EVALUATION OF STATIC AND KINETIC PREDICTION TEST DATA AND COMPARISON WITH FIELD MONITORING DATA

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EVALUATION OF STATIC AND KINETIC PREDICTION TEST

DATA AND

COMPARISON WITH FIELD MONITORING DATA

by

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ABSTRACT

The Database for Acid Rock Drainage (DBARD) and a detailed study of the tailings impoundment at Gibraltar - McLeese Operations, British Columbia have provided the basis for this study evaluating the ability of Acid Rock Drainage (ARD) prediction data to indicate on-site water quality.

Analysis of the database has shown that sites with similar geologic or geographic settings cannot be compared directly, although experience from previous work at other sites can aid new sites in developing waste characterization programs. The static prediction data is dependent on geochemistry of the sample and the prediction method and procedure. Improved methods of data interpretation can account for these factors. Identification of "indicator" elements can be used to calculate acid generating and neutralization potentials from site specific correlations and be included in kinetic tests and on-site monitoring programs to characterize oxidation and dissolution reactions. The water quality and oxidation/neutralization rates for the DBARD kinetic tests are not predicted by the static test data due to the short time frame of the tests, the time lag to ARD and/or the inaccurate values of the static test data. Kinetic tests need to be initiated as early as possible to allow stable conditions to be established and the maximum amount of time for leaching. Various methods proposed to calculate neutralization depletion rates were shown to provide similar rates. With longer term kinetic tests, the assumption that calculated oxidation/neutralization rates can be extrapolated into the future needs to be verified through additional test work.

Interpretation of the Gibraltar static prediction data for the tailings inferred a potential for ARD. This potential is indicated after approximately 3 years of kinetic testwork with increasing oxidation/neutralization reaction rates, although the pH is neutral. Oxidation and neutralization reactions are also occurring on-site, although water quality is predominantly affected by the chemistry and infiltration/migration of the tailings pond supernatant. Water quality changes during supernatant migration are attributed to physical processes, chemical reactions and/or mixing of waters with different compositions. These factors all contribute to the ultimate water

quality on-site suggesting that extrapolation of laboratory data is more qualitative than quantitative.

Recommendations for analyses, data manipulation, criteria for interpretation, and reporting of ARD prediction data have been made for the different stages of waste characterization: 1) mineralogical characterization, 2) static testing, and 3) kinetic testing.

SOMMAIRE

La base de données sur le drainage rocheux acide (DBARD) et les résultats d'une étude détaillée sur le parc à résidus du site McLeese de la société Gibraltar en Colombie-Britannique ont servi de base à la présente étude visant à évaluer dans quelle mesure les données de prévision sur le drainage rocheux acide (DRA) peuvent indiquer la qualité de l'eau *in situ*.

L'analyse de la base de données a montré qu'on ne peut pas comparer directement des sites dont le cadre géologique ou géographique est semblable, même si l'expérience acquise par des travaux antérieurs à d'autres sites peut faciliter l'élaboration de programmes de caractérisation des déchets à de nouveaux sites. Les données de prévision statiques reposent sur la géochimie de l'échantillon ainsi que sur la méthode et la procédure de prévision. Les méthodes améliorées d'interprétation des données peuvent tenir compte de ces facteurs. Des éléments * indicateurs + peuvent servir à calculer les potentiels d'acidification et de neutralisation à partir de corrélations propres à chaque site et être utilisés dans des essais cinétiques et dans les programmes de suivi *in situ* pour caractériser les réactions d'oxydation et de dissolution. La qualité de l'eau et les vitesses d'oxydation/neutralisation aux fins des essais cinétiques de DBARD ne sont pas prévues par les données d'essais statiques étant donné la courte durée des essais, le décalage temporel du DRA et(ou) les valeurs inexactes des données d'essais statiques. Des essais cinétiques devront être entrepris dès que possible pour établir des conditions stables et pour laisser au lessivage le temps maximal pour se réaliser. Diverses méthodes proposées pour calculer les taux de diminution de la neutralisation ont donné des taux semblables. Si on allonge la durée des essais cinétiques, l'hypothèse selon laquelle les taux d'oxydation/neutralisation peuvent être extrapolés dans l'avenir devra être vérifiée par des essais additionnels.

L'interprétation des données de prévision statiques de Gibraltar s'appliquant aux résidus indique un potentiel de drainage rocheux acide. Ce potentiel apparaît après trois ans environ d'essais cinétiques au cours desquels les taux de réaction de l'oxydation/neutralisation ont augmenté, même si le pH est neutre. Les réactions d'oxydation et de neutralisation se reproduisent sur les sites, mais la qualité de l'eau est principalement affectée par la composition chimique et l'infiltration/migration des surnageants du parc à résidus. Les changements de la qualité de l'eau durant la migration des surnageants sont attribués à des processus physiques, des réactions chimiques et(ou) au mélange

d'eaux de composition différente. Ces facteurs contribuent tous à la qualité ultime de l'eau *in situ,* ce qui porte à conclure que l'extrapolation des données de laboratoire est plus qualitative que quantitative.

Des recommandations ont été formulées pour les analyses, la manipulation des données, les critères d'interprétation et la présentation des données de prévision du DRA et ce, à différentes étapes de la caractérisation des déchets : 1) caractérisation minéralogique, 2) essais statiques, et 3) essais cinétiques.

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1.0   INTRODUCTION

Acid Rock Drainage (ARD) remains a major obstacle for environmental protection and reclamation at mine sites.   To protect the environment and satisfy regulatory requirements, exploration and mining companies are required to conduct laboratory and on-site investigations, during all stages of a mine operation from exploration to closure, that include: 1) waste characterization, to assess ARD potential by static and kinetic prediction techniques and 2) baseline and on-going environmental studies, including water quality monitoring.   These data allow owners/operators of new and existing mines to complete waste management plans to prevent the generation of ARD and the migration of contaminated runoff during operation and after closure.

The generation of ARD is the net result of two types of reactions broadly referred to as acid generating (sulphide oxidation) and acid neutralizing (mineral dissolution).   ARD is primarily a function of the mineralogy of the material and the availability of water and oxygen. At mining operations sulphide minerals in waste material, such as waste rock and tailings, and in mine structures, such as pits and underground workings, can be exposed to air and water leading to the generation of ARD.   There are many factors that affect the potential for ARD, and since these vary from site to site, predicting ARD can be difficult, costly and of uncertain reliability. The issue of long-term, or perpetual, care at historic mines and at some active mines has focused attention on the need to improve prediction methods for an assessment of the ARD potential during the early stages of mine development.

Initially, mine wastes are characterized using static prediction techniques that attempt to quantify the acid producing and acid neutralizing potential of the waste component.   The most commonly used static prediction technique is the (Standard) Acid Base Accounting (ABA) method of Sobek et al (1978). Waste characterization studies also include kinetic prediction tests, using laboratory and field techniques, to provide information regarding the rate of ARD generation.   These tests have generally focused on the rates of sulphide oxidation and metal leaching (Sobek et al, 1978; BC AMD Task Force, 1989; Coastech Research Inc., 1991).   More recently, kinetic procedures are also being used to evaluate the rate at which neutralizing minerals are depleted (Bradham and Carruccio, 1990; Lapakko, 1990; White and Jeffers, 1994;

White et al, 1994; Morin et al, 1995a). In addition to static and kinetic tests, site investigations can be carried out which include water quality monitoring to assess long-term ARD generation and water quality.

The overall objective of this thesis is to determine the ability of the ARD prediction techniques to approximate on-site water quality. This requires an understanding of both the chemical reactions that contribute to ARD as well as the factors affecting relative reaction rates of the different reactions. In Chapter 2.0 the geochemical evolution of ARD and reaction kinetics are reviewed. Various static and kinetic prediction test and interpretation methods are then discussed. The prediction data manipulation and interpretation are based, in part, on the concepts of alkalinity/acidity and carbonate equilibria and these are reviewed after the prediction techniques. Static prediction data are presented and analyzed primarily by statistical methods and, to a limited extent, kinetic and on-site monitoring data are analyzed by these methods. A review of statistical analysis is also presented in order to assess the application of statistical methods in ARD waste characterization studies.

With this understanding of the geochemical evolution of ARD and the prediction methods and interpretation, the first part of this project is to assess the relationship between static data, kinetic data and geology. This first phase is based on the assessment of data in the Database of Acid Rock Drainage (DBARD), a computer database initiated in 1990 to be a repository of static and kinetic test data, which is presented in Chapter 3.0.

Once the relation between the various laboratory methods has been considered, the second part of this thesis presents a detailed study at one mine site where laboratory prediction tests have been completed and on-site water quality has been monitored. The site selected is Gibraltar-McLeese Lake Operations (Gibraltar) near Williams Lake, British Columbia. The available data allow for a site specific assessment of how the ARD prediction laboratory methods approximate on-site water quality. This assessment is presented in Chapter 4.0.

In conjunction with the DBARD assessment, a review was made of the interpretation and reporting methodology of ARD prediction data. Recommendations for analyses, data manipulation, interpretation and reporting of ARD prediction data is presented in Chapter 5.0.

1.1   OBJECTIVES

The overall objective of this thesis is to determine the ability of ARD prediction techniques to approximate on-site water quality. This will be based on the following specific objectives:

1. Investigate the relationship between static prediction parameters and lithogeochemistry and geologic deposit type.

2. Assess current interpretations of kinetic prediction data and its relation to the corresponding static prediction data.

3. Determine the ability of static and kinetic prediction methods to identify on-site water quality.

4. Assess current interpretive and reporting methodologies used to present and assess ARD prediction data.

2.0   BACKGROUND

In this chapter a review of the chemical reactions, and their kinetics, contributing to ARD will be presented. This will be followed by a review of the various ARD prediction techniques and interpretations. Manipulation and interpretation of prediction data are based, in part, on alkalinity/acidity and the carbonate system, and a review of these concepts is also presented. Statistical methods are commonly used in waste characterization and a review of these statistical analyses is presented at the end of the chapter.

2.1   REVIEW OF ACID ROCK DRAINAGE

2.1.1   GEOCHEMICAL EVOLUTION

Acid rock drainage (ARD) is the result of a complex combination of inorganic and organic processes and reactions taking place when sulphide-bearing geologic material is exposed to air and water. At mining operations, exposed material includes waste, such as waste rock and tailings, or mine structures, such as open pits and underground workings.   Our current understanding of the processes is based on numerous studies of ARD generation in waste material and mine structures using field studies, geochemical mass balance techniques and computer speciation programs.   Oxidation (acid generating) and mineral dissolution (acid neutralizing) reactions have been used to describe tailings porewater chemistry (Boorman and Watson, 1976; Blowes et al, 1987, 1991, 1992) and migration of contaminant plumes (Morin et al 1988a, 1988b; Morin and Cherry, 1988). Notable work was completed by Kleinmann et al (1981) who simplified the geochemical evolution of ARD into three stages and by Morin et al (1988a, 1988b) and Morin and Cherry (1988) who suggested reasons for the typically observed "step-wise" decrease in pH.

Kleinmann et al (1981) simplified the various ARD processes into three stages. The first, or alkaline, stage of ARD generation occurs in neutral or alkaline conditions and is primarily chemical oxidation of pyrite by molecular oxygen to sulphate and ferrous iron:

$$FeS_2 + 7/2\ O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad\qquad (1)$$

The second, or transition, stage occurs in the pH range of approximately 2.5 to 4.5 and represents the oxidation of ferrous iron by molecular oxygen to ferric iron which occurs as ferric iron hydroxide:

$$Fe^{2+} + 5/2\ H_2O + 1/4\ O_2 = Fe(OH)_3\ (s) + 2H^+ \tag{2}$$
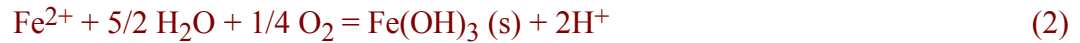
The third, or acidic stage, occurs once neutralizing minerals have been consumed and the lack of a buffering capacity results in decreasing pH. Under low pH conditions there is an increase in bacterial activity (primarily *T. ferrooxidans*) which catalyze pyrite oxidation. Ferric iron, produced by the oxidation of ferrous iron, also acts as an oxidizing agent for pyrite. These reactions may be written:

$$Fe^{2+} + 1/4O_2 + H^+ = Fe^{3+} + 1/2\ H_2O \tag{3}$$

$$FeS_2 + 14\ Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{4}$$

The third stage is below pH approximately 2.5, and the solution chemistry is characterized by high concentrations of sulphate and total iron and a high Fe^{3+}/Fe^{2+} ratio.

Neutralization of ARD is primarily through carbonate mineral dissolution (Kleinmann et al, 1981; Morin et al 1988a, 1988b) represented by the reactions:

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3 \tag{5}$$

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \tag{6}$$

Two equations are used to describe calcite dissolution because carbonate ions occur as different species in solution, depending on pH, due to ion hydrolysis. Carbonate equilibria is presented in more detail with the review of alkalinity and acidity (Section 2.2).

Carbonate, and hydroxide minerals, are consumed (i.e. dissolved) during neutralization reactions depending on the "equilibrium pH" of each mineral (Morin et al 1988a, 1988b). The "equilibrium pH" describes the pH above which the mineral precipitates and below which it

dissolves. Minerals identified by Morin et al (1988a, 1988b), with corresponding equilibrium pH, are: $Fe(OH)_3$ (3.0 - 3.7), $Al(OH)_3$ (4.3 - 5.0), $FeCO_3$ (5.1 - 6.0) and $CaCO_3$ (5.5 - 6.9). Acidic conditions generated by sulphide oxidation (equations 1 to 4) are initially buffered by calcite dissolution (equations 5 and 6). With continued sulphide oxidation and hydrogen ion release, calcite is depleted and the pH is then buffered by siderite dissolution, followed by $Al(OH)_3$ and $Fe(OH)_3$. This leads to a "step-wise" decrease of the pH, and with continued sulphide oxidation, the neutralizing minerals are depleted in order.

In some tailings impoundments the dissolved species are at sufficient concentrations that minerals precipitate to form a "hardpan" layer. Hardpan layers are composed of melanterite (ferrous iron sulphate) and gypsum (calcium sulphate; Blowes et al, 1991, 1992) or ferric iron oxides and jarosites (hydrated ferric iron sulphate; Blowes et al, 1991). These layers serve as an important barrier to oxygen diffusion into the tailings which limits pyrite oxidation. The hardpan layers also attenuate metal ions by adsorption and co-precipitation processes (Blowes et al, 1991, 1992). These hardpan layers have also been identified in waste rock piles by Lister (1994).

Research has primarily focused on the oxidation reactions and the role of calcite in neutralization because of its reactivity and resultant neutralizing capacity. More attention is currently being directed toward the role of silicates in the neutralization processes (Lapakko, 1994: Sherlock et al, 1995). Neutralization by silicates may be represented by equations showing either complete dissolution (congruent dissolution) or alteration (incongruent dissolution). The difference between these is that complete dissolution results in all ions going into solution and alteration introduces certain ions from the mineral to solution leading to the alteration of the original mineral to another mineral. An example is anorthite (calcium silicate) dissolution (equation 7) and alteration to kaolinite (equation 8):

$$CaAl_2Si_2O_8 + 2H^+ + 6H_2O = Ca^{2+} + 2Al^{3+} + 2H_4SiO_4 + 6OH^- \qquad (7)$$

$$CaAl_2Si_2O_8 + 2H^+ + H_2O = Ca^{2+} + Al_2Si_2O_5(OH)_4 \qquad (8)$$

Factors that determine whether silicate dissolution is congruent or incongruent include the mineral structure and composition as well as external environmental factors. In natural

systems, chemical weathering of silicate minerals is more commonly alteration with montmorillinite (smectite) and kaolinite clay minerals as end-products (Blanchard, 1984).

Silicate neutralization in ARD systems is identified by elevated concentrations of silica and aluminum in tailings water (Blowes et al, 1992) and waste rock drainage (Alpers and Nordstrom, 1990). Morin et al (1988a) suggest that ARD has elevated silica and aluminum concentrations due to alumino-silicate mineral dissolution and that minimal precipitation of secondary amorphous silica and allophane (amorphous alumino-silicate) occurs. Secondary amorphous silica and goethite have also been identified in waste rock piles by Alpers and Nordstrom (1990) who concluded, using computer speciation programs, that acid neutralization, in the pH range of 1.0 to 1.5, was the result of albite, chlorite, sericite, epidote and calcite dissolution, with the largest pH increase due to chlorite dissolution. Blowes and Ptacek (1994) also suggest that the source for aluminum ions for gibbsite $(Al(OH)_3)$ precipitation, during the step-wise pH decrease, is alumino-silicate dissolution.

An important natural analogue to ARD is gossan formation. A gossan is the ferriginous weathered product of a sulphide body (Nickel, 1983) formed by oxidizing and leaching of sulphide minerals above the water table. Acid generation during the oxidation of the sulphides during gossan formation is buffered by carbonate and silicate mineral dissolution and alteration (Thornber 1983). Silicate buffering is indicated by the presence of secondary kaolinite and silica polymorphs (Blanchard, 1984).

Other processes that contribute to neutralization include (Stumm and Morgan, 1981; Moss and Edmunds, 1992; Kirchner, 1992):

- alkalinity of local soil, surface water, groundwater
- ion exchange capacity of soil and rock
- biomass (*via* respiration/decay and adsorption/uptake processes)

In natural systems, there exists a steady state condition that represents a balance of elemental cycles. If there is excess acid introduced to a system, as in ARD, this may lead to acidified water, depleted solid and degraded biomass. The interaction and rates of the various acid generating and acid consuming processes and reactions determines the rate of ARD generation as well as the impact potential for a site.

2.1.2   KINETICS

Sulphide Oxidation

Summaries of factors that determine the sulphide oxidation rate are presented within Kleinmann et al (1981), Lowson (1982), Bierens de Hann (1991), Morin et al (1991) and Nicholson (1994). The more important factors include:

- oxidant

- particle size (surface area) and morphology

- temperature

- pH

- bacteria (iron and sulphur oxidizing)

An important factor of sulphide oxidation is the presence of an oxidant. In ARD processes, oxygen and ferric iron are the more common oxidants (Lowson, 1982; Hering and Stumm, 1990). As suggested by the "stages" of ARD (Kleinmann et al, 1981), oxygen is the more significant oxidant at neutral pH conditions and ferric iron is more significant at lower pH conditions.

In addition to the presence of an oxidant, other factors have been identified that contribute to the rate of sulphide oxidation such as surface area. The surface area is dependent on the grain size and morphological form of the mineral (Lowson, 1982). Nicholson (1994) suggests that the rate of oxidation is proportional to the available surface area.

The temperature dependence of the oxidation rate constant follows the Arrhenius Equation:

$$k_0 = Ae^{-E_0/RT} \tag{9}$$

where: k_0 = rate constant
A = Arrhenius factor
E_0 = activation energy
R = gas constant
T = temperature

The E_0 value for pyrite oxidation is between 60 to 90 kJ/ mole. This range is higher than the E_0 value for transport controlled reactions (approximately 20 kJ/mole) and lower than the energy necessary to break crystal bonds (160 to 400 kJ/mole), suggesting that surface reactions are reducing the activation energy (Lasaga, 1984). The Arrhenius relationship suggests that an increase in temperature increases the rate of reaction and the higher the E_0 value the larger the change. Sulphide oxidation reactions are exothermic; for example, equation 1 would release 1440 kJ/mole (Lowson, 1982). As a result, oxidation of sulphides can lead to a temperature increase in the system which increases the rate of oxidation. Since temperature is readily measured, it has been used to determine the oxidation rates in waste rock piles (Harries and Ritchie, 1981).

The decrease of pH below 2.5 leads to an increase in the numbers of bacteria that catalyze the iron and sulphur oxidation reactions (Kleinmann et al, 1981). The bacteria *Thiobacillus ferrooxidans* can increase pyrite and ferrous iron oxidation rates by a factor of 10 to 100 (Nicholson, 1994). Other bacteria (*Thiobacillus thiooxidans*) catalyze sulphur oxidation (Gould et al, 1994). Iron and sulphur oxidizing bacteria also exist in more neutral conditions, however, the rates of inorganic oxidation are faster at higher pH values than the bacterial rates. Lower pH conditions lead to a significant increase in the rates of microbiological processes relative to the chemical reactions. In the pH range of 1 to 3.5 and with temperatures up to 40°C, pyrite and ferrous oxidation catalysis by bacteria is most effective (Gould et al, 1994). Sulphur oxidation by bacteria is most effective in the pH range 0.5 to 4 and in the temperature range 25° to 30°C (Gould et al, 1994). Taylor and Wheeler (1984) suggest that, during ARD generation, the microbial oxidation is more common in aerobic, unsaturated conditions while chemical reactions are dominant in anaerobic, water saturated systems. This indicates that microbial processes are more significant in ARD from waste rock piles, mine workings and open pit walls and relatively minor within the saturated zone of tailings impoundments.

Mineral Dissolution and Alteration

Factors that contribute to carbonate and silicate dissolution and alteration are (Morse, 1983; Sverdrup, 1990; Sherlock et al, 1995):

- pH
- partial pressure of carbon dioxide (P_{CO_2})

- stable, equilibrium conditions

- temperature

- mineral size and morphology

- redox conditions

- concentration of other ions and organics

The more important rate determining factors are pH, P_{CO_2} and equilibrium conditions. The pH dependence is due to mineral dissolution and alteration that involves surface reactions between the hydrogen ions in solution and the ions held within the crystal lattice (Lasaga, 1984; Wieland et al 1988; Sverdrup, 1990).

The presence or absence of carbon dioxide is important in controlling the dissolution rate of carbonates. There is an increased solubility in open system dissolution (i.e. gas is able to enter solution) relative to closed system dissolution (i.e. no gas exchange; Stumm and Morgan, 1981).

Temperature is another factor that contributes to the rate of carbonate and silicate dissolution. The rate dependence is described by the Arrhenius Equation (equation 9) with activation energy values for silicates of 40 to 80 kJ/ mole and calcite of 35 kJ/mole (Lasaga, 1984). Most minerals have a solubility proportional to temperature except carbonate and sulphate minerals. The latter have decreased solubility with increasing temperature due to a change in the equilibrium constant (Stumm and Morgan, 1981). During sulphide oxidation, the associated temperature increase will increase the oxidation rate but could decrease the solubility of calcite resulting in reduced neutralization capacity.

Another factor that influences the dissolution rate of carbonates and silicates is mineral composition and structure. The more complex the bonding in a mineral lattice the more stable the mineral. Natural minerals have impurities and variable composition which affect whether mineral dissolution will be congruent (dissolution) or incongruent (alteration).

Redox conditions may also affect silicate and carbonate mineral dissolution due to the presence of ions of various oxidation states in the crystal lattice. Hering and Stumm (1990) cite examples where a mineral is more soluble either in the oxidized state, for example Mn-oxides, Fe-oxides and Fe-silicates, or in the reduced state, for example Cr_2O_3 and V_2O_3.

As a mineral dissolves or alters, the presence of ions in solution can increase the solubility of the mineral due to complexing and the formation of aqueous species (Stumm and Morgan, 1981). Ions in solution can also be adsorbed onto the crystal surface and block the reactive sites, thereby decreasing solubility. Identified inhibitors of calcite dissolution, via adsorption processes, include magnesium, phosphate, organics, sulphate and metals (Terjesen et al, 1961; Morse, 1983). In ARD processes, therefore, the increased concentration of metals and sulphate due to sulphide oxidation could lead to a decrease in solubility of the calcite.

It is possible to classify different mineral types, and the minerals within each type, on the basis of their reactivity (e.g. Sverdrup, 1990; Lasaga, 1984). With respect to mining wastes, Jambor (1994) suggests a general sequence of sulphide reactivity (from readily decomposed to increased resistance):

pyrrhotite > galena - sphalerite > arsenopyrite - pyrite > chalcopyrite

The relative reactivity of carbonate minerals as suggested by Evangelou et al (1985), from most reactive to least, is:

calcite > dolomite - ankerite > siderite

Sverdrup (1990) has presented a detailed classification of mineral reactivity based on laboratory experiments (Table 2.1). Ritchie (1994) has compared rates of oxidation and dissolution/alteration reactions in a waste rock environment. Based on field observations the rate of sulphide oxidation was identified as approximately the same as calcite dissolution under natural conditions, although for many other carbonates and silicates, dissolution and alteration rates are significantly slower then sulphide oxidation.

Table 2.1: Reactivity Classification of Neutralizing Minerals (after Sverdrup, 1990)

Mineral Group	Typical Minerals
Dissolving	calcite, aragonite, dolomite, magnesite, brucite
Fast Weathering	anorthite, nepheline, olivine (forsterite), garnet, jadeite, leucite, spodumene, diopside, wollastonite

Intermediate Weathering	sorosilicates (epidote, zoisite), pyroxenes (enstatite, hypersthene, augite, hedenbergite), amphiboles (hornblende, glaucophane, tremolite, actinolite, anthophyllite), phyllosilicates (serpentine, chrysotile, talc, chlorite, biotite)
Slow Weathering	plagioclase feldspars (albite, oligoclase, labradorite), clays (vermiculite, montmorillinite)
Very Slow Weathering	K-feldspars, muscovite
Inert	quartz, rutile, zircon

2.1.3   ARD PREDICTION METHODS

The purpose of waste characterization is to determine the ARD potential for a site. Interpretation of prediction data are used for site plans, treatment and control measures. This is particularly apparent in Provincial Mining Acts that require mine sites to be physically and chemically stable during and after operation.

Prediction of the ARD potential is an iterative process that is carried out during exploration, development, operation and closure of a mine site with prediction methods including the following assessments (BC AMD Task Force, 1989; Price and Errington, 1995):

- previous work/mining in area
- environmental and geological models
- tests that determine metal leaching
- static tests
- kinetic tests in the laboratory or field
- mathematical models

Of these methods, the static and kinetic predictive tests are used extensively in British Columbia and most other jurisdictions. These methods are outlined below.

Static Methods

Static prediction methods measure the theoretical balance between acid producing and neutralizing components of a waste material. The first test to be widely employed was the acid base accounting (ABA) method by Sobek et al (1978) which can be termed the standard ABA.

Various other methods have been developed and are summarized in Coastech Research Inc. (1991). These methods include:

- Modified ABA
- BC Research Initial Test
- Net Acid Production (NAP) Test
- APP / S ratio

The standard and modified ABA tests are the most commonly used static tests in British Columbia, although in the early 1980's, the BC Research initial test was preferred. The NAP and APP/S methods have only limited application in waste charaterization studies and are not discussed in further detail in this thesis.

The above techniques involve laboratory methods to determine AP (acid potential) and NP (neutralizing potential) values for a sample. In general, the AP is determined by analyzing a sample for sulphur content and multiplying by 31.25 to convert to units of kg as calcite per tonne (kg $CaCO_3$/t) of material. The standard ABA test assumes that:

- all the sulphur is in sulphide (S^{2-})
- pyrite (ferrous iron sulphide) completely oxidizes to sulphate and ferric iron
- ferric iron precipitates as $Fe(OH)_3$

In the modified ABA procedure, determination of AP considers the sulphur already in oxidized form, i.e. sulphate, which would not contribute to the acid potential of the sample. AP is therefore based on the sulphide content of the sample.

In the standard and modified ABA tests, the NP is determined by digesting a sample in excess acid and back-titrating the solution with base to a predetermined pH. The amount of acid consumed during digestion is then calculated using the amount of base added during the titration. The principal differences between the static prediction tests is the digestion conditions. Differences in the various static tests, summarized in Coastech Research Inc. (1991) and other proposed techniques, are the result of identified shortcomings of the standard ABA test. Lawrence (1990) suggests that boiling during the NP determination of the standard ABA method may introduce components to solution that influence the NP value. The modified ABA (Lawrence, 1990) uses low temperature digestion over a longer time period and uses sulphide-sulphur to estimate AP. Lapakko (1994) suggests that the low pH conditions of the standard acid

digestion may lead to dissolution of carbonate minerals and least stable silicates (olivine, pyroxene, calcic plagioclase) which would contribute to NP values, while the more stable silicates (K-feldspar, mica and quartz) will not. He suggests a procedure in which the acid digestion is carried out to a pH value of 6.0 in order that only the neutralizing capacity of carbonates is measured. The BC Research Initial method involves titrating, with acid, a sample in water to pH of 3.5 and using the amount of acid added to reach this pH to determine the NP. The end pH of 3.5 is based on the premise that below this pH bacteria will catalyze the sulphide oxidation. Therefore, if the acid production is not sufficient to lower pH below 3.5, then biochemical oxidation, and ARD, will not occur.

The results of an ABA test can be interpreted in two ways. In the first, the Net NP (net neutralizing potential) is calculated by taking the arithmetic difference of NP and AP. A Net NP value less then -20 can be interpreted to indicate that the sample has a high ARD potential and if greater then +20, a low potential (BC AMD Task Force, 1989). Data between -20 and +20 requires further study by kinetic techniques to evaluate the ARD potential. The second interpretation of ABA data, which has found increased use recently, uses the NP:AP ratio to determine the ARD potential rather than the Net NP value. This is because the NP:AP ratio reveals the relative proportion of acid generating and acid consuming components. Interpretation of NP:AP values varies with different jurisdictions. In British Columbia, Price and Errington (1995) propose that for initial classification of waste material, a sample with NP:AP ratio less than 1, has a high potential for ARD. If the ratio is greater than 4, then the sample has a low potential for ARD. Those samples with NP:AP ratios between 1 and 4 require further kinetic testing.

More recently, field-based prediction methods have been proposed (Kwong, 1993; Brodie et al, 1991). These field techniques involve a visual determination of the sulphur and carbonate content and the use of weighting factors, for example grain size, structural features and crystal morphology, to assess the ARD potential.

Kinetic Methods

Kinetic methods are used to test the interpretation of the static test data, determine the long term rate of acid generation (sulphide oxidation) and metal leaching, test proposed control and mitigation measures and more recently, determine the depletion rate of the neutralization

potential. The various kinetic methods that have been proposed include both laboratory and field techniques (Coastech Research Inc., 1991) and include:

- Humidity Cells
- Columns
- BC Research Cofirmation test
- Shake Flasks
- Soxhlet extraction
- Field test pads

The differences between the tests are based on the complexity, scale, duration, cost and data requirements. Humidity cells and columns are commonly used in British Columbia to determine the rate of ARD generation. Most of these tests measure metal and sulphate concentration, pH and alkalinity of the leachate over time. This allows the rate of sulphide oxidation, based on the assumption that sulphate in solution is the result of oxidation, and the rate of metal release to be determined, both expressed on either a weight or surface area basis. To a limited extent, kinetic test data have included the determination of the NP depletion by considering molar ratios and oxidation rates (Morin and Hutt, 1994; Morin et al, 1995a, 1995b) and metal leaching rates for calcium and magnesium (Lapakko, 1987, 1990; Bradham and Carrucio, 1990; White and Jeffers, 1994; White et al 1994). Lapakko (1987) and Ferguson and Morin (1992) determined the occurrence of ARD by plotting the molar ratio of measured sulphate to alkalinity over time and noted an increase in this ratio prior to the decrease in pH. Morin and Hutt (1994) and Morin et al (1995a, 1995b) have used kinetic test data to determine the "safe" NP:AP ratio and NP depletion rates by plotting the molar ratio of cations from neutralizing minerals (calcium, magnesium, potassium, sodium, strontium) to sulphate. A review of these rate calculations will be presented in Chapter 3 with the database analysis.

As a final note to ARD prediction data, many protocols for waste characterization have been developed independently with many investigators having different approaches and interpretations for ARD prediction data. For example, static prediction methods have similarities in that all quantify the acid producing and consuming potential. However, a variety of acronyms have been identified in the literature (Table 2.2). Some of these names differ due to to differences in test methods. Many names, however, are based on the same test procedure. There

are also various approaches to the data collection and manipulation of data from kinetic testing. One can recognize from this that a guideline to reporting ARD prediction is necessary and recommendations for reporting, based on the review of the database, are presented in Chapter 5.

Table 2.2: Examples of Acronyms from Static Prediction Tests

AP	Acid Potential	NP	Neutralization Potential
APPS	Acid Producing Potential	ACP	Acid Consuming Potential
MPA	Maximum Potential Acidity	AC	Acid Consumption
PA	Potential Acidity	ANC	Acid Neutralizing Capacity
AGC	Acid Generating Capacity	NC	Neutralization Capacity
SAP	Sulphide Acid Potential		

2.2   REVIEW OF ALKALINITY AND CARBONATE EQUILIBRIA IN ARD PREDICTION

The carbonate system is complex and involves the transfer of carbon among three phases: gas, liquid and solid. When carbon dioxide (CO_2) is brought into contact with water it dissolves forming carbonic ions (H_2CO_3) until an equilibrium state is reached. Carbonic ions will dissociate to hydrogen ions (H^+), bicarbonate ions (HCO_3^-) and carbonate ions (CO_3^{2-}) depending on the pH. Below pH 6.3 carbonic ions are the dominant species in solution, between pH 6.3 and 10.3 bicarbonate ions are dominant and above pH 10.3 carbonate ions are dominant. These aqueous species will form as a result of carbonate mineral dissolution (equation 5 and 6) with pH determining the form in solution.

Alkalinity is the buffering capacity of a water sample determined by titrating the sample with an acid to a specific pH and the amount of acid added is expressed as calcite equivalents per litre (mg as $CaCO_3$/L). Alkalinity is also referred to as the acid neutralizing capacity (ANC). In most natural surface and groundwater alkalinity is represented by equation 10 (Stumm and Morgan, 1981; Drever, 1988):

$$\text{Alkalinity} = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] - [H^+] \qquad (10)$$

Other constituents that contribute to alkalinity are species capable of combining with hydrogen during titration. Examples are hydroxide complexes, HS^-, S^{2-}, $H_3SiO_4^-$, $H_2BO_3^-$ and dissociated organic acids. Since borate, silicic acid, bisulphides, organic anions, hydrogen and hydroxide ions are in relatively low concentrations in natural waters, the carbonate system is generally used to define alkalinity (termed carbonate alkalinity).

Various reactions will effect alkalinity. For example, the precipitation of calcite (equation 5) indicates that for every mole of carbonic species lost from solution as a result of calcite precipitation, there are two moles of hydrogen ions generated and alkalinity is not conserved. Another example is the oxidation of metals, such as Fe^{2+}, that will hydrolyze upon oxidation and produce protons. Other reactions that affect alkalinity include: photosynthesis, nitrification, denitrification, sulphide and metal oxidation, sulphate reduction, and mineral precipitation or dissolution. Degassing of carbon dioxide ($HCO_3^- + H^+ = CO_2 + H_2O$) does not affect the alkalinity since for every mole of carbon dioxide generated, one mole of hydrogen ions is also lost and alkalinity is conserved.

The opposite of alkalinity is acidity which describes the capacity of a water to donate protons (Stumm and Morgan, 1981) and is also referred to as base neutralizing capacity (BNC). Sources of acidity are dissolved or suspended hydrolyzed constituents including gases, such as CO_2 or H_2S; inorganic ions such as Fe^{3+}, Al^{3+}, or HSO_4^-, dissolved organics, such as humic and fulvic acids; and suspended material such as clays and metal hydroxides. Acidity is determined by titrating a water sample with a base to a specific pH and the amount of base added is expressed as mg as $CaCO_3/L$.

The application of alkalinity and acidity to ARD prediction occurs in both static and kinetic methods. The determination of NP is based on the introduction of ions to solution during digestion that would contribute to the alkalinity (or ANC) of the water. Alkalinity and acidity measurements are also used to interpret kinetic test data, but given the various reactions that can affect alkalinity, the measurements may not be representative of the neutralization reactions that have occurred. This limits alkalinity measurements to a more qualitative interpretation of kinetic test data.

The buffer intensity (β) is a measure of a solution's ability to resist changes in pH. The carbonate system is most important in affecting the buffer intensity and neutralizing capacity of

natural waters. However, there are other heterogeneous chemical, biological and geochemical processes that may contribute to the buffering of solutions (Stumm and Morgan, 1981; Drever, 1988; Morel and Hering, 1993). Theoretically, silicate minerals have a greater neutralizing capacity than the carbonate minerals. However, these reactions are slower than the more reactive carbonates. It is for this reason that the more important buffering within near surface natural waters is by the carbonate system. Under ARD conditions, once the carbonate neutralizing capacity is exhausted then silicate dissolution is the dominant acid neutralization reaction.

2.3 REVIEW OF STATISTICAL METHODS IN ARD PREDICTION

The field of statistics can be broadly divided into two areas: descriptive and inferential statistics. The former includes the collection, presentation and description of data with common descriptors being histograms, mean, mode, standard deviation and variance of samples. Inferential statistics uses descriptive statistics of a sample set to make inferences for the population. These statistical analyses may be completed using parametric or non-parametric techniques with the difference between these techniques described in the following.

For most parametric statistical methods, it is a requirement that the sample sets be collected randomly from the individual populations (Rock, 1988) and that sampling from one population cannot be related to sampling from another population, i.e. the sources of these data are not the same or related (referred to as independent sampling). In addition, many statistical methods are based on a normal, or gaussian, distribution. Most geochemical data are skewed, usually lognormal, which Ott (1990) suggests is due to successive random dilution processes occurring from the initial to the final concentration. Parametric analytical techniques assume a normal distribution either naturally or as a result of data transformation. Common data transformations include square root, logarithmic, reciprocal, and angular.

ARD and environmental data are commonly analyzed using parametric methods, primarily descriptive statistics. Two important limitations of these analysis are the distribution of the data and the detection limits (Helsel, 1987). For analysis it is usually assumed that the distribution is normal and/or that the parametric methods are sufficiently "robust" to compensate for the non-normal distribution. If these data are below the detection limit it tends to be either

disregarded or represented by a minimum value which introduces a bias into the data set leading to an incorrect assessment by statistical analysis. Helsel (1987) proposes non-parametric methods be used for the statistical analysis of geochemical data. Non-parametric (or distribution free) tests are independent of the data distribution and are therefore unaffected by it. These methods are based on ranking and/or weighting of the data (Helsel, 1987; Rock, 1988).

Regression and Correlation

A common statistical analysis, particularly in waste characterization studies, is linear regression or correlation analysis. Regression analysis determines an equation to predict the value of the dependent variable (y) given values for the independent variables (x_1, x_2, ..., x_m) (Rock, 1988). Correlation analysis determines the relationship between the variables, or the effect of the independent variables on the dependent variable.

Time Series Analysis

The main objective of time series analysis is to identify patterns in data, that can be extrapolated to future conditions, providing a basis for prediction (Parl, 1967). The components of time series data include secular trends (long term), cyclical variations (intermediate), seasonal variations (short term) and irregular variations.

Statistical methods are used extensively in waste characterization studies and ARD prediction. Waste characterization studies involve sampling ore, waste rock material and tailings to determine the ARD potential. Sampling strategy is site specific since the number and type of specimens collected depends on the character of the lithologies present (BC AMD Task Force, 1992; Price and Errington, 1995). Design of an ARD prediction sampling program should ensure that representative samples are collected with detailed descriptions of geology, mineralogy, and weathering. As a guideline, the British Columbia Ministry of Energy, Mines and Petroleum Resources (Price and Errington, 1995) has proposed the following:

Mass of Rock Type (tonnes)	Minimum Number of Samples
< 10,000	3
< 100,000	8
<1,000,000	26
10,000,000	80

There are situations where these minimum number of samples is sufficient. There are situations, however, where these may not be sufficient if one considers inhomogenieties of either the in-situ material, for example the geology and structural features, or the excavated material (tailings and waste rock), for example layering and particle size distribution. There is also the consideration of the "representativeness" of the samples, for example are they the worst-case or average, are they fresh or weathered samples, are they surface samples or taken at depth? These are some of the considerations used to develop sampling strategies for individual sites and results in the sampling density to be site specific; commonly based on either a systematic grid or stratified sampling. There is also statistical considerations in determining the number of samples required. In general, there is no correct number of samples, although statistical methods need between 30 to 100 to satisfy the Central Limit Theorum (Helsel, 1987; Rock, 1988).

Statistical analysis of AP, NP, Net NP and NP:AP values are commonly completed by parametric techniques of descriptive statistics. In general, the samples are divided into the lithologic units and the mean, minimum, maximum and standard deviation is used to characterize the ARD potential. These descriptive statistics of the sample sets are used to make inferences about the population (or the entire lithologic unit). These characterizations are then used in mine operation, closure and waste material disposal plans since the purpose of testing material is to allow for classification and planning, based on the ARD potential of the material, to prevent the generation of ARD and the migration of contaminated runoff.

Regression/correlation techniques have been used for a proposed waste classification scheme at the Windy Craggy property in northern British Columbia (Claridge and Downing, 1993; Downing and Giroux, 1993); to predict water quality from existing waste rock piles at Bell Mine (Morin and Hutt, 1993b); and the monitoring frequency of waste pile seepage at Island Copper (Morin et al 1993). At Windy Craggy, correlation between lithologies and calcium content were extrapolated to the deposit block model, to ensure that any potentially acid generating mine blocks were disposed of safely. At the Bell and Island Copper Mine sites, the correlation between the logarithmic copper concentration and pH were used to predict short and long term peak metal concentrations as well as long term water quality from the waste rock dumps. Time series analysis has not been used in ARD prediction investigations and may have application in long term kinetic tests and on-site monitoring data to determine short and long

term trends in the data that can be extrapolated into the future, providing a temporal prediction of water quality.

3.0   ACID ROCK DRAINAGE DATABASE REVIEW

3.1 INTRODUCTION

Two databases, DBARD (database for acid rock drainage) and WasteDB (database for waste rock dump monitoring), managed by the Chair of Mining and Environment at the University of British Columbia have been evaluated. DBARD (Morin and Hutt, 1993a; Lawrence, 1994b; Lawrence and Harries, 1995) was developed through the initiative of the BC AMD Task Force in 1990 to store and retrieve data from ARD test work. WasteDB (Lawrence, 1994a) was initiated in 1993 to identify sites which currently monitor on-site water quality related to either existing or potential ARD in waste rock piles. The WasteDB does not contain the on-site monitoring data but does provide the information on what kind of data are available at different mine sites and how to access them.

This chapter of the thesis will present a review of DBARD using data from metal deposits within British Columbia. Background to the development and structure of DBARD will be presented, followed by the analyses of the static and kinetic prediction data in the database. The static test data are analyzed by: comparing data between sites based on geographic location and geology, assessment of paste pH as a screening tool, and determining the relation between the data and lithogeochemistry. The evaluation of kinetic test data follows the static data analysis and involves the assessment of different rate calculations and the relationship between the static prediction data and the determined rates. The majority of the prediction data in DBARD is from static tests and, as a result, form the basis for the largest part of the analysis. In evaluating the prediction data, various analysis and interpretative methods were identified in the literature related to static and kinetic prediction data collection and interpretation. Given the current variety of approaches to waste characterization, a guideline for reporting ARD prediction data is presented in Chapter 5.0 to streamline ARD reporting and to facilitate future database analysis.

3.2   DBARD

3.2.1   HISTORY

A brief synopsis of the history and programs used by DBARD will be presented in this text. More detailed information can be attained from Morin and Hutt (1993a), Lawrence (1994b) and Lawrence and Harries (1995).

The database initially used dBASE III Plus software and, in early 1992, the preliminary Version 2.0 (alpha) was released (Morin and Hutt, 1993a).   In 1992, custodianship of the database passed to the Chair of Mining and Environment, University of British Columbia to continue data input and improve database format. The final release of Version 2.0 occurred in 1994.   The next phase of DBARD, completed 1995, includes continued data entry and conversion to Paradox for Windows software (Lawrence and Harries, 1995; Lawrence and Sherlock, 1995).

3.2.2   DBARD DATA FILES AND STRUCTURE

The data files that comprise DBARD (in dBASE III and Paradox) include information related to mine site, sample location and lithology, static prediction data, kinetic prediction data, short term metal leaching data, and whole rock chemistry. The data entered in each file has been extracted from mine permit submission documents, the BC AMD Task Force 1987 survey, annual environmental and reclamation reports and other reports from the individual sites.

The mine information database includes coal and metal operations, primarily in British Columbia, with additional national and international sites. The type of information within this file includes mine name, owner/operator, location, commodity, grades, deposit type and principle sulphide and carbonate minerals present. There are currently 120 mines listed with 3 industrial mineral, 26 coal and 91 metal deposits. The sample and geology databases include sample identification, location description and lithology/mineralogy.

The static prediction test database includes data from 69 sites with 9 being coal deposits and 60 metal deposits. Only metal deposits are considered in this thesis. The information in this file includes mine identification, sample identification, paste pH, total sulphur, sulphide-S, sulphate-S, organic-S, acid potential (AP), sulphide acid potential (SAP), neutralization potential (NP), carbonate neutralization potential (CNNP) determined from carbon content, the net

neutralization potential (Net NP) which is the arithmetic difference of NP and AP, the refined net neutralization potential (RNNP) which is the arithmetic difference between NP and SAP, the ratio of NP:AP and NP:SAP. Review of the information sources indicates that there are numerous terms and calculations used in waste characterization programs to present and interpret static test data. The terms and calculations in DBARD are presented here. It should be noted that in DBARD the units of the static data (AP and NP) are in equivalents of calcite, that is, kilograms as calcite per tonne of material (kg as $CaCO_3$/tonne). For internal consistency some of the static data have been converted to these units prior to entry to the database. For example, for the BC Research Initial Test, the sulphuric acid equivalent (kg as H_2SO_4/tonne) is converted to calcite equivalent by multiplying by 1.02.

The kinetic prediction test data file includes 80 individual samples from 9 deposits. Information includes the mine identification, sample identification and description, the number and type of cycles, the parameters monitored, and measured concentrations. The concentrations from the leachate analysis are reported as either parts per million (ppm or milligrams per litre) or parts per hundred (%). For this thesis, the results of 54 kinetic tests from 8 mine sites were considered since corresponding static data are available.

The sample lithogeochemistry analysis data are from 55 sites and includes mine name, sample identification, analysis technique, parameters monitored and measured concentrations. Concentrations in this case have been entered as either parts per million (ppm) or parts per hundred (%). For this thesis, 22 sites have been considered for analysis as there is geochemistry data with corresponding static prediction data.

The metal leaching data are from one-time batch tests used to describe the short term leaching characteristics of a sample (e.g. SWEP test). These tests do not define the time dependent leaching rates and are affected by accumulated oxidation products. Within DBARD there are 79 samples from 13 sites, of which 4 are coal and 9 are metal deposits, which have data from these types of tests. These data were not assessed as part of this thesis.

3.3 DATA ANALYSIS

The analysis of the data in DBARD is presented in this section with static data considered first, followed by kinetic prediction data. The static test data are analyzed by: comparing data

between sites based on geographic location and geology (using genetic deposit type); assessment of the paste pH as a screening tool; and determining the relation between the data and lithogeochemistry. Evaluation of kinetic test data involves the assessment of the calculation of sulphide oxidation and NP depletion rates and the relationship between these rates and static prediction data.

3.3.2 STATIC TEST DATA

Static Prediction and Geology

One objective of establishing DBARD is to facilitate comparison between sites. New British Columbia government ARD guidelines (Price and Errington, 1995) recommend comparisons between sites as one component of the waste characterization program since it is possible that new sites can use the experience gained at other sites. Price and Errington (1987) and Kwong (1993) suggest that different deposit types have differing ARD potential and an understanding of the deposit type may aid in the prediction of ARD. Classification of ore deposits can be based on commodity, morphology and origin. For this project, deposits are grouped genetically (Evans, 1980; McMillan et al, 1991) and are ranked, from highest ARD potential to lowest (Kwong, 1993):

1. sedimentary exhalative massive sulphides (sedex)
2. volcanogenic massive sulphides (VMS)
3. calc-alkaline suite porphyry
4. epithermal Au-Ag
5. mesothermal vein Au
6. alkaline suite porphyry
7. skarn

The first analysis of the static prediction data was to determine the relationship between static prediction data and broader scale geologic features, using the premise that mine sites with similar mineralogy (geologic deposit type) or geographic location can be compared.

A summary of the static prediction data including: mine name, deposit type, prediction method and the descriptive statistics (including number of samples, minimum value, maximum value and mean value) for paste pH, AP, NP, Net NP and the NP:AP ratio is presented in Appendix 1. These data for paste pH, Net NP and NP:AP are presented for ore (Figure 3.1a, b, c), waste rock (Figure 3.2a, b, c) and tailings (Figure 3.3a, b, c) showing the minimum, maximum and mean values, for each mine site, grouped by deposit type. For this analysis the calc-alkaline and alkaline porphyry deposit types have been grouped together, and referred to as porphyry, since there is insufficient information in DBARD to distinguish the two deposit types. Also, mine sites numbered 30, 33, 34, 35 and 36 (Appendix 1) have not been included in Figures 3.1 to 3.3 as they do not have static prediction data in DBARD.
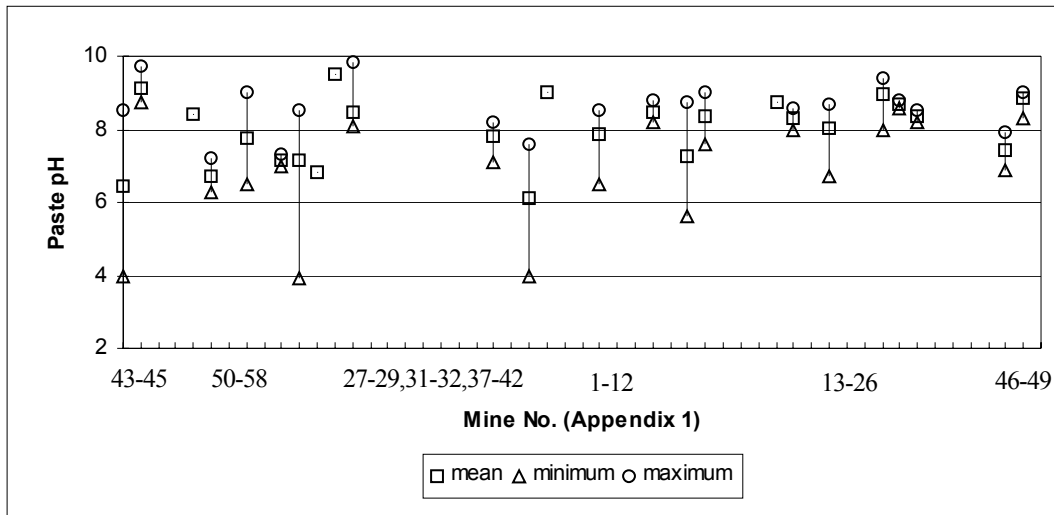
Figure 3.1a: Mean, minimum and maximum paste pH values for ore at DBARD sites
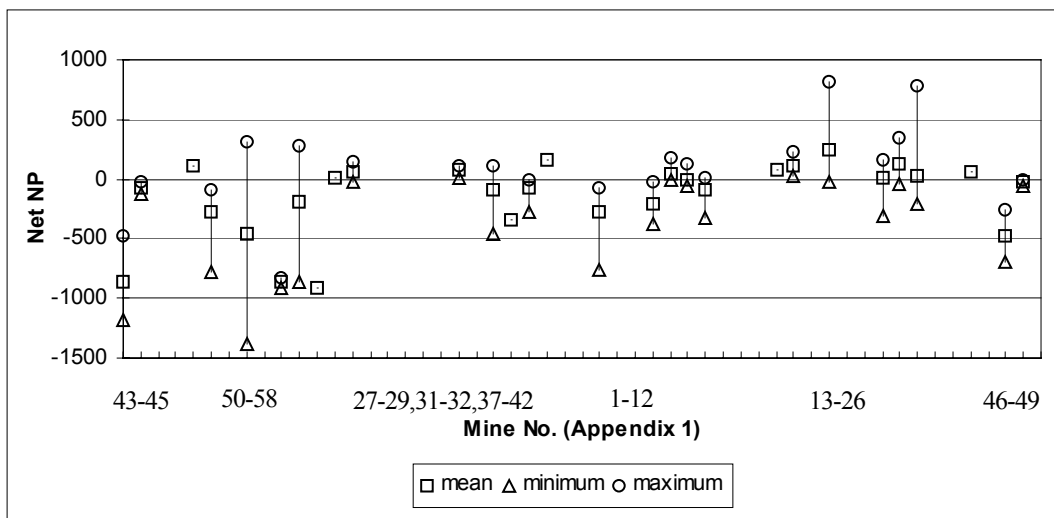
Figure 3.1b: Mean, minimum and maximum Net NP values for ore at DBARD sites
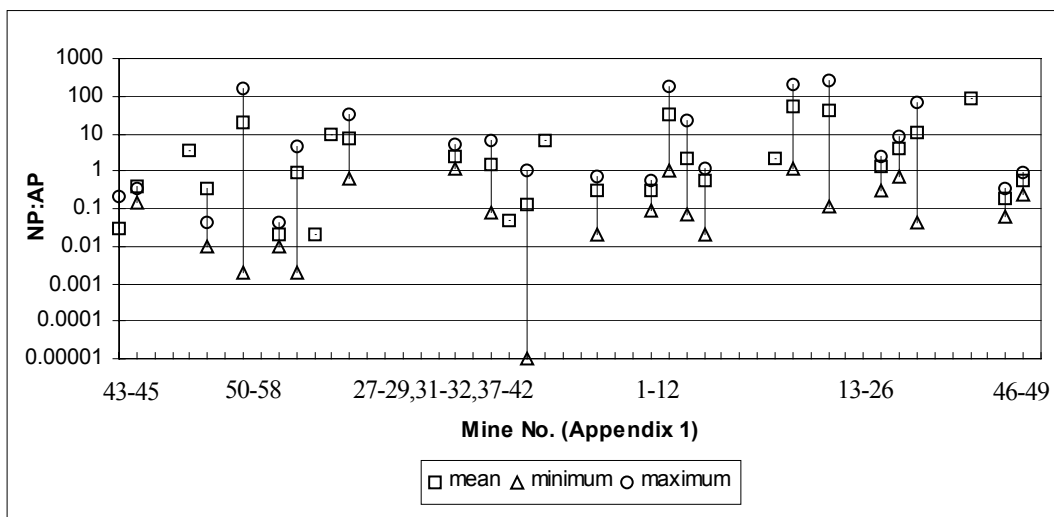
Figure 3.1c: Mean, minimum and maximum NP:AP values for ore at DBARD sites
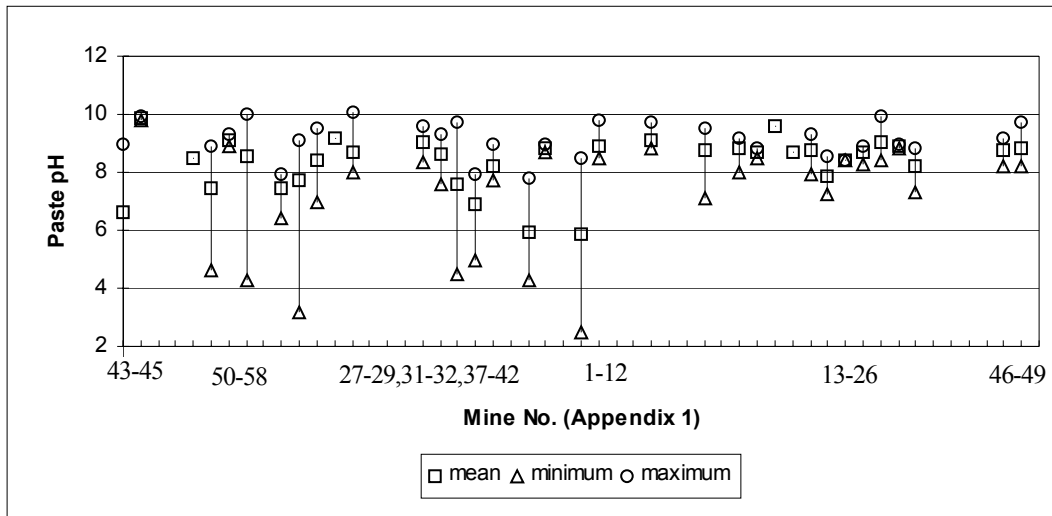
Figure 3.2a: Mean, minimum and maximum paste pH values for waste rock at DBARD sites
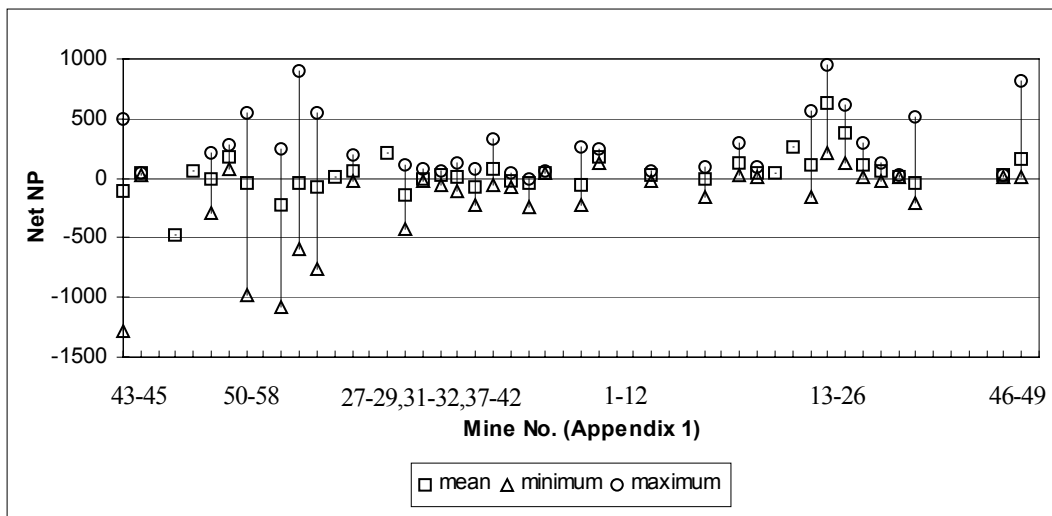
Figure 3.2b: Mean, minimum and maximum Net NP values for waste rock at DBARD sites
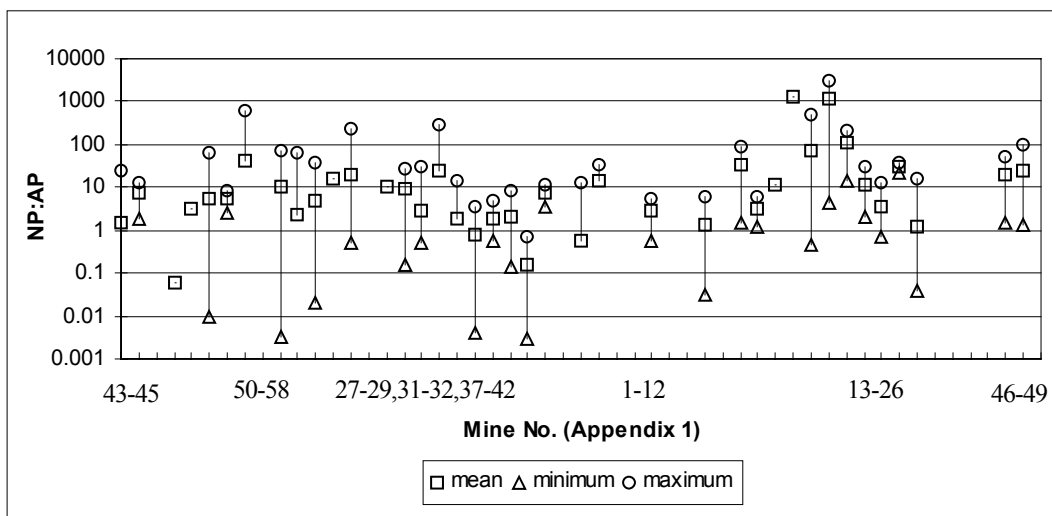
Figure 3.2c: Mean, minimum and maximum NP:AP values for waste rock at DBARD sites

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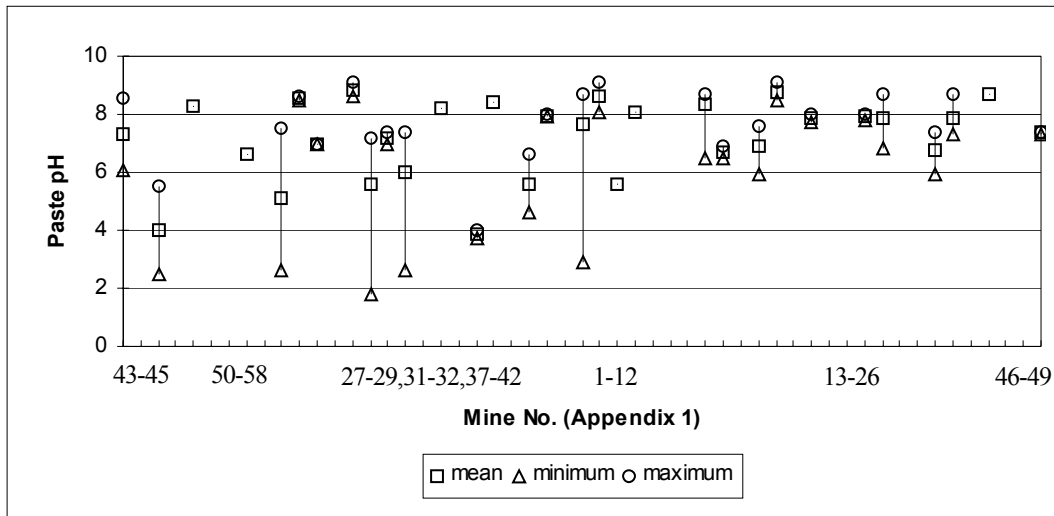
Figure 3.3a: Mean, minimum and maximum paste pH values for tailings at DBARD sites
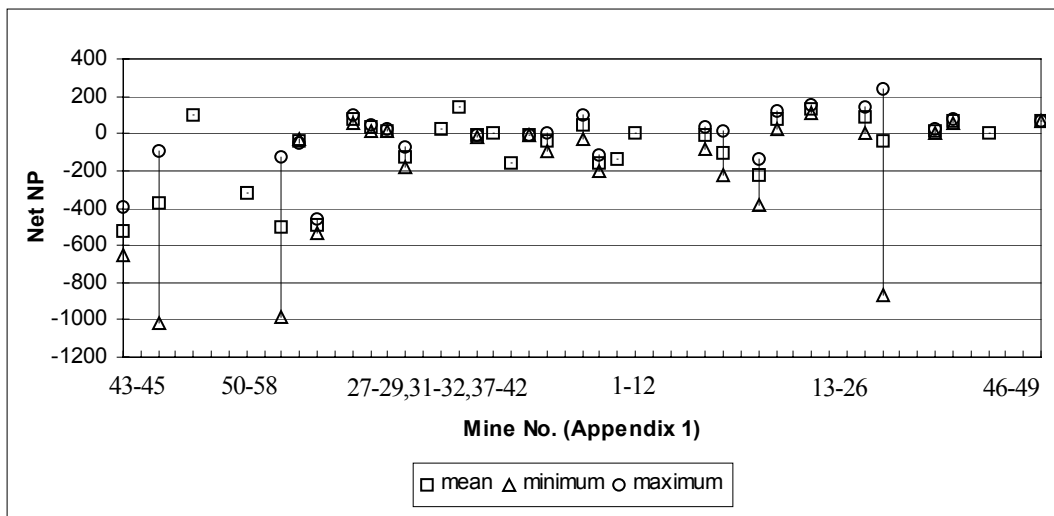
Figure 3.3b: Mean, minimum and maximum Net NP values for tailings at DBARD sites
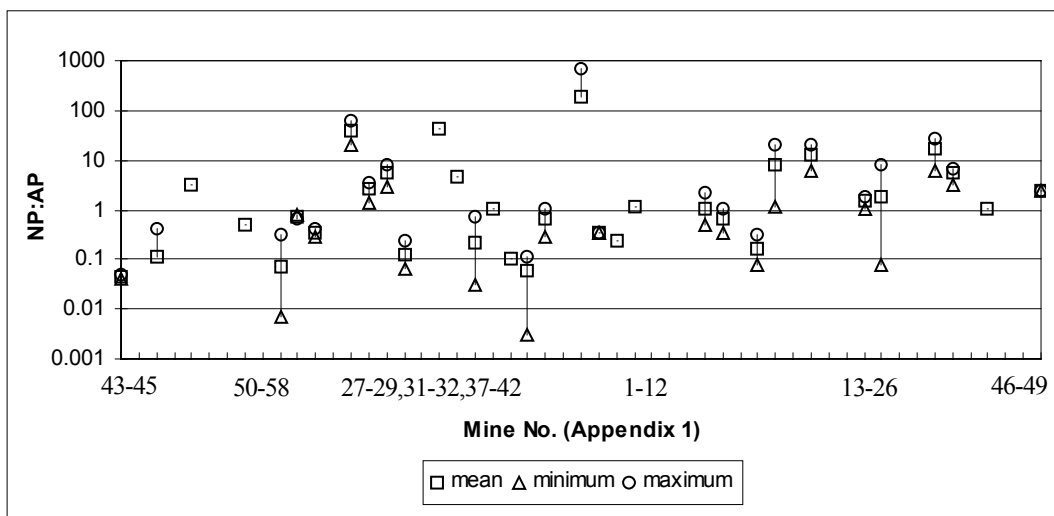
Figure 3.3c: Mean, minimum and maximum NP:AP values for tailings at DBARD sites

The data included in this analysis indicate that there is a broad range of values for static prediction data regardless of deposit type. Nonparametric statistical analysis (not presented) using the Kruskal-Wallis comparison of means test, was used to compare the mean values of Net NP and NP:AP since the data do not have a normal distribution. This analysis determines if the mean values of the deposit types are statistically different. For ore samples, the Net NP and NP:AP are not statistically different for epithermal, mesothermal and porphyry deposits. VMS, sedex and skarn deposits are also not statistically different. The epithermal, mesothermal and porphyry deposits, however, are statistically different than the VMS, sedex and skarn deposits. For waste rock, Net NP and NP:AP are not statistically different for mesothermal, porphyry and skarn deposits. The epithermal, sedex and VMS deposits are also not statistically different. The mesothermal, porphyry and skarn deposits, however, are statistically different from the epithermal, sedex and VMS deposits. For tailings samples, Net NP and NP:AP is not statistically different for all deposit types except VMS. This indicates that, in general, the Net NP and NP:AP for the different deposit types do not statistically differ. These descriptive statistics, however, are based on an overall consideration of the site, that is all the data from the site. More recent waste characterization studies evaluate the ARD potential based on the various lithologies of the site. For example, Figure 3.4a, b, c presents mean, maximum, and minimum values for paste pH, Net NP and NP:AP for one mine site (Mine No. 57; Appendix 1) where seven different waste lithologies (or waste units) have been identified. This illustrates that at an individual mine site the static test data can be variable. Non-parametric statistical analysis was used to compare the mean values of Net NP and NP:AP ratios of these different lithologies and indicates that waste units 2 and 4 are not statistically different and waste units 1, 3, 5, 6 and 7 are also not statistically different, although these two groups are statistically different.
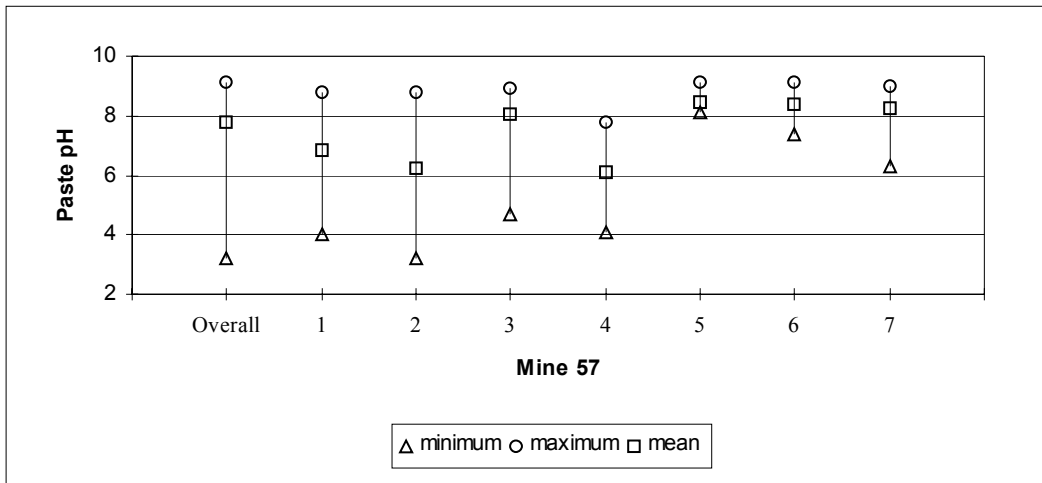
Figure 3.4a: Minimum, maximum and mean paste pH for individual waste rock units at Mine 57
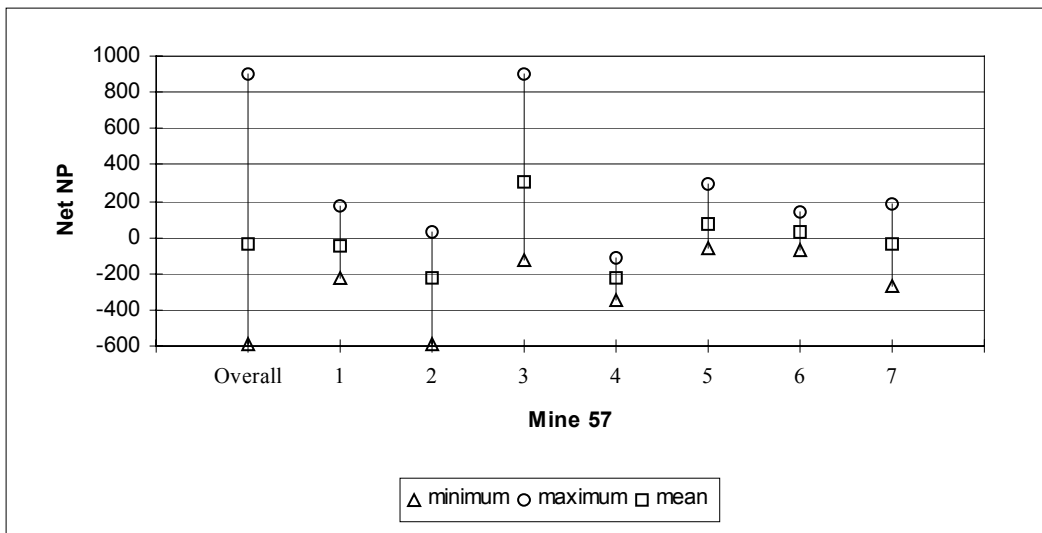
Figure 3.4b: Minimum, maximum and mean Net NP for individual waste rock units at Mine 57
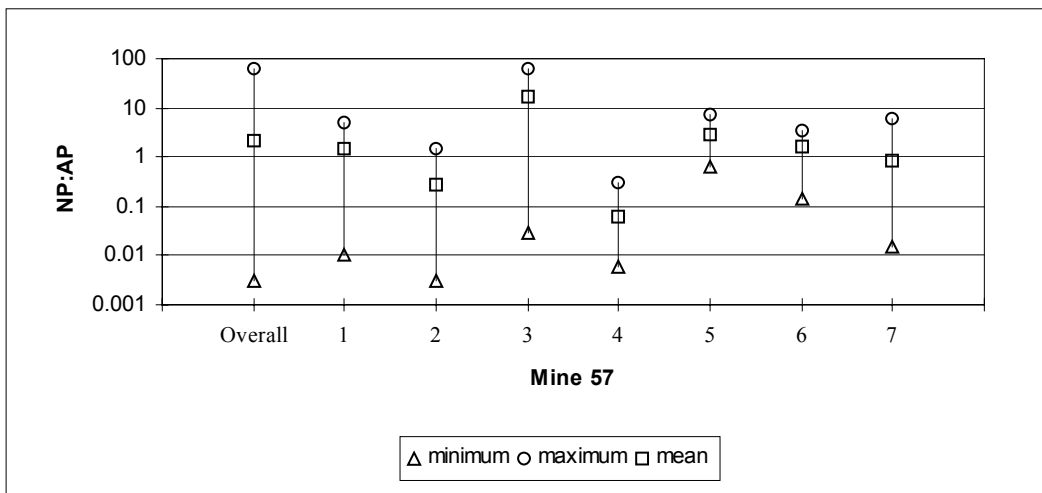
Figure 3.4c: Minimum, maximum and mean NP:AP for individual waste rock units at Mine 57

Waste rock NP and AP data from epithermal deposits in the Toodoggone mining district are plotted in Figure 3.5a. A broad range in static prediction data from adjacent mine sites with similar mineralogy and lithology is recognized suggesting there is no correlation between NP and AP between the sites. This lack of correlation is also recognized in other mining districts in British Columbia. For example, Figure 3.5b is a plot of NP and AP for various deposit types from another mining district, the Iskut-Eskay Creek. The lack of any NP-AP correlation between sites suggests that, although it may be appropriate at new sites to consider neighbouring sites prediction data as a guideline to the sampling program or methodology, direct comparison between the sites may not provide a true indication of the ARD potential. Differences between sites can exist due to different geology, lithology/mineralogy, alteration and weathering. Differences between sites can also exist due to the use of different static prediction tests. Lawrence et al (1994) and Lawrence and Wang (in prep) report that the measured NP can vary significantly for a sample depending on either the static test used or the procedural variations in the same test.

Paste pH and Waste Characterization

Paste pH (the pH of a paste made from mixing finely ground sample with water) is often used as an initial screening tool in waste characterization studies and its use is recommended in the British Columbia ARD guidelines (Price and Errington, 1995). For example, materials with a paste pH less than 3.5 will be considered a potential source of ARD while samples with either more then 0.3 wt% sulphide-S or a paste pH less than 5.0 would require further testing (Price and Errington, 1995). Ferguson and Morin (1992) plot the NP:AP ratio versus the paste pH and suggest that paste pH measurements can infer NP:AP ratios, thereby indicating the ARD
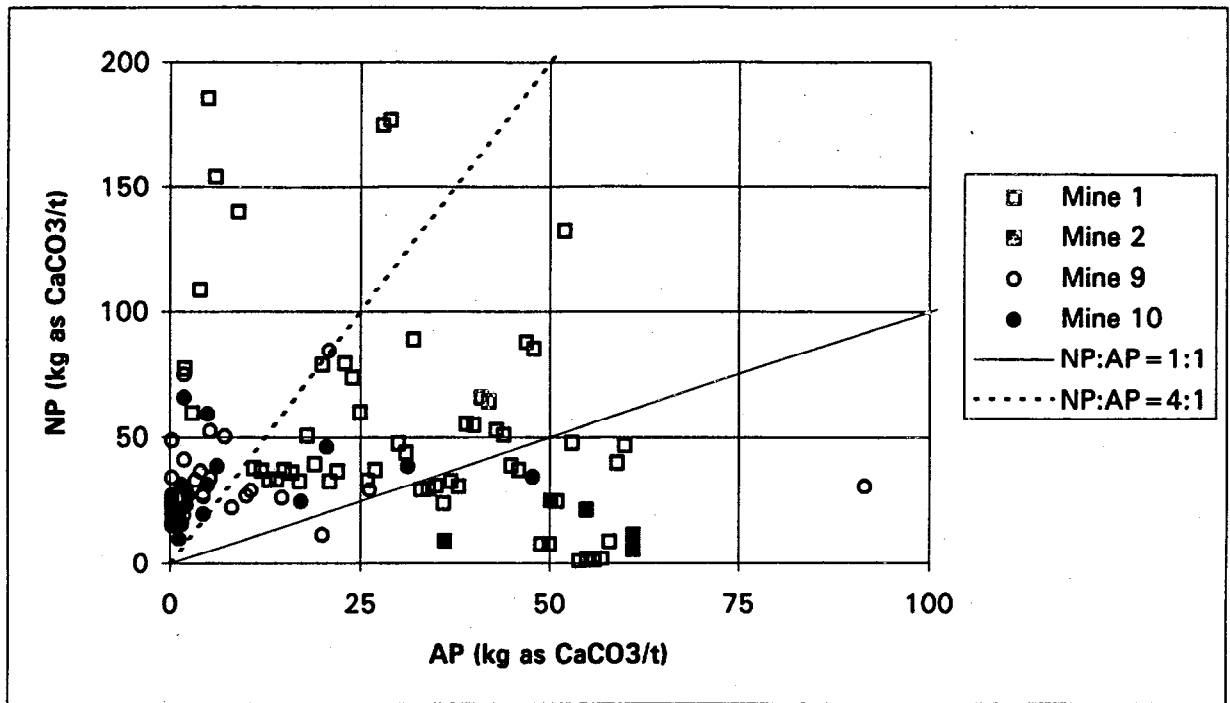
Figure 3.5a: NP and AP data for epithermal deposits in the Toodoggone Mining District
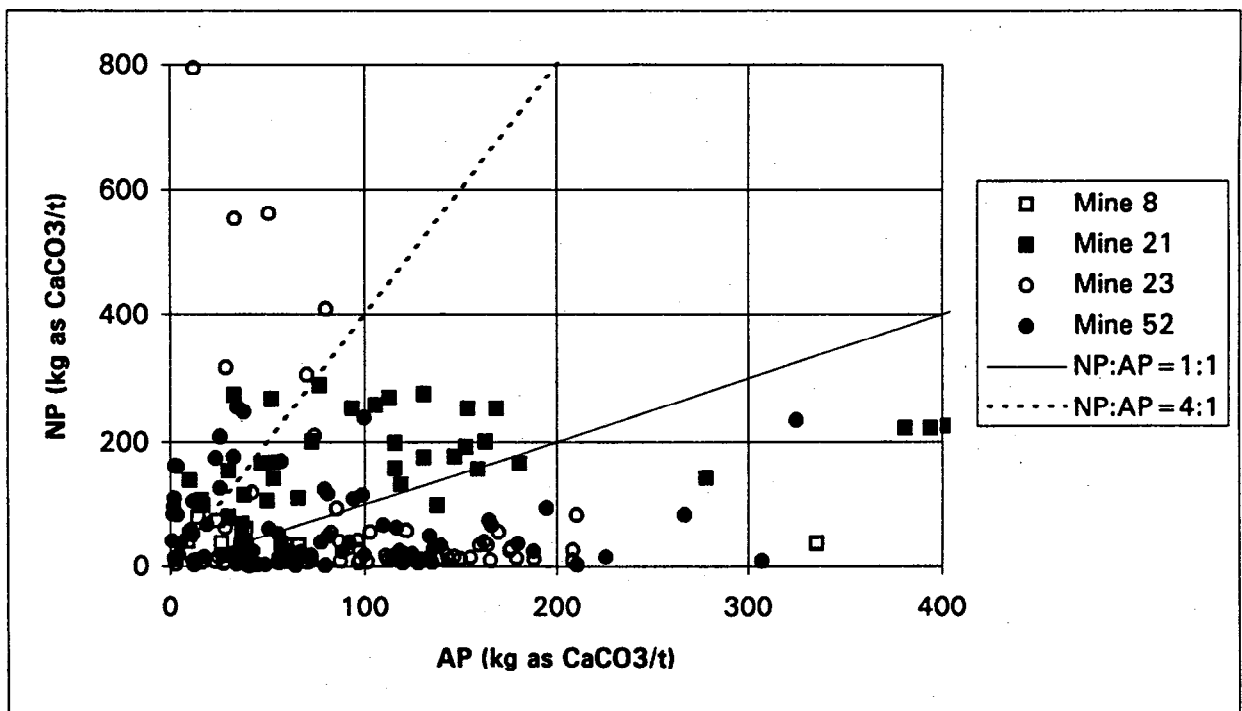
Figure 3.5b: NP and AP data for all deposit types in the Iskut-Eskay Mining District

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potential. Plots of NP:AP versus paste pH for DBARD data, grouped by deposit type, are presented in Figures 3.6 (a to f). Skarn deposit data have not been plotted as there is minimal data available. The samples with paste pH values below 7.0 generally have NP:AP ratios less then 4:1, with exceptions for sedex and tailings. Such correlation allows for a quick, relatively inexpensive technique to approximate the NP:AP ratio based on the field measurements of paste pH. These correlations may not exist at all sites and would need to be identified and calibrated for a site by initially collecting sufficient samples to characterize the paste pH and NP:AP for the individual waste units.

Statistical analysis of NP:AP and paste pH allows for a further quantification of their relationship. If the dependent variable is defined as the paste pH and the independent is the NP:AP ratio, distribution plots of the data (not shown) would indicate that the distribution is not normal but skewed. The data, therefore, can be transformed to a normal distribution by converting to its natural logarithm. Using SYSTAT, regression analysis determined the best fit equation in the general form: $\ln(\text{paste pH}) = b_0 + b_1 \ln (\text{NP:AP})$. These best fit equations are included in Figure 3.6 (a to f).

Static Prediction and Lithogeochemistry

To investigate the relationship between static prediction data and lithogeochemistry, DBARD data was examined to determine if either whole rock chemistry or carbon dioxide content correlate with NP determination. Claridge and Downing (1993) noted a correlation between neutralization potential and calcium content at the Windy Craggy deposit, northwestern British Columbia, and suggested that assay data can be used to estimate the NP. Graphs of
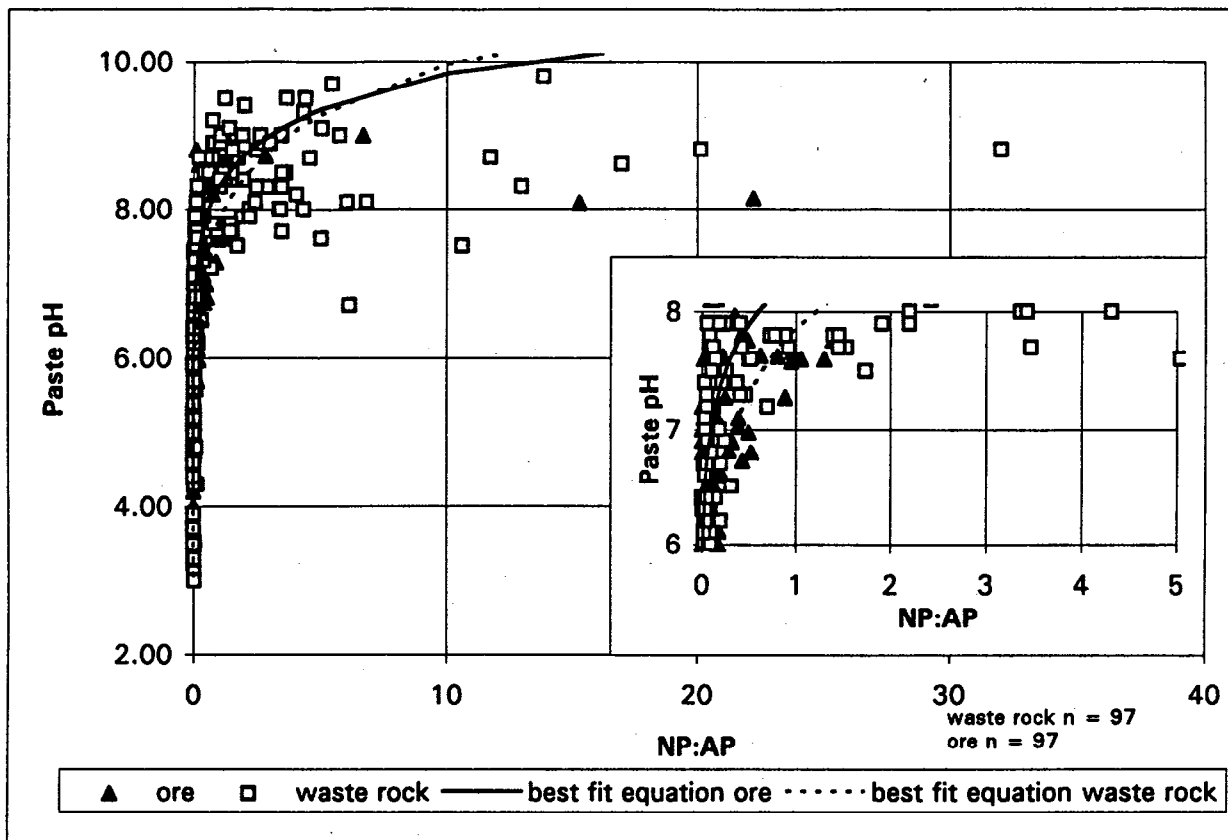
Figure 3.6a: Paste pH and NP:AP data for epithermal deposits
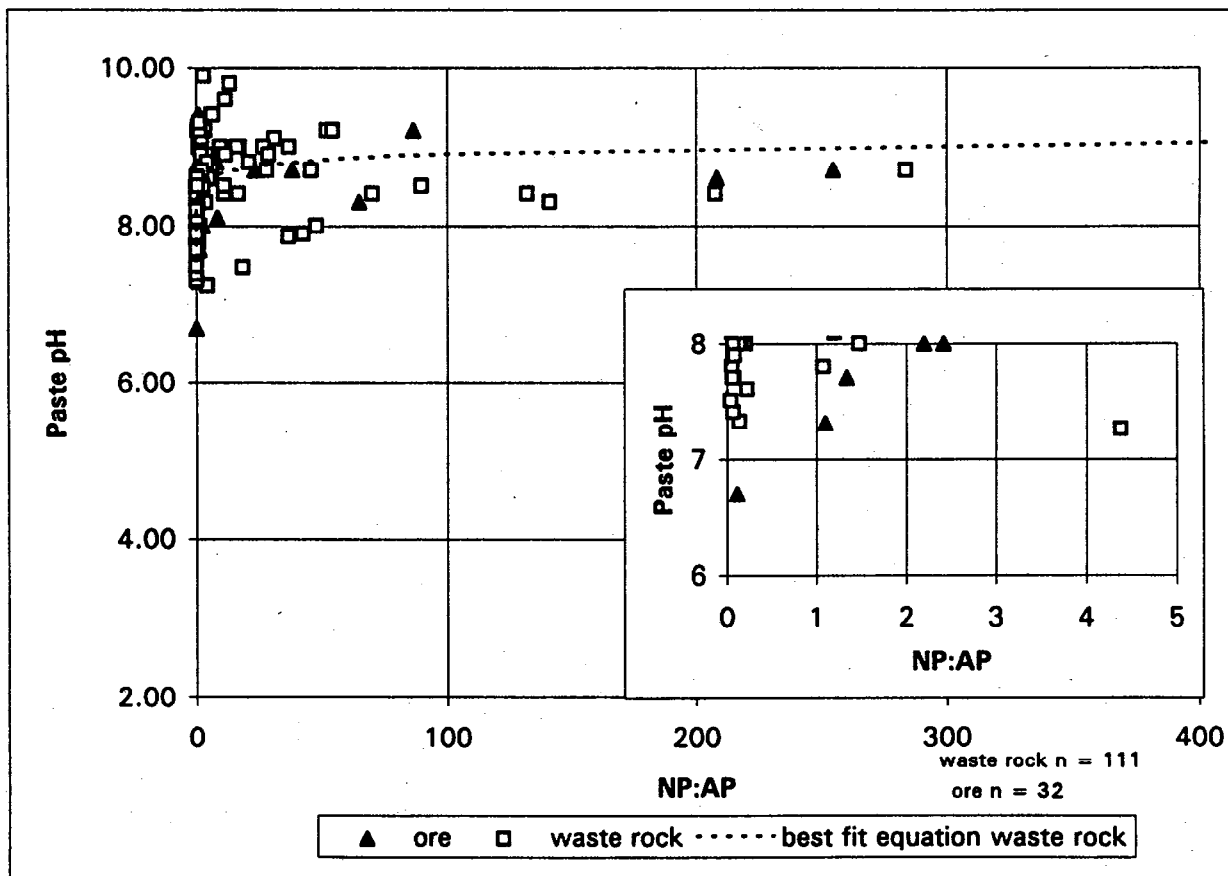
Figure 3.6b: Paste pH and NP:AP data for mesothermal deposits

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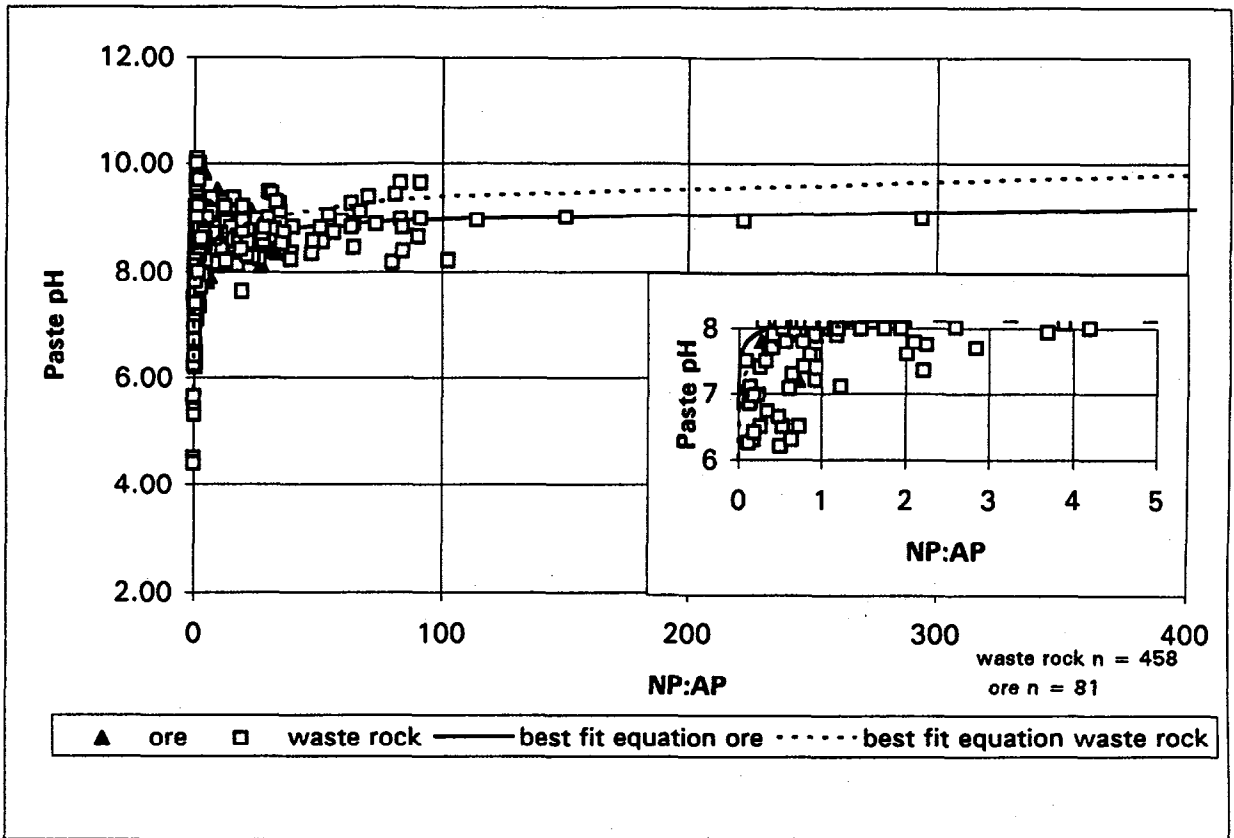
Figure 3.6c: Paste pH and NP:AP data for porphyry deposits
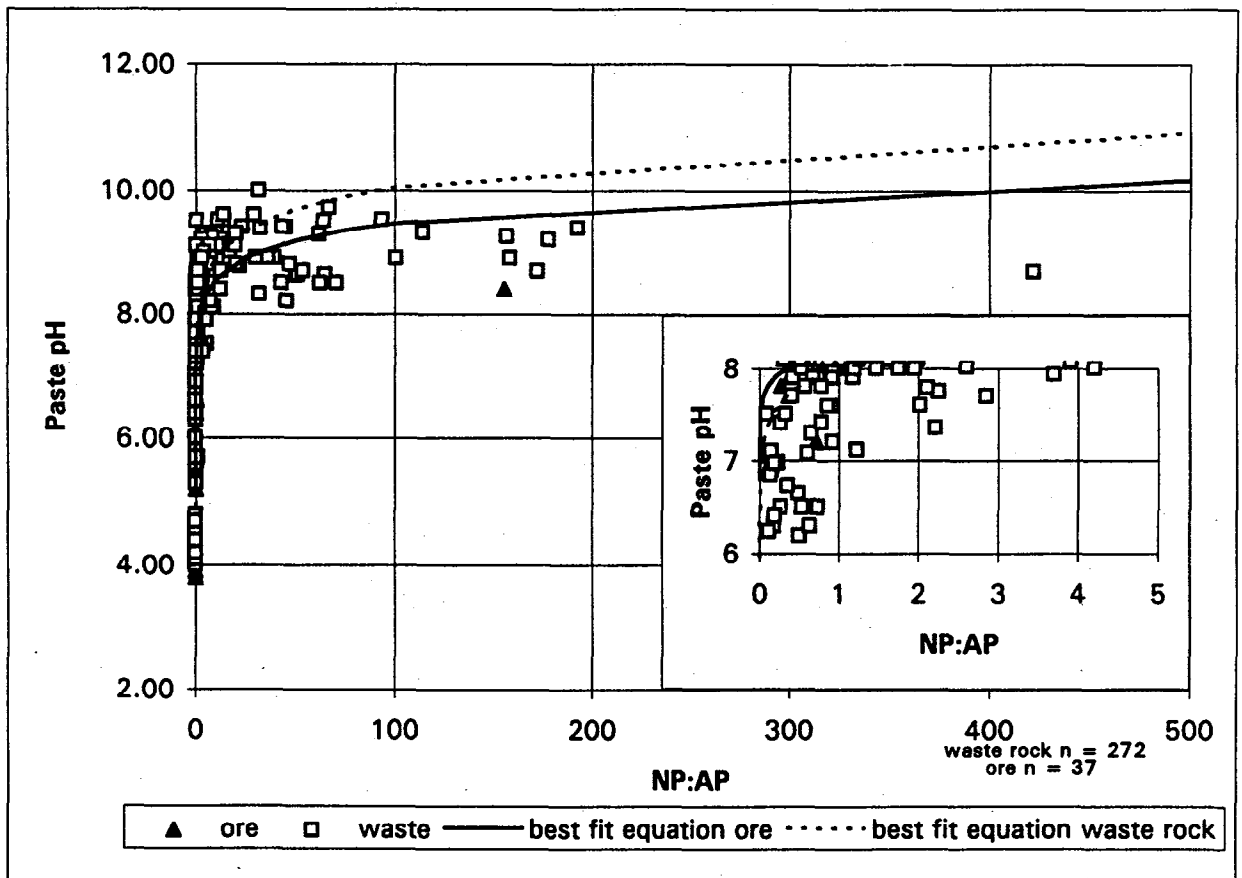
Figure 3.6d: Paste pH and NP:AP data for VMS deposits

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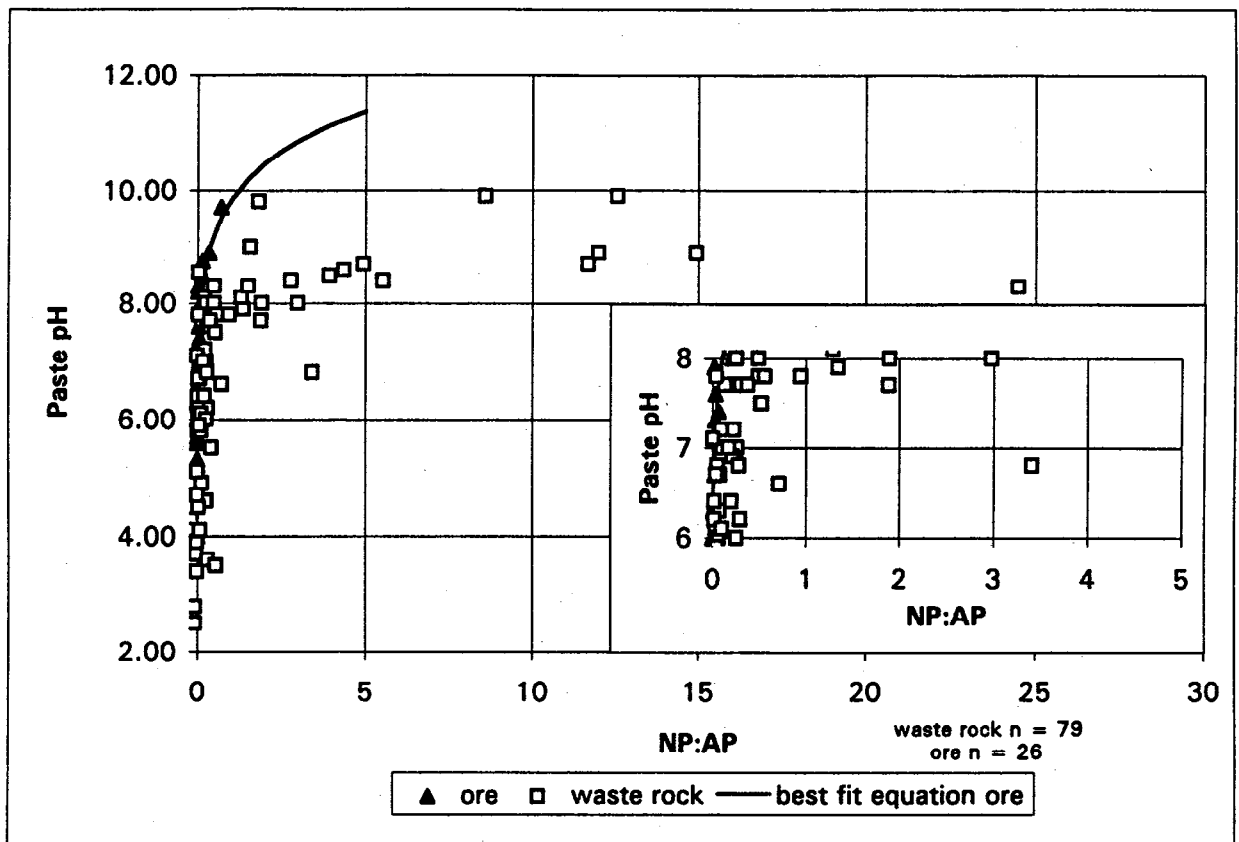
Figure 3.6e: Paste pH and NP:AP data for sedex deposits
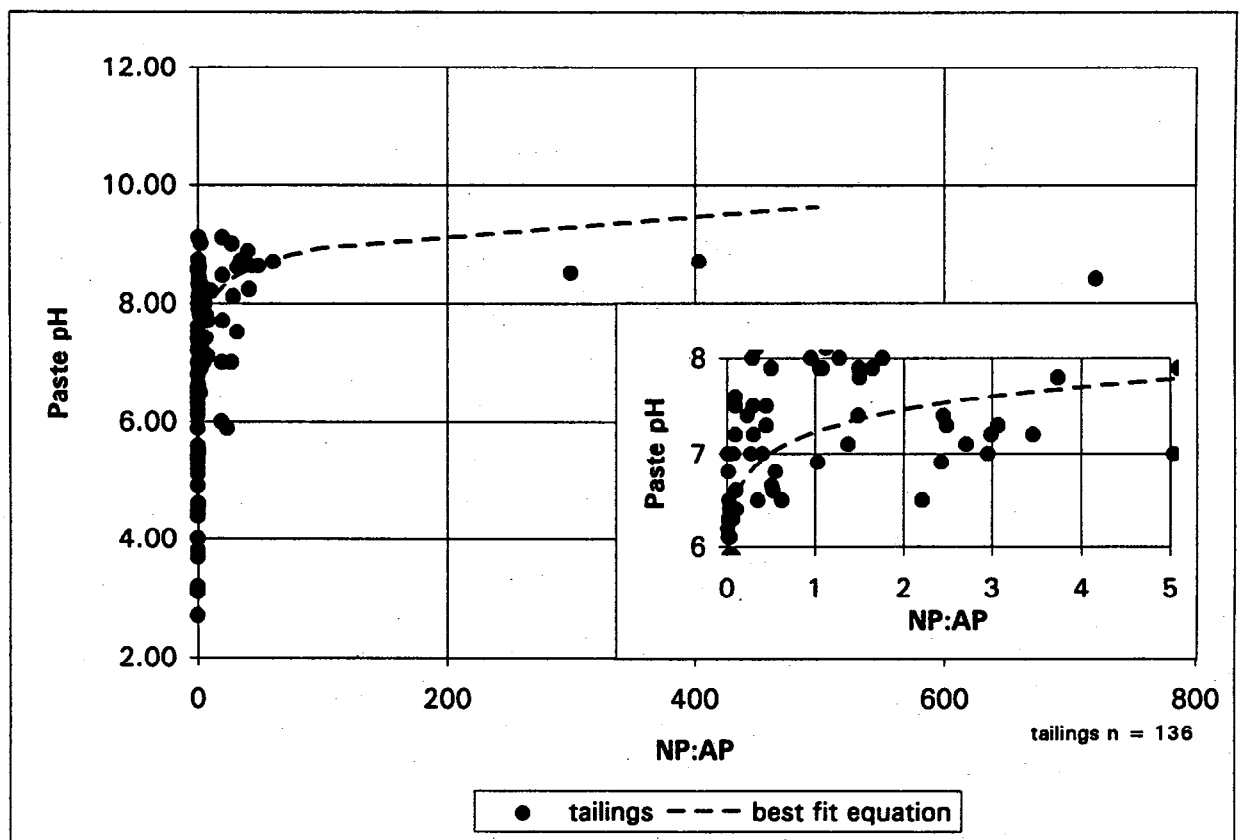
Figure 3.6f: Paste pH and NP:AP data for tailings

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calcium, magnesium, sodium, potassium, aluminum and iron (ppm) and NP were generated using DBARD data. Calcium plus magnesium versus NP is presented in Figure 3.7a (tailings) and 3.7b (waste rock), with the results supporting the findings of Claridge and Downing. In general, there are trends between NP and calcium and magnesium with an NP value of 75 to 100 kg $CaCO_3$/t dividing these data into groups. Other data available in DBARD would suggest that these trends are due to the mineralogy of the sample. The first correlation with NP (labeled A, Figure 3.7a, b) occurs in samples with a higher magnesium content than calcium. The lithologic description extracted from the data sources indicates that these samples have more mafic minerals (e.g. greenstones, pyroxenites). The second correlation (labeled B, Figure 3.7a, b) occurs in samples containing a higher calcium content than magnesiumn. The lithologic description indicates that these samples have more felsic and carbonate minerals. A third trend, presented in Figure 3.7a inset, occurs at NP values less than 100. Sodium, potassium, iron and aluminum do not correlate with NP (not presented).

The carbon dioxide content of samples has been analyzed in order to determine the carbonate content of the sample and its correlation to NP (Morwijk Enterprises Ltd., 1992; Lister, 1994; Lawrence and Wang, in prep). Graphs of NP and CNNP (carbon dioxide NP) for waste rock and tailings are presented in Figure 3.8a, b and indicate that there is a correlation between NP and CNNP. Samples with NP greater than CNNP suggests the presence of other non-carbonate minerals contributing to NP (Lapakko, 1994; Lawrence and Wang, in prep). Samples with CNNP greater than NP, for example data from Mine 43 (Figure 3.8b), suggests either the presence of iron carbonates (siderite) that contribute to the CO_2 determination but are unreactive in the static prediction tests (Morwijk, 1992) or the presence of carbon, not within

Figure 3.7: Calcium plus magnesium content and NP for a) tailings and b) waste rock samples in DBARD. Line A is the relationship between NP and magnesium rich lithologies and line B is the relationship between NP and calcium rich lithologies. A third trend in the inset, is the realtionship at NP values less than 100.

Figure 3.7a: Calcium plus magnesium content and NP for tailings samples in DBARD
(mines are grouped by deposit type)
Line A is relationship between NP and magnesium rich lithologies and B is
the relationship between NP and calcium rich lithologies. A third trend in the
inset, is the relationship at NP values less the 100.
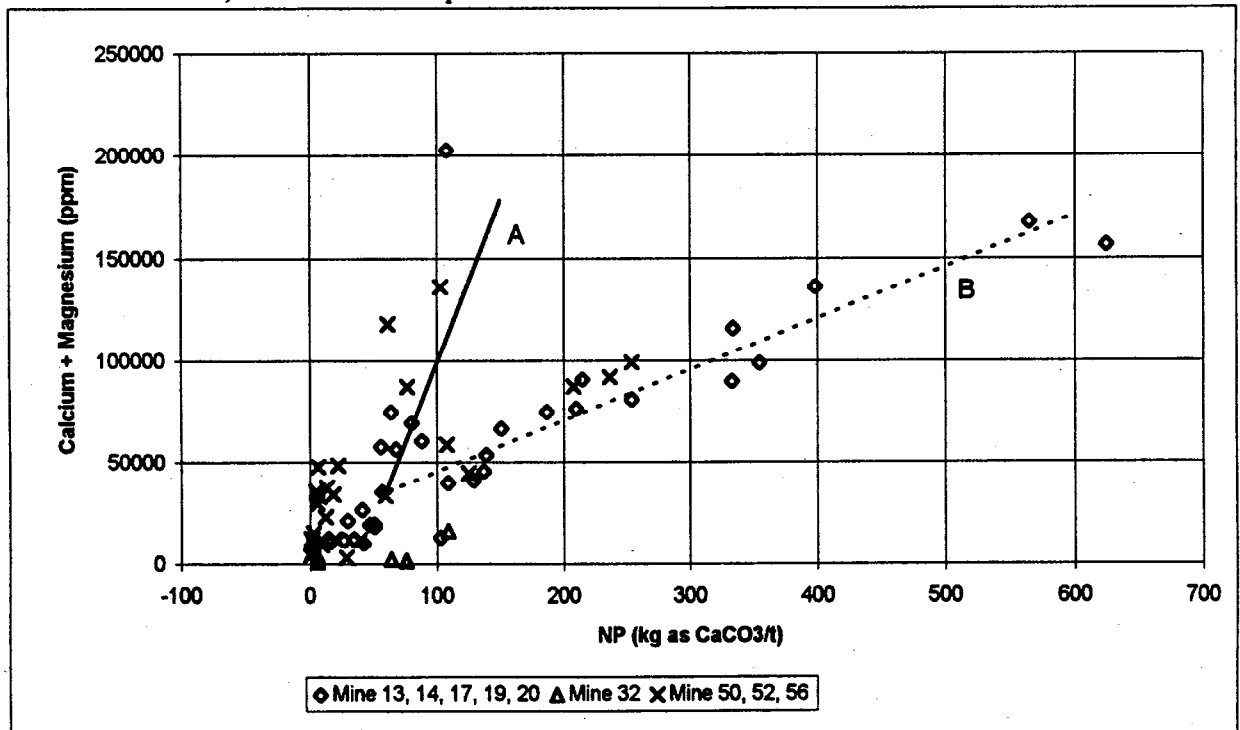
Figure 3.7b: Calcium plus magnesium content and NP for waste rock samples in DBARD
(mines are grouped by deposit type)
Line A is relationship between NP and magnesium rich lithologies and B is
the relationship between NP and calcium rich lithologies.
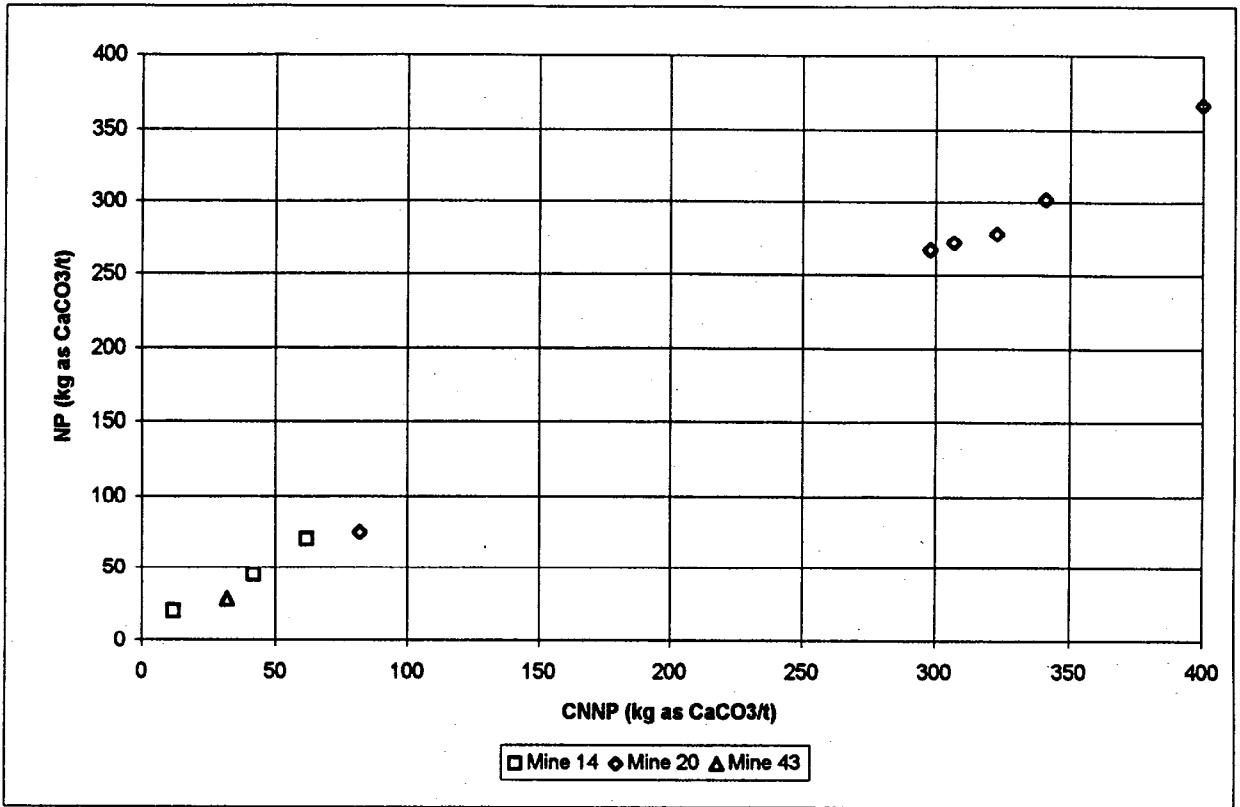
Figure 3.8a: NP and CNNP for tailings samples in DBARD
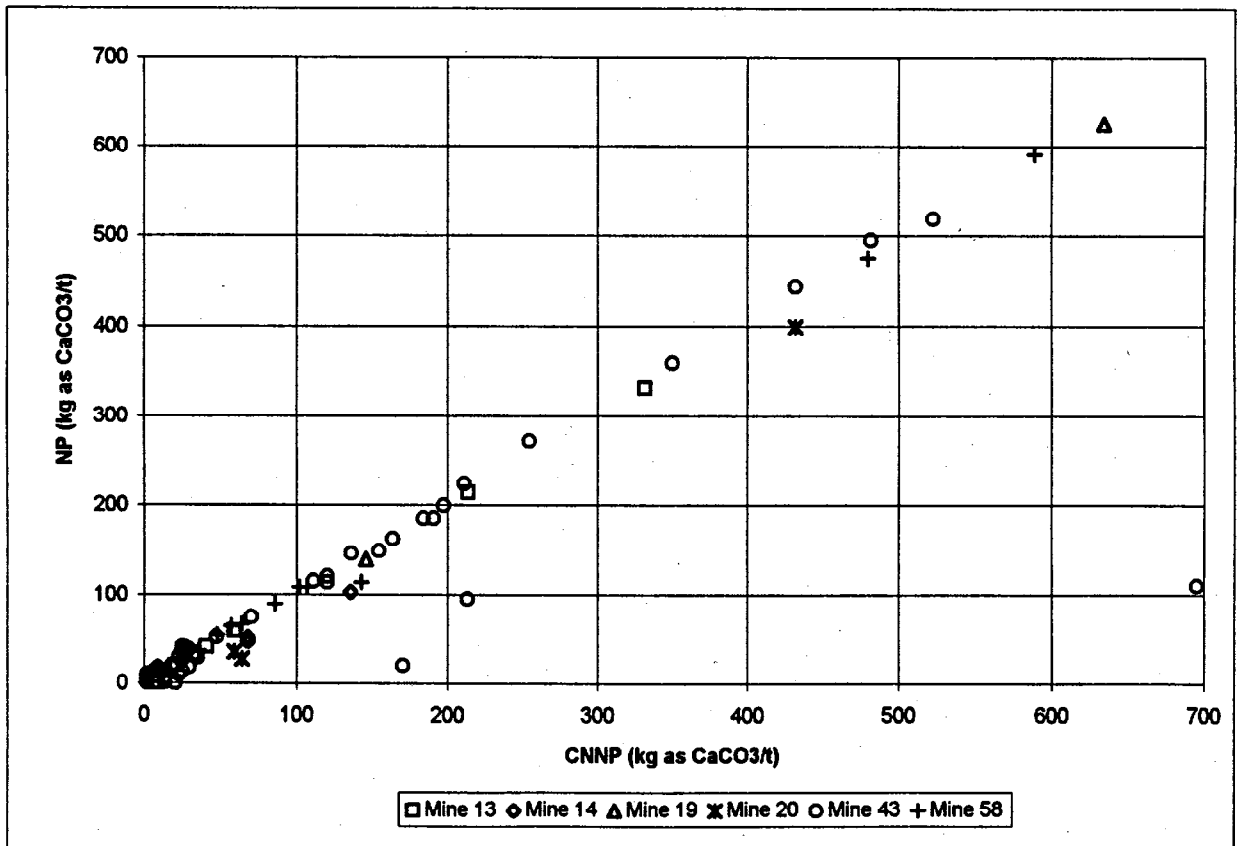
Figure 3.8b: NP and CNNP for waste rock samples in DBARD

carbonate minerals, but contributing to the CO_2. Measuring inorganic and organic carbon content in a sample can be completed by various laboratory methods and these methods currently tend not to be reported. Therefore, without knowing how CO_2 content has been measured, it is difficult to assess the differences between it and NP.

Other considerations in analyzing the static test data include NP variation with static test method for the same lithologic unit at a site, and also how static test data varies with sampling density and interval. Lawrence and Wang (in prep) have demonstrated that the different static test methods, when applied to the same sample, may result in a range of NP values. Brady et al (1994) determined that sample interval and drill hole density at a site affected the variation and range of ARD prediction data. However, this data are not available in DBARD since many sites use only one static prediction method and sampling density and interval tends not to be reported. For these reasons, these other considerations cannot be assessed.

3.3.3   KINETIC TEST DATA

The focus of simulated field weathering tests has been to confirm the interpretation of the static tests, to determine the rate and temporal variation of reactions contributing to ARD, and to test proposed control options (BC AMD Task Force, 1989). In DBARD there are eight mine sites with kinetic and corresponding static prediction data.

Kinetic prediction tests generally determine the rate of sulphide mineral oxidation by the occurrence of sulphate in the leachate assuming: all oxidized sulphur is released to solution; all the sulphur is oxidized completely to sulphate; and precipitation of gypsum or other sulphate minerals does not limit the sulphate concentration. Sulphide oxidation is often expressed on a cumulative basis as total mg SO_4/kg and rates are calculated on either a weight (e.g. mg SO_4/kg/week) or a surface area basis (e.g. mg SO_4/m^2/week). For this thesis, sulphide oxidation has been calculated on a weight basis only.

Another focus of kinetic tests has been to determine the rate of metal release to the environment. Analysis of aqueous metals in the test leachate indicate the rate at which metals are depleted from the sample, assuming all ions are released to solution and are not limited by precipitation. Metal depletion is commonly expressed on a cumulative basis as total mg/kg and rates are calculated on either a weight or surface area basis.

Rate calculations can also include a determination of the depletion of neutralizing minerals. This has not been a common component of kinetic testing until recently. NP depletion is an important consideration in ARD prediction and is dependent on the type of neutralizing minerals present (Morin, 1990b; Day, 1990). There is no general agreement as to the method of calculating NP depletion, but most methods assume either carbonate or silicate dissolution is the neutralizing reaction and that secondary mineral precipitation, mainly gypsum, is not limiting leachate concentration. Lapakko (1987, 1990) suggests that calcium and magnesium concentration in solution (mmoles/litre) can be used to identify the combined dissolution of carbonate and silicate minerals. Assuming only calcium carbonate minerals are available to neutralize, Bradham and Carrucio (1990) calculated NP depletion rates using calcium depletion rates (i.e. mg Ca/kg/week). White and Jeffers (1994) and White et al (1994) use calcium plus magnesium (from carbonate and silicate dissolution) leaching rates (as mg Ca+Mg/kg/week) to determine the NP depletion. Morin and Hutt (1994) and Morin et al (1995a, 1995b) use sulphide oxidation rates and molar ratios (ions from neutralizing mineral dissolution to sulphate ions) to determine the type and rate of neutralization. Calcium, magnesium, barium and strontium ions represent carbonate dissolution and calcium, sodium and potassium ions represent silicate dissolution. Morin and Hutt (1994) and Morin et al (1995a) suggest using the molar ratio of calcium to sulphate initially to identify either carbonate or silicate minerals as the neutralizing minerals with ratios between one and two representing carbonate dissolution and ratios less then one representing silicate dissolution. Another approach might be to consider sulphide oxidation rates and alkalinity measurements. However, NP depletion calculations based on alkalinity measurements do not represent the true rate since there are reactions occurring within the kinetic test cell that are not conserving alkalinity, as discussed in Chapter 2.

An important consideration of kinetic tests is the relationship with static prediction tests. In British Columbia, regulatory guidelines have been proposed that samples with NP:AP ratios from static tests between 1 and 4 have an uncertain ARD potential and require additional testing using kinetic techniques (Price and Errington, 1995). Those ratios below 1 are interpreted to have an ARD potential and those greater then 4 have no potential. Ferguson and Robertson (1994) propose a ratio between 1 to 2 as being uncertain. Given the expense and time

requirements to complete kinetic tests, it is important to determine what may be valid interpretation of static tests.

Analysis of the DBARD kinetic data focused on sulphide oxidation and NP depletion rates, the relationship between kinetic and corresponding static prediction data, and the time lag to ARD (Appendix 2). The kinetic tests in DBARD were carried out for a relatively short term, typically less then 20 weeks. Sulphide oxidation and neutralization reactions may not have established in this time period and will limit the interpretation and conclusions of these data.

The fifty-four kinetic tests in DBARD were divided into three groups based on the trend in pH during the test: type 1 (pH >5.0), type 2 (pH>5.0 decreasing to pH <5.0) and type 3 (pH<5.0). The pH value of 5.0 used to separate these tests is suggested by Morin et al (1995a) who identified kinetic tests with inert samples and low rates of acid generation with pH 5.0 in the leachate. The lowest pH measured during a test, which generally occurs towards the end of the test, was used as an indicator of neutral or acidic test conditions. Also, the highest measured pH, usually near the beginning of the test, determined if test conditions were initially neutral or acidic. On this basis, there are thirty-nine type 1, seven type 2, seven type 3 kinetic tests and one test that was initially acidic and then the pH rose to over 5.0 during the test.

The comparison of minimum pH measured during the kinetic test and AP indicates that acidic conditions can occur at AP values of 15 kg as $CaCO_3$/t, equivalent to 0.5% S (Figure 3.9a). The comparison of minimum pH measured and NP indicates that acidic conditions did not occur in samples at NP values greater than 75 kg as $CaCO_3$/t (Figure 3.9b). Relative to the Net NP, all the type 2 and 3 tests have negative values (Figure 3.9c) and relative to the NP:AP ratio, these same tests have values less then 1.0 (Figure 3.9d). For both Net NP and NP:AP there are samples with values below 0.0 and 1.0, respectively, that remained alkaline throughout the kinetic test which may reflect the short time-frame of the tests, the time lag to acidic conditions,
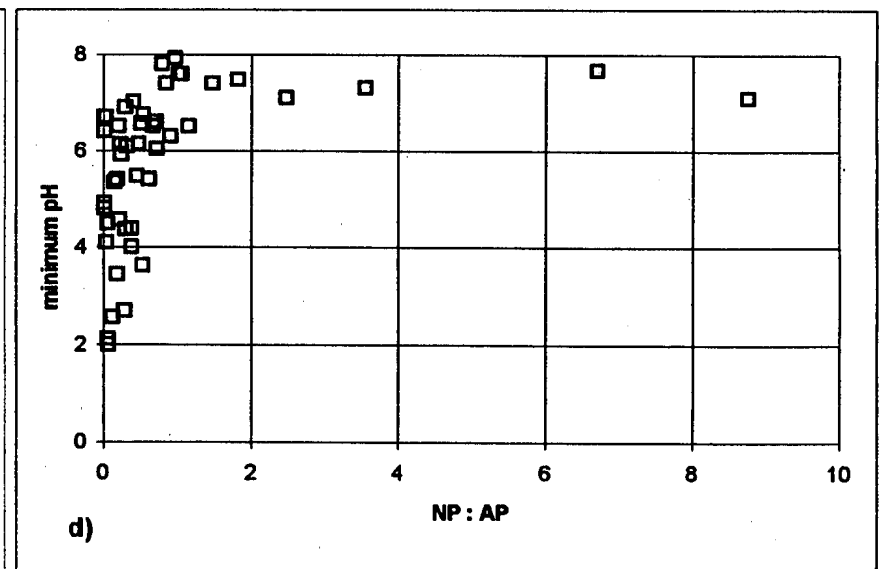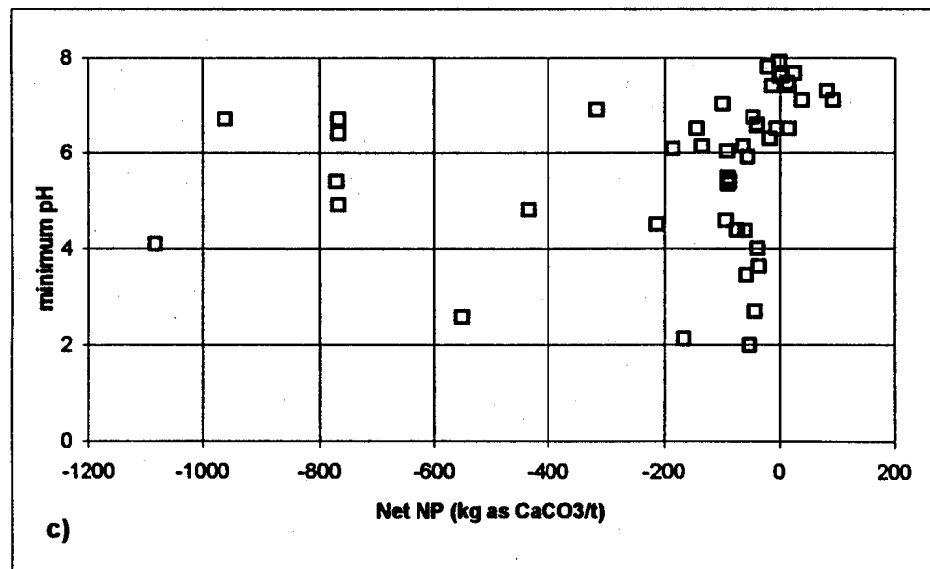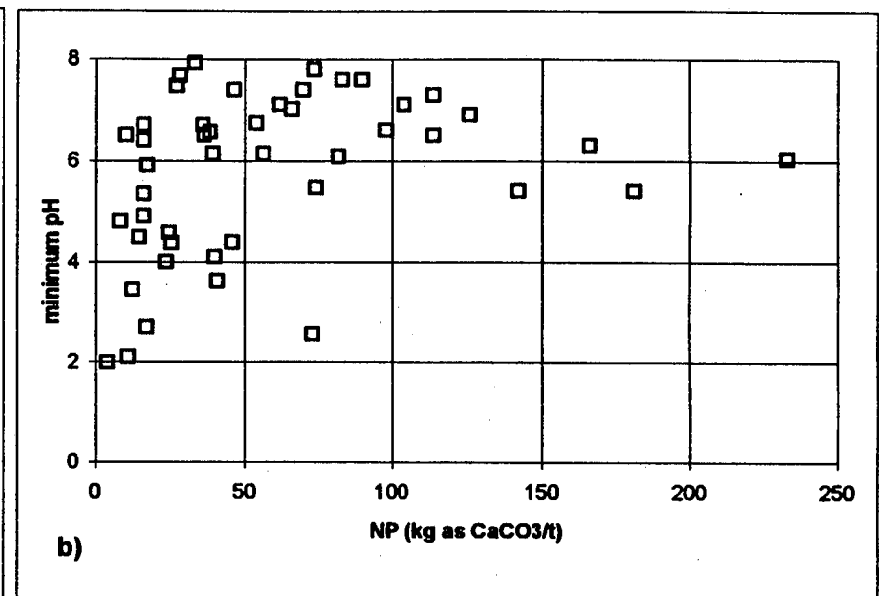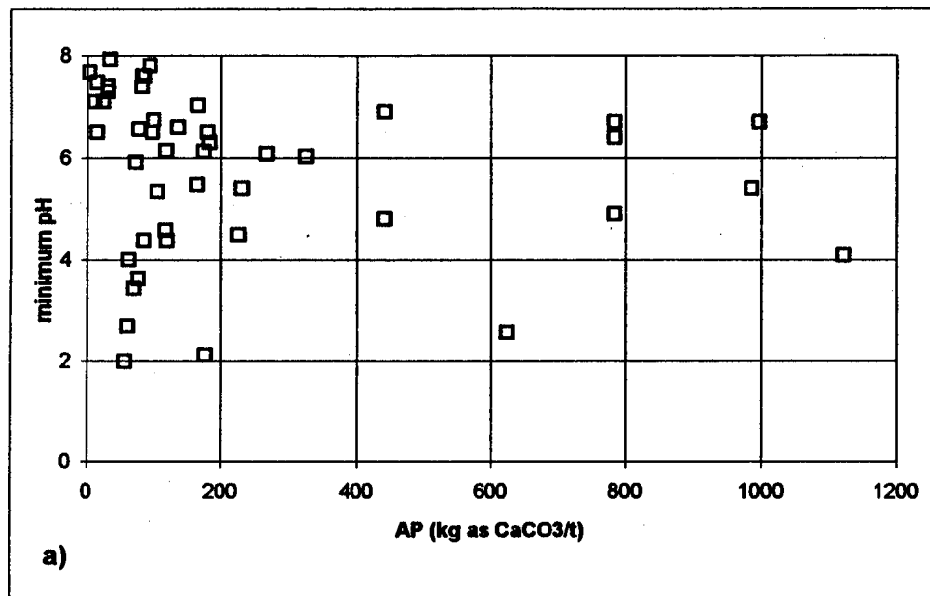
Figure 3.9: Minimum pH from kinetic test data and a) AP, b) NP, c) Net NP and d) NP/AP

or over/under estimated values for the static prediction data. The implication of the lack of relationships is that the static prediction data does not provide an indication of the minimum pH during the kinetic test.

Rates of Sulphide Oxidation

Kinetic prediction tests generally determine the rate of sulphide mineral oxidation by the occurrence of sulphate in the leachate. The rate of sulphate production represents the rate of sulphide oxidation and, for the kinetic cells considered in this thesis, are summarized in Appendix 2. Overall, the mean rates of sulphate production range from 9 to 1290 mg SO_4/kg/wk and those samples with the highest average rate generate the lowest pH conditions (Figure 3.10). When subdivided by deposit type (included in Appendix 1), there is no apparent relation between sulphate production rate and geologic model (Figure 3.10). It is probable that these rates are related to differences in the type, form, and abundance of the sulphides in the sample. Unfortunately, details of this nature have not been documented in DBARD. Differences may also arise from differing test conditions such as leaching cycle and temperature.

The comparison between sulphide oxidation rate and AP (Figure 3.11a) reveals sulphide oxidation rate is independent of AP. The highest sulphide oxidation rate was not from the sample with the highest AP suggesting that the highest sulphur content does not necessarily generate the highest sulphide oxidation rates and that other mineralogical factors are determining the overall oxidation rate. Low rates (< 50 mg/kg/week) of sulphide oxidation correspond with positive values of Net NP and higher rates (> 100 mg/kg/week; with one exception) correspond with negative Net NP values (Figure 3.11b). The highest sulphide oxidation rates were not
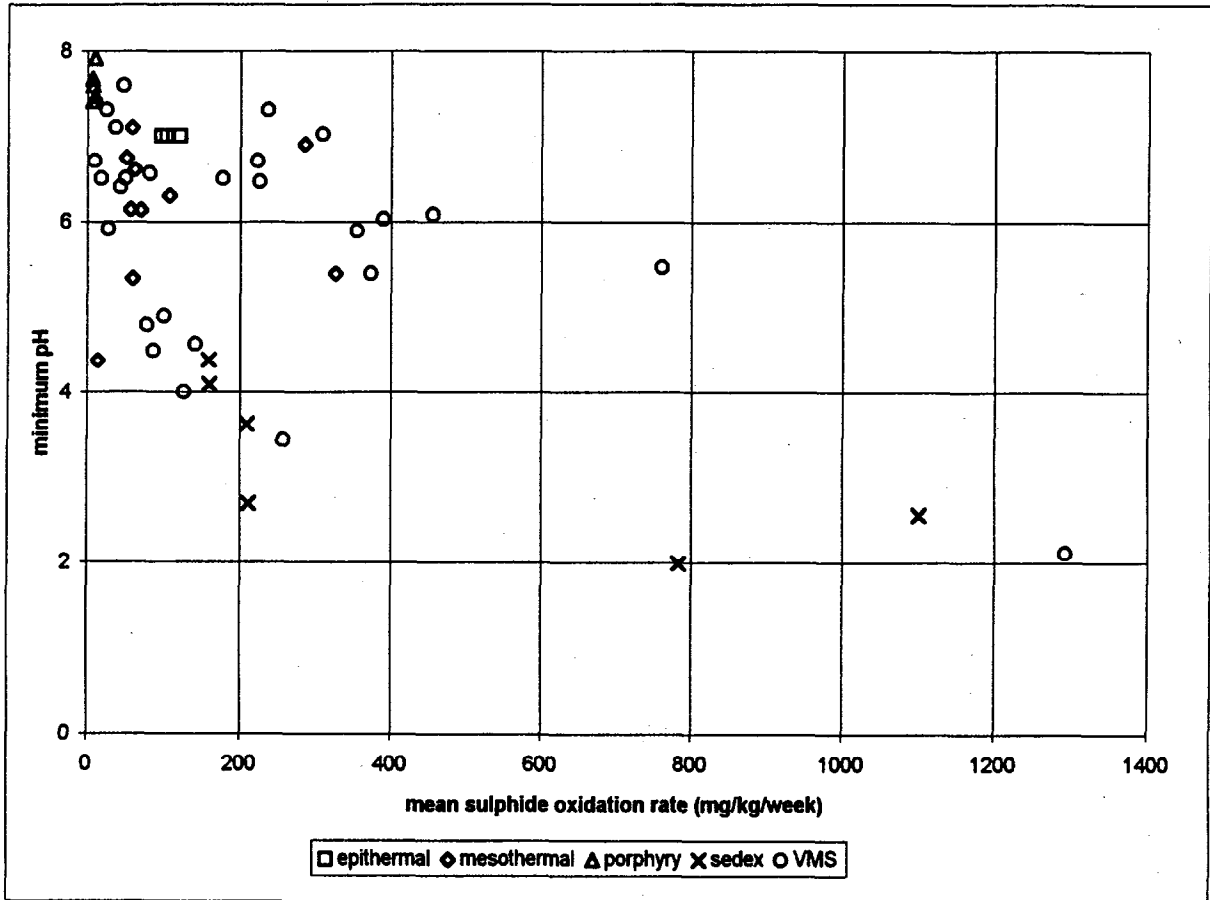
Figure 3.10: Minimum pH and mean sulphide oxidation rate for kinetic test data in DBARD
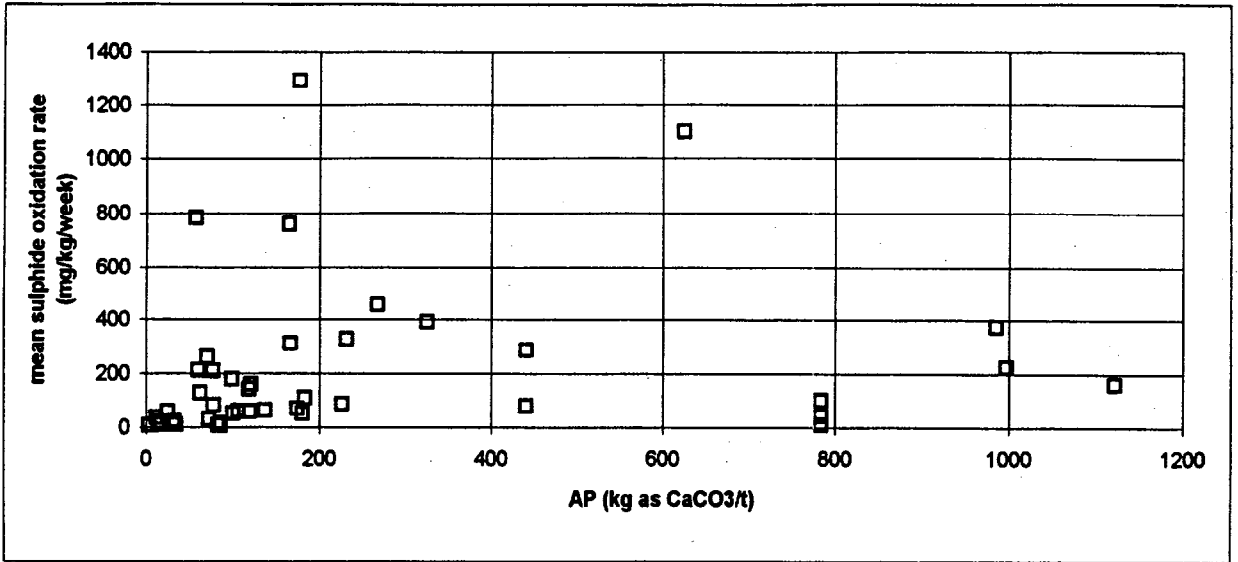
Figure 3.11a: Mean sulphide oxidation rate and AP for kinetic tests in DBARD
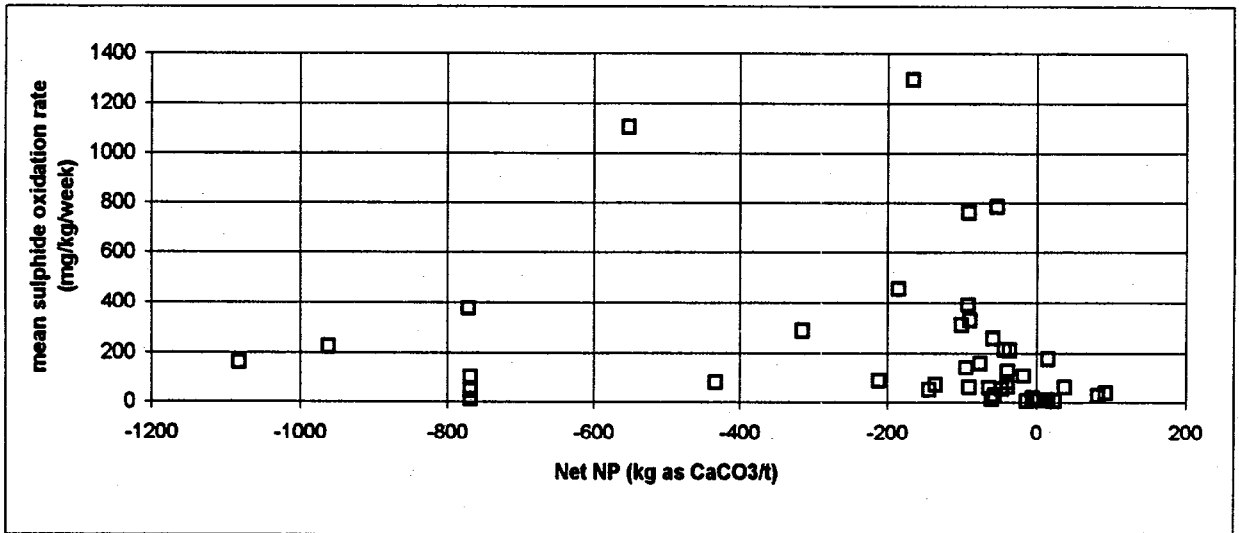
Figure 3.11b: Mean sulphide oxidation rate and Net NP for kinetic tests in DBARD
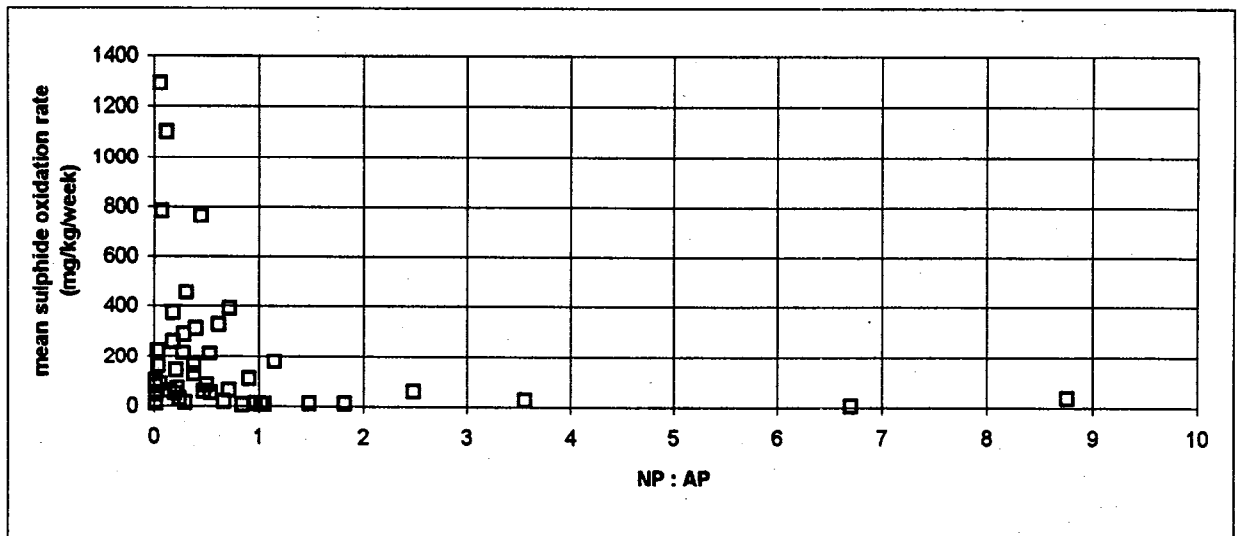
Figure 3.11c: Mean sulphide oxidation rate and NP:AP for kinetic tests in DBARD

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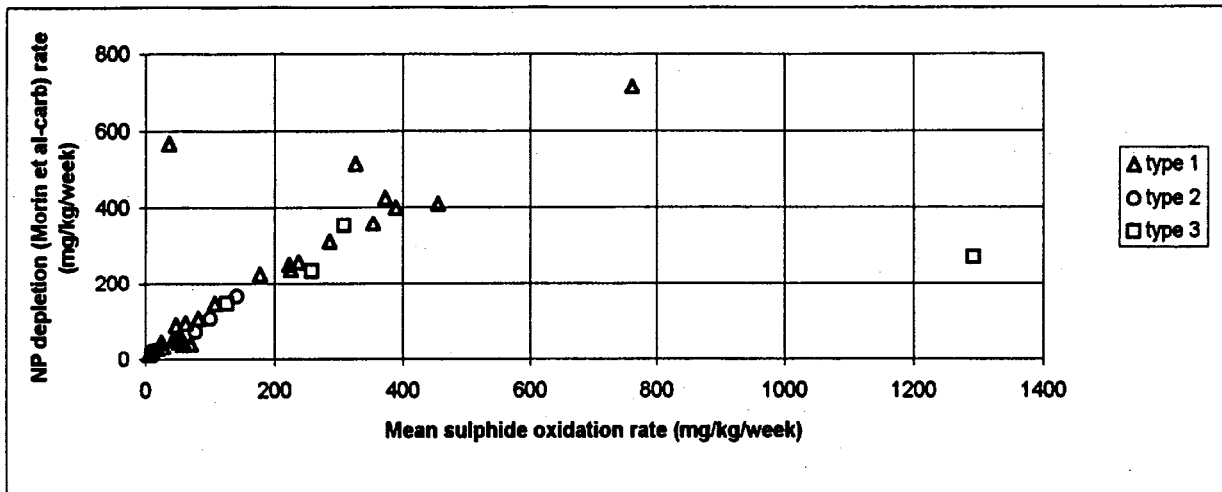
Figure 3.12a: Mean sulphide oxidation rate and NP depletion rate using
Morin et al (1995a) carbonate ratio
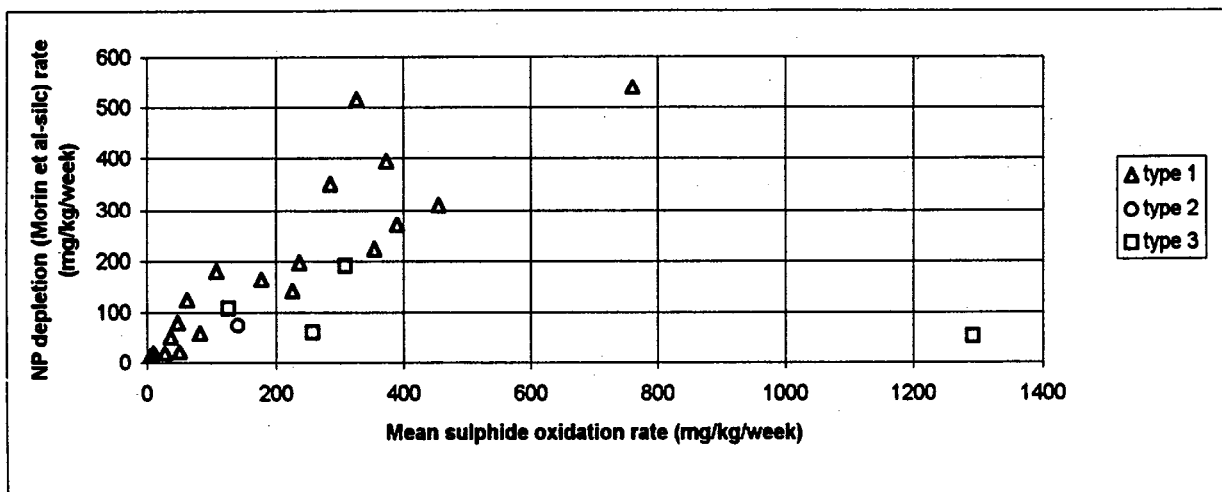
Figure 3.12b: Mean sulphide oxidation rate and NP depletion rate using
Morin et al (1995a) silicate ratio
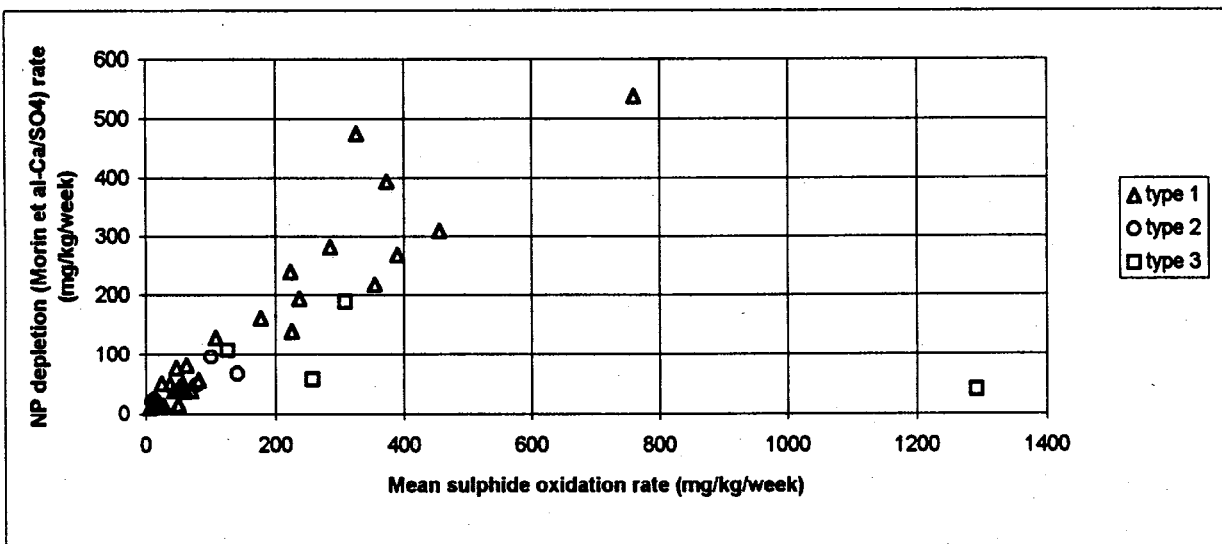
Figure 3.12c: Mean sulphide oxidation rate and NP depletion rate using
Morin et al (1995a) calcium to sulphate ratio

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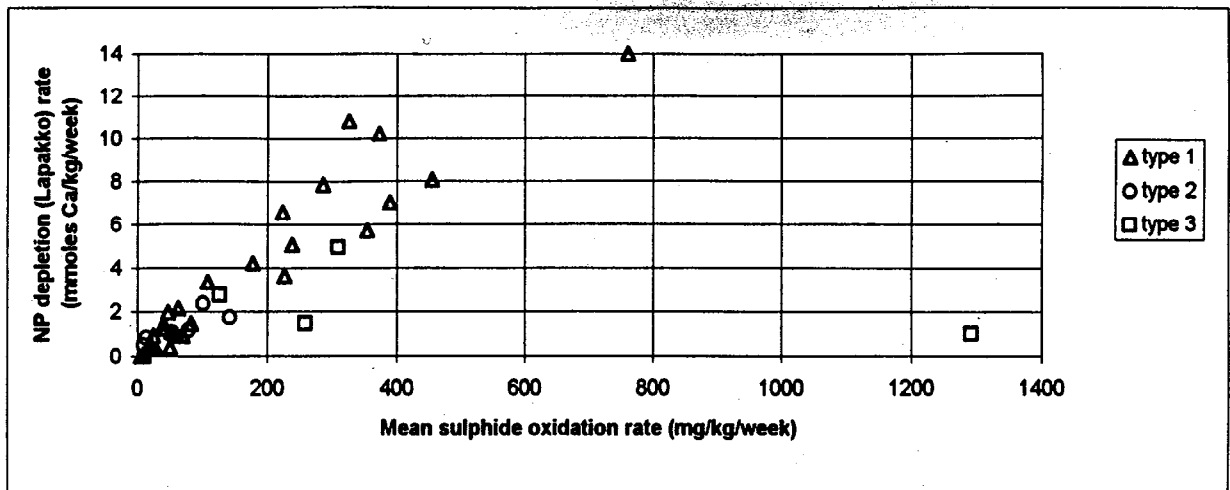
Figure 3.12d: Mean sulphide oxidation rate and NP depletion rate using
Lapakko (1987, 1990)
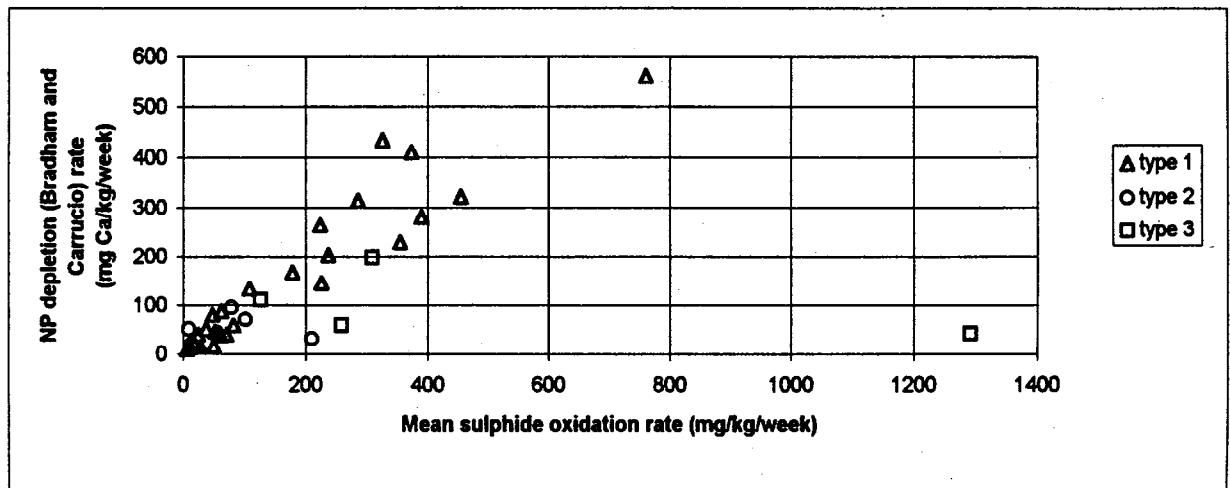
Figure 3.12e: Mean sulphide oxidation rate and NP depletion rate using
Bradham and Carrucio (1990)
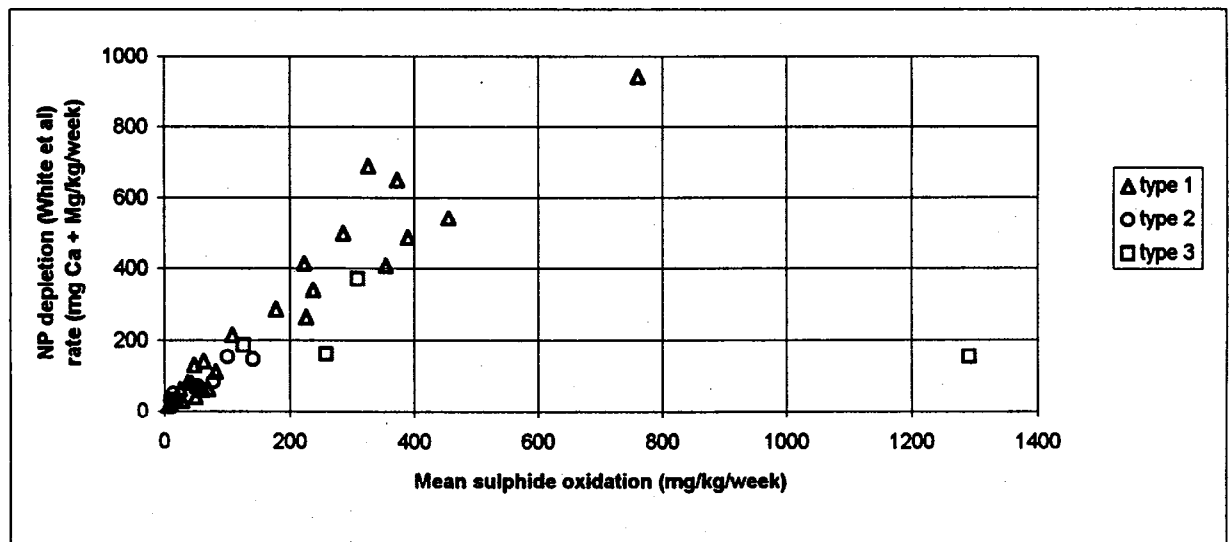
Figure 3.12f: Mean sulphide oxidation rate and NP depletion rate using
White and Jeffers (1994) and White et al (1994)

generated by the samples with the most negative Net NP value suggesting that the largest difference between NP and AP does not infer the highest sulphide oxidation rates. The highest sulphide oxidation rates occur in samples having the lowest NP:AP ratios (Figure 3.11c). However, even at ratios close to zero the sulphate production rate extends over four orders of magnitude. Morin et al (1995a, 1995b) have documented similar findings based on the analysis of their data. Thus, there is little correlation between the rate of sulphide oxidation determined from kinetic tests and the Net NP and NP:AP values from static tests.

Rates of Neutralization

The rate of neutralization represents the consumption of NP of a sample. As discussed previously, proposed methods for determining this depletion rate can be based on: 1) metal leaching rates for calcium and/or magnesium (Lapakko, 1987, 1990; Bradham and Carrucio, 1990; White and Jeffers, 1994; White et al, 1994); and 2) molar ratios and sulphide oxidation rates (Morin et al, 1995a, 1995b). For comparison, the rates determined by these methods are converted to calcite equivalents, that is mg $CaCO_3$/kg/week or moles $CaCO_3$/kg/week, and presented in Appendix 2. Overall, the mean rates of NP depletion range from 9 to 700 mg $CaCO_3$/kg/week.

An important consideration for sulphide oxidation rates and NP depletion rates is how the pH conditions within the kinetic cell change over time: Are pH changes due to depleting NP past a critical level or are sulphide oxidation rates exceeding neutralizing mineral dissolution? Figure 3.12 (a - f) presents the mean NP depletion rate, calculated by the various methods referenced

above, versus the mean sulphide oxidation rate and grouped according to the pH classification of the cells (Type 1, 2 or 3). In general, the pH conditions within the tests are independent of the two rates. Cells classified as type 2 have relatively low sulphide oxidation and NP depletion rates. The method of Morin et al (1995a, 1995b; Figure 3.12a, b, c) indicate a correlation between NP depletion and sulphide oxidation since the NP calculations are based on the rate of oxidation. Methods based on metal leaching data (Lapakko, 1987; Bradham and Carrucio, 1990; White and Jeffers, 1994; White et al, 1994), that are calculated independent of the oxidation rates, also indicate a correlation between NP depletion and sulphide oxidation (Figure 3.12e, f, g) suggesting that NP depletion rate corresponds to sulphide oxidation rate and the resulting decrease in pH. This suggests that NP depletion rates can be calculated by any of these proposed methods. It should be noted that the kinetic tests included in this analysis were run for relatively short terms. The initial period of kinetic tests are characterized by elevated and fluctuating data due to flushing of existing oxidation/dissolution products, cation exchange processes, oxidation/dissolution reactions and many other reactions that lead to "noisy" data. For this reason, it is unknown if the kinetic tests in DBARD have reached conditions such that the leachate chemistry is the result of predominant oxidation and dissolution reactions.

The calculation of these sulphide oxidation and NP depletion rates make it possible to calculate an estimated time required to deplete acid producing and neutralizing minerals in mine wastes. Lapakko (1987, 1990), Bradham and Carrucio (1990), White and Jeffers (1994) and White et al (1994) have completed laboratory testwork in which NP depletion, from carbonate dissolution only, coincided in time with decreasing pH conditions. The trend, in more recent waste characterization studies, is for longer term kinetic tests and additional consideration for the data interpretation may include the contributions from different minerals to acid generation and neutralization. Therefore, additional work is required to assess the accuracy of calculated mineral depletion rates and the validity of assumptions such as constant oxidation and dissolution rates over time. Acid generating and neutralizing minerals have variable composition and relative reactivity. This suggests that an individual ion, for example calcium, may be introduced to solution by dissolution of different minerals, for example calcite and plagioclase. Also, the dissolution rates of these minerals differ with plagioclase being slower then calcite and, over time, these differences may lead to neutralization by different minerals as well as different NP

depletion rates. A similar arguement can be made for the acid generating reactions since sulphides also exhibit different relative stability and oxidation rates (Ritchie, 1994; Kwong, 1995).

3.4 SUMMARY

The review of DBARD is summarized and discussed in the following.

1. As an initial approach, proposed mine sites can be compared with other mines that are in similar geologic or geographic settings. These comparisons are based on the assumption that the factors that affect acid generation are constant for the sites being compared. It is unlikely that deposits will be comparable because host rocks, mineralogy, alteration, structural elements and other non-geologic factors (e.g. physiography and climate) will be dissimilar. The review of DBARD has indicated that adjacent sites, or sites of similar geology, cannot be compared directly when determining ARD potential from static prediction data. However, experience from previous work at other sites could aid new sites in determining waste characterization programs.

2. Paste pH is used as an initial screening tool, in conjunction with the static prediction data, to interpret ARD potential. Paste pH may also provide an estimate of NP:AP values. This correlation between paste pH and NP:AP would need to be identified and established on a site specific basis with a consideration of the on-site geology, structural elements, alteration and weathering. If available, using field measurements of paste pH allows for a quick, relatively inexpensive technique to approximate the NP:AP ratio.

3. NP determination from static prediction tests correlates with sample geochemistry particularly the concentration of calcium, magnesium and carbon. A similar mineralogical dependence of AP is already applied in waste characterization by accounting for the different sulphur species present and determining AP from the sulphide-sulphur content. The review of DBARD indicates that an understanding of the sample mineralogy/lithology is necessary to aid in the interpretation of the static prediction data. Correlation between geochemistry and NP would need to be established on a site specific basis. The identification of "indicator" elements (i.e. ion concentration that correlate with AP or NP values) can be used to estimate

NP values from geochemical data. These indicator elements can also be used to characterize oxidation and neutralization reactions in kinetic tests.

4. Current interpretation of static prediction data includes that the lower the NP:AP value the higher the oxidation rate and, corresponding, lower pH. The review of DBARD indicates that minimum pH values do not correlate with either static prediction data or the mean rates of sulphide oxidation. Also, sulphide oxidation rates are not predicted by static prediction data. These findings suggest that there is no relationship between the static and kinetic prediction data as currently interpreted. An improvement to the static and kinetic data interpretation would be the consideration of mineralogical components that are contributing to the ARD potential. Given the short time frame of the kinetic tests in DBARD, it is also important to establish kinetic cells as soon as possible to allow stable conditions to be established and the maximum amount of time for leaching.

5. Proposed calculations for NP depletion rates use either 1) metal leaching rates for calcium and/or magnesium, or 2) molar ratios and sulphide oxidation rates. Similar rates are determined by these methods and suggest that NP depletion rate changes correspond to changes in sulphide oxidation rate. These rate calculations can be used to determine the time to AP and NP depletion, although the accuracy of these calculated depletion rates and the validity of assuming constant rates over time needs to be considered during the interpretation of long term kinetic test data.

Regulatory agencies and other individuals involved in ARD prediction have attempted to develop single tests and criteria to determine the ARD potential for a site. Guidelines for testing and interpretations are necessary as a starting approach to waste characterizarion. It is also necessary, however, that the facility exist to consider other tests and/or interpretations given the numerous factors, and their interrelationship, that determine ARD generation potential. The review of DBARD has indicated that current interpretation methods of static and kinetic prediction data are limited by the lack of understanding the role of geologic factors in determining the ARD potential. These prediction data may also be limited by the lack of understanding of what is being measured in the static and kinetic tests.

With the review of DBARD, and mine submission reports data, information that tends not to be reported/recorded was identified. These additional data would aid in the interpretation of

ARD prediction data and determining the relationship between the static and kinetic data. These data would also prove useful in any future database reviews. Recommendations for collecting and reporting ARD prediction data are presented in Chapter 5.0.

4.0 STUDY AREA - GIBRALTAR TAILINGS IMPOUNDMENT

4.1 INTRODUCTION

Gibraltar Mine, near Williams Lake, British Columbia was the site selected to assess the ability of ARD prediction techniques to approximate on-site water quality. Gibraltar has been in production since 1972 and has ARD predic0tion data and long-term water quality data making it a suitable site to compare prediction and monitoring data.

Gibraltar Mines Ltd. has inititated studies related to closure of the mine including: 1) identification of on-site ARD potential and 2) potential ARD mitigation strategies. Elevated copper concentrations and acidic conditions were noted in drainage from the waste rock piles in the 1980's leading to the commercial heap leaching of the waste rock piles to recover additional copper and the treatment of surface drainage. Many of the studies initiated by Gibraltar are related to the post mining water quality of the leached waste rock piles and their physical stability. Gibraltar Mines Ltd. is also investigating closure options for the tailings impoundment area. The detailed study of this thesis will focus on the tailings impoundment area.

In this chapter, background information related to the mine site and a review of the existing on-site conditions will be presented followed by the assessment of prediction and on-site monitoring data. The initial analysis assesses the static test data from different procedures and the relationship between static test data, lithogeochemistry and mineralogy. Kinetic test data are then considered by identifying variations in water quality, the calculated rates of sulphide oxidation and NP depletion, and the relationship between the static and kinetic prediction data. The water quality monitoring data are then described and analyzed in order to determine if ARD conditions currently exist in the tailings impoundment area. Finally, the relationship between the laboratory data and on-site water quality is discussed.

4.2 BACKGROUND

4.2.1 MINE SITE LOCATION AND DESCRIPTION

The Gibraltar Mine is located approximately 160 km south of Prince George, British Columbia on the western flank of Granite Mountain (Figure 4.1). The minesite is accessed by a 20 kilometer paved road from Highway 97. The mine has been in operation since 1972 and covers an area of approximately 1,885 hectares including orebodies, waste rock piles, plantsite and tailings impoundment (Patterson and Wambolt, 1994; Wambolt et al, 1995). Mining and milling operations ceased for a ten month period (November 1993 to September 1994) due to depressed copper prices.

Ore occurs in six zones: Gibraltar West, Gibraltar East, Pollyanna, Granite Lake, Gibraltar North and Sawmill (Figure 4.2; Bysouth et al, in press). Mining has occurred in all zones except Gibraltar North and Sawmill. Ore is mined by open pit methods at 163,000 tonnes per day (180,000 tons/day; Patterson and Wambolt, 1994; Wambolt et al, 1995). Concentration of the ore is by conventional crushing, grinding and flotation processes at a metallurgical plant located to the north of the open pits (Figure 4.1). Tailings from the rougher/scavenger flotation cells of the plant are discharged *via* pipeline to the impoundment area approximately 5 km north of the open pit-plant area.
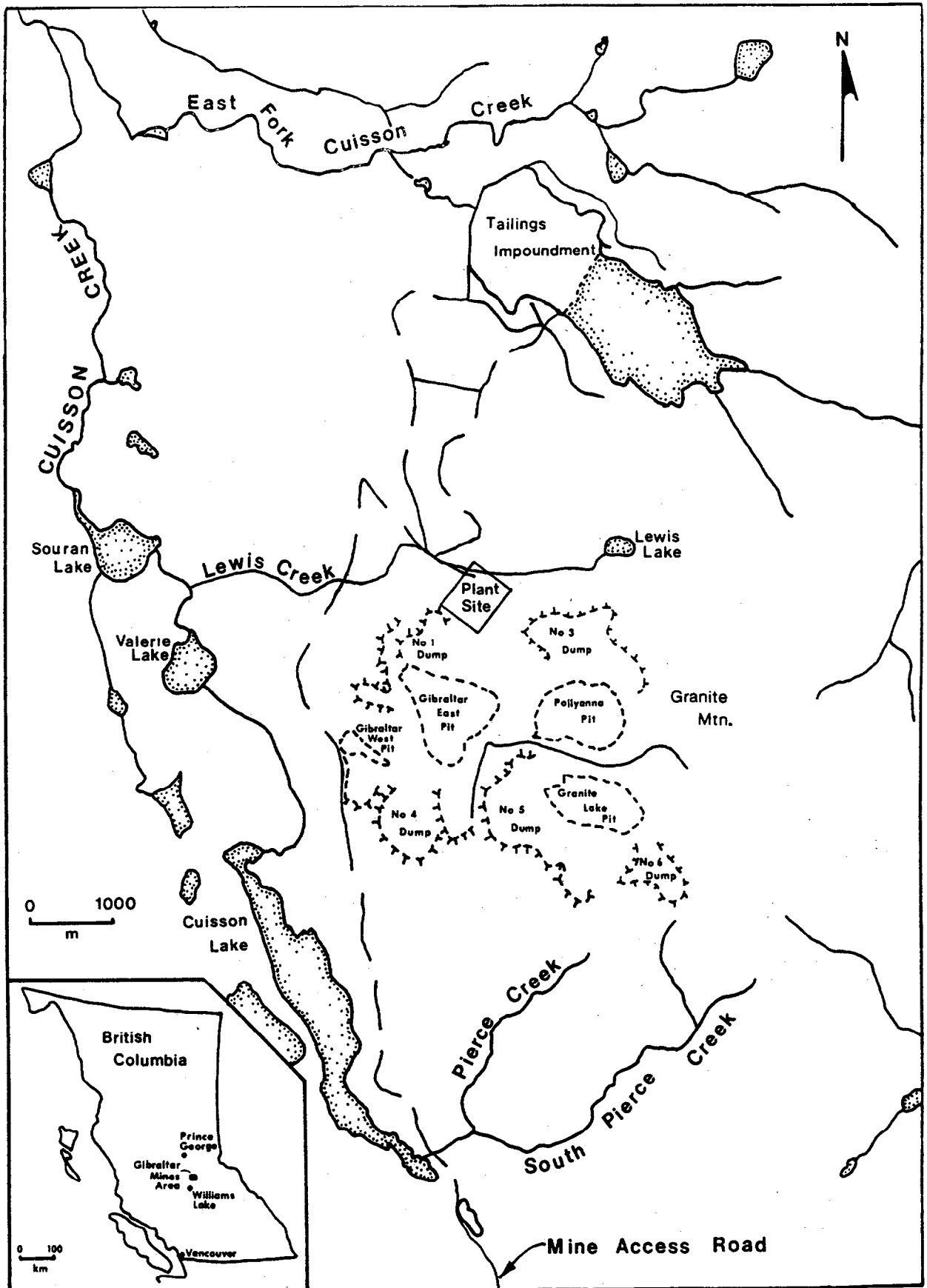
Figure 4.1: Location Map for Gibraltar - McLeese Lake Operations
(after Klohn Leonoff Ltd., 1993 and Wambolt et al, 1995)

LEGEND

QUATERNARY

glacial till, ablation moraine and outwash

TERTIARY

Endako Group basalt

CRETACEOUS

Sheridan Stock granodiorite to tonalite

TRIASSIC
Granite Mountain Batholith

Leucocratic Phase

Granite Mtn. Phase: trondhjemite

Mine Phase: tonalite

Border Phase: diorite to quartz diorite

PERMIAN
Cache Creek Group

Contact Phase: meta-andesite, diorite, skarn

greenschists, andesitic breccia, marble

graphitic phyllite

mineralized zones

fault zones

Figure 4.2: Geology Map for Gibraltar - McLeese Operations
(from Bysouth et al, in press)

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Figure 4.2: Geology Map for Gibraltar - McLeese Lake Operations
(from Bysouth et al, in press)

Copper is also recovered by heap leaching waste rock piles using sulphuric acid followed by solvent extraction and electrowinning (SX-EW). The SX-EW plant is located northeast and adjacent to the metallurgical plant.

Since 1989, Gibraltar has operated under a zero discharge policy to ensure a low risk of impact to the environment. Approximately 80% of the process water is made up recycled tailings water. All flows from the leached piles are collected and channelled to the SX-EW plant where the copper is extracted and the barren solution (or raffinate) is distributed back to the waste rock piles for further leaching. Excess solution from the leached and unleached waste rock piles, generated by rainfall or snowmelt, is treated with lime and discharged to the tailings impoundment.

4.2.2 PHYSIOGRAPHY

Gibraltar is in the Cariboo Plateau of the Central Interior (Campbell et al, 1990). Land use is principally agricultural (grazing and minor forage production), logging, mining and tourism. This plateau is generally flat or has gently rolling topography. In the area of the mine site, elevation ranges from 850 metres along the eastern site boundary in the area of the Cuisson Creek to approximately 1350 metres along the western site boundary at Granite Mountain (Figure 4.1). In the area of the tailings impoundment, elevation ranges from approximately 1000 metres at East Fork Cuisson Creek northwest of the Main Tailings Dam to 1200 metres at ridges south and northeast of the impoundment.

In the upper elevations, the mine site is classified as continental humid climatic region and as biogeoclimatic Engelmann spruce-alpine fir zone that is characterized by Engelmann spruce (*Picea engelmannii*) and alpine fir (*Abies lasiocarpa*) (Campbell et al, 1990; Wambolt et al, 1995). The lower elevations are classified as continental subhumid zone and as Cariboo aspen-lodgepole and pine-douglas fir zone that is characterized by trembling aspen (*Populus*

tremuloides), lodgepole pine (*Pinus contorta*) and interior Douglas fir (*Pseudotsuga menziesii*) (Campbell et al, 1990; Wambolt et al, 1995).

4.2.3 GEOLOGY

Regional Geology

The Granite Mountain Batholith, which hosts the Gibraltar ore bodies, is located within a wedge of Mesozoic and Paleozoic rocks bounded on the west by the Fraser fault system and on the east by the Pinchi fault system (Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). Rock units within the mine area include those of the Cache Creek and Quesnel terranes.

The oldest rocks are the regionally metamorphosed sedimentary and volcanic rocks of the Permian Cache Creek Group (Figure 4.2; Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). This Group is comprised mainly of andesitic to basaltic flows and volcanoclastic rocks, metamorphosed to greenschist facies. Lenses of limestone, recrystallized to marble, form a minor but widespread component of the predominantly volcanic assemblage. Locally, these units are metamorphosed, by the Granite Mountain Batholith, to epidote-chlorite-garnet skarn (Bysouth et al, in press).

The Cache Creek Group is intruded by the Late Triassic to Early Jurassic Granite Mountain Batholith and the Cretaceous Sheridan Stock (Figure 4.2; Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). The Granite Mountain Batholith, approximately 20 by 10 km in plan view, is a zoned, peraluminous, subalkaline intrusion. The batholith and adjacent Cache Creek Group rocks have a penetrative foliation and are metamorphosed to upper greenschist facies. The Sheridan Stock is composed of diorite to granodiorite rocks and lacks the deformation and alteration of the older rocks suggesting a post regional metamorphism and ore stage mineralization emplacement (Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press).

Flat lying basaltic flows of the Miocene Endako Group cap the dissected plateau west of the Granite Mountain Batholith (Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). The area has been intensely glaciated at least twice and most of the bedrock is covered

by impervious lodgement till, accompanied in places by ablation moraine and glaciofluvial deposits (Tipper, 1971; Klohn Leonoff Ltd., 1992).

Ore Deposit Geology

Five of the six separate ore bodies (Pollyanna, Gibraltar East, Gibraltar West, Gibraltar North and Granite Lake) occur in the Granite Mountain batholith in a broad zone of deformation and hydrothermal alteration (Figure 4.2; Bysouth et al, in press). The sixth ore zone, Sawmill, is along the southern edge of the batholith at the contact between the batholith and Cache Creek Group.

The Granite Mountain batholith is a composite body of three major phases: Border Phase diorite, Mine Phase tonalite and Granite Mountain trondhjemite (Bysouth et al, in press). Contacts between the major phases are gradational over widths ranging from two metres to several hundred metres.

The Border Phase diorite and the contact with the mafic Cache Creek Group comprise a broad hybrid zone of assimilation and recrystallization (Figure 4.2). The outer, predominatly volcanic, portion of the hybrid zone is the Contact Phase and the inner, predominantly plutonic, part of the hybrid zone is the Border Phase diorite (Bysouth et al, in press). Typical Border Phase diorite consists of 45-50% saussuritized plagioclase, 35% chloritized hornblende and 15% fine quartz.

The Mine Phase tonalite is the host rock for the majority of the Gibraltar ore bodies. It has a relatively uniform composition of saussuritized plagioclase, chlorite and quartz (Drummond et al, 1976; Bysouth et al, in press). The chlorite is an alteration product of biotite ± hornblende and the plagioclase is variously altered to albite-epidote-zoisite and muscovite. Accessory minerals include magnetite and rutile. Typical mineral assemblage of the tonalite is 30% quartz, 50% plagioclase and 20% chlorite.

The north part of the batholith consists of the Granite Mountain trondhjemite composed of 45% saussuritized plagioclase, ≥45% quartz and 10% chloritized biotite.

Associated with all ore grade mineralization are narrow zones of fine grained rock, termed the Leucocratic Phase because of the quartz plagioclase composition and general lack of

mafic minerals (Bysouth et al, in press). The leucocratic phase consists of phenocrysts (25-30% quartz, 70-75% plagioclase) in a groundmass of felsite with 5-10% sericite.

Ore Mineralization

At Gibraltar, ore grade mineralization is associated with an extensive chlorite and sericite alteration assemblage, with pyrite and chalcopyrite the principal sulphide minerals (Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). Fine grained chalcopyrite accounts for up to 60% of the contained copper and is disseminated in the phyllosilicate foliation lamellae and coarser grained chalcopyrite occurs in quartz veins and shear zones. A pyrite halo is formed around the ore bodies (Bysouth et al, in press). Pyrite is also associated with the ore in the Gibraltar West and Gibraltar North zones, as massive zones 3 to 7 m wide.

Minor amounts of other sulphides are also present. Bornite is associated with magnetite and chalcopyrite in the Pollyanna and Sawmill zones, molybdenite is associated with chalcopyrite in the Pollyanna, Granite Lake and Sawmill zones and sphalerite is present in the Gibraltar West and Gibraltar North zones (Sutherland-Brown, 1973; Drummond et al, 1976; Bysouth et al, in press). The sulphide minerals suggests a metal zoning from Pollyanna to Gibraltar North, with a westerly decrease in molybdenum and a corresponding increase of zinc, gold and silver (Drummond et al, 1976; Bysouth et al, in press).

Supergene enrichment is absent or confined to small zones within the deposits. The exception is Gibraltar East which is capped by 15-30 m of supergene enrichment, underlying a leached zone, interpreted to be a remnant of pre-glacial, or interglacial, weathering (Bysouth et al, in press). Chalcocite constitutes 85% of the secondary copper mineralization principally as coatings on pyrite and chalcopyrite (Drummond et al, 1976; Gibraltar Mines Ltd., 1995; Bysouth et al, in press). Cuprite represents appproximately 10% of the secondary mineralization followed by lesser amounts of malachite, azurite and native copper and trace amounts of covellite and chrysocolla (Drummond et al, 1976; Gibraltar Mines Ltd, 1995; Bysouth et al, in press).

4.2.4 HYDROLOGY AND HYDROGEOLOGY

The principal watershed draining the area of the mine site is Cuisson Creek and a series of lakes called Cuisson, Valerie (or Bushie) and Souran (or Teapot) (Figure 4.1). The Cuisson

Creek system is to the west of the mine site and flows northwesterly 11 kilometres to the Fraser River. Drainage to the south of the mine site flows into Pierce Creek and South Pierce Creek, both of which ultimately flow into Cuisson Creek. North of the plant area is Lewis Creek which drains into Cuisson Creek. Lafrenie Creek directs flow westerly from the east side of the open pit area to the surface drainage collection system.

4.3 EXISTING CONDITIONS OF THE TAILINGS IMPOUNDMENT

4.3.1 DESCRIPTION

The tailings impoundment is located approximately 5 km north of the mine site in a northwesterly trending valley (Figure 4.3). The tailings impoundment covers an area of approximately 450 ha and the valley below the impoundment ranges in elevation from 1065 metres in the southeastern corner to 975 metres at the northwestern corner over approximately 4.5 km (Klohn Leonoff Ltd., 1992, 1993).

The main tailings dam is up to 90 metres high and approximately 2400 metres long (Klohn Leonoff Ltd., 1992, 1993) and is raised by direct deposition of tailings underflow from cyclones located across the crest of the dam (Klohn-Crippen Consultants Ltd., 1994; Patterson and Wambolt, 1994; Wambolt et al, 1995). The cyclone overflow is discharged onto the tailings beach. During the winter months (approximately December to April), unclassified whole tailings are discharged onto the tailings beach by spigotting from a discharge point located near the south abutment of the Main Dam crest. In 1994, the elevation of the main dam crest ranged from 1079 to 1088 metres (Klohn-Crippen Consultants Ltd., 1994). The beach elevation is approximately 3 metres below the dam crest and slopes southwesterly over approximately 1200 metres to the tailings pond. The pond water elevation in January 1994 was 1070 metres and is reported to have risen from 1057 metres in December 1987 (Klohn-Crippen Consultants Ltd., 1994).

Rockfill finger drains were installed in the base of the dam to maintain the phreatic surface near the foundation (Figure 4.3). These drains have undergone inspection and
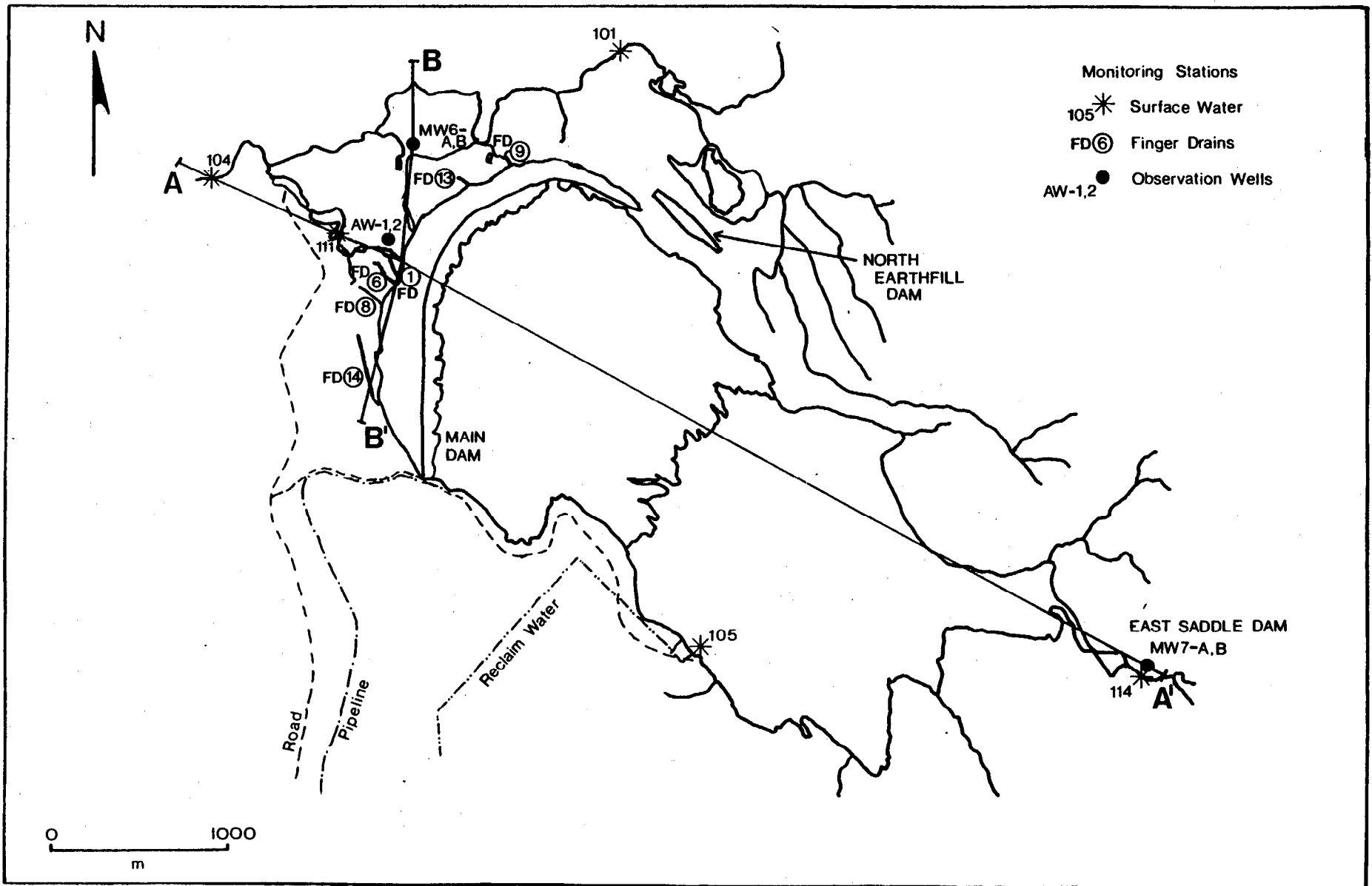
Figure 4.3: Location of Monitoring Stations in Area of the Gibraltar Tailings Impoundment   (from Wambolt et al, 1995)

rehabilitation during the early 1990's (Klohn Leonoff Ltd., 1992, 1993). A seepage collection pond is located approximately 450 metres northwest of the main dam and water is pumped from the collection pond back into the tailings impoundment (Patterson and Wambolt, 1994; Wambolt et al, 1995).

Low saddle dams are located near the eastern and northern sides of the tailings impoundment (Figure 4.3). Phase I of the North Earthfill Dam was constructed in 1990 along the north side of the tailings impoundment near the northern abutment of the Main Tailings Dam. (Klohn-Crippen Consultants Ltd., 1994). It has an elevation of 1080 metres and is approximately 600 metres long. The East Saddle Dam was constructed in 1985-86 on the eastern end of the tailings pond with an elevation of 1085 metres. Two diversion ditches were constructed along the north side of the tailings impoundment to direct surface runoff from the tailings pond to East Fork Cuisson Creek.

4.3.2 PREVIOUS WORK

Gibraltar conducts and sponsors research programs to assist in the closure plan for the mine site. Many of these programs are investigating post-mining water quality conditions and physical stability of the open pits, waste rock piles and the tailings impoundment and are described in other documents (e.g. Patterson and Wambolt, 1994; Wambolt et al, 1995). Since the focus of this study is the tailings impoundment area, the following is a discussion of previous work in this area.

Physical Stability

Geotechnical drilling and test pit programs in the area of the Main Tailings Dam were completed in the early 1970's during dam construction (Klohn Leonoff Ltd., 1992). During the 1980's, test pit programs were also completed in the area of the East Saddle Dam.

During the 1990's, Klohn-Crippen Consultants Ltd. (1994) completed performance studies on the Main Tailings Dam to assess the stability of the impoundment. In general, the tailings dams have a good particle size distribution, water drainage and an adequate slope angle for stability.

Additional testing on the tailings dam and beach include measures to secure sands and suppress dust. Asphalt - organic applications were tested in 1993 and forty acres of the beach

were seeded with fall rye and fertilized in 1994. Vegetation metal uptake is also being investigated in the area below the Main Dam and on the tailings beach.

Waste Characterization

Chemical stability of the tailings is related to its ARD potential with waste characterization including static and kinetic prediction tests and whole rock lithogeochemistry. These investigations were initiated in 1992 by on-site environmental staff (Patterson and Wambolt, 1994; Wambolt et al, 1995) and, for this thesis, are identified by the following phases:

Phase I:

This phase was initiated in early 1992 and provides an estimate of the ARD potential for the tailings dam and beach. It involved the collection of 80 surface samples, from the dam and beach, followed by static prediction tests. In general, the tailings have a neutral paste pH, low AP and low NP values, and have localized areas with a high potential for ARD (i.e. NP:AP ratios less than 1.0; Patterson and Wambolt, 1994). Given these results, kinetic testwork was inititated in July 1992 with three humidity cells having NP:AP ratios of 0.5, 0.7 and 1.0 which represent the range of NP:AP ratios identified from the static testwork. Kinetic testing continues today and is planned for several more years.

Phase II:

As part of a geotechnical study of the dam, 33 samples were collected from 3 geotechnical drill holes to assess the variation of ARD potential with depth. The findings of this phase indicate that little oxidation of the sands has occurred and sufficient buffering capacity is available to neutralize any acid generated (Patterson and Wambolt, 1994). Analysis of lithogeochemistry results noted a correlation between NP and the calcium and carbon content of the sample that was attributed to the presence of carbonate minerals and lime in the tailings.

Phase III:

This program, completed July 1993, evaluated the variation of ARD potential with particle size fraction. Three bulk samples were collected from the main tailings line, sieved to five different size fractions with static prediction testing and lithogeochemistry analysis

conducted on each fraction. In general, the samples with the highest ARD potential were found in the finer grained material relative to the coarse material suggesting that particle size has some control on ARD potential (Patterson and Wambolt, 1994). A correlation between carbon content and NP was also noted.

Phase IV:

In August 1993, the relation of ARD potential to particle size and distance from discharge point was determined by sampling 3 flow lines. Static prediction tests, on 31 samples, indicated that the Net NP is independent of particle size distribution conflicting with the findings of Phase III. Lithogeochemistry indicated that carbon content of these samples was higher than the measured NP and was interpreted to be due to the presence of organic reagents, used in the mill, contributing to the measured carbon content.

Phase V:

In September 1993, variations in ARD potential relative to spigot location of the cyclones was assessed. Sixty samples, from three surface transects across the high ARD potential zones identified in Phase I, indicated that ARD potential decreases with distance from the cyclone due to differential settling occuring along the flow path. Lithogeochemistry data identified the correlation between NP and carbon content.

On-going work in the area of the tailings impoundment includes geophysical surveys to identify anomolous water quality zones in the area of the tailings impoundment. This study is part of a Ph.D. research program (M. Davies, personal communication) at UBC and uses *in-situ* geophysical techniques to characterize geotechnical aspects, hydrogeology and geochemistry of mine waste facilities and affected environments. Poulin et al (in press) have investigated the use of tailings to control ARD within the waste rock by mixing the two mine waste products. Lawrence and Wang (in prep) have included nine samples from the Phase I investigation in their larger project to evaluate NP determination from different static prediction tests.

4.3.3 GEOLOGY

The description of ore deposit geology and mineralization (Section 4.2.3) provides an indication of the composition of material deposited into the tailings impoundment.

In the area of the tailings impoundment, the bedrock and surficial geology are poorly described. The bedrock has been identified in geotechnical and hydrogeological studies as being weathered diorite of the Granite Mountain Batholith (Klohn Leonoff Ltd., 1992) and Bysouth et al (in press) describe the bedrock as trondhjemite of the Granite Mountain Phase.

The surficial geology has been studied in various geotechnical and hydrological studies (Klohn Leonoff Ltd., 1992) and, in general, the majority of the surficial material is described as silt to sand till-like material with discontinuous lenses and pockets of sand and gravel (Klohn Leonoff Ltd., 1992). Geologic cross-sections A and B of the tailings impoundment (shown in Figure 4.3) are presented in Figure 4.4 a, b.

4.3.4 CLIMATE

The McLeese Lake Granite Mountain climate station is located at the Gibraltar mine site and has a recorded mean total annual precipitation of 502 mm based on 15 years of records

Figure 4.4: Geologic Cross-sections a) A-A' and b) B-B' across Gibraltar Tailings
Impoundment
(after Klohn Leonoff, 1992)
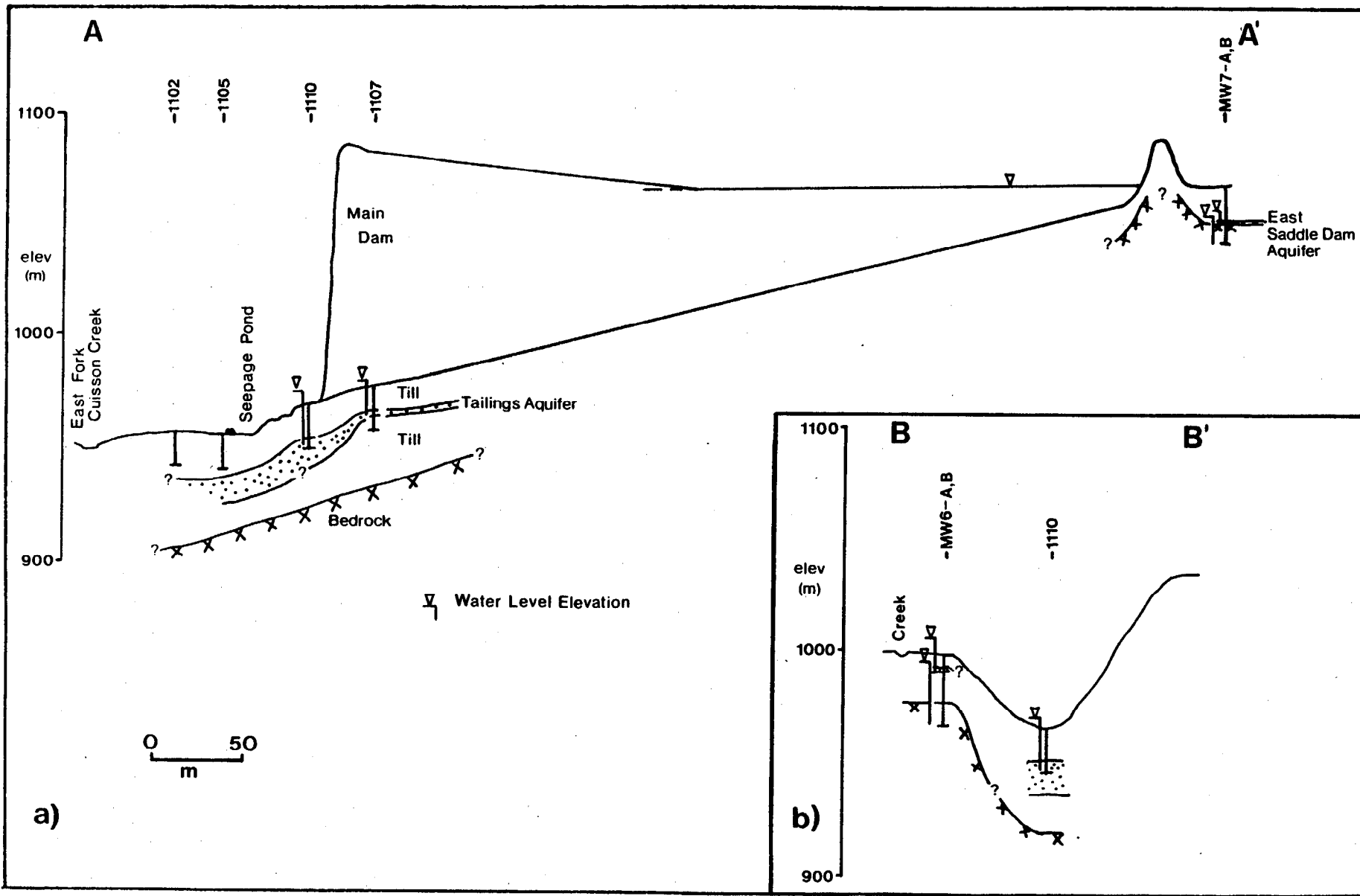
Figure 4.4: Geologic Cross-sections a) A-A' and b) B-B' across Gibraltar Tailings Impoundment   (after Klohn Leonoff, 1992)

(Klohn Leonoff Ltd., 1992). Of this total precipitation, approximately 67% occurs as rain and 33% as snow (Klohn Leonoff Ltd., 1993).

Mean daily temperatures range from -8.1° C in January to 14.3° C in July (Klohn Leonoff Ltd., 1992). Regional annual runoff, including groundwater and surface water, is estimated to be 25 to 100 mm/year, evapotranspiration is approximately 325 to 400 mm/year, and lake evaporation approximately 400 to 500 mm/year (Klohn Leonoff Ltd., 1992, 1993).

4.3.5 HYDROLOGY AND HYDROGEOLOGY

To the north and west of the tailings impoundment, the area is drained by the East Fork Cuisson Creek which flows to Cuisson Creek (Figure 4.1). To the east of the tailings impoundment, drainage is to a swamp which ultimately drains into the Quesnel River.

Klohn Leonoff Ltd. (1992) has developed a hydrogeology model for the mine site and tailings area in order to identify potential contaminant sources and flow paths. In the tailings impoundment area, two aquifers have been delineated: the Tailings and East Saddle Aquifers (Figure 4.4). Although bedrock groundwater flow has not been defined, groundwater flow in bedrock in the open pit area is through major north-south trending faults with minor flow *via* east-west faults. Water level elevations within the surficial aquifers are presented on the geologic cross-sections (Figure 4.4 a, b).

The Tailings Aquifer is a silty sand and gravel sandwiched between silty to sandy till units and follows the valley underneath the impoundment (Klohn Leonoff Ltd., 1992). Recharge to this aquifer is principally from the tailings impoundment and discharge is to East Fork Cuisson Creek northwest of the Main Tailings Dam. Artesian conditions exist in this aquifer below the Main Dam and may have existed prior to the construction of the Dam (Klohn Leonoff Ltd., 1992).

The East Saddle Aquifer is also in the valley occupied by the impoundment although it may not be connected to the Tailings Aquifer. The unit is clean sand and gravel that overlies bedrock in the area of the East Saddle Dam. The unit is unsaturated and may be connected to the tailings impoundment by either extending beyond the East Saddle Dam to the base of the impoundment or *via* bedrock faults and fractures. This aquifer discharges to a low lying wet area east of the impoundment.

4.3.6 WATER QUALITY MONITORING

Gibraltar has an extensive ground and surface water quality monitoring program at background stations, in the open pits and tailings impoundment, and downstream of the mine site. Fifty-four stations are established, eighteen of which are in the tailings impoundment area with the locations summarized in Table 4.1 and identified on Figure 4.3. Sampling follows accepted sampling and QA/QC protocols. Samples were analyzed on-site prior to 1992. Recent samples, however, are analyzed by Induced Couple Plasma (ICP) and Gas Flame Atomic Adsorption (GFAA) at a commercial laboratory in Vancouver.

Table 4.1: Sampling Stations in the Area of the Gibraltar Tailings Impoundment

Gibraltar I.D.	Location	Frequency
101	East Fork Cuisson Creek above influence	Monthly
104	East Fork Cuisson Creek below seepage pond ditch	Monthly
105	Tailings Pond Supernatant	Monthly
111	Seepage Pond Supernatant	Quarterly
114	Saddle Dam Drainage	Quarterly
116	Beaver Pond Ditch	Annual
AW-1	Artesian Well #1	Annual
AW-2	Artesian Well #2	Annual
MW-6A	Monitoring Well 6A	Quarterly
MW-6B	Monitoring Well 6B	Quarterly
MW-7A	Monitoring Well 7A	Semi-Annual
MW-7B	Monitoring Well 7B	Semi-Annual
FD-01	Finger Drain #1	Quarterly
FD-06	Finger Drain #6	Annual
FD-08	Finger Drain #8	Annual
FD-09	Finger Drain #9	Quarterly

FD-13	Finger Drain #13	Annual
FD-14	Finger Drain #14	Quarterly

The parameters analyzed and the years for which data are available are summarized in Table 4.2. The metals are analyzed for total and dissolved concentrations and pH is measured in the field and laboratory.

Table 4.2: Parameters Monitored On-site at Gibraltar Tailings Impoundment and Years of Available Data

Location / PARAMETER	101	104	105	111	114	AW-1	AW-2	MW6A	MW6-B	MW7-A	MW7-B	FD-01	FD-06	FD-08	FD-09	FD-13	FD-14
Aluminum	1988-94	1992-94	1988-94	1988-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Alkalinity	1980-94	1992-94		1992-94	1992-94			1992-94	1992-94	1992-94	1992-94						
Barium	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Calcium	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Copper	1980-94	1992-94	1980-94	1980-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Iron	1980-94	1992-94	1980-94	1980-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Hardness	1980-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Potassium	1980-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Magnesium	1980-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Manganese	1980-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Molybdenum	1980-94	1992-94	1980-94	1980-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Sodium	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Phosphorus	1991-94	1992-94		1993-94	1992-94			1992-94	1992-94	1992-94	1992-94						
Lead	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
pH field	1991-94	1992-94	1991-94	1991-94	1992-94	1991-94	1991-94	1992-94	1992-94	1992-94	1992-94	1991-94	1991-94	1991-94	1991-94	1991-94	1991-94
pH lab	1980-94	1992-94	1980-94	1980-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Silicon	1994		1994	1994		1994	1994					1994	1994	1994	1994	1994	1994
Tin	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Sulphate	1980-94	1992-94	1980-94	1980-94	1992-94	1988-94	1988-94	1992-94	1992-94	1992-94	1992-94	1988-94	1988-94	1988-94	1988-94	1988-94	1988-94
Strontium	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94
Zinc	1992-94		1992-94	1992-94		1992-94	1992-94					1992-94	1992-94	1992-94	1992-94	1992-94	1992-94

4.3.7 ARD PREDICTION DATA

A summary of the available ARD test work is presented in Table 4.3. These data are from the previous work completed by Gibraltar environmental staff described in Section 4.2.3. Other data is available from Lawrence and Wang (in prep) and analysis of a whole tailings sample collected in February 1995 for this thesis.

Table 4.3: Summary of Available ARD Prediction Test Work for Gibraltar Tailings

Phase	Number of Samples Static tests	Number of Samples Kinetic tests	Whole Rock Analysis (ICP)
I	80	3	
II	33		33
III	3*		3*
IV	31*		31*
V	60		60

* ABA and whole rock analysis conducted on individual sieve fractions.

4.4 DATA ANALYSIS

4.4.1 STATIC PREDICTION DATA

NP determination from Different Static Prediction Methods

Lawrence and Wang (in prep) have investigated different static prediction tests, applied to the same sample, in order to evaluate NP determination methods. Included in this research are nine samples from the Phase I ARD waste characterization of the Gibraltar tailings. Table 4.4a and b presents the Gibraltar sample data from Lawrence and Wang (in prep) and available static prediction data from Wambolt et al (1995). The methods included in Lawrence and Wang (in prep) are: Standard ABA (Sobek et al, 1978), Standard ABA with 2 variations, a variation of the Modified ABA (after Lawrence, 1990), inorganic carbon analysis and a new method suggested by Lapakko (1994). The variations to the Standard ABA are changes to the acid normality and/or volume used for digestion.

For the Standard ABA, the "fizz rating" for all of the Gibraltar samples was "slight", therefore, 40 ml of 0.1 N HCl were added for the digestion according to the specified procedure.

The two variations of this method involved adding lesser and greater amounts of acid according to the fizz ratings of "none" and "moderate", respectively. An exception to these fizz ratings was for sample 54-2, where the Standard ABA digestion for a "moderate" fizz rating was used and the two variations involved digestion conditions for "slight" and "strong" fizz ratings. The variation of the Modified ABA involved the addition of sample to distilled water prior to addition of acid that was determined from the fizz rating. Also included in Table 4.4a and b, is sample 1995-t which underwent Standard ABA and Modified ABA testing. The two variations to the Standard ABA were attempted on this sample, however, the "none" and "slight" fizz rating digestions of this sample resulted in alkaline pH conditions (due to the presence of lime) and NP could not be determined.

In general, the NP and AP values differ from one test to another (Figure 4.5a) with the largest difference in the Standard ABA - variation 2 of Lawrence and Wang (in prep) where NP values increase with digestion conditions. Lawrence and Wang (in prep) suggest that the Standard ABA values exceed the Modified ABA and CNNP (NP calculated using carbon content) values due to an overestimation of NP from the extreme digestion conditions. The CNNP values (Figure 4.5b) differ due to the analytical techniques used. Wambolt et al (1995)

Table 4.4a: Summary of Acid Potential and Neutralization Potential from Different Static Test Methods for Gibraltar Tailings

	Source of Data	Sample 8-2	8-10	22-18	44-22	52-16	54-2	54-6	58-14	62-8	1995-t
AP	Wambolt et al (1995)	18	15	34	58	18	60	33	33	32	
	Lawrence and Wang (in prep)	18	18	32	57	17	66	33	35	24	
	This research										21
SAP	Wambolt et al (1995)	14	12	28	57	17	53	28	32	21	
NP method:											
Standard ABA	Wambolt et al (1995)	12	15	13	19	18	30	17	15	23	
Standard ABA	Lawrence and Wang (in prep)	12	20	10	18	18	83	20	9	18	
Standard ABA	This research										25
Standard ABA-variation 1	Lawrence and Wang (in prep)	11	18	3	15	14	28	17	6	17	
Standard ABA-variation 2	Lawrence and Wang (in prep)	36	49	20	21	66	103	321	19	61	
Modified ABA	Lawrence and Wang (in prep)	11	14	8	15	17	29	11	10	16	
Modified ABA	This research										32
CNNP (total)	Wambolt et al (1995)	10	14	14	14	15	34	19	10	11	
CNNP (total)	This research	13	7	12	11	23	43	18	19	13	14
CNNP (inorganic)	Lawrence and Wang (in prep)	8	11	6	18	9	31	10	12	11	
CNNP (inorganic)	This research	9	11				33				10

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Table 4.4b:Summary of Calculated Net NP and NP:AP Ratios from Different Static Prediction Methods for Gibraltar Tailings

	Source of Data	Sample 8-2	8-10	22-18	44-22	52-16	54-2	54-6	58-14	62-8	1995-t
Net NP (=Std NP-AP)	Wambolt et al (1995)	-6	0	-21	-39	0	-30	-16	-18	0	
(=Std NP-AP)	Lawrence and Wang (in prep)	-6	-2	-22	-39	1	-36	-16	-29	-7	
(=Std NP-AP)	This research										4
(=Std NP-var 1-AP)	Lawrence and Wang (in prep)	-7	0	-29	-42	-3	-38	-16	-29	-7	
(=Std NP-var 2-AP)	Lawrence and Wang (in prep)	18	31	-12	-36	49	37	-2	-16	37	
(=Mod NP-AP)	Lawrence and Wang (in prep)	-7	-4	-24	-42	0	-37	-22	-25	-8	
(=Mod NP-AP)	This research										11
(=CNNP(total)-AP)	Wambolt et al (1995)	-8	-1	-20	-44	-3	-26	-14	-23	-7	
(=CNNP(total)-AP)	This research			-13	-25	4		-13	-6	-8	-8
(=CNNP(inorg)-AP)	Lawrence and Wang (in prep)	-10	-7	-23	-39	-8	-35	-23	-23	-13	
(=CNNP(inorg)-AP)	This research	-9	-4				-27				-11
NP:AP (=Std NP/AP)	Wambolt et al (1995)	0.7	1.0	0.4	0.3	1.0	0.5	0.5	0.5	1.0	
(=Std NP/AP)	Lawrence and Wang (in prep)			0.3	0.3	1.1		0.6	0.3	0.7	
(=Std NP/AP)	This research										1.2
(=Std NP/SAP)	Wambolt et al (1995)	0.8	1.3	0.5	0.3	1.1	0.6	0.6	0.5	1.1	
(=Std NP-var 1/AP)	Lawrence and Wang (in prep)	0.6	1.0	0.1	0.3	0.8	0.4	0.5	0.2	0.7	
(=Std NP-var 2/AP)	Lawrence and Wang (in prep)	2.0	2.7	0.6	0.4	3.9	1.6	0.9	0.5	2.5	
(=Mod NP/AP)	Lawrence and Wang (in prep)	0.6	0.8	0.2	0.3	1.0	0.4	0.3	0.3	0.7	
(=Mod NP/AP)	This research										1.5
(=CNNP(total)/AP)	Wambolt et al (1995)	0 6	0.9	0.4	0.2	0.8	0.6	0.6	0.3	0.7	
(=CNNP(total)/AP)	This research	0.7	0.5	0.5	0.3	1.2	0.7	0.6	0.8	0.6	0.6
(=CNNP(inorg)/AP)	Lawrence and Wang (in prep)	0.4	0.6	0.2	0.3	0.5	0.5	0.3	0.3	0.5	
(=CNNP(inorg)/AP)	This research	0.5	0.7				0.6				0.5

values are determined by Leco furnace analysis which provides a total carbon (inorganic and organic) result and Lawrence and Wang (in prep) used carbon coulimetric techniques to measure inorganic carbon only.

Lawrence and Wang (in prep) also plot back titration curves from the NP determination to describe mineralogical contributions to NP. This qualitative assessment is based on the premise that, during digestion, ions are introduced to solution due to the dissolution of minerals. When the solution is back-titrated, these ions can precipitate and give the titration curve a distinctive shape depending on the pH range in which the solution is buffered. Three samples from Gibraltar were included in this assessment by Lawrence and Wang (in prep). These back titration curves are included in Appendix 3. The back titration curve for sample 1995-t, determined during this research, is presented in Figure 4.6. The back titration for this sample was continued beyond pH 7 (end point for the standard static prediction method) to pH 12. The Figure shows two major inflections for both the Standard ABA and Modified ABA curves at approximately pH 3-4 and pH 10-11. These inflection points represent the buffering by the carbonate species. There is also a minor inflection at approximately pH 4-5 which Lawrence and Wang (in prep) also identified and suggest that aluminum is precipitating in this pH range and buffering pH. Lawrence and Wang (in prep) also found that increasing acid digestion normality and volume results in an increase in this small inflection and concluded that this increase resulted in a greater dissolution of alumino-silicates.
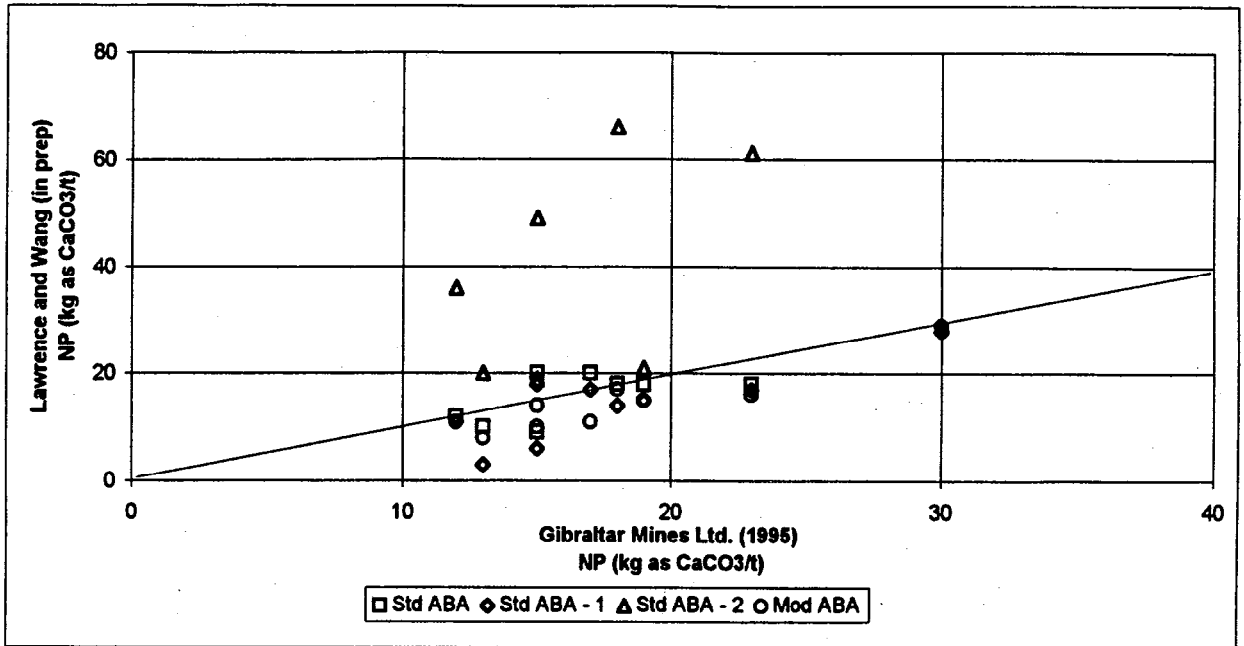
Figure 4.5a Comparison of NP Determined by Standard and Modified ABA Methods from
Gibraltar Mines Ltd. (1995) and Lawrence and Wang (in prep); keyed to Table 4.4
(Std ABA = standard acid base accounting, Std ABA -1 and Std ABA - 2 = standard acid base
accounting with variations; Mod ABA = modified acid base accounting)
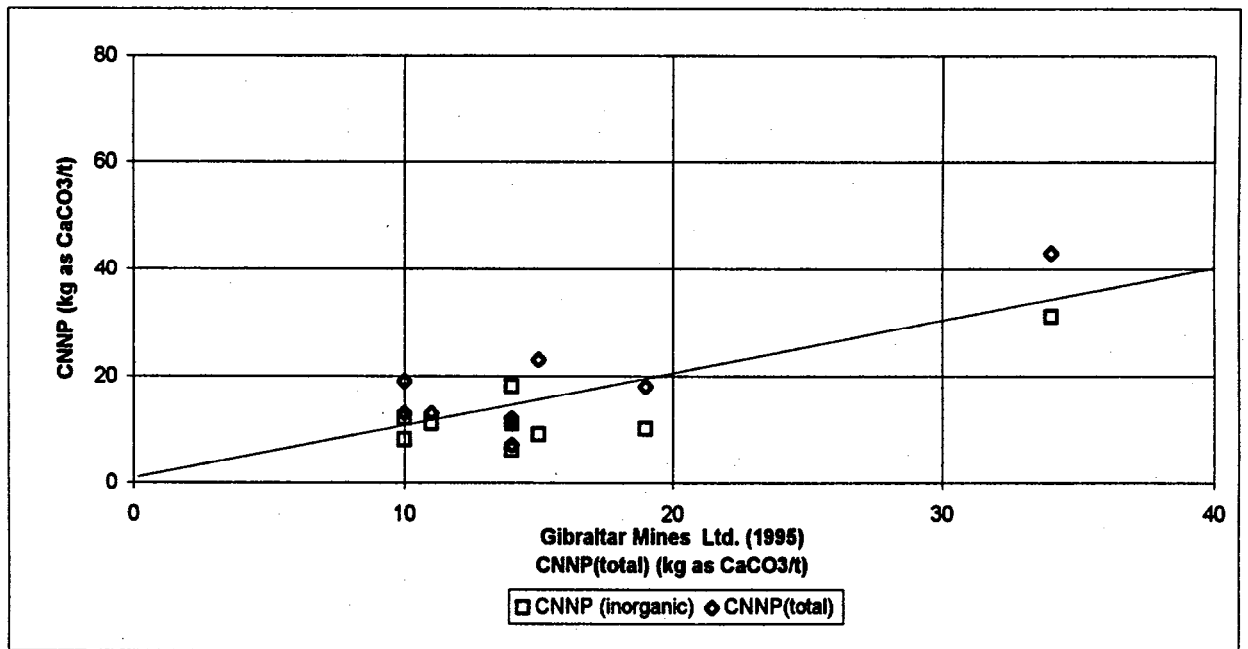
Figure 4.5b Comparison of NP Determined by Total and Inorganic Carbon ABA Methods from
Gibraltar Mines Ltd. (1995), Lawrence and Wang (in prep) and this research; keyed
to Table 4.4
(CNNP(Total) - NP detemined from total carbon content; CNNP(inorg) - NP determined from
inorganic carbon content)
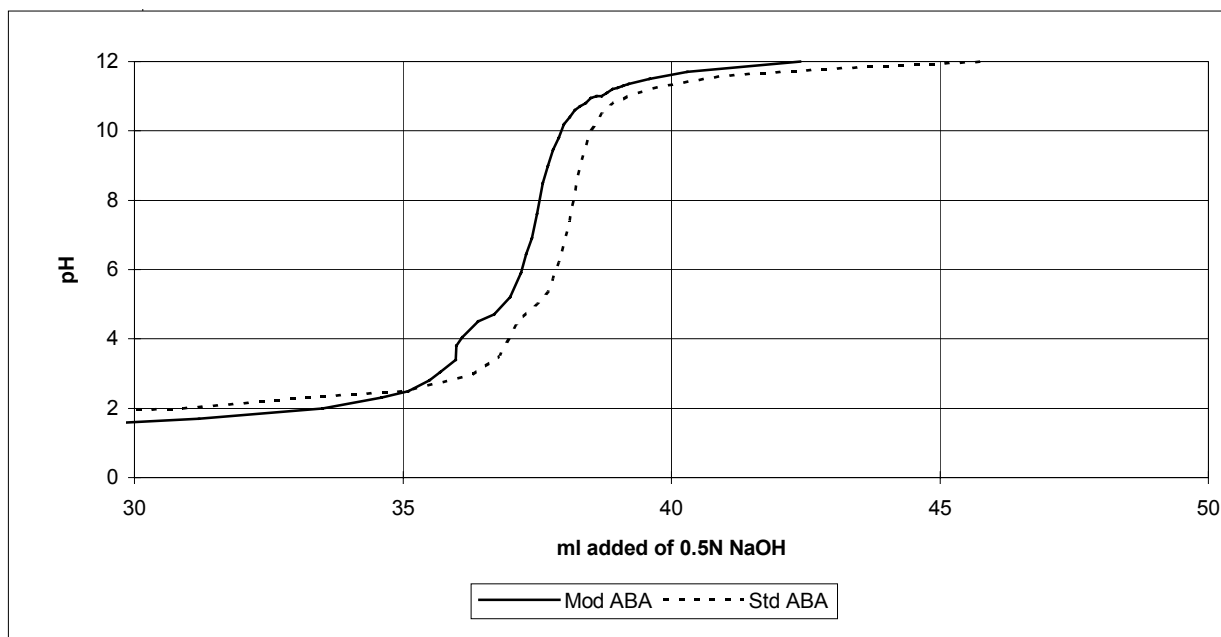
Figure 4.6: Back Titration Curve for Standard and Modified ABA tests of Sample 1995-t. NP from Modified ABA is 32 kg as CaCO$_3$/t and from Standard ABA is 25 kg as CaCO$_3$/t.

The implication to the differences between AP and NP is the resultant variations in the interpretative calculations of Net NP and/or NP:AP ratio. Lawrence et al (1994) indicate that variation in NP and AP may result in significant variations in the Net NP and NP:AP that affect interpretation. Thus, a sample that is considered acid generating from one static test may be non-acid generating in another. Although the variations are relatively minor in the Gibraltar samples (Table 4.4a, b), there is sufficient variation that interpretation of the ARD potential may change depending on the criteria considered. For example, Gibraltar sample 54-2 (Table 4.4a, b) has NP ranging from 28 to 103 kg CaCO$_3$/t resulting in NP:AP ratios of 0.4 to 1.6. If a criteria of NP:AP less then 1 is used to differentiate potentially acid and non-acid generating then the interpretation of the potential of this sample varies between methods. These differences are also significant since the NP and AP values are relatively low in the Gibraltar tailings.

Lithogeochemistry, NP and AP

Evaluation of the relationship between lithogeochemistry and the NP and AP values allows minerals contributing to NP and AP to be identified and aid in the interpretation of water

quality in kinetic tests and on-site. ICP lithogeochemical data from 139 samples (from Phase II to V) suggest correlations between NP, AP and geochemistry. Data histograms (not presented) indicate that the distribution of the NP, AP and individual ICP metal data are skewed and, prior to statistical treatment, the data was converted to its natural logarithm. The Pearson correlation matrix (calculated using SYSTAT) indicates statistically significant correlations between NP and carbon, calcium, sodium, phosphorous and strontium (Table 4.5a) and between AP and cobalt, iron, manganese and phosphorous (Table 4.5b). Statistically significant correlations were also identified between: 1) carbon and calcium, manganese, sodium, phosphorous and strontium and 2) calcium and potassium, magnesium, manganese, sodium, phosphorous and strontium. Calcium and carbon correlation with NP suggests that carbonate minerals are contributing to NP while correlation between NP and calcium and sodium suggests contribution from alumino-silicate minerals. Correlation between iron and AP suggests pyrite as the principal acid generating mineral present. The relationship between the other metals and either NP or AP can be attributed to their similar behaviour and substitution within the minerals. For example, strontium, magnesium and manganese substitute for calcium and manganese and cobalt substitute for iron (Stumm and Morgan, 1981; Hem, 1992).

Table 4.5a: Pearson Correlation Matrix for Neutralization Potential (NP) and Geochemistry (calculated using SYSTAT for Windows)

	lnAl	lnBa	lnC	lnCa	lnFe	lnK	lnMg	lnMn	lnNa	lnP	lnSr	lnTi
lnAl	1.0											
lnBa	**0.5**	1.0										
lnC	0.3	0.2	1.0									
lnCa	**0.5**	**0.5**	**0.8**	1.0								
lnFe	**0.5**	0.0	0.2	0.3	1.0							
lnK	**0.6**	**0.8**	0.3	**0.5**	0.1	1.0						
lnMg	**0.9**	0.2	0.2	**0.4**	**0.5**	**0.4**	1.0					
lnMn	**0.5**	0.1	**0.4**	**0.4**	**0.6**	0.2	**0.6**	1.0				
lnNa	**0.5**	**0.7**	**0.5**	**0.7**	0.0	**0.8**	0.1	0.2	1.0			
lnP	**0.5**	0.2	**0.4**	**0.5**	**0.7**	0.3	**0.5**	**0.5**	0.3	1.0		
lnSr	**0.6**	**0.8**	**0.5**	**0.8**	0.2	**0.8**	0.4	**0.4**	**0.8**	**0.5**	1.0	
lnTi	0.2	0.3	-0.3	-0.1	-0.2	0.3	0.1	-0.2	0.2	0.0	0.3	1.0
lnNP	0.3	0.3	**0.9**	**0.9**	0.2	0.3	0.1	0.3	**0.6**	**0.5**	**0.6**	-0.3

Critical value = 0.366; alpha = 0.05; n = 149
bold values are statistically significant

Table 4.5b: Pearson Correlation Matrix for Sulphur Content (Acid Potential) and Geochemistry (calculated using SYSTAT for Windows)

	lnCo	lnCr	lnCu	lnFe	lnMn	lnMo	lnNi	lnZn	lnP	lnS
lnCo	1.0									
lnCr	0.0	1.0								
lnCu	-0.1	0.2	1.0							
lnFe	**0.8**	0.1	0.0	1.0						
lnMn	**0.5**	0.2	-0.1	**0.6**	1.0					
lnMo	-0.2	**0.4**	**0.7**	0.0	-0.1	1.0				
lnNi	**0.5**	**0.6**	0.1	**0.4**	**0.5**	0.3	1.0			
lnZn	**0.4**	0.3	0.1	**0.6**	**0.7**	0.1	**0.5**	1.0		
lnP	**0.6**	0.3	-0.3	**0.7**	**0.5**	-0.2	0.0	**0.4**	1.0	
lnS	**0.7**	-0.3	-0.2	**0.7**	**0.3**	-0.3	0.0	0.2	**0.4**	1.0

Critical value = 0.335; alpha = 0.05; n = 149
bold values are statistically significant

The mineral assemblage of the tailings has been determined using petrographic techniques, x-ray diffraction (XRD) techniques and whole rock geochemistry determined by x-ray fluorescence (XRF) techniques. The samples included in these tests are from the Phase I investigation (Section 4.3.2). Also included in these analyses, and additional static testing, is a whole tailings sample collected in February 1995. Table 4.6 summarizes the sources and type of information available for the samples included in the mineralogical characterization analysis.

Table 4.6: Summary of Available Laboratory Analysis for Gibraltar Samples in Mineralogical Characterization Study

Sample	Wambolt et al (1995) Static Prediction	Lawrence and Wang (in prep) Static Prediction	Petrography +35 Sieve Fraction	This XRD	Research Whole Rock XRF	Static Prediction Tests
8-2	*			*	*	
8-10	*			*	*	
22-18	*	*		*	*	
44-22	*	*	*		*	
52-16	*	*	*	*	*	
54-2	*			*	*	
54-6	*	*		*	*	
58-14	*	*	*	*	*	
62-8	*	*	*		*	
1995-t			*	*	*	*

Polished thin sections were made from the +0.5 mm (No. 35) sieve fraction of samples 44-22, 52-16, 58-14, 62-8 and 1995-t. Insufficient sample was retained on the sieve to warrant thin sections of samples 22-18 and 54-6. These thin sections allow for the identification of mineral assemblages in both transmitted and reflected light. Point counting, and modal

distribution for each point, was determined for 100 grains in each thin section and used to determine the overall mineral distribution.

Ten samples (-200 mesh) were submitted to Geochemical Laboratories, Earth and Planetary Sciences, McGill University, for whole rock oxide analysis, using XRF techniques. This laboratory uses a Philips PW2400 3kW automated XRF spectrometer system and the results are included in Appendix 3. The major elements (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K and P) and trace elements (Ba, Ce, Co, Cr, Cu, Ni, Sc, V and Zn) were analyzed using 32 mm diameter fused beads prepared from a 1:5 (sample:lithium tetraborate) mixture. Other trace elements were determined by analyzing 40 mm diameter pressed pellets prepared from a mixture of sample with 20 wt% Hoerchst Wax C Micropowder. The oxide analysis was used to complete CIPW normative calculations (developed by petrologists Cross, Idding, Pirsson and Washington) using the computer based program NewPet (Memorial University, 1994). Normative calculations are based on the combination of the oxide components into a set of water-free mineral components according to a prescribed order thought to be the order of mineral crystallization in a magma. These calculations are applicable to the Gibraltar samples and would provide representative mineralogic descriptions since the host formation, the Granite Mountain batholith, is crystalline in nature and has undergone minimal alteration.

Samples which were analyzed by XRD include 22-18, 52-16, 54-6, 58-14 from the Lawrence and Wang (in prep) study and 8-2, 8-10, 54-2 and 1995-t.   These analyses were completed at the Department of Geological Sciences, University of British Columbia, using a Siemens D5000 x-ray diffractometer running at 40kV and 30mA and using Cu$k\alpha$ radiation. Samples from Lawrence and Wang (in prep) were prepared by grinding with a mortar and pestle and smear mounted on standard thin section glass. The other samples included were ground to minus 200 mesh and smear mounted on thin section glass. Spectra of these samples were collected from 3-60° 2θ using a step size of 0.02° 2θ with a counting time of 1 second per step. The diffraction plots attained are included in Appendix 3 and the minerals identified represent the major minerals present within the sample as minerals with less then 3% distribution would not be identified by XRD.

The results of the normative calculations are presented in Table 4.7 and indicate that the samples are composed primarily of quartz (34-45%), feldspar (34-50%) which includes albite

and anorthite, and hypersthene (4-6%). Hypersthene was not identified in either thin section or XRD analysis and most likely this calculation represents the identified occurrence of chlorite. Thin sections and XRD analysis indicate that the feldspar crystals are altered primarily to epidote, muscovite and trace zoisite. Epidote and zoisite are included in the anorthite calculation and muscovite is represented by the orthoclase calculation. Calcite comprises 0.7 to 4% of the mineral assemblage. The sulphide modal distribution (0.6-2%) was calculated by assuming all the sulphur occurred in pyrite. The equivalent iron was accounted for in the ferrous iron oxide concentration prior to normative calculations. Sulphur occurs in other sulphide minerals, primarily chalcopyrite and trace molybdenite, as identified in polished thin section. Other opaque minerals identified in polished thin section are magnetite and hematite. Sulphur may also occur in

sulphate minerals, however, the concentration of sulphate is relatively low (0.05 to 0.2%) in these samples. Petrology indicates that pyrite is the major form of sulphur present in these samples.

Figure 4.7 presents the mineral modal distribution from Table 4.7 and CNNP (Figure 4.7a, b), NP (Figure 4.7c, d) and AP (Figure 4.7e, f). Although there is limited data, trends in these graphs suggest that with decreasing feldspar, primarily sodium-calcium silicates (albite, anorthite, epidote), there is an increase in calcite content and CNNP (Figure 4.7a to d). This may be attributed to the saussaritization of the silicates. Due to the assumptions for the calculations, there is an excellent correlation between AP and pyrite content (Figure 4.7f). The other minerals present are muscovite (potassium silicate), chlorite (magnesium-iron silicate) and quartz which do not affect the NP and AP values.

The analysis of static prediction data, lithogeochemistry and mineralogical characterization has identified carbonate (calcite) and Na-Ca silicate (feldspar, epidote) minerals contributing to NP and pyrite contributing to AP. This provides a guide to the chemical parameters which can be monitored in the kinetic tests to evaluate NP and AP depletion. In this case, these parameters are calcium, sodium and strontium for NP and sulphate, iron, cobalt and manganese for AP. Other minerals identified, but not contributing to NP or AP in the static tests, are muscovite (potassium silicate), chlorite (magnesium-iron silicate) and quartz. Knowledge of the sample mineralogy allows for an improved interpretation of the static prediction data. Both carbonate and silicate minerals contribute to NP depending on the analytical method used. Since it is the buffering capacity of the carbonate minerals that is important in maintaining neutral pH conditions, the inclusion of silicates results in an overestimation of NP. In addition to a mineralogical
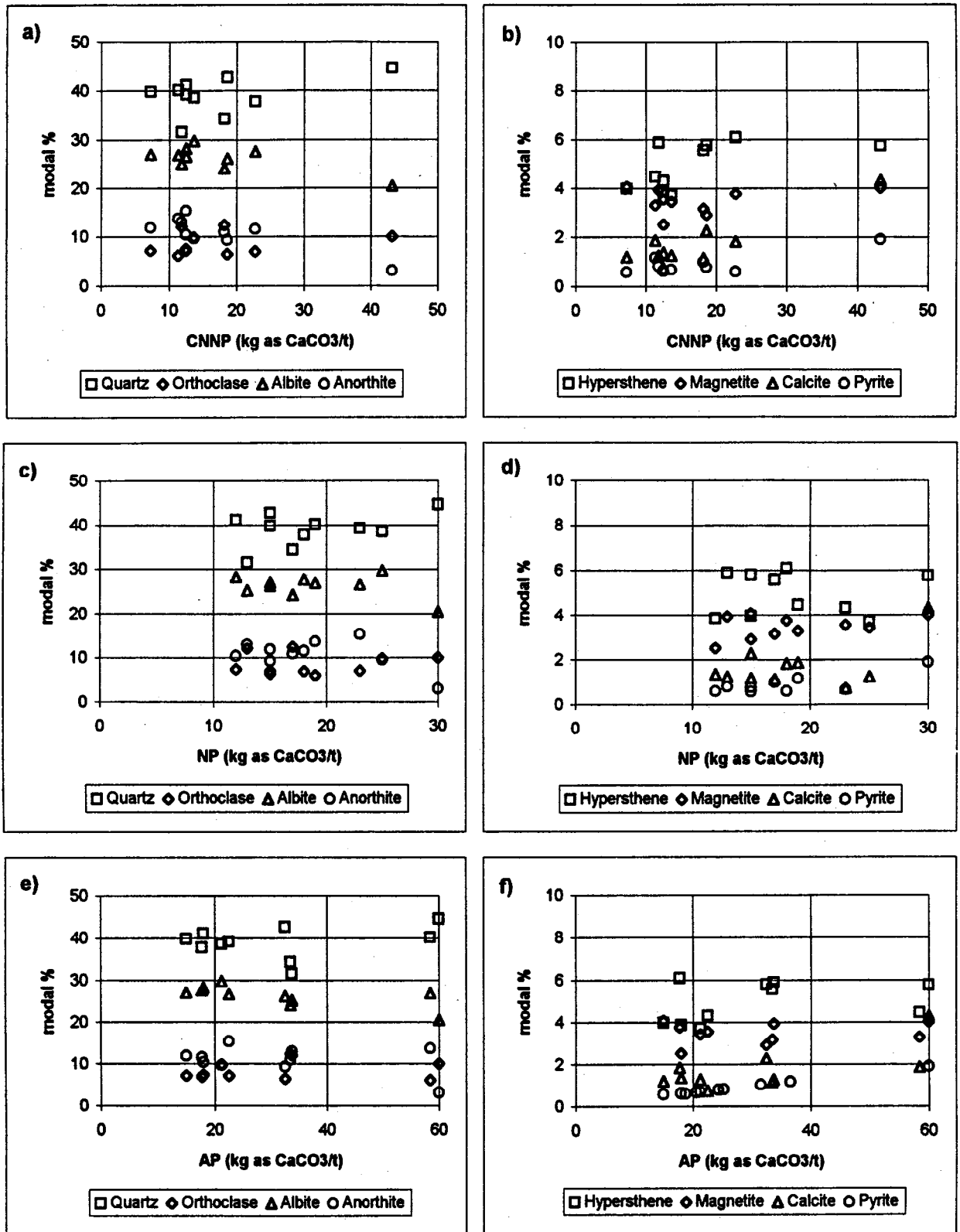
Figure 4.7: a) CNNP(total) and modal distribution of quartz, orthoclase (muscovite), albite and
anorthite and b) hypersthene (chlorite), magnetite, calcite and pyrite
c) NP and modal distribution of quartz, orthoclase (muscovite), albite and
anorthite and d) hypersthene (chlorite), magnetite, calcite and anorthite
e) AP and modal distribution of quartz, orthoclase (muscovite), albite and
anorthite and f) hypersthene (chlorite), magnetite, calcite and pyrite

understanding, it is important to know the digestion conditions used during the static tests since NP values vary for the different static methods. For the Gibraltar samples these variations are small, however, they may be significant given the low values for NP.

Samples included in this mineralogical analysis are from one surface layer of the Main Dam and extrapolating the findings to the entire tailings impoundment would be incorrect. Geologic descriptions indicate that sulphide mineralization varies from pit to pit which may lead to variations of AP within the tailings, depending on the production from the individual pits. Work by Gibraltar Mines Ltd. has identified variations in the tailings due to particle size. Also, mineralogical variations in the host rock may lead to differences in NP.

These techniques demonstrate some of the methods used to characterize lithogeochemistry of geologic materials and how the data correlates with the static prediction data. The methods have identified calcite and calcium-sodium silicate minerals contributing to the NP and that pyrite is the principal mineral contributing to AP. Lime was not identified during the mineral characterization, although it is present in the tailings impoundment. With this understanding of mineralogy and lithogeochemistry, identification of the chemical parameters that would indicate NP and AP depletion during kinetic tests is available.

4.4.2 KINETIC PREDICTION DATA

Three kinetic humidity cells were initiated in July 1992 as part of the Phase I of the ARD waste characterization studies described in Section 4.3.2. Testing of these cells continues today and is planned for several more years. The test cycle is 3 days of dry air followed by 3 days of moist air and the final step is 1 day of leaching with 500 ml of distilled water. The leachate is collected, volume measured and analyzed by ICP for metals. Other measurements of the leachate include pH, alkalinity, acidity, conductivity and sulphate. Analysis frequency has decreased from weekly initially, to monthly intervals and is currently quarterly. Kinetic test data were made available for this project on Excel for Windows spreadsheets. The three samples selected for kinetic testing represent the range of NP:AP values from the static prediction data of Phase I. Table 4.8 presents the static test data for these samples from Wambolt et al (1995) and Lawrence and Wang (in prep) and the mineralogy from Section 4.4.1.

The samples selected for kinetic testing represent the range of NP:AP ratios identified in the Phase I waste characterization with Cell 1 having the lowest ratio (0.5), Cell 2 having the highest (1.0) and Cell 3 having an intermediate value (0.7). An understanding of the mineralogy allows for an improved consideration of NP and AP. For example, one can account for the proportion of sulphur in sulphate minerals as well as account for the proportion of inorganic carbon, representing carbonate content, contributing to NP. With these components taken into account, various calculations, presented in Table 4.8, show differences in the NP:AP ratios and, although the ratios vary, Cell 1 has the lowest ratio and Cell 2 has the highest. In these samples selected for kinetic testing, the lowest NP:AP ratio is in the sample with the highest calcite and pyrite and lowest feldspar content.

Table 4.8: ABA Data for Gibraltar Kinetic Humidity Cells

	Cell 1	Cell 2	Cell 3
Sample	54-2	8-10	8-2
paste pH	7.87	8.38	8.36
AP　　　　(t as $CaCO_3$/kt)	60	15	18
SAP	53	12	14
NP　　　　(t as $CaCO_3$/kt)	31	16	13
CNNP (total)	34	14	10
CNNP (inorganic)	33	11	9
Net NP (t as $CaCO_3$/kt)	-35	-1	-5
NP:AP	0.5	1.1	0.7
NP:SAP	0.6	1.3	0.9
CNNP (total):AP	0.6	0.9	0.6
CNNP (total):SAP	0.6	1.2	0.7
CNNP (inorganic):AP	0.6	0.7	0.5
CNNP (inorganic):SAP	0.6	0.9	0.6
Mineralogy (%)　　　quartz	43.7	39.5	40.8
feldspar	23.5	38.6	38.4

muscovite	10.0	7.1	7.4
chlorite	5.7	4.0	3.8
magnetite	4.0	4.0	2.5
hematite	0.0	0.9	0.6
calcite	4.3	1.2	1.4
pyrite	1.9	0.6	0.6

Description of Data

Based on the static prediction data analysis, identification of chemical parameters representing NP and AP depletion are calcium, sodium, and strontium for NP (from calcite and silicate dissolution) and sulphate, iron, cobalt and manganese for AP (from sulphide oxidation). Parameters considered in this study are sulphate, pH, alkalinity, calcium, strontium, sodium, iron, cobalt and manganese. Other parameters considered for this thesis are copper, molybdenum, zinc, lead, magnesium and phosphorus.

The initial period of testing is characterized by fluctuating and elevated concentrations of parameters until an equilibrium state is reached. For these samples, this period is approximately 4 to 5 months (16 to 20 weeks) and stable conditions are reached by November 1992. Most of the parameters have relatively constant leachate concentrations and neutral pH conditions from 1992 to 1994. During the latter part of 1994 and into 1995, some of the parameter concentrations increased, principally in Cells 1 and 2.

pH, Sulphate and Alkalinity

Figures 4.8a, b and c present the pH and sulphate and alkalinity concentrations within the kinetic cells. The pH (Figure 4.8a) fluctuates, however, it remains neutral in the three cells. The sulphate concentration (Figure 4.8b) is relatively constant at 26 mg/L in Cell 1, 11 mg/L in Cell 2 and 10 mg/L in Cell 3.   During 1995, however, there is an increase in concentration in Cells 1 and 2 to 60 mg/L and 35 mg/L, respectively. This increase in sulphate concentration suggests an increase in sulphide oxidation. Table 4.8 indicates that the sulphate content inititally in these samples has been leached during the initial months of the test. The alkalinity (Figure 4.8c) has

fluctuated since 1992, however, the concentration within the three cells is between 10 to 20 mg as $CaCO_3/l$.

Calcium, Sodium and Strontium

Figures 4.9a and b present the calcium and strontium concentrations within the kinetic cells. The calcium concentrations (Figure 4.9a) are relatively unchanged at 16 mg/L in Cell 1, 11 mg/L in Cell 2 and 10 mg/L in Cell 3, however, there is an increase during 1995 to 30 mg/L and 20 mg/L in Cells 1 and 2, respectively. If sulphide oxidation is occurring, this increased concentration may be the result of acid neutralization through the dissolution of calcite. Strontium (Figure 4.9b) shows a similar trend to calcium with relatively constant concentrations of 0.02 mg/L in Cell 1 and Cell 2 and 0.01 mg/L in Cell 3 and increasing to 0.04 mg/L and 0.03 mg/L in Cells 1 and 2. The sodium concentration is below detection limits in all three cells since 1992.

Iron, Cobalt and Manganese

Figures 4.9c presents the concentration of manganese in the kinetic cells. The iron and cobalt concentrations in the three cells are below detection limits since 1993. Manganese concentration (Figure 4.9c) remained constant at 0.06 mg/L in Cell 1, 0.02 mg/L in Cell 2 and 0.01 mg/L in Cell 3 and has increased to 0.25 mg/L in Cell 1 during 1995. If manganese is substituting for calcium, increased neutralization may account for the increase in manganese concentration. Increasing sulphate concentrations suggest that oxidation of the sulphide minerals is occurring, however, iron and cobalt remain below detection limits. This may reflect either the precipitation of secondary minerals within the cell limiting the concentration in solution or minimal oxidation of these sulphide minerals is occurring.
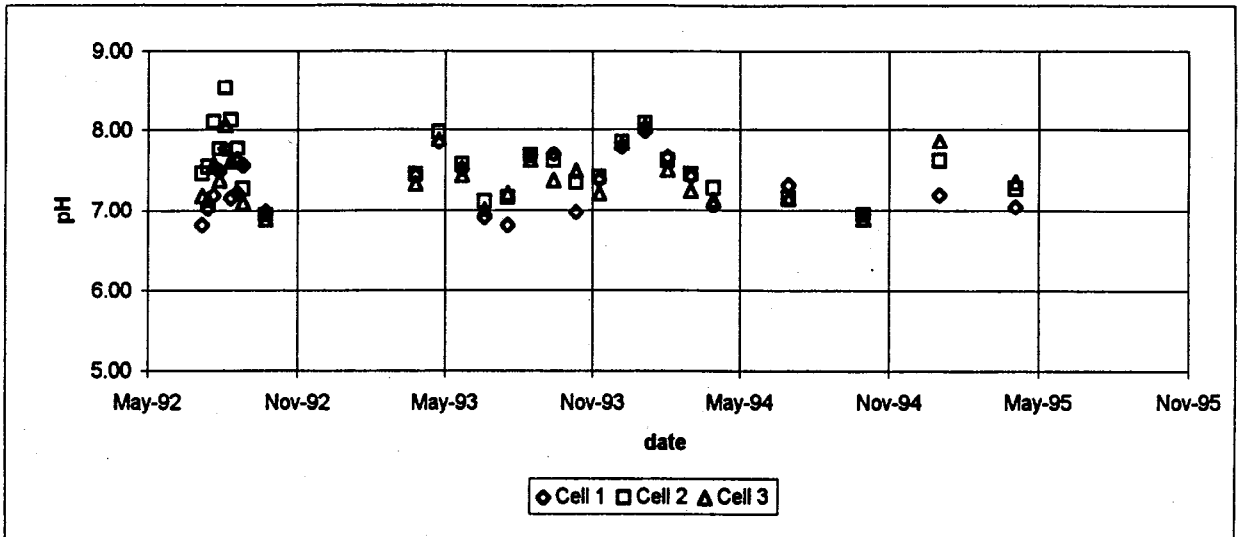
Figure 4.8a: pH Measurements from Gibraltar Humidity Cells 1, 2 and 3
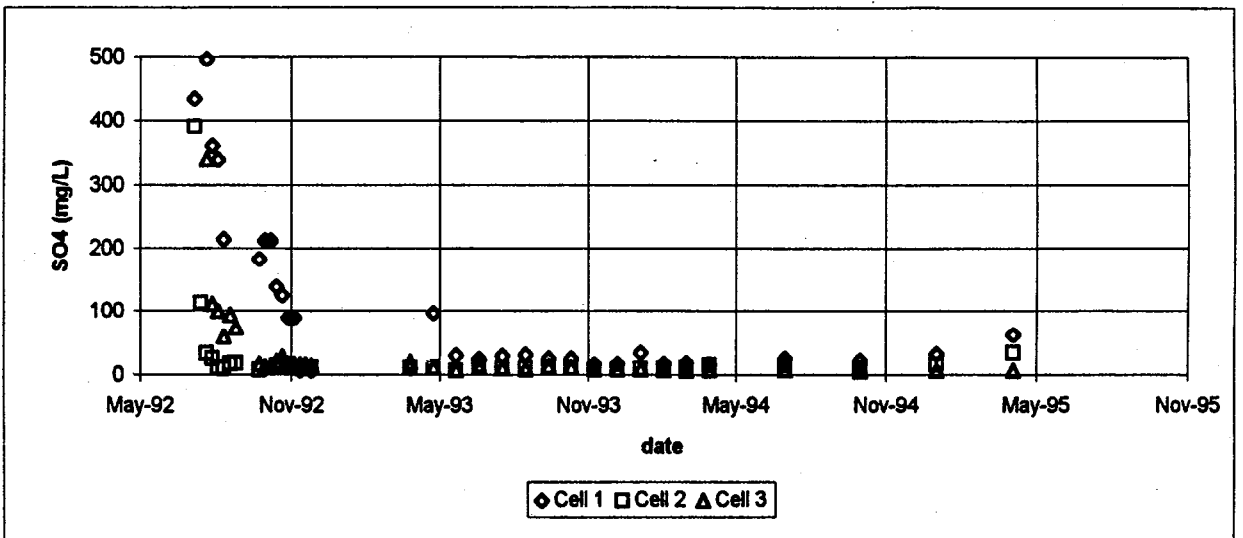
Figure 4.8b: Sulphate Concentrations (mg/L) from Gibraltar Humidity Cells 1, 2 and 3
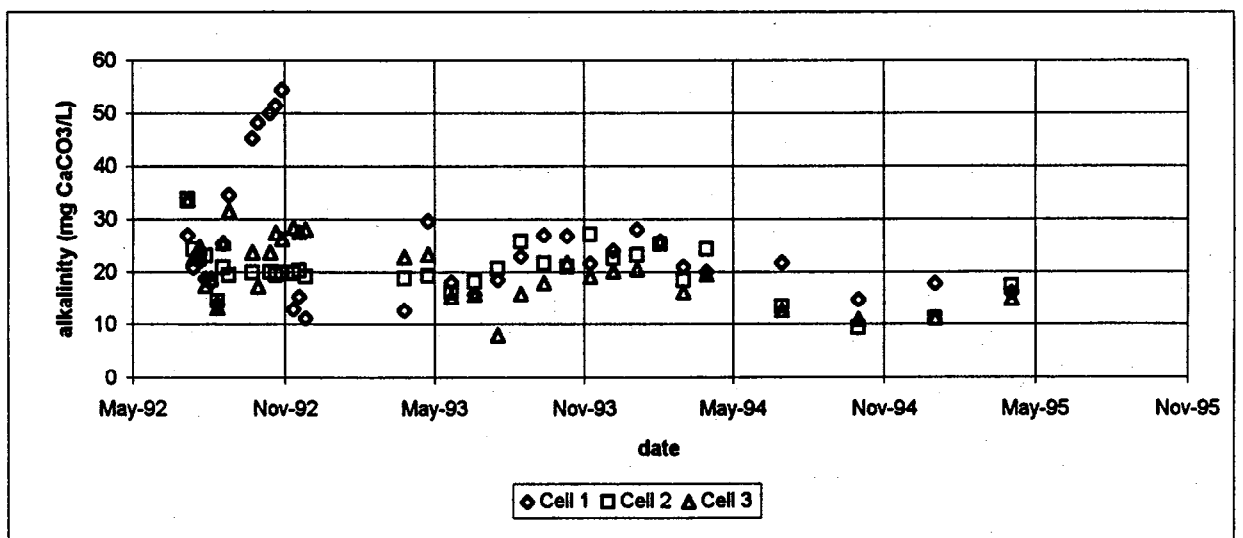
Figure 4.8c: Alkalinity Concentrations (mg CaCO3/L) from Gibraltar Humidity Cells 1, 2 and 3
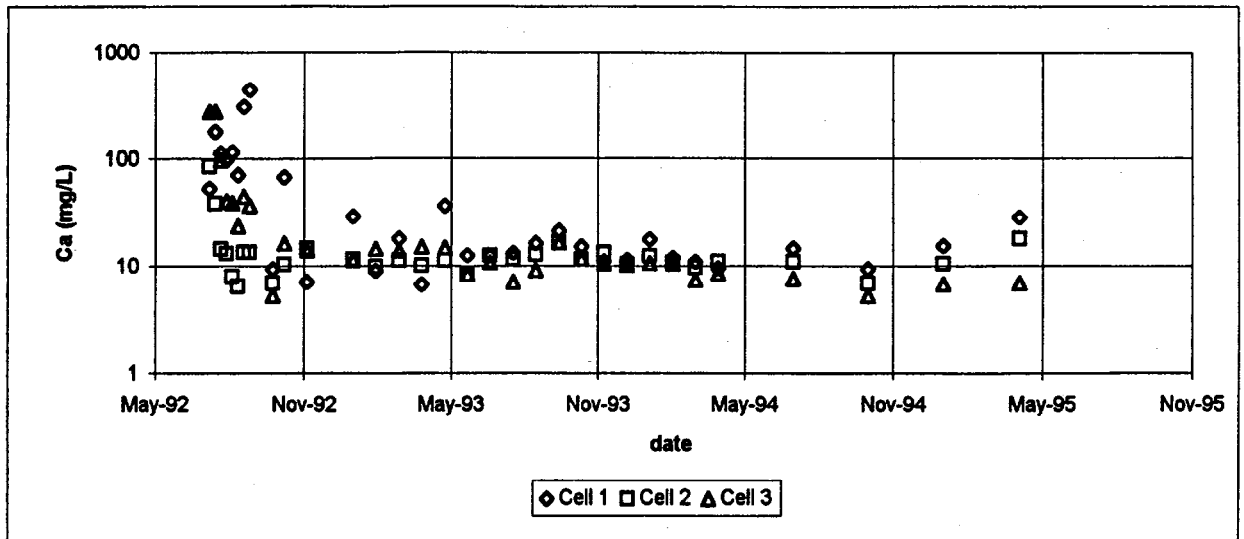
Figure 4.9a: Calcium Concentrations (mg/L) from Gibraltar Humidity Cells 1, 2 and 3
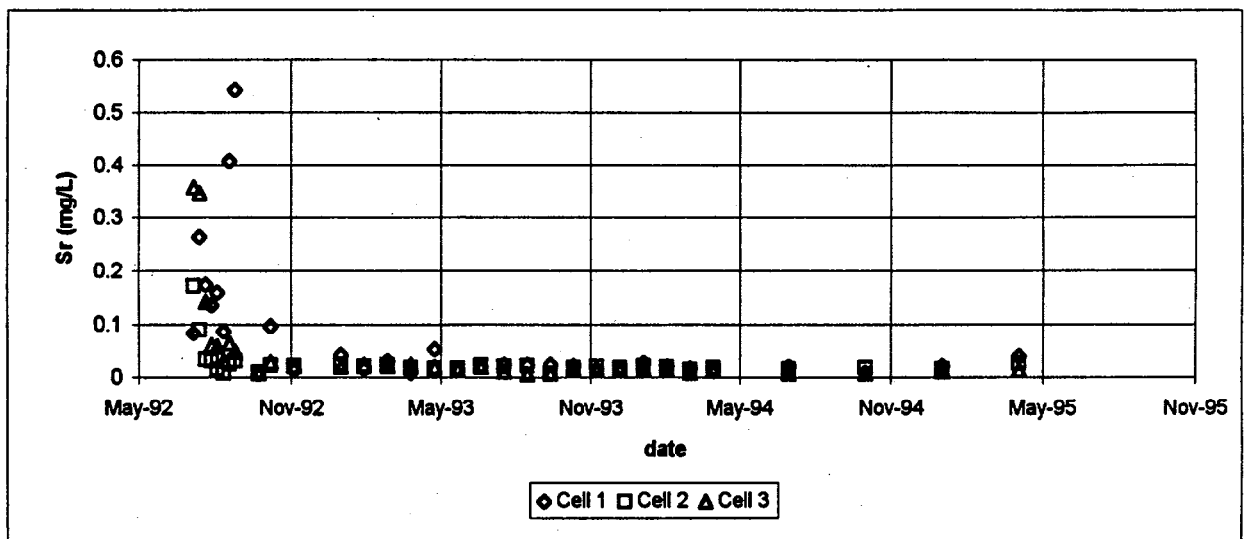
Figure 4.9b: Strontium Concentrations (mg/L) from Gibraltar Humidity Cells 1, 2 and 3
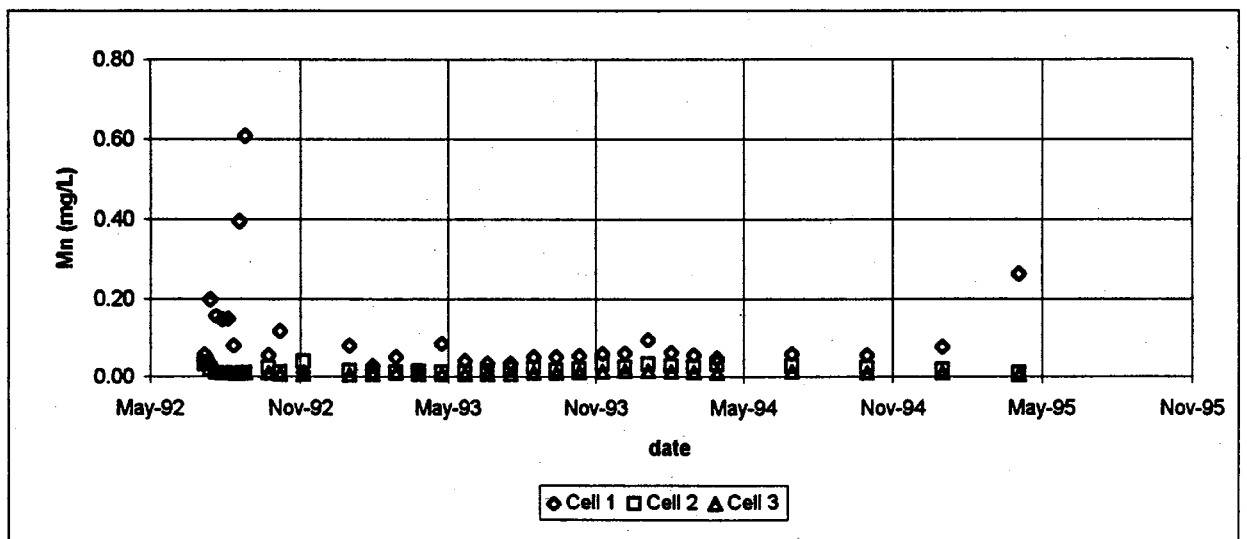
Figure 4.9b: Manganese Concentrations (mg/L) from Gibraltar Humidity Cells 1, 2 and 3

Figures 4.10a, b, c present the concentrations of other metals during the kinetic test period. Copper, lead, and phosphorus are below detection limits and not presented. The concentrations are relatively constant with molybdenum (Figure 4.10a) at 0.01 mg/L in Cells 1 and 2, 0.02 mg/L in Cell 3, zinc (Figure 4.10b) at 0.01 mg/L in Cells 1, 2, and 3, and magnesium (Figure 4.10c) at 3 mg/L in Cell 1, 0.4 mg/L in Cell 2, and 0.26 mg/L in Cell 3. The only change noted is an increase in 1995 in the molybdenum concentration to 0.08 mg/L in Cell 2 and 0.12 mg/L in Cell 3.

Molar Ratio Analysis

Molar ratios have also been used to interpret kinetic test data. Lapakko (1990) uses an increase of the molar ratio of sulphate to alkalinity to predict the on-set of decreasing pH in kinetic cells. Figure 4.11 presents the Gibraltar kinetic test data and during 1995 the sulphate to alkalinity molar ratio within Cell 1, and possibly Cell 2, is increasing and may indicate the on-set of ARD conditions within these cells. Other molar ratios considered in this analysis include (Figure 4.12a to f): calcium/sulphate, sodium/sulphate, iron/sulphate, calcium/sodium, calcium/iron, and sodium/iron in order to assess the value of using these ratios to determine NP to AP depletion and the preferential depletion of the neutralizing minerals. To assess the preferential oxidation of the sulphide minerals, molar ratios considered include (Figure 4.12 g to I): copper/iron, molybdenum/iron and manganese/iron. The molar ratios indicate the relative rate of leaching for the parameters and any changes to the ratio will reflect a mass gain, or loss, to solution.
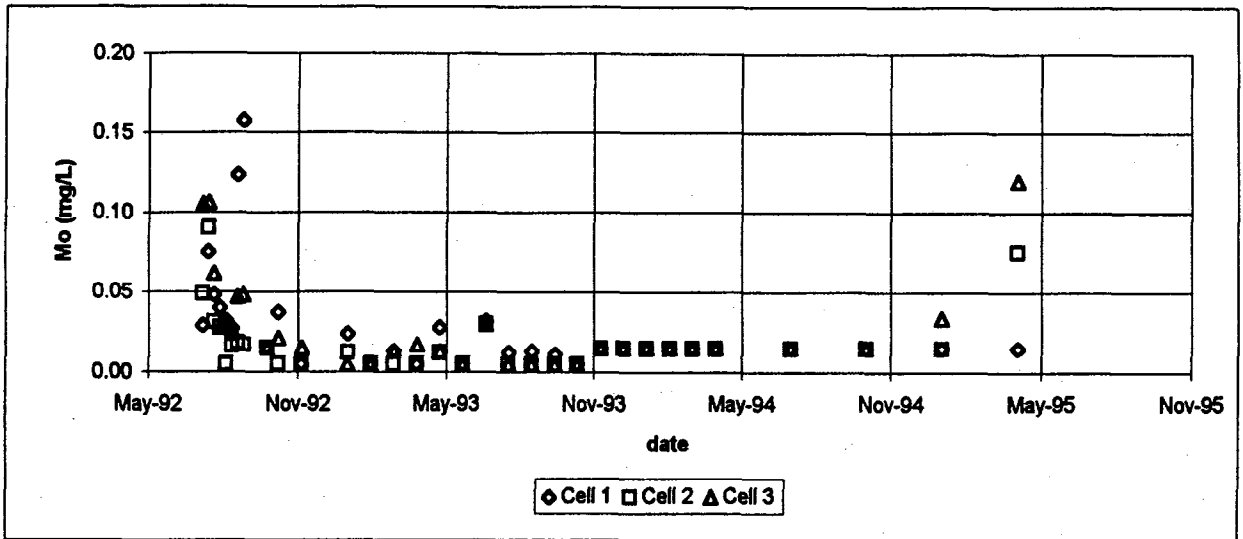
Figure 4.10a: Molybdenum Concentration (mg/L) from Gibraltar Humidity Cells 1, 2 and 3
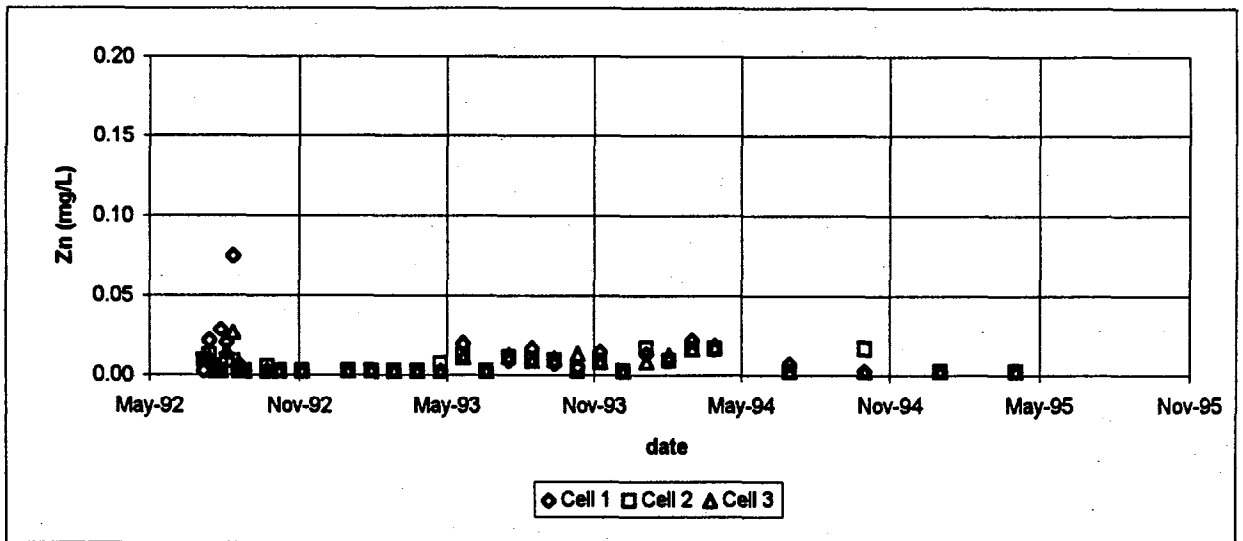
Figure 4.10b: Zinc Concentration (mg/L) from Gibraltar Humidity Cells 1, 2 and 3
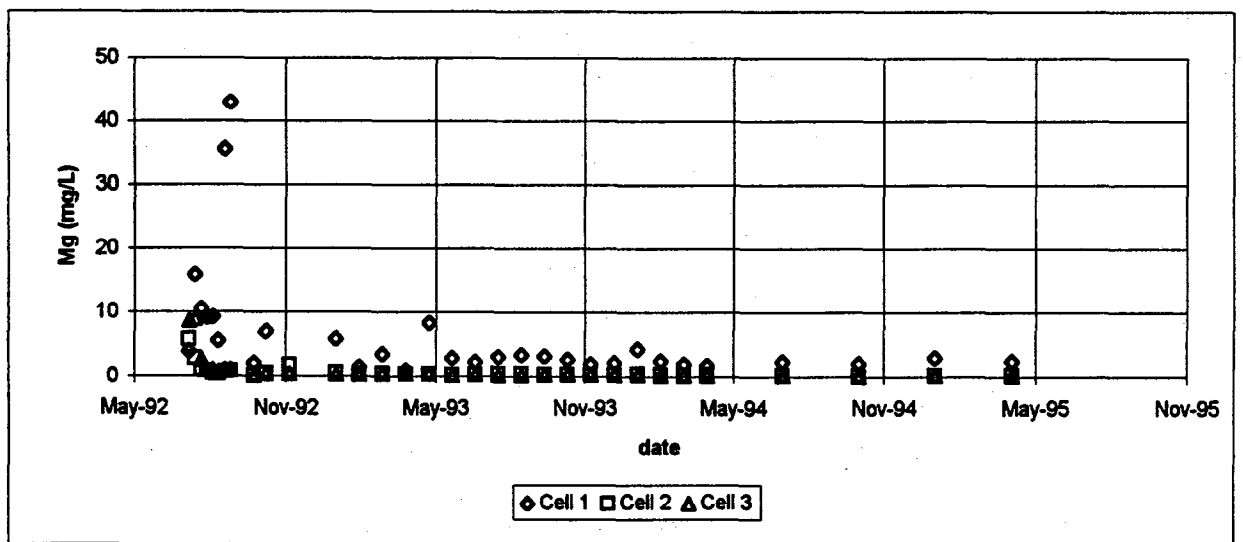
Figure 4.10c: Magnesium Concentration (mg/L) from Gibraltar Humidity Cells 1, 2 and 3

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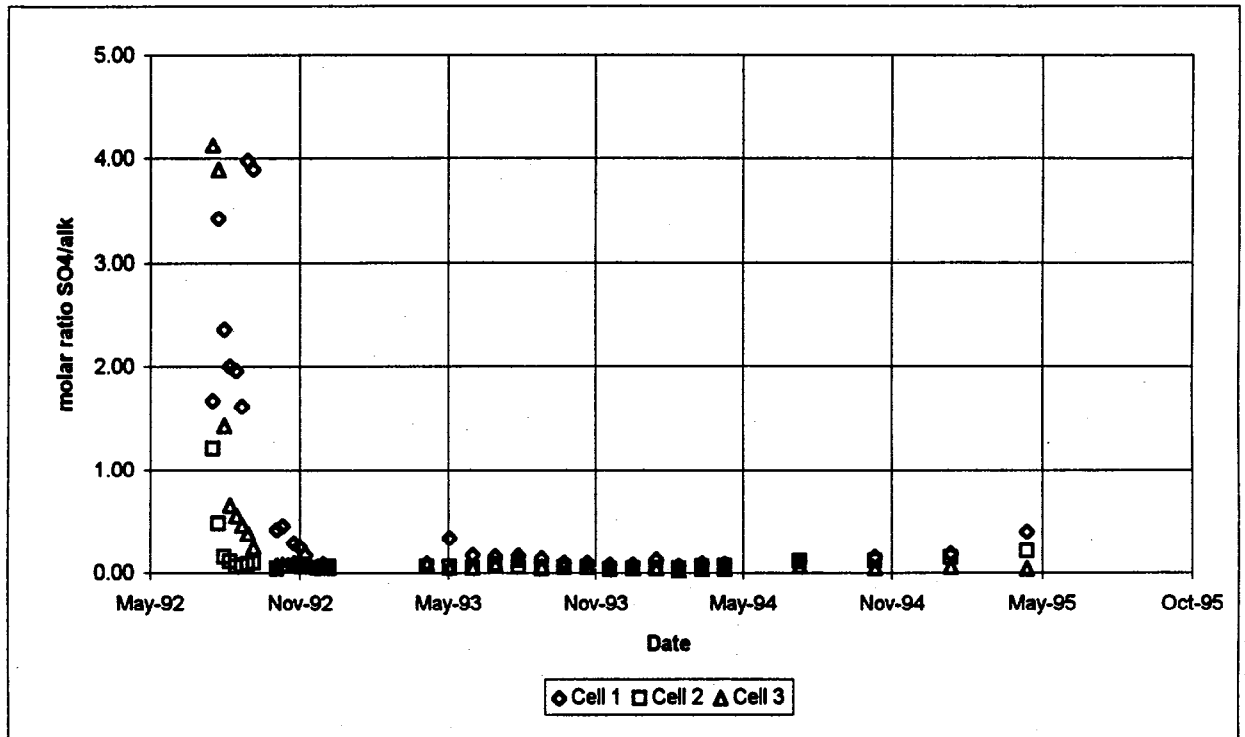
Figure 4.11: Molar ratio of Sulphate to Alkalinity from Gibraltar Humidity Cells 1, 2 and 3

Figures 4.12 a, b and c present the molar ratios of calcium, sodium and iron to sulphate. Calcium to sulphate (Figure 4.12a) increased during the initial five months and have remained relatively constant. The decrease in the sodium and iron to sulphate (Figure 4.12b, c) ratio in Cells 1 and 2 is attributed to the increase in sulphate concentration and unchanged sodium and iron concentrations (both are below detection limits). Figures 4.12d presents the molar ratios of calcium/sodium and indicates that in Cells 1 and 2 this ratio is increasing, indicating preferential leaching of the calcium. Figure 4.12e to i present the molar ratios of calcium, sodium, copper, molybdenum and manganese to iron. Changes in the calcium to iron ratio (Figure 4.12e) in Cells 1 and 2 reflect the increased concentration of calcium and unchanged iron concentration in the leachate. The sodium to iron and copper to iron ratios (Figure 4.12f, g) are constant in all three cells since these parameters are below detection limits. The molybdenum to iron ratio (Figure 4.12h) is increasing in Cell 2 and 3 reflecting the increasing molybdenum concentrations in these cells. The manganese to iron ratio (Figure 4.12i) is increasing in Cell 1 indicating a preferential leaching of manganese.
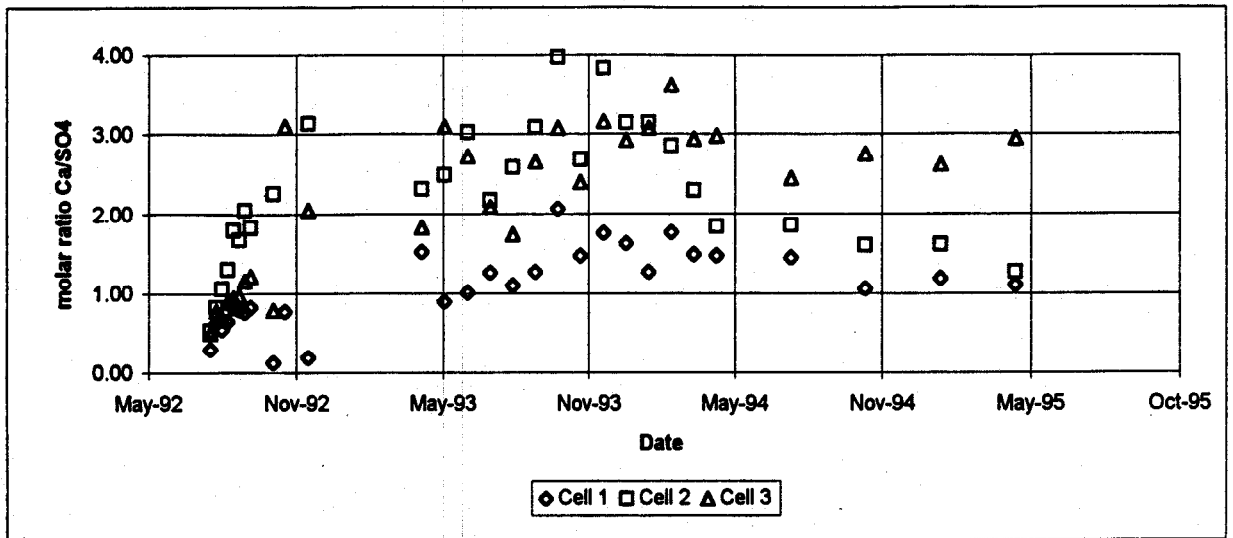
Figure 4.12a: Molar ratio of Calcium to Sulphate from Gibraltar Humidity Cells 1, 2 and 3
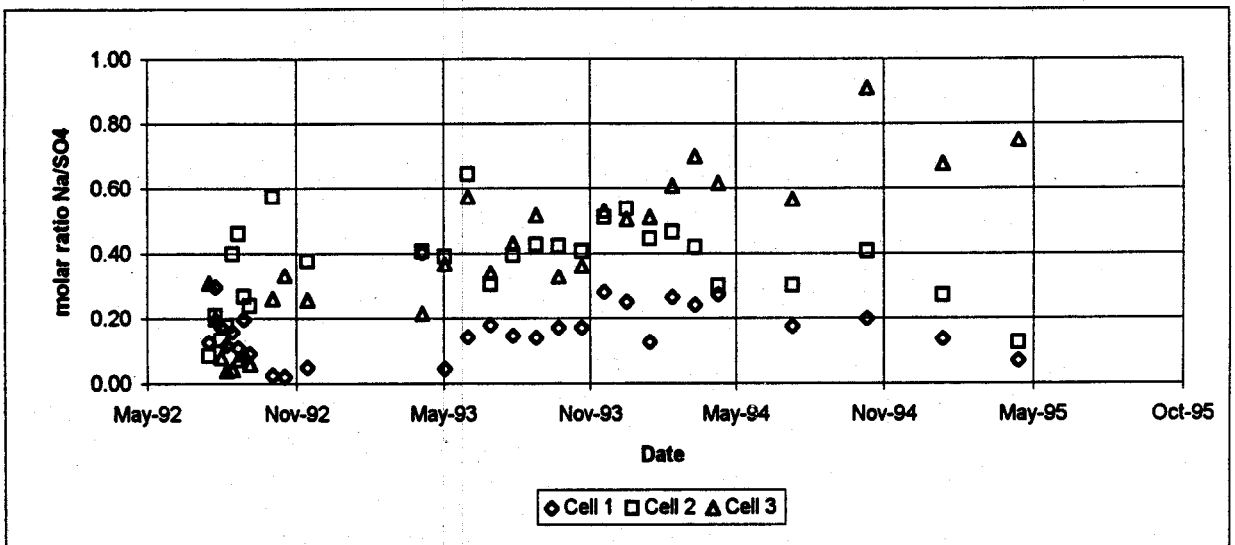
Figure 4.12b: Molar ratio of Sodium to Sulphate from Gibraltar Humidity Cells 1, 2 and 3
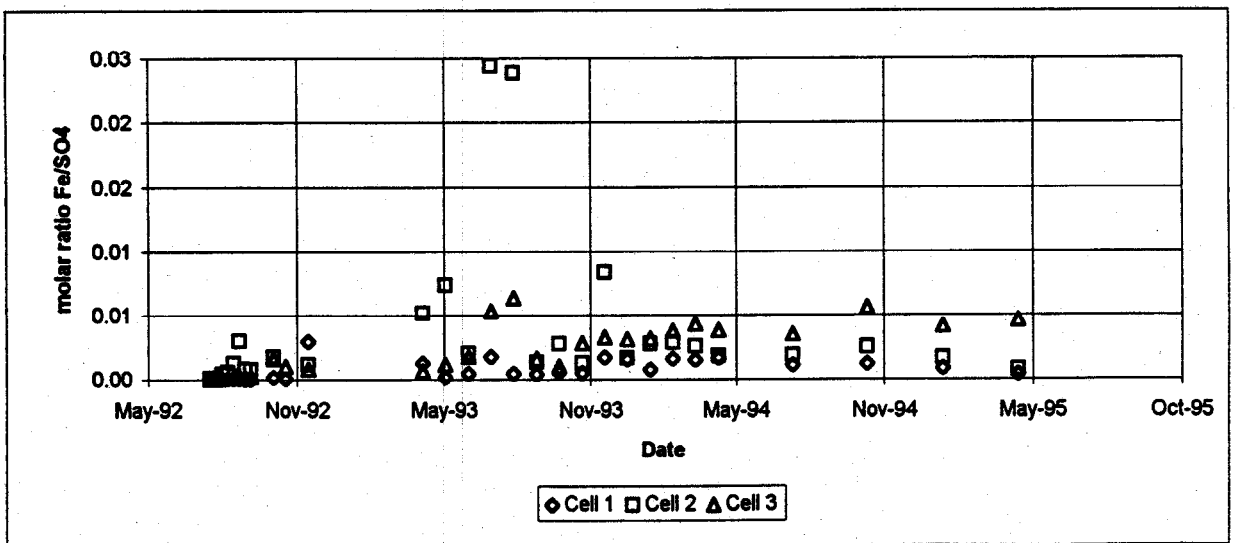
Figure 4.12c: Molar ratio of Iron to Sulphate from Gibraltar Humidity Cells 1, 2 and 3
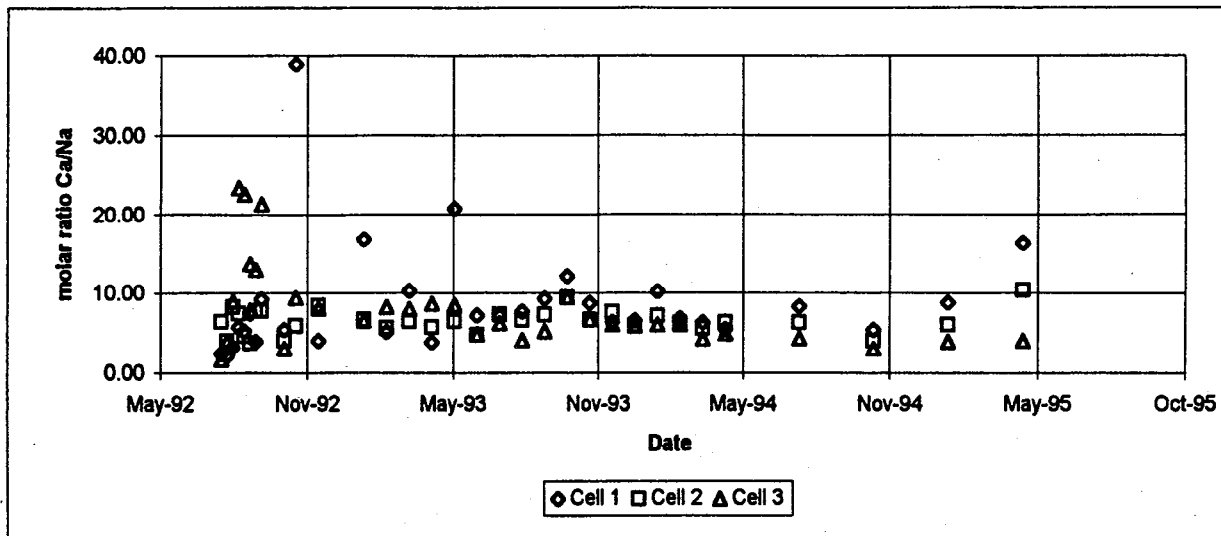
Figure 4.12d: Molar ratio of Calcium to Sodium from Gibraltar Humidity Cells 1, 2 and 3
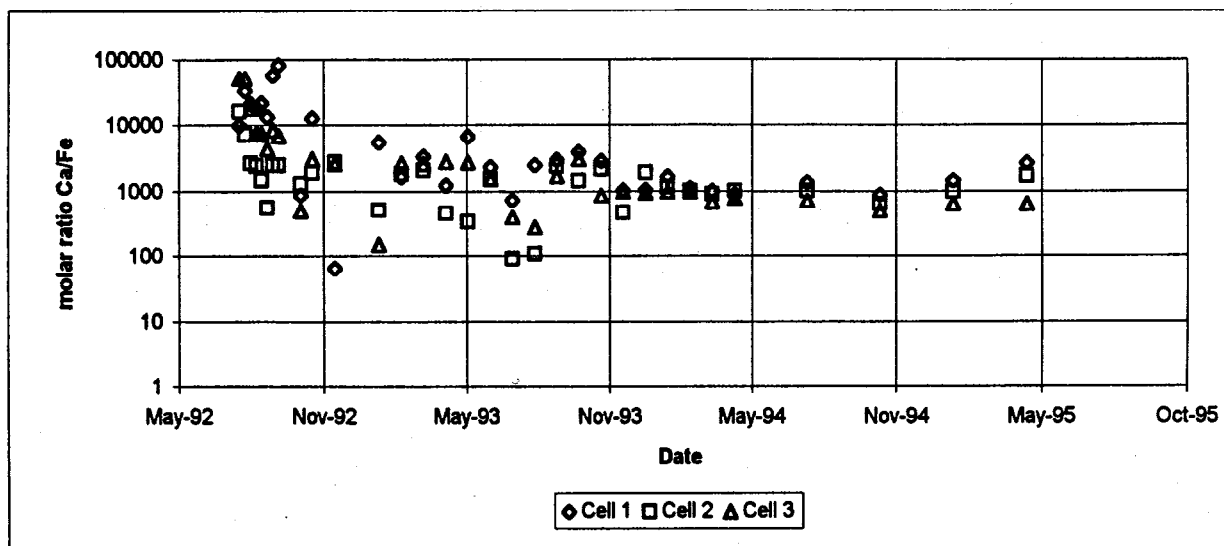
Figure 4.12e: Molar ratio of Calcium to Iron from Gibraltar Humidity Cells 1, 2 and 3
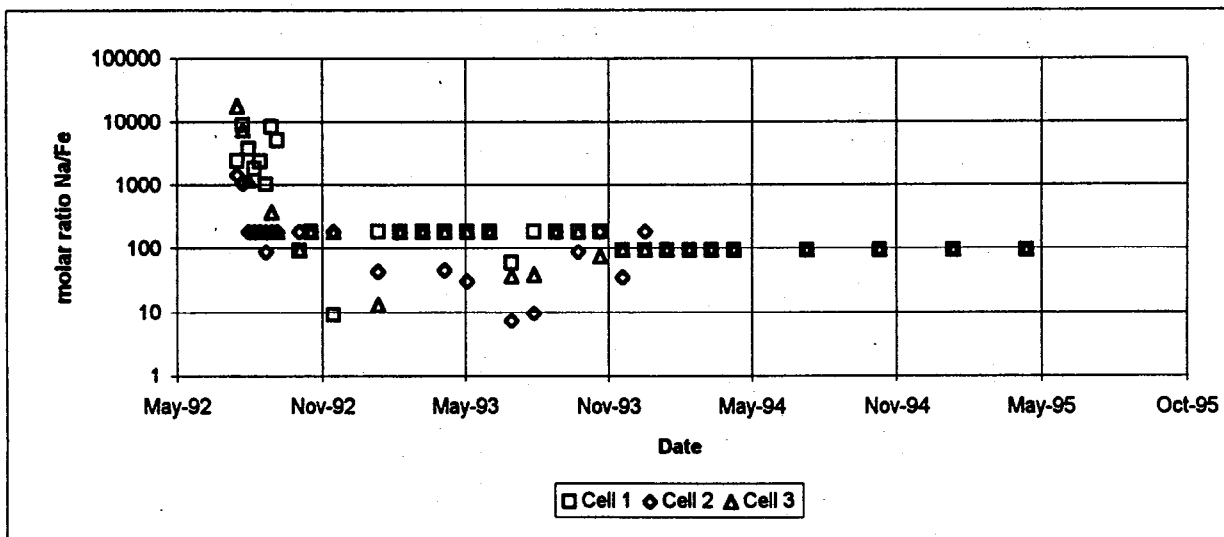
Figure 4.12f: Molar ratio of Sodium to Iron from Gibraltar Humidity Cells 1, 2 and 3

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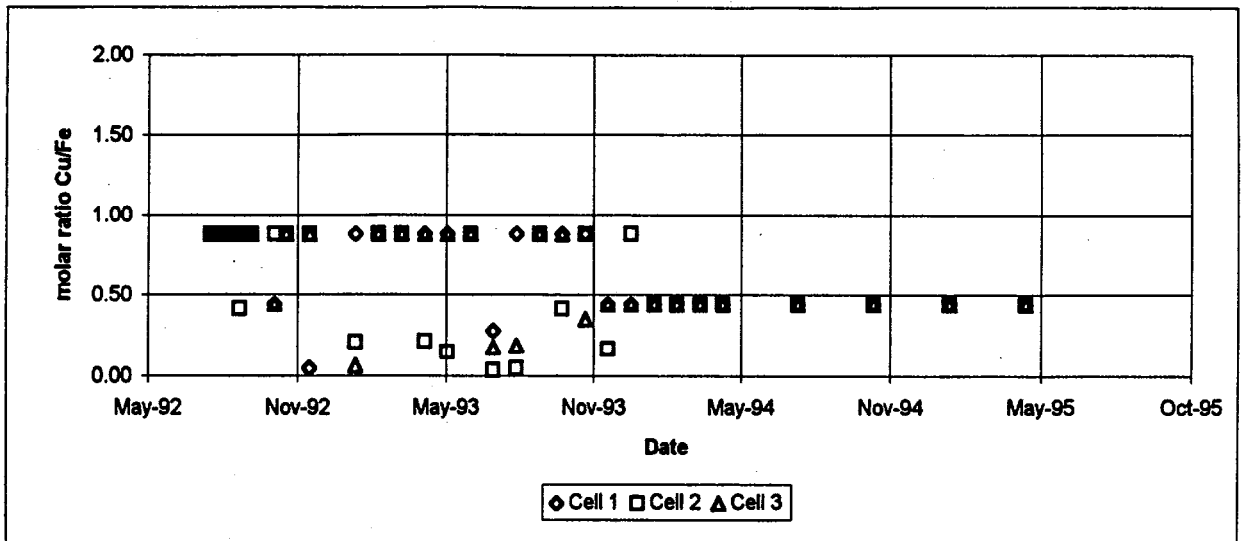
Figure 4.12g: Molar ratio of Copper to Iron from Gibraltar Humidity Cells 1, 2 and 3
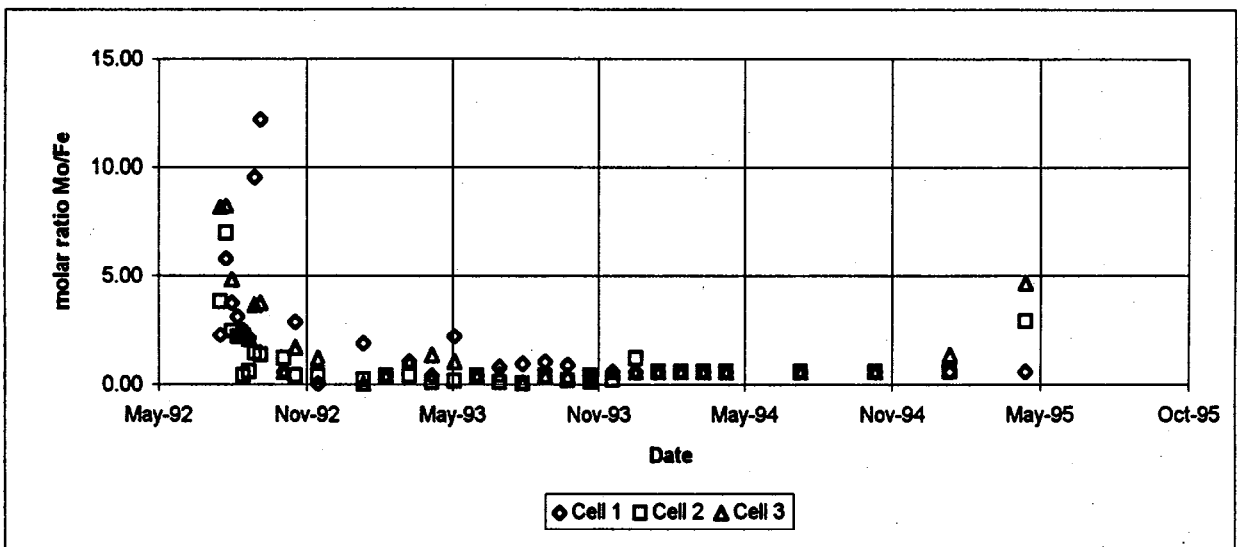
Figure 4.12h: Molar ratio of Molybdenum to Iron from Gibraltar Humidity Cells 1, 2 and 3
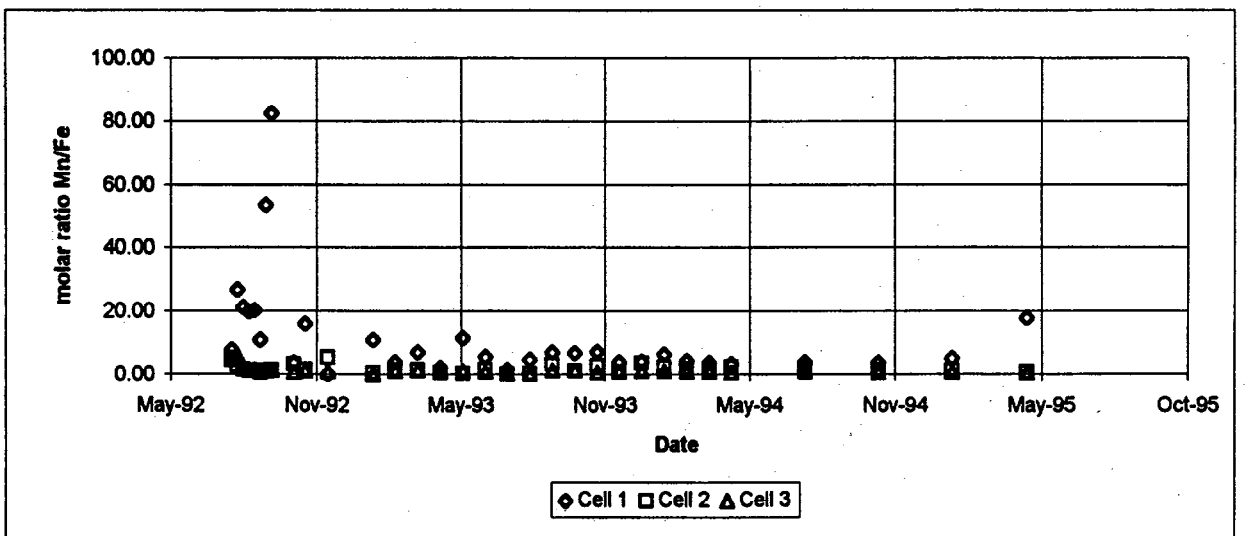
Figure 4.12i: Molar ratio of Manganese to Iron from Gibraltar Humidity Cells 1, 2 and 3

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The implications of the results of these kinetic tests include:

1) Approximately 4 to 5 months (16 to 20 weeks) was necessary to remove the sulphate present at the start of testing and to reach a steady state;

2) Some parameters are introduced to solution and occur above detection limits during steady state conditions. These ions are calcium, strontium, sulphate, magnesium, molybdenum, manganese and zinc inferring that oxidation and neutralization reactions are occurring; and

3) Once stable conditions are attained in the cells, changes in the concentration and molar ratios would indicate the on-set of ARD conditions. Although pH conditions are neutral in all three cells, changes in concentration and molar ratio suggest that increasing oxidation and dissolution reactions may just be starting in Cells 1 and 2.

NP and AP Depletion Rates

The Gibraltar kinetic prediction tests have been established to verify the interpreted ARD potential from the static prediction testing of Phase I. The rate of sulphide mineral oxidation is determined by the occurrence of sulphate in the leachate assuming: all oxidized sulphur is released to solution, all the sulphur is completely oxidized to sulphate and precipitation of gypsum or other sulphate minerals does not limit the sulphate concentration. The rate of NP depletion can also be calculated using the concentration of ions in solution attributed to mineral dissolution. Both AP and NP depletion are considered in the following analysis with calculated rates summarized in Table 4.10 and shown in Figures 4.13 (Cell 1), 4.14 (Cell 2) and 4.15 (Cell 3).

Sulphide Oxidation Rate

The sulphide oxidation rate, shown in Table 4.9, are expressed on a weight basis and determined using either measured sulphate concentration or calculated sulphate concentration from measured conductivity. The mean rates are 2 to 12 mg as CaCO3/kg/week (or 1.9 to 11.5 mg as SO4/kg/week) since November 1992 (Table 4.9). During 1995, the rates have increased in Cells 1 (Figure 4.13) and 2 (Figure 4.14) to as high as 75 and 30 mg as $CaCO_3$/kg/week, respectively. This increase in sulphide oxidation suggests the onset of ARD conditions within these cells.

Calculations using these rates include the determination of AP depleted and the percent remaining based on the mean sulphide oxidation rates and the different AP values. These calculations are summarized in Table 4.10. In general, the depletion of AP has been minimal since November 1992 with over 95% of the original content still present. Ritchie (1994) and Kwong (1995) suggest that different sulphide minerals have different relative oxidation rates resulting in some sulphides, for example pyrite, being more stable than others, for example sphalerite. Although pyrite is the principal sulphide mineral in the Gibraltar sample, there may be preferential oxidation occurring of the trace sulphides (i.e. chalcopyrite, molybdenum, bornite) and other opaque minerals resulting in the time lag to pyrite oxidation.
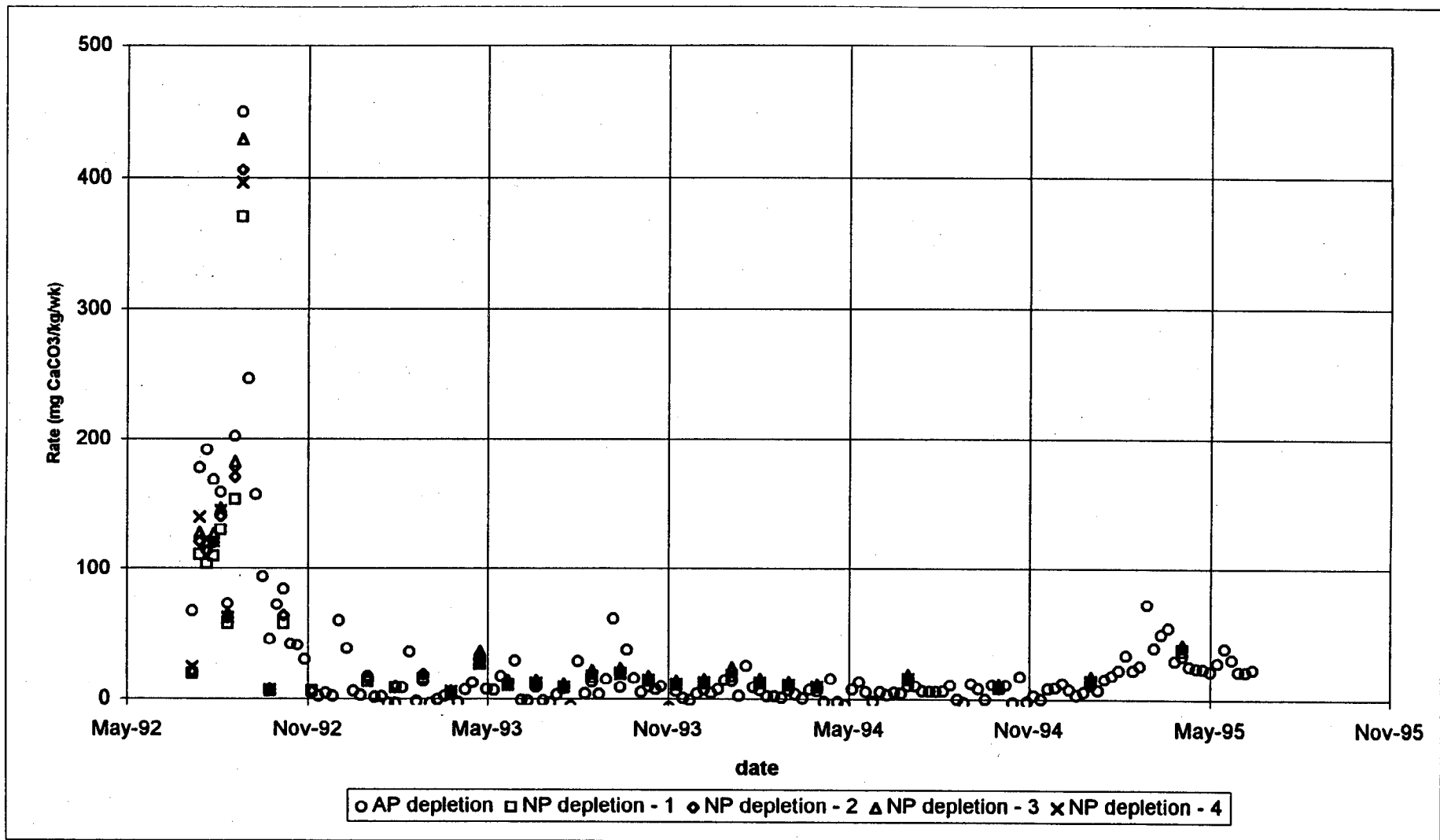
Figure 4.13: AP and NP Depletion Rates in Gibraltar Humidity Cell 1

(AP depletion calculated from measured sulphate concentrations and calculated sulphate concentration from conductivity measurements;

NP depletion-1 calculated based on Bradham and Carrucio, 1990; NP depletion-2 calculated based on White et al, 1994;

NP depletion-3 calculated based on Morin et al, 1995a carbonate ratio; NP depletion-4 calculated based on Morin et al, 1995a silicate ratio)
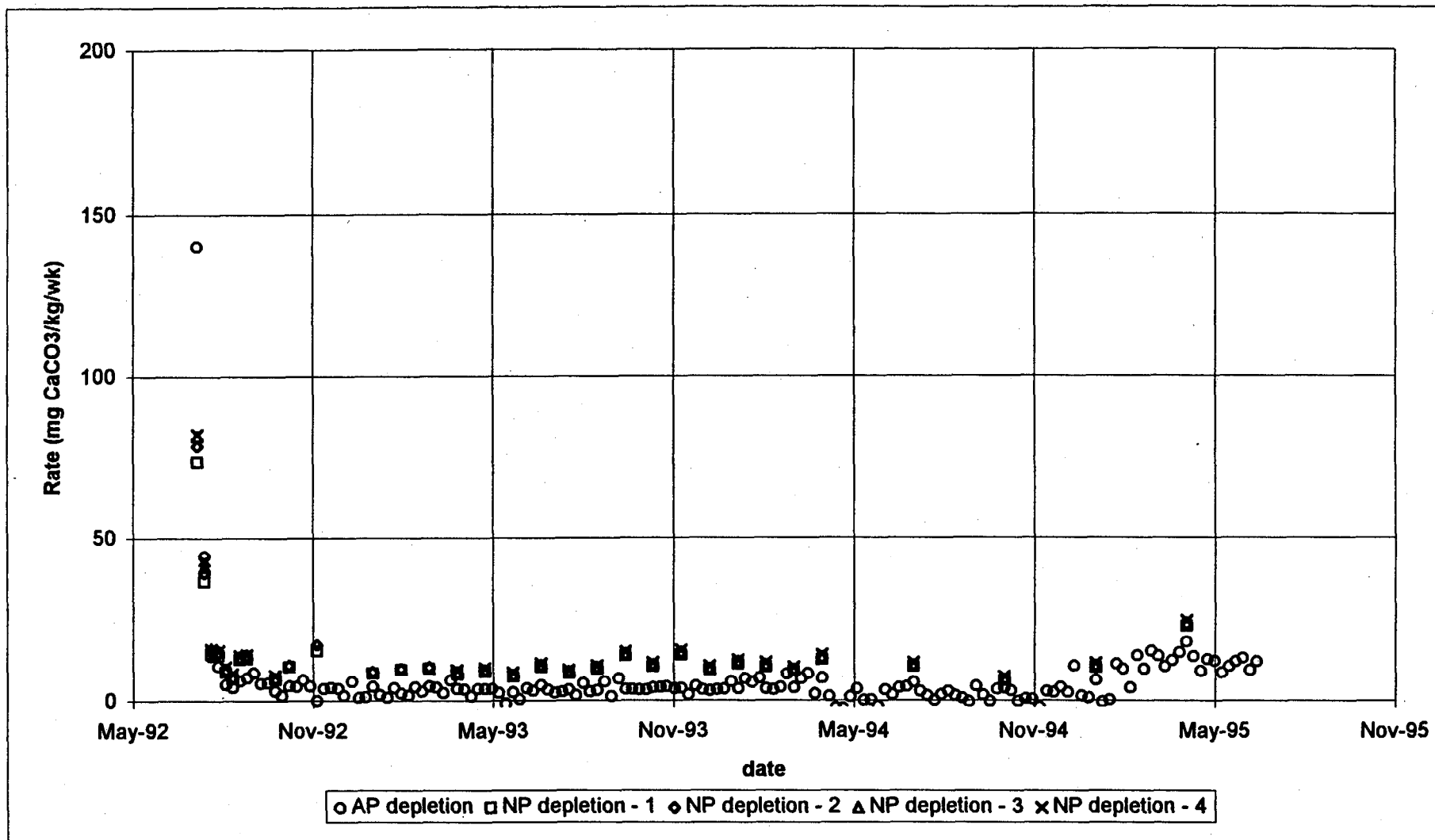
Figure 4.14: AP and NP Depletion Rates in Gibraltar Humidity Cell 2

(AP depletion calculated from measured sulphate concentrations and calculated sulphate concentration from conductivity measurements;
NP depletion-1 calculated based on Bradham and Carrucio, 1990; NP depletion-2 calculated based on White et al, 1994;
NP depletion-3 calculated based on Morin et al, 1995a carbonate ratio; NP depletion-4 calculated based on Morin et al, 1995a silicate ratio)
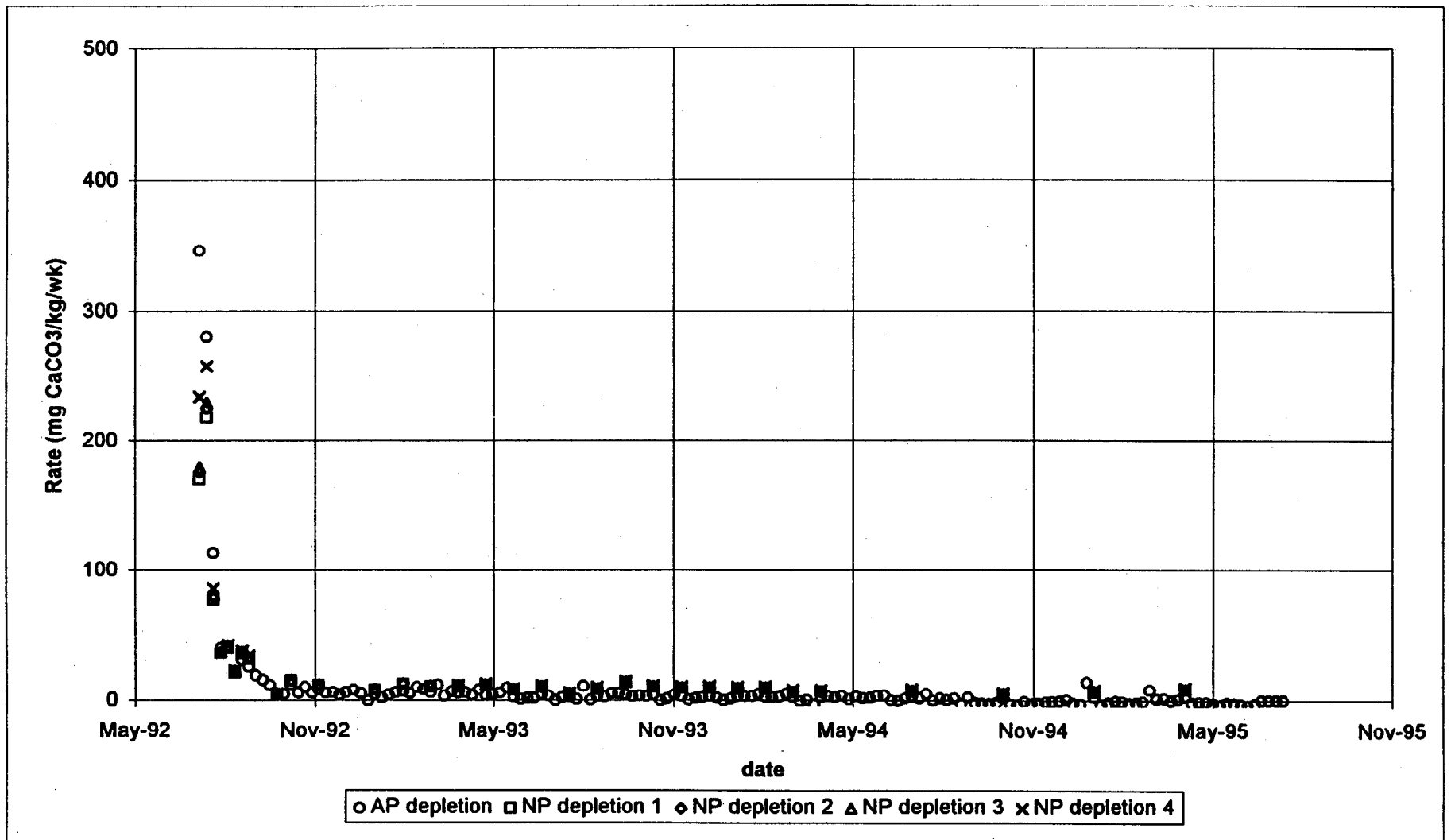
Figure 4.15: AP and NP Depletion Rates in Gibraltar Humidity Cell 3

(AP depletion calculated from measured sulphate concentrations and calculated sulphate concentration from conductivity measurements; NP depletion-1 calculated based on Bradham and Carrucio, 1990; NP depletion-2 calculated based on White et al, 1994; NP depletion-3 calculated based on Morin et al, 1995a carbonate ratio; NP depletion-4 calculated based on Morin et al, 1995a silicate ratio)

Table 4.9: Calculated AP and NP Depletion Rates for Gibraltar Kinetic Humidity Cells from November 1992 to May 1995

Cell	calculated AP depletion rate based on: SO4 production (mg as CaCO3/kg/week)				calculated NP depletion rate based on: Bradham and Carrucio (1990) (mg as CaCO3/kg/week)			
	n	mean	min	max	n	mean	min	max
1	138	11.98	-6.34	72.19	22	13.18	4.54	36.42
2	138	4.25	-2.41	17.92	22	10.62	6.01	22.78
3	138	2.19	-4.05	13.70	22	8.84	4.62	13.33

Cell	calculated NP depletion rate based on: Lapakko (1987) (mmoles as CaCO3/kg/week)				White and Jeffers; White et al (1994) (mg as CaCO3/kg/week)			
	n	mean	min	max	n	mean	min	max
1	22	0.13	0.05	0.36	22	15.61	5.22	39.62
2	22	0.11	0.06	0.23	22	11.05	6.20	23.30
3	22	0.09	0.05	0.13	22	9.06	4.74	13.55

Cell	calculated NP depletion rate based on: Morin et al (1995a) - carbonate ratio (mg as CaCO3/kg/week)				Morin et al (1995a) - silicate ratio (mg as CaCO3/kg/week)			
	n	mean	min	max	n	mean	min	max
1	18	18.01	5.65	41.81	18	14.99	5.49	38.15
2	18	11.19	6.32	23.63	18	11.86	7.21	24.51
3	18	8.81	4.82	13.69	18	9.67	5.67	14.43

Table 4.10: Calculated Percent AP and NP Depleted in Gibraltar Humidity Cells

AP Depletion Calculations		Cell 1	Cell 2	Cell 3
Mean sulphide oxidation rate (mg as $CaCO_3$/kg/week)	from Table 4.9	11.98	4.25	2.19
Cumulative flux S (mg $CaCO_3$/kg)	from Nov. 1992 to May 1995	498	177	91
Percent Remaining of Original	using original % reported from:			
% total - S	Wambolt et al (1995)	97.4	96.3	98.4
	this research	97.4	97.0	98.5
% Sulphide - S	Wambolt et al (1995)	93.8	94.7	97.0
NP Depletion Calculations				
Mean NP Depletion rate	from Table 4.9 using:			
(mg or mmoles as	Bradham and Carrucio (1990)	13.18	10.62	8.84
$CaCO_3$/kg/week)	Lapakko (1987)	0.13	0.11	0.09
	White et al (1994)	15.61	11.05	9.06
	Morin et al (1995a) carbonate ratio	18.01	11.19	8.81
	Morin et al (1995a) silicate ratio	14.99	11.86	9.67
Cumulative flux $CaCO_3$	from Nov. 1992 to May 1995 using:			
(mg or moles $CaCO_3$/kg)	Bradham and Carrucio (1990)	1713	1381	1149
	Lapakko (1987)	0.017	0.014	0.015
	White et al (1994)	2029	1437	1178
	Morin et al (1995a) carbonate ratio	2341	1455	1145
	Morin et al (1995a) silicate ratio	1949	1542	1257
Percent Remaining of Original	using calculations of:			
Calcite	Bradham and Carrucio (1990)	96.0	88.3	91.6
(from Table 4.7)	Lapakko (1987)	96.0	88.3	91.6
	White et al (1994)	95.3	87.8	91.3
	Morin et al (1995a) carbonate ratio	94.6	87.7	91.6
	Morin et al (1995a) silicate ratio	95.5	86.9	90.8

Table 4.10: Calculated Percent AP and NP Depleted in Gibraltar Humidity Cells

AP Depletion Calculations		Cell 1	Cell 2	Cell 3
Mean sulphide oxidation rate (mg as CaCO$_3$/kg/week)	from Table 4.9	11.98	4.25	2.19
Cumulative flux S (mg CaCO$_3$/kg)	from Nov. 1992 to May 1995	498	177	91
Percent Remaining of Original	using original % reported from:			
% total - S	Wambolt et al (1995)	97.4	96.3	98.4
	this research	97.4	97.0	98.5
% Sulphide - S	Wambolt et al (1995)	93.8	94.7	97.0
NP Depletion Calculations				
Mean NP Depletion rate	from Table 4.9 using:			
(mg or mmoles as	Bradham and Carrucio (1990)	13.18	10.62	8.84
CaCO$_3$/kg/week)	Lapakko (1987)	0.13	0.11	0.09
	White et al (1994)	15.61	11.05	9.06
	Morin et al (1995a) carbonate ratio	18.01	11.19	8.81
	Morin et al (1995a) silicate ratio	14.99	11.86	9.67
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(mg or moles CaCO$_3$/kg)	Bradham and Carrucio (1990)	1713	1381	1149
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	Morin et al (1995a) silicate ratio	95.5	86.9	90.8

The rate of neutralization has been calculated by various methods reported in the literature. Lapakko (1987) uses calcium and magnesium concentration in solution (mmoles/L) to determine the dissolution rate of carbonate and silicate minerals. Carbonate dissolution rates were also considered by Bradham and Carrucio (1990) using calcium depletion rates (mg Ca/kg/week). White and Jeffers (1994) and White et al (1994) use calcium and magnesium leaching rates to determine NP depletion. Morin and Hutt (1994) and Morin et al (1995a) use sulphide oxidation rate and molar ratios (ions from neutralizing mineral dissolution to sulphate ions) to determine the type and rate of neutralization. Ions representing carbonate dissolution are calcium, magnesium, barium and strontium and ions from silicate mineral dissolution are calcium, sodium and potassium. NP depletion rates have been calculated and summarized in Table 4.10 and included in Figures 4.13, 4.14 and 4.15. In general, the rates are relatively similar at 9 to 19 mg $CaCO_3$/kg/week. The similar rates may be attributed to the predominance of calcium ions in solution from neutralizing mineral dissolution. In the Gibraltar samples, NP is from carbonate and silicate minerals, however, given the pH conditions and knowing the higher relative reactivity of carbonate to silicate (Sherlock et al, 1995), the neutralization occurring is predominantly by calcite dissolution. Also, NP depletion rates respond to changes in the sulphide oxidation rates and there is an increase in Cells 1 and 2 during 1995 to approximately 40 and 25 mg as $CaCO_3$/kg/week, respectively.

Calculations of the amount of calcite depleted since November 1992 and the percent remaining are included in Table 4.10. The authors listed above of the different NP depletion calculations use either the original calcium content of the sample from ICP analysis or the NP of the sample to calculate the amount of NP depleted as a percentage. Both carbonate and silicate minerals contain calcium and are contributing to NP as discussed in Section 4.1. Therefore, to calculate the amount depleted using either calcium content or NP would not be representative of the dissolution occuring, which is currently limited to carbonate dissolution. For this thesis the percentage of NP depleted is based on the amount of calcite present, identified through CIPW normative calculations and, based on mean NP depletion rates, approximate the calcite content remaining to be over 85% of the original calcite content.

Relation between Static and Kinetic Prediction Data

Assessment of static prediction data has indicated:

1. NP values vary with digestion conditions of different static test methods. The differences identified in the Gibraltar samples are relatively small, but may be important given the low NP values;

2. Sample mineralogy also affect AP and NP values. A mineralogical study identified pyrite as the principal sulphide mineral present contributing to AP with minor chalcopyrite, bornite and molybdenite. Sulphur also occurs in other species, namely sulphate, in the tailings but was not identified in the mineralogical study. Both carbonate and sodium-calcium silicates minerals are contributing to NP, however, the carbonate minerals would be the important buffering material in order to maintain a neutral pH. The identification of minerals contributing to AP and NP allows for the identification of chemical parameters that could be used to identify oxidation and dissolution reactions occuring within the humidity cells. In the Gibraltar case, calcium, strontium and sodium concentration in the leachate indicate NP mineral dissolution and iron, cobalt, manganese and sulphate concentration are due to sulphide mineral oxidation.

3. Differences in NP and AP values, due to differences in test method and/or mineralogy, lead to differences in interpretation depending on criteria used to differentiate potentially acid generating from non-acid generating. This is evident in the various interpretations of the static prediction data for the Gibraltar humidity cells where interpreted ARD potential differs between the methods.

Assessment of kinetic prediction data has indicated:

1. The leachate chemistry is highly variable in the first 16 to 20 weeks of the test during which time the existing sulphate would be leached. Once stable conditions were established certain chemical parameters occur in solution above detection limits, in this case, calcium, strontium, sulphate, magnesium, molybdenum, manganese and zinc, suggesting oxidation and dissolution reactions are occurring. Interpretation of these data suggest that oxidation of the trace sulphides is occurring and calcite dissolution is the predominant neutralization reaction.

2. Changes in concentration and molar ratios, during the latter part of 1994 and 1995, suggest increased oxidation/neutralization reaction rates although the pH is still neutral.

3. The oxidation and NP depletion rates can be determined from the measured leachate chemistry with the mean sulphide oxidation rate being 2 to 12 mg $CaCO_3$/kg/week and the NP depletion being 9 to 19 mg $CaCO_3$/kg/week. Using these rates, calculations indicate that over 95% of the original sulphide content and over 85% of the original calcite content is still present in the cells after three years of kinetic testing. Also, there is an increase in sulphide oxidation during the latter part of 1994 and 1995 and a corresponding increase in NP depletion suggesting the on-set of ARD conditions within two of the cells.

An important limitation of static prediction tests is that the rates and extent of acid producing and neutralizing reactions are not determined and the methods do not distinguish the reactive acid generating and neutralizing minerals from the less reactive. Therefore, the interpretation of static data provides an indication if ARD will occur but not when and to what extent. An important purpose of kinetic tests is to verify the interpretations of the static tests and determine the rate of ARD generation. For example, the interpretation of static prediction data for the Gibraltar tailings indicated a potential for ARD and humidity cells were initiated. After approximately three years of leaching the pH is still neutral and sulphate and metal concentrations are relatively low. During 1995, there is an indication that ARD conditions may be starting in Cells 1 and 2, which have the lowest and highest NP:AP ratios, respectively. Also, the cell (1) with the highest NP and AP has the highest calculated AP and NP depletion rates. This same cell also has the lowest NP:AP ratio.

With this assessment of the static and kinetic data, the next consideration is the on-site monitoring data and the relationship between it and the laboratory prediction data.

4.4.3 ON-SITE MONITORING DATA

Gibraltar has an extensive ground and surface water quality monitoring program at background stations, in the open pits and tailings impoundment, and downstream of the mine site. Fifty-four stations are established, sixteen of which are in the tailings impoundment area with the locations summarized in Table 4.1 and identified on Figure 4.3. Sampling follows accepted sampling and QA/QC protocols. Samples were analyzed on-site prior to 1992. Recent samples, however, are analyzed by ICP, GFAA and other accepted methods at an independent commercial laboratory in Vancouver.

The location of the monitoring sites are given in Figure 4.3 and the available data are summarized in Tables 4.1 and 4.2. For data presentation and discussion, the locations have been grouped into surface water sites (stations 101, 104, 105 and 114), finger drain sites (stations FD-01, FD-06, FD-08, FD-09, FD-13, and FD-14) and observation wells (stations AW-1, 2, MW-6A, B, and MW-7A, B). These data were made available for this thesis by the environmental staff at Gibraltar on Excel for Windows spreadsheets.

Description of Data

The static and kinetic prediction data indicate that calcium, sodium, and strontium occur within minerals contributing to NP and iron, cobalt and manganese occur in minerals contributing to AP. Parameters considered for this thesis are sulphate, pH, alkalinity (Figures 4.16a, b, c to 4.19a, b, c), calcium, strontium and sodium (Figure 4.20a, b, c to 4.22a, b, c) and iron and manganese (Figure 4.23 a, b, c to 4.24a, b, c). Other parameters include copper, molybdenum, magnesium and phosphorus (Figures 4.25a, b, c to 4.28a, b, c). Cobalt, zinc and lead are below detection limits and are not presented.

pH, Sulphate and Alkalinity

Field pH (Figures 4.16a, b, c) conditions are neutral at most stations except within the tailings supernatant (station 105) which is more alkaline. These pH conditions exist in the supernatant due to the addition of lime to maintain tailings viscosity. Similar neutral pH conditions occur in the laboratory analysis of the same samples (Figure 4.17a, b, c). Sulphate concentration (Figure 4.18a, b, c) at the background surface water (station 101) is relatively low at 7 mg/L compared to the elevated concentration within the tailings supernantant (station 105) and seepage pond (station 111) at 650 mg/L. For unknown reasons the concentration at station 105 (Figure 4.18a) has increased since 1989. The finger drain stations (Figure 4.18b) have elevated sulphate concentrations relative to the tailings supernatant at 700 to 1100 mg/L. In both surface water (station 104) and observation wells (stations MW6-A,B and AW-1,2) the sulphate concentration is elevated relative to background levels up to 100 to 350 mg/L. This increase below the Main Tailings Dam is attributed to leakage from the impoundment through the underlying Tailings Aquifer to discharge in East Fork Cuisson Creek. In the area of the East Saddle Dam sulphate concentrations are low at 3 to 10 mg/L. Alkalinity (Figure 4.19a, b) is

monitored at the surface water and observation well stations and has a relatively constant concentration of 100 to 130 mg as $CaCO_3$/l in the surface water and 150 to 225 mg as $CaCO_3$/l in the ground water.

Figure 4.16: Field pH at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment

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Figure 4.17: Laboratory pH at a) Surface Water Stations, b) Finger Drain Stations and
c) Observation Well Stations Gibraltar Tailings Impoundment

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Figure 4.18: Sulphate Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain
Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
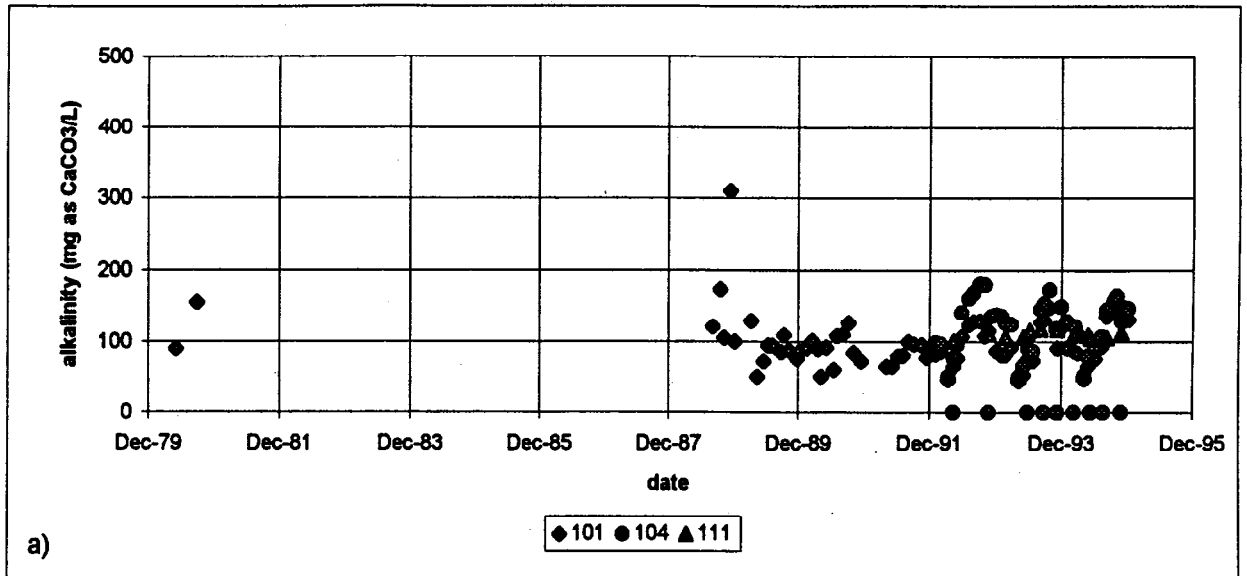
Figure 4.19: Alkalinity (mg as CaCO3/L) at a) Surface Water Stations and b) Observation Well Stations Gibraltar Tailings Impoundment

Calcium, Sodium and Strontium

These parameters are unavailable for stations 104, 114, MW6-A, B and MW7-A, B. The calcium concentrations (Figure 4.20a, b, c) are elevated within the tailings supernatant (station 105) and seepage pond (station 111), at 250 to 300 mg/L, relative to the background station 101 at 30 mg/L. The finger drains (Figure 4.20b) have either similar or elevated concentrations (as high as 375 mg/L) relative to the tailings supernatant. Observation wells below the Main Dam (stations AW-1,2) have calcium concentrations of 80 to 100 mg/L. Sodium concentrations (Figure 4.21a, b, c) show similar trends to the calcium with background levels of 2 mg/L in the surface water (station 101) and elevated concentrations in the tailings supernatant (station 105), seepage pond (station 111) and finger drains at 80 to 110 mg/L, and observation wells (stations AW-1,2), at 30 to 40 mg/L. Strontium concentrations (Figure 4.22a, b, c) are 0.13 mg/L at the background surface water station (station 101), 0.5 to 1.0 mg/L in the tailings supernatant and finger drains and 0.5 mg/L in observation wells AW-1 and AW-2.

Iron, Cobalt and Manganese

Of these ions, cobalt is not monitored on-site and manganese is not available for stations 104, MW6-A,B and MW7-A,B. Iron concentrations (Figure 4.23a, b, c) fluctuate significantly in the tailings supernatant, seepage pond and finger drains. This is particularly evident after December 1991, which corresponds to the time water quality analysis shifted from on-site to the contract laboratory. Since 1992, iron concentrations are from 0.08 to 0.14 mg/L at the surface water locations and below detection limits at observation well locations. The concentrations within the tailings supernantant (station 105) and seepage pond (station 111) are at or below

Figure 4.20: Calcium Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Station and c) Observation Well Stations Gibraltar Tailings Impoundment

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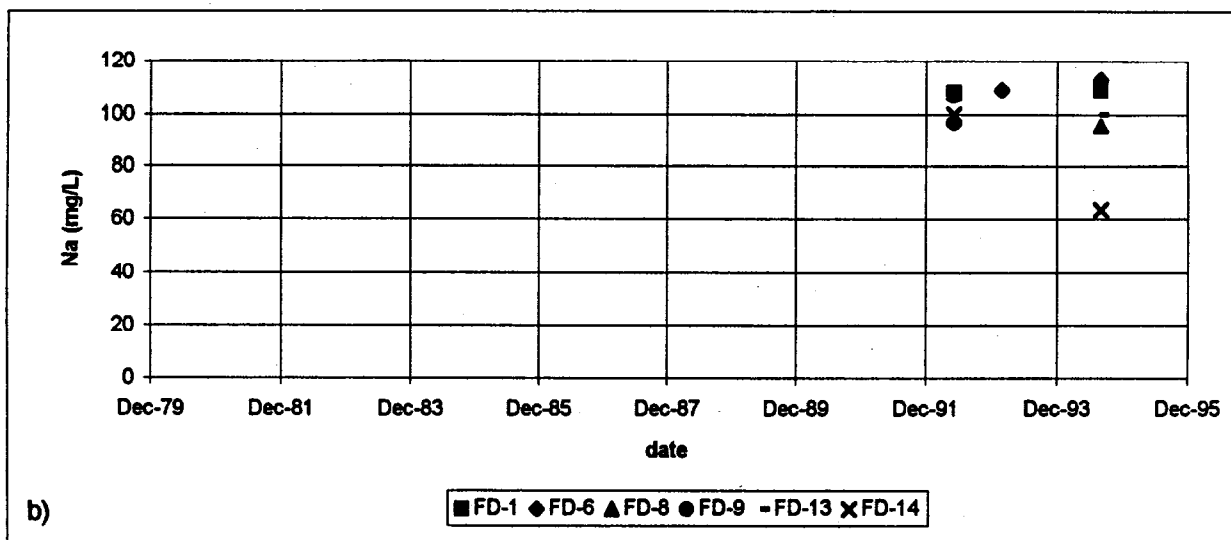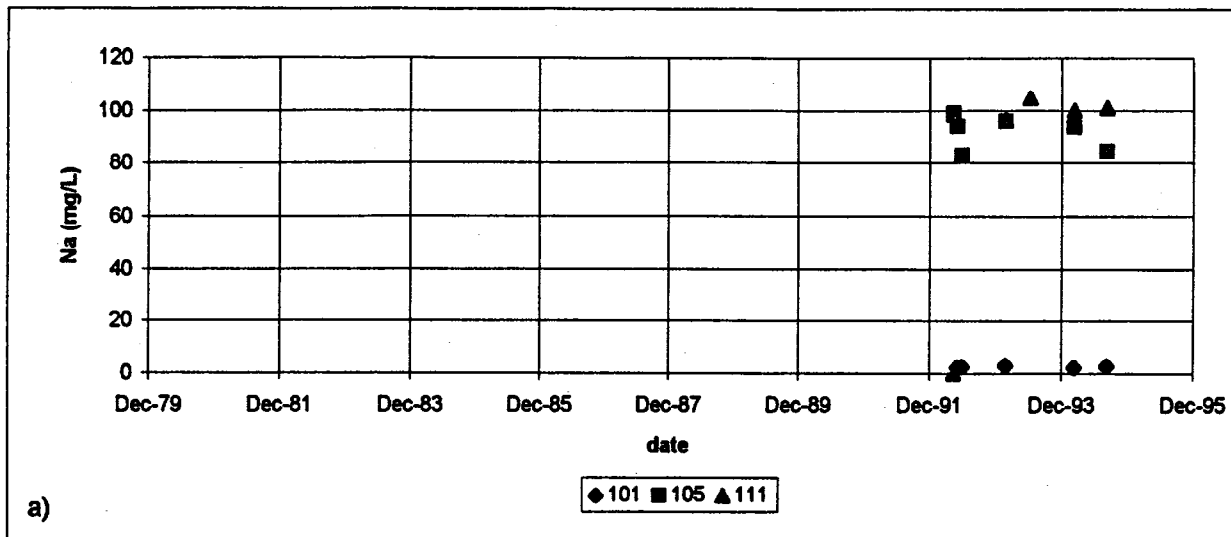
Figure 4.21: Sodium Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Station and c) Observation Well Stations Gibraltar Tailings Impoundment
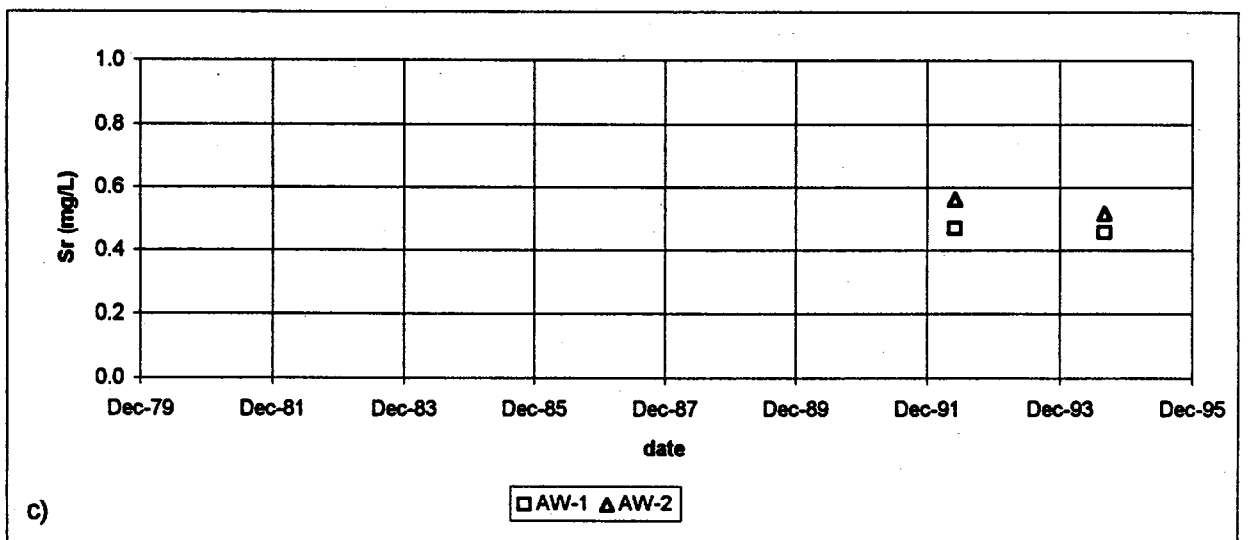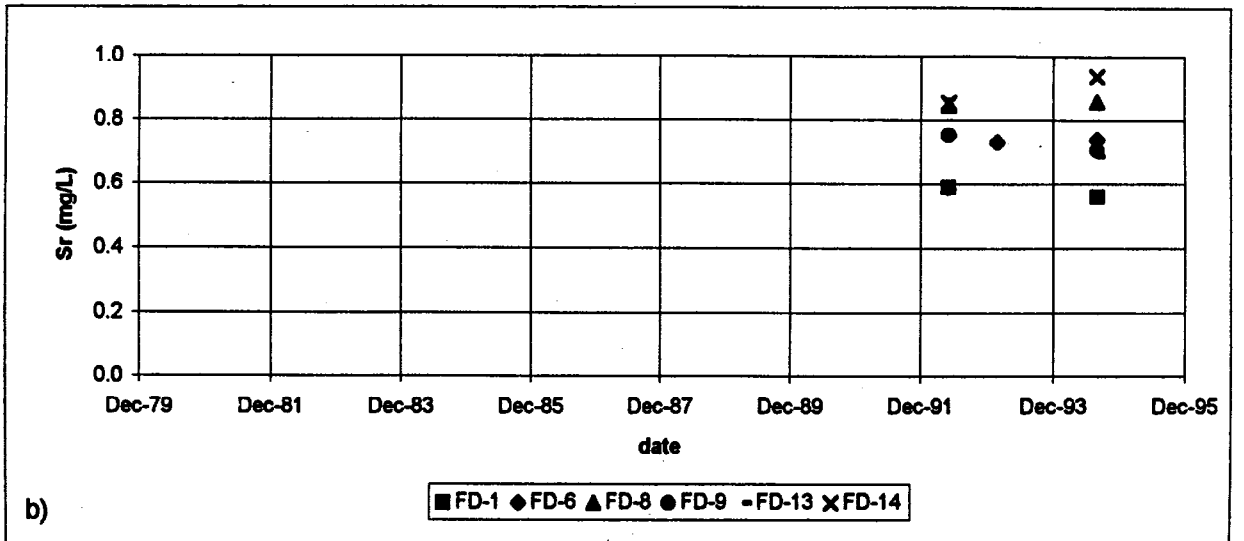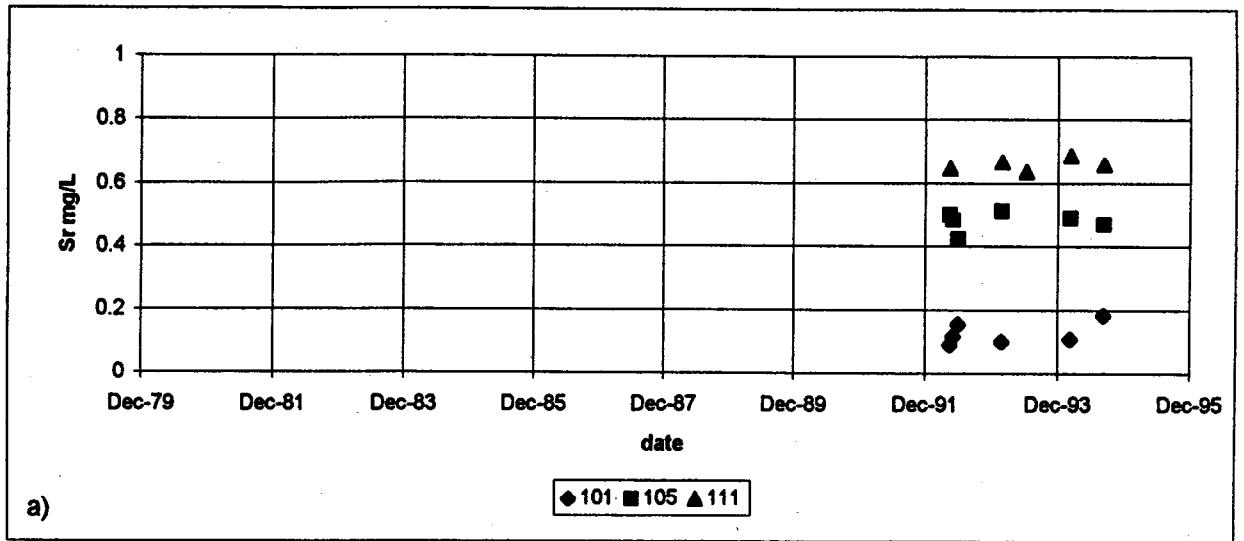
Figure 4.22: Strontium Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
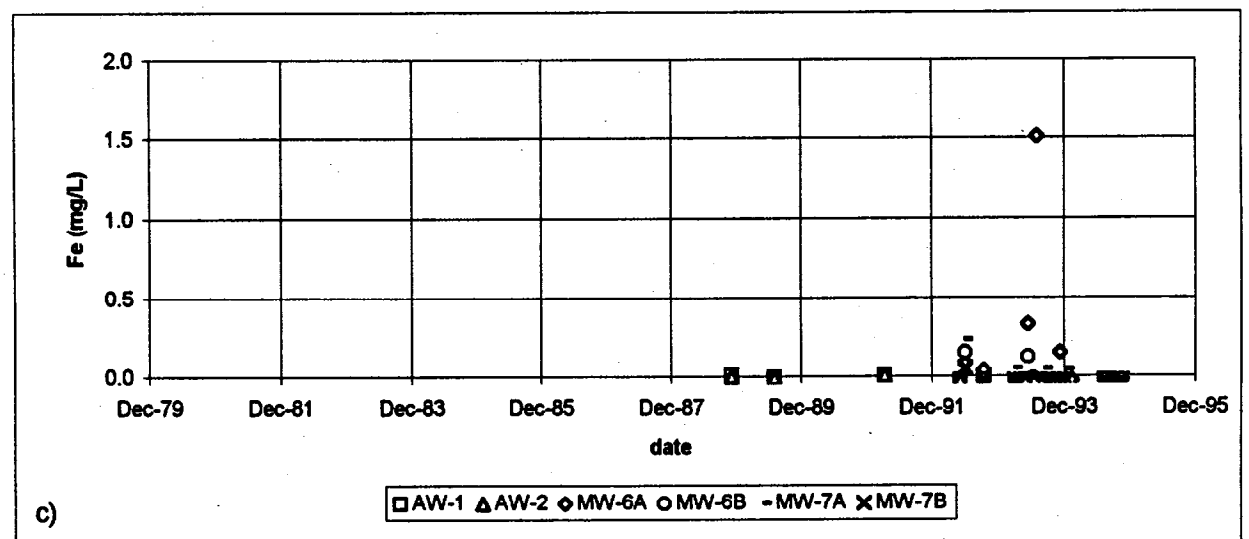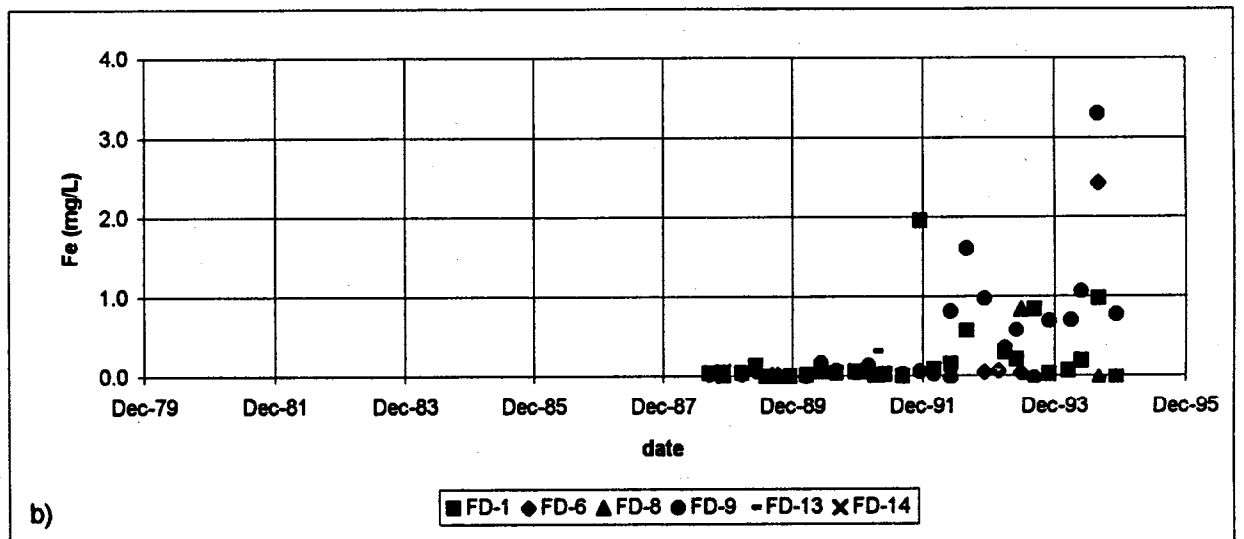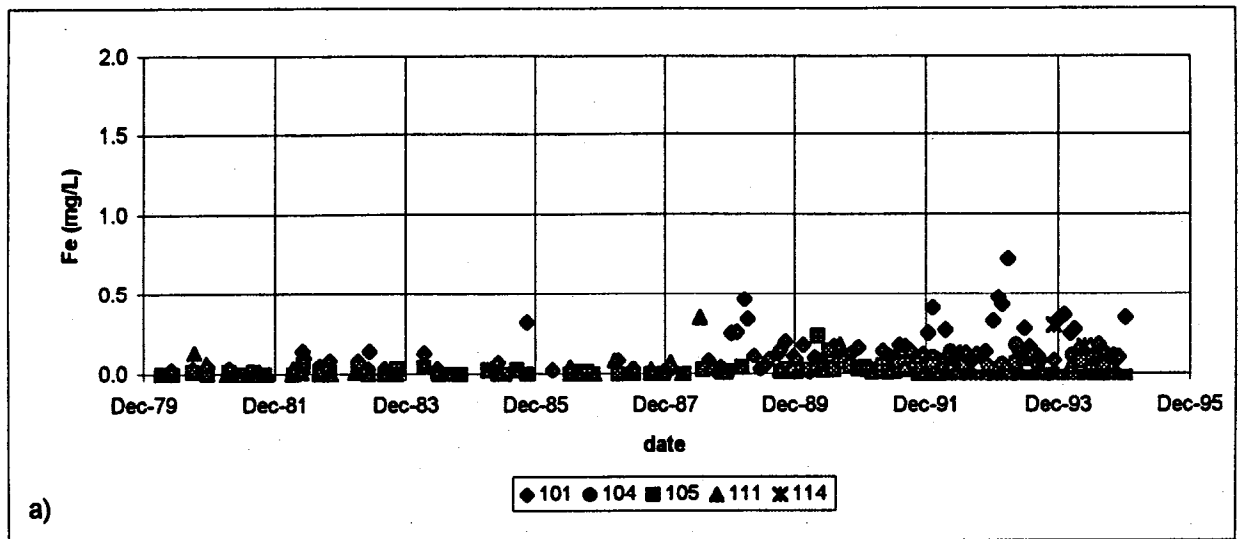
Figure 4.23: Iron Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
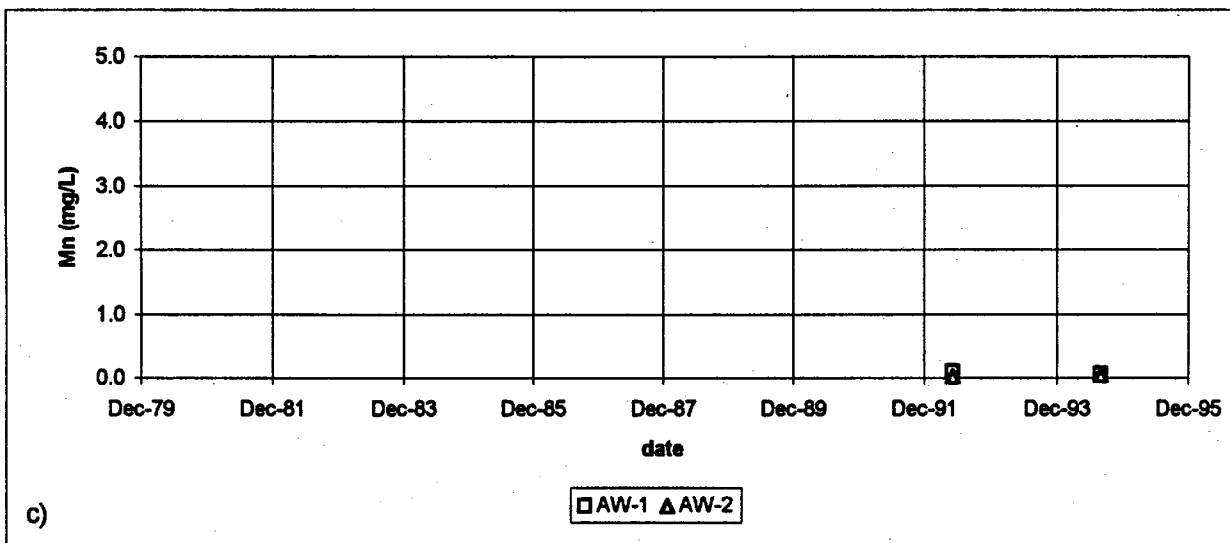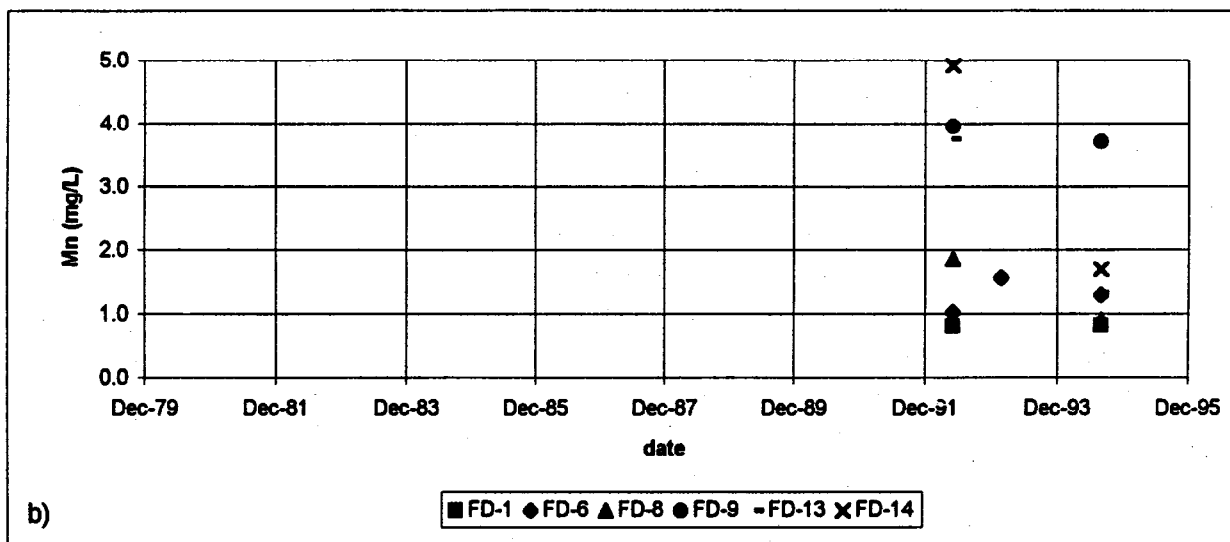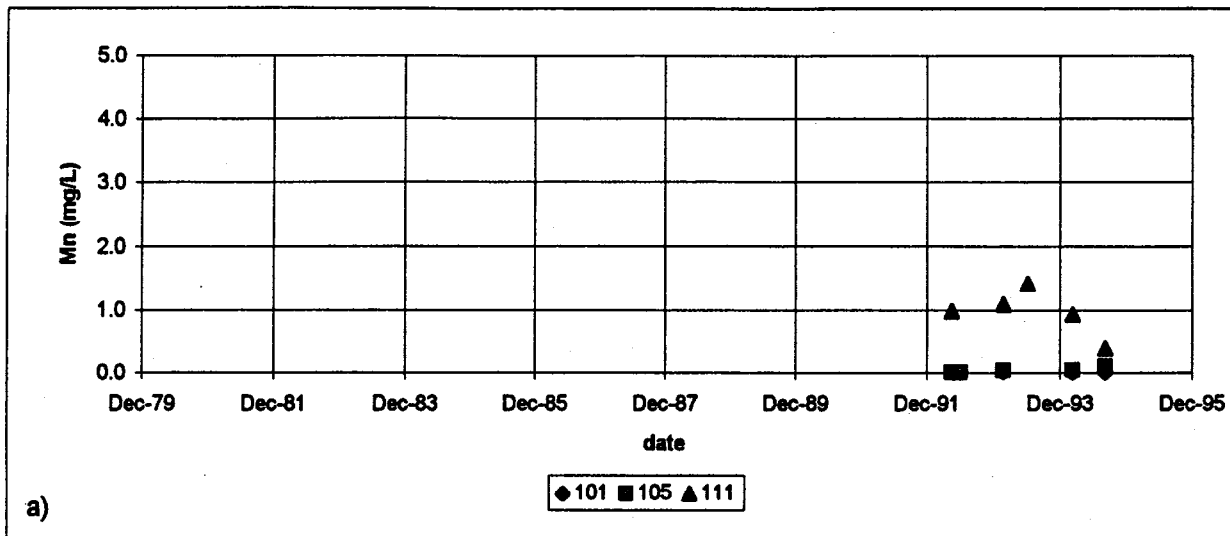
Figure 4.24: Manganese Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment

detection limits. In the finger drains, iron concentrations are between 0.03 to 0.9 mg/L, but has been as high as 3.5 mg/L. Manganese concentrations (Figure 4.24a, b, c) are 0.01 mg/L in the background surface water station (station 101) and elevated to 0.04 to 1.0 mg/L in the tailings supernatant and seepage pond. Manganese concentrations at the finger drains are 1 to 4 mg/L and below the Main Dam the observation wells are 0.02 to 0.07 mg/L.

Copper, Molybdenum, Zinc, Lead, Magnesium and Phosphorus

Similar trends between the stations are observed for copper, molybdenum, magnesium and phosphorus (Figure 4.25a, b, c to 4.28a, b, c). Zinc and lead are below detection limits at all locations and are not presented. At the background surface water stations (stations 101, 114) the range of concentrations are 0.006 mg/L copper, below or at detection limits molybdenum, 5 mg/L magnesium, and 0.01 mg/L phosphorus. Within the tailings supernatant (station 105) and seepage pond (station 111) these concentrations are elevated relative to the surface water background stations at 0.01 to 0.07 mg/L copper, 0.4 to 0.6 mg/L molybdenum, 5 to 12 mg/L magnesium and 0.01 mg/L phosphorus. The finger drains have similar concentrations to the supernatant and seepage pond except station FD-14, where molybdenum concentrations are lower and copper and magnesium concentrations are higher. In the observation wells, copper is 0.002 to 0.004 mg/L, molybdenum is 0.002 to 0.01 mg/L, magnesium is 20 mg/L and phosphorus is 0.01 to 0.04 mg/L, except at MW6-A where phosphorus concentrations are approximately 1 mg/L.
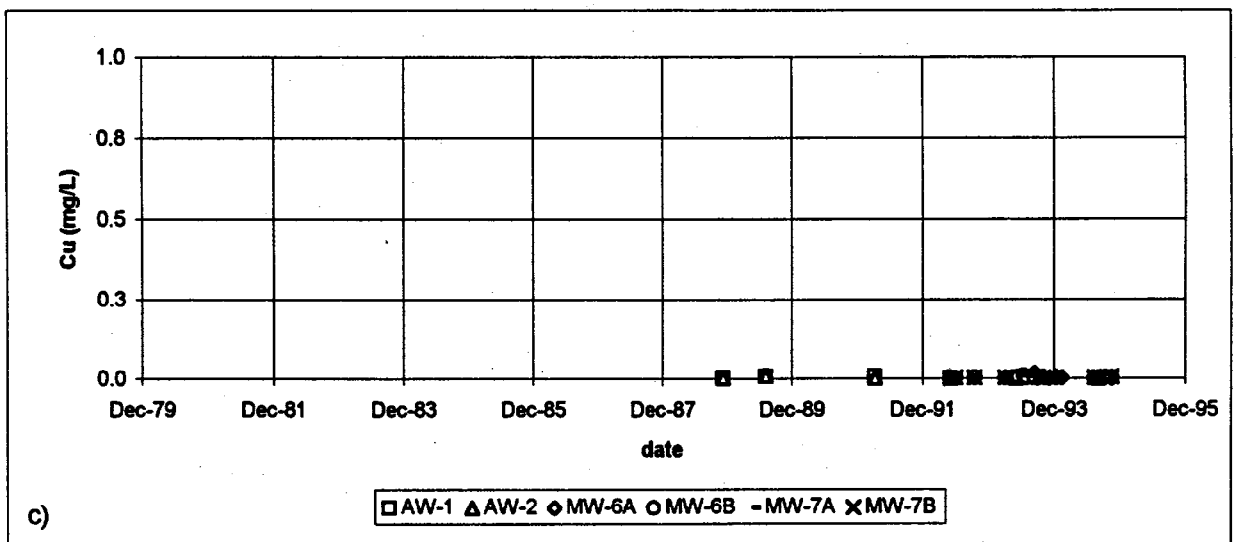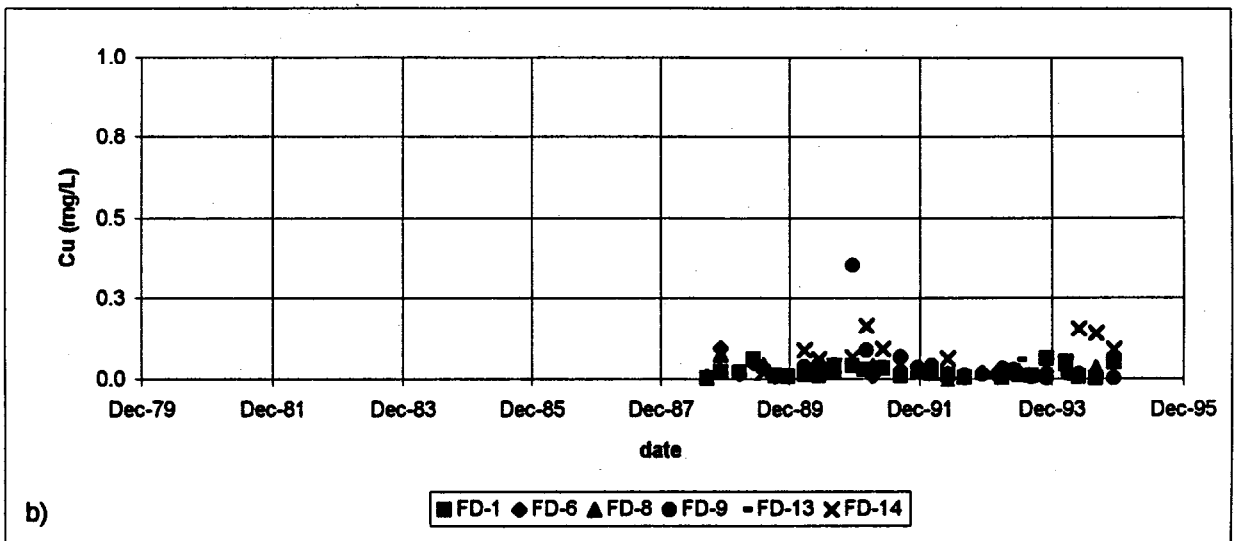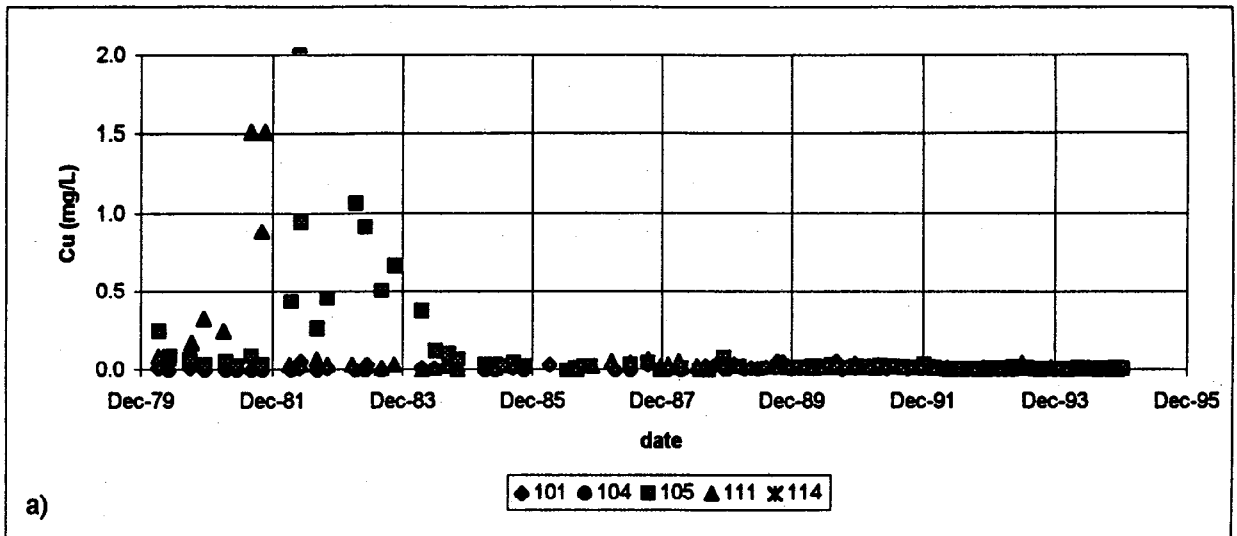
Figure 4.25: Copper Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
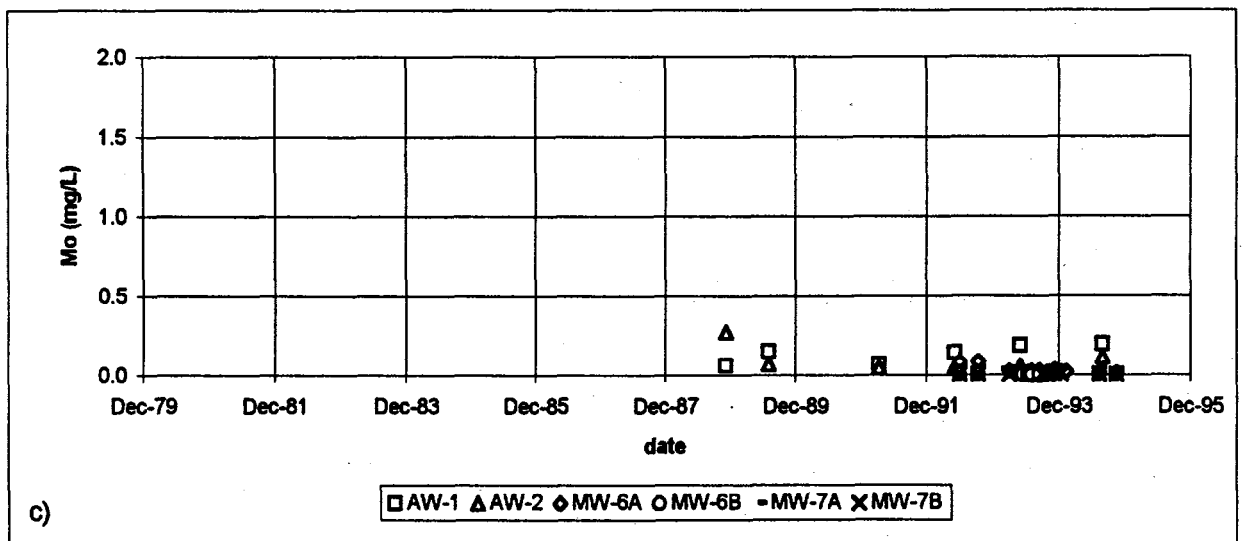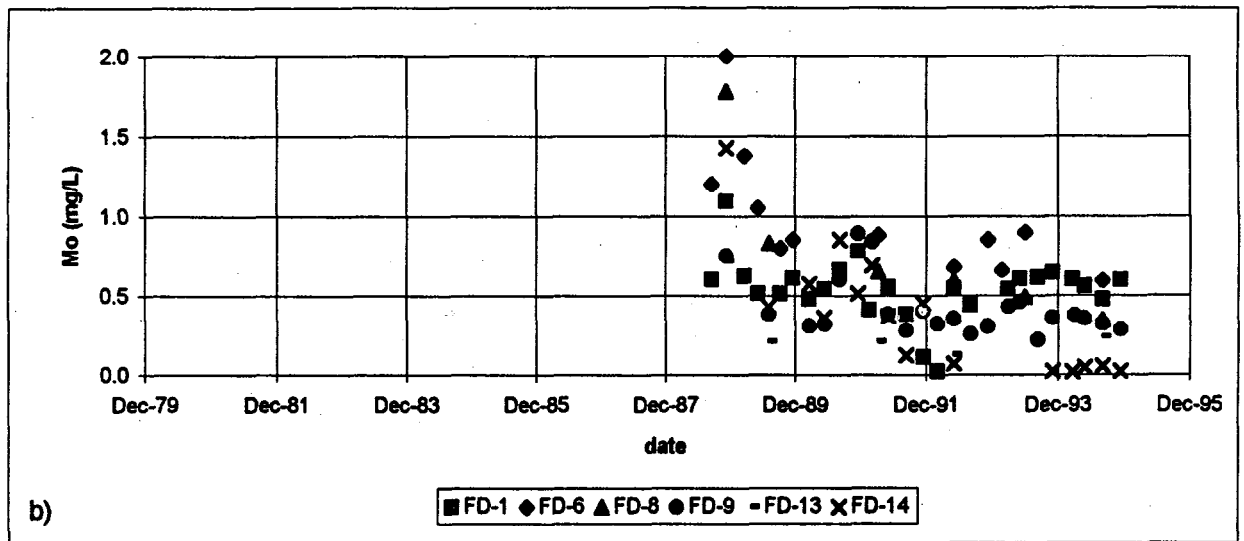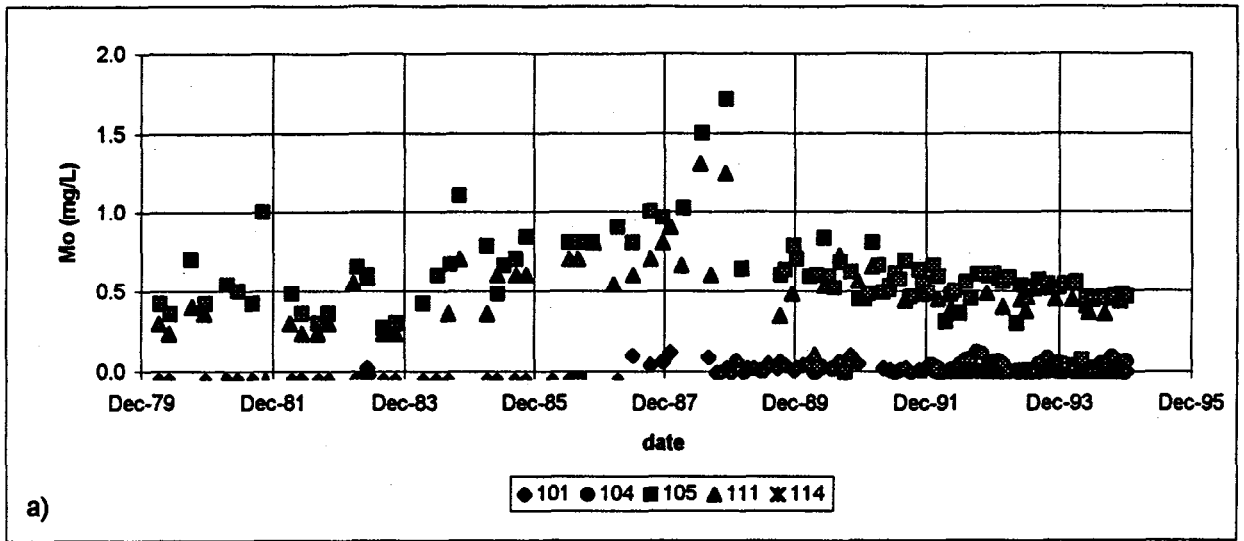
Figure 4.26: Molybdenum Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
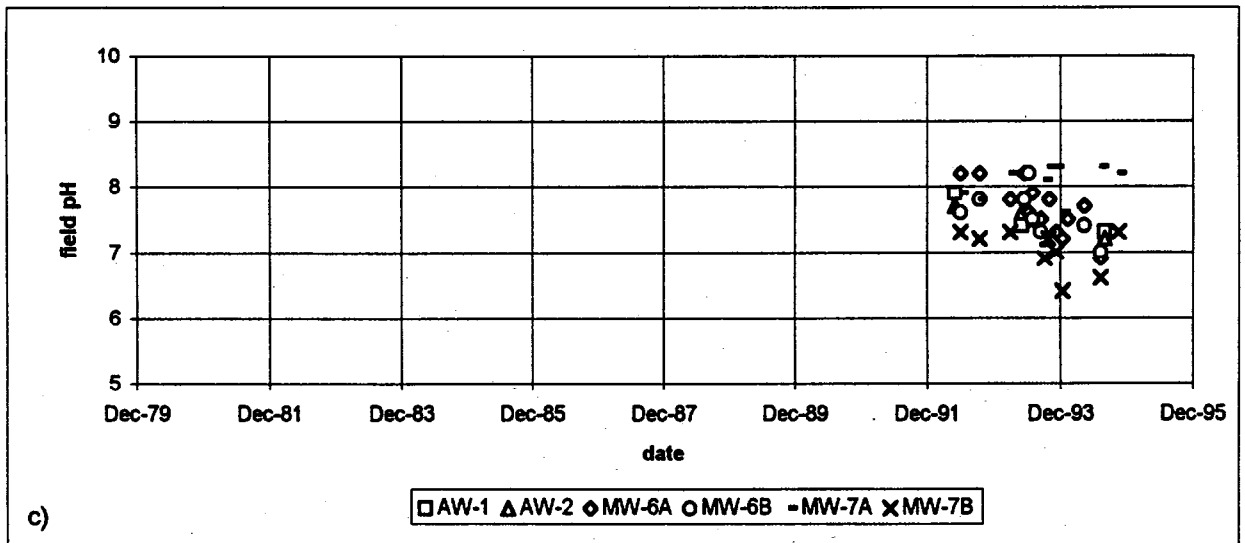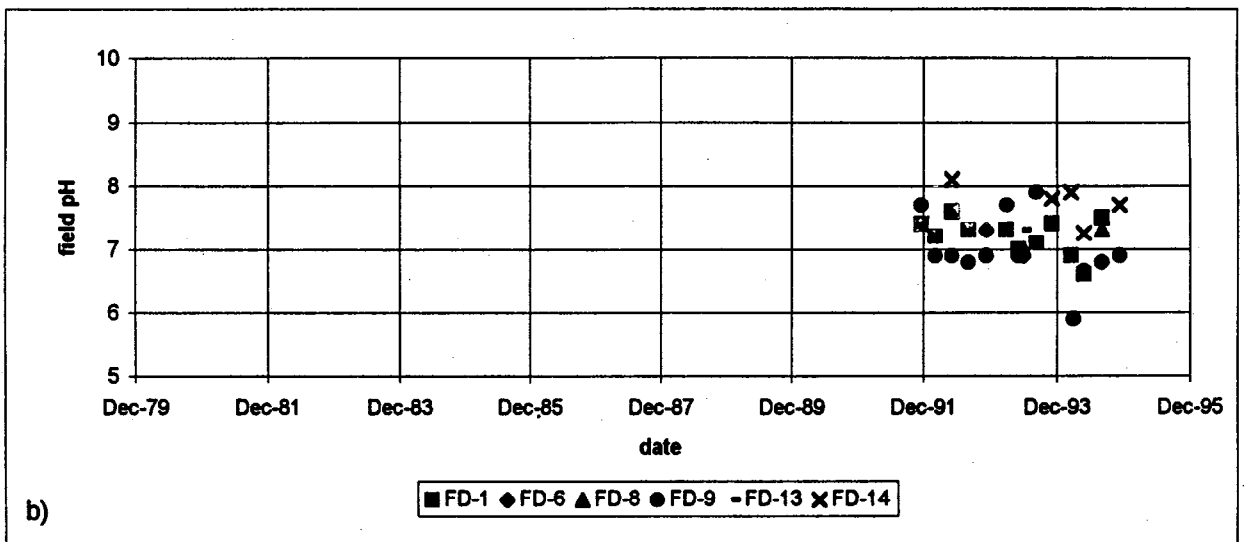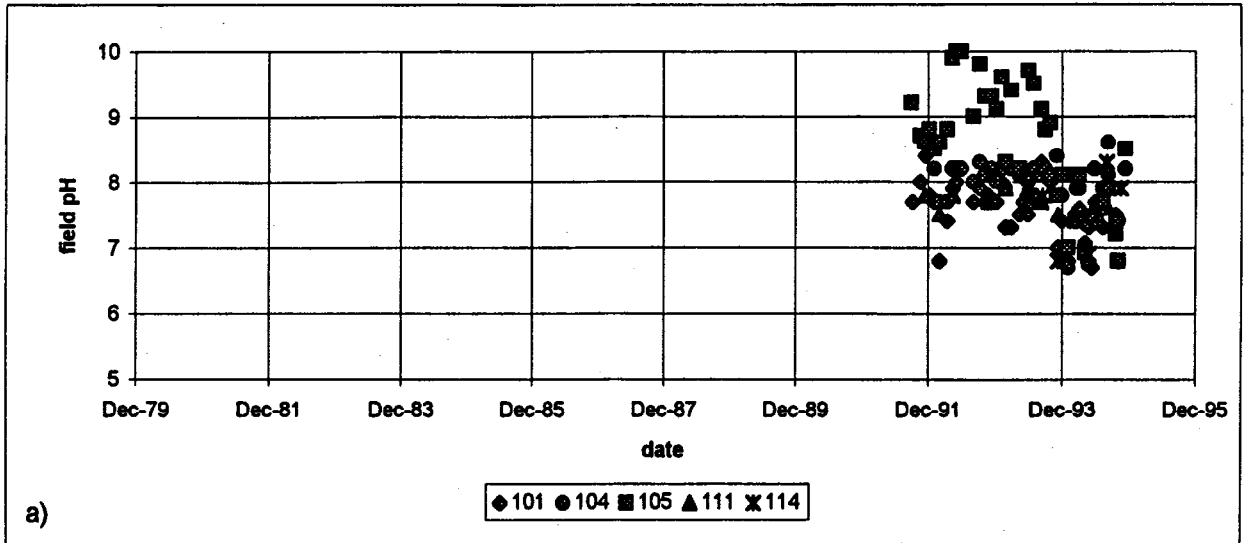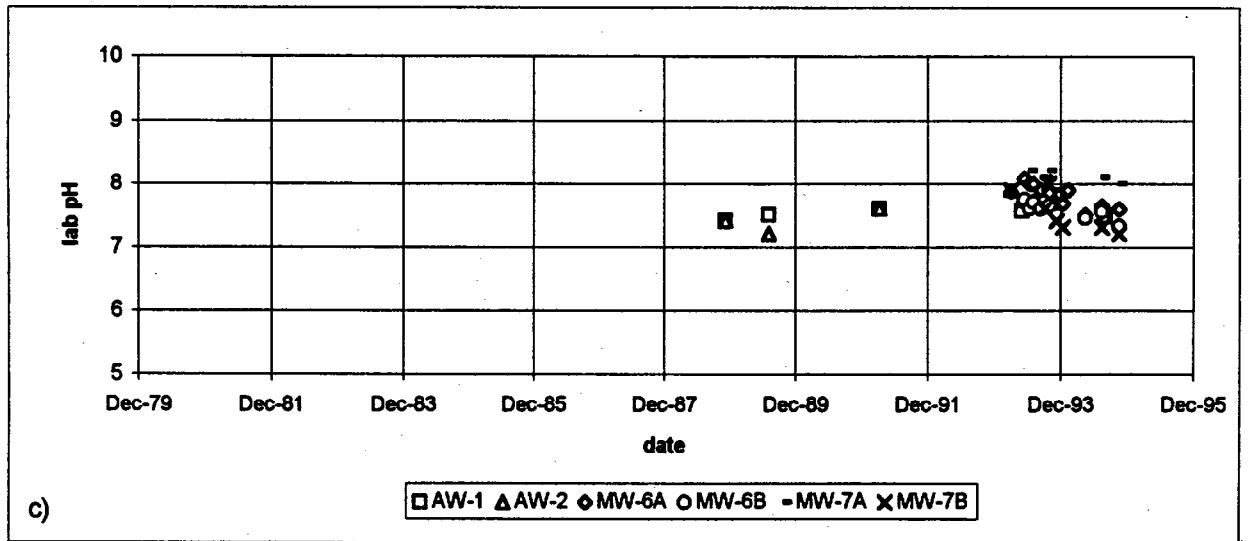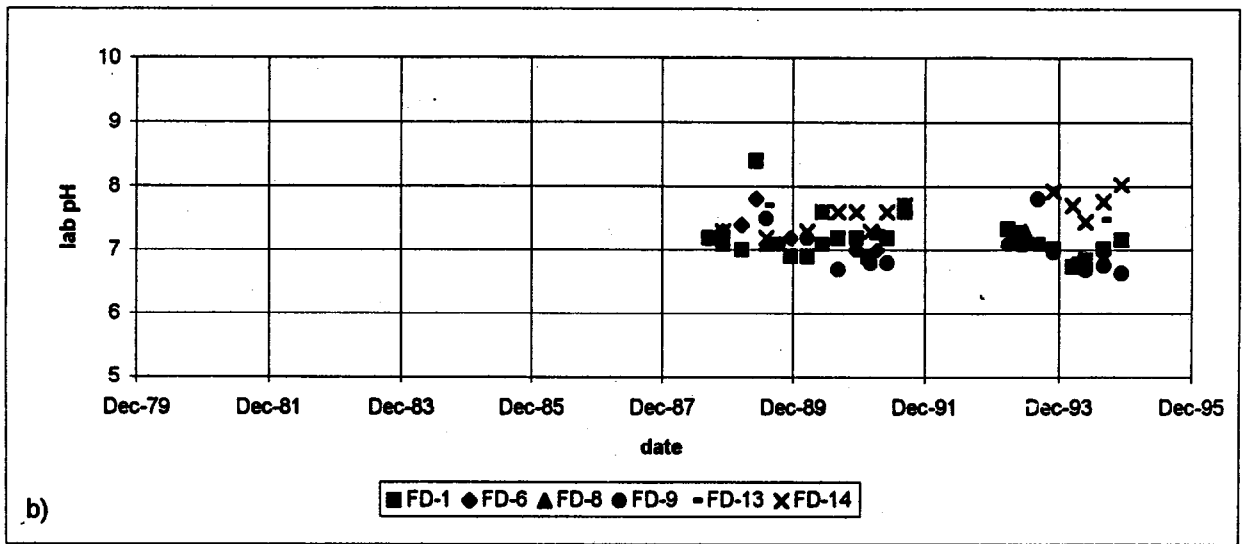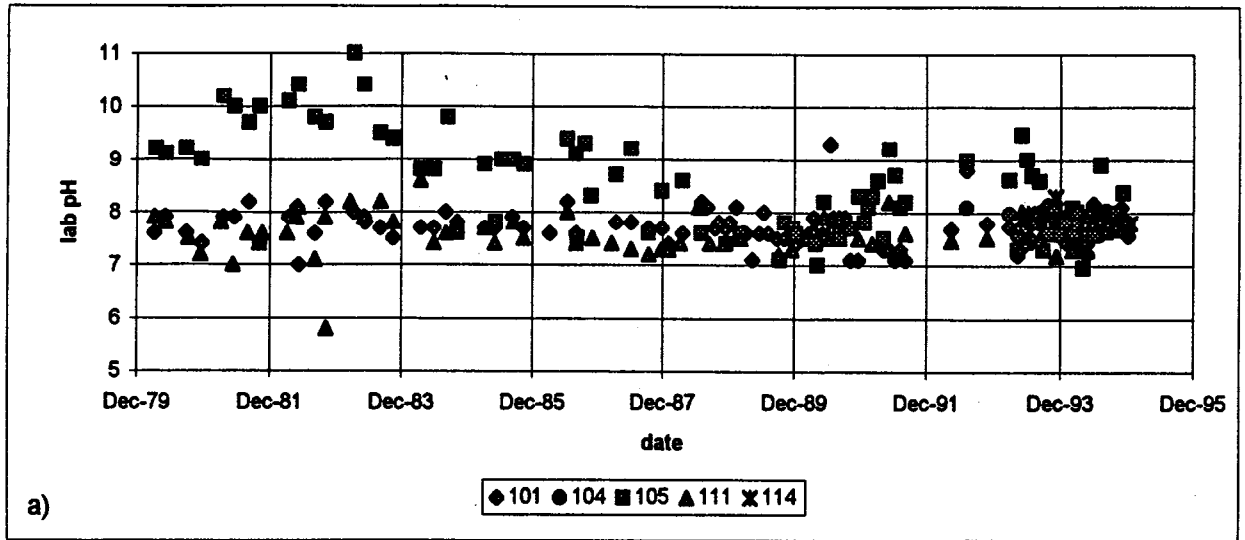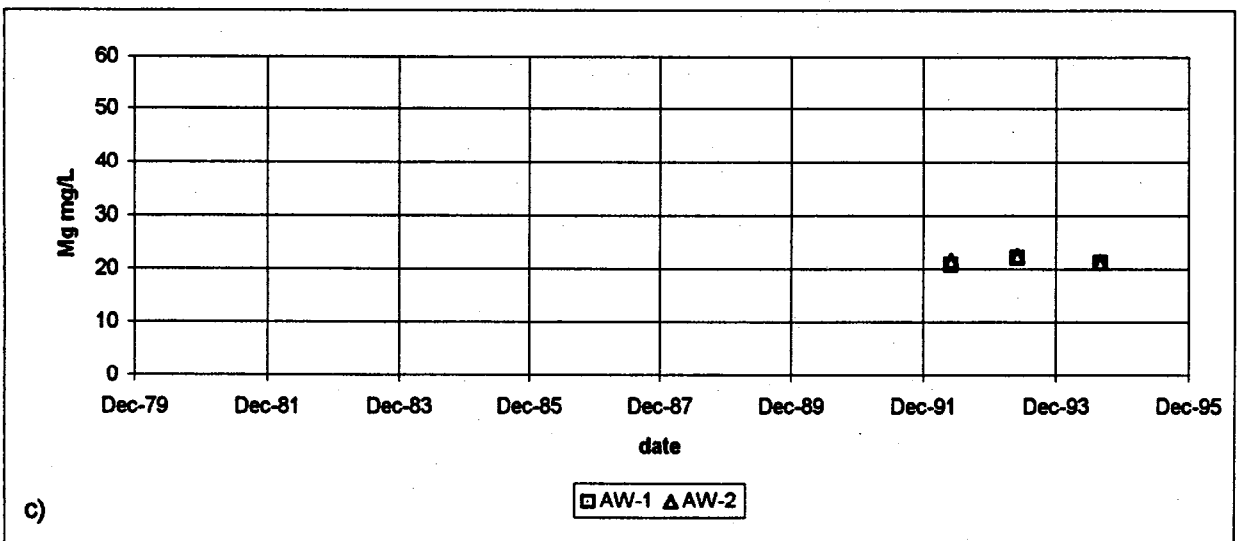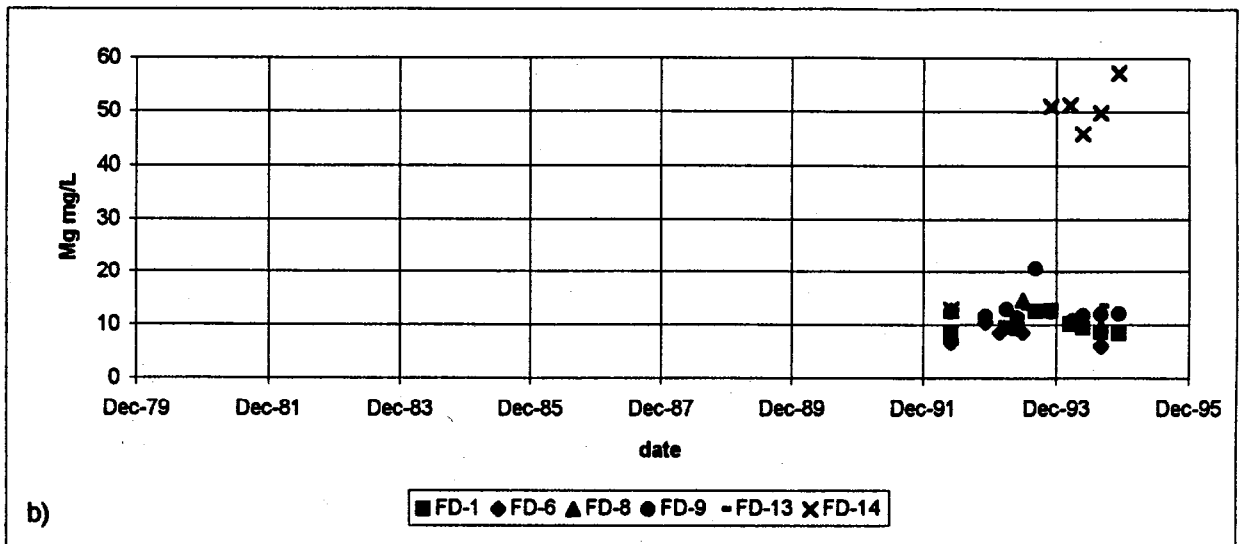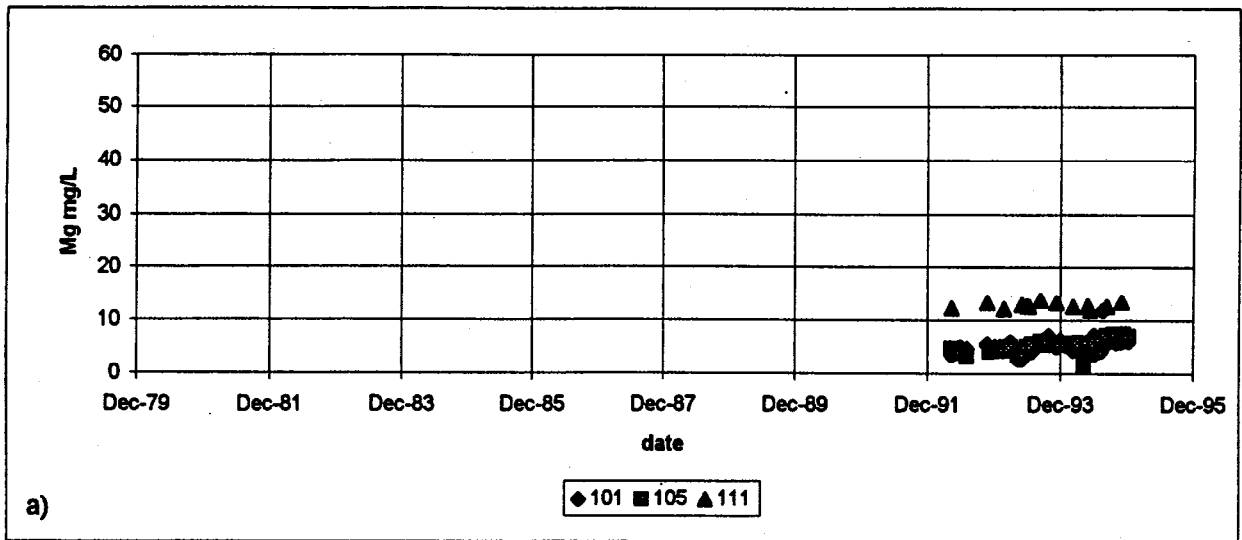
Figure 4.27: Magnesium Concentration (mg/L) at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
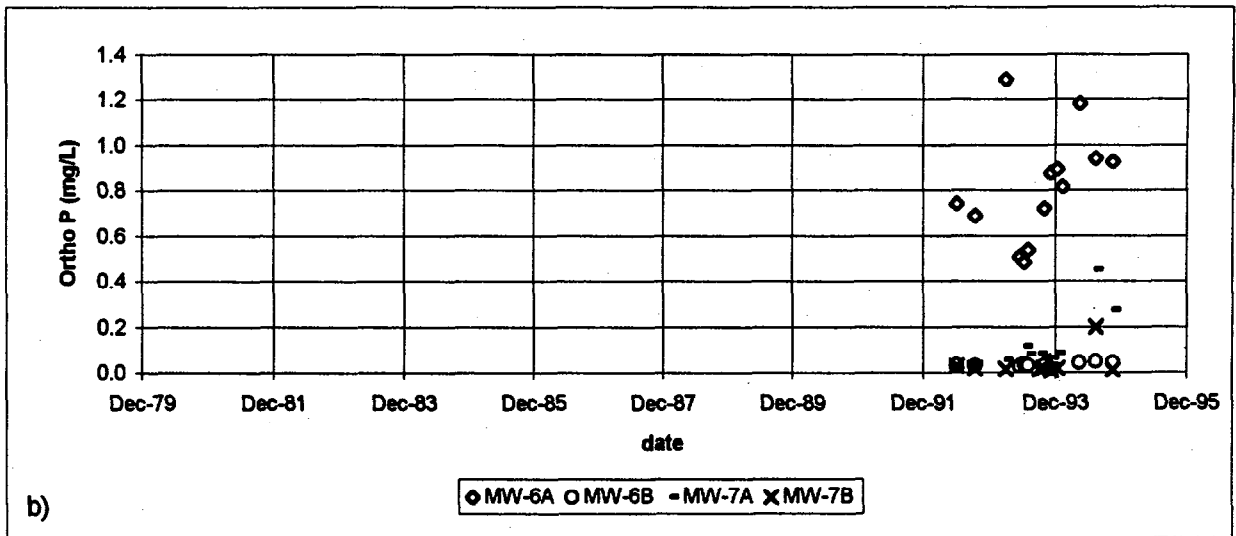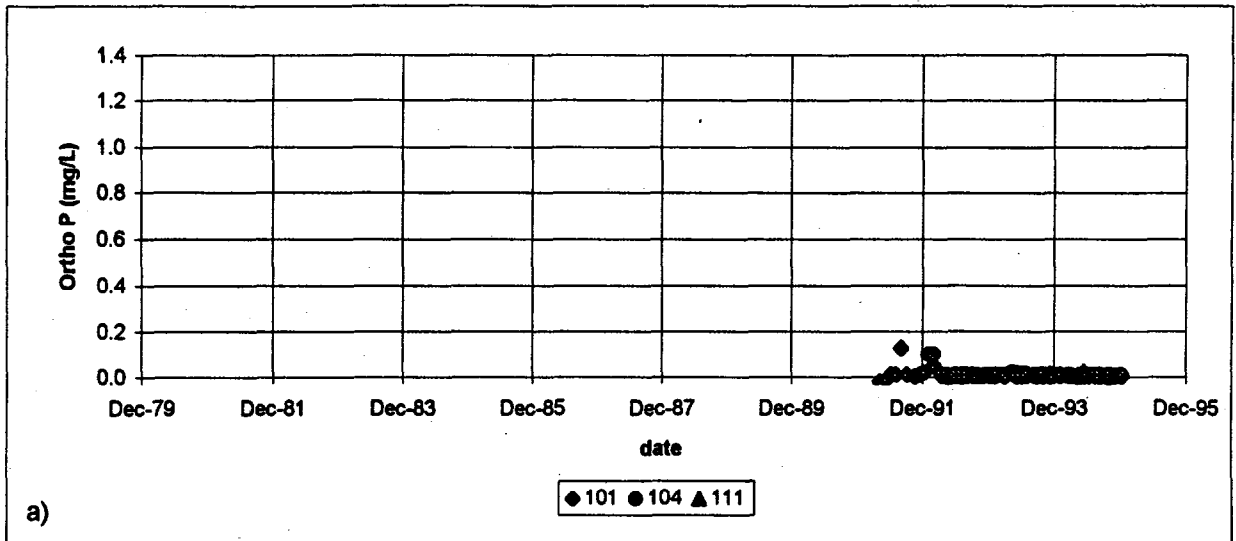
Figure 4.28: Phosphorus Concentration (mg/L) at a) Surface Water Stations and b) Observation Well Stations Gibraltar Tailings Impoundment

In general, the on-site monitoring data indicates that the tailings supernatant has elevated concentrations of most parameters relative to the background surface and ground water concentrations and the finger drains of the Main Tailings Dam have elevated concentrations relative to the tailings pond supernatant. Given this trend in concentration from tailings pond supernatant to finger drains, there is a suggestion that ARD conditions may exist within the tailings impoundment resulting in the increase of concentration as water flows through it. In order to investigate this possibility, molar ratios were used to identify any mass losses or gains during migration from the tailings pond to the finger drains.

Molar Ratio Analysis

The molar ratios used to interpret the on-site monitoring data are similar to those presented in the kinetic test data analysis. The first ratio considered is sulphate to alkalinity (Figure 4.29a, b). The elevated ratio in the seepage pond (station 111) and observation wells MW6-A and MW6-B is the result of elevated sulphate concentration at these locations. For unknown reasons, there is a decreasing trend in this ratio at station 111 and an increasing trend at station MW6-B.

Other molar ratios considered in this analysis include: calcium/sulphate (Figure 4.30a, b, c), sodium/sulphate (Figure 4.31a, b, c), iron/sulphate (Figure 4.32a, b, c), molybdenum/sulphate (Figure 4.33a, b, c), calcium/sodium (Figure 4.34a, b, c), calcium/iron (Figure 4.35a, b, c), sodium/iron (Figure 4.36a, b, c), copper/iron (Figure 4.37a, b, c), molybdenum/iron (Figure 4.38a, b, c) and manganese/iron (Figure 4.39a, b, c). The significance of these ratios are that an indication of the relative rate of leaching is available and any changes to the ratio would reflect a mass gain, or loss, to solution of the parameters.

Figures 4.30a, b, c to 4.33a, b, c present the molar ratios of calcium, sodium, iron and molybdenum to sulphate. The calcium/sulphate (Figure 4.30a, b, c) ratio is relatively high at the background surface water station (station 101) due to the low sulphate content. The tailings supernatant, seepage pond, finger drains and observation wells below the Main Dam have similar ratios for calcium to sulphate. The sodium/sulphate (Figure 4.31a, b, c) ratio shows a similar trend as the calcium/sulphate with background values relatively high and similar, but lower than background values in the supernatant, seepage pond, finger drains and observation wells. Iron to sulphate ratios (Figure 4.32a, b, c) are low at all stations except at station 101. There is also an

increase in this ratio in the surface water and finger drains stations corresponding to the time when zero discharge was initiated. Molybdenum to sulphate (Figure 4.33a, b, c) is used by Gibraltar to identify and track the migration of tailings water from the impoundment. Similar ratios exist between the tailings pond, finger drains and seepage pond, except at FD-14. The ratios at this location and at stations MW6-A,B are lower then the tailings impoundment.
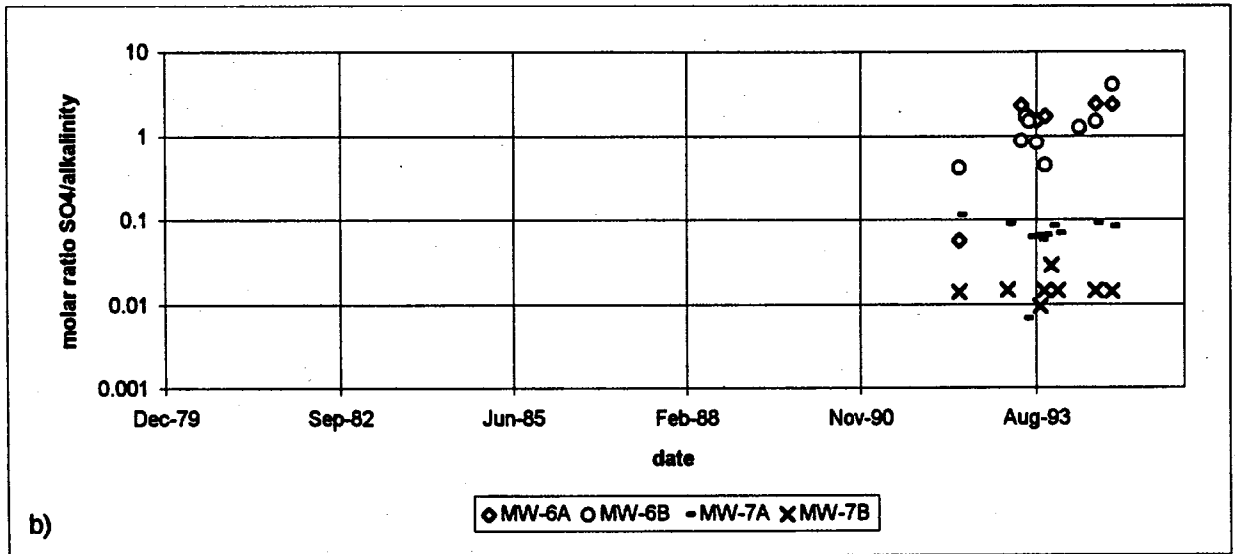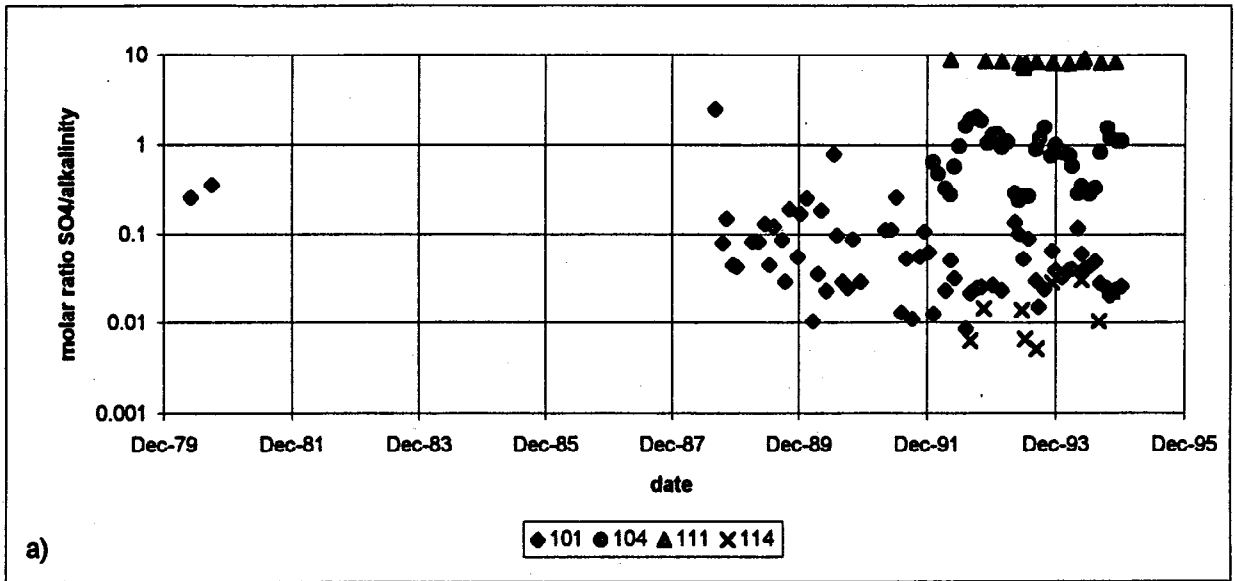
Figure 4.29: Molar ratio of Sulphate to Alkalinity at a) Surface Water Stations and
b) Observation Well Stations Gibraltar Tailings Impoundment
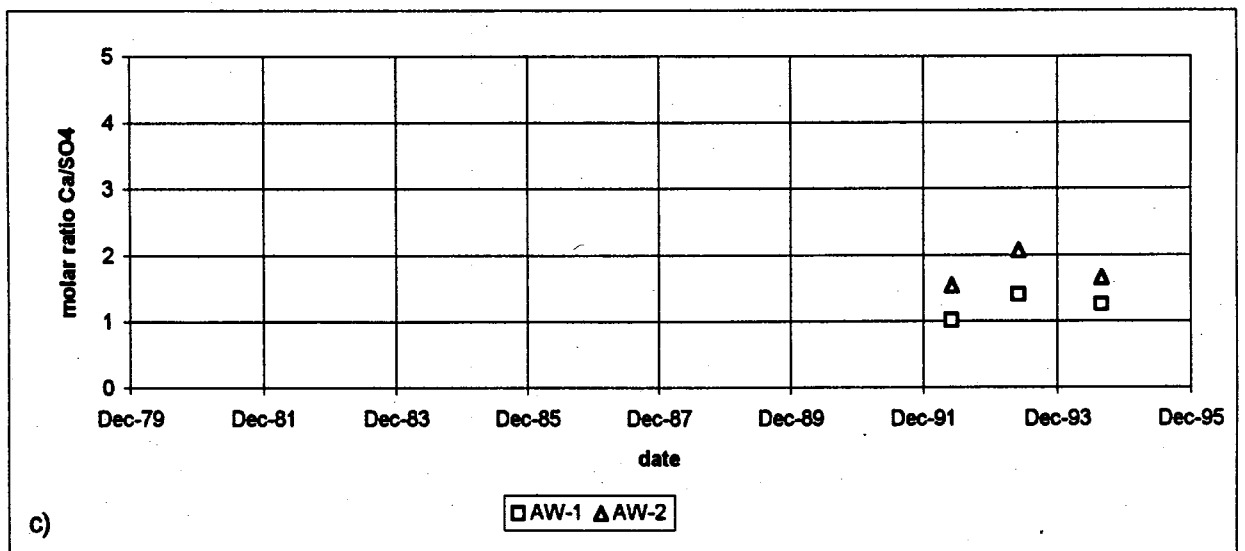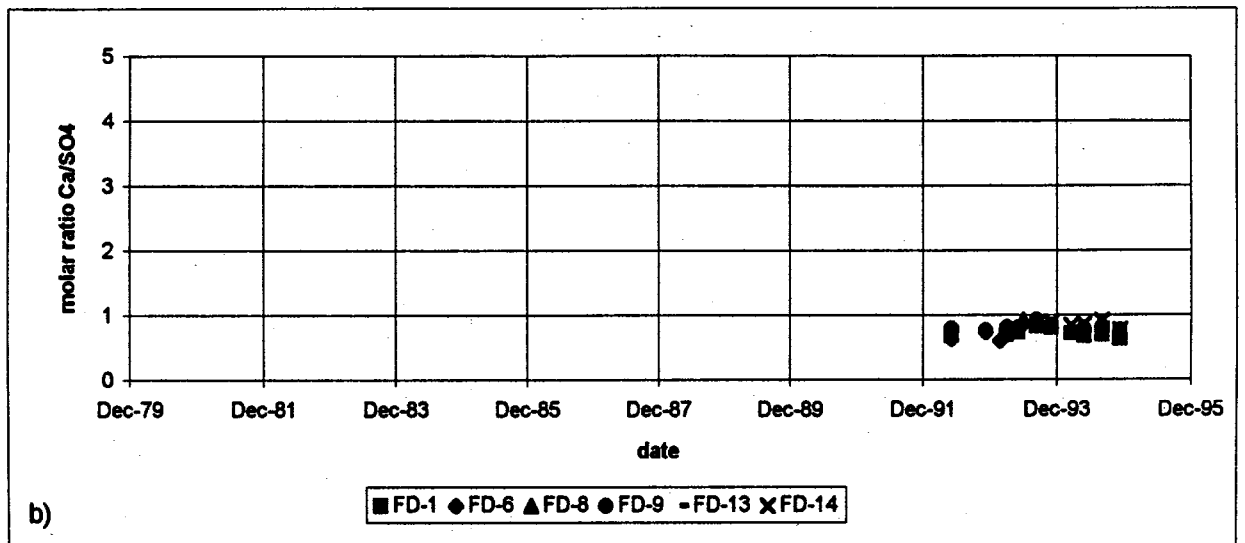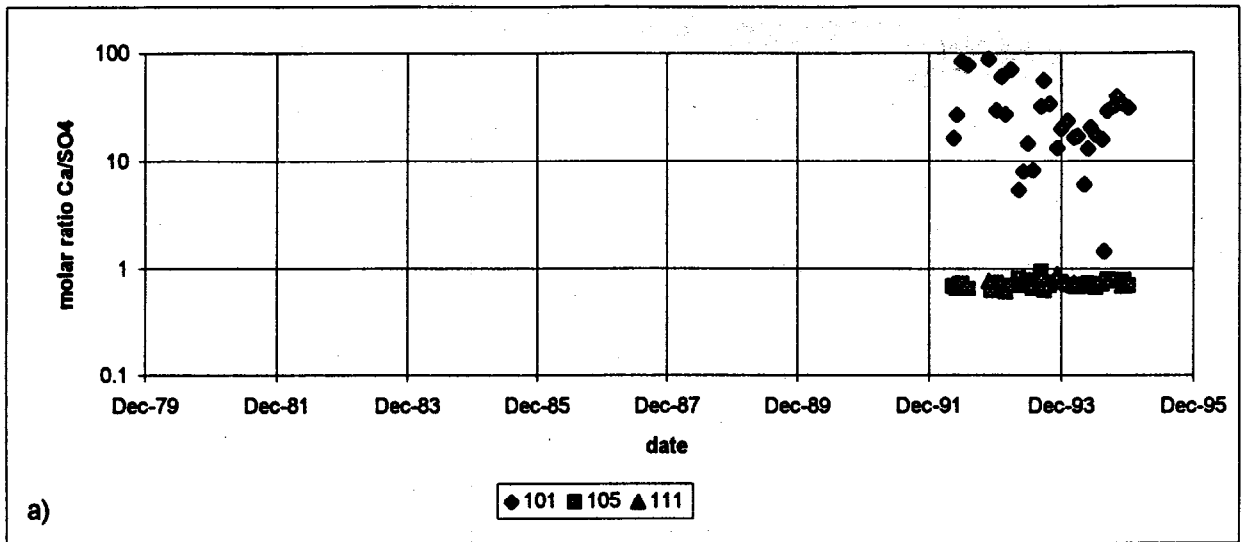
Figure 4.30: Molar ratio of Calcium to Sulphate at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations, Gibraltar Tailings Impoundment
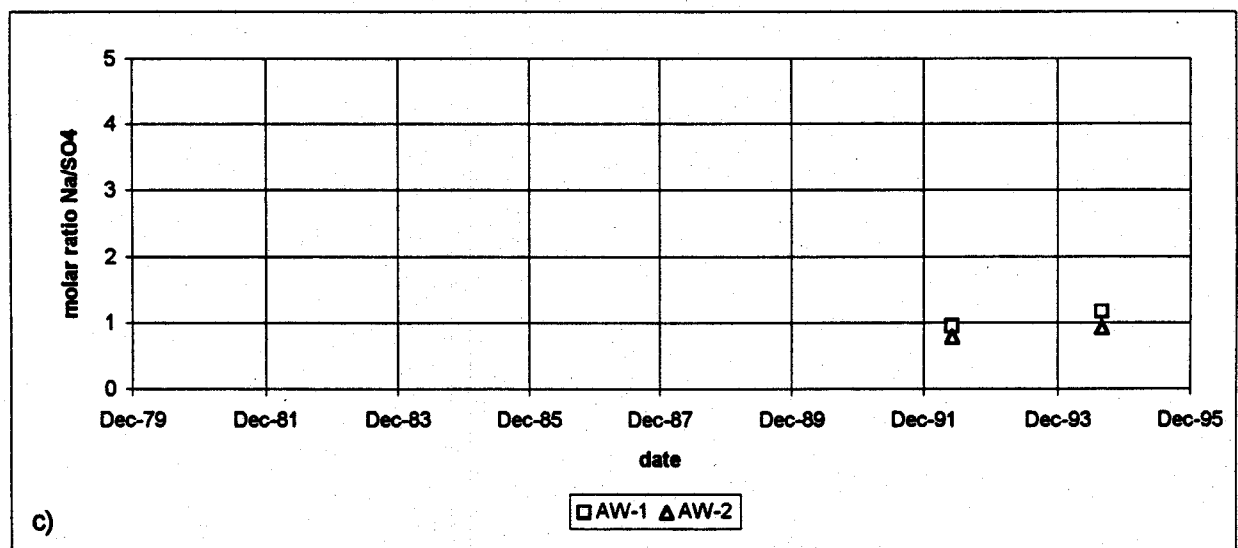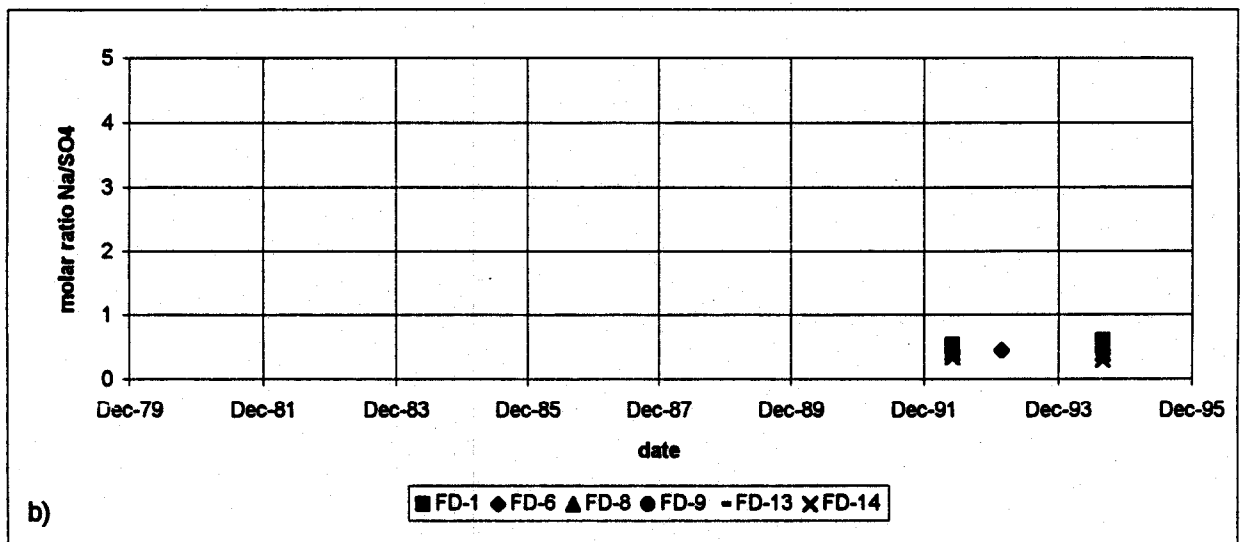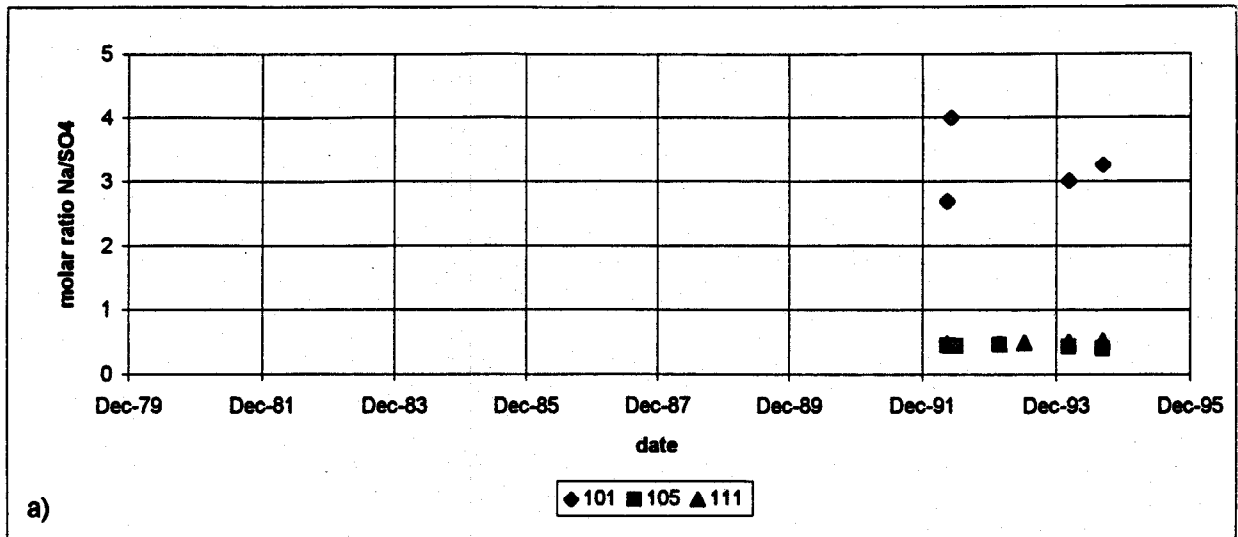
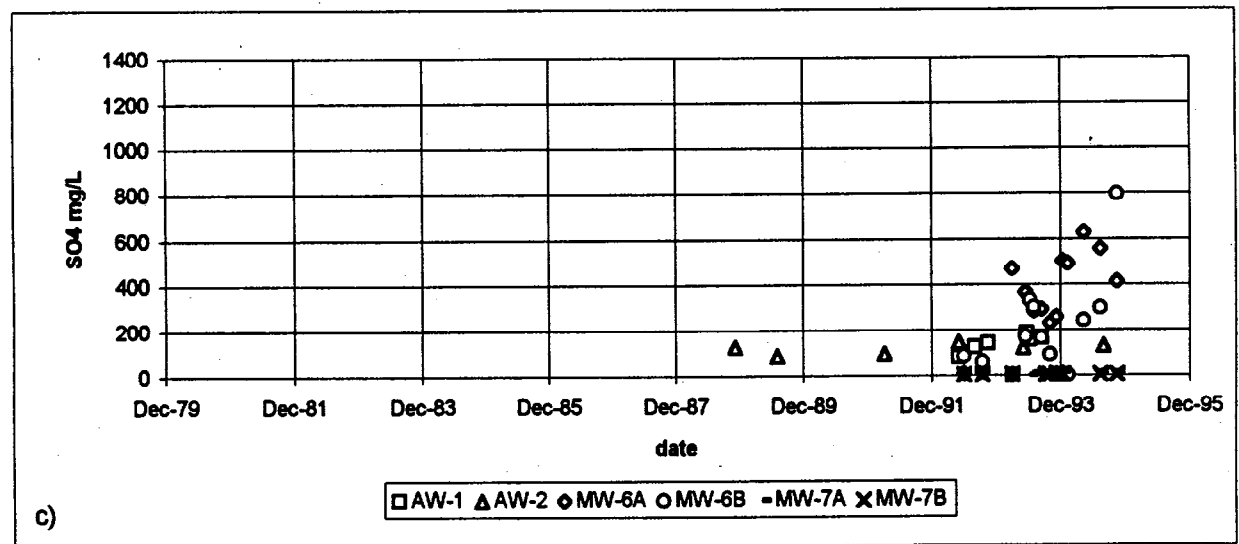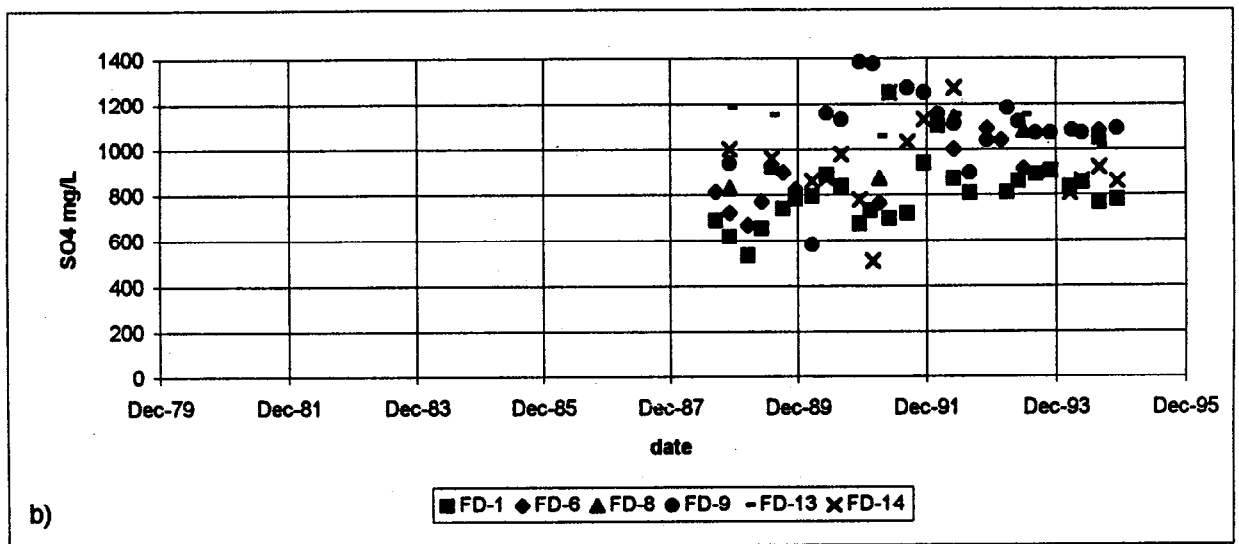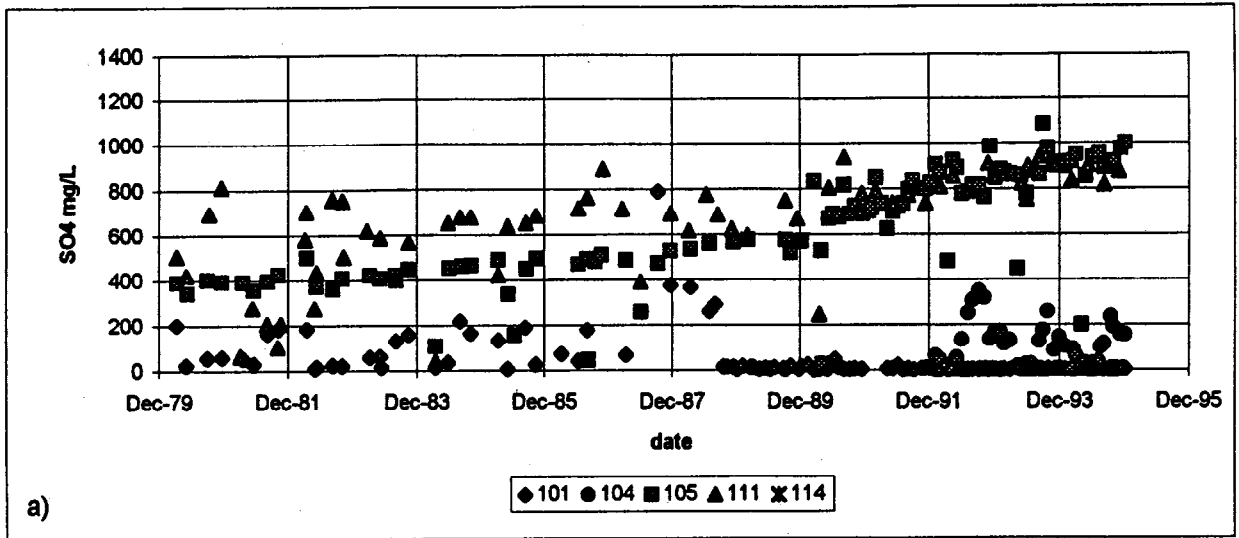Figure 4.31: Molar ratio of Sodium to Sulphate at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations, Gibraltar Tailings Impoundment
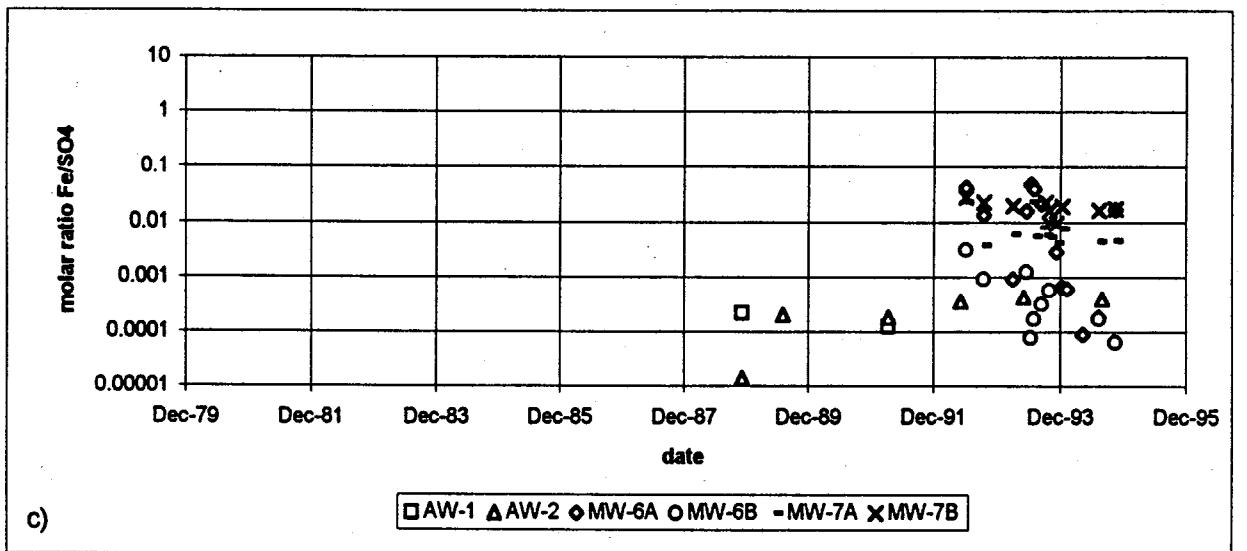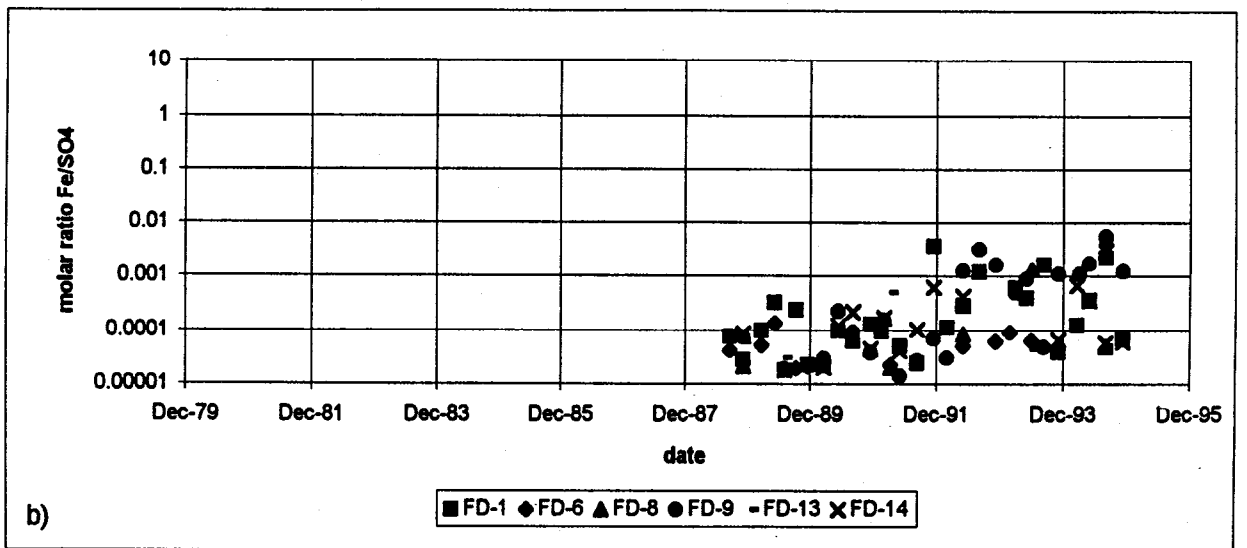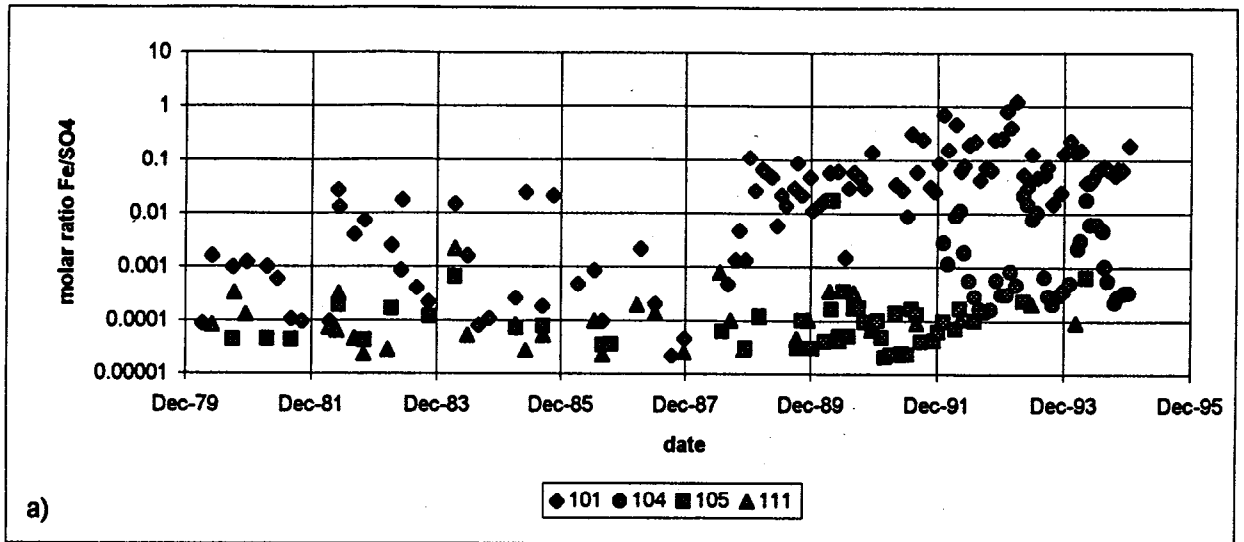
Figure 4.32: Molar ratio of Iron to Sulphate at a) Surface Water Stations, b) Finger Drain
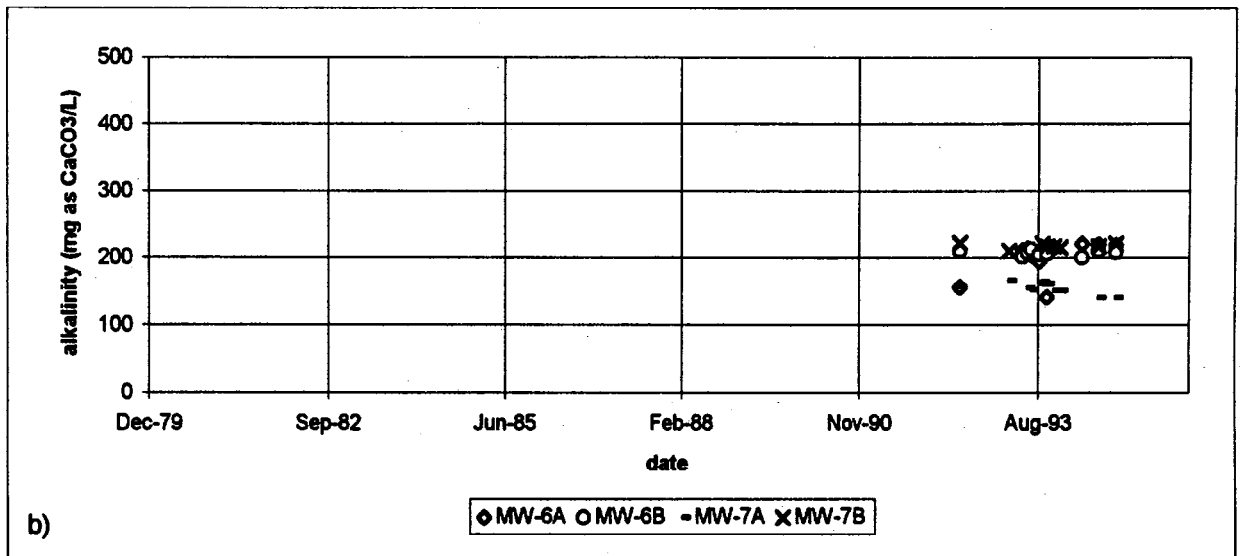Stations and c) Observation Well Stations, Gibraltar Tailings Impoundment
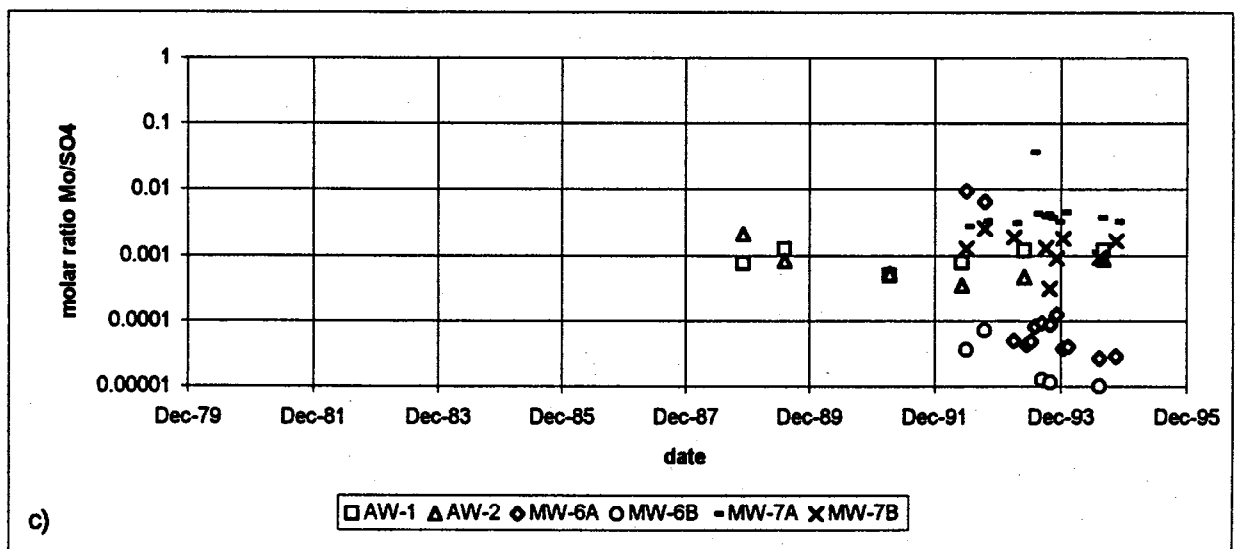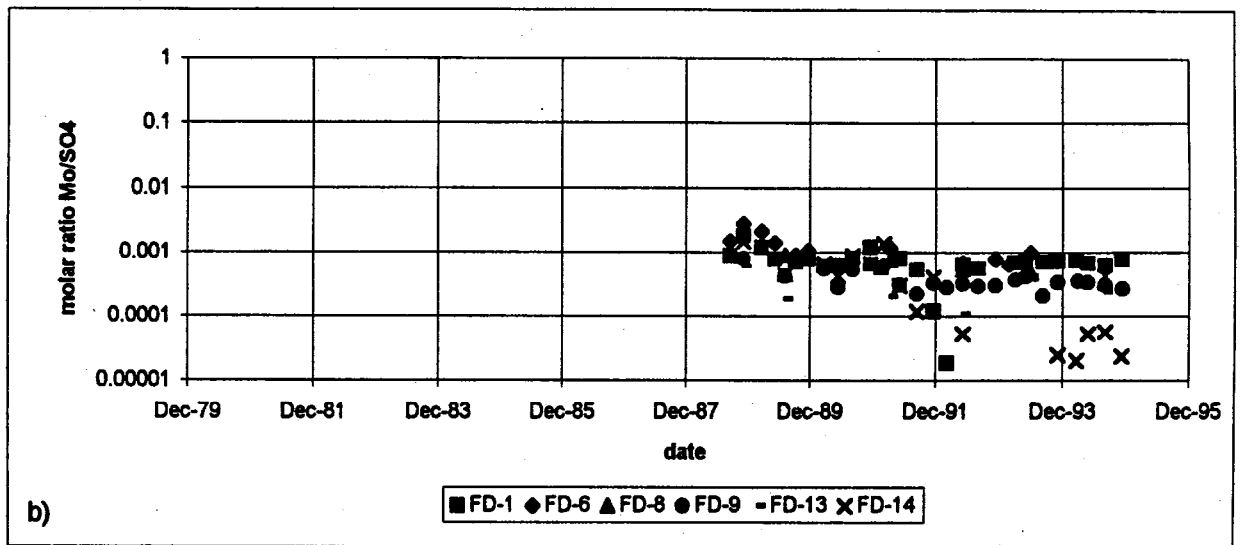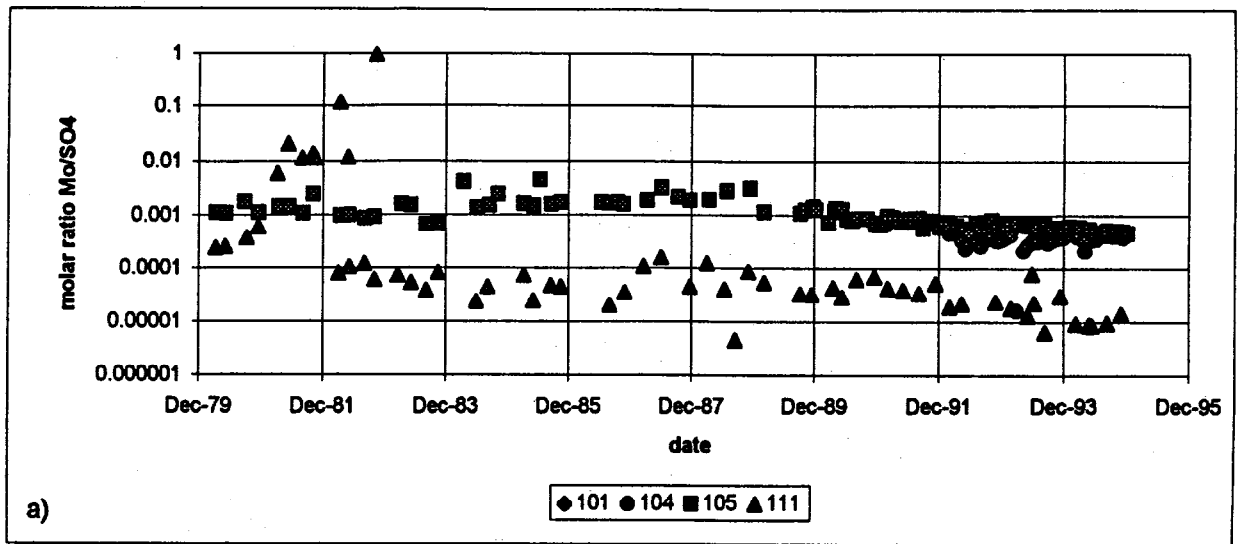
Figure 4.33: Molar ratio of Molybdenum to Sulphate at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations, Gibraltar Tailings Impoundment

Since sulphate concentration is very high relative to the individual metals, Figure 4.34a, b, c presents the molar ratio of calcium/sodium to assess preferential leaching of the neutralizing minerals. This ratio is similar in the tailings supernatant, seepage pond and finger drains.

Figures 4.35a, b, c to 4.39a, b, c present the molar ratios of calcium, sodium, copper, molybdenum and manganese to iron. The calcium/iron ratio (Figure 4.35a, b, c) in the tailings supernatant (station 105) and seepage pond (station 111) is higher then the background surface water (station 101) and the observation wells (stations AW-1,2), however, the finger drain ratio is either similar to background surface water and observation well concentrations (i.e. FD-9, 13) or similar to supernatant/seepage pond concentrations (i.e. FD-1, 6, 8 and 14). The sodium/iron ratio (Figure 4.36a, b, c) also indicates that the tailings supernatant and seepage ponds ratio is higher then the background levels and that the finger drains have ratios similar either to the background surface water and observation wells (i.e. FD-1, 9, 13 and 14) or to the tailings supernatant (i.e. FD-6, 8). The copper to iron ratio (Figure 4.37a, b, c) and molybdenum to iron ratio (Figure 4.38a, b, c) is relatively similar at all the monitoring stations. Also, there is a decreasing trend recognizable at most of the stations for both of these ratios suggesting an increase in iron concentration relative to copper and molybdenum. The manganese to iron ratio (Figure 4.39a, b, c) also indicates that the tailings supernatant and seepage pond has a higher value than the background surface water and observation wells, also, the finger drains have ratios similar either to the supernatant/seepage pond (i.e. FD-6, 8, 13 and 14) or to the background surface water and observation wells (i.e. FD-1, 9).
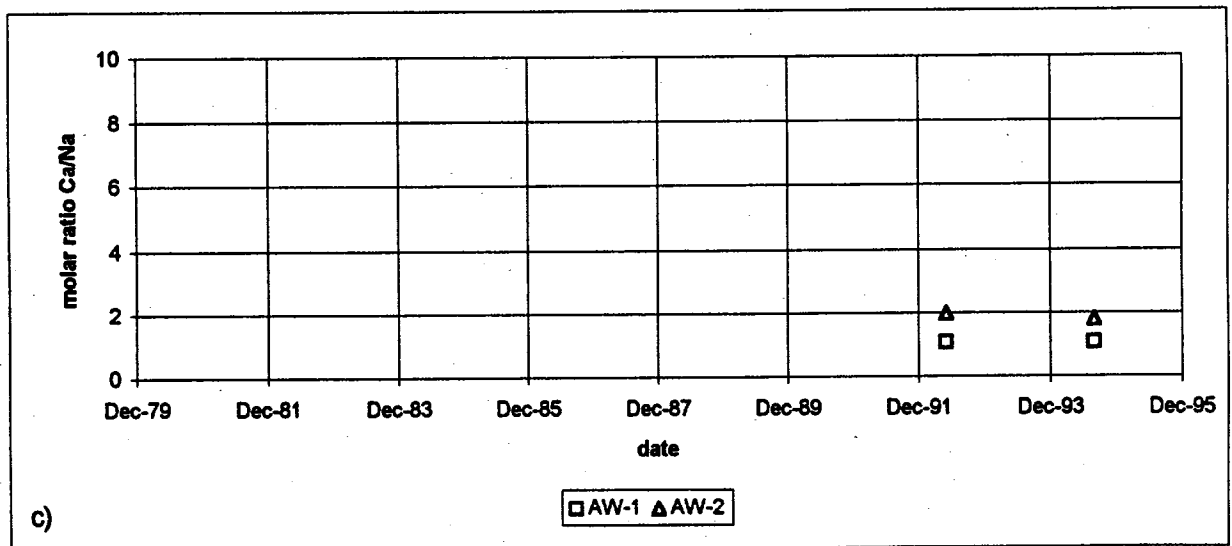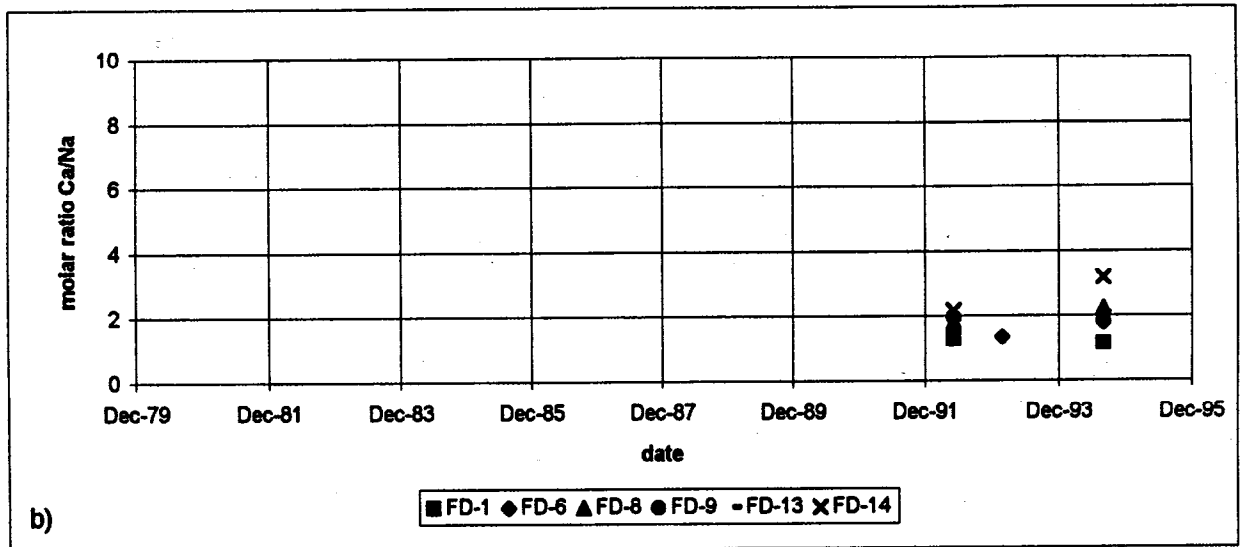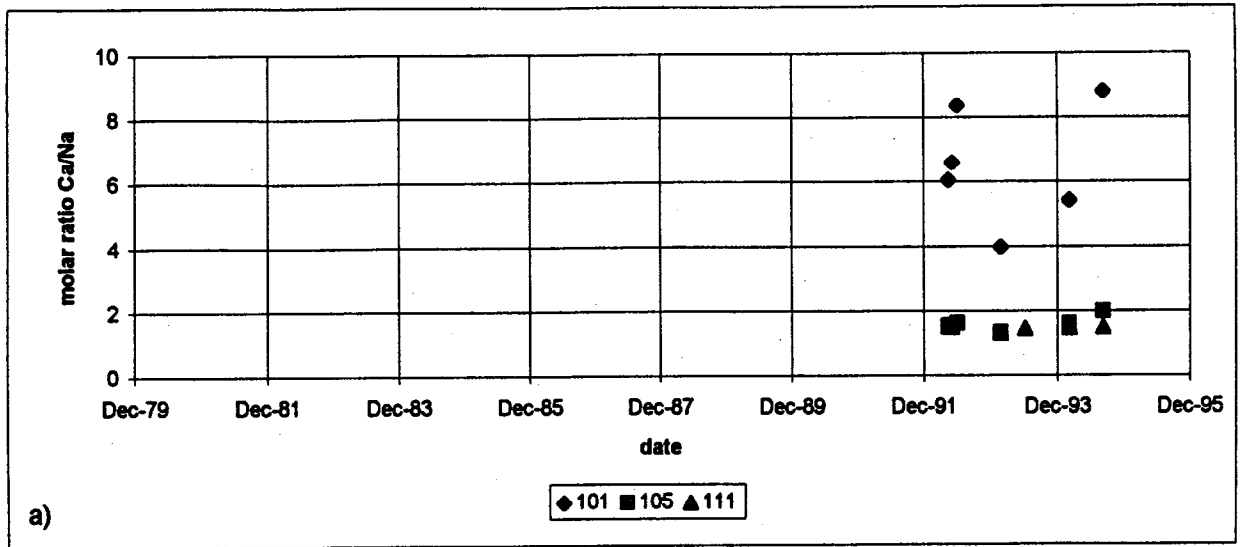
Figure 4.34: Molar ratio of Calcium to Sodium at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations, Gibraltar Tailings Impoundment
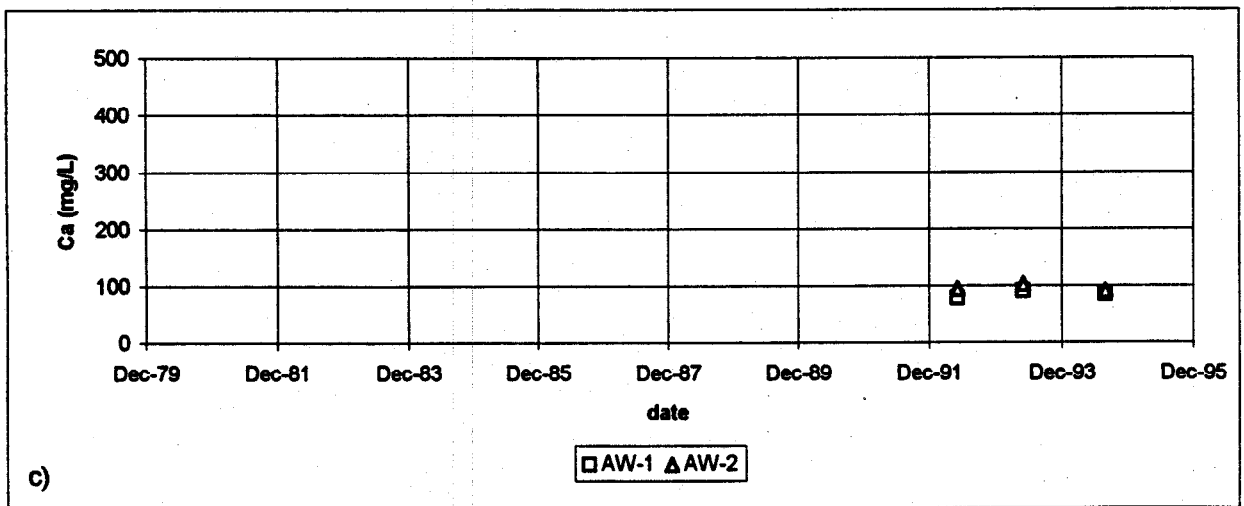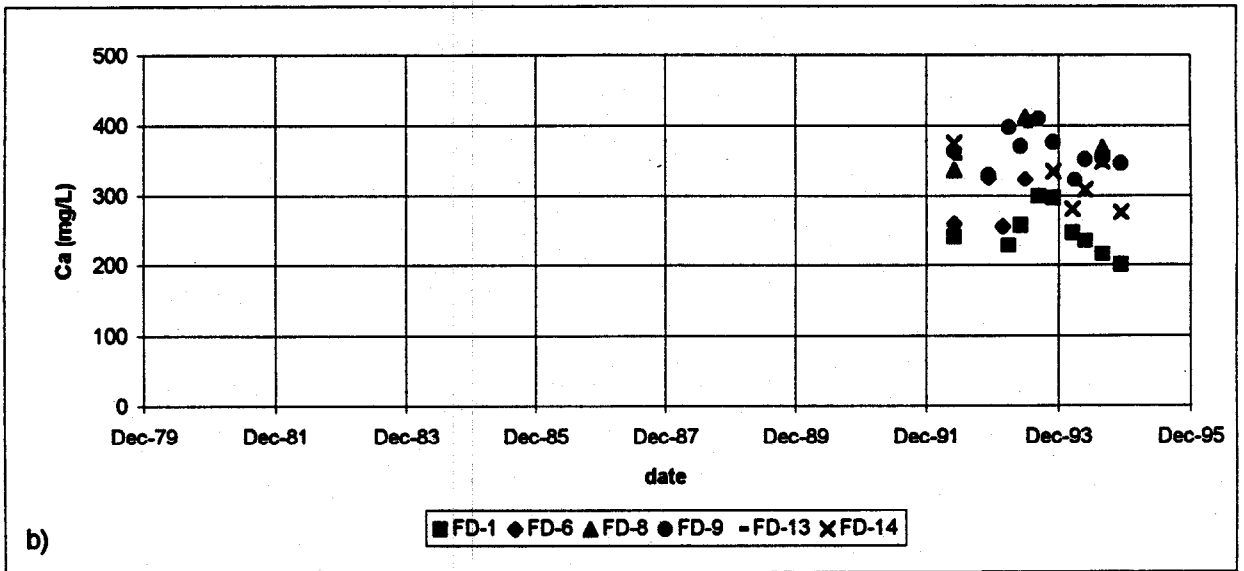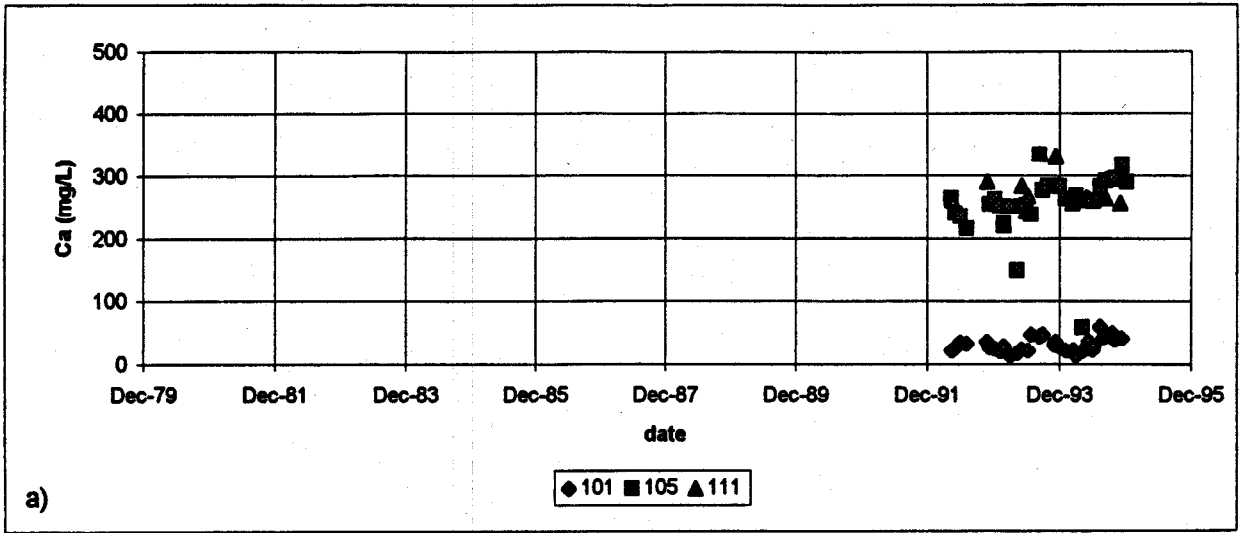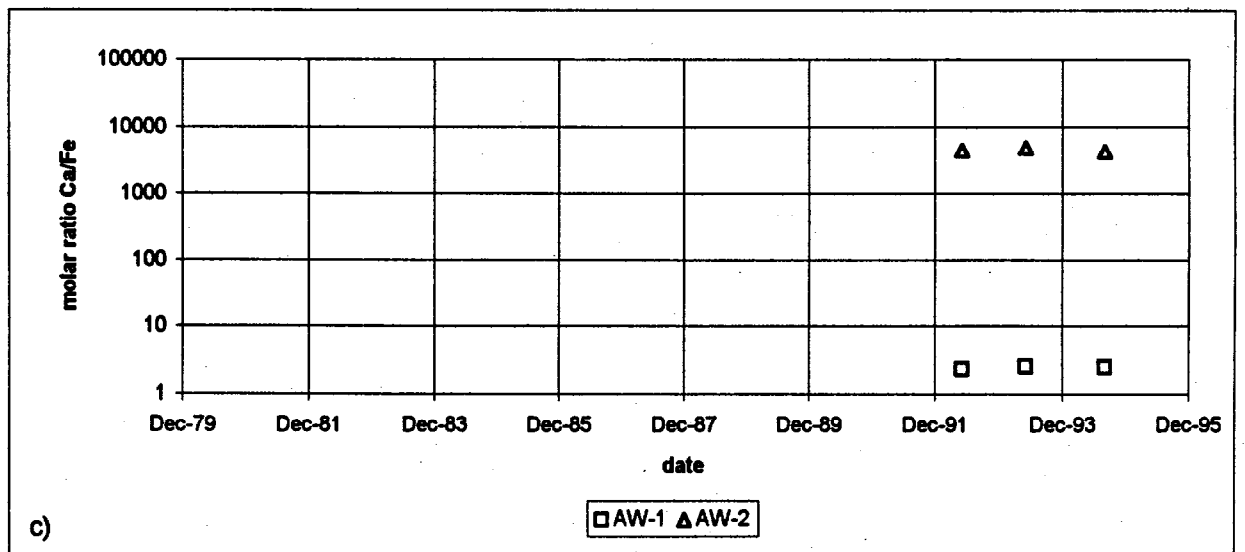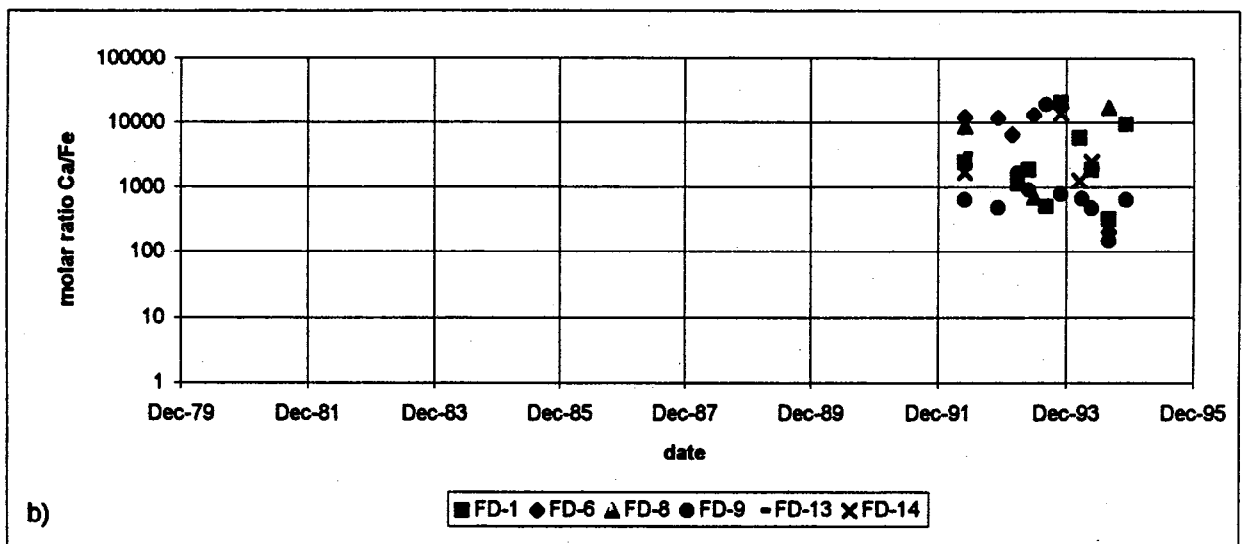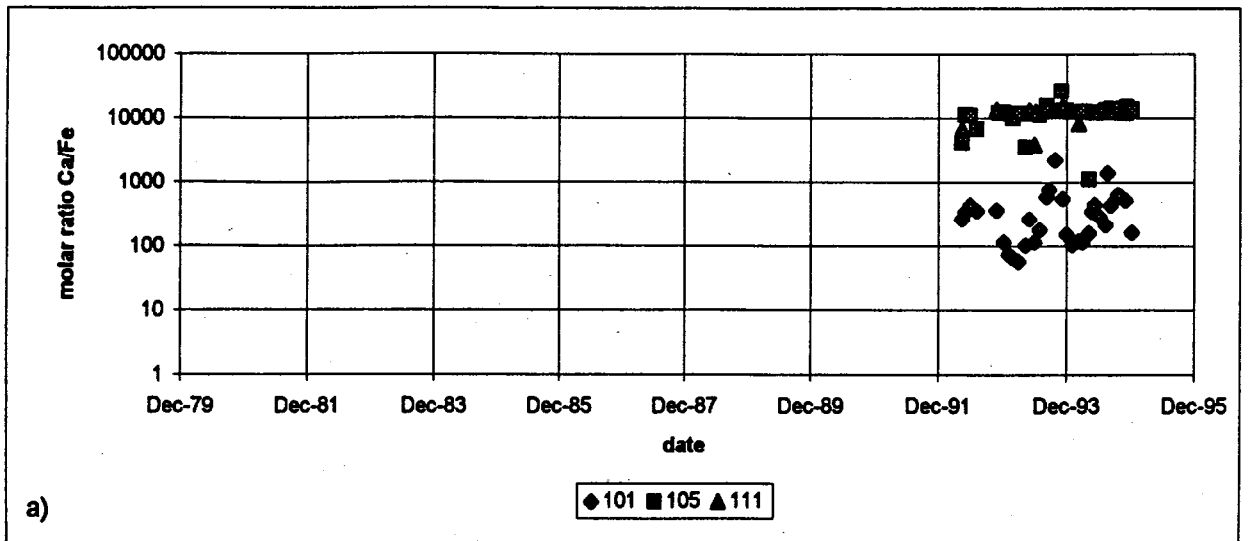
Figure 4.35: Molar ratio of Calcium to Iron at a) Surface Water Stations, b) Finger Drain Station and c) Observation Well Stations Gibraltar Tailings Impoundment
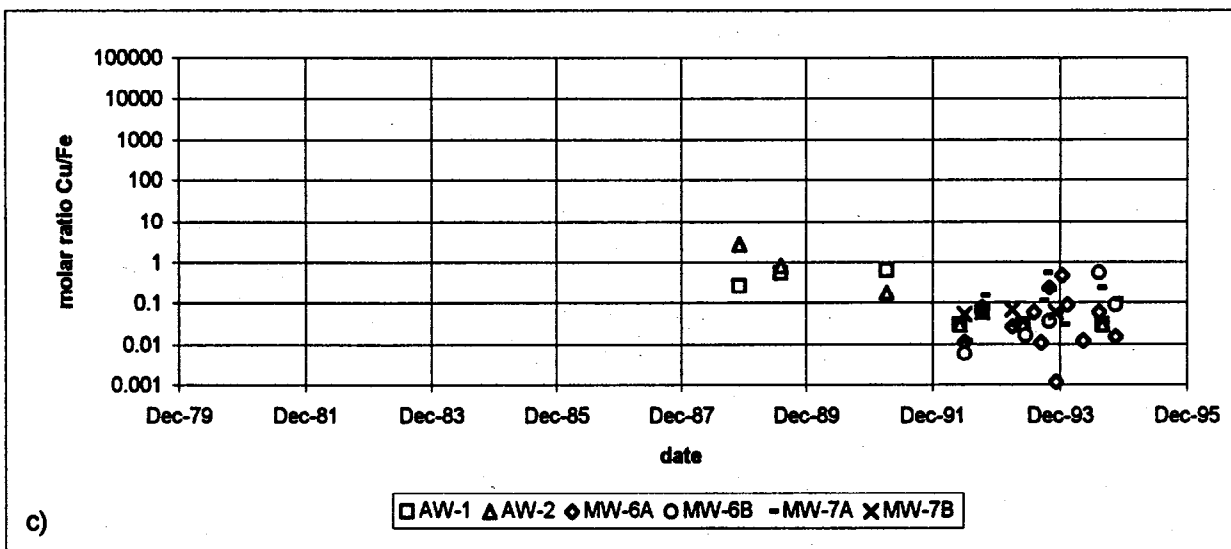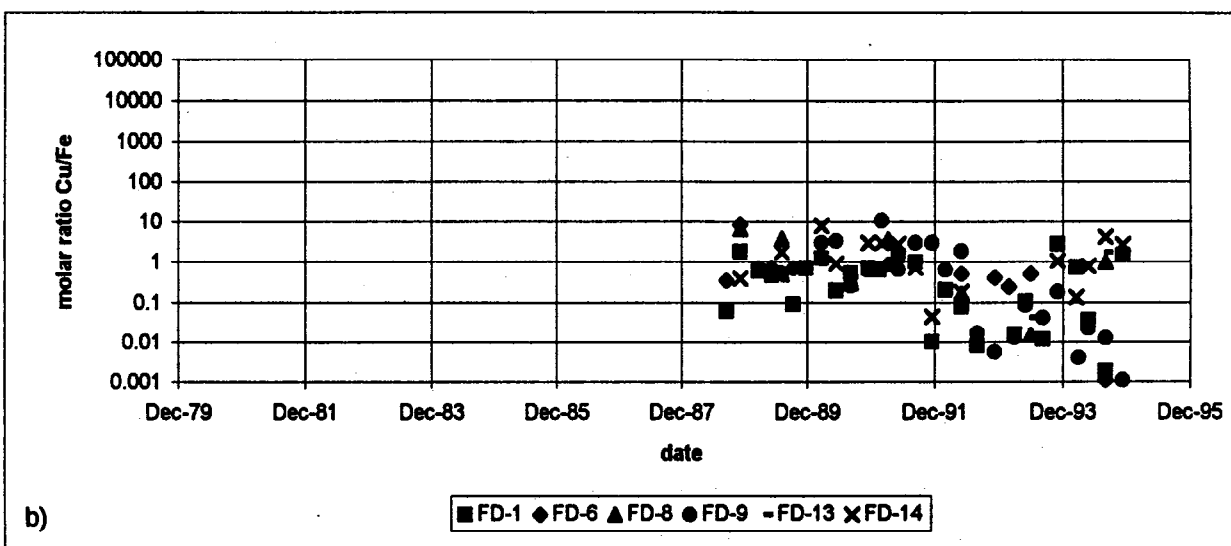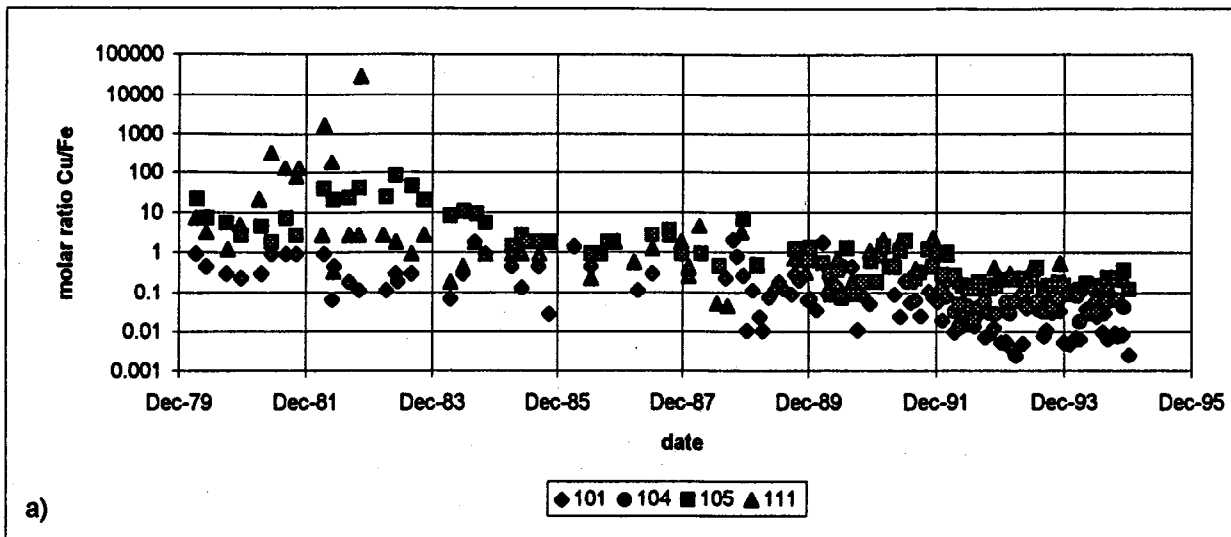
Figure 4.37: Molar ratio of Copper to Iron at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
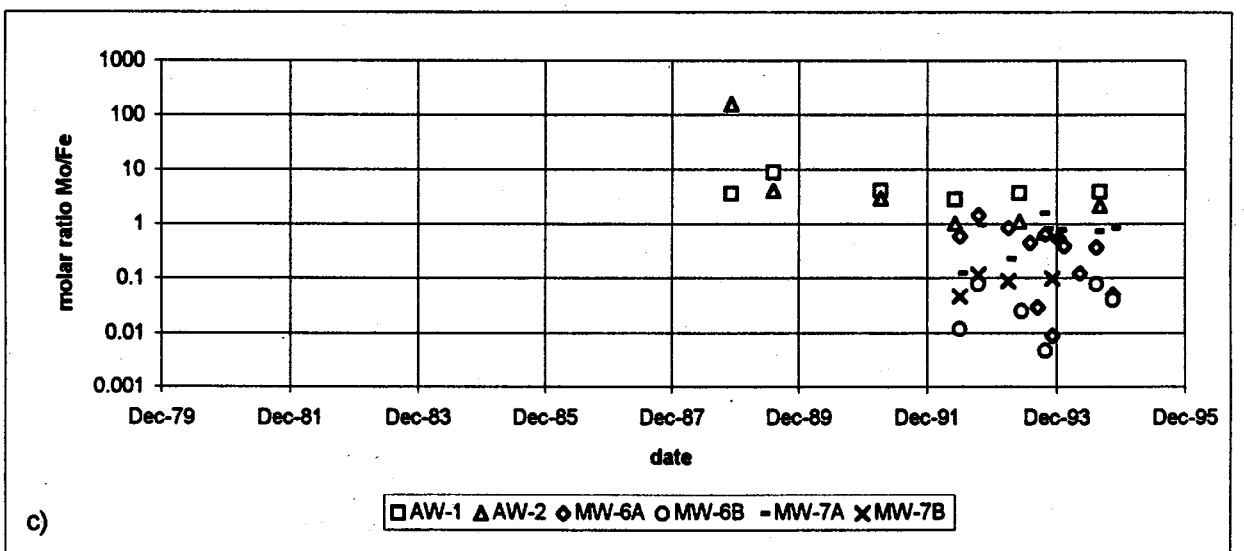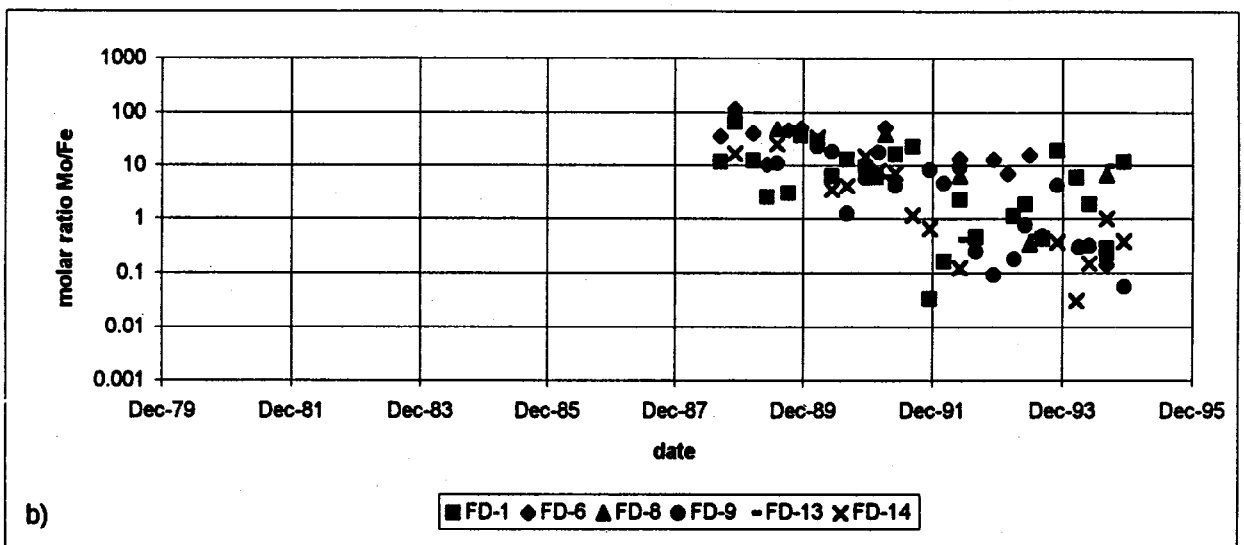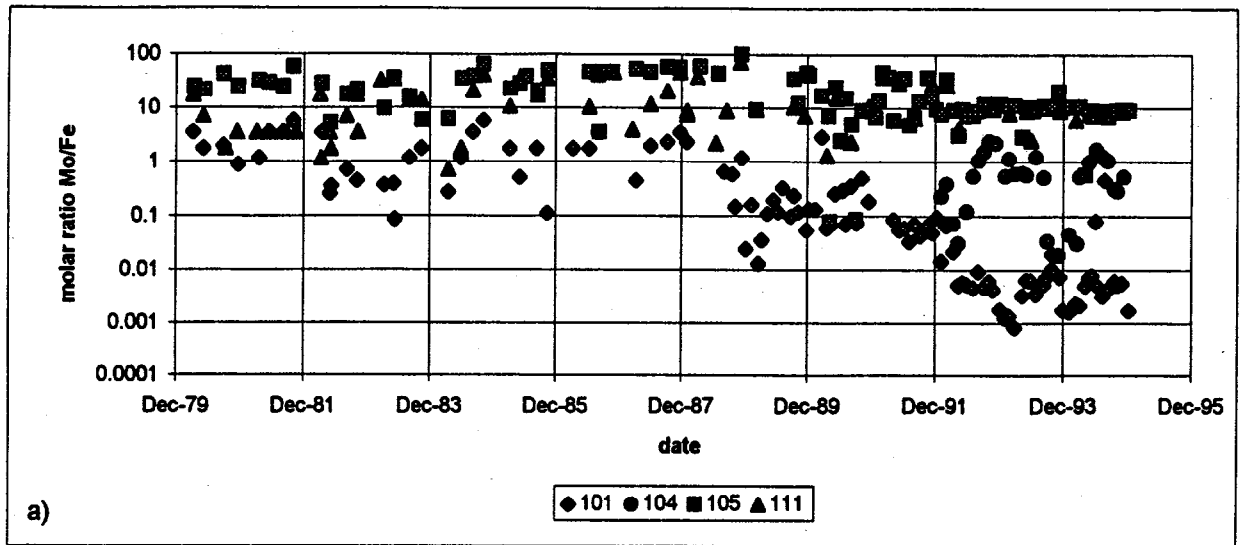
Figure 4.38: Molar ratio of Molybdenum to Iron at a) Surface Water Stations, b) Finger Drain
Stations and c) Observation Well Stations Gibraltar Tailings Impoundment
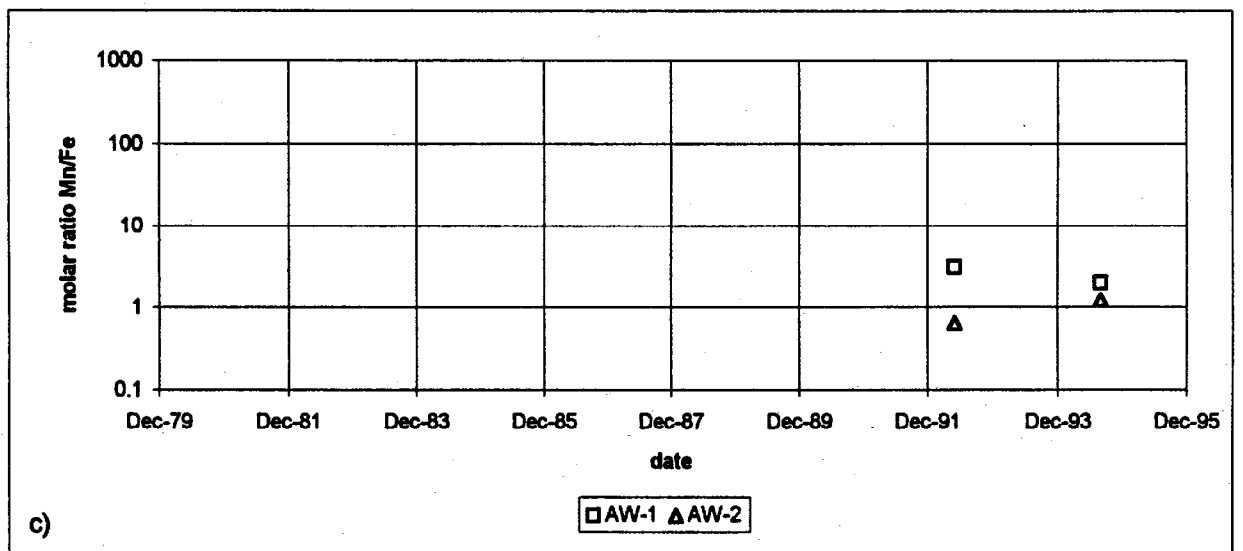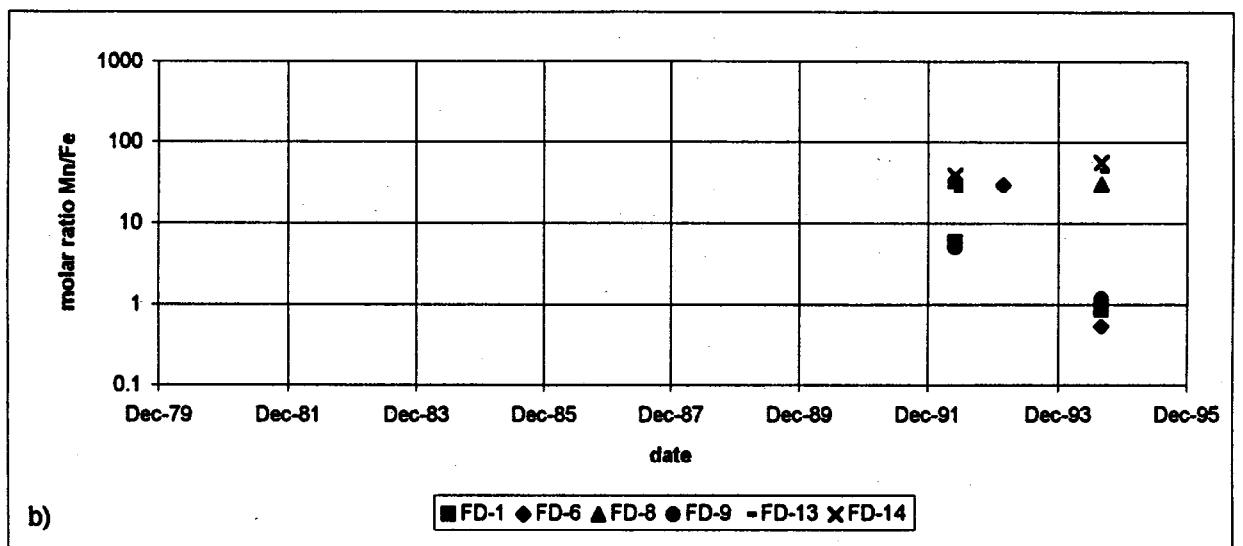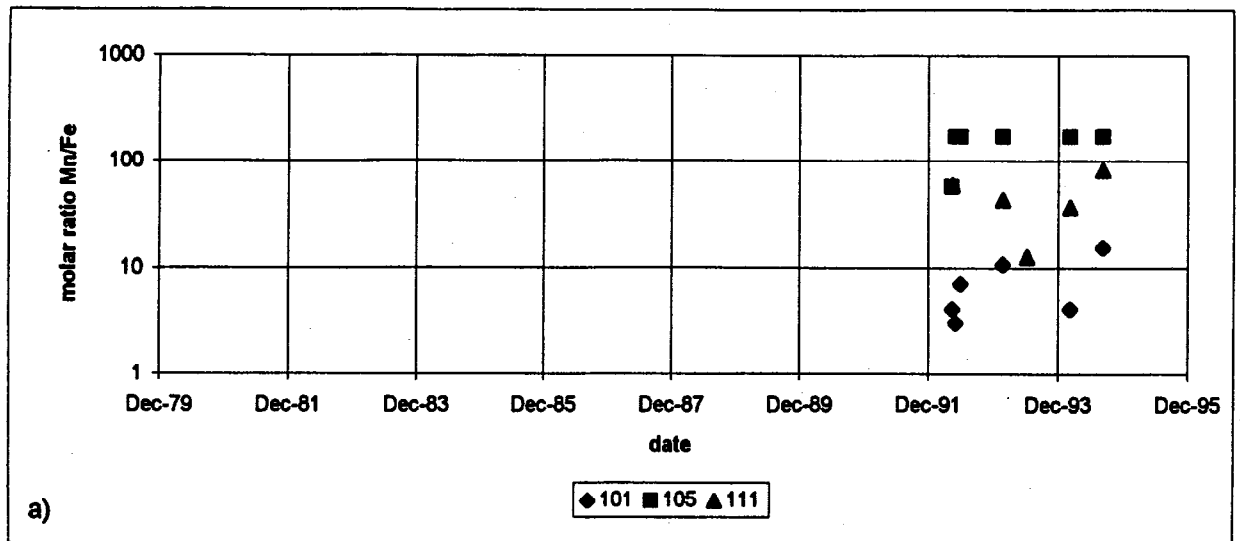
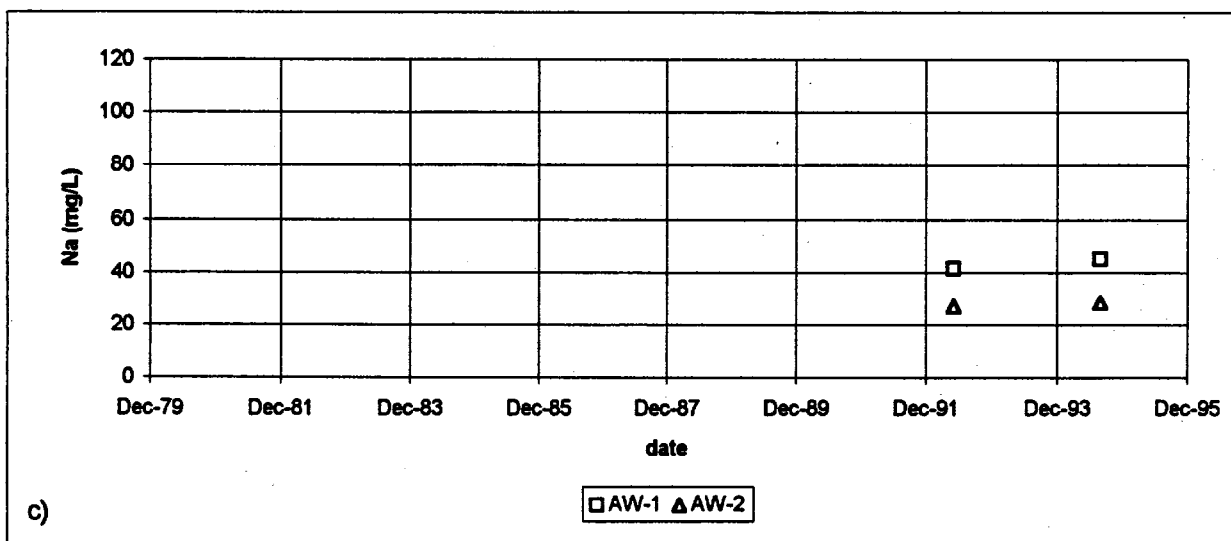Figure 4.39: Molar ratio of Manganese to Iron at a) Surface Water Stations, b) Finger Drain Stations and c) Observation Well Stations Gibraltar Tailings Impoundment

In general, the on-site monitoring data indicates that the concentration of most parameters is elevated in the tailings supernatant, seepage pond, and finger drains relative to the background surface water concentrations. The concentration of parameters in surface water and observation wells in the East Saddle Dam area are low indicating that leakage from the tailings pond to the area east of the impoundment is not occurring. In observation wells below the Main Dam, the concentrations are elevated relative to background levels due to leakage of water from the tailings impoundment through the Tailings Aquifer to discharge in East Fork Cuisson Creek. Also, the finger drain concentrations are elevated relative to the supernatant, however, molar ratios of parameters in the tailings supernatant and the finger drains are similar suggesting that there is no loss or gain of mass along the flow path. This suggests that the increase in concentration is the result of physical processes, for example, evaporation or dilution. However, some of the molar ratios are indicating that some parameters are losing or gaining mass during migration. For example, at monitoring stations FD-1, FD-9, FD-13, FD-14 and MW6-A,B. This change in mass could be due to chemical reactions occurring along the flow path and/or mixing of waters with differing compositions. Chemical reactions and processes could include oxidation and neutralization reactions occurring in the subaerial portion of the Main Dam. In the area of finger drains 1, 9, 13 and observation well MW6-A, B ground water elevations (Figure 4.4b) suggest that mixing of different waters may be occurring and may also be occurring in Finger Drain 14. It is difficult to assess whether it is mixing of waters or water-rock interactions during supernatant migration, or a combination of both, that result in the observed concentration changes without a better understanding of the hydrogeology in the tailings impoundment area.

Relationship between Laboratory Prediction Methods and On-site Water Quality

The purpose of waste characterization is to determine the ARD potential for a site by addressing: 1) do the individual waste units have a potential for ARD?; 2) will this potential be realized and when?; 3) if ARD conditions do occur, to what level and time period?; and 4) how will water quality and environment be affected by ARD? The answers to these questions are based on the interpretation of the static and kinetic prediction data and, depending on those interpretations, used for site, mine and closure plans.

Interpretation of the static prediction data can be based on either Net NP or NP:AP ratio, with the latter currently preferred. In British Columbia, Price and Errington (1995) propose that

if the NP:AP ratio is less then 1, then the sample has a high potential for ARD. If the ratio is greater then 4, then the sample has a low potential. Those samples with NP:AP ratios between 1 and 4 require further kinetic testing. The guidelines recognize these criteria as being conservative and are used until the proponent can show, through additional work, that the acid generating and neutralizing components are favourably balanced. The Gibraltar tailings have NP:AP values between 0.13 and 8.7 (mean is 1.25) for all samples and have been interpreted has having a potential for ARD (Patterson and Wambolt, 1994). Lawrence and Wang (in prep) have demonstrated that, for Gibraltar and other sites, the NP values vary when determined by different static methods. The Gibraltar samples included in this analysis have NP:AP values of 0.3 to 1.0 (Wambolt et al, 1995) and Lawrence and Wang (in prep) report that these same samples have NP:AP ratios ranging from 0.2 to 3.9. The implication of a variable NP value is the resultant variation in the NP:AP ratio and corresponding interpretation depending on the criterion used.

Given the low values of NP and AP for the Gibraltar tailings, it was uncertain if the ARD potential would be realized and kinetic tests were initiated (Patterson and Wambolt, 1994). The initial period (16-20 weeks) of these kinetic tests is characterized by fluctuating and elevated concentration of parameters until stable conditions are established. It was once accepted practice that kinetic tests were completed in 20 weeks. Recently, waste characterization studies include much longer term tests, although 20 week tests are still specified for some assessments. Interpretation of the Gibraltar kinetic data suggests that sulphide oxidation and calcite dissolution has been occurring since the initiation of these tests. After three years of continued kinetic testing, recent increases in sulphide oxidation and calcite dissolution reactions rates suggest the on-set of ARD conditions in the cells. This infers that the kinetic tests have verified the interpretation of the static test data that a potential for ARD exists and that the potential has been realized after three years of kinetic testing. This potential is also realized on-site as interpretation of the water quality data suggests that oxidation and neutralization reactions are occurring in the subaerial portion of the Main Dam of the tailings impoundment. The Gibraltar study demonstrates the importance of establishing kinetic cells as early as possible to allow stable conditions to be established and the maximum amount of time for leaching. The significance of this is that, although the interpretation of static prediction data provides an indication of the ARD potential, it does not provide an indication of when ARD will occur. The kinetic laboratory tests

suggests that, in this case, a three year period is needed before increased oxidation and neutralization reactions occur. On-site, however, it is impossible to determine the time-frame for these reactions due to the unknown conditions contributing to water quality. Thus, interpretation of static prediction data indicates the potential for ARD although the realization and time lag to the these conditions are only determined by long term, continued kinetic testing.

The next point of waste charaterization to address is at what rate and for what time period will ARD be generated by the Gibraltar tailings. Although static and kinetic test data indicate ARD conditions will establish in these tailings, current kinetic leachate water quality does not exceed British Columbia water quality guidelines for aquatic life (British Columbia Ministry of Environment, Lands and Parks, 1994). Only continued testing of the kinetic cells will determine the worst-case concentrations and rates that will be attained in the kinetic cell leachate.

The interpretation of kinetic test data are principally the calculation of sulphide oxidation and NP depletion rates. By knowing the original AP and NP content and these depletion rates, the time required to deplete acid producing and neutralizing minerals in mine wastes can be calculated. Lapakko (1987, 1990), Bradham and Carrucio (1990), White and Jeffers (1994) and White et al (1994) have completed laboratory testwork in which NP depletion, from carbonate dissolution only, coincided with decreasing pH conditions. Additional work, however, is required to assess the accuracy of calculated mineral depletion rates and the validity of assumptions such as constant oxidation and dissolution rates over time. Acid generating and neutralizing minerals have variable composition and relative reactivity. This can result in an individual ion, for example calcium, being introduced to solution by dissolution of different minerals, for example, from calcite and plagioclase. In this case, the dissolution rates of these minerals differ with plagioclase being slower than calcite. Over time, therefore, neutralization by different minerals may lead to different NP depletion rates. A similar arguement can be made for the acid generating reactions since sulphides also exhibit different relative stabilities and oxidation rates (Ritchie, 1994; Kwong, 1995). Suggested additional work is kinetic testing of samples with a prescribed mineralogy to ensure the occurrence of a variety of sulphide oxidation and neutralization reactions. These tests could assess the assumptions of constant AP and NP depletion rates, although these tests would have the same limitations as most kinetic tests, namely the long time frame.

Quantitative extrapolation of the controlled conditions of a laboratory to operating mine sites like Gibraltar, is tenuous due to constantly fluctuating environmental conditions. Interpretation of the Gibraltar monitoring data has indicated that a significant proportion of surface and ground water quality in the area of the tailings impoundment is affected by the tailings supernatant. The on-site monitoring data also indicates that the water quality changes during migration from the tailings pond to the finger drains and during leakage from the impoundment to the local ground water aquifers. These changes may be the result of physical processes, chemical reactions and/or mixing of waters with different compositions. These influences on ultimate water quality cannot be easily simulated in laboratory kinetic testing and can probably only be accounted for by the development of models that link geochemical reactions and hydrogeology.

Some of the reactions contributing to the water quality changes are sulphide oxidation and neutralizing mineral dissolution. It would be impossible, however, to determine the rates of these reactions since the water quality is influenced more by the supernatant. This suggests that in the absence of more sophisticated approaches, the extrapolation of these laboratory data interpretations is more qualitative than quantitative. For example, identification of preferential depletion of minerals and the formation of secondary minerals in the laboratory tests can be used in the interpretation of existing and future water quality on-site, although the laboratory determined depletion rates cannot be extrapolated directly to the field.

The final consideration is related to the existing conditions of the tailings impoundment that determine the ultimate water quality of the area and its impact to the environment. One consideration at Gibraltar is that most of the tailings are currently underwater and only the Main Dam is subaerial and available for sulphide oxidation reactions. Although an ARD potential exists and it is realized in the laboratory tests and on-site, currently most of the tailings are subaqueous which prohibits sulphide oxidation. Interpretation of the on-site monitoring data also suggests that the local environment has some capacity to neutralize and immobilize some of the ions in solution. It is difficult, however, to assess whether it is mixing of waters or water-rock interactions during supernatant migration, or a combination of both, that result in the observed concentration changes without a better understanding of the hydrogeology in the tailings impoundment area.

5.0   RECOMMENDATIONS FOR ARD PREDICTION TESTING, REPORTING AND INTERPRETATION

Waste characterization studies have evolved over the past few decades with the increasing awareness of the impact to the environment by ARD. Prior to the late 1970's the affect of ARD was not considered. During the 1980's and 1990's, regulatory agencies and mining companies have improved ARD prediction protocols by increasing the number and types of samples and analyses to characterize the mine material. Further refinements of waste characterization studies continue today resulting from increased knowledge and experience in ARD prediction, prevention, control and treatment.

Reporting and interpretation of ARD prediction data has also evolved over the past few decades. What once took a page or two to discuss in the mine plan, now comprises large documents solely on waste characterization. Given that ARD reporting protocols have been developed independently, there are different approaches and interpretations to ARD prediction data. Many investigators and government agents are recognizing the need to improve data collection and reporting in order to completely assess current interpretive methods.

With the review of DBARD and mine submission reports, various data and information pertinent to the review were identified, however, this information tends to be unreported or unrecorded. In an effort to aid groups involved with ARD prediction, the following is presented as a guideline to reporting ARD prediction data with recommended analytical and interpretive methods.

It should be noted that, although the sequence of the following analyses and tests represents the order in which they are often completed during waste characterization studies, ARD testing should be an iterative process. In many cases it is necessary to complete additional tests and analysis as a result of data and interpretation from subsequent tests. In addition, tests completed at a later stage of waste characterization can be used to re-interpret the results of earlier analysis. This applies particularly to the results of the kinetic tests which can often allow a more thorough interpretation of static test data and mineralogical analysis.

5.1 MINERALOGICAL CHARACTERIZATION

An initial part of waste characterization is the division of the on-site waste units. This is usually based on the geologic units identified during the exploration and development phases of the site. During waste characterization these divisions are further refined and possibly divided differently based on the acid generation potential. Mineralogical characterization is based on geochemistry, mineralogy and, in some cases, particle size.

5.1.1 GEOCHEMISTRY

The geochemistry of a sample can be reported as element or oxide content depending on the analysis used. Common techniques used to determine the concentration of the major and trace elements are Induced Coupled Plasma (ICP), Atomic Adsorption (AA) and X-ray Fluorescence (XRF). Determining which technique to use will depend on the elements to be analyzed, detection limits required, number of samples and cost. Commonly, ICP analysis is used to determine elemental concentrations of a sample.

One important consideration in interpreting available geochemical data from ICP and AA is understanding the digestion conditions used in these analytical techniques. Digestions commonly used are aqua-regia or hydrofluoric-perchlorate-nitric. Aqua-regia digestions will not completely digest some of the minerals, particularly silicates. Although this affects the accuracy of the concentrations obtained, it does permit an interpretation of the static prediction data. For example, elements not completely digested by aqua-regia are aluminum, calcium, magnesium, potassium and sodium. This suggests, for example, that if calcium is present in a sample in both carbonate and silicate minerals, digestion by aqua-regia would introduce calcium from the carbonate predominantly. It is important to understand the analytical techniques completed given the recent trend to measure "indicator" (or "surrogate") elements. These elements correlate with the neutralization potential and, by using correlation equations, the neutralization potential can be calculated from elemental concentration. Indicator elements may also be applicable to determining the acid potential. It is recommended that any indicator elements also be used to monitor and characterize oxidation and dissolution reactions in kinetic testing.

The various sulphur species have to be measured in order to establish the sulphide-sulphur content of the samples. This is accomplished by measuring the total sulphur content, determined by Leco furnace techniques, and sulphate content, determined by HCl dissolution

techniques. The arithmetic difference between these two sulphur measurements represents the sulphide - sulphur content and this value is used to determine the Sulphide Acid Potential (SAP). Standard ABA uses the total sulphur content to determine the Acid Potential (AP). If barite is suspected in the sample it is necessary to estimate its content using barium analysis since barite is insoluble in HCl and would not be accounted for by these dissolution techniques.

Analysis of inorganic carbon content of samples is also recommended for the calculation of the carbonate mineral content. There are various forms of carbon present that must also be considered when analyzing for carbon content. Total carbon represents the organic and inorganic carbon content of the sample and is commonly determined by Leco furnace techniques. Of interest is the inorganic carbon content that can be used to calculate the Carbonate Neutralization Potential (CNP). Inorganic carbon content may also prove to be a useful indicator element at sites.

5.1.2 MINERALOGICAL ANALYSIS

An understanding of the mineralogy of the different lithologies is important in the collection and interpretation of prediction data. Methods used for mineralogical analysis range from simple visual examination of core or hand specimens, petrographic microscope techniques, to more sophisticated analysis such as x-ray diffraction (XRD). Normative calculations also provide an inferred modal distribution based on the geochemistry of a sample, although these may not be applicable at all sites since the calculations are based on the assumption of crystallization from a magma. It is recommended that mineralogical analysis include at least visual examinations and petrographic microscope techniques.

Mineralogical features noted during the mineralogical analysis by visual and petrographic methods include components that are relevant to the ARD potential for example:

- types and modal distribution of sulphide/opague, carbonate, and silicate minerals
- crystal size, fabric, habit, deformation and form
- association and occurrence of the minerals
- presence of secondary minerals as coating/replacement

5.1.3 PARTICLE SIZE ANALYSIS

Analysis or mineralogical examination of size fractions of tailings and other materials can provide useful information on the distribution of AP and NP, namely, does static test data correlate with particle size? This may occur, for example, if differential settling occurs along flow paths as tailings are disposed. This type of analysis includes sieving the samples, with very fine fractions separated using specific analytical techniques, and each size fraction undergoing mineralogical characterization and static prediction tests. In addition to mineralogic/lithologic descriptions, particle characteristics for the individual sieve fractions should include shape and angularity. If the particles are sufficiently large enough, for example from waste rock piles, then additional testing could include the particle competence and slaking potential.

5.1.4 REPORTING OF DATA

The various methods and techniques used to characterize the mineralogy should be specified. If non-standard techniques are used, these should be described in detail. Reporting of the mineralogical characterization should include: the laboratory where the analysis was completed and when; the analytical method; description of sample preparation; and digestion conditions where applicable. The data to be reported from the geochemical analysis includes:

- waste characterization unit
- elemental analysis from ICP scan
- sulphur species concentrations
- inorganic carbon concentration

The data to be reported from the particle size analysis includes the above list, if available, and:

- sieve sizes used and % retained
- particle shape and angularity
- competence/slaking potential

The mineralogical analysis should result in detailed descriptions of the individual units identified in the waste characterization studies. The description of each unit should include the full lithologic name and any abbreviations that will be referred to. Each unit should have a

detailed lithologic summary based on the interpretations of the geochemical and mineralogical characterization focusing on the mineralogy, modal distribution, crystal size and form and the association of the minerals.

5.2 STATIC PREDICTION TESTING

5.2.1 TEST METHODS

Of the various methods available, it is recommended that the Modified ABA (Lawrence, 1990) test be used as other research (Lawrence and Wang, in prep) suggests it provides a more representative value of the neutralization potential. It is recognized that a preference is commonly given to the Standard ABA method given its practical aspects, namely the minimal laboratory time and space requirements. This test may be still be used, although it is important to have the "fizz" rating and digestion conditions used in each test noted. These data should also be reported for each Modified ABA test completed.

It is also recommended that the inorganic carbon content measured be used to aid in the interpretation of the Modified or Standard ABA data. Since the inorganic carbon represents the carbonate content, it could be used to assess the overestimation of NP that may result from the Standard ABA tests and to verify the NP values from the Modified ABA tests. Inorganic carbon content of samples also indicates the proportion of NP attributed to carbonate dissolution. For example, if the neutralization potential exceeds the carbonate neutralization potential (determined from sample carbon content) it indicates that there may be an overestimation of NP due to silicate dissolution. If carbonate neutralization potential exceeds the neutralization potential it suggests the presence of siderite (iron carbonate) which does not contribute to the neutralization potential but would be included in the inorganic carbon content.

Paste pH should also be recorded in order to determine if a correlation exists between it and the static prediction data. If there is a correlation, using field measurements of paste pH allows for a quick, relatively inexpensive technique to approximate the ARD potential.

Other information that should be reported by the laboratory completing the static prediction tests are the end pH of the digestion and the back titration curves. Both of these

would provide an indication of the degree of digestion and the contributions of carbonate and silicate minerals to NP.

5.2.2 CALCULATIONS AND TERMS

The following terms and calculations are recommended for use in static prediction tests. All investigators, whether they use the following calculations or their own, should detail the calculations and terms used in their waste characterization studies. This information tends to be the least reported/recorded and is probably the most significant.

The first consideration is the acid generating potential:

Acid Potential: $\qquad$ AP = (% S - total) x 31.25
(kg as $CaCO_3$/t)

Sulphide Acid Potential: $\qquad$ SAP = (% S - sulphide) x 31.25
(kg as $CaCO_3$/t)

Mineralogical descriptions would indicate the type, availability, and associations of the sulphide minerals and provide a qualitative identification of the sulphide minerals contributing to the acid potential. The SAP value quantifies the acid potential and represents of the amount of sulphide minerals present to oxidize.

The second consideration is the acid neutralizing potential:

Neutralization Potential: $\qquad$ NP = from Standard ABA or Modified
ABA procedures
(kg as $CaCO_3$/t)

Carbonate Neutralization Potential: $\qquad$ = (%CO_2 - inorganic) x 22.73
CNP $\qquad$ or
(%C - inorganic) x 83.33
(kg as $CaCO_3$/t)

In considering neutralization, qualitative identification of minerals contributing to NP can be determined from mineralogical characterization and the back titration curves. The above calculations quantify the available NP and the contributions of silicate and carbonate minerals.

With AP, SAP, NP and CNP determined by laboratory methods, the following calculations are recommended to interpret the ARD potential:

Net Neutralization Potential: $\qquad$ NNP = NP - AP

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$$\text{(kg as } CaCO_3/t)$$

Neutralization Potential Ratio:	NPR	=	NP / AP

Refined Net Neutralization Potential:	RNNP	=	NP - SAP

$$\text{(kg as } CaCO_3/t)$$

Refined Neutralization Potential Ratio:	RNPR	=	NP / SAP

Carbonate-Sulphide Net Neutralization
Potential: CNNP   =   CNP - SAP

$$\text{(kg as } CaCO_3/t)$$

Carbonate-Sulphide Neutralization Potential
Ratio: CNPR   =   CNP / SAP

Of these calculations, the CNPR is recommended for interpretation of the ARD potential as it represents the proportion of carbonate to sulphide content in the sample.

5.2.3 REPORTING OF DATA

Information which should be included when reporting static prediction data includes:

Sample I.D/Location	% S - sulphide	NP determination method	NNP
Waste Unit	% S - total	Fizz Rating	NPR
Sample/Analysis Date	% S - sulphate	Acid digestion (normality/volume)	RNNP
Laboratory	AP	pH after digestion	RNPR
Paste pH	SAP	NP	CNNP
		% C - inorganic	CNPR
		CNP	

5.3 KINETIC PREDICTION TESTING

5.3.1 TEST METHODS

Outlining the objectives of the kinetic testing is important given that these determine how the test and analysis is completed. Kinetic tests are used to: test the interpretation of the static test data; determine the rate of acid generation (sulphide oxidation) and metal leaching; determine water quality; test pr oposed control and mitigation measures; and, more recently, determine the depletion rate of the neutralization potential. As a result of these various objectives there are different types of kinetic tests and procedures. For example, humidity cells

(Lawrence, 1990) can be used to determine the time-lag and worst-case reaction rates since procedures of these tests do not represent field conditions and are such that flushing removes all oxidation/neutralization products and washes all the particles. Interpretation of these data provides an indication of preferential depletion of the acid generating and neutralizing minerals. Larger scale trickle - leach humidity cells (Broughton et al, 1992), column leach tests and on-site field plots provide a better indication of the water quality that would result from weathering since procedures are more representative of field conditions. Interpretation of field plot water quality data are often limited since insufficient data tends to be collected. This is particularly evident if the site is remote and not easily accessible. These larger scale kinetic tests can be modified to test proposed mitigation measures and resultant water quality. An important feature of the test method selected is that it should be consistent with the objective of the test.

In detailing the objectives of the the kinetic testing, it is important to fully outline the procedure of the kinetic tests and the selection and preparation of samples included in the testing. Kinetic testing should be initiated as soon as possible in waste characterization studies to allow stable conditions to be established and the maximum amount of time for leaching. Although an absolute time frame for these tests cannot be recommended, it is recognized that these tests often require approximately 20 to 30 weeks just to reach stable conditions.

It is important to identify the analytical techniques used to determine the leachate water quality. ICP and AA techniques are commonly used and recommended. Noting analytical techniques is important, particularly if correlation equations are used to estimate the concentration of one parameter from the measurement of another. For example, one approach is to use measured conductivity value to calculate sulphate concentration. Care should be used when using concentrations determined by these correlation techniques, to calculate depletion rates as it may not be representative of the actual concentration and rate. Another consideration is the use of data below detection limits to calculate depletion rates. This also requires special consideration when using this data to calculate depletion rates as assuming values at detection limits, or at some proportion of the detection limits, may not represent the true concentration and rate.

An important consideration of the kinetic testing is the sampling interval. Many test procedures are based on weekly sampling intervals, however, with more and more tests

completed over a long term (i.e. years), weekly samples may prove to be too detailed and costly. It is recommended that sampling interval initially be weekly until stable conditions are reached and continued at this interval until these conditions are characterized. Some parameters, such as pH, conductivity, temperature and redox potential, can be monitored simply and inexpensively on a weekly basis for the duration of the test. Other parameters, namely the ICP analysis, may have a reduced sampling frequency, to monthly or even quarterly, once stable conditions are attained. These sampling intervals should be reviewed if: 1) test conditions change, for example if testing stops for a period and is re-initiated or if cells are moved to another location, and 2) water quality changes, for example if oxidation and neutralization reaction rates are increasing.

The parameters in the leachate analysis should include:

- pH
- alkalinity/acidity
- conductivity
- sulphate concentration
- individual metal concentrations

Redox potential can also be measured, although measurements of low ionic strength solution are often erratic from week to week and interpretation should be carried out carefully. In determining the metals to include in the analysis, the multi - elements included in a typical ICP scan provide an overall indication of the water quality. If indicator elements have been identified, the analysis could be limited to these parameters. If there are metals of concern, for example, mercury, selenium, arsenic, antimony and base metals, not available in the ICP analysis, these should also be included in the sampling and analyzed by more sensitive or accurate techniques such as AA. It is recommended that the ICP scan be utilized, in addition to any indicator or metals of concern not included in this analysis. This provides an overall water quality, parameters to calculate depletion rates and may provide information needed as a result of changing regulations and permit requirements.

Parameters to be included in the analysis, together with the sampling interval, should be reviewed periodically to ensure that testing is meeting the objectives of the test and remains cost effective.

5.3.2 CALCULATIONS AND TERMS

Recommended calculations and terms for use in kinetic testing are presented in the following. All investigators, whether they use the following calculations or their own, should detail the calculations and terms used for manipulating kinetic test data in their waste characterization studies.

The first consideration is the sulphide oxidation rate and the time until sulphide is depleted which is calculated using the leachate sulphate concentration values and the sulphide-sulphur content of the sample at the start of the test.

$$\text{Cumulative } SO_4 \text{ Produced} = \text{cumulative total of:}$$
$$\frac{(SO_4 \text{ concentration per cycle x leachate volume})}{\text{sample weight}}$$
$$(\text{mg as } SO_4/kg)$$

$$\text{Sulphide oxidation rate} = \frac{(\text{cumulative } SO_4 \text{ extracted from one cycle} - \text{cumulative } SO_4 \text{ extracted from an earlier cycle})}{\text{time difference between cycles}}$$
$$(\text{mg as } SO_4/kg/week)$$

$$\text{\% S - sulphide remaining} = \frac{((\text{original \% S-sulphide x sample weight x } 10^6 - (\text{cumulative } SO_4 \text{ x } 32/96))}{(\text{original \% S-sulphide x sample weight x } 10^6)} \text{ x100}$$
$$(\%)$$

$$\text{Time to Deplete AP} = \frac{(\text{\% S-sulphide remaining x} (\text{original \%S-sulphide x sample weight x } 10^6))}{\text{sulphide oxidation rate x } 32/96}$$
$$(\text{weeks})$$

The next consideration is the leaching rates of the individual metals. These calculations should focus on the identified indicator elements and metals of concern in order to characterize the reactions introducing them to solution.

$$\text{Cumulative Metal Produced} = \text{cumulative total of}$$
$$\frac{(\text{metal concentration per cycle x leachate volume})}{\text{sample weight}}$$
$$(\text{mg as metal/kg})$$

$$\text{Metal leaching rate} = \frac{(\text{cumulative metal extracted from one cycle} - \text{cumulative metal extracted from an earlier cycle})}{\text{time difference between cycles}}$$

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$$\text{(mg as metal/kg/week)}$$

% metal remaining $\quad = \dfrac{((\text{original \% metal x sample weight x } 10^6) - \text{cumulative metal})}{\text{original \% metal x sample weight x } 10^6} \text{ x } 100$

(%)

Time to Deplete metal $\quad = \dfrac{(\text{\% metal remaining x } (\text{original \% metal x sample weight x } 10^6))}{\text{metal leaching rate}}$

(weeks)

There are two proposed methods to calculate the NP depletion. The first is based on the leaching of calcium and/or magnesium using the calculations for the individual metals presented above. The second method uses molar ratios of ions from neutralizing minerals to sulphate and the calculated oxidation rate. The molar ratio to use for these calculations will depend on the predominant neutralizing mineral present, that is carbonate or silicate. The calcium to sulphate ratio is sufficient to calculate neutralization depletion rates if the minerals contributing to neutralization cannot be distinguished.

Molar Ratios to calculate:

carbonate ratio $\quad = \dfrac{((\text{Ca concentration/40.08}) + (\text{Mg concentration/24.31}) + (\text{Sr concentration/87.62}) + (\text{Ba concentration/137.34}))}{(\text{SO}_4 \text{ concentration/96})}$

silicate ratio $\quad = \dfrac{((\text{Ca concentration/40.08}) + 0.5(\text{Na concentration/22.99}) + 0.5(\text{K concentration/39.09}))}{(\text{SO}_4 \text{ concentration/96})}$

calcium to sulphate ratio $\quad = \dfrac{(\text{Ca concentration/40.08})}{(\text{SO}_4 \text{ concentration/96})}$

NP depletion rate $\quad = $ selected molar ratio x sulphide oxidation rate x (100/96)

(mg as $CaCO_3$/kg/week)

Cumulative NP Produced $\quad = $ cumulative SO_4 produced x (100/96) x selected molar ratio

(mg as $CaCO_3$/kg)

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% NP remaining = $\underline{\text{(original NP - cumulative NP)} \times 100}$
                              original NP
(%)

Time to Deplete metal = $\underline{\text{(% NP remaining} \times \text{(sample weight} \times 10^6))}$
                              NP depletion rate
(weeks)

It has been recognized that the initial 20 to 30 week period is often characterized by elevated and fluctuating concentrations due to the flushing of existing oxidation/neutralization products. Calculations completed using this data may not represent oxidation and neutralization reactions that are occurring. It is recommended that running averages of the last five calculated sulphide oxidation, metal leaching and NP depletion rates be completed in order to "smooth" the data. These running averages should be used in determing the percent remaining and time to depletion.

The NP depletion calculations presented follow the procedures of the original authors. An improvement to these calculatives is using the original mineralogical content rather than the original calcium (used for % remaining calculations based on metal leaching rates) or NP (used for % remaining calculations based on molar ratios and sulphide oxidation rate). Calcium and NP values may reflect both carbonate and silicate contributions, thus using the original modal distribution provides a more representative calculation of its depletion.

Calculations can be carried out to determine other molar ratios which represent the proportion of moles in solution. Molar concentrations are calculated by dividing the leachate concentrations by the ion molecular weight and using the molar concentrations to determine the molar ratio. The ratios to calculate depend on the "indicator" elements identified and the following molar ratios are recommended, but not limited to:

sulphate / alkalinity   - an increase in this indicates the on-set of increased
                                                    oxidation and neutralization reaction rates and
                                                    ARD conditions

calcium / sodium or magnesium   - to determine preferential leaching of neutralizing
                                                    minerals

calcium or magnesium or sodium or potassium / sulphate
                                                    - to characterize dissolution and oxidation reactions

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calcium or magnesium or sodium or potassium / iron

- to characterize dissolution and oxidation reactions

Other calculations that can be carried out include saturation index values for secondary minerals that may precipitate. This would apply principally to sulphate minerals which would limit the concentration of sulphate and calcium in the leachate and lead to erroneous rate calculations.

5.3.3 REPORTING OF DATA

Prior to reporting the kinetic test data, there should be a compilation of information related to the samples included in the kinetic testing. This would principally be the static prediction data, geochemical analysis and mineralogic/lithogic description.

Data to report kinetic tests includes:

Laboratory	Calculated sulphate production rates and cumulative total
Date/Cycle Number	Calculated individual metal leaching rates and cumulative total
Leachate Volume	Calculated NP depletion rate and cumulative total
Conductivity	% S, metal and NP remaining
Redox	time to deplete AP, NP and metals
pH	Molar ratios
Alkalinity / Acidity	
Sulphate concentration	
Individual metal concentrations	

5.4 INTERPRETATION AND WASTE CHARACTERIZATION

Since waste characterization is iterative and tends to be phased, it is important to identify the individual phases included in the waste characterization as each phase tends to have individual objectives. It is also important to identify and describe the work completed for each phase since interpretations from one phase may be either applied to previous work for re-interpretation or used to determine additional test work. Each phase of the waste characterization should be identified by its objective(s), time of completion, the number of samples collected and analyses completed, and findings/conclusions.

The criteria used to interpret static and kinetic prediction data should also be presented. As a guideline it is recommended that for Neutralization Potential Ratio (=NP/AP) and Refined Neutralization Potential Ratio (=NP/SAP) values less than 1 be interpreted as acid generating, values greater than 3 as non-acid generating and those values between 1 and 3 as uncertain potential. It is recommended that the Carbonate Sulphide Potential Ratio (=CNP/SAP) be used to interpret the ARD potential. In this case the zone of uncertainty would lie between 1 and 2. These guidelines should be used as an initial classification for the data and used in conjunction with other geologic and non-geologic factors of the sample, and on-site, to determine site specific interpretation criteria for the ARD potential. If investigators use other criteria to distinguish acid and non-acid generating components, then a detailed description of their derivation or source should be given.

Interpretation of the kinetic test data is dependent on the objectives and procedures of the test and the discussion should address the individual objectives of the test. The interpretation could include, but not limited to, the oxidation and neutralization reactions rates and time to depletion, the leaching rates of indicator elements and metals of concern, the characterization of mass gains or losses and preferential depletion from molar ratios, and the resultant water quality from weathering.

Following the discussion of the static criteria used and the discussion of the kinetic test data interpretations, there should be a summary of the on-site waste units and their interpreted ARD potential.

6.0 CONCLUSIONS AND RECOMMENDATIONS

This chapter will summarize the findings of this thesis by discussing each of the objectives, presented in Section 1.0.

The first objective of this thesis was to investigate the relationship between static prediction parameters and lithogeochemistry and geologic deposit type. This was completed with a review of DBARD and a detailed study of the tailings impoundment at Gibraltar. The review of DBARD has indicated that adjacent sites, or sites of a similar deposit model, cannot be compared directly when determining ARD potential from static prediction data. However, experience from previous work at other sites could aid new sites in determining waste characterization programs. Paste pH provides a quick indication of NP:AP values and should be used as an ARD charaterization tool. This indicator is site specific and the correlation between paste pH and NP:AP would need to be established at individual sites.

The review of DBARD also indicated that NP determination from static prediction tests are dependent on mineralogy (i.e. whole rock chemistry) particularly the concentration of calcium, magnesium and carbon. These dependences would need to be established on a site specific basis as there is a correlation of these factors with lithology. The detailed study at Gibraltar has identified correlations between NP and calcium, carbon, strontium and sodium as well as between AP and iron, cobalt and manganese. In this case, minerals that may be contributing to AP are pyrite and minor chalcopyrite, bornite and molybdenite. Minerals contributing to NP are calcium carbonate and sodium-calcium silicate minerals. Identification of minerals contributing to AP and NP has been incorporated in the Gibraltar study by identifying chemical parameters that can be used in the interpretation of kinetic test data and on-site monitoring data to characterize oxidation and dissolution reactions. The DBARD review and detailed study suggests that an understanding of the mineralogy/lithology of the waste characterization units is essential to interpret ARD prediction data.

The Gibraltar tailings have NP:AP values between 0.3 and 1.5 and have beeen interpreted as having a potential for ARD. For Gibraltar, and other sites, Lawrence and Wang (in prep) suggest that NP values vary with different static test methods depending on the digestion conditions and the sample mineralogy. The implication of this is that the resultant variation of

the NP:AP ratios and corresponding interpretation of the ARD potential depend on the classification criterion used.

The second objective of this research was to assess current interpretations of kinetic prediction data and their relation to the static prediction data. Although the kinetic tests in DBARD are relatively short term (less then 20 weeks), the review indicates that the static prediction data do not correlate with either the minimum pH values or the mean rates of sulphide oxidation from the kinetic tests. There are proposed calculations for NP depletion rates using either: 1) metal leaching rates for calcium and magnesium or 2) various molar ratios and sulphide oxidation rates. Although similar rates are determined by these methods, additional work is needed to assess the accuracy of these calculated depletion rates and the validity of assuming constant rates over time.

The Gibraltar study indicates that the kinetic leachate chemistry is highly variable in the first 16 to 20 weeks of testing until stable conditions are established. More recent waste characterization studies have incorporated longer term kinetic tests than the previously accepted 20 week test. Once stable conditions were established in the Gibraltar cells, certain chemical parameters occur in solution above detection limits, in this case, calcium, strontium, sulphate, magnesium, molybdenum, manganese and zinc, suggesting sulphide oxidation and calcite dissolution reactions are occurring. In addition, changes in concentration and molar ratios in the cell leachate indicate increased oxidation and neutralization reactions rates and the possible on-set of ARD conditions. The Gibraltar study demonstrates the importance of establishing kinetic cells as early as possible since to allow stable conditions to be established and the maximum amount of time for leaching. The interpretation of the static test data indicates a potential for ARD and the realization and time lag to these conditions can only be determined by long term kinetic testing. Calculated sulphide oxidation and NP depletion rates indicate that, after three years of testing, approximately 95% of the original sulphide and 85% of the original calcite are still present in these Gibraltar samples.

The third objective of this thesis was to determine the ability of static and kinetic prediction methods to identify on-site water quality using the detailed study of the Gibraltar tailings impoundment. Interpretation of the on-site monitoring data has indicated that a significant proportion of surface and ground water in the tailings impoundment area is affected

by the tailings supernatant. These data also indicate that the water quality changes during migration from the tailings pond to the finger drains of the Main Dam and during leakage from the impoundment to the local ground water aquifers. These changes may be the result of physical processes, chemical reactions and/or the mixing of waters of different compositions. These factors all contribute to the ultimate water quality on-site. Although the static prediction data interpretations indicate that a potential for ARD exists within the tailings which is subsequently identified in laboratory kinetic tests, extrapolation of laboratory interpretations is more qualitative than quantitative. For example, the calculated depletion rates cannot be directly extrapolated to the field. The identification of preferred mineral depletion and formation of secondary minerals identified in the laboratory tests can be used, in conjunction with the understanding of other factors on-site, to interpret existing and future on-site water quality.

The fourth objective of this thesis was to assess current interpretive and reporting methodology used to assess ARD prediction data. The review of DBARD has indicated that ARD reporting protocols have been developed independently and, as a result, there are different approaches and interpretations of ARD prediction data. Data and information that are either unrecorded or unreported were also identified. In an effort to aid groups involved in ARD prediction, a guideline to waste characterization testing, data collection, interpretation and reporting is presented. The steps recommended include:

1. Mineralogical characterization summarizing the geochemical, mineralogical and particle size analyses completed to describe the minerology/lithology of the individual waste units. Recommended procedures include ICP to determine the geochemistry and visual descriptions and petrographic microscope methods to identify mineralogy;

2. Static prediction characterization summarizing the tests completed and the calculations used to interpret the data. Recommended tests are the Modified ABA or Standard ABA with digestions conditions, end pH, and back titration curves reported. Inorganic carbon content and indicator elements should also be determined. Interpretation of the ARD potential should be based on the carbonate to sulphide ratio (CNPR).

3. Kinetic prediction characterization summarizing the objectives, procedures, leachate water quality and calculations completed. The test and analyses used should be consistent with the required objectives. Although a maximum time cannot be recommended, these tests should

be considered long term tests as approximately 20 to 30 weeks are required to establish stable conditions. Initially sampling should be carried out at weekly intervals and include the analysis of alkalinity/acidity, pH, conductivity, sulphate concentration and individual metal concentrations (from ICP). The sampling interval and analysis should be reviewed after stable conditions occur, if test conditions change, or as water quality changes. Calculations should include cumulative flux, leaching rate, % sulphur, metal and NP remaining, and time to deplete for both acid and neutralization potential. Other information to be derived from the leachate water quality can include molar ratios using the indicator elements to characterize the oxidation and neutralization reactions; and

4. Waste Characterization summarizing the criteria used to interpret the static and kinetic test data and the classification of the waste units on-site based on the interpreted ARD potential. As a guideline, the CNPR should be used to interpret the static test data with values less than 1 considered acid generating greater than 3 as non-acid generating and between 1 and 3 as uncertain. These criteria should be used as an initial interpretative tool and used in conjunction with kinetic test data and other geologic and non-geologic components of the samples and on-site to assess the ARD potential

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APPENDIX 1

Summary Table of Descriptive Statistics for Static Test Data in DBARD

Appendix 1: Summary Table of Descriptive Statistics for Static Test Data in DBARD Ore

Mine No	Deposit Type*	method**	n	Paste pH			AP			NP			Net NP			NP:AP		
				mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1	Epith	mod?	29	6.1	4.0	7.6	86.5	2.2	280.6	1.1	0.01	5.4	-81.5	-280.3	0.3	0.13	1E-05	1.05
2	Epith	?	1	9.0			28.0			187.0			159.0			6.68		
3	Epith																	
4	Epith																	
5	Epith	sobek	6	7.8	6.5	8.5	348.2	18.9	772.0	48.4	6.7	105.0	-274.5	-757.4	-78.9	0.29	0.02	0.74
6	Epith																	
7	Epith																	
8	Epith	sobek	4	8.5	8.2	8.8	239.8	59.4	411.3	35.4	32.9	38.0	-204.4	-374.1	-25.8	0.29	0.09	0.56
9	Epith	sobek?	23				14.4	0.5	50.4	59.6	24.1	176.8	45.2	0.5	175.0	33.58	1.01	180.41
10	Epith	?	25	7.3	5.6	8.7	25.7	1.3	78.0	17.7	0.8	131.9	-7.0	-59.1	126.3	2.05	0.07	22.25
11	Epith	BC	9	8.4	7.6	9.0	130.8	51.0	328.0	48.4	6.7	105.0	-82.5	-321.3	11.0	0.57	0.02	1.22
12	Epith																	
13	Mesoth																	
14	Mesoth																	
15	Mesoth	sob/BC	1	8.8			71.0			148.0			77.0			2.08		
16	Mesoth	sobek	4	8.3	8.0	8.6	94.5	1.1	158.0	210.5	180.0	241.0	115.9	33.5	228.3	53.38	1.20	208.50
17	Mesoth																	
18	Mesoth	?	8	8.0	6.7	8.7	73.6	3.2	210.9	312.6	2.1	813.9	243.2	-16.6	810.8	41.19	0.11	255.10
19	Mesoth																	
20	Mesoth																	
21	Mesoth	sobek	8	9.0	8.0	9.4	176.6	106	438.0	190.3	98.0	275.0	13.8	-312.0	156.0	1.37	0.29	2.42
22	Mesoth	?	4	8.7	8.6	8.8	48.9	27.6	67.5	170.3	17.0	416.0	121.4	-43.3	348.5	3.90	0.70	7.97
23	Mesoth	sobek	6	8.3	8.2	8.5	113.0	12.3	208.8	141.0	7.1	793.6	28.0	-200.5	781.4	10.87	0.04	64.78
24	Mesoth																	
25	Mesoth																	
26	Mesoth	BC	1				0.6			54.0			53.4			86.38		
27	Porph	?	1	9.5			2.2			20.0			17.8			9.13		
28	Porph	sobek	61	8.5	8.1	9.8	18.5	2.0	63.0	74.2	25.0	152.0	55.1	-17.0	143.0	7.46	0.64	33.00
29	Porph																	
30	Porph																	

Mine No	Deposit Type*	Ore method**	n	Paste pH mean	min	max	AP mean	min	max	NP mean	min	max	Net NP mean	min	max	NP:AP mean	min	max
31	Porph																	
32	Porph																	
35	Porph																	
37	Porph																	
38	Porph																	
39	Porph	?	6				86.8	28.1	131.3	164.9	146.2	179.5	78.7	18.0	118.1	2.35	1.14	5.19
40	Porph																	
41	Porph	?	12	7.8	7.1	8.2	200.2	21.0	500.0	110.2	378.0	150.0	-90.0	-462.0	113.0	1.45	0.08	6.38
42	Porph	BC	1				361.4			18.5			-342.9			0.05		
43	Sedex	sobek	23	6.5	4.0	8.5	894.3	488	1178	51.7	-9.0	209.0	-868.4	-1187	-480	0.03	0.00	0.21
44	Sedex	BC	3	9.1	8.8	9.7	100.3	70.3	155.6	33.6	24.0	52.8	-66.7	-131.6	-22.2	0.40	0.15	0.34
45	Sedex																	
46	Skarn																	
47	Skarn	?	2	7.4	6.9	7.9	554.5	381	728	83.0	40.0	126.0	-471.5	-688	-255	0.19	0.06	0.33
48	Skarn	BC	3	8.8	8.3	9.0	37.8	18.8	67.2	17.3	10.8	25.0	-20.5	-51.0	-2.5	0.58	0.24	0.91
49	Skarn																	
50	VMS																	
51	VMS	BC	1	8.4			44.7			152.1			107.4			3.40		
52	VMS	sobek?	5	6.7	6.3	7.2	387.0	165	952.0	116.9	14.4	233.0	-270.2	-771.0	-91.8	0.35	0.01	0.04
53	VMS																	
54	VMS	sobek	8	7.7	6.5	9.0	547.5	2.0	1470	93.9	2.0	311.0	-451.6	-1385	309.0	19.80	0.00	155.50
55	VMS																	
56	VMS	?	2	7.2	7.0	7.3	891	863	919	21.0	12.1	30.0	-870	-907	-833	0.02	0.01	0.04
57	VMS	sobek	10	7.2	3.9	8.5	301.2	83.4	871.9	113.9	2.0	369.0	-187.3	-869.9	285.6	0.93	0.002	4.42
58	VMS	sobek?	11	6.8			934.0			19.6			-914.5			0.02		

total n = 278

* deposit type: epith - epithermal; mesoth - mesothermal; porph - porphyry;
sedex - sedimentary exhalative; skarn - skarn; VMS - volcanogenic massive sulphide
** method: sobek - Standard ABA; mod - Modified ABA; BC - BC Research Initial Test; ? - unknown

Appendix 1

Mine No	Deposit Type*	Waste Rock method**	n	Paste pH			AP			NP			Net NP			NP:AP		
				mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1	Epith	mod?	20	5.9	4.3	7.8	21.4	7.2	239.4	3.0	0.2	17.8	-44.9	-238.8	-2.9	0.16	0.003	0.73
2	Epith	?	2	8.9	8.7	9.0	13.0	4.0	22.0	61.5	47.0	76.0	48.5	43.0	54.0	7.60	3.45	11.75
3	Epith																	
4	Epith	sobek	197	5.9	2.5	8.5	71.2	0.1	225.0	15.8	-6.7	317.5	-55.5	-221.0	255.0	0.56	-0.22	13
5	Epith	sobek	6	8.9	8.5	9.8	21.0	ND	61.6	197.3	140.0	268.9	179.8	133.1	253.1	14.42	undef	31.99
6	Epith																	
7	Epith																	
8	Epith	sob/BC	7	9.1	8.8	9.7	26.6	9.1	59.4	56.2	32.9	78.9	29.6	-26.5	64.1	2.99	0.55	5.45
9	Epith																	
10	Epith																	
11	Epith	BC	43	8.7	7.1	9.5	72.8	12.0	159.4	69.4	4.9	149.0	-3.5	-149.4	92.0	1.37	0.03	5.75
12	Epith																	
13	Mesoth	sobek	6	8.8	8.0	9.2	16.2	1.1	54.1	136.3	57.0	334.0	120.2	25.9	299.3	35.02	1.48	89.58
14	Mesoth	sobek	3	8.7	8.5	8.8	26.0	17.0	40.0	67.0	47.0	103.0	41.0	7.0	86.0	3.22	1.18	6.06
15	Mesoth	BC	1	9.6			3.8			43.6			39.9			11.64		
16	Mesoth	sobek	1	8.7			0.2			267.9			267.7			1340		
17	Mesoth	sobek	20	8.8	7.9	9.3	30.6	0.3	293.0	148.2	16.0	565.0	117.7	-164.0	561.0	68.79	0.44	467.7
18	Mesoth	?	5	7.9	7.3	8.6	23.1	0.3	61.3	659.5	268.8	942.0	636.5	207.5	942.0	1220	4.38	3039
19	Mesoth	sobek	2	8.4	8.4	8.4	6.5	3.0	10.0	382.0	139.0	625.0	375.5	129.0	622.0	111	13.9	208
20	Mesoth	sobek	3	8.7	8.3	8.9	41.7	0.9	107.0	153.7	27.0	399.0	112.0	18.0	292.0	11.50	2.06	28.7
21	Mesoth	sob/?	16	9.0	8.4	9.9	48.5	10.0	119.0	114.0	36.0	167.0	65.9	-18.0	128.0	3.64	0.67	13.38
22	Mesoth	?	2	8.9	8.8	9.0	0.8	0.3	1.3	19.0	11.0	27.0	18.2	10.7	25.7	28.72	20.77	36.67
23	Mesoth	sobek	52	8.2	7.3	8.8	102.5	2.8	210.6	63.5	2.0	559.9	-38.8	-199.8	518.8	1.26	0.04	16.51
24	Mesoth																	
25	Mesoth																	
26	Mesoth																	
27	Porph	?	1	9.2			0.9			15.5			14.6			16.49		
28	Porph	sobek	205	8.7	8.0	10	9.6	0.4	73.5	66.7	1.0	205.0	57.2	-23.0	202.0	18.90	0.53	222.5
29	Porph																	
30	Porph																	

Appendix 1

Mine No	Deposit Type*	Waste Rock method**	n	Paste pH			AP			NP			Net NP			NP:AP		
				mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
31	Porph	sobek	1				23.1			241.0			217.9			10.42		
32	Porph	sobek	5				581.4	4.1	1538	83.0	64.0	109.0	-136.1	-433.4	104.9	9.14	0.149	26.83
35	Porph																	
37	Porph	BC	17	9.0	8.3	9.6	37.2	2.0	66.3	37.4	11.0	105.2	0.2	-29.7	78.6	2.87	0.488	29.57
38	Porph	sob/mod	52	8.7	7.6	9.3	6.6	0.0	91.6	28.6	10.1	65.5	22.5	-55.0	63.6	24.70	undef	293
39	Porph	?	123	7.6	4.5	9.7	58.3	1.1	150.3	61.8	0.0	182.3	5.0	-107.7	121.0	1.80	undef	14.51
40	Porph	?	20	6.9	4.9	7.9	124.5	24.4	261.3	48.6	0.6	94.6	-76.0	-226.1	69.0	0.76	0.004	3.695
41	Porph	?	29	8.2	7.7	9.0	117.6	31.0	193.8	197.5	67.0	496.0	79.8	-59.0	322.0	1.87	0.572	4.925
42	Porph	BC	5				46.7	5.9	94.0	23.6	10.2	51.0	-23.0	-80.5	45.1	2.03	0.14	8.6
43	Sedex	sobek	76	6.6	1.1	9.0	176.6	14.7	1309	74.1	-4.0	519.0	-102.5	-1282	497.8	1.49	-0.08	24.49
44	Sedex	BC	3	9.9	9.8	9.9	11.9	4.4	26.8	47.2	37.8	55.3	35.3	21.7	50.9	7.66	1.81	12.57
45	Sedex																	
46	Skarn																	
47	Skarn	?	3	8.8	8.2	9.2	7.8	0.5	18.0	27.3	25.0	29.0	19.5	10.0	24.0	19.12	1.56	50
48	Skarn	BC	10	8.8	8.2	9.7	13.6	1.1	42.2	168.2	15.5	824.3	154.6	7.1	814.0	24.76	1.32	96.92
49	Skarn																	
50	VMS	sobek	1				506.3			29.0			-477.0			0.06		
51	VMS	BC	1	8.5			30.9			95.6			64.6			3.09		
52	VMS	sobek	72	7.5	4.6	8.9	62.8	1.3	307.2	54.2	0.3	254.0	-8.5	-299.3	219.6	5.60	0.01	64.64
53	VMS	BC	2	9.1	8.9	9.3	44.7	40.6	48.8	227.3	128.6	326.1	182.6	79.8	285.4	5.34	2.64	8.04
54	VMS	BC/sob	77	8.6	4.3	10	175.7	0.0	1236	119.5	1.0	566.0	-41.4	-974.5	553.0	41.68	undef	606.3
55	VMS																	
56	VMS	sobek?	4	7.4	6.4	7.9	299.8	1.8	1078	67.9	3.0	256.0	-232.9	-1078	252.0	10.34	0.003	67.72
57	VMS	sob/BC	97	7.8	3.2	9.1	106.1	1.0	587.5	74.0	0.0	916.0	-32.0	-587.5	901.3	2.20	undef	62.1
58	VMS	sobek?	18	8.4	7.0	9.5	183.6	3.0	784.0	107.1	7.0	591.0	-76.4	-766.0	543.0	5.02	0.02	36

total n = 1208

* deposit type: epith - epithermal; mesoth - mesothermal; porph - porphyry;
sedex - sedimentary exhalative; skarn - skarn; VMS - volcanogenic massive sulphide
** method: sobek - Standard ABA; mod - Modified ABA; BC - BC Research Initial Test; ? - unknown

Appendix 1

Mine No	Deposit Type*	Tailings method**	n	Paste pH			AP			NP			Net NP			NP:AP		
				mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
1	Epith	mod?	6	5.6	4.6	6.6	7.3	3.1	13.0	0.5	0.01	1.0	-6.8	-12.3	-3.0	0.06	0.003	0.11
2	Epith	?	2	8.0	7.9	8.0	95.5	64.0	127.0	52.5	37.0	68.0	-43.0	-90.0	4.0	0.68	0.29	1.06
3	Epith																	
4	Epith	sobek	8	7.7	2.9	8.7	8.1	0.1	46.0	52.7	-5.2	102.0	44.4	-25.3	101.0	187	-0.3	720
5	Epith	sobek	2	8.6	8.1	9.1	241.4	175.3	307.5	83.9	59.3	108.4	-157.6	-199.1	-116.0	0.35	0.34	0.35
6	Epith	sobek	1	5.6			185.3			45.0			-140.0			0.24		
7	Epith	?	1	8.1			30.1			34.0			3.9			1.13		
8	Epith																	
9	Epith																	
10	Epith																	
11	Epith	sobek?	8	8.4	6.5	8.7	93.5	29.1	165.0	80.3	61.0	111.5	-13.1	-83.5	31.9	1.04	0.49	2.10
12	Epith	sobek	3	6.7	6.5	6.9	283.5	241.3	340.6	176.3	121.0	281.0	-107.3	-220.0	12.0	0.64	0.36	1.04
13	Mesoth																	
14	Mesoth	sobek	3	6.9	5.9	7.6	260.7	160.0	425.0	38.7	12.0	62.0	-222.0	-383.0	-135.0	0.16	0.08	0.31
15	Mesoth	sob/BC	2	8.8	8.5	9.1	53.6	6.3	119.1	131.3	123.5	140.9	77.5	21.8	117.3	8.20	1.18	19.76
16	Mesoth																	
17	Mesoth	?	2	7.9	7.7	8.0	14.5	8.0	21.0	144.5	132.0	157.0	130.0	111.0	149.0	12.95	6.30	19.60
18	Mesoth																	
19	Mesoth																	
20	Mesoth	sobek	6	7.9	7.8	8.0	173.4	69.1	222.0	260.2	75.0	367.0	86.8	6.0	145.0	1.47	1.09	1.77
21	Mesoth	sobek?	17	7.9	6.8	8.7	324.8	33.0	1090	208.0	83.0	288.0	-38.5	-870.0	240.0	1.81	0.08	8.27
22	Mesoth																	
23	Mesoth																	
24	Mesoth	sobek	5	6.7	5.9	7.4	1.5	0.2	3.6	15.2	3.5	24.7	13.7	3.3	21.1	16.77	5.95	27.00
25	Mesoth	sobek	3	7.9	7.3	8.7	18.1	12.8	27.8	140.6	86.0	299.0	69.7	58.0	76.0	5.48	3.07	6.85
26	Mesoth																	
27	Porph																	
28	Porph	sobek	7	8.8	8.6	9.1	2.2	1.6	3.0	81.4	59.0	96.0	79.0	56.0	94.0	38.86	19.7	60.00
29	Porph	sobek	5	5.6	1.8	7.2	44.1	17.1	118.1	36.4	-23.0	64.0	33.8	18.0	42.0	2.54	1.38	3.46
30	Porph																	

Appendix 1

Mine No	Deposit Type*	Tailings method**	n	Paste pH			AP			NP			Net NP			NP:AP		
				mean	min	max	mean	min	max	mean	min	max	mean	min	max	mean	min	max
31	Porph	sobek	4	7.2	7.0	7.4	2.8	2.6	3.0	17.8	14.0	21.6	14.0	11.0	19.0	5.63	2.99	7.94
32	Porph	sobek	4	6.0	2.6	7.4	349.0	103.1	1313	11.3	-14.0	24.5	-126.8	-179.0	-75.0	0.13	0.06	0.24
35	Porph																	
37	Porph																	
38	Porph	?	1	8.2			0.6			24.6			24.0			41.00		
39	Porph	?	1				40.9			183.8			142.9			4.49		
40	Porph	sobek	3	3.8	3.7	4.0	11.6	4.7	27.2	5.1	0.2	19.7	-8.2	-21.0	-4.5	0.22	0.03	0.72
41	Porph	sobek?	1	8.4			109.0			114.0			5.0			1.05		
42	Porph		1				175.0			18.0			-157.0			0.10		
43	Sedex	sobek	2	7.3	6.1	8.6	634.4	450.0	818.8	24.1	20.2	28.0	-526.2	-656.4	-396.1	0.05	0.04	0.05
44	Sedex																	
45	Sedex	sobek	5	4.0	2.5	5.5	398.7	155.6	1047	23.6	-28.0	64.7	-375.1	-1015	-90.9	0.12	-0.07	0.42
46	Skarn	BC	1	8.7			53.8			54.1			0.3			1.01		
47	Skarn																	
48	Skarn																	
49	Skarn	?	2	7.4	7.3	7.4	44.1	43.8	44.4	109.1	109.0	109.2	65.0	64.6	65.4	2.47	2.45	2.49
50	VMS																	
51	VMS	BC	1	8.3			46.0			144.0			98.1			3.13		
52	VMS																	
53	VMS																	
54	VMS	BC	1	6.7			655.9			336.0			-319.9			0.51		
55	VMS																	
56	VMS	sobek	24	5.1	2.6	7.5	799.1	184.1	1375	19.2	-4.3	56.1	-498.4	-984.0	-128.1	0.07	0.01	0.30
57	VMS	BC	2	8.6	8.5	8.6	151.3	139.7	162.8	108.5	108.0	109.0	-42.8	-31.7	-53.8	0.72	0.77	0.67
58	VMS	sobek?	2	7.0	7.0	7.0	759.4	737.5	781.3	263.2	206.0	320.4	-496.2	-531.5	-460.8	0.34	0.28	0.41

total n = 136

* deposit type: epith - epithermal; mesoth - mesothermal; porph - porphyry;
  sedex - sedimentary exhalative; skarn - skarn; VMS - volcanogenic massive sulphide
** method: sobek - Standard ABA; mod - Modified ABA; BC - BC Research Initial Test; ? - unknown

Appendix 1

APPENDIX 2

Summary Table of Kinetic Test Data in DBARD

Appendix 2: Summary of Kinetic test data in DBARD

Mine No	Sample	YR	Type*	CYCLE	TEST TIME wks	MASS	pH Type**	min	max	Time lag to pH <6.0	<5.0	<4.0	<3.0	SO4 production rate (mg/kg/week) n	mean	min	max
11	1	1989	H	3dry/3moist/1leach	10	200 g	1	7.00	7.20					10	96.8	41.6	164.7
	2	1989	H	3dry/3moist/1leach	10	200 g	1	7.00	8.10					10	103.3	63.4	141.1
	3	1989	H	3dry/3moist/1leach	10	200 g	1	7.00	7.60					10	120.9	47.3	278.1
21	1	1988	H	continuous humid with 2 days/wk leach	10	183 g	1	6.60	8.90					5	62.3	57.4	65.6
	2	1988	H	continuous humid with 2 days/wk leach	10	200 g	1	6.90	8.60					5	285.5	157.5	455.0
	3	1988	H	continuous humid with 2 days/wk leach	10	200 g	1	6.30	8.70					5	107.5	52.5	142.5
	4	1988	H	continuous humid with 2 days/wk leach	10	195 g	1	5.40	8.00					5	326.2	169.2	512.8
23	1	1989	H	3dry/3moist/1leach	373	1 kg	1	5.34	7.85	24				28	59.6	3.0	170.0
	2	1989	H	3dry/3moist/1leach	373	1 kg	1	6.13	7.68					28	69.9	21.0	287.5
	3	1989	H	3dry/3moist/1leach	373	1 kg	1	7.10	8.18					28	58.5	12.0	205.0
	4	1989	H	3dry/3moist/1leach	373	1 kg	1	6.74	7.92					28	51.5	15.0	167.5
	5	1989	H	3dry/3moist/1leach	373	1 kg	2	4.37	7.51	0	12			28	14.0	2.5	85.0
	6	1989	H	3dry/3moist/1leach	373	1 kg	1	6.14	7.81					28	56.4	26.0	135.0
38	1	1990	H	3dry/3moist/1leach	13	1 kg?	1	7.47	8.67					13	9.8	2.5	27.5
	2	1990	H	3dry/3moist/1leach	13	1 kg?	1	7.67	8.38					13	6.4	2.5	15.0
	3	1990	H	3dry/3moist/1leach	10	1 kg	1	7.92	8.97					10	10.2	5.0	22.5
39	1	1990	C	3moist/3dry/1leach	20	50 kg?	1	7.40	8.30					20	6.4	3.5	14.1
	2	1990	C	3moist/3dry/1leach	20	50 kg?	1	7.60	8.40					20	7.6	4.2	16.2
	3	1990	C	3moist/3dry/1leach	20	50 kg?	1	7.60	8.40					20	7.4	3.8	14.8
	4	1990	C	3moist/3dry/1leach	20	50 kg?	1	7.40	8.30					20	9.2	4.4	21.3
	5				63		1	7.40	8.30								
	6				25		1	7.80	8.30								

Appendix 2: Summary of Kinetic test data in DBARD

Mine No	Sample	YR	Type*	CYCLE	TEST TIME wks	MASS	pH Type**	min	max	Time lag to pH <6.0	<5.0	<4.0	<3.0	SO4 production rate (mg/kg/week) n	mean	min	max
43	1	1991	H	3dry/3moist/1leach	35	1 kg	3	2.69	5.03	0	2	4	23	35	211.9	94.0	417.1
	2	1991	H	3dry/3moist/1leach	35	1 kg	2	3.62	7.37	9	13	25		35	209.6	129.3	560.6
	3	1991	H	3dry/3moist/1leach	35	1 kg	3	1.99	3.28			0	10	35	783.2	188.2	4833.0
	4	1991	H	3dry/3moist/1leach	35	1 kg	2	4.38	7.76	22	30			35	159.1	87.8	414.4
	5	1991	H	3dry/3moist/1leach	35	1 kg	2	4.09	7.51	20	28			35	160.2	101.9	274.9
	6	1991	H	3dry/3moist/1leach	35	1 kg	3	2.56	4.52		0	5	24	35	1101.5	488.9	4359.2
52	1	1990	H	cont moist/leach	17	1 kg	3	4.00	5.98	0	8			18	126.6	83.0	235.2
	2	1990	H	cont moist/leach	17	1 kg	1	7.10	7.85					18	36.9	17.8	90.6
	3	1990	H	cont moist/leach	17	1 kg	3	7.02	5.77	5				18	308.7	225.1	546.5
	4	1990	H	cont moist/leach	17	1 kg	1	6.50	7.52					18	177.4	115.4	414.3
	5	1990	H	cont moist/leach	17	1 kg	2	4.57	6.08	2	6			18	141.5	105.4	375.0
	6	1990	H	cont moist/leach	17	1 kg	1	6.56	7.18					18	81.7	47.3	230.7
	7	1990	H	cont moist/leach	25	1 kg	1	6.50	7.20					26	49.8	17.1	114.2
	8	1990	H	cont moist/leach	25	1 kg	1	5.91	6.93					26	27.9	18.8	63.1
	9	1990	C	cont moist/leach	16	31.2 kg	1	6.46	7.02					17	225.8	24.5	579.7
	10	1990	C	cont moist/leach	16	30.1 kg	1	7.30	7.74					17	237.3	46.6	610.1
	11	1990	C	cont moist/leach	14	30.7 kg	1	7.60	7.85					9	47.3	13.9	81.0
	12	1990	C	cont moist/leach	14	31.4 kg	1	5.89	7.19					9	354.3	120.4	602.1
	13	1992	H	cont moist/leach	29	1 kg	3	2.11	3.88			0	9	22	1292.4	204.0	3979.6
	14	1992	H	cont moist/leach	29	1 kg	3	3.44	5.43		2	9		23	258.0	177.3	443.0
	15	1992	H	3.5dry/3.5moist/leach	17	750 g	1	5.47	7.01					17	760.7	500.6	1267.9
	16	1992	H	3.5dry/3.5moist/leach	17	750 g	1	6.08	6.84					17	455.2	232.9	1177.3
	17	1992	H	3.5dry/3.5moist/leach	17	750 g	1	6.03	7.30					18	389.7	152.1	802.9
	18	1992	H	3.5dry/3.5moist/leach	17	750 g	1	5.40	6.99					17	372.8	189.3	665.4
	19	1992	H	3.5dry/3.5moist/leach	17	750 g	2	4.49	6.48					18	86.5	34.9	303.3

Appendix 2: Summary of Kinetic test data in DBARD

Mine No	Sample	YR	Type*	CYCLE	TEST TIME wks	MASS	pH Type**	min	max	Time lag to pH				SO4 production rate (mg/kg/week)			
										<6.0	<5.0	<4.0	<3.0	n	mean	min	max
58	1	1990	H	3dry/3moist/1leach	13	200 g	2	4.90	7.30	7				14	100.9	52.5	162.5
	2	1990	H	3dry/3moist/1leach	13	200 g	1	6.70	7.90					14	223.2	110.2	318.2
	3	1990	H	3dry/3moist/1leach	13	200 g	1	6.50	7.70					14	18.7	6.8	33.0
	4	1990	H	3dry/3moist/1leach	13	200 g	2	4.80	7.40	7	13			14	78.2	15.0	132.5
	5	1990	H	3dry/3moist/1leach	13	200 g	1	7.30	8.50					14	24.8	3.8	41.3
	6	1990	H	3dry/3moist/1leach at 7 deg C	13	200 g	1	6.40	7.60					13	43.3	15.0	98.8
	7	1990	H	3dry/3moist/1leach at -20 deg C	13	200 g	1	6.70	7.60					13	9.8	1.3	56.3

Type: H - humidity cell; C - column

pH type - 1 - pH>5.0; 2 - pH>5.0 to pH<5.0; 3 - pH<5.0

Mine No	Sample	NP depletion rates using Morin et al (1995a) - Carb (mg/kg/week)				Morin et al (1995a) - Silc (mg/kg/week)				Morin et al (1995a) - Ca (mg/kg/week)				Lapakko (1990) (mmoles/kg/week)			
		n	mean	min	max	n	mean	min	max	n	mean	min	max	n	mean	min	max
11	1																
	2																
	3																
21	1	2	95.10	86.78	103.72	2	124.55	112.05	137.05	2	81.51	75.03	87.99	3	2.17	1.87	2.44
	2	2	308.30	247.03	369.58	2	349.71	292.77	406.64	2	281.49	221.57	341.30	3	7.84	5.54	9.47
	3	2	145.79	115.24	176.36	2	181.74	155.48	208.01	2	127.64	95.49	159.78	3	3.35	2.39	3.99
	4	2	512.99	242.71	783.28	2	515.16	252.04	778.27	2	475.63	215.09	736.17	3	10.80	5.37	18.40
23	1	13	44.94	6.40	141.51					12	40.89	22.97	118.84	12	1.02	0.57	2.97
	2	13	40.38	3.43	124.30					12	38.44	21.10	109.48	12	0.96	0.53	2.74
	3	13	37.19	1.56	138.48					12	37.46	12.11	127.32	12	0.94	0.30	3.18
	4	13	44.93	1.56	147.44					12	45.20	7.99	133.57	12	1.13	0.20	3.34
	5	13	23.08	0.06	78.14					12	23.62	0.06	72.03	12	0.85	0.35	3.15
	6	13	52.59	4.70	144.30					12	49.90	24.96	126.08	12	1.07	0.62	1.79
38	1	13	16.76	3.34	38.34	13	18.60	5.60	42.08	13	13.41	1.25	31.21	13	0.13	0.03	0.78
	2	13	11.50	3.75	19.87	13	13.60	6.69	22.76	13	9.25	1.25	16.23	13	0.01	0.03	0.40
	3	10	21.20	14.05	32.52	10	20.32	13.41	31.49	10	16.40	11.23	24.94	10	0.02	0.28	0.62
39	1																
	2																
	3																
	4																
	5																
	6																

Mine No	Sample	NP depletion rates using Morin et al (1995a) - Carb (mg/kg/week)				Morin et al (1995a) - Silc (mg/kg/week)				Morin et al (1995a) - Ca (mg/kg/week)				Lapakko (1990) (mmoles/kg/week)			
		n	mean	min	max	n	mean	min	max	n	mean	min	max	n	mean	min	max
43	1																
	2																
	3																
	4																
	5																
	6																
52	1	11	144.60	61.23	243.42	11	107.99	43.25	176.14	11	105.73	41.72	171.63	11	2.76	1.09	4.48
	2	11	567.52	27.70	110.85	11	51.66	23.91	100.58	11	48.95	23.24	94.43	11	1.28	0.61	2.46
	3	11	350.98	266.70	572.72	11	191.41	135.34	261.63	11	188.78	133.93	260.35	11	4.93	3.49	6.79
	4	11	223.04	122.24	433.52	11	164.37	96.11	310.37	11	160.90	95.69	300.50	11	4.20	2.50	7.84
	5	11	163.51	111.41	352.51	11	75.02	44.16	186.97	11	66.73	43.06	150.89	11	1.74	1.12	3.94
	6	11	105.80	58.07	236.36	11	59.85	34.14	119.61	11	56.18	32.63	106.98	11	1.47	0.85	2.79
	7	14	55.56	30.19	110.12	14	21.30	11.25	35.70	14	15.23	6.02	31.16	14	0.40	0.16	0.81
	8	14	31.58	22.46	50.46	14	18.53	11.40	39.52	14	13.75	9.75	20.63	14	0.36	0.25	0.54
	9	17	234.12	24.31	582.84	17	142.07	13.67	333.54	17	139.50	13.52	313.84	17	3.64	0.35	8.19
	10	14	254.44	49.88	604.52	14	198.23	33.77	445.00	14	194.04	33.34	438.11	8	5.07	0.87	11.40
	11	9	89.49	21.63	234.23	9	80.18	19.41	208.18	9	76.13	18.29	198.69	9	1.99	0.48	5.19
	12	9	356.54	137.04	587.45	9	223.78	94.56	351.97	9	217.86	93.26	344.74	9	5.70	2.44	9.02
	13	22	266.43	151.08	670.01	22	53.36	10.18	318.71	22	39.74	8.49	151.49	22	1.04	0.22	3.95
	14	23	231.06	107.40	350.24	23	61.44	34.61	124.25	23	56.42	34.61	81.70	23	1.47	0.90	2.13
	15	18	714.55	397.91	1191.70	18	538.87	362.32	753.92	18	537.80	362.32	753.92	18	14.00	9.45	19.70
	16	18	409.20	229.99	1002.27	18	309.91	196.39	661.14	18	308.99	196.39	661.14	18	8.06	5.12	17.30
	17	18	398.47	163.86	840.11	18	269.61	133.60	495.97	18	268.70	133.60	495.97	18	7.01	3.49	12.90
	18	18	422.88	211.09	661.91	18	393.68	192.09	641.05	18	392.68	192.09	639.70	18	10.20	5.01	16.70
	19	18	84.84	33.96	325.99	18	37.62	16.50	129.05	18	36.46	16.50	126.34	18	0.95	0.43	3.30

Appendix 2

Mine No	Sample	NP depletion rates using Morin et al (1995a) - Carb (mg/kg/week)				Morin et al (1995a) - Silc (mg/kg/week)				Morin et al (1995a) - Ca (mg/kg/week)				Lapakko (1990) (mmoles/kg/week)			
		n	mean	min	max	n	mean	min	max	n	mean	min	max	n	mean	min	max
58	1	13	105.83	46.16	172.02					13	95.30	34.33	159.16	13	2.38	0.86	3.98
	2	13	247.86	186.19	349.42					13	239.40	175.90	348.95	13	6.58	4.83	9.59
	3	12	27.11	9.02	92.00					12	18.06	3.40	73.76	12	0.50	0.09	2.03
	4	13	73.12	21.97	132.12					13	47.63	13.73	84.26	13	1.19	0.34	2.11
	5	13	45.85	22.16	61.25					11	50.24	25.59	93.62	13	0.96	0.50	1.25
	6	11	53.28	27.65	98.25					13	38.53	19.97	49.93	11	1.26	0.64	2.34
	7	13	21.53	11.75	46.78					13	20.62	11.23	43.69	13	0.52	0.28	1.09

Appendix 2

Mine No	Sample	Bradham + Carrucio (1990) (mg/kg/week)				White et al (1994) (mg/kg/week)				method	paste pH	ABA AP	NP	NNP	NP:AP
		n	mean	min	max	n	mean	min	max						
11	1														
	2														
	3														
21	1	3	86.98	75.14	97.68	3	140.29	120.91	157.28	sobek?	NA	137.0	98.0	-39.0	0.72
	2	3	314.38	221.88	379.38	3	497.00	353.99	595.68	sobek?	NA	441.0	126.0	-315.0	0.29
	3	3	134.17	95.62	160.00	3	214.43	155.83	254.58	sobek?	NA	183.0	166.0	-17.0	0.91
	4	3	433.55	215.38	737.18	3	687.20	344.79	1162.33	sobek?	NA	231.0	142.0	-89.0	0.61
23	1	12	40.95	23.00	119.00	12	66.35	37.29	193.38	sobek?	7.32	106.3	16.0	-90.3	0.15
	2	12	38.49	21.12	109.62	12	61.67	33.83	175.86	sobek?	8.15	174.4	39.4	-135.0	0.23
	3	12	37.51	12.12	127.50	12	59.28	18.92	202.25	sobek?	8.70	25.0	62.1	37.1	2.48
	4	12	45.26	8.00	133.75	12	71.56	12.43	212.98	sobek?	8.47	100.6	54.1	-46.5	0.54
	5	12	31.54	0.06	126.25	12	49.98	0.01	202.97	sobek?	8.62	85.6	25.3	-60.3	0.30
	6	12	43.03	2.00	71.88	12	68.90	38.95	115.54	sobek?	8.44	119.7	56.4	-63.3	0.47
38	1	13	13.43	1.25	31.25	13	22.11	2.72	51.22	mod	8.83	15.0	27.0	12.2	1.82
	2	13	9.26	1.25	16.25	13	15.21	2.88	26.60	mod	8.86	4.0	28.0	23.5	6.70
	3	10	16.42	11.25	25.00	10	27.31	18.52	41.67	mod	8.27	34.3	33.2	-1.1	0.97
39	1											82.8	69.8	-13.0	0.84
	2											85.9	89.9	4.0	1.05
	3											83.4	83.1	-0.3	1.02
	4											31.6	46.6	15.0	1.48
	5														
	6										8.20	95.0	73.5	-19.5	0.79

Appendix 2

Mine No	Sample	Bradham + Carrucio (1990) (mg/kg/week)				White et al (1994) (mg/kg/week)				method	paste pH	ABA AP	NP	NNP	NP:AP
		n	mean	min	max	n	mean	min	max						
43	1									sobek	6.80	60.0	17.0	-43.0	0.28
	2									sobek	7.50	77.0	41.0	-36.0	0.53
	3									sobek	4.10	57.0	4.0	-53.0	0.07
	4									sobek	7.70	121.0	46.0	-75.0	0.38
	5									sobek	6.70	1121.8	40.0	-1081.8	0.04
	6									sobek	5.80	625.0	73.0	-552.0	0.12
52	1	11	110.35	43.55	179.14	11	186.67	75.29	306.44	sobek	7.90	61.9	23.5	-38.4	0.38
	2	11	51.09	24.26	98.56	11	82.71	39.43	159.52	sobek	8.10	11.9	104.0	92.1	8.76
	3	11	197.04	139.79	271.74	11	369.78	256.27	515.24	sobek	7.50	166.3	66.3	-100.0	0.40
	4	11	167.94	99.88	313.65	11	285.22	165.54	539.35	sobek	7.60	99.1	114.0	14.9	1.15
	5	11	69.95	44.94	157.50	11	146.01	96.55	323.35	sobek	7.40	118.4	24.3	-94.1	0.21
	6	11	58.64	34.05	111.60	11	110.48	62.84	224.03	sobek	8.00	77.5	38.4	-39.1	0.50
	7	14	15.90	6.28	32.53	14	40.43	19.17	79.18	sobek	8.40	180.0	36.4	-143.7	0.20
	8	14	14.35	10.17	21.53	14	29.24	20.74	45.07	sobek	7.90	72.8	17.3	-55.5	0.24
	9	17	145.65	14.12	327.67	17	263.35	26.17	614.36	sobek					
	10	14	202.61	34.82	457.48	14	338.41	60.57	775.90	sobek					
	11	9	79.50	19.10	207.49	9	128.72	30.97	336.20	sobek					
	12	9	227.99	97.59	360.76	9	408.67	168.81	642.14	sobek					
	13	22	41.48	8.08	158.12	22	153.60	72.95	449.55	sobek		176.6	10.6	-166.0	0.06
	14	23	58.89	36.12	85.28	23	160.16	106.55	238.08	sobek		70.3	12.3	-58.0	0.18
	15	18	561.32	378.17	786.90	18	941.13	601.26	1383.63	sobek		164.7	74.2	-90.8	0.45
	16	18	322.51	204.98	690.06	18	540.27	333.55	1205.70	sobek		266.9	81.8	-185.2	0.31
	17	18	280.45	139.45	517.67	18	486.53	228.46	939.06	sobek		325.0	233.0	-92.0	0.72
	18	18	409.86	200.49	667.68	18	648.42	318.84	1045.74	sobek		985.3	181.0	-771.0	0.18
	19	18	38.05	17.22	131.87	18	78.08	33.57	283.24	sobek		226.3	14.4	-211.6	0.06

Mine No	Sample	Bradham + Carrucio (1990) (mg/kg/week)				White et al (1994) (mg/kg/week)				method	paste pH	ABA AP	NP	NNP	NP:AP
		n	mean	min	max	n	mean	min	max						
58	1	13	95.43	34.38	159.38	13	152.21	57.86	252.41	sobek?	7.00	784.0	16.0	-768.0	0.02
	2	13	263.70	193.75	384.38	13	413.11	605.22	597.24	sobek?	7.10	997.0	36.0	-961.0	0.04
	3	12	19.90	3.75	81.25	12	34.66	8.16	133.78	sobek?	7.90	15.0	10.0	-5.0	0.67
	4	13	47.69	13.75	84.38	13	83.70	24.46	149.11	sobek?	7.70	441.0	8.0	-433.0	0.02
	5	13	38.69	20.00	50.00	13	62.69	34.46	81.94	sobek?	8.60	32.0	114.0	82.0	3.56
	6	11	50.31	25.62	93.75	11	79.30	40.58	147.37	sobek?	7.00	784.0	16.0	-768.0	0.02
	7	13	20.65	20.65	43.75	13	32.42	17.67	69.12	sobek?	7.00	784.0	16.0	-768.0	0.02

Appendix 2

APPENDIX 3

Analysis of Gibraltar Tailings Samples:

    1. Back titration curves from Lawrence and Wang (in prep)

    2. XRF analysis

    3. XRD analysis

Appendix 3: Back Titration Curves from Lawrence and Wang (in prep)

Sample	Gibraltar Tails-8-2	Gibraltar Tails-8-2	Gibraltar Tails-8-2
Fizz	none	slight	moderate
weight (g)	2	2	2
HCl (vol)	20	40	40
HCl (N)	0.1	0.1	0.5
NaOH (N)	0.1	0.1	0.5

pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne	pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne	pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne
1.7	0.00	1.000	50.0	1.30	0.00	2.000	100.0	0.6	0.00	10.000	500.0
2.0	5.84	0.708	35.4	2.0	23.99	0.801	40.0	2.0	31.97	2.008	100.4
2.5	8.16	0.592	29.6	2.5	27.34	0.633	31.7	2.5	33.13	1.718	85.9
3.0	9.15	0.543	27.1	3.0	28.79	0.561	28.0	3.0	33.64	1.590	79.5
3.5	9.86	0.507	25.4	3.5	29.52	0.524	26.2	3.5	34.06	1.485	74.3
4.0	11.15	0.443	22.1	4.0	30.44	0.478	23.9	4.0	34.51	1.373	68.6
4.5	12.77	0.362	18.1	4.5	32.50	0.375	18.8	4.5	35.91	1.023	51.1
5.0	13.70	0.315	15.8	5.0	33.21	0.340	17.0	5.0	36.41	0.898	44.9
6.0	15.03	0.249	12.4	6.0	34.75	0.263	13.1	6.0	37.01	0.748	37.4
7.0	15.60	0.220	11.0	7.0	35.32	0.234	11.7	7.0	37.09	0.727	36.4

Appendix 3: Back Titration Curves from Lawrence and Wang (in prep)

Sample	Gibraltar Tails-8-10		
Fizz	none		
weight (g)	2		
HCl (vol)	20		
HCl (N)	0.1		
NaOH (N)	0.1		

pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne
2.1	0.00	1.000	50.0
2.0		1.000	50.0
2.5	4.38	0.781	39.1
3.0	5.26	0.737	36.9
3.5	5.86	0.707	35.4
4.0	7.37	0.632	31.6
4.5	9.54	0.523	26.2
5.0	10.19	0.491	24.5
6.0	12.08	0.396	19.8
7.0	12.83	0.359	17.9

Sample	Gibraltar Tails-8-10		
Fizz	slight		
weight (g)	2		
HCl (vol)	40		
HCl (N)	0.1		
NaOH (N)	0.1		

pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne
1.30	0.00	2.000	100.0
2.0	18.84	1.058	52.9
2.5	22.44	0.878	43.9
3.0	23.78	0.811	40.6
3.5	24.51	0.775	38.7
4.0	25.95	0.703	35.1
4.5	29.11	0.545	27.2
5.0	29.54	0.523	26.2
6.0	31.43	0.429	21.4
7.0	32.06	0.397	19.9

Sample	Gibraltar Tails-8-10		
Fizz	moderate		
weight (g)	2		
HCl (vol)	40		
HCl (N)	0.5		
NaOH (N)	0.6		

pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne
0.9	0.00	10.000	500.0
2.0	22.04	3.322	166.1
2.5	23.58	2.855	142.8
3.0	24.93	2.446	122.3
3.5	26.00	2.122	106.1
4.0	26.53	1.961	98.1
4.5	28.55	1.349	67.5
5.0	29.14	1.171	58.5
6.0	29.46	1.074	53.7
7.0	29.79	0.974	48.7

Appendix 3: Back Titration Curves from Lawrence and Wang (in prep)

Sample	Gibraltar Tails-54-2		Gibraltar Tails-54-2		Gibraltar Tails-54-2	
Fizz	slight		moderate		strong	
weight (g)	2		2		2	
HCl (vol)	40		40		80	
HCl (N)	0.1		0.5		0.5	
NaOH (N)	0.1		0.5		0.5	

pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne	pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne	pH	NaOH ml	mg equiv acid per g	kg CaCO3 per tonne
1.3	0.00	2.000	100.0	0.81	0.00	10.000	500.0	0.4	0.00	20.000	1000.0
2.0	19.40	1.030	51.5	2.0	28.10	2.975	148.8	2.0	65.03	3.743	187.1
2.5	20.00	1.000	50.0	2.5	29.15	2.713	135.6	2.5	66.57	3.358	167.9
3.0	21.20	0.940	47.0	3.0	29.73	2.568	128.4	3.0	67.31	3.173	158.6
3.5	21.73	0.914	45.7	3.5	30.05	2.488	124.4	3.5	67.90	3.025	151.3
4.0	22.57	0.872	43.6	4.0	30.42	2.395	119.8	4.0	68.50	2.875	143.8
4.5	24.12	0.794	39.7	4.5	31.78	2.055	102.8	4.5	70.19	2.453	122.6
5.0	25.01	0.750	37.5	5.0	32.26	1.935	96.8	5.0	70.79	2.303	115.1
6.0	28.06	0.597	29.9	6.0	33.08	1.730	86.5	6.0	71.60	2.100	105.0
7.0	28.73	0.564	28.2	7.0	33.33	1.668	83.4	7.0	71.77	2.058	102.9

Appendix 3: Summary of XRF Analysis for Gibraltar Tailings Samples

Sample	SiO2	TiO2	Al2O3	FeO	Fe2O3	MnO	MgO	CaO	Na2O	K2O	P2O5	BaO	Co	Cu	Ni	Zn	LOI	S	CO2
8-2	69.84	0.43	14.190	2.010	2.29	0.058	1.50	2.93	3.23	1.22	0.117	745.00	15	1568	7	335	2.03	0.61	0.55
8-10	68.94	0.46	14.170	2.300	2.38	0.071	1.56	3.11	3.12	1.18	0.087	667.00	<d/l	971	4	239	2.08	0.58	0.32
22-18	61.34	0.48	17.110	2.490	3.63	0.107	2.16	3.26	2.78	1.91	0.128	1038.00	13	2009	8	520	3.62	0.81	52
44-22	67.70	0.44	13.960	2.540	3.09	0.078	1.53	3.76	3.03	0.99	0.102	581.00	22	764	<d/l	233	2.29	1.17	0.5
52-16	67.77	0.50	14.540	2.980	1.94	0.077	1.65	3.40	3.18	1.15	0.104	657.00	10	1412	<d/l	352	2.15	0.6	1
54-2	64.90	0.47	14.190	3.950	2.58	0.125	1.87	3.04	2.25	1.58	0.159	629.00	<d/l	949	<d/l	330	4.18	1.89	1.9
54-6	62.89	0.46	16.460	3.630	2.53	0.105	2.10	2.85	2.68	1.97	0.137	884.00	<d/l	710	3	298	3.69	1.01	0.8
58-14	69.63	0.40	13.740	2.410	2.17	0.080	1.39	3.17	2.99	1.06	0.091	704.00	16	1587	<d/l	388	2.19	0.78	0.82
62-8	68.97	0.47	13.960	2.260	2.54	0.067	1.51	3.52	3.04	1.17	0.098	577.00	17	1267	<d/l	316	2.01	0.66	0.55
1995-t	69.17	0.37	14.100	1.840	2.29	0.047	1.43	2.68	3.39	1.60	0.099	889.00	15	844	8	247	1.96	0.68	0.6
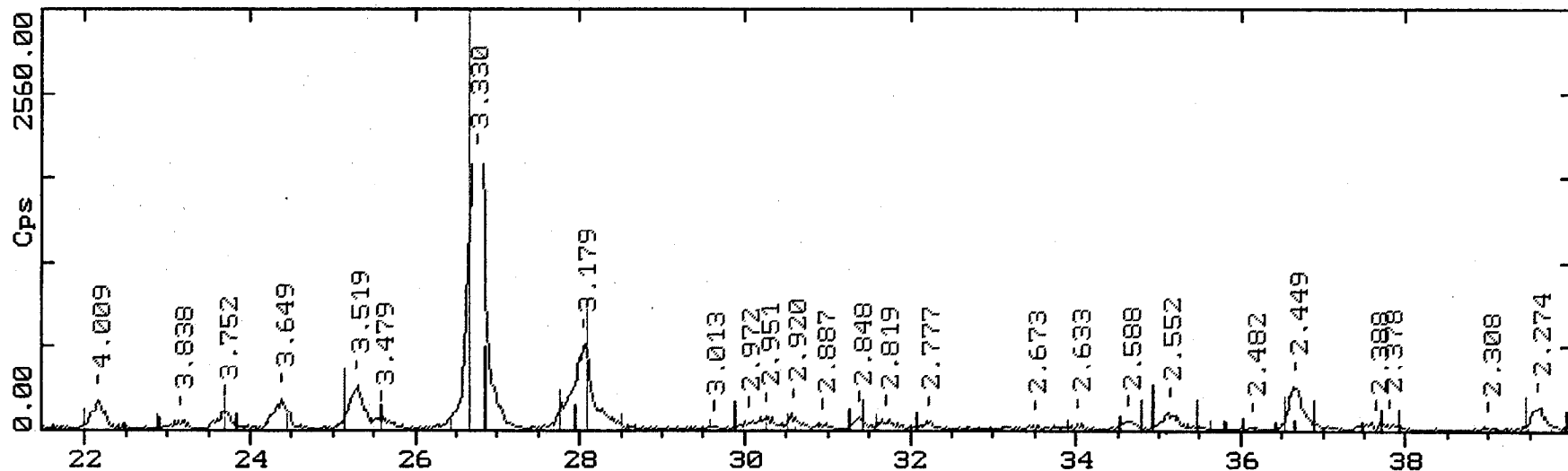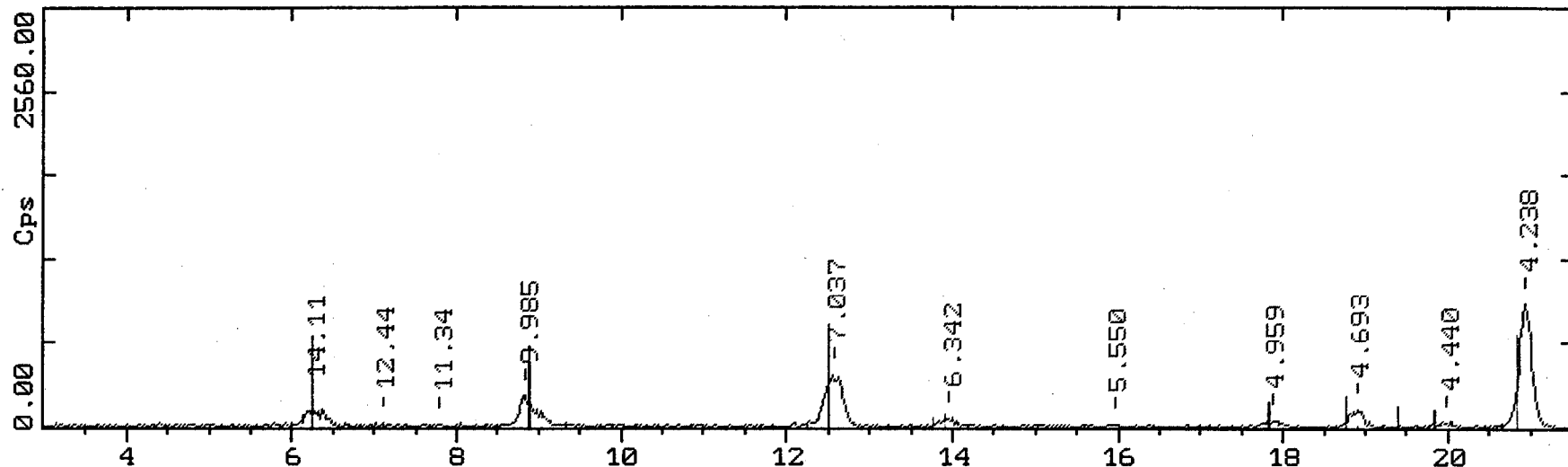
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10-0393 * NaAlSi3O8 Albite ordered (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)
 6-0263 I KAl2(Si3Al)O10(OH,F)2 Muscovite IT M RG (WL: 1.5406Ao)
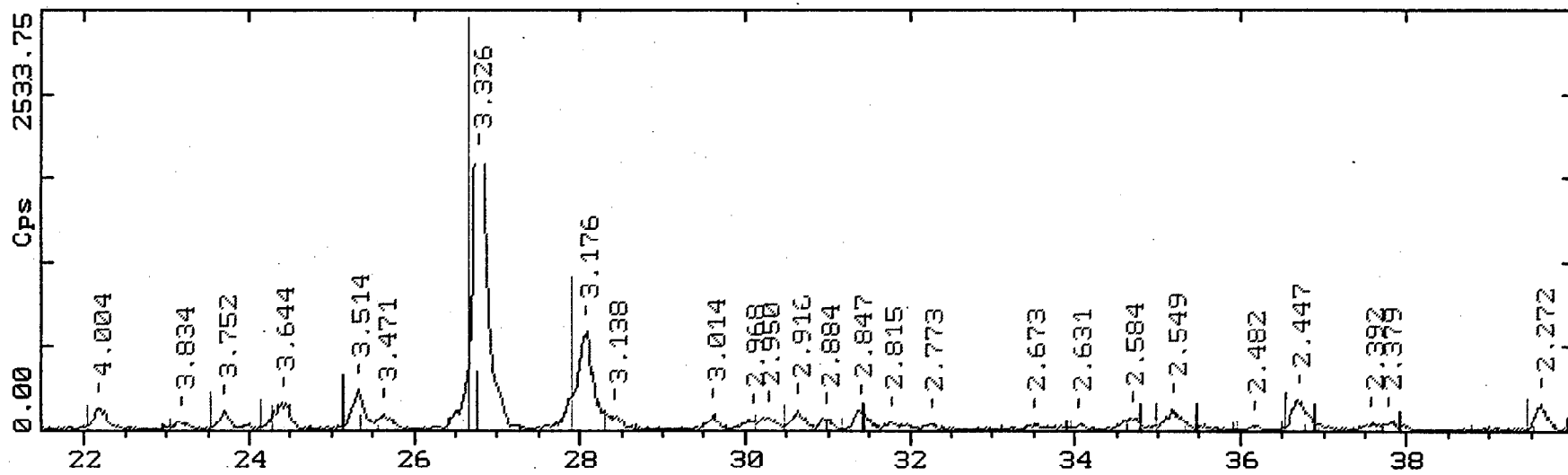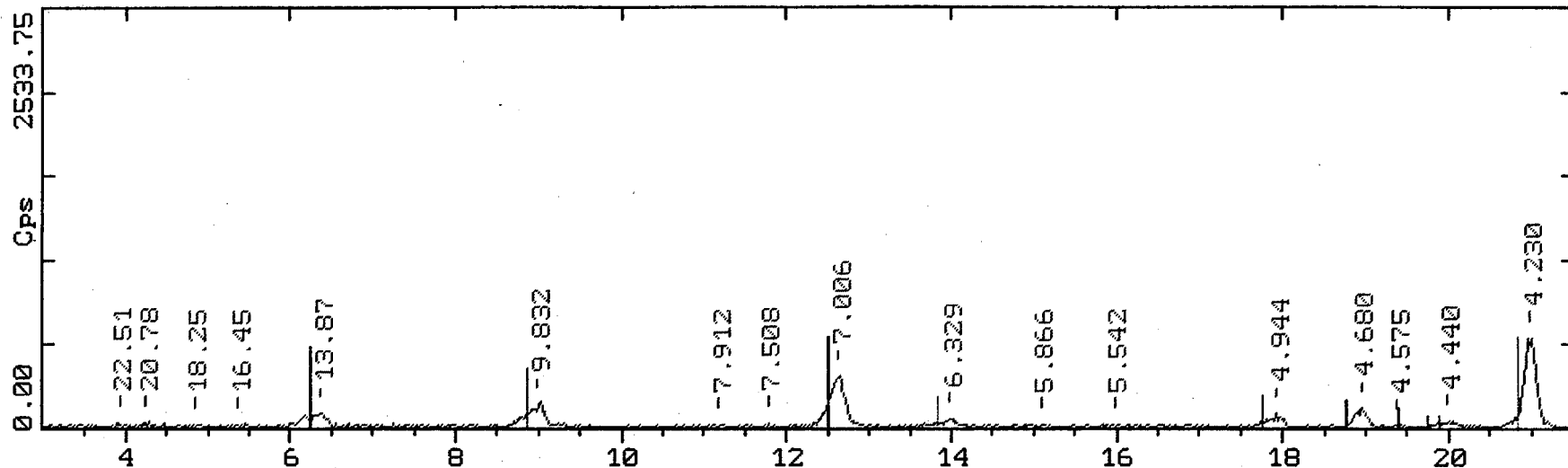
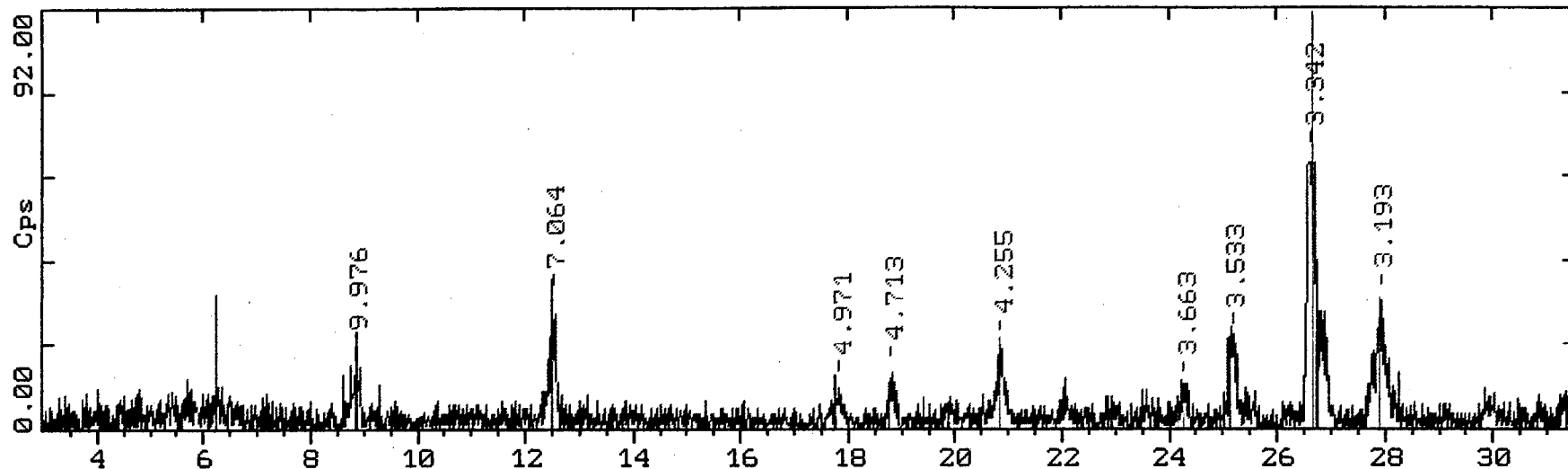C:\D5000\DATA\GS8-10.RAW GS8-10 (CT: 0.8s, SS:0.020dg, WL: 1.5406Ao)
33-1161 * SiO2 Quartz syn (WL: 1.5406Ao)
 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)
 7-0042 I (K,Na)(Al,Mg,Fe)2(Si3.1Al0.9)O10(OH)2 Muscovite IT T RG (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)
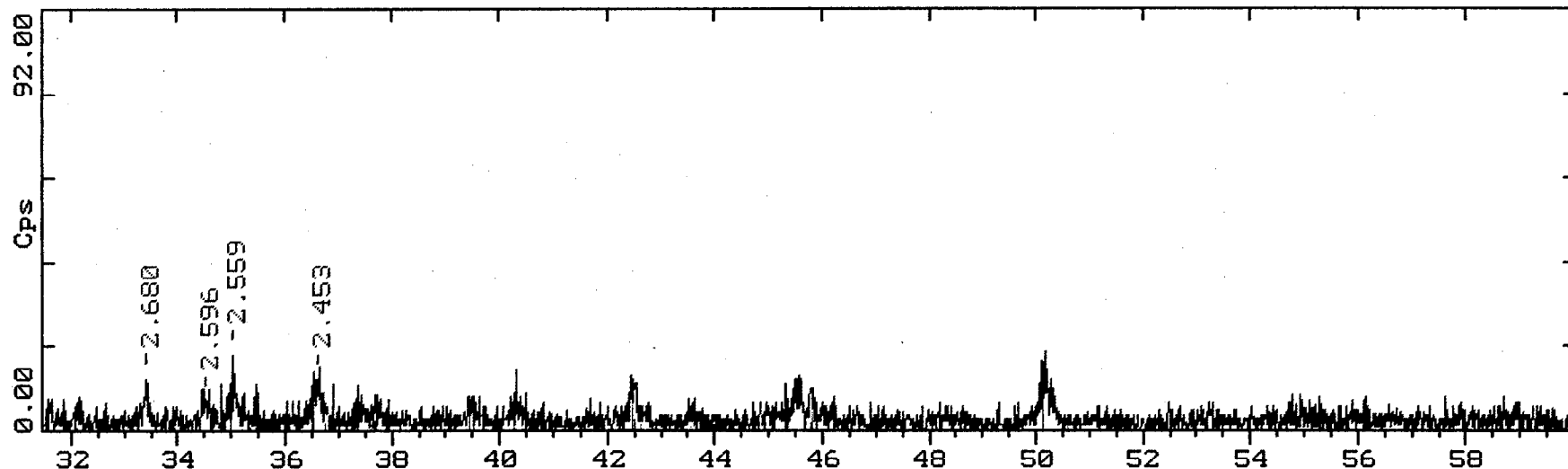
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 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)
 7-0042 I (K,Na)(Al,Mg,Fe)2(Si3.1Al0.9)O10(OH)2 Muscovite IT T RG (WL: 1.5406Ao)
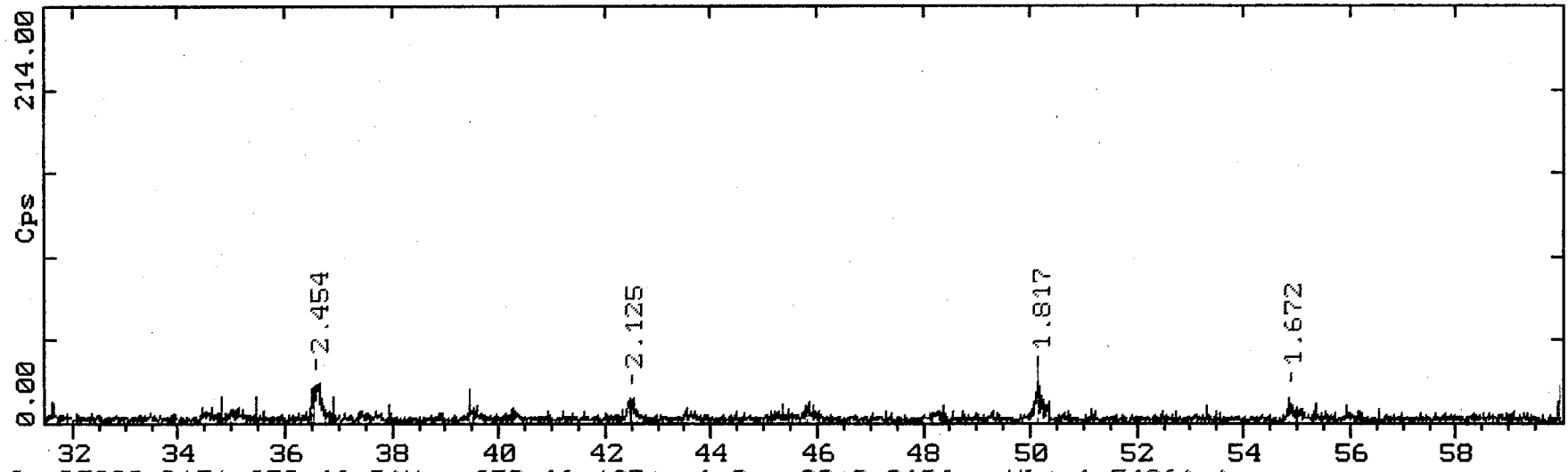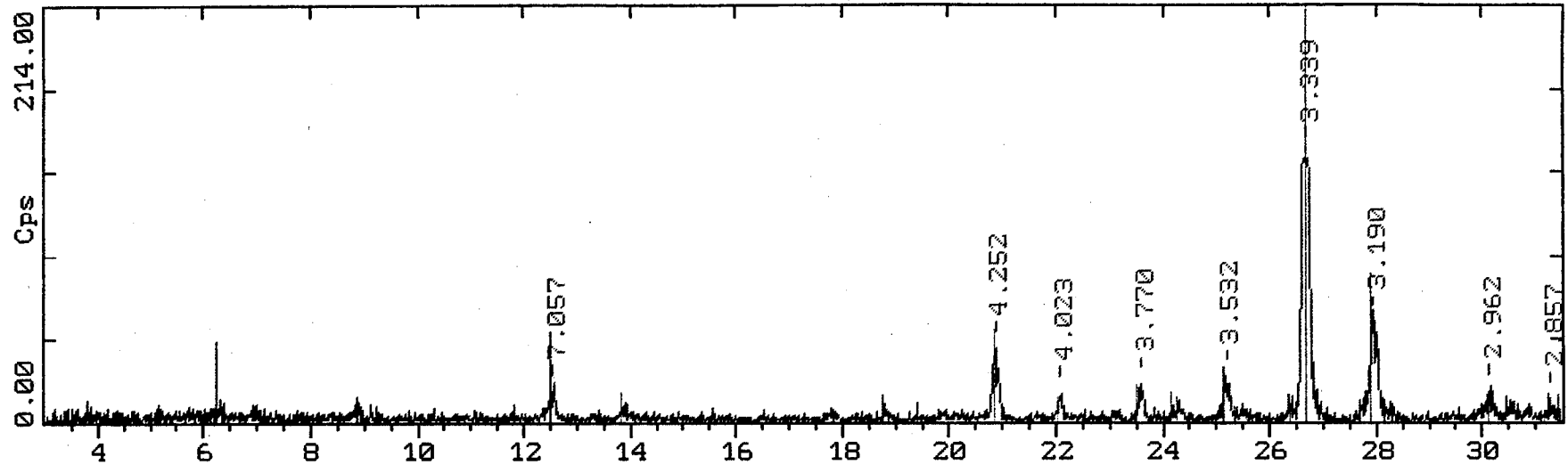
C:\D5000\DATA\G52-16.RAW   G52-16 (CT: 1.0s, SS:0.010dg, WL: 1.5406Ao)
 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)
33-1161 * SiO2 Quartz syn (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)

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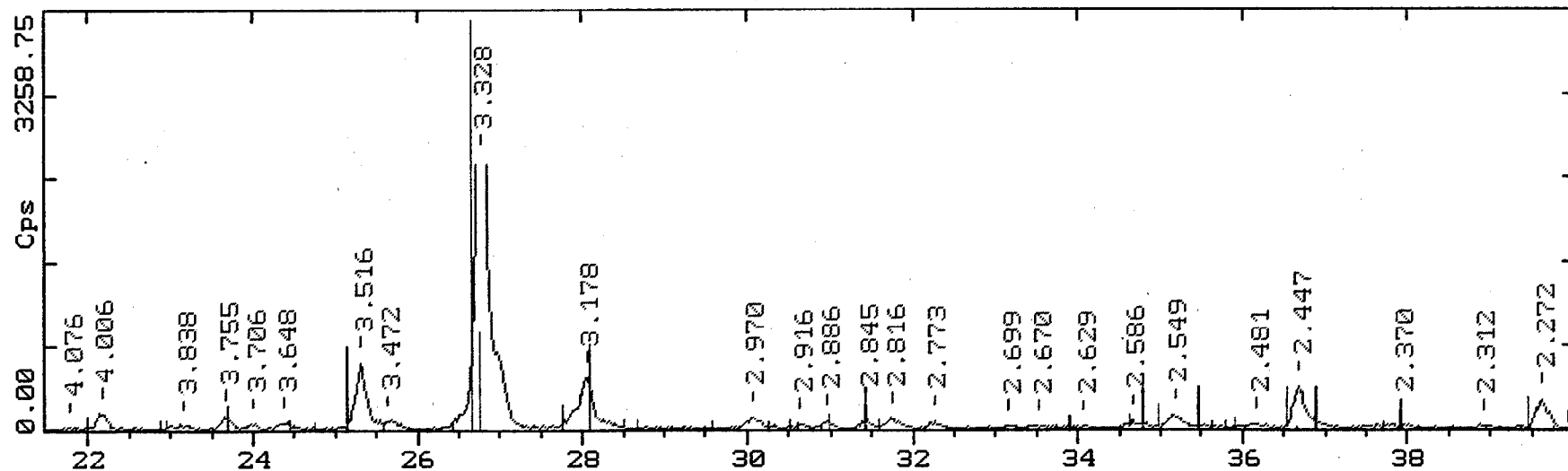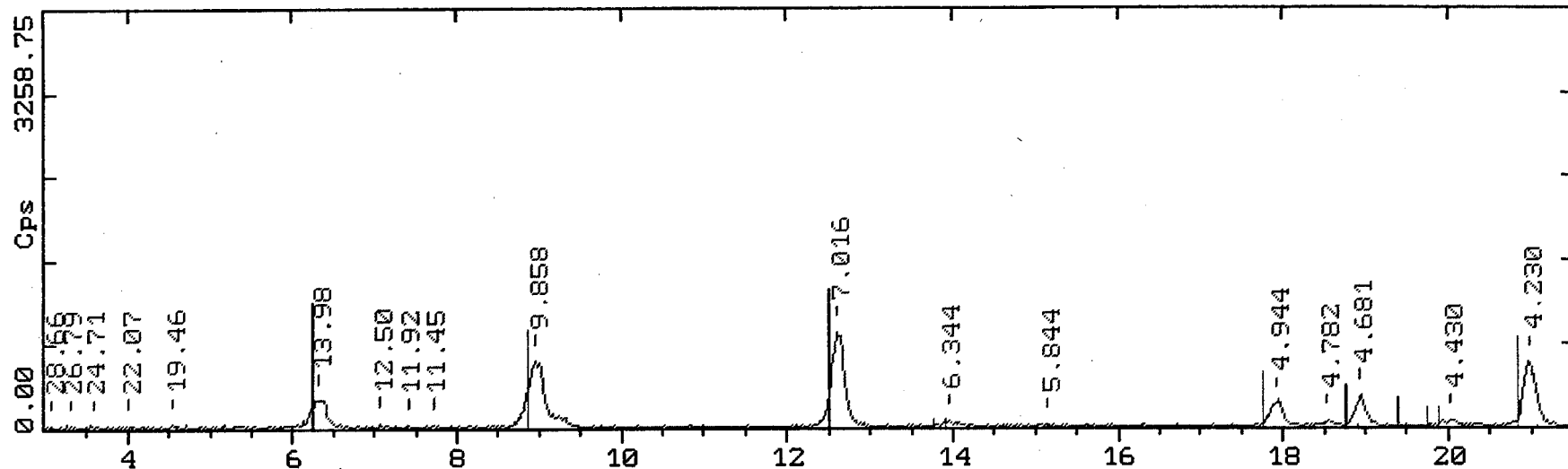
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33-1161 * SiO2 Quartz syn (WL: 1.5406Ao)
 7-0042 I (K,Na)(Al,Mg,Fe)2(Si3.1Al0.9)O10(OH)2 Muscovite IT T RG (WL: 1.5406Ao)
10-0393 * NaAlSi3O8 Albite ordered (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)
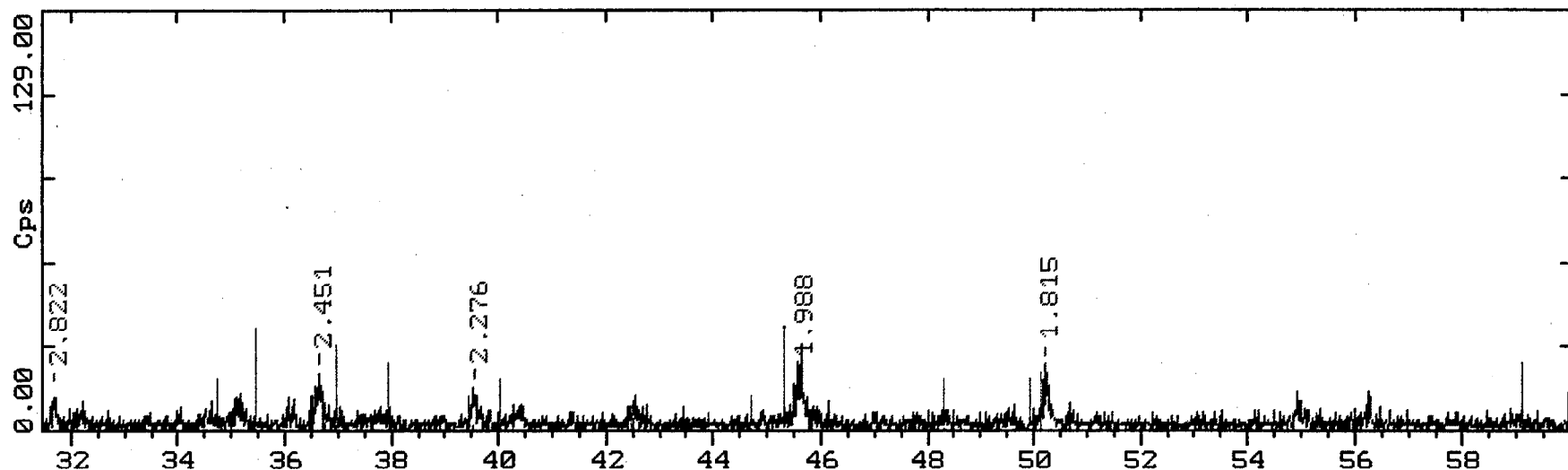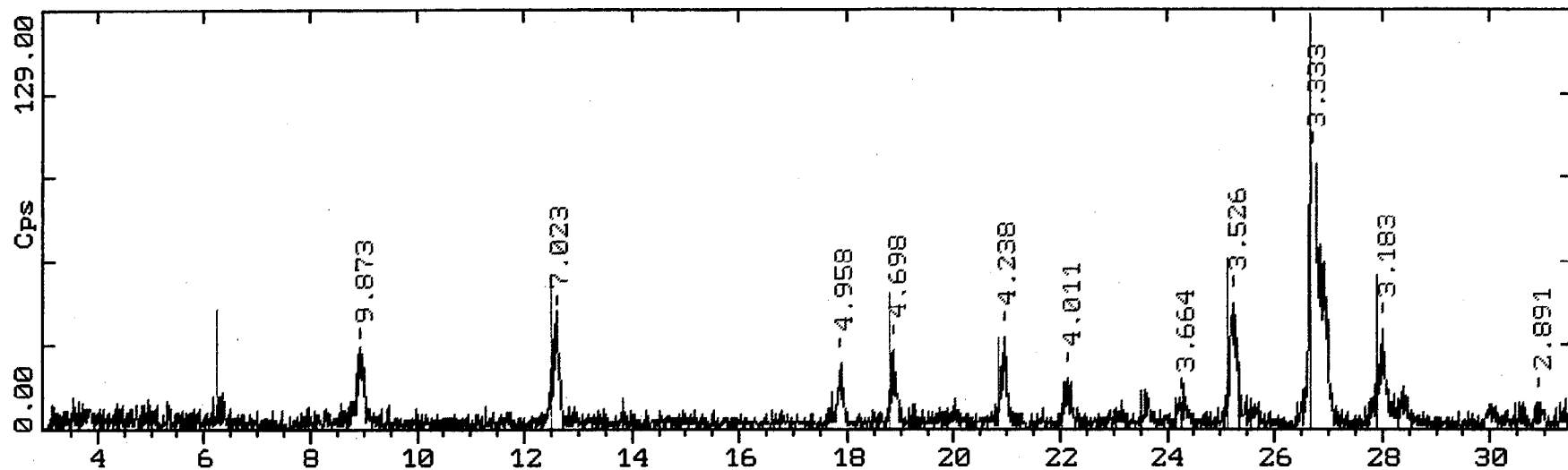
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33-1161 * SiO2 Quartz syn (WL: 1.5406Ao)
12-0242   (Mg,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG (WL: 1.5406Ao)
 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)

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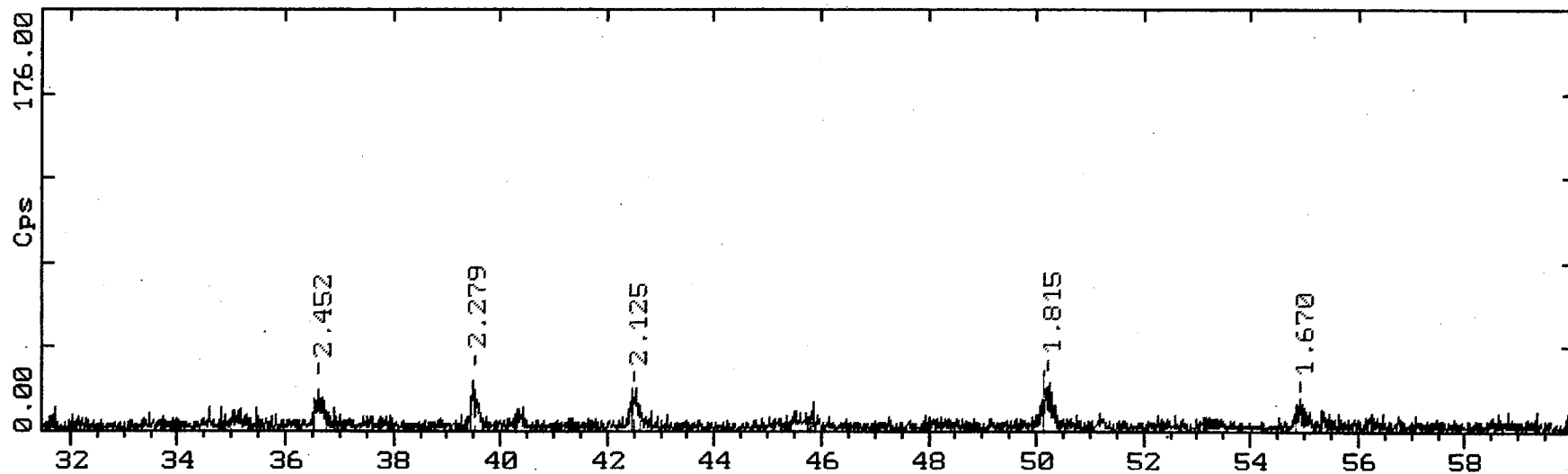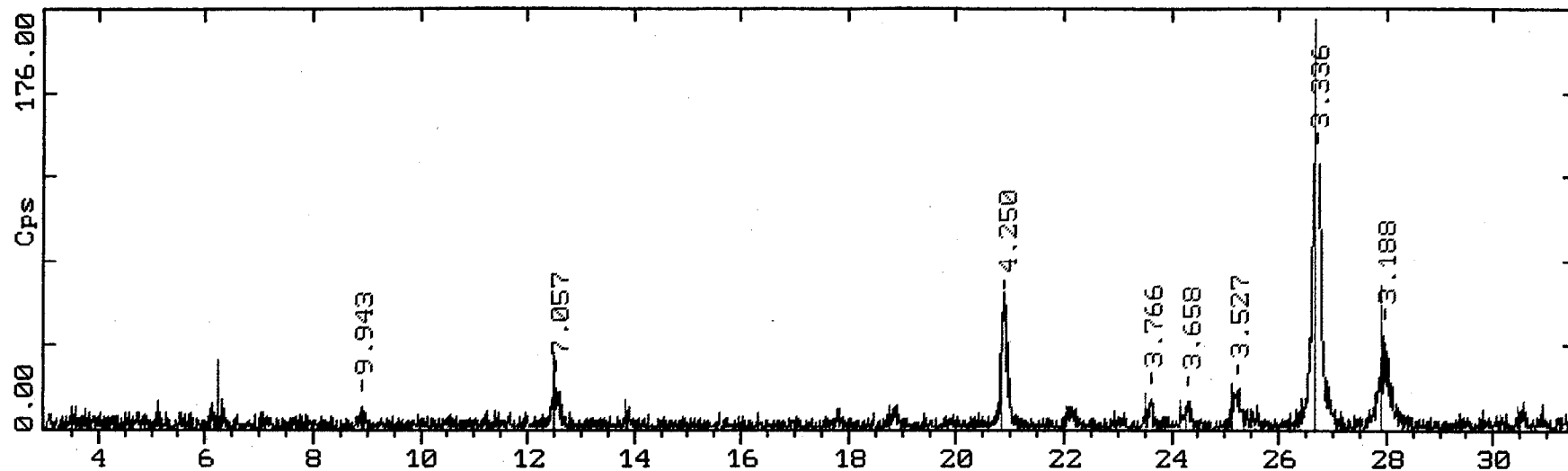
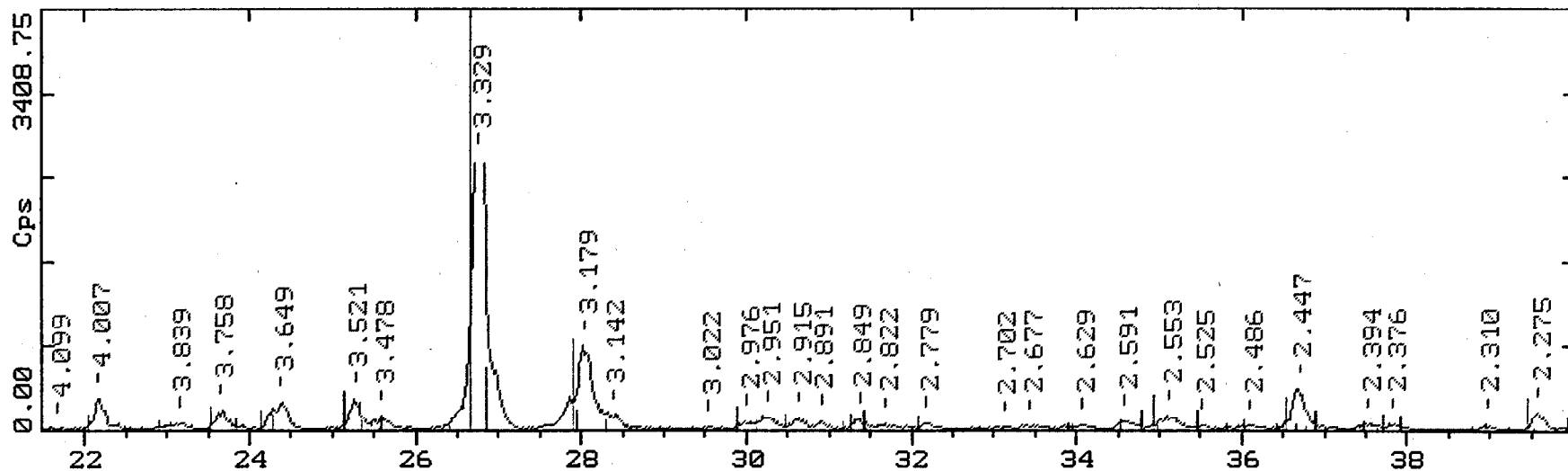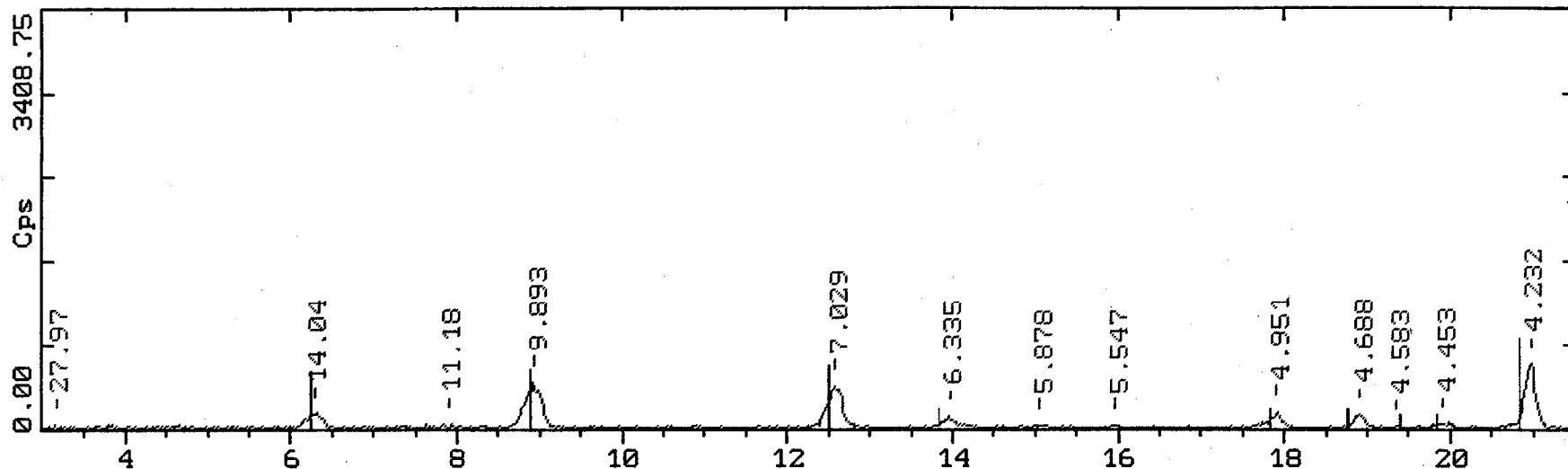C:\D5000\DATA\G58-14.RAW   G58-14 (CT: 1.0s, SS:0.010dg, WL: 1.5406Ao)
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 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)

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33-1161 * SiO2 Quartz syn (WL: 1.5406Ao)
 9-0466 * NaAlSi3O8 Albite low (WL: 1.5406Ao)
 6-0263 I KAl2(Si3Al)O10(OH,F)2 Muscovite IT M RG (WL: 1.5406Ao)
 7-0078   (Mg,Fe,Al)6(Si,Al)4O10(OH)8 Clinochlore IT M I I b RG ferrian (WL: 1.5406Ao)