Garrels, 1965, pages 231 and 231.

For the system Cu-O-H, copper exhibits three stable oxidation states within the stability field of water: +II, +I and 0. In the absence of S and C species, native (elemental) copper is a stable species. In the oxidizing-reducing transition zone, copper(+I) (cuprous) oxide $Cu_2O$ (the mineral cuprite) is the most stable species in alkaline conditions. In the Eh-pH area of our interest, parallelogram ABCD, the most stable oxidation state is +II. Below pH 6.5, all $10^{-6}$ copper(+II) stays in solution as $Cu^{2+}$ (cupric) ions. Above pH 6.5, cupric ions are transformed to $CuO$ (the mineral tenorite). However, the transformation from aqueous $Cu^{2+}$ ions to $CuO$ is not a redox reaction, $Cu^{2+}$ can not combine directly with free $O_2$; it has to find a non-redox route to $CuO$. Actually $Cu^{2+}$ first combines with two $OH^-$ to form amorphous
Figure 19  Eh-pH Diagram for Part of the System Cu-O-H. The assumed activity of dissolved $\Sigma$Cu=$10^{-6}$. 

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Figure 20 Eh-pH Diagram for Part of the System Cu-S-O-H. The assumed activities of dissolved species are: $ECu=10^{-6}$, $ES=10^{-3}$.
Figure 21  Eh-pH Diagram for Part of the System Cu-S-C-O-H. The assumed activities of dissolved species are: ECu=10^{-6}, ES=10^{-3}, EC=10^{-3}. 
cupric hydroxide, which dehydrates one water molecule to form CuO, as the following reactions show:

\[
\text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 \text{ (amorphous)} \quad \text{(very fast)} \quad (8)
\]

\[
\text{Cu(OH)}_2 \text{ (amorphous)} \rightarrow \text{CuO} \text{ (crystal)} + \text{H}_2\text{O} \quad \text{(slow)} \quad (9)
\]

The first reaction, precipitation of amorphous cupric hydroxide, does not occur until pH is greater than 7.1, given a total Cu activity of $10^{-6}$. Therefore, the conversion of Cu$^{2+}$ to CuO (namely the removal of Cu$^{2+}$ from solution) can not occur until pH is greater than 7.1. The first reaction is labelled "very fast" because it is an ion-ion reaction in solution. The second one is slow because it is a conversion from one solid to another. Note that the conversion from Cu$^{2+}$ to CuO is an alkalinity-consuming reaction and is favoured in higher pH.

The reverse conversion, i.e., from CuO to aqueous cupric ions does occur at pH 6.5 as the Eh-pH diagram shows through the reaction

\[
\text{CuO} \text{ (crystal)} + 2\text{H}^+ \rightarrow \text{Cu}^{2+} + \text{H}_2\text{O} \quad \text{(not very fast)} \quad (10)
\]

which is a hydrolysis reaction. It is also an acid-consuming reaction. It is not very fast because it is a surface reaction. It can be fast if the CuO crystal is finely powdered, which usually does not happen in nature.
The introduction of S into Cu-O-H system completely alters the lower half of the Eh-pH diagram, but the upper half remains identical (see Figure 20). The stability field of native copper becomes much smaller, and the predominant grounds of minerals chalcocite (Cu₂S) and covellite (CuS) occur near the lower water stability limit. Since both of these stability fields are far removed from the parallelogram ABCD, which encompasses surface water conditions, the sulfides are unstable at earth's surface. They oxidize to convert S(-II) to S(+VI) in SO₄⁻ and to convert Cu(+I) as in Cu₂S to Cu(+II), either as aqueous Cu²⁺ or as CuO depending on pH values. The oxidation of copper sulfides obeys mechanisms similar to those of the oxidation of pyrite in general, that is to say, copper sulfides are oxidized either by free oxygen O₂ or by in-solution oxidizing agents such as Fe³⁺, both are often promoted by bacteria. The oxidation of pyrite is explained in detail in the literature review. Without going into details, we write the overall oxidation reactions as follows:

Chalcocite:

\[
\begin{align*}
\text{Cu}_2\text{S} + 2\frac{1}{2}\text{O}_2 + 2\text{H}^+ & \rightarrow 2\text{Cu}^{2+} + \text{SO}_4^{2-} + \text{H}_2\text{O} \\
\text{Cu}_2\text{S} + 4\text{H}_2\text{O} + 10\text{Fe}^{3+} & \rightarrow 2\text{Cu}^{2+} + \text{SO}_4^{2-} + 10\text{Fe}^{2+} + 8\text{H}^+
\end{align*}
\]

Covellite:

\[
\begin{align*}
\text{CuS} + 2\text{O}_2 & \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \\
\text{CuS} + 8\text{Fe}^{3+} + 4\text{H}_2\text{O} & \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} + 8\text{Fe}^{2+} + 8\text{H}^+
\end{align*}
\]

Note how the above oxidations differ in the view point of acid-base balance: the oxidation of covellite by oxygen (in air) has no effect on acid-base balance, the oxidation of chalcocite by oxygen consumes acid, and the oxidation of both by Fe³⁺ generates acid. (This is a very
superficial statement and not exactly true. See the discussion on the oxidation of chalcopyrite below for explanation). Other primary copper sulfides may also occur in igneous formations, they will oxidize in a manner similar to chalcocite or covellite.

The oxidation of copper sulfides is always undergoing at surface conditions therefore the release of copper is continuous. Like the oxidation of pyrite, the oxidation of copper sulfide is a surface reaction thus is generally slow. The oxidation rate is highly dependent of the surface area to mass ratio and the total percentage of copper sulfide in the waste dump. The concentration of cupric ions in drainage is a result of the balance between oxidation rate, frequency and amount of precipitation, equilibrium control, etc.

In Figure 21, carbon is added to the system Cu-S-H-O. In the new diagram, the lower part (reducing conditions) remains unchanged, the upper part is reshaped with the new malachite (\(\text{Cu}_2(\text{OH})_2\text{CO}_3\)) phase replacing tenorite (CuO). Malachite is an oxidized copper mineral formed at or near earth surface conditions. At a total Cu activity of \(10^{-6}\), it is stable at pH>7.2 but dissolves at pH≤7.2 to yield \(\text{Cu}^{2+}\), hydroxide alkalinity and carbonate alkalinity. Malachite acts as an acid neutralizer at a higher pH (7.2) than tenorite does (6.5). At pH≥11.5, malachite dissolves to form \(\text{CuO}_2^-\) in a highly alkalinity consuming reaction.

In the Eh-pH diagram of Cu-Fe-S-H-O system (not provided in this thesis but can be found in Garrels, 1965, pages 231 and 232), at very reducing conditions very close to but within the lower water stability limit, one can find a variety of stable sulfides of copper and/or iron depending on pH. These include, approximately in the order from low to high pH,
chalcopyrite CuFeS₂, covellite CuS, pyrite FeS₂, Cu₉S₅, Cu₅FeS₄, chalcopyrite CuFeS₂, and the oxide magnetite Fe₃O₄. It is interesting that the oxide magnetite can form at such highly reducing conditions. In the area defined by parallelogram ABCD, the predominant stable species are aqueous Cu²⁺, Fe³⁺ and Fe²⁺ at very acidic pH values; aqueous Cu²⁺ and solid Fe₂O₃ (or Fe(OH)₃) at less acidic pH values; and solid CuO and Fe₂O₃ (or Fe(OH)₃) at pH values approximately ranging from neutrality to very high (between 12 and 13). At even higher pH values, CuO starts to dissolve to yield CuO₂⁻, a soluble copper species. This structure of Eh-pH diagram is expected from our knowledge of the Eh-pH diagrams of the systems Cu-S-H-O and Fe-S-H-O.

Upon exposure to earth’s surface conditions, the various sulfides will oxidize to a common product SO₄²⁻, as well as dissolved metal ions at lower pH or metal oxides (or other forms such as malachite) at higher pH. Magnetite will slowly transform to hematite. Among the oxidation reactions is that of chalcopyrite as discussed below.

The oxidation of chalcopyrite by oxygen

$$\text{CuFeS}_2 + 4\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{SO}_4^{2-} \quad \text{(slow)}$$  (15)

does not produce acid itself, but the oxidation followed by hydrolysis of the ferrous ions does:

$$\text{Fe}^{2+} + 2\frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \rightarrow \text{Fe(OH)}_3 + 2\text{H}^+$$  (16)
If microbiological oxidation is pronounced, Fe\textsuperscript{2+} will be oxidized by bacteria, mainly *Thiobacillus ferrooxidans*, to Fe\textsuperscript{3+}:

\[
\text{Fe}^{2+} + \frac{1}{4}\text{O}_2 + \text{H}^+ \rightarrow \text{Fe}^{3+} + \frac{1}{2}\text{H}_2\text{O} \quad \quad (17)
\]

(by bacteria)

When the activity ratio of Fe\textsuperscript{3+}/Fe\textsuperscript{2+} in solution is great enough, the oxidation of chalcopyrite by Fe\textsuperscript{3+} takes place significantly:

\[
\text{CuFeS}_2 + 8\text{H}_2\text{O} + 16\text{Fe}^{3+} \rightarrow 17\text{Fe}^{2+} + \text{Cu}^{2+} + 2\text{SO}_4^{2-} + 16\text{H}^+ \quad \quad (18)
\]

Note that although this reaction shows 16 H\textsuperscript{+} ions being generated, they will be consumed when 16 Fe\textsuperscript{2+} ions of the 17 Fe\textsuperscript{2+} ions are oxidized by bacteria back to Fe\textsuperscript{3+} via reaction (17). Upon a complete circle consisting of reactions (17) and (18), the net result (the sum of reactions (17) and (18)) is reaction (15): one CuFeS\textsubscript{2} is broken down to one Cu\textsuperscript{2+}, one Fe\textsuperscript{2+} and two SO\textsubscript{4}\textsuperscript{2-}. It is the Fe\textsuperscript{2+} generated in this process that gives up two H\textsuperscript{+} ions (acid) through reaction (16). The role of bacteria and the 16 Fe\textsuperscript{2+}/Fe\textsuperscript{3+} is exactly that of a catalyst - speeding up the reaction but yielding no net change in themselves. From the same perspective, the oxidation of chalcocite and covellite by Fe\textsuperscript{3+}, when mediated by bacteria, will not generate any acidity, but rather the overall result would be that delineated by the equations (11) and (13).

**Solubilization of Cu** At ICM, secondary oxidized copper minerals such as tenorite or malachite are absent. So neither can copper be released from the hydrolysis of oxidized
Cu(+II) minerals nor can alkalinity or acid-consuming capability derive from them. The aqueous Cu$^{2+}$ ions come from the oxidation of primary sulfide minerals, the most abundant of which is chalcopyrite. The breakdown of copper sulfides or copper-iron sulfides yield cupric ions, ferrous ions and sulfate ions. The oxidation of chalcocite consumes acid; that of covellite neither consumes nor generates acid; and that of chalcopyrite generates acid. The acid is generated by oxidation followed by hydrolysis of aqueous Fe$^{2+}$ ions to solid Fe(OH)$_3$, which is the short term, metastable compound of iron at earth surface conditions when pH is approximately greater than 3.0 and which will slowly dehydrate to transform to hematite in the long run (see next section for detailed discussion of iron species).

**Removal of Dissolved Cu$^{2+}$** In an short term, at a Cu$^{2+}$ activity of the order of magnitude of 10$^6$, all cupric ions will stay in solution when pH is less than 7.0, even though they might be over-saturated with respect to tenorite or malachite. At greater pH values, part of the dissolved Cu$^{2+}$ will be removed from solution as hydroxide. In a long term and at the same activity level, all Cu$^{2+}$ will remain in solution at surface conditions if pH is approximately less than 6.5. At greater pH, part of the Cu$^{2+}$ will be removed either as tenorite or as malachite, depending on the total activity of carbon species. The short term removal of Cu$^{2+}$ has importance in considering chemical treatment plant as a pollution abatement option while the long term removal may be of significance in evaluating passive treatment of drainage.

The copper activity of 10$^6$ translates to a concentration of 128 µg/l. This value has been exceeded in NDD and EMO drainage by a factor of 10-20 for some of the high-concentration drainage flows. For example, the highest concentrations in NDD and EMO for the period
January, 1988 - January, 1989 are 2400 µg/l and 1200 µg/l. For these concentrations of dissolved copper to be stable in solution, the pH must be 0.3-0.5 unit less than pH 7.0. This problem is examined again in the section on solubility control.

5.3.2.6 Iron

Figures 22 and 23 provide the Eh-pH diagrams for the Fe-O-H and Fe-S-O-H systems at a total dissolved activity of $\Sigma Fe = 10^{-6}$ and at total dissolved activities of $\Sigma Fe = 10^{-6}$, $\Sigma S = 10^{-3}$, respectively. In the typical drainage at ICM, $\Sigma Fe = 5.0 \times 10^{-6}$, $\Sigma S = 4.67 \times 10^{-3}$.

The element iron has three oxidation states: +III, +II and 0. The oxidation state 0 is unstable in contact with water thus does not appear in the Eh-pH diagrams in the stability field of water. Fe(+III) is stable at relatively oxidizing conditions while Fe(+II) is stable at relatively reducing conditions.

The introduction of S into the Fe-O-H system only changes the lower part of Eh-pH diagram near the lower water stability limit, the upper part is unaffected. The upper parts are different in the two diagrams because of the different choices of the stable solid iron species. In Figure 22, Fe(OH)$_3$ and Fe(OH)$_2$ are chosen as stable species while in Figure 23 hematite (Fe$_2$O$_3$) and magnetite (Fe$_3$O$_4$) are selected. Since hematite is thermodynamically more stable than Fe(OH)$_3$, it pushes the Fe$^{3+}$/Fe$_2$O$_3$ boundary, the Fe$^{2+}$/Fe$_2$O$_3$ boundary and the
Figure 22  Eh-pH Diagram for Part of the System Fe-O-H Assuming Fe(OH)$_3$ as Stable Fe(+III) Phase. The assumed activity of dissolved Fe=10$^{-6}$. 

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Figure 23  Eh-pH Diagram for Part of the System Fe-S-O-H Assuming Hematite as the Major Fe(+III) Phase. The assumed activities of dissolved species are: $E_{Fe}=10^{-6}$, $ES=10^{-3}$. 
Fe$_3$O$_4$/Fe$_2$O$_3$ boundary outwards to occupy a larger territory. One can construct an Eh-pH diagram of Fe-S-O-H system with Fe(OH)$_3$ and Fe(OH)$_2$ being the major Fe(+III) and Fe(+II) solid phase species by superimposing the lower part of Figure 23 onto Figure 22. Figure 23 can be used to assess the dissolution of the minerals hematite and magnetite for various Eh-pH conditions. Figure 22 is suitable for evaluating the precipitation of dissolved iron from solutions, because observations have shown that when the pH of a solution containing dissolved iron is raised, Fe$^{3+}$ and Fe$^{2+}$ will be removed as Fe(+III) and Fe(+II) hydroxides (usually amorphous), not hematite or magnetite (both usually crystalline). This can be explained as follows: The formation of Fe(OH)$_3$ and Fe(OH)$_2$ is simply the combination of Fe$^{3+}$ and Fe$^{2+}$ ions with OH$^-$ ions in solution due to electrostatic attraction; all three ions are highly dispersed hence the reaction is very fast. However, Fe$^{3+}$ and Fe$^{2+}$ can not form hematite or magnetite directly, because firstly they are already in oxidized forms thus can not combine with free dissolved oxygen for which an electron donor must be available in order to form ion oxides, secondly a free oxide ion O$^-$ is not present in natural environments. They must extract O$^-$ from some species that contains it: This is usually OH$^-$ (or H$_2$O) in natural environments. Fe$^{3+}$ and Fe$^{2+}$ combine with OH$^-$ to form hydroxides:

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3 \text{ (solid)} \quad (19)
\]

\[
\text{Fe}^{2+} + 2\text{OH}^- \rightarrow \text{Fe(OH)}_2 \text{ (solid)} \quad (20)
\]

Reaction (20) takes place when pH is approximately greater than 8.8 and the Eh is very low at an activity of dissolved Fe$^{2+}$=10$^{-6}$ and is favoured by higher pH values. In contrast,
reaction (19) occurs at a pH as low as 3.1. In fact, reaction (19) is written for alkaline solutions where OH⁻ activity is reasonably high. In acidic solutions where OH⁻ activity is extremely low, Fe³⁺ hydrolyses to break down water into H⁺ and OH⁻, OH⁻ combines with Fe³⁺ while H⁺ is left behind in the solution, giving rise to acid mine drainage. Reaction (19) thus becomes:

$$\text{Fe}^{3+} + 3\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(\text{solid}) + 3\text{H}^+ \quad (21)$$

In the pH range from 3.1 to 8.8, Fe²⁺ is reduced to ferric hydroxide:

$$\text{Fe}^{2+} + 2\frac{1}{2}\text{H}_2\text{O} + \frac{1}{4}\text{O}_2 \rightarrow \text{Fe(OH)}_3(\text{solid}) + 2\text{H}^+ \quad (22)$$

Eventually, however, given enough time, Fe(OH)₃ and Fe(OH)₂ will transform to hematite or magnetite depending on Eh-pH conditions. The transformation of ferric hydroxide is simply a dehydration process:

$$2 \text{Fe(OH)}_3(\text{solid}) \rightarrow \text{Fe}_2\text{O}_3(\text{hematite}) + 3\text{H}_2\text{O} \quad (23)$$

The direct dehydration of ferrous hydroxide yield ferrous oxide FeO (the mineral wuestite):

$$\text{Fe(OH)}_2(\text{solid}) \rightarrow \text{FeO} + \text{H}_2\text{O} \quad (24)$$
Ferrous oxide is not a stable species (see Figures 22 and 23), thus in nature the above route is not taken. Ferrous hydroxide either oxidizes completely to hematite at relative oxidizing conditions:

\[ 2\text{Fe(OH)}_2(\text{solid}) \rightarrow \text{Fe}_2\text{O}_3(\text{hematite}) + \text{H}_2\text{O} + 2\text{H}^+ + 2e^- \quad (25) \]

or oxidizes partially to magnetite at relative reducing conditions:

\[ 3\text{Fe(OH)}_2(\text{solid}) \rightarrow \text{Fe}_3\text{O}_4(\text{magnetite}) + 2\text{H}_2\text{O} + 2\text{H}^+ + 2e^- \quad (26) \]

Reactions (25) and (26) are only half reactions, they require electron acceptors to complete. When free oxygen (whether gaseous or dissolved) are available, oxygen acts as the electron acceptor:

\[ \frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad (27) \]

The coupling of the half reaction (27) with half reactions (25) and (26) gives rise to:

\[ 2\text{Fe(OH)}_2(\text{solid}) + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3(\text{hematite}) + 2\text{H}_2\text{O} \quad (28) \]

\[ 3\text{Fe(OH)}_2(\text{solid}) + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4(\text{magnetite}) + 3\text{H}_2\text{O} \quad (29) \]

However, in the natural environments where Fe(OH)$_2$ is formed, the condition is often anoxic, that is, without free oxygen. An example of anoxic conditions is that of the bottom
of a stratified lake where biological activities are abundant. At such conditions, some other electron acceptor other than free oxygen must be available to facilitate the transformations represented by reactions (25) and (26). The oxidized species in the redox pairs that appear in Figure 10 may act as such electron acceptors at appropriate Eh-pH and activity settings. For example, if ammonium ion $NH_4^+$ is in significant concentration (such as due to the biological activity at the bottom of an anoxic lake), it can be reduced to nitrate to take up electrons:

$$NH_4^+ + 3H_2O + 8e^- \rightarrow NO_3^- + 10H^+$$  \hspace{1cm} (30)

Coupling of this half reaction with half reaction (26) yields:

$$12Fe(OH)_2 + NH_4^+ \rightarrow 4Fe_3O_4 \text{(magnetite)} + NO_3^- + 5H_2O + 18H^+$$ \hspace{1cm} (31)

One more possibility is the direct oxidation of ferrous ions by oxygen to hematite or magnetite:

$$2Fe^{2+} + 2H_2O + \frac{1}{2}O_2 \rightarrow Fe_2O_3 \text{(hematite)} + 4H^+$$ \hspace{1cm} (32)

$$3Fe^{2+} + 3H_2O + \frac{1}{2}O_2 \rightarrow Fe_3O_4 \text{(magnetite)} + 6H^+$$ \hspace{1cm} (33)

Reactions (32) and (33) are unlikely to take place in nature to any significant degree in a short term, because the formation of crystalline hematite and magnetite is an extremely
slow process. Much faster processes, such as that represented by reaction (20), (22) or the oxidation of Fe$^{2+}$ to Fe$^{3+}$ in solution

$$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^- \quad (34)$$

predominate in nature. Note that when reaction (34) is coupled with reaction (27), reaction (17) results, but not necessarily with the involvement of bacteria all the time.

From Figure 22, it can be seen that in the parallelogram ABCD, which represents the possible conditions in surface waters, the most stable species of iron can be Fe$^{3+}$, Fe$^{2+}$, and Fe(OH)$_3$. The Fe(OH)$_3$ field occupies the majority of the area in ABCD, thus it is likely the most stable species to form in ICM drainage flows. As has been discussed above, although Fe$^{3+}$ should transform to hematite at pH values approximately greater than 1.3 according to Figure 23, this does not take place in a short term for kinetic considerations. Instead, Fe$^{3+}$ precipitates as ferric hydroxide at pH values roughly greater than 3.1 at 10$^{-6}$ total Fe activity. The ferric ion activity in even the most acidic drainage (that of EMO with a pH of 4.2, see Table 18) should be three orders of magnitude less than 10$^{-6}$ (since [Fe$^{3+}$]·[OH]$^-$ = constant, OH$^-$ activity one order of magnitude greater corresponds to Fe$^{3+}$ activity three orders of magnitude less), namely, 10$^{-9}$, which corresponds to 0.215 µg/l assuming the activity coefficient of Fe$^{3+}$ to be 0.26 (computed from Debye-Hückel formula). The concentrations in other drainage streams with higher pH values are virtually zero. The above, however, are thermodynamic conclusions and should be applied with caution. The above rules are expected to be followed in ordinary conditions due to the rapid rate of hydroxide precipitation except where the bacteria *Thiobacillus ferroxidans* are extremely
active. The bacteria are believed to be able to maintain the Fe$^{3+}$ concentration somewhat higher than that dictated by thermodynamic equilibrium.

In the Eh-pH range defined by parallelogram ABCD, dissolved ferrous ions at an activity of $10^{-6}$ starts to transform to ferric hydroxide (reaction (22)) at pH values ranging from 3.1 to 5.4 depending on Eh values of the solution. The appropriate pH of the precipitation of Fe$^{2+}$ can be assumed to be 3.9, that along the line EF in Figure 22, due to lack of Eh measurements in the ICM drainage. Under this assumption, all $10^{-6}$ activity of Fe$^{2+}$ (112 pg/l in concentration) stays in solution below pH 3.9, but at pH 5.0 the activity of Fe$^{2+}$ will decrease to approximately $10^{-8}$, which corresponds to 1.12 µg/l. However, reaction (22) involves the oxidation of Fe(+II) to Fe(+III), therefore is much slower than the formation of ferric hydroxide from ferric ions, which involves only electrostatic attraction. Some deviation in Fe$^{2+}$ activity from the thermodynamic equilibrium is expected in reality. This is why in the ICM drainage concentrations of Fe$^{2+}$ as high as 830 µg/l have been detected (see Table 17).

Figure 23 demonstrates that pyrite occupies most of the area near the lower water stability limit. Pyrite is the most widespread primary sulfide in the world. Since the stability field of pyrite is too remote from the area defined by ABCD, which covers ordinary surface aerated water Eh-pH conditions, pyrite is not stable at earth’s surface. Almost any oxidants at earth surface conditions can play the role of oxidizing pyrite. The most common one is of course oxygen. According to Kleinmann, Fe$^{3+}$ becomes the major oxidant in place of oxygen when pH≤2.5 and Eh≥650 mv (approximate) (Kleinmann, 1981). The oxidation of pyrite is continuously undergoing at the earth’s surface. It is clear that the rate of release
of iron and sulfur is not limited by thermodynamic equilibrium, but by kinetics of the reactions. The biochemistry of pyrite oxidation has been discussed in the literature review of this thesis. At ICM, the dissolved iron are determined by the reconciliation among the rate of pyrite oxidation (which is determined by the total sulfur content, surface area to mass ratio of pyrite, bacteria activity, supply of water and oxygen, Eh-pH conditions, etc.), the frequency and amount of rain, and the rate of Fe²⁺/Fe³⁺ removal by precipitation as ferric hydroxide.

*Solubilization of Fe and S* At ICM, the rate of release of Fe²⁺ and SO₄²⁻ depends on the rate of pyrite oxidation. The concentrations of Fe³⁺ and Fe⁹⁺ reflects the balance among thermodynamic trends, bacteria activity, and kinetic considerations. Currently, the total Fe concentration in all the ICM drainage streams is basically that of Fe²⁺, the concentration of Fe³⁺ is extremely low due to the Eh-pH conditions in the present drainage. The concentration of Fe²⁺ (hence the total Fe concentration) is often higher than that governed by the equilibrium because the removal of Fe²⁺ via reaction (22) is slower than the generation of Fe²⁺ by the oxidation of pyrite, which in practice has bee proven to be relatively fast, especially when bacteria is actively involved.

The steady-state cycling of Fe²⁺/Fe³⁺ by bacteria oxidation of Fe²⁺ and pyrite reduction of Fe³⁺ generate neither net Fe²⁺ or Fe³⁺ nor net acidity. It is the oxidation of one unit of pyrite FeS₂, no matter abiotic or biological, that liberates two sulfate ions, two H⁺ and one Fe²⁺ ion, which upon hydrolysis generates another two H⁺ ions (reaction (22)). The kinetics of pyrite oxidation will be further discussed in the section headed by "kinetic considerations".
**Removal of Dissolved Fe** The state of existence of iron mobilized from pyrite depends on the Eh-pH conditions of the solution (see Figure 22). Assuming that line EF represents the average Eh-pH conditions that are likely to occur in the nature, we have calculate the equilibrium activities of dissolved iron species in the pH range 2-9. Note that the complexation of dissolved iron species with dissolved sulfur species is not considered. The result of the calculation is shown in Figure 24. It can be seen that at pH values greater than 2 the dissolved ferrous iron is so dominant that the total Fe activity is indiscernible from the Fe$^{2+}$ activity on the plot except near pH 2. The activities of dissolved iron species increase exponentially with the lowering of pH. For example, the total dissolved iron will be less than $10^{-6}$ in activity (112 μg/l in concentration) when pH is greater than 3.9. At pH 2, the drainage solution can hold $2.88 \times 10^{-3}$ Fe$^{3+}$ (620,000 μg/l in concentration) and $7.50 \times 10^{-3}$ Fe$^{2+}$ (840,000 μg/l), the ferric/ferrous ion concentration ratio is roughly one. At this pH, however, the formation of soluble complexes (actually ion pairs) such as FeSO$_4^+$, FeSO$_4^-$, FeHSO$_4^{2+}$ and FeHSO$_4^+$ becomes significant and increases as pH is further lowered due to the increasing iron activity. The concentrations of these ion pairs are not limited by equilibria with solid phase Fe(OH)$_3$ but by equilibria with the ions they consist of. Therefore, the total dissolved iron concentration can be much higher than the sum of the equilibrium concentrations of ferric and ferrous ions. At pH 4.5, the activity of Fe$^{2+}$ in equilibrium with Fe(OH)$_3$ is $10^{-7.13}$ (8.4 μg/l) and that of Fe$^{3+}$ is virtually zero ($10^{-10}$). In more sensible but less accurate words, we can state that the thermodynamics of the drainage system is such that under pH 2.5, all the iron mobilized by pyrite oxidation stays in the drainage; between pH 2.5 and 4.5, the iron released by pyrite is partially precipitated; and above pH 4.5, virtually all the iron is removed as ferric hydroxide. Two points should be emphasized, however. The first is that it is assumed that the occurrence of natural Eh-pH
Figure 24  Activities of Fe Species in Equilibrium with Fe(OH)₃
conditions follows line EF; deviations from line EF (as natural waters always do) lead to somewhat different answers, but the methodology still applies. The second is that these are thermodynamic (equilibrium) conclusions.

Data collected at ICM suggest that the drainage are over-saturated with respect to ferric hydroxide. According to the thermodynamics, the total iron concentration should not be detectable in all drainage streams but EMO which frequently had pH values below 4.5. This deviation from equilibrium, as has been mentioned above, is due to the kinetics: The iron release is faster than its removal. We can use our understanding of the system in practical applications. One example is that drainage samples for chemical analysis should be acidified upon collection to maintain highly oxidizing and acidic conditions to preserve the dissolved iron in solution (although other considerations also apply). This has been almost a standard practice for environmental sampling. Another example is that almost all the dissolved iron (and some other dissolved metal species) can be removed from a drainage simply by aging in a pond, although deliberate aeration can accelerate the process. Once a drainage water is no longer in contact with pyrite, the supply of fresh Fe$^{2+}$ is eliminated, thermodynamic equilibrium will be reached in time so that Fe$^{2+}$ will be removed as Fe(OH)$_3$.

5.3.2.7 Lead

Figure 25 displays the Eh-pH diagram for the system Pb-S-C-O-H at assumed activities of dissolved species $\Sigma$Pb=$10^{-6.6}$, $\Sigma$S=$10^{-3}$, $\Sigma$C=$10^{-3}$. The same activities in the ICM typical
Figure 25  Eh-pH Diagram for Part of the System Pb-S-C-O-H. The assumed activities of dissolved species are: $\Sigma Pb = 10^{-8.6}$, $\Sigma S = 10^{-3}$, $\Sigma C = 10^{-3}$. 
drainage are $\Sigma \text{Pb}=4.8\times10^9$, $\Sigma \text{S}=4.67\times10^3$ and $\Sigma \text{C}=1.11\times10^3$ (Table 18). Pb level in the drainage to be released to the environment is regulated at ICM to be less than 50 µg/l. With a few exceptions, the Pb levels in ICM land drainage are within the permit value.

Pb is a very heavy (molar mass 207 g/mol), environmentally toxic, group IV metal element. Its toxicity to man is cumulative. It has four oxidation states: 0, +II, +III, +IV. In the presence of S, Pb(0) is not stable in contact with water thus does not appear in the stability field of water. At $\Sigma \text{Pb}=10^{-8}$, Pb$^{2+}$ occupies a large field up to pH 8.1. Between pH 8.1 and 9.4, PbCO$_3$ (the mineral cerussite) is the stable phase provided the condition is not extremely oxidizing. When pH is greater than 9.4, PbCO$_3$ transforms to PbO (massicocot). At very oxidizing, near-neutral to alkaline conditions, Pb(+II) is oxidized to Pb(+III) as Pb$_3$O$_4$ (minium) and Pb(+IV) as PbO$_2$ (plattnerite). Another Pb(+II) species PbSO$_4$ (anglesite) which would be stable at acidic, oxidizing conditions does not occur in the Eh-pH diagram because $\Sigma \text{Pb}$ is too low. At higher $\Sigma \text{Pb}$ and/or $\Sigma \text{S}$ activities, the Pb$^{2+}$/PbCO$_3$ boundary will shift to the left by a great deal, and anglesite will occur in the diagram when $\Sigma \text{Pb}$ is high enough (approximately $10^5$). At reducing conditions, PbS (galena) is the stable species in the pH range 0-14. Within the parallelogram ABCD, the most stable species is Pb$^{2+}$.

Lead can occur in nature as galena, anglesite, cerussite, massicocot, minium and plattnerite, depending on the conditions of formation. ICM rocks are igneous thus we expect the primary sulfide galena to be the dominant Pb mineral. Galena probably occurs in association with other sulfides such as pyrite and chalcopyrite, which occupy a similar field in the Eh-pH diagram. Galena is unstable at surface oxygenated conditions as designated
by parallelogram ABCD, therefore it oxidizes readily. Like the situation with pyrite, the release of Pb$^{2+}$ and SO$_4^{2-}$ is not equilibrium-controlled, but kinetics-controlled. It is necessary to differentiate two kinetics measured on different scales. First of all, the word "kinetics" means in chemistry the study of the rate of a chemical reaction, the rate controlling factors, the rate's mathematical expression (the reaction orders), the reactions's elementary reactions, the reaction's activation energy and the rate's temperature response. In the context of acid mine drainage study, the kinetics either can be measured as the rate of the release of reaction products (such as Fe$^{2+}$ or Pb$^{2+}$) per unit weight of pure solid reactants (such as pyrite or galena) (the first one); or can be measured as the rate of the release of reaction products to each unit volume of drainage (the second one). The difference between the two is that the second is affected by all the factors that affect the first one, as well as the over-all content of solid reactants (such as pyrite), the frequency and amount of flushing water. We use the second interpretation of the word kinetics. The concentration of a reaction product (such as Fe$^{2+}$ or Pb$^{2+}$) is usually not directly related to the kinetics of the reaction, since once a reaction product is released into the drainage, it can be removed by other mechanisms that are not part of the kinetics of the reaction that release the product.

According to Figure 25, the concentration of Pb$^{2+}$ in equilibrium with cerussite is $10^{-8}$ in activity (4.3 $\mu$g/l in concentration) at pH 8.1, and $10^{-6}$ (431 $\mu$g/l) at pH 6.5. Similar calculations result in the following: $10^{-8.43}$ (1.6 $\mu$g/l) at pH 8.6, $10^{-6.94}$ (50 $\mu$g/l) at pH 7.2.

*Solubilization of Pb* The solubilization of Pb from galena is kinetics-controlled. An examination of the drainage pH values and Pb$^{2+}$ concentrations in the ICM drainage
streams that derive directly from the North Dump reveals that the \( \text{Pb}^{2+} \) in all drainage flows except NDD and TED are under-saturated with respect to cerussite. Thus the \( \Sigma \text{Pb} \) in all drainage streams except NDD and TED represents 100% of the Pb mobilized from galena. The slow release rate (hence the low \( \Sigma \text{Pb} \) concentration) in drainage is due to the scarcity of lead minerals in the ICM waste rock, because if the slow rate of Pb release were due to other limiting factors other than the low galena content, we would expect Pb release rate to increase in strongly acidified areas such as EMO where the release rates of other metals (such as Fe, Mn, Zn) have greatly increased. But in fact the \( \text{Pb}^{2+} \) level in EMO is approximately the same as other drainage streams (except NDD). The only drainage that contains \( \Sigma \text{Pb} \) in concentrations greater than the permit level (50 \( \mu \text{g/l} \)) is NDD, which usually contains about ten times greater \( \Sigma \text{Pb} \) concentration than other streams. The origin of the NDD dissolved lead can almost certainly be traced to the Old Marginal Dump, which is very likely to contain much higher percentage of galena than average waste rocks due to its higher degree of sulfide mineralization. The \( \text{Pb}^{2+} \) in NDD is sometimes over-saturated with respect to cerussite. So is the \( \text{Pb}^{2+} \) in TED to which NDD reports along with the \( \text{Pb}^{2+} \) it carries. The over-saturation is possible for kinetic reasons, as has been discussed previously.

It seems safe to concluded therefore that \( \Sigma \text{Pb} \) does not constitute a concern at ICM (except NDD), since the limiting factor responsible for low Pb concentration is the availability, thus the low Pb release rate can not be significantly accelerated by further acidification. The Old Marginal Dump deserves some attention since it is a warehouse of Pb for NDD.
Removal of Dissolved Pb  At ICM, the concentration of ΣPb has been very low, mostly within the range 0.5-7.5 µg/l. At such low concentrations, Pb²⁺ will neither be removed as carbonate (ΣC=10⁻³) below pH 8.0 nor be removed as sulfate (ΣS=4.7x10⁻³). To reduce the dissolved ΣPb below 50 µg/l (current ICM permit level) by cerussite precipitation, a pH greater than 7.2 and time to allow equilibrium to be reached is required. The removal of Pb²⁺ as hydroxide is discussed in the solubility control section.

5.3.2.8 Manganese

Figures 26 and 27 present the Eh-pH diagrams of the systems Mn-O-H and Mn-C-S-O-H at an assumed activity of ΣMn=10⁻⁶.⁴ and activities ΣMn =10⁻⁶, ΣC=10⁻³ and ΣS=10⁻³, respectively. The activities in the ICM typical drainage are ΣMn=5.0x10⁻⁵, ΣS=4.67x10⁻³ and ΣC=1.11x10⁻³ (Table 18).

Mn is a very active transition metal. Its oxidation states are 0, +II, +III, +IV, +VII. The oxidation states 0 and +VII are not stable in the water stability field thus do not occur in the Eh-pH diagrams. The Mn²⁺ field occupies much of Eh-pH diagram in both figures from acidic to relatively alkaline conditions except at high Eh. In parallelogram ABCD, Mn²⁺ is the most stable species except the most oxidizing and alkaline corner. Under oxidizing and very alkaline conditions, Mn forms oxide minerals of oxidation states +IV (MnO₂, pyrolusite, todorokite, etc.) and +III (Mn₂O₃). At transitional Eh and very high pH, the stable phase is Mn₃O₄ (hausmannite), an oxide of mixed oxidation states (+III and +II). At reducing and alkaline conditions hydroxide and carbonate are formed. The sulfide of Mn (MnS,
Figure 26  Eh-pH Diagram for Part of the System Mn-O-H. The assumed activity of dissolved ΣMn=10^{-6}.
Figure 27 Eh-pH Diagram for Part of the System Mn-C-S-O-H. The assumed activities of dissolved species are: $\Sigma Mn = 10^{-6}$, $\Sigma S = 10^{-3}$, $\Sigma C = 10^{-3}$. 

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alabandite) occupies only a very small field. This explains the rare occurrence of alabandite in the nature.

The nature of Mn-bearing minerals at ICM can not be determined from available information with certainty. The oxidation of MnS neither generates nor consumes acid:

\[
\text{MnS} + 2\text{O}_2 \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} \tag{35}
\]

The reactions that release Mn
\(\text{Mn}^{2+}\) from all other minerals that occur in Figure 27 are acid-consuming (or alkalinity-generating):

\[
\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O} \tag{36}
\]

\[
\text{Mn}_2\text{O}_3 + 6\text{H}^+ + 2\text{e}^- \rightarrow 2\text{Mn}^{2+} + 3\text{H}_2\text{O} \tag{37}
\]

\[
\text{Mn}_3\text{O}_4 + 8\text{H}^+ + 2\text{e}^- \rightarrow 3\text{Mn}^{2+} + 4\text{H}_2\text{O} \tag{38}
\]

\[
\text{MnCO}_3 + \text{H}^+ \rightarrow \text{Mn}^{2+} + \text{HCO}_3^- \tag{39}
\]

\[
\text{HCO}_3^- + \text{H}^+ \rightarrow \text{H}_2\text{CO}_3
\]
\[
\rightarrow \text{CO}_2(\text{g}) + \text{H}_2\text{O} \tag{40}
\]

\[
\text{Mn(OH)}_2 + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\text{O} \tag{41}
\]
Of these reactions, (36), (37) and (38) are reduction half reactions. Since the $\Sigma$Mn concentration in the ICM drainage is increasing very rapidly recently, it is worthwhile to examine the role of above acid-consuming reactions in the overall acid-base balance of the dump-drainage system if the major Mn mineral at ICM were oxides or carbonate or hydroxide. For convenience, let us assume the major Mn mineral is rhodochrosite ($\text{MnCO}_3$) and take EMO drainage as an example. Other minerals are similar. The average $\Sigma$Mn concentration in 1988 in EMO drainage is 4600 $\mu$g/l ($8.37 \times 10^{-5}$ molar concentration), the highest $\Sigma$Mn is 25,000 $\mu$g/l ($4.55 \times 10^{-4}$). The pH range of EMO in the same period is 4.2-4.8, within which $\text{H}_2\text{CO}_3$ (aqueous) is the predominant carbonate species. Each $\text{MnCO}_3$ releases one $\text{Mn}^{2+}$ and consumes two $\text{H}^+$ via Reactions (39) and (40). Thus each mole of $\text{MnCO}_3$ is equivalent to one mole of $\text{CaCO}_3$ with respect to acid consumption. Using the total annual drainage volume 243,600 m$^3$ and the total tonnage 4,670,000 tonnes for EMO, the alkalinity released by $\text{MnCO}_3$ is 2,034 kg $\text{CaCO}_3$ (using average $\Sigma$Mn) and 11,084 kg $\text{CaCO}_3$ (using highest $\Sigma$Mn). These are equivalent to $4.36 \times 10^{-4}$ kg $\text{CaCO}_3$/tonne and $2.37 \times 10^{-3}$ kg $\text{CaCO}_3$/tonne. The total annual release of alkalinity (used in consuming acidity) is 300 tonnes $\text{CaCO}_3$ in 1988 (Appendix II). The percentages of the alkalinity released by $\text{MnCO}_3$ are 0.68% and 3.7% respectively. These percentages are just marginally significant.

It is also possible that Mn appears as silicates (such as spessartite, $\text{Mn}_3\text{AL}_2\text{Si}_5\text{O}_{12}$) or as replacement constituents of more complicated silicate minerals (such as metamorphic mineral tourmaline), or as constituents of other minerals. We will not discuss these minerals in further detail except noting that the release of Mn from silicates is usually non-redox, slow, incongruent dissolution processes that consume acidity.
An interesting feature of the Mn-C-S-O-H system is that the stable phases at alkaline, from very oxidizing to transitional Eh conditions are all at a higher oxidation state than Mn$^{2+}$. These oxides therefore will act as oxidizing agents from near-neutral to acidic conditions in the same Eh range, as illustrated by Reactions (36), (37) and (38). The consequence of this is that, if the Mn oxides exist in appreciable quantities in the waste rocks, the oxidation of sulfides continue even oxygen is not present, since the Mn oxides replace oxygen as the major oxidants. This may take two routes: First, if water is available, water may be oxidized to release oxygen:

$$2\text{H}_2\text{O} \rightarrow 4\text{H}^+ + \text{O}_2 + 4\text{e}^- \quad (42)$$

The coupling of reactions (36), for example, with (42) yields:

$$2\text{MnO}_2 + 4\text{H}^+ \rightarrow 2\text{Mn}^{2+} + \text{O}_2 + 2\text{H}_2\text{O} \quad (43)$$

The oxygen so produced will be transported to other locations to be used to oxidize sulfide, for instance, pyrite:

$$\text{FeS}_2 + 3\frac{3}{2}\text{O}_2 + 3\frac{1}{2}\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3 + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (44)$$

The overall reaction, assuming all the oxygen produced in Reaction (43) is used in Reaction (44), is

$$\text{FeS}_2 + 7\frac{1}{2}\text{MnO}_2 + 11\text{H}^+ \rightarrow \text{Fe(OH)}_3 + 7\frac{1}{2}\text{Mn}^{2+} + 2\text{SO}_4^{2-} + 4\text{H}_2\text{O} \quad (45)$$
It can be seen from Reactions (42)-(45) that water is only needed to initiate the reaction. The overall reaction generates water so the water is self-sufficient. The problem is $\text{H}^+$ ions, for each $\text{FeS}_2$ oxidized consumes 11 $\text{H}^+$ ions. If there is no net acidity input into the system, the acidity is soon exhausted, raising the pH until the Mn oxides are stable thus no longer reduced to $\text{Mn}^{2+}$.

In the second route, the Mn oxides may oxidize sulfide directly (also take the reaction between pyrite and $\text{MnO}_2$ as an example) in one single step. The reaction is the same as Reaction (45), but without water and oxygen being electron transferring media. Although the limitation imposed by acidity availability still applies, the more stringent requirement is imposed by the reaction itself: It is a solid-solid-solute electron transfer reaction that takes geologic time to occur substantially, thus is not considered in our study.

The above discussion has potential practical significance. For example, if the waste rock contains $\text{MnO}_2$ (which could even be intentionally added), after the dump is sealed off from air, the pyrite oxidation (which does not produce but rather consumes acid in the absence of oxygen, Reaction (45)) may continue for a short time, during which the pH quickly picks up, then the oxidation will stop completely. The $\text{MnO}_2$ function as a "negative feedback": the faster the pyrite is oxidized by $\text{MnO}_2$, the faster the pH rises, and thus the sooner the oxidation stops. Mn oxides are as efficient acid consumers as $\text{CaCO}_3$ in that each $\text{Mn}^{2+}$ or $\text{Ca}^{2+}$ released to a solution will eliminate two $\text{H}^+$ from it. The difference between limestone and Mn oxides is that the breakdown of Mn oxides (except MnO) is a redox process while that of $\text{CaCO}_3$ a simple dissolution process. The idea of using Mn oxides as acid production abatement agents has not been seen elsewhere. Since the above discussion is largely based
on thermodynamics, the feasibility of this idea needs to be evaluated based on kinetic studies.

*Solubilization of Mn*  In the parallelogram ABCD, Mn$^{2+}$ is the most stable species. At ICM, the $\Sigma$Mn concentrations in all the drainage streams are under-saturated with respect to Mn oxides. The concentration of Mn$^{2+}$ therefore is kinetics-controlled rather than equilibrium controlled. The identities of the major Mn-bearing minerals have not been determined.

*Removal of Dissolved Mn*  Mn$^{2+}$ is a quite soluble species and is not removed from the ICM drainage as hydroxide or carbonate (see Section 5.3.3).

5.3.2.9  Molybdenum

Figure 28 presents the Eh-pH diagram for the system Mo-S-O-H at assumed dissolved species activities of $\Sigma$Mo=10$^{-8}$, $\Sigma$S=10$^{-3}$. The activities in the ICM typical drainage are $\Sigma$Mo=8.3x10$^{-8}$, $\Sigma$S=4.67x10$^{-3}$.

Molybdenum is one of ICM's revenue-generating metals. The mine effluent to be released to the environment is required to contain less than 500 $\mu$g/l by the environment permit. So far, the $\Sigma$Mo levels in the drainage streams emanating from the North Dump have been far below the permit level.
Figure 28  Eh-pH Diagram for Part of the System Mo-S-O-H. The assumed activities of dissolved species are: $\Sigma Mo=10^{-6}$, $ES=10^{-3}$.  

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The metal Mo (oxidation state 0) is not stable in contact with water. The oxidation states that occur in the water stability field are +IV, +V and +VI. The Mo(+/VI) occupies the majority of the Eh-pH diagram as two oxo-anions. The sulfide MoS₂ (molybdenite) is the stable species at reducing conditions. At transitional Eh and low pH conditions, Mo(+V) as MoO₂⁺ is the stable species. The mineral ilsemannite (Mo₈O₂₈, a Mo(+V)-Mo(+VI) mixture, or Mo₂O₆·MoO₃) occupies a triangle area near the MoS₂ field, between Mo(+V) and Mo(+VI).

The major Mo-bearing mineral at ICM is certainly molybdenite. In the parallelogram ABCD, the stable species is the soluble oxo-anion HMoO₄⁻. In the activity range of our interest, ΣMo is obviously under-saturated, therefore the concentration of ΣMo is controlled by the kinetics of MoS₂ oxidation. The low concentrations of ΣMo in ICM drainage are obviously limited by the low molybdenite content in the waste rock, just like the situation with lead (see Section 5.3.2.7). The ΣMo in the drainage will not be elevated by further acidification, as proved by the low ΣMo level in EMO drainage. Therefore, ΣMo does not constitute an environmental concern at ICM.

5.3.2.10 Zinc

Figure 29 presents the Eh-pH diagram of the system Zn-C-S-O-H at the assumed activities ΣZn=10⁻⁶.⁴, ΣC=10⁻³, ΣS=10⁻³. In the typical ICM drainage, these activities are 5.0x10⁵, 1.1x10⁻³, 4.67x10⁻³, respectively.
Figure 29  Eh-pH Diagram for Part of the System Zn-C-S-O-H. The assumed activities of dissolved species are: $\Sigma Zn=10^{-6}$, $\Sigma S=10^{-3}$, $\Sigma C=10^{-3}$. 
Although zinc only exhibits one oxidation state $\text{Zn}^{(+II)}$ in nature, the system is affected by $E_{\text{H}}$ because of the stability of sphalerite $\text{ZnS}$. Sphalerite is the most stable species between the lower water stability limit and the sulfate-sulfide boundary at pH>2.1 for $10^6 \Sigma \text{Zn}$ activity or at pH>1.14 for $10^4 \Sigma \text{Zn}$ activity. $\text{Zn}^{2+}$ is very soluble and occupies a large stability field from very acidic to near-neutral conditions above the sulfate/sulfide boundary. From near-neutral to alkaline conditions and above the sphalerite field, the stable $\text{Zn}^{(+II)}$ species are $\text{ZnCO}_3$ (smithsonite), $\text{ZnO}$ (zincite) and the soluble complex $\text{ZnO}_2^{2-}$. The $\text{ZnCO}_3/\text{ZnO}$ boundary is located at pH 8.1 and is not dependent of $\Sigma \text{Zn}$ activity. At $10^4 \Sigma \text{Zn}$ activity, $\text{ZnCO}_3$ occupies a narrow field between pH 7.5 and 8.1 while $\text{ZnO}_2^{2-}$ predominates at pH>13. At an $10^6 \Sigma \text{Zn}$ activity, the $\text{Zn}^{2+}/\text{ZnCO}_3$ border shifts to approximately pH 8.6 (to the right of the $\text{ZnCO}_3/\text{ZnO}$ boundary), therefore $\text{ZnCO}_3$ is unstable. The $\text{Zn}^{2+}/\text{ZnO}$ border appears at pH 8.8. The $\text{ZnO}/\text{ZnO}_2^{2-}$ boundary shifts to the left to pH 12. In the parallelogram ABCD, assuming $\Sigma \text{Zn}$ activity to be $10^4$, $\text{Zn}^{2+}$ is stable except at pH values greater than 7.5.

Zinc commonly occurs in nature either as the primary sulfide sphalerite or as secondary minerals such as smithsonite and zincite. Other rarer zinc minerals also exist in nature. At ICM, the major zinc-bearing mineral is probably sphalerite due to the igneous nature of the formation. Like calcite, smithsonite and zincite behave as acid consumers below approximately neutral pH:

$$\text{ZnCO}_3 + H^+ \rightarrow \text{Zn}^{2+} + \text{HCO}_3^- \quad (46)$$

$$\text{ZnCO}_3 + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2\text{CO}_3$$

$$\text{H}_2\text{CO}_3 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$$

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ZnO + 2 H⁺ → Zn²⁺ + H₂O \hspace{1cm} (48)

The oxidation of sphalerite neither produces nor consumes acid:

ZnS + 2O₂ → Zn²⁺ + SO₄²⁻ \hspace{1cm} (49)

The oxidation of sphalerite may also be facilitated by ferric ions with the involvement of bacteria in a fashion similar to the bacteria-enhanced oxidation of pyrite. An examination of the pH values and ΣZn concentrations recorded for the drainage streams around the North Dump reveals that all the drainage streams are under-saturated with respect to ZnCO₃, ZnO and Zn(OH)₂, even for the EMO drainage whose dissolved ΣZn once peaked to 36,000 µg/l (2.75x10⁻⁴ M activity). This fact implies that the concentration of ΣZn in the ICM drainage is not controlled by equilibria between dissolved ΣZn and secondary precipitates, neither is it controlled by the equilibrium between dissolved ΣZn and the primary sulfide sphalerite, which requires the total destruction of sphalerite. The ΣZn levels are limited by the kinetics of the oxidation of sphalerite.

The concentration of ΣZn has rapidly increased lately. The levels of ΣZn are in the same orders of magnitude as those of ΣMn. It is estimated that if the major zinc-bearing minerals were secondary minerals (smithsonite or zincite), the alkalinity released by the dissolution of such minerals would have accounted for 0.5-5% of the total alkalinity released in the EMO drainage in 1988. But the major zinc-bearing minerals are more likely to be primary minerals, especially sphalerite. If this is true, the solubilization of zinc will have no influence on the acid-base balance of the drainage, but will contribute a small percentage
of sulfate to the drainage. For example, in 1988 the EMO drainage contained 500-2,200 mg/l (5.2x10^{-3} - 2.3x10^{-2} mol/l) sulfate (Table 17) and 1,000-36,000 µg/l (1.53x10^{-5} - 5.5x10^{-4} mol/l) dissolved $\Sigma$Zn. That is to say, approximately 0.3-2.4% of the total sulfate derived from sphalerite. The largest contribution to total sulfate by the oxidation of Mn-bearing minerals would occur when we assume all the dissolved $\Sigma$Mn derived from MnS (which is very unlikely). This percentage is 2.0% for EMO drainage in 1988. The input of sulfate from sources other than pyrite, sphalerite and alabandite is insignificant. Therefore, the contribution to total sulfate by sulfides other than pyrite is at most 5%. This provides the justification for an assumption we use elsewhere in this thesis for calculation purposes. The assumption is that all the sulfate in the drainage derives from the oxidation of pyrite.

Solubilization of Zn The concentration of $\Sigma$Zn is controlled by the kinetics of sphalerite oxidation. More advanced stages of pyrite oxidation will be accompanied by more advanced stages of sphalerite oxidation because of their common rate-limiting factors.

Removal of Dissolved Zn$^{2+}$ So far in ICM drainage streams, all the zinc released by oxidation has been carried out, removal of dissolved zinc by precipitation is negligible. This is further discussed in the section on solubility control.
5.3.2.11 Cadmium

Figure 30 presents the Eh-pH diagram of the system Cd-C-S-O-H for assumed activities of \( \Sigma_{\text{Cd}}=10^{-8}, \Sigma_{\text{C}}=10^{-3}, \Sigma_{\text{S}}=10^{-3} \). In the ICM typical drainage, these activities are: \( \Sigma_{\text{Cd}}=4.9 \times 10^{-8}, \Sigma_{\text{C}}=1.1 \times 10^{-3}, \) and \( \Sigma_{\text{S}}=4.67 \times 10^{-3} \).

The permitted level of \( \Sigma_{\text{Cd}} \) in the mine drainage to be released to the environment is 10 \( \mu \)g/l because of the environmental toxicity of cadmium. This level has been marginally exceeded in NDD, TED, NDS, EMO, and EDD. The Eh-pH diagram of cadmium is very much like that of zinc (Figure 29). Cadmium has only two oxidation states in nature, Cd(0) and Cd(+II). CdS (greenockite) occupies all the area below the sulfate/sulfide boundary except at very acidic conditions. Experience has shown that in nature Cd rarely forms its own sulfide but rather occurs in other sulfide minerals such as sphalerite as impurities, perhaps because the element is too sparse in the crust. In oxidizing conditions, \( \text{Cd}^{2+} \) reigns a large field from near-neutral to acidic conditions. In mildly alkaline to alkaline conditions are the predominant fields of CdCO\(_3\) and Cd(OH)\(_2\), which dissolves to yield the complex oxo-anion \( \text{CdO}_2^{2-} \) at very alkaline conditions. In the parallelogram ABCD, \( \text{Cd}^{2+} \) is the predominant species.

**Solubilization of Cd** At ICM, Cd released to the solution is not removed either as carbonate or as hydroxide. High concentrations of \( \Sigma_{\text{Cd}} \) are observed to almost always correspond to high concentrations of \( \Sigma_{\text{Zn}} \), which can indicate an association of Cd with Zn minerals. The concentration of \( \Sigma_{\text{Cd}} \) is controlled by the kinetics of oxidation and at the same time is subject to the availability of Cd-bearing minerals.
Figure 30  Eh-pH Diagram for Part of the System Cd-C-S-O-H. The assumed activities of dissolved species are: \( \Sigma \text{Cd}=10^{-8}, \) \( \Sigma C=10^{-3}, \) \( \Sigma S=10^{-3}. \)
Removal of Dissolved Cd  Cd$^{2+}$ is under-saturated with respect to either carbonate or hydroxide at ICM. To reduce the Cd$^{2+}$ concentration in the solution to under 10 μg/l (permit level) as carbonate, a pH approximately greater than 8 is required (assuming dissolved ΣC activity to be 10$^{-3}$). To achieve the same purpose by hydroxide precipitation, pH should be greater than 10.6.

5.3.2.12 Arsenic

Figure 31 presents the Eh-pH diagram for the system As-S-O-H at assumed activities ΣAs=10$^{-6}$, ΣS=10$^{-8}$. The corresponding activities in the ICM typical drainage are ΣAs=8.3x10$^{-10}$, ΣS=4.67x10$^{-3}$.

Arsenic is very poisonous and is restricted at ICM by the permit to below 100 μg/l in the drainage to be released to the environment. ΣAs levels in current ICM drainage flows are commonly two orders of magnitude lower than the permit level. Arsenic is a metalloid element and exhibits six oxidation states in nature: -II, -I, 0, +II, +III, and +VI. The oxidation states -II and -I do not appear in the Eh-pH diagram. In reducing conditions As occurs as AsS (realgar), As$_2$S$_3$ (orpiment) and natural As. In approximately transitional zone it exists as As$_2$O$_3$ (arsenolite), arsenous acid and its various dissociation species. In oxidizing conditions, As occurs as arsenic acid and its dissociation products, all of which are soluble. When iron is introduced into the system, new stable phases include FeAsS (arsenopyrite), FeAs$_2$ (loellingite) and Fe(AsO$_4$)$_2$·2H$_2$O (scorodite). At ICM, arsenic probably exists in various sulfide minerals that contains iron.
Figure 31  Eh-pH Diagram for Part of the System As-S-O-H. The assumed activities of dissolved species are: ΣAs=10^{-6}, ΣS=10^{-3}.
Solubilization of As  At a ΣAs activity of 10^{-6} arsenic is totally soluble as arsenic acid or its ionization products. The ΣAs in the ICM drainage flows is well under-saturated. The reason for this is obviously the scarcity of As-bearing minerals in ICM waste rocks. Therefore the advancement of acidification will not cause arsenic to be mobilized faster to elevate the ΣAs concentration in the ICM drainage, as demonstrated by the fact that EMO drainage contains minimum arsenic despite its very acidic pH.

Removal of Dissolved As  At ICM, dissolved ΣAs is not removed by precipitation and need not be removed to satisfy the permit since the ΣAs in the drainage is already so low and will not rise significantly in the future. Dissolve ΣAs does not constitute a concern at ICM.

5.3.3 Solubility Control

Solubility product control, or more exactly equilibrium ion activity product control refers to the limitations set on the activities of ions in a solution by relatively insoluble compounds which are composed of these ions. For example, the equilibrium chemistry requires that the activities of Fe^{3+} and OH^- in a solution must be such that their ion activity product [Fe^{3+}][OH^-]^3 should be less than or equal to 3 \times 10^{-39}, the solubility product (or equilibrium ion activity product) of Fe(OH)_3. One particular ion may be a constituent of many insoluble compounds and must obey the activity restrictions set by all such insoluble compounds. The maximum allowable activity of an ion in a solution at thermodynamic equilibrium is determined by the compound that requires lowest equilibrium activity of the ion. When the activity of an ion is smaller than the maximum allowable activity, the solution is under-
saturated with respect to all solid phases containing the ion. A solution under-saturated in a certain ion can be in equilibrium when all solid phases containing the ion as a constituent are absent, otherwise the solid will dissolve to raise the activity of the ion, thus the system is not at equilibrium. A solution-solid system can be over-saturated in some ions due to kinetic considerations (such as extremely slow reaction rate, lack of crystallization seeds, etc.). Such systems are never at true thermodynamic equilibrium.

We will only consider the solubility control of ion activities by ionic or highly polar covalent compounds whose elements do not change oxidation states upon dissolution. These compounds will dissolve to yield the ions they are composed of in solution and are referred to as strong electrolytes. Highly insoluble electrolytes are expected to exercise major ion activity control in many solutions where the total content of organic substances is low, partly because the precipitation of such solids involves only electrostatic attractions between ions thus is rapid relative to redox reactions which involve electron transfer, and other reactions. Oxides are not considered because the metal ions in basic oxides (such as CaO, Fe$_2$O$_3$ etc.) are most frequently removed from solutions as hydroxides (which are in fact hydrated oxides and are considered) while acidic oxides are often weak electrolytes and do not include the metal elements in which we are interested. We have also excluded the compounds whose dissolutions are redox reactions, since these have already been considered in the previous sections. Complexation of ionic metal species with organic ligands also exerts an important, even primary control over ionic activities of metal ions as well as total activities of metals under certain conditions. This is treated in the next section.
The previous discussion of the Eh-pH diagrams has in fact dealt implicitly with the solubility controls of many metal ions by hydroxides, oxides, carbonates (when carbon species are considered in the Eh-pH diagrams), and sulfates (when sulfur species are considered). This section will view the solubility control systematically and find out the major activity controllers for some of the important metal species in the ICM drainage.

Table 19 is a compilation of the solubility products of some strong electrolytes formed by the metals of our interest and anions present in the ICM drainage. In Section 5.3.1, we mentioned that the major anions in the ICM drainage include HSO₄⁻, SO₄²⁻, OH⁻, HCO₃⁻, CO₃²⁻, Cl⁻, and perhaps NO₃⁻ and the ionization products of phosphoric acid H₂PO₄⁻, HPO₄²⁻ and PO₄³⁻. Of these, nitrates, chlorides, hydrogen sulfates and bicarbonates of all the metals we are interested in are too soluble to commit any significant ion activity control, so they will be dropped from the list. Although phosphate could impose control over some ion activities when present in significant activities (concentrations), especially in alkaline conditions, we believe that the total phosphate concentration is too low in the ICM drainage to assume this responsibility. In addition, at the pH range of our concerns, the predominant phosphate species are hydrogen phosphate ions and di-hydrogen phosphate ions whose salts are usually soluble, and the activity of phosphate ion is at least four orders of magnitude less than the total inorganic phosphate activity below pH 8.5. For example, let us make an approximate calculation using Pb₃(PO₄)₂, the phosphate salt that has the lowest solubility product (7.9x10⁻⁴⁸) in Table 19. Assuming a total inorganic phosphorus activity of 10⁻⁷ M, at pH 8.5, the activity of PO₄³⁻ would be 10⁻¹¹. From [Pb³⁺]³²[PO₄³⁻]² = 7.9x10⁻⁴₈, [Pb³⁺]= 2x10⁻⁷. This activity is greater than the activity of Pb²⁺ in equilibrium with lead carbonate at pH 8.5 (assumed activity of ΣC=10⁴, see Figure 35) so the activity of Pb²⁺ will be
Table 19  Solubility Products of Salts and Bases of Interest at 25°C and 1 atm

<table>
<thead>
<tr>
<th>Cations</th>
<th>Carbonates</th>
<th>Chlorides</th>
<th>Hydroxides</th>
<th>Sulfates</th>
<th>Sulfides</th>
<th>Phosphates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca^{2+}</td>
<td>3.84 x 10^-9</td>
<td>3.63 x 10^11*</td>
<td>4.0 x 10^-5</td>
<td>2.5 x 10^-5</td>
<td>d.</td>
<td>1 x 10^-26</td>
</tr>
<tr>
<td>Mg^{2+}</td>
<td>1 x 10^-5</td>
<td>1.76 x 10^33*</td>
<td>7.1 x 10^-12</td>
<td>3.09 x 10^-5*</td>
<td>d.</td>
<td>1 x 10^-32</td>
</tr>
<tr>
<td>Al^{3+}</td>
<td>N/A</td>
<td>s.</td>
<td>3.5 x 10^-34</td>
<td>v.s.</td>
<td>d.</td>
<td>5.8 x 10^-19</td>
</tr>
<tr>
<td>Fe^{2+}</td>
<td>2.1 x 10^-11</td>
<td>9.14 x 10^-7*</td>
<td>8 x 10^-16</td>
<td>sl.s. ((\text{FeSO}_4\cdot7\text{H}_2\text{O}))</td>
<td>4.2 x 10^-17 ((\text{FeS})) N/C, ins. v.s. ((\text{FeSO}_3\cdot4\text{H}_2\text{O})) ((\text{Fe}_3(\text{PO}_4)_2\cdot8\text{H}_2\text{O}))</td>
<td></td>
</tr>
<tr>
<td>Fe^{3+}</td>
<td>N/A</td>
<td>8.3 x 10^11*</td>
<td>3 x 10^-39</td>
<td>v.s.</td>
<td>sl.d.</td>
<td>2.08 x 10^-41*</td>
</tr>
<tr>
<td>Cu^{2+}</td>
<td>2.3 x 10^-10</td>
<td>6.02 x 10^-33*</td>
<td>1.3 x 10^-20</td>
<td>4.43 x 10^-22*</td>
<td>6 x 10^-36 ((\text{CuS})) N/C, ins.</td>
<td></td>
</tr>
<tr>
<td>Cu^{+}</td>
<td>N/C, ins.</td>
<td>1.2 x 10^-6</td>
<td>N/A</td>
<td>d.</td>
<td>3 x 10^-48 ((\text{Cu}_2\text{S})) N/A</td>
<td></td>
</tr>
<tr>
<td>Zn^{2+}</td>
<td>1.7 x 10^-11</td>
<td>1.14 x 10^-7*</td>
<td>3.3 x 10^-13</td>
<td>1.23 x 10^-3*</td>
<td>2 x 10^-24 ((\text{ZnS})) N/C, ins.</td>
<td></td>
</tr>
<tr>
<td>Mn^{2+}</td>
<td>5 x 10^-10</td>
<td>v.s.</td>
<td>2 x 10^-13</td>
<td>2.45 x 10^-12*</td>
<td>2.3 x 10^-13 ((\text{MnS}))</td>
<td>1 x 10^-22</td>
</tr>
<tr>
<td>Mo^{5+}</td>
<td>N/A</td>
<td>d.</td>
<td>2.3 x 10^-8*</td>
<td>N/A</td>
<td>N/C, ins.</td>
<td>N/A ((\text{Mo}_2\text{O}_5\cdot3\text{H}_2\text{O}))</td>
</tr>
<tr>
<td>Mo^{6+}</td>
<td>N/A</td>
<td>s. d.</td>
<td>N/C, ins. ((\text{MoO}_3\cdot2\text{H}_2\text{O}))</td>
<td>N/A</td>
<td>N/C, sl.s. ((\text{MoS}_2))</td>
<td>N/A</td>
</tr>
<tr>
<td>Pb^{2+}</td>
<td>7.4 x 10^-14</td>
<td>2 x 10^-5</td>
<td>1.2 x 10^-15</td>
<td>1.82 x 10^-8*</td>
<td>1 x 10^-20 ((\text{PbS}))</td>
<td>7.9 x 10^-43</td>
</tr>
<tr>
<td>Cd^{2+}</td>
<td>1.0 x 10^-12</td>
<td>2.75*</td>
<td>8.1 x 10^-15</td>
<td>1.13*</td>
<td>2 x 10^-28 ((\text{CdS}))</td>
<td>N/C, ins.</td>
</tr>
</tbody>
</table>

Notes:
1. In constructing this table, the following references are consulted: Bailar et. al. 1984; CRC Handbook of Chemistry and Physics, 47th edn.; Dreyer, 1982; and Brookins, 1988. See Bibliography at the back of this report.
2. Entries indicated with an "*" are computed from Standard Free Energies of Formation at 25°C found in the References listed above.
3. Abbreviations used: v.=very, s.=soluble, ins.=insoluble, d.=decompose, sl.=slightly, N/A =not available, usually because the substance does not form or is not stable, N/C=non-computable due to lack of thermodynamic data.
4. Scope of phrasal expressions: very soluble = greater than 10 grams per 100 ml of water, soluble = between 1 and 10 grams per 100 ml, slightly soluble = approximately around 0.1 gram per 100 ml.
controlled by carbonate instead of phosphate. Therefore, the role of phosphates in solubility
control is also insignificant at ICM. What we have left to consider are carbonates,
hydroxides and sulfates. Some words about sulfides before we proceed. Sulfides of metals
are generally very insoluble in water (in the sense that they dissolve to give \( M^{n+} \) and \( S^- \), see
the solubility products in Table 19) except those of alkaline and alkaline earth metals,
which are unstable in contact with water. At reducing conditions in the water stability field
below the sulfate/sulfide boundary, the predominant species are aqueous \( H_2S \) at \( pH<7 \) and
\( HS^- \) at \( 7< pH<14 \) (Figures 12 and 13). The \( S^+ \) ions become the predominant species only at
\( pH>14 \). Assuming a \( \Sigma S \) activity of \( 10^{-3} \) M, we find the activity of \( S^- \) to be \( 5 \times 10^{-11} \) M at \( pH \)
7. Even at such a small activity, sulfide is able to control the activities of some metals due
to the extremely small solubility products of these metals. For example, with a solubility
product of \( 2 \times 10^{-28} \), sphalerite (ZnS) can have at most an activity of \( 4 \times 10^{-18} \). However, the
above picture changes completely in oxidizing conditions, i.e., above the sulfate/sulfide
boundary. At the same \( \Sigma S \) activity (\( 10^{-3} \) M) and \( pH (7.0) \), the predominant sulfur species
is \( SO_4^{2-} \) at \( pH>1.8 \). The activity of \( S^+ \) ions in equilibrium with the \( 10^{-3} \) M \( SO_4^{2-} \) at \( pH 7 \) is
calculated to be \( 1.47 \times 10^{-50} \) M. At such an activity, \( S^+ \) will definitely not exercise any control
over any metal ion activities via the formation of sulfides.

The equation of solubility product for sulfates \( [M^{2+}] \cdot [SO_4^{2-}] = K_{sp} \) can be written as
\[ \log[M^{2+}] = \log K_{sp} + p[SO_4^{2-}] \], thus the plot of \( \log[M^{2+}] \) versus \( p[SO_4^{2-}] \) (which is defined as
\( -\log[SO_4^{2-}] \)) is a straight line. Using the \( K_{sp} \) values given in Table 19, we have constructed
Figure 32. It turned out that only \( Pb^{2+} \), \( Ca^{2+} \) and \( Mg^{2+} \) appear in the \( [M^{2+}]-[SO_4^{2-}] \) range of
our interest. The straight lines represent the metal ion activities in equilibrium with their
sulfates.
Figure 32  Logarithmic Concentration Diagram Showing the Activities of Some Metal Ions in Equilibrium with Their Sulfates at 25°C.

pSO₄⁻⁻ ( = p(Total S) at pH>2)
For metal hydroxides, \([M^{n+}]^\circ \cdot [OH^-]^\circ = K_{sp}\), thus \(\log[M^{n+}] = \log K_{sp} - n\log[OH^-]\), or \(\log[M^{n+}] = \log K_{sp} + 14n - n\cdot pH\). Using the \(K_{sp}\) in Table 19, \(\log[M^{n+}]\) is plotted against \(pH\) in Figure 33. A point on a particular straight line indicates the activity of the metal ion concerned in equilibrium with its hydroxide at the corresponding \(pH\). Note the difference in slope between +2 ions and +3 ions.

Figure 34 is constructed in the same way as Figure 32. Much more metal ions appear in this figure than in Figure 32 because generally carbonates are less soluble than sulfates. Figure 34 may be difficult to use because the \(CO_3^{2-}\) is a function of both \(\Sigma C\) activity and \(pH\) due to the equilibrium between \(CO_3^{2-}\) and \(HCO_3^-\) and between \(HCO_3^-\) and \(H_2CO_3\) (Figure 15). A diagram showing the activities of various metal ions in equilibrium with their corresponding carbonates for a specific \(\Sigma C\) activity is more convenient. Figure 35 is constructed for this purpose.

To construct Figure 35, we need to choose a \(\Sigma C\) activity. For this reason, let us first consider the \(\Sigma C\) activity in a water in equilibrium with atmosphere at \(pH 7\). The partial pressure of \(CO_2\) in the standard atmosphere at sea level is quite low, 0.0003 (or \(10^{-3.52}\)) atm (which is also equal to the mole fraction of carbon dioxide in the atmosphere). According to Henry's law, at equilibrium, the activity of carbonic acid (dissolved carbon dioxide) is \(a_{H_2CO_3} = p_{CO_2} \cdot K_{CO_2}\), where \(K_{CO_2} = 10^{-1.47}\) at 25°C. Therefore \(a_{H_2CO_3} = 10^{-4.99} \approx 10^{-5}\). The total carbon activity is calculated as:
Figure 33 Logarithmic Concentration-pH Diagram Showing the Activities of Various Metal Ions in Equilibrium with Their Hydroxides at 25°C.
Figure 34  Logarithmic Concentration Diagram Showing the Activities of Various Metal Ions in Equilibrium with Their Carbonates at 25°C.
Figure 35  Logarithmic Concentration-pH Diagram Showing the Activities of Various Metal Ions in Equilibrium with Their Carbonates at 25°C.
\[ a_{\text{EC}} = a_{\text{H}_2\text{CO}_3}(1 + K_1/a_{\text{H}^+} + K_1\cdot K_2/a_{\text{H}^+}^2) \]
\[ = 5.3 \times 10^{-5} \]
\[ = 10^{-4.28} \]

where \( K_1 \) and \( K_2 \) are the first and the second dissociation constants of carbonic acid and equal to \( 4.3 \times 10^{-7} \) and \( 4.7 \times 10^{-11} \) at 25°C. The same calculation at pH 8 leads to a \( \Sigma \text{C} \) activity of \( 10^{-3.35} \). Considering the flushing water in the dumps to be approximately neutral, the dumps to be well aerated and the flushing water is approximate in equilibrium with the pore air in the dumps, the \( \Sigma \text{C} \) activity in the flushing water will be in the order of magnitude of \( 10^{-4} \). This activity value is assumed in Figure 35. In reality, the flushing water could be much more acidic on one hand, which will reduce the \( \Sigma \text{C} \) activity in water in equilibrium with atmosphere, on the other hand, the partial pressure of carbon dioxide in the pore air in the dumps could be much higher than that in the atmosphere due to biological activities and/or release of carbon dioxide by the acid consumption reactions of carbonate (such as calcite), which tends to increase the \( \Sigma \text{C} \) activity. Therefore, the \( \Sigma \text{C} \) activity in real situations probably fluctuates between \( 10^2 \) and \( 10^5 \). The construction of a diagram similar to Figure 35 with a different \( \Sigma \text{C} \) activity involves only a vertical displacement of all the curves but that of CO\textsubscript{3}\textsuperscript{2-} by a distance determined by the difference between the new \( \Sigma \text{C} \) activity and \( 10^4 \). For example, if a similar diagram is to be constructed for \( 10^{-3} \Sigma \text{C} \) activity, all the curves in Figure 35 simply shift down by one unit, except the curve of CO\textsubscript{3}\textsuperscript{2-} which shifts up by one unit.

Using Figures 32 through 35, we can determine the saturation state (i.e. over-saturation, under-saturation, or equilibrium) of a particular metal ion with respect to sulfate if we
know ΣS activity (calculated form concentration) and pH, or SO₄⁻ activity; or with respect to hydroxide if we know the pH; or with respect to carbonate if we know either CO₃⁻ activity or the ΣC activity along with pH. We can also determine the conditions for precipitation of various ions as hydroxides, carbonates and sulfates.

An comparison of Figure 32 with Figures 33 and 35 reveals that at the conditions typical of the ICM drainage, i.e., ΣS=10⁻², ΣC=10⁻³, the maximum activity of Ca²⁺ is controlled by its sulfate at pH<7.5 and by its carbonate at pH>7.5; that of Mg²⁺ by its sulfate at pH<9.7 and by its hydroxide at pH>9.7; and that of Pb²⁺ by its sulfate below pH 6.3 and by its carbonate above pH 6.3. If the activity of ΣC decreases to 10⁻⁴ but other conditions remain unchanged, Mg²⁺ is not affected, but Ca²⁺ and Pb²⁺ are. The pH values of the transition from sulfate control to carbonate control become pH 8.5 for Ca²⁺ and pH 7.1 for Pb²⁺. The activities of all other ions will be controlled either by carbonates or by hydroxides, but not by sulfates.

In Figures 36 and 37, we have combined Figure 33 and 35 into one plot at two different ΣC activities. The intersection point of the hydroxide line and the carbonate curve of a particular metal ion defines the transition pH, above which its hydroxide controls its activity while below which its carbonate does. The information obtained in Figures 36 and 37, along with that from the analysis of activity control by sulfates, are presented in Table 20.

Figure 38 summarizes the above discussions graphically. It shows in bold lines the maximum activities of various ions as allowed by their equilibrium with sulfates, carbonates
Figure 36. Logarithmic Concentration-pH Diagram Showing the Activities of Various Metal Ions in Equilibrium with Both Their Carbonates and Their Hydroxides at 25°C. Assumed activity of EC=10⁻⁴.
Figure 37 Logarithmic Concentration-pH Diagram Showing the Activities of Various Metal Ions in Equilibrium with Both Their Carbonates and Their Hydroxides at 25°C. Assumed activity of ΣC=10^{-3}. 
Table 20  The pH Ranges of Metal Ion Activity Control by Sulfates, Carbonates and Hydroxides (ΣS activity is assumed to be 10⁻²)

<table>
<thead>
<tr>
<th>Ions</th>
<th>Sulfate Ctrl.</th>
<th>Carbonate Ctrl.</th>
<th>Hydroxide Ctrl</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΣC=10⁻³</td>
<td>ΣC=10⁻⁴</td>
<td>ΣC=10⁻³</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>2-7.5</td>
<td>2-8.5</td>
<td>7.5-14.5</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>2-9.7</td>
<td>2-9.7</td>
<td>Nil</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>&lt;10.1</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>Nil</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>&lt;11.6</td>
</tr>
<tr>
<td>Mn²⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>&lt;10.7</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>2-6.3</td>
<td>2-7.1</td>
<td>6.3-11.6</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>Nil</td>
<td>Nil</td>
<td>&lt;11.4</td>
</tr>
</tbody>
</table>
Figure 38  Activity-pH Diagram Showing the Maximum Activities of Various Metal Ions as Controlled by Their Equilibrium with Sulfates, Carbonates and Hydroxides at 25°C. Assumed activities are: EC=10^{-3}, ES=10^{-2}.
and hydroxides for a selected set of conditions. As a matter of fact, we can modify Figure 38 for any combinations of $\Sigma C$ and $\Sigma S$ activities corresponding to those of particular drainage steams, then plot the pH and the activities of various metal ions in the streams onto the diagram to determine their saturation states.

Applying the composition of the typical ICM drainage (Table 18) to Figure 38, we find that all the metal ions are under-saturated except $\text{Ca}^{2+}$, which is approximately in equilibrium with gypsum ($\text{CaSO}_4$).

An examination of the analytical results of the EMO drainage samples in 1988 using the same principles as above shows that the drainage is under-saturated in all the metal cations except $\text{Ca}^{2+}$, which is over-saturated with respect to gypsum by a factor from 1 to 3 in most samples and is slightly under-saturated in the rest of the samples. This may imply that the sulfate level and the calcium level in the EMO drainage is controlled by gypsum precipitation. The major reason for the under-saturation of the metal cations is the low pH in EMO (4.2-4.8), which raises the activities of cations in equilibrium with their carbonates and hydroxides but has no effect on the activities of cations in equilibrium with sulfates approximately above pH 2.

In a similar exercise performed on the water quality data of NDD in the period January - October, 1988, we have found the following: In cases where pH is near-neutral (6.5-7.5), the activities of all metal ions except $\text{Zn}^{2+}$, $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ in the drainage are 1-3 (mostly 2) orders of magnitude lower than the equilibrium activities (namely under-saturated). $\text{Zn}^{2+}$ is also under-saturated but its activity is in the same order as the equilibrium activity.
Ca\textsuperscript{2+} and Mg\textsuperscript{2+} are under-saturated with respect to their sulfates by one order. In the only case where pH is 4.4, however, all the metals except Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Pb\textsuperscript{2+} become under-saturated by 3-6 orders. Pb\textsuperscript{2+} and Mg\textsuperscript{2+} are under-saturated with respect to their sulfates by one order of magnitude while Ca\textsuperscript{2+} is under-saturated by a factor of 2.

The importance of pH on the saturation states of various metal ions in the ICM drainage can best be demonstrated in Table 21, which is an analysis similar to the ones above carried out on the TED drainage data collected in 1988. TED is the stream that has exhibited the highest pH values in all the drainage streams originating directly from the North Dump.

The following have been observed from Table 21:

<table>
<thead>
<tr>
<th>Date</th>
<th>pH</th>
<th>Sulph.</th>
<th>Ca</th>
<th>Mg</th>
<th>Pb</th>
<th>Cu</th>
<th>Fe</th>
<th>Pb</th>
<th>Mn</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Jan 88</td>
<td>8.1</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-2</td>
<td>O+2</td>
<td>U-1</td>
<td>U-1</td>
<td>U-1</td>
<td>O+0</td>
<td>U-1</td>
</tr>
<tr>
<td>Feb 88</td>
<td>7.1</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-2</td>
<td>U-1</td>
<td>U-2</td>
<td>U-1</td>
<td>U-2</td>
<td>U-1</td>
<td>U-2</td>
</tr>
<tr>
<td>Mar 88</td>
<td>8.1</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-2</td>
<td>O+1</td>
<td>U-1</td>
<td>U-1</td>
<td>U-2</td>
<td>O+0</td>
<td>U-1</td>
</tr>
<tr>
<td>Apr 88</td>
<td>8.4</td>
<td>U</td>
<td>U-3</td>
<td>U-1</td>
<td>U-2</td>
<td>O+2</td>
<td>U-1</td>
<td>E</td>
<td>U-1</td>
<td>O+0</td>
<td>U-1</td>
</tr>
<tr>
<td>May 88</td>
<td>8.6</td>
<td>U</td>
<td>U-3</td>
<td>U-1</td>
<td>U-1</td>
<td>O+2</td>
<td>U-1</td>
<td>E</td>
<td>U-1</td>
<td>O+0</td>
<td>U-1</td>
</tr>
<tr>
<td>Jun 88</td>
<td>8.5</td>
<td>U</td>
<td>U-3</td>
<td>U-1</td>
<td>U-1</td>
<td>O+2</td>
<td>U-1</td>
<td>E</td>
<td>U-1</td>
<td>E</td>
<td>U-1</td>
</tr>
<tr>
<td>Jul 88</td>
<td>8.0</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-1</td>
<td>O+1</td>
<td>U-1</td>
<td>U-1</td>
<td>U-2</td>
<td>U-1</td>
<td>U-2</td>
</tr>
<tr>
<td>Aug 88</td>
<td>8.1</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-1</td>
<td>O+1</td>
<td>U-1</td>
<td>U-0</td>
<td>U-3</td>
<td>U-1</td>
<td>U-2</td>
</tr>
<tr>
<td>Sep 88</td>
<td>4.5</td>
<td>U</td>
<td>U-4</td>
<td>U-1</td>
<td>U-1</td>
<td>U-5</td>
<td>U-5</td>
<td>U-3</td>
<td>U-6</td>
<td>U-5</td>
<td>U-6</td>
</tr>
<tr>
<td>Oct 88</td>
<td>6.8</td>
<td>U</td>
<td>U-3</td>
<td>U-0</td>
<td>U-1</td>
<td>U-0</td>
<td>U-3</td>
<td>U-2</td>
<td>U-2</td>
<td>E</td>
<td>U-2</td>
</tr>
</tbody>
</table>

Note: U=Under-saturated, O=Over-saturated, E=Approximate Equilibrium. +2=Over-saturated by 2 orders, -3=Under-saturated by 3 orders, +0 or -0 = Over- or Under-saturated, but in the same order. w.r.t.= With respect to.
All the over-saturation and equilibrium states occurred above pH 8.0 (except one case). In other words, below pH 8.0, all the metal ions are under-saturated, thus have not been precipitated prior to their appearance in the seeps.

All the metal ions except Ca²⁺ and Mg²⁺ are dramatically much more under-saturated in the only drainage with a pH of 4.4 than in all others whose pH values range from 6.8 to 8.6. The equilibrium activities of Ca²⁺ and Mg²⁺ ions are controlled by their sulfates and do not change in the pH range 2-7.

The only metal ions that achieved either equilibria or over-saturation are Cu²⁺, Pb²⁺, and Zn²⁺, and they did so at pH values greater than 8. It appears that the activities of Pb²⁺ and Zn²⁺ are controlled by their equilibria with their activity-limiting compounds, since the two were either under-saturated, or at equilibria, or slightly over-saturated, but never over-saturated by one order of magnitude or more. Cu²⁺ is different, however, in that it was over-saturated for many times by 1-2 orders of magnitude with respect to its equilibrium activity defined by its activity-limiting compound. This is not surprising because it has been well documented that in natural waters some solutes are often over-saturated by a factor of 1-1000, but rarely by a factor greater than 1000 (Drever, 1982). This phenomenon is again attributable to slow reaction kinetics.

The conclusions are clear from the discussion of solubility control and the examination of the three representative streams at ICM (EMO - lowest pH and heaviest contamination,
NDD - heavy contamination in metals, pH near-neutral but less than 8.0, TED - intermediate metal contamination and wide pH variation 4.4-8.6):

- Below pH 8.0, no metal ions are removed from any of the ICM drainage streams. This is perhaps contrary to our chemical intuition but is theoretically and practically true.

- The ability of the drainage in holding dissolved metal species (excluding Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and Pb\textsuperscript{2+} due to sulfate control) is greatly enhanced by decreases in pH. Between the approximate pH range 6-8, the drainage is able to carry metal ions in activities 1-2 orders of magnitude higher than the present levels. Below pH 6.0, the drainage's capability of holding dissolved metal ions is virtually unlimited as far as the mobilization of metal constituents from minerals is concerned.

- Above pH 8.0, there is probably some precipitation of Cu(OH)\textsubscript{2}, PbCO\textsubscript{3} and ZnCO\textsubscript{3} in the dump or drainage courses to reduce the levels of Cu\textsuperscript{2+}, Zn\textsuperscript{2+}, and Pb\textsuperscript{2+} in the ICM drainage.

- In acidic to approximately neutral pH values, the activities of Ca\textsuperscript{2+}, Mg\textsuperscript{2+} and Pb\textsuperscript{2+} are controlled by the formation of their sulfates, as the sulfate activity is generally quite high in the ICM drainage, although the activity of Pb\textsuperscript{2+} has never reached such a magnitude as to be precipitated as lead sulfate despite the high sulfate activities (see Section 5.3.2.7). In drainage streams such as EMO, when sulfate, calcium and magnesium are high, the sulfate control mechanism will operate to adjust their
activities (concentrations). Gypsum (or jarosite if iron concentration is high and pH is low) can precipitate within the dump or in the drainage ditches.

- Below pH 10, the activity controlling compounds are carbonates rather than hydroxides for most metals (excluding Cu$^{2+}$). To reduce effectively the activities (concentrations) of all metal ions in concern at ICM to satisfactory levels by the precipitation of hydroxides, the pH has to be raised above 11.

Having presented the principles of the mechanisms that affect the concentrations of various metals in a solution, we now use the element iron to exemplify how these principles operate interactively to determine its actual concentration in drainage streams. All the concerned metals should be examined in such a comprehensive way in order for their actual concentrations in the drainage to be explained by chemical principles. Otherwise, conclusions based on incomplete considerations may be erroneous and misleading.

Now assume redox reactions and simple ionic compound solubility control are the major mechanisms of controlling the activities of iron species in solution. Neglect the ion pairs Fe(OH)$^+$, Fe(OH)$_2^+$, Fe(OH)$_3^+$, and others (they can be shown to be in negligible concentrations), the iron species in solution are Fe$^{2+}$ and Fe$^{3+}$. The processes in determining the activities of ferrous and ferric ions in solution include:

1. The solubilization of iron from sulfides (essentially pyrite) by oxidation. This is a relatively slow, surface redox reaction. The reaction rate is determined by a variety of factors as discussed previously. The reaction is very thermodynamically favourable. There will be no equilibrium between the
sulfides and surface oxygenated water before all sulfides are completely oxidized, since sulfides are unstable at such conditions.

(2) The control of Fe$^{3+}$ activity by ferric hydroxide (Figure 33). The precipitation of ferric hydroxide is fast.

(3) The control of Fe$^{2+}$ by iron(II) carbonate below pH 10.2 (approximate) and ferrous hydroxide above pH 10.2 (Figure 38). These reactions are fast.

(4) The control of Fe$^{2+}$ by Fe(OH)$_3$ (Figure 24). The reaction is slow because of its redox nature.

(5) The equilibrium between Fe$^{2+}$ and Fe$^{3+}$, which is dependent of the Eh of the solution. The reaction rate is intermediate when abiotic and fast when biological.

(6) The control of both ferric and ferrous ions by hematite. This is ignored due to the slowness of the reactions.

The compounds formed in (3) (ferrous carbonate or hydroxide) are always only meta-stable with respect to ferric hydroxide, but they do form due to their fast reaction kinetics when conditions are appropriate. Now the activities of Fe$^{2+}$, Fe$^{3+}$ and total Fe are determined as follows. If the release of Fe (process (1)) is so slow that both Fe$^{2+}$ and Fe$^{3+}$ are under-saturated with respect to processes (2), (3) and (4) above (note the ferric/ferrous ratio is determined by the Eh of the solution), no iron will be removed from solution. The activity of total iron is solely determined by the rate of iron solubilization while the activities of ferrous and ferric ions are determined by the solution Eh. At pH 4.5 and Eh 0.6 V (approximate) which are typical for the EMO drainage, the above conditions are satisfied when the Fe$^{2+}$ activity is less than $10^{-7}$ and Fe$^{3+}$ activity is less than $10^{-10}$ (Figure 24). These
activities translate to concentrations 11 μg/l Fe²⁺ and 0.02 μg/l Fe³⁺. At pH 6 and Eh 0.5, the same calculation leads to 10^{10.1} Fe²⁺ in activity (0.009 μg/l in concentration) and 10^{14.3} Fe³⁺ in activity (0.000001 μg/l). These conditions are certainly unrealistic to fulfil, even in the EMO drainage (see Table 13), which is the most acidic of all the ICM drainage streams. The pH values of drainage have to be below 4.0 for the total iron concentration to be solely controlled by the oxidation of pyrite.

Next, if the release of iron is fast enough so that the iron activity in the solution is over-saturated with respect to processes (2) and (4) but not (3) above, we would expect the activity of Fe³⁺ to be roughly in equilibrium in solution with Fe(OH)₃ while Fe²⁺ is over-saturated to a certain degree with respect to Fe(OH)₃. At this time, Fe²⁺ will oxidize both to Fe(OH)₃ directly by oxygen and to Fe³⁺, which will be precipitated as Fe(OH)₃. At pH 4.5, the concentrations of iron species in solution should be: Fe³⁺ approximately 0.02 μg/l, Fe²⁺ 1.1 μg/l - 11 g/l. It is clear at this pH Fe²⁺ will not be over-saturated with respect to process (3). At pH 8.0, the concentration of Fe³⁺ should be virtually zero, and the concentration of Fe²⁺ should be below 450 μg/l.

Last, if the iron release by pyrite oxidation is fast and the pH of the drainage is high, the iron in solution may be over-saturated with respect to processes (2), (3) and (4). Note this over-saturation is impossible at low pH values. At pH 8.0, the over-saturation of Fe²⁺ with respect to carbonate occurs when the release of iron exceeds 450 μg/l. The ferrous ions will be removed as ferrous carbonate (total C activity is assumed at 10^{-3}).
Examination of the total Fe concentrations shows that all the ICM drainage streams are under-saturated relative to carbonate and ferrous hydroxide, but most are over-saturated with respect to Fe(OH)$_3$, even the most acidic EMO drainage. The aging of the ICM drainage, therefore, should bring the total iron activity towards that defined in Figure 24.

5.3.4 Other Processes

In accounting the acid-base balance and the contaminant balance, processes other than redox reactions and salt precipitation (both discussed above) are also involved. These include complexation, chelation, hydration, simple dissolution, hydrolysis, carbonation, ion exchange, adsorption-desorption, and co-precipitation. They are briefly discussed below.

Complexation, Chelation and Hydration

Complexation is the chemical association of a metal atom or ion with a ligand, both of which are capable of independent existence, through coordination covalent bonds to form new species (complexes). A coordination covalent bond is formed between a donor atom or ion, which has an unshared pair of electrons, and an acceptor atom or ion, which has unoccupied orbitals that can accommodate the electron pair. All metal ions have the ability to form complex ions. Those with small radius and high charge, especially those that also have vacant d orbitals - the transition metal ions - do so most readily. But even the sodium ion, with its comparatively large radius and its small charge, forms complexes. The difference lies in the stability.
Complexation is important in considering the contaminant levels of a natural water, because it can alter the total concentration of metals (which we measure in the laboratory chemical analysis) remarkably. If the complex formed is very soluble, the total concentration of the metal involved in the complex formation will be greatly increased. The complex is a new substance thus does not have to satisfy the solubility and redox requirements that the metal has to before complexation. For example, the formation of the complex \( [\text{Au(CN)}_2]^2- \) brings about the total dissolution of otherwise insoluble elemental gold. The complexation of \( \text{Zn}^{2+}, \text{Cu}^{2+} \) and \( \text{Al}^{3+} \) with \( \text{OH}^- \) tremendously increases the total concentration of these metals in alkaline conditions relative to near-neutral conditions. However, if the complex formed is highly insoluble, the total concentration of the metal involved in the complex formation may be controlled by the dissociation constant of the complex rather than by the solubility products of the relatively insoluble compounds of the metal.

Common inorganic ligands in nature are: \( \text{F}^-, \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{CN}^-, \text{NCS}^-, \text{NO}_2^-, \text{OH}^-, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{SO}_3^{2-}, \text{NH}_3, \text{H}_2\text{O}, \text{CO}, \text{NO} \). Many kinds of organic ligands exist which usually bond to metal atoms or ions through \( \text{N} \) atoms or \( \text{O} \) atoms.

If an organic ligand has several electron donor atoms which are simultaneously bound to a central metal species to form a complex, the ligand is then called a chelating agent, or a bi-, tri-, quadri-dentate according to the number of coordinating atoms in the ligand. The complex so formed contains organic rings around the central metal species. The chemical agent EDTA is an example of quadridentate. In nature, some plants and microorganisms are capable of excreting chelating agents, therefore the chelation process may be important.
in the destruction of some minerals by bringing the metal constituents into solution by chelation. At ICM, we believe chelation play an insignificant role in the overall metallic species (contaminants) balance.

Although water is a common ligand capable of complex formation, we rarely view the resulting species as complexes. The word "hydration" is used to refer to the association of chemical species (such as ions, molecules, or salts) with water. Hydration can take place through two mechanisms: that caused by the electrostatic attraction between charged species (such as Ca\(^{2+}\), Cu\(^{2+}\) and SO\(_4^{2-}\)) and the water dipoles, and that caused by the coordination covalent bonding between a metal species (such as Cu\(^{2+}\), Fe\(^{3+}\), etc.) and water molecules (as a ligand). The latter belongs to the category of complexation and is relatively stronger than the electrostatic hydration. In this regard, hydration and complexation are overlapping concepts. When metal ions are precipitated from solution, all or part of the coordinated water molecules will be retained and incorporated in the crystalline salts formed, depending on the abundance of free, unbounded water molecules in the solution from which the salts are precipitated. Such is the mechanism of the formation of ZnSO\(_4\).7H\(_2\)O, ZnSO\(_4\).6H\(_2\)O, CuSO\(_4\).5H\(_2\)O etc. The crystalline water molecules in these compounds can be gradually driven off by intensive heating, first the relatively weakly bound ones at a lower temperature, then the more strongly bound ones at a higher temperature. The great availability of free water molecules in dilute solutions (such as the ICM drainage) makes water the most competitive ligands to prevent the formation of complexes of metal ions with other ligands which are usually at much lower activities. The hydration of metal ions, either by electrostatic association or by complexing, usually does not alter the thermodynamic properties of the metal ions in solution, since it has been dealt
with in the formulation of activity coefficients and the equilibrium constants. Therefore, hydration does not comprise a concern in considering the metal species (contaminants) balance at the ICM drainage. There is another kind of hydration which involves the combination of water into the crystalline structure by anhydrous minerals formed in the absence of water. This process modifies the crystalline structure, but does not affect the solution chemistry.

Of the common ligands listed above, only Cl\(^-\), OH\(^-\), CO\(_3\)\(^-\), SO\(_4\)\(^-\), and H\(_2\)O are present in the ICM drainage in detectable concentrations. Of these, Cl\(^-\), CO\(_3\)\(^-\) and SO\(_4\)\(^-\) are weak ligands and act as significant complexing agents only when they are very concentrated, which is not the case in the ICM drainage. OH\(^-\) does not form complexes significantly with the metal ions of our interest below pH 9. H\(_2\)O has been discussed above. Therefore, complexation, hydration and chelation will not affect the consideration of metal species balance in the ICM drainage. However, these processes do play a role in chemical treatment plants of polluted water. The pH of the precipitation tanks may be high enough to solubilize Zn and Cu as complexes. Chelation may also increase the total concentrations of some metals. These factors should be taken into consideration in the design of the treatment plant if such an option is selected.

*Simple Dissolution, Hydrolysis and Carbonation*

Again, these are not mutually-exclusive, but rather overlapping concepts defined according to different criteria. Simple dissolution refers to the transfer of mineral constituents from the solid mineral phases to the solution as dissolved species without the involvement of
redox reactions. In congruent dissolution, all mineral constituents are transferred into dissolved species, such as the dissolution of rock salt (NaCl) and other brine minerals, of gypsum, calcite and dolomite, and of some magnesian minerals. Incongruent dissolution converts some of the mineral constituents into dissolved species while leaving others in a solid residual mineral, such as the dissolution of most aluminosilicates in nature. Hydrolysis refers to the process in which amphoteric species (usually an ion) from mineral dissolution combine with either $\text{H}^+$ or $\text{OH}^-$ to form a weakly dissociated species or a highly insoluble compound, resulting a shift in pH of the solution. The formation of $\text{Fe(OH)}_3$ from $\text{Fe}^{3+}$ and gibbsite $\text{Al(OH)}_3$ from the dissolution of aluminosilicates are examples of hydrolysis. Carbonation is actually a hydrolysis process involving carbonate species. It is used to refer to the weathering of calcium-, magnesium- and iron-bearing rocks by the formation of carbonate or bicarbonate salts of these metal elements, which are relatively soluble. Its use has largely been discontinued due to the ambiguity in its definition.

The importance of simple dissolution of minerals lies in the fact that most igneous silicate minerals weather by this mechanism. Our primary interests in silicate mineral weathering are how it affects the acid-base balance and the metal contaminant balance of the drainage. Most of the silicate dissolution processes are acid-consuming. In nature, silicate minerals are commonly weathered by the attack of dissolved carbon dioxide (or carbonic acid), which is universally available from the atmosphere and biological activities. The carbonic acid is converted to bicarbonate ions (at near-neutral conditions) or carbonate ions (at alkaline conditions) with the release of $\text{H}^+$ ions, which is necessary for the dissolution (often incongruent) of silicate minerals. It has been observed that the weathering of silicate minerals by dissolved carbon dioxide is a slow process and can be considered negligible in
contaminant release (if it were not, the majority of rivers and streams would have been polluted), and most probably also negligible in acid consumption, insomuch as acid mine drainage generation is concerned. However, theoretically the silicate weathering process should be accelerated by the lowering of pH as much more H⁺ and acidity becomes available. H⁺ penetrates the outer residual shell of silicates being weathered (as many researchers believe to be present) readily and diffuses to the fresh silicate surface rapidly due to its tiny size. At ICM where some streams (such as EMO) have low pH values, whether the silicate weathering has been accelerated to such a degree as to deserve considerations in the acid-base balance and the metal contaminant balance still remains to be investigated.

Ion Exchange

As the name states, this refers to the exchange of an ion in solution for an ion with the same type of charge in a solid (often crystalline) structure. Ion exchange is often driven by a concentration gradient across the solution-solid interface. In the weathering of rocks, we are primarily concerned about cation exchanges. Within the soil layer penetrated by plant roots, cation exchange is often an important mechanism to deliver mineral nutrients to plants for their growth. In the process, the H⁺ ions present in plant roots exchange for ions such as K⁺, Na⁺, Ca²⁺, etc. with the interstitial water, which may in turn exchange with surrounding clay minerals. If the exchange chain travels far enough to reach some clay minerals in contact with unweathered silicate minerals, exchange may take place between the two, thus accelerating the breakdown of the silicate minerals into clay minerals. The net result of ion-exchange between plant roots and silicate minerals is neither acid-
consuming or acid-generating, nor contaminant-releasing (although it does result in new mineral formation), thus is ignored in this thesis. The ion-exchange reactions between silicate minerals and fresh water is acid-consuming as the silicates absorbs $\text{H}^+$ from water to make the water alkaline. But this exchange only takes place in the initial stage when dry, fresh silicate minerals are brought into contact with water; it reaches saturation very quickly as silicate minerals are in continued contact with water through the weathering process. The net results brought about by this reaction is negligible in a long term.

*Adsorption, Desorption and Coprecipitation*

Adsorption is the attachment of dissolved species to the surfaces of solids, often colloids; desorption is the reverse process. They can be physical or chemical. Chemisorptions are actually surface chemical reactions while physical sorptions are mostly of electrostatic nature. In reality, these two are often indistinguishable. Coprecipitation occurs when a dissolved species is incorporated as a minor component in a solid phase as that phase itself is precipitated. Coprecipitation is often indistinguishable from adsorption thus sometimes is included by the word adsorption. In natural waters transition metals are strongly adsorbed by oxides and hydroxides (particularly of aluminum, iron and manganese). This adsorption is most pronounced when the oxides or hydroxides are finely divided, e.g., as colloids. It has been found that in some natural waters the adsorption of many transition metals by hydrous manganese and iron oxides exerts primary controls over the concentrations of these metals (Dreyer, 1982). As a general rule, the adsorption of transition metal ions on to oxides and hydroxides is most remarkable in alkaline conditions, decreases as pH drops, and disappears totally when pH is low enough. The transition from
high adsorption to non-adsorption occurs in a narrow pH range. This can be explained (at least partially) by two arguments: first, at higher pH (greater than the point of zero charge), oxides and hydroxides bear negative surface charges, which favour the adsorption of positively charged metal ions or metal complexes which are positively charged; second, transition metals usually do not adsorb as metal ions due to their large hydrated shells, but adsorb as metal-hydroxy complexes (such as Zn(OH)$^+$, Pb(OH)$^+$, etc.) which only form when pH is greater than a particular value for a particular metal and which do not possess a large hydrated shell. The pH characteristic of the transition from non-adsorption to high adsorption is often the pH at which the metal-hydroxy complex becomes predominant.

At ICM, the influence of the adsorption of transition metals by oxides and hydroxides is ignored, primarily because we do not have any information on the composition of the suspended solids and the colloidal portion of the drainage. We believe this will not introduce significant errors into our conclusions regarding the solution chemistry due to the following considerations:

- Some of the ICM drainage streams, such as EMO drainage which is our primary concern have low pH values (4.2-4.5 for EMO), which prohibits the adsorption.

- In the ICM drainage, the total suspended solids and perhaps colloids are relatively low while the total dissolved metal species relatively high (such as Mn, Zn, Cu, and Fe in EMO), so that even the solid surfaces are saturated with adsorption of these transition metals, the amount adsorbed would still account only a small portion of the total dissolved species. Therefore, if the total concentration of a metal is greatly in excess of the natural (baseline) level, the concentration of the metal can not have
been controlled by its adsorption on to any solids, despite that it may be heavily adsorbed.

- For those drainage streams whose pH values are high enough for the adsorption to occur, we would expect that only the one or two most competitive metals are adsorbed significantly, while others are relatively unaffected.

However, we can not rule out the possibility that the total concentrations of some metals are controlled by their adsorption on to solid surfaces, particularly those whose total concentrations are very small.

5.3.5 Bacterial Action

The involvement of bacteria in the generation of acid mine drainage has been reviewed in Section 2.1 of this thesis. The goal of the present section is to evaluation the degree of bacteria involvement in ICM drainage, with the emphasis being given to EMO drainage.

Let us first discuss the relationship of drainage pH and interstitial pH within the pore spaces in an acid-generating dump. The moisture retained in a dump between rain storms acidifies quickly and experiences a great dilution when the next rain storm comes. The interstitial pH within the dump should be lower than the drainage pH before the acidity is diluted. But the interstitial pH can not be predicted from the drainage pH by simply considering the dilution effect. For example, one can not conclude that the interstitial pH
is 2 units lower than that of the drainage purely based on a 100-fold dilution. Other factors have to be considered, such as the buffering capacity of various minerals. For example, Fe(OH)$_3$ starts to consume acid when pH reaches roughly 3.0, the interstitial pH at places where Fe(OH)$_3$ is present can not be much lower than 2.5 before Fe(OH)$_3$ is completely dissolved. Kleinmann found in laboratory experiments that interstitial pH values were typically 0.2-0.5 below the corresponding drainage pH (Kleinmann, Crerar and Pacelli, 1981). As to pH control, he also demonstrated that the drainage pH of a dump is controlled primarily by the role played by bacteria, presumably *Thiobacillus ferrooxidans*. He proposed the three-stage acidification model to characterize the acid generation from pyrite-containing materials and divided the three stages at pH 4.5 and 2.5, which were considered to correspond to major changes in the role of bacteria (see Section 2.1). Others have demonstrated the step-like control of drainage pH in the course of acidification of pyritic dumps which contain readily available neutralizing materials (SRK and Norecol, 1989). In addition, each rain storm disrupts the lowering of pH in pore spaces such that at the end of each rain event, the pH of the pore spaces which have been flushed will approach that of the drainage. It seems fair to say that the interstitial pH values are normally less than that of the drainage but the difference is small. The value of this statement is that we can use the pH of the drainage to represent that of the pore spaces without incurring a large error.

In Section 5.3.2, we assumed that the redox potential of natural waters is controlled primarily by the redox pairs H$_2$O/O$_2$ and H$_2$O$_2$/O$_2$. However, Kleinmann presented evidences to show that the Eh seems to be dominated by the Fe$^{2+}$/Fe(OH)$_3$ redox pair in many AMD environments (Kleinmann, Crerar and Pacelli, 1981). He also showed that increased
bacteria involvement in the acid production will cause the Eh of the system to rise, the pH to decrease and the total Fe concentration to increase.

The total dissolved iron and pH values in the EMO drainage all indicate that EMO is currently in stage II of the acidification process in view of Kleinmann's three stage model. Bacteria are involved in both the direct oxidation of pyrite and the oxidation of Fe\(^{2+}\) to Fe\(^{3+}\). The contributions of chemical oxidation and biochemical oxidation of pyrite are both significant in this stage. The steady state cycling of ferrous and ferric ions by bacterial oxidation of ferrous ions to ferric ions and pyrite reduction of ferric ions to ferrous ions has not been reached. In other words, the bacterial involvement in pyrite oxidation has not reached its maximum. If there is enough pyritic material available, the bacterial oxidation will increase and the pH will decrease, provided the acid consuming potential will be gradually exhausted. The onset of stage III is signalled by an enormous increase in total dissolved Fe (to hundreds to thousands of mg/l), by a high ferrous/ferric ratio (greater than 1), and by a pH lower than 2.5. In stage III, the abiotic oxidation of Fe\(^{2+}\) to Fe\(^{3+}\) ceases; the abiotic, direct oxidation of pyrite becomes insignificant; all the acidity is generated by the oxidation of pyrite (and other sulfides) by Fe\(^{3+}\), which itself is produced by bacteria from Fe\(^{2+}\).

5.3.6 Kinetic Considerations

It is unfortunate that general quantitative descriptions of the rate of pyrite oxidation, acid-neutralization and acid generation are so scarce, especially for real-field situations, given
the vital importance of such information in the planning of pollution control and abatement. The limited existing quantitative expressions are almost unexceptionally established in controlled laboratory conditions. Qualitatively, the rate of acid generation is considered to follow the curve outlined in Figure 39 (after SRK and Norecol, 1989). The controlling factors of acid generation rate include sulfide content, presence of neutralizing materials, bacterial activity, availability of oxygen and water, pH, passage of time and other less important ones such as climate and surface vegetation. Some of the above factors are interactive with the rate of oxidation, such as pH and bacterial activity. The maximum oxidation rate is achieved when the steady-state cycling of ferrous and ferric ions by bacterial oxidation and pyrite reduction is reached.

Prediction of future acidity and metal release requires a set of kinetic tests to start with. Such information is not available in this study. The calculation in Appendix II is based on the assumption that the current rate of acidity release will continue in the future. In reality, the release rate is likely to increase in both EMO and the Caps due to the availability of acid producing materials and all the necessary ingredients of pyrite oxidation, if these dumps are not treated one way or another. Therefore, the duration of acid generation is probably shorter than that calculated in Appendix II, while the acidity and metal load in the drainage will be greater than the present level.

It took from five to ten years at ICM for various acid-generating dump areas to go acid or show indications of acid generation in the drainage (metal level elevation). EMO was the most acidic dump and was built in 1981. It was found generating acid in 1986. The Old North Dump was deposited in early 70s and showed no indication of acid generation until
Figure 39  Schematic Diagram Showing the Rate of Acid Production over Time
(After SRK and Norecol, 1989)
mid 80s. The initial period is necessary because oxidation is slowest at the very beginning because of low pH and little bacteria involvement; because the pH decrease and the acidity buildup is often disrupted by rainstorms; and the most reactive acid-consuming materials are available at the initial stage. The length of initial acidification stage depends on many variables such as S content, the content and nature of acid-consuming materials, dump porosity, total surface area of reactive sulfides, etc. After the initial acidification, acid generation will be accelerated due to lowering of pH and increased bacteria involvement.

5.3.7 Underwater Disposal Considerations

If the finished pit is to be flooded either with fresh water or with sea water, underwater disposal of reactive wastes or polluted drainage is among the potential options of acid mine drainage abatement at ICM.

Acid mine drainage abatement measures must be based on the fact that in the North Dump problematic areas are isolated and account for only a small portion of the entire North Dump. The majority of the North Dump only gives rise to mild AMD problems. Underwater disposal options may include the removal of the reactive acid-generating waste materials from the North Dump and their placement in the pit bottom before flooding the pit, or the collection of polluted drainage followed by its introduction into the pit bottom after the pit is flooded.
The first option above may be enhanced by the placement of a layer of crushed limestone on the top of the reactive wastes. The purpose of this limestone layer is to trap the metal pollutants in the bottom before they are stabilized by reduction to sulfides, or carbonates, or oxides in the initial stage of flooding. This option is most effective in preventing further acid and pollutant production but is costly.

The purpose of the second option above is to retain the pollutants and the acidity in the drainage in the flooded pit bottom. The pit bottom is generally expected to be anaerobic and reducing. The acidity input from the drainage will not make the pit bottom acidic because of its relatively small quantity compared to the pit and will be gradually consumed, for example, by the reduction of sulfate by decomposing organic debris below the sulfate/sulfide boundary but above the carbon dioxide/methane boundary, or by the reduction of some dissolved metal ions (such as $\text{Fe}^{2+}$ and $\text{Cu}^{2+}$) to their sulfides (pyrite and chalcocite) which are acid-consuming reactions.

There are a few methods of flooding the pit after the mine's closure. They are:

1) Turn the pit into a fresh water lake closed from the sea by natural drainage water accumulation, or more quickly by pumping water from fresh water sources such as Marble river or Francis Lake.

2) Turn the pit into a salt lake closed from the sea by first introducing sea water from Rupert Inlet by a channel then disconnecting the channel.

3) Turn the pit into a salt lake open to the sea by a connecting channel.

4) Turn the pit into a salt lake semi-closed to the sea by a controlled connecting channel.
Water balance has to be studied to prevent the lake from overflowing or drying up in 1) and 2) above. The surface fresh water drainage courses around the pit area should then be altered accordingly. The conditions at the flooded pit bottom depends primarily on the circulation patterns of water and biological activity (supply of organic matters to the lake bottom). Generally, the lake bottom will be anoxic and reducing in 1) and 2) above, perhaps in 3) and 4).

The underwater disposal of reactive wastes is not greatly influenced by the choice of flooding methods since its purpose is to seal the acid generating materials from oxygen. For the polluted drainage to be disposed of in the flooded pit bottom, the pit bottom should be anaerobic and reducing, preferably with a relatively high pH (>9) so that the acidity input from the drainage will be neutralized instantly and the dissolved metals will be removed immediately as carbonates or hydroxides (Figure 38), which later will be reduced to various sulfides or carbonates or oxides. It may be beneficial to reduce the total amount of polluted drainage to be put in the pit bottom by diverting the unpolluted water such as that to the north east of the North Dump within the End Creek watershed away from the North Dump area. Another consideration in this option is the difference in the densities of the pit bottom water and the incoming drainage water. This difference should be reduced to such an extent that the incoming drainage water will not trigger an upward density current to spread the polluted water throughout the entire water body. This problem may be solved by mixing the drainage water with the pit bottom water (or other water of similar density) prior to the placement of the drainage water in the pit bottom. If the pit is going to be filled with fresh water, the density problem is less marked.
The introduction of acidic, polluted drainage into the pit bottom can be realized by using a corrosion-resistant pipeline, or by constructing a tunnel connecting the pit bottom and a surface drainage discharge point. There is still much to be investigated if this option is chosen.
6.0 CONCLUSIONS

1. A typical, contaminated ICM drainage in resemblance to EMO has a pH of 4.5, a total ionic strength of 0.0426 and a few species in concentrations much higher than natural levels. The activity coefficients depart markedly from unity for all the species in consideration, thus have to be taken into consideration when examining the solution chemistry of the drainage.

2. Metal solubilization is caused by the oxidation of sulfides and less importantly the dissolution of silicate minerals. The rate of metal release depends on many factors including sulfur content, surface area to mass ratio of reactive sulfides, bacterial activity, frequency and amount of rain, Eh-pH conditions, surface vegetation, temperature, etc.

3. The important processes in determining the levels of dissolved species in ICM drainage include rates of mineral constituent release and removal of dissolved species by precipitation of highly insoluble compounds, as well as the amount of precipitation. The removal of dissolved species by adsorption is not considered. The most important insoluble compounds in the ICM drainage environment are carbonates, hydroxides, and sulfates.
4. The typical drainage is under-saturated with respect to most of the metal species considered, usually by more than one order of magnitude. This implies that for these metal species, chemical equilibrium with their most insoluble compounds is not a limiting factor of their levels. They can be virtually as high as their release rate can afford. It is over-saturated, however, with respect to Cu in some streams, and is in approximate equilibrium with Pb and Zn in other streams. This means the equilibrium chemistry will set an upper limit for the levels of these metals.

5. Levels of dissolved species can often be up to 2 orders of magnitude higher than is dictated by the equilibrium with their most insoluble species, as has been demonstrated in this study.

6. The removal of metal contaminants by formation of carbonates and hydroxides usually does not happen below pH 8. In acidic conditions, Pb and Ca may be removed from solution by the precipitation of their sulfates when sulfate concentration is high; all other metals are highly soluble. Above pH 8 and below pH 10, most metals are removed as carbonates when they are concentrate enough, except Cu$^{2+}$ and Fe$^{3+}$, which are removed as hydroxides in this range. Increased total carbon activity will assist this carbonate removal process to function more efficiently and at a lower pH. Therefore, growth of surface vegetation helps the removal of metal contaminants by increasing the total carbon activity. Above pH 10, most metals will be removed as hydroxides, but such a pH is not likely to occur in the dump or drainage.
7. There is no barrier to sulfide oxidation at present. Oxygen and water, the two major reactants for sulfide oxidation can enter the dump almost freely.

8. *Thiobacillus ferrooxidans* are believed to have been involved significantly in the sulfide oxidation process in EMO. The steady-state Fe$^{2+}$/Fe$^{3+}$ cycling, which is the most advanced stage of bacterial involvement in pyrite oxidation, has not been reached in EMO.

9. The Caps are weakly acid-generating, very porous, and contain no glacial till. They are however underlain by a layer of glacial till-rich layer of older North Dump, which helps neutralize the acidity in the drainage that leaves the Caps mostly from underneath. The Caps have a thermodynamic potential to generate acid for 650 years. The current acid release rate is 730 tonnes H$_2$SO$_4$/year, of which 87% is neutralized within the dump by 640 tonnes CaCO$_3$ equivalent/year acid-consuming materials. The APP and the ACP are consumed at a proportional rate so that the acid-consuming material will last almost the entire acid-generating life of the dump.

10. EMO is very acid-generating and contains virtually no glacial till. It is not underlain by a cushion of till-rich, acid-consuming layer, as is other areas in the North Dump. Therefore it is the most problematic area in the North Dump. Its oxidation will continue for 600 years at the current rate. The current rate of acid release is 370 tonnes H$_2$SO$_4$/year, of which 80% is being neutralized within the dump by 300 tonnes CaCO$_3$ equivalent/year acid consuming materials. The ACP is being
used up faster than the APP so that after 300 years the ACP within the dump will be exhausted. The pH could drop dramatically after that time.

11. The Old North Dump area, especially the Old Marginal Dump is related to the high loads of Pb and Mo in NDD. This indicates that active oxidation is undergoing in some locations, which mobilizes the metal contaminants; but the acidity is neutralized before the seepage reaches NDD.

12. Other areas of the North Dump are less problematic than the ones discussed above because the dump materials are a mixture of rock and glacial till, which is underlain by a till-rich layer.

13. Without some kind of abatement measures, the North Dump will produce approximately 3,500,000 cubic meters of contaminated drainage per year which will not meet the provincial objectives with respect to some heavy metals. By diverting EDL drainage and TCR drainage which are very slightly polluted, the contaminated drainage can be reduced to 2,600,000 cubic meters per year.

14. As acid generation proceeds and pH drops in the future, the concentrations of Zn, Mn, Cu, and perhaps Cd (all of which are much more soluble in acidic conditions) in the ICM drainage could increase dramatically, since the only control over these concentrations when pH is below 4.5 are the oxidation rate, which will accelerates in the future. The concentration of Fe will only increase remarkably when pH is less than 3.0. The levels of As, Mo, and Pb will not be elevated significantly relative to
the present levels since their concentrations are limited by their low content in the ICM waste rocks. Therefore they do not constitute concerns in environmental pollution in the ICM drainage. The only exception may be Mo and Pb in the Old Marginal Dump, which probably contains much more of these metals than the waste rocks. The concentrations of Ca, Mg, Pb, and \( \text{SO}_4^- \) are mutually-limiting by the corresponding solubility products of their sulfates, which do not change with pH.

15. At ICM, the initial acidification of potential acid producing materials took from five to ten years. After the initial acidification, the acid generation process will accelerate. The Caps were deposited on the North Dump in 1985. According to the length of acidification demonstrated at ICM (5-10 years) and taking into consideration of the fact that the Caps is weakly acid-generating, highly porous, and contains no till, we expect that the Caps will start to generate acid around 1992. The direct indication of this happening will be the elevation of dissolved metals in NDS and TCR.

16. Effective abatement measures must be applied to the EMO area, the Caps area and the Old North Dump area to avoid further drainage quality deterioration and to satisfy the environmental standards for drainage quality. The rest of the North Dump can be treated with less stringent abatement measures. Surface drainage courses should be altered to reduce the unnecessary water intake by the North Dump.
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I. Calculation of the Pathway of an Enclosed Area

In this appendix, significant digits in all figures are underlined. Insignificant digits are included here to reduce intermediate round-off errors. When actually reporting the figures, one should only quote the underlined digits, after rounding off the first non-underlined digit, as the significant figures.

An area which is believed to be a self-contained watershed is chosen on the map. This area is located to the north east of the pit, and the boundary of this area is defined by End Creek water shed boundary on the north, the west and the east, by the End Creek/Trey Creek water shed boundary on the south, and by the Ten Eighty Ditch (TED) on the south west. The area of this region is 1,767,424 m$^2$ (19,024,400 square feet). In the production year 1988, i.e., from September 27, 1987 to September 24, 1988,

\[
\text{Total Mine Site Precipitation} = 2042.2 \text{ (mm)}
\]

\[
\text{Total Volume of Rain and Snow Water Falling on the Area} = 2.0422 \times 1,767,424 = 3,609,433 \text{ (m}^3\text{)}
\]

Assume 21.7% evaporation,

\[
\text{Total Evaporation} = 3,609,433 \text{ m}^3 \times 21.7% = 783,247 \text{ m}^3
\]

\[
\text{Total Volume of Water Running off or Percolating into the Dump within the Enclosed Area} = 3,609,433 - 783,247 = 2,826,186 \text{ m}^3
\]

\[
\text{Total TED Flow in this Period} = 2,598,090 \text{ m}^3
\]

Since TED flow data is not available for September, 1987 - September, 1988, the data for November, 1987 - November, 1988 was used above. This was the only available data of this kind. Of the total TED flow, 15% comes from NDD,

\[
\text{Flow from NDD} = 2,598,090 \times 0.15 = 389,714 \text{ m}^3
\]

Therefore,

\[
\text{Total Volume of Runoff and Seepage from the Enclosed Area} = 2,598,090 \times 0.85 = 2,208,377 \text{ m}^3
\]
The Volume of Water that Goes into the Ground Water System
\[= 2,826,186 - 2,208,377 \]
\[= 617,548 \text{ m}^3\]

II. Calculation of the Pathway of the Rain Water Falling on EMO

The technique used in this calculation is more or less the same as that employed in the above calculation. The basic assumption in this calculation is: All the rain water falling directly on the EMO area either evaporates or infiltrates or runs off. The runoff, if any, reports to the EMO ditch. Furthermore, the part that infiltrates either goes to recharge the aquifer or seeps into the EMO ditch.

From September 27, 1987 to September 24, 1988,

Mine Site Precipitation = 2042.2 mm

Total Area of EMO = 152,320 m²

Annual Total Volume of Rain Water Falling on EMO = \(152,320 \times 2.0422\) = 311,150 m³

Adopt an evaporation rate of 21.7% (from previous calculation),

Rain Water Evaporated = 311,150 \times 21.7\% \]
\[= 67,520 \text{ m}^3\]

Rain Water Infiltration into and Runoff from EMO = 311,150 - 67,520
\[= 243,630 \text{ m}^3\]

Total Volume of Drainage from EMO into EMO ditch = 221,050 m³

The last figure above is for the period November 20, 1987 - November 19, 1988, thus a time offset exists between this figure and other figures we use in this calculation. We had to use this figure in the calculation because this was the only available complete year drainage volume. An error is introduced in doing so. However, if the total precipitation and the pattern of precipitation are similar in 1987 and 1988 for the months October and November, this error will be small. The precipitation record in 1988 was not yet available at the time of the calculation. Therefore,

Rain Water that Goes into Ground Water Aquifer = 234,630 - 221,050
\[= 22,580 \text{ m}^3\]

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In this appendix, significant digits in all figures are underlined. Insignificant digits are included here to reduce intermediate round-off errors. When actually reporting the figures, one should only quote the underlined digits, after rounding off the first non-underlined digit, as the significant figures.

I. Eastern Most Outslope

Area of Upper EMO = 340,000 ft$^2$

Area of Lower EMO = 1,300,000 ft$^2$

Total Area of EMO = 1,640,000 ft$^2$ = 152,361 m$^2$ = 15.24 Ha.

Average Depth of Upper EMO = 40.0 ft

Average Depth of Lower EMO = 58.3 ft

Volume of Upper EMO = 340,000 ft$^2 \times 40.0$ ft = 13,600,000 ft$^3$

Volume of Lower EMO = 1,300,000 ft$^2 \times 58.3$ ft = 75,790,000 ft$^3$

Total Volume of EMO = 13,600,000 ft$^3 + 75,790,000$ ft$^3$ = 89,390,000 ft$^3$ = 2,531,239 m$^3$

If we use the average bulk density of the entire North Dump, 1,965 kg/m$^3$, we obtain

Mass of Waste Material in EMO, Calculated from Volume and Average Bulk Density = 2,531,239 m$^3 \times 1.965$ tonne/m$^3$ = 4,973,846 tonnes

Mass of Material in EMO from Haulage Records = 5,147,577 tons x 0.9071847 tonne/ton = 4,669,803 tonnes

Relative Error of the Two Tonnages Obtained Above = (5,482,727 - 5,147,577) / [(5,482,727 + 5,147,577) / 2] = 6.306%
This error is presumably due to the error in the assumption of the average bulk density. Of course, we will adopt the tonnage from the Haulage Records for the following calculations.

Average Acid Production Potential (APP)  
\[ = 51.15 \text{ kg H}_2\text{SO}_4 /\text{tonne} \]

Average Acid-Consuming Potential (ACP)  
\[ = 18.67 \text{ kg H}_2\text{SO}_4 /\text{tonne} \]

Precipitation at the Mine Site from September 27, 1987 - September 24, 1988  
\[ = 2042.2 \text{ mm} \]

Annual Volume of Rain Falling on EMO  
\[ = 152,361 \text{ m}^2 \times 2.0422 \text{ m} \]  
\[ = 311,152 \text{ m}^3 \]

At 21.7% evaporation rate, 78.3% will percolate (and slightly run off) EMO.

Total Percolation and Runoff  
\[ = 311,152 \text{ m}^3 \times 78.3% \]  
\[ = 243,632 \text{ m}^3 \]

Average Sulfate Concentration in EMO Drainage in 1988  
\[ = 1500 \text{ mg SO}_4^{2-} /\text{l} \]  
\[ = 1.50 \text{ kg SO}_4^{2-} /\text{m}^3 \]

Sulfate Released in 1988  
\[ = 1.50 \text{ kg SO}_4^{2-} /\text{m}^3 \times 243,632 \text{ m}^3 \]  
\[ = 365,448 \text{ kg SO}_4^{2-} \]  
\[ = 365.4 \text{ tonnes SO}_4^{2-} \]

Assume that all sulfate comes from the oxidation of sulfides and that sulfate removal from drainage by precipitation and other mechanisms is negligible. The above sulfate release can be converted into

Sulfuric Acid Leached out from Sulfides in 1988  
\[ = 365,448 \text{ kg SO}_4^{2-} \times (98.0 \text{ kgH}_2\text{SO}_4 / 96.0 \text{ kgSO}_4^{2-}) \]  
\[ = 373,062 \text{ kg H}_2\text{SO}_4 \]  
\[ = 373.1 \text{ tonnes H}_2\text{SO}_4 \]

Total Potential Tonnage of Sulfuric Acid Contained in EMO  
\[ = 4,669,803 \text{ tonnes} \times 51.15 \text{ kg H}_2\text{SO}_4 /\text{tonne} \]  
\[ = 238,860,424 \text{ kg H}_2\text{SO}_4 \]  
\[ = 238,860 \text{ tonnes H}_2\text{SO}_4 \]

If EMO continues to release sulfuric acid at the present rate (373.1 tonnes of H$_2$SO$_4$ per year),
Number of Years Needed for EMO to Release All the Sulfuric Acid Contained in Sulfides

\[
= \frac{238,860 \text{ tonnes } \text{H}_2\text{SO}_4}{(373 \text{ tonnes } \text{H}_2\text{SO}_4/\text{year})} \]

\[
= 640.4 \text{ years}
\]

In 1988, the Average Acidity of the Drainage from EMO

\[
= 300 \text{ mg CaCO}_3 \text{ equiv./l} \]

\[
= 0.300 \text{ kg CaCO}_3 \text{ equiv./m}^3
\]

Total Annual Acidity Released in 1988

\[
= 243,632 \text{ m}^3 \times 0.300 \text{ kg CaCO}_3 \text{ equiv./m}^3 \]

\[
= 73,090 \text{ kg CaCO}_3 \text{ equiv.} \]

\[
= 73.09 \text{ tonnes CaCO}_3 \text{ equiv.}
\]

If we assume the acidity in EMO is all from sulfuric acid,

Acidity Consumed by Acid-Consuming Material in EMO in 1988

\[
= 373.1 \text{ tonnes} - 73.09 \text{ tonnes} \]

\[
= 300.0 \text{ tonnes}
\]

(Note: 1.00 tonne \text{H}_2\text{SO}_4 = 1.00 \text{ tonne CaCO}_3 \text{ equiv.})

Percentage of Acidity Consumed by EMO Material in Total Acidity Released by Sulfides

\[
= \frac{300.0 \text{ tonnes}}{373.1 \text{ tonnes}} \times 100\% \]

\[
= 80.41\%
\]

Average Acid Consuming Potential of EMO

\[
= 18.67 \text{ kg CaCO}_3 \text{ equiv./tonne}
\]

Total Acid Consuming Capability Contained in EMO

\[
= 18.67 \text{ kg CaCO}_3 \text{ equiv./tonne} \times 4,669,803 \text{ tonnes} \]

\[
= 87,185,222 \text{ kg CaCO}_3 \text{ equiv.} \]

\[
= 87,185 \text{ tonnes CaCO}_3 \text{ equiv.}
\]

If the acid consuming capability of EMO continues to be consumed at the current rate of 300.0 tonnes \text{CaCO}_3 \text{ equiv.} per year,

Number of Years Needed before the Acid Consuming Capability of EMO Is Depleted

\[
= \frac{87,185 \text{ tonnes CaCO}_3 \text{ equiv.}}{(300.0 \text{ tonnes CaCO}_3 \text{ equiv./year})} \]

\[
= 290.6 \text{ years}
\]

After 291 years, because the acid consuming capability of EMO will have been depleted, all 373 tonnes of \text{H}_2\text{SO}_4 will appear in the EMO drainage for the remaining 349 years. This is equivalent to

Concentration of \text{H}_2\text{SO}_4 \text{ in the Drainage Emanating from EMO
= 373.1 tonnes H$_2$SO$_4$ / 243,632 m$^3$ drainage
= 373,000,000 g / 243,632,000 l
= 1.531 g/l

Since the molar mass of H$_2$SO$_4$ is 98.0 g/mol,

Molar Concentration of H$_2$SO$_4$ in the Drainage
= (1.531 g/l) / (98.0 g/mol)
= 0.01562 mol/l

Molar Concentration of H$^+$ in the Drainage
= (0.01562 mol H$_2$SO$_4$/l) x (2 mol H$^+$/mol H$_2$SO$_4$)
= 0.03124 mol H$^+$/l

Therefore,

pH of the Drainage
= -log(0.3124)
= 1.505

Of course this is an idealized calculation and the pH 1.51 should be regarded as a lower limit.

II. The Caps

Total Area of Caps
= 4,318,943 ft$^2$
= 401,243 m$^2$
= 40.124 Ha.

Total Tonnage of Caps
= 10,051,791 tons
= 9,118,831 tonnes

Average APP of the Caps
= 52.29 kg H$_2$SO$_4$/tonne

Average ACP of the Caps
= 43.51 kg CaCO$_3$/tonne

Annual Precipitation from September 27, 1987 - September 24, 1988
= 2042.2 mm

Annual Total Volume of Rain Water Falling on Caps
= 401,243 x 2.0422
= 819,418 m$^3$

At an evaporation rate of 21.7%, 78.3% of total rain water will percolate or run off the Caps.

Rain Water Infiltration into and Runoff from the Caps
= 819,418 m$^3$ x 78.3%
= 641,604 m$^3$

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Assume that the sulfate load in the drainage along the Old Trey Creek (TCR) represents that in the seeps form the Caps. (The Caps are underlain by a thick layer of porous older dump material thus there is no stream emanating exclusively from the Caps). The annual mean of sulfate in TCR is 1120 mg SO$_4^-$ /l.

Sulfate Concentration in Drainage Seeping from the Caps

$= 1120 \text{ mg SO}_4^- / l$

This translates to

Sulfuric Acid Released by the Caps

$= 1120 \times (98.0/96.0)$

$= 1143 \text{ mg H}_2\text{SO}_4 / l$

$= 1.143 \text{ kg H}_2\text{SO}_4 / m^3$

Total Sulfuric Acid Contained in the Caps

$= 52.29 \text{ kg H}_2\text{SO}_4 / \text{tonne x 9,118,831 tonnes}$

$= 476,824 \text{ tonnes H}_2\text{SO}_4$

Annual Release of H$_2$SO$_4$ from the Caps

$= 1.143 \text{ kg H}_2\text{SO}_4 / m^3 \times 641,604 \text{ m}^3/\text{year}$

$= 733.4 \text{ tonnes H}_2\text{SO}_4/\text{year}$

Number of Years for the Acid Producing Capability to be Exhausted

$= \frac{(476,824 \text{ tonnes H}_2\text{SO}_4)/}{(733.4 \text{ tonnes H}_2\text{SO}_4/\text{year})}$

$= 650.2 \text{ years}$

Before appearing as seeps along the Old Trey Creek water course, the drainage from the Caps has already been neutralized by the underlying layer composed largely of till which has a relatively large acid consuming potential. The tills are effective in neutralizing acids because of their fine particle size. We could use the Old Trey Creek sulfate load to represent that of the Caps because the sulfate released by the Caps is not removed by its flowing through the till-rich layer (or the removal is negligible). This is not the case with acidity. All the acidity contained in the drainage immediately beneath the Caps is lost en route before its reporting to TCR ditch. We have no information on the acidity of the water draining the Caps, therefore can not make a justifiable assessment as to how many years are needed before the acid consuming capability of the Caps is depleted.

Nevertheless, if we were to make such an assessment regardless of what has been mentioned above, we can use the acidity in EMO, which is 300 mg CaCO$_3$ equiv./l, as a guide. The APP of EMO is 51.15 kg/tonne and that of the Caps 52.29 kg/tonne. The concentration of sulfate in EMO ditch is 1500 mg/l and that from the Caps 1120 mg/l. We observe from these that roughly equal APP resulted in roughly equal sulfate release. Now that the ACP of EMO is 18.67 kg/tonne and that of the Caps 43.51 kg/tonne, it is almost certain that the acidity in the Caps drainage will be less than that in EMO drainage. For
calculation purpose, we will assume arbitrarily that the acidity in the Caps drainage is half of that in EMO, namely 150 mg/l.

Acidity in the Caps Drainage = 150 mg CaCO₃ equiv./l
= 0.150 kg/m³

Total Acidity Released to the Caps Drainage
= 0.150 kg/m³ x 641,604 m³/year
= 96.24 tonnes/year

By the same reasoning as in EMO calculation,

Acid Consumed by Acid Consuming Material in the Caps
= 733.4 tonnes/year - 96.24 tonnes/year
= 637.2 tonnes/year

which is numerically equal to the consumption of acid-consuming material.

Percentage Acidity Consumed
= 637.2/733.4
= 86.88 %

Total Acid-Consuming Capability of the Caps
= 43.51 kg/tonne x 9,118,831 tonnes
= 396,760 tonnes CaCO₃ equiv.

Number of Years Needed before Acid Consuming Capability in the Caps is Exhausted
= 396,760/637.2
= 622.7 years

This is to say, the acid-consuming material will last almost as long as the acid-producing material does. If this were true, the drainage from the Caps would carry only a small acidity through its acid-generating life, and its pH will not lower considerably. Meanwhile, after the journey within the till-rich cushion layer, the drainage will hardly contain any acidity or perhaps contain some alkalinity, the only effect down stream would be elevated levels of sulfate and relatively soluble metals, such as Mn and Zn, much like the water quality exemplified by today's TCR drainage.

However, this is only a very rough estimate and one has to bear in mind the assumptions we have made in the calculation when applying these figures. It will be very beneficial to this calculation if an analysis of sulfate and total acidity could be performed on the seeps directly draining the Caps, so that this calculation can be updated with real parameters of the Caps drainage.