# ASSESSING THE SUBAQUEOUS STABILITY OF OXIDIZED WASTE ROCK

## MEND Project 2.36.3

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# MEND

## PROJECT 2.36.3

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# ASSESSING THE SUBAQUEOUS STABILITY OF OXIDIZED WASTE ROCK

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*Prepared For:*

**THE MINE ENVIRONMENT NEUTRAL DRAINAGE (MEND) PROGRAM**

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# *EXECUTIVE SUMMARY*

Waste rock is typically stored in a subaerial environment, a setting that may promote the oxidation of sulphide minerals and therefore be conducive to the initiation of acid rock drainage (ARD) and commensurate trace metal release. To mitigate this problem several strategies are currently being employed and tested by the mining industry including the subaqueous disposal of sulphide-rich waste rock. Subaqueous disposal has a number of features that make it attractive as a long-term storage option. However, the secondary mineral assemblages that accumulate during subaerial exposure could have a profound influence on the geochemical behaviour of the waste when submerged, such that deleterious effects on water quality may result. In order to assess adequately the environmental implications of placing oxidized waste rock underwater, techniques must be developed to allow proponents and government agencies to evaluate scientifically, and ultimately predict, the potential water quality impacts of this waste rock management strategy.

The ultimate objective of this project was to design a laboratory test protocol that could be used to quantify the chemical stability of waste rock oxidation products in a range of subaqueous environments. To this objective, the report first examines the mechanisms that control the formation and stability of secondary minerals in waste rock dumps, identifies the minerals that may be present in the dumps and evaluates their subsequent stability in a subaqueous setting. Second, the report examines available laboratory methods and their applicability to assessing metal release from oxidized waste rock.

The extent of oxidation is spatially variable in a subaerial waste rock dump; hence the distribution of weathering products is heterogeneous. The climate and physical characteristics of a waste rock dump indirectly control the extent of these weathering products by regulating the intensity of various physico-chemical conditions such as pH, temperature, dump hydrology and mineral weathering. A general indication of the mineralogical form taken by metal precipitates can be inferred from the site-specific physico-chemical conditions and the elemental constituents of the waste rock. An

indication of which elements will be retained as major or minor components of secondary minerals in oxidized waste rock can be obtained by determining the elements associated with various types of ore deposits and their relative mobilities. However, iron and sulphate secondary minerals are common in all oxidized sulphide-rich waste rock dumps and exert a major control on the mobility of other less abundant elements.

The subaqueous stability of a mineral is controlled by the thermodynamic and kinetic properties of the mineral which are in turn influenced by variable characteristics such as surface area, crystallinity, solution chemistry and temperature. Four general mineral dissolution categories have been examined including: water soluble; pH sensitive; reducible; and oxidizable. Water soluble precipitates found in waste rock dumps are typically hydrated sulphate minerals and many of these minerals produce acidity upon their dissolution. Carbonate minerals and adsorbed cations are extremely pH sensitive and are soluble in acidic solutions. Mature oxyhydroxide and sulphate minerals are typically insoluble in oxic waters but are susceptible to reductive dissolution. Organic matter and sulphide minerals, which are susceptible to oxidation have also been examined, although it is acknowledged that subaqueous storage minimizes sulphide oxidation.

A number of test methods were examined to evaluate the subaqueous stability of oxidized waste rock including: partial extractions; sequential extractions; shake flask; column; and tank tests. Sequential extraction tests are best suited for use as an initial screening tool for the evaluation of metal release from subaqueous waste rock. Shake flask, column and tank tests have been used to determine the subaqueous stability of oxidation products. However, they do not discriminate between the geochemical processes or mineral phases responsible for the release of metals to solution. Partial extraction tests are limited to simulating one environmental condition and thus one standard test cannot be applied to examine a range of receiving environments. In contrast, sequential extraction can be used to evaluate metal release for a range of extreme environmental conditions. The application of sequential extraction methods to assess subaqueous stability of oxidized waste rock is comparable to the use of acid-base accounting (ABA) to assess the acid generating characteristics of subaerially-exposed waste rock. Extractions are more powerful, however, because they provide data on the element-phase associations which are lacking in ABA testing.

A four step sequential extraction scheme is proposed to examine metal partitioning in oxidized waste rock by targeting the following four phases:

- F1: water soluble (*e.g.*, hydrated sulphates);
- F2: exchangeable/adsorbed/bound to carbonates;
- F3: total reducible (*e.g.*, oxyhydroxides); and
- F4: total oxidizable (*e.g.*, sulphides and organic matter).

In order to determine the elemental composition of the sample prior and subsequent to the application of the proposed extraction scheme, two analytical techniques have been considered. These are XRF and acid digestion followed by ICP-MS analysis. The applicability of these techniques should be assessed during the verification and standardization phase for the proposed extraction procedure, with the optimum method being chosen at that stage. Determination of whole rock elemental abundances in the initial and residual fractions is critical for the interpretation of results from the proposed extraction procedure.

It is of utmost importance to note that sequential extractions are "operationally-defined", therefore an extraction procedure that provides an accurate representation of metal partitioning in one type of sample (*i.e.*, soil) may not be effective in another (*i.e.*, waste rock). Thus, prior to utilizing sequential extractions directly for assessing metal release from oxidized waste rock, verification and validation of the proposed procedure is required.

The proposed sequential extraction method can be used as an effective tool to assess metal-phase associations in waste rock when more direct methods (*e.g.*, SEM, XRD, *etc.*) become to expensive and time consuming due to the fine grained/amorphous nature of many secondary minerals. Although the extraction alone cannot predict quantitative water quality impacts due to kinetic controls on mineral dissolution, when combined with kinetic or *in-situ* testing it is an effective tool to assess environmental risk associated with the subaqueous disposal of oxidized waste rock.

# *SOMMAIRE*

Les stériles sont généralement entreposés à l'air libre. Cet environnement subaérien peut favoriser l'oxydation des minéraux sulfurés et ainsi être propice au déclenchement du drainage rocheux acide (DRA) et de l'émission correspondante de métaux présents à l'état de traces. L'industrie minière utilise et évalue présentement plusieurs stratégies, dont l'emplacement subaquatique des stériles riches en sulfures, dans le but de remédier ce problème. L'emplacement subaquatique présente un certain nombre de caractéristiques qui la rende attrayante comme solution d'entreposage à long terme. Cependant, les associations minérales secondaires qui s'accumulent au cours de l'exposition subaérienne pourraient influer considérablement sur le comportement géochimique des déchets immergés, par exemple en entraînant des effets nocifs sur la qualité de l'eau. Afin d'évaluer adéquatement les conséquences environnementales de l'entreposage subaquatique de stériles oxydés, on doit mettre au point des techniques permettant aux proposants et aux organismes gouvernementaux de faire une évaluation scientifique et, ultimement, de prévoir les impacts potentiels de cette stratégie de gestion des stériles sur la qualité de l'eau.

L'objectif ultime de ce projet était de concevoir un protocole d'essai en laboratoire qui pourrait servir à quantifier la stabilité chimique des produits d'oxydation des stériles dans divers environnements subaquatiques. À cette fin, on a d'abord examiné les mécanismes régissant la formation et la stabilité des minéraux secondaires dans les haldes de stériles, on a identifié les minéraux pouvant être présents dans ces haldes et on a évalué leur stabilité subséquente dans un environnement subaquatique. On a ensuite examiné les méthodes de laboratoire disponibles et la possibilité de les appliquer à l'évaluation des émissions de métaux par les stériles oxydés.

Dans une halde de stériles à l'air libre, l'importance de l'oxydation varie en fonction de l'emplacement; la distribution des produits d'altération est donc hétérogène. Le climat et les caractéristiques physiques d'une halde de stériles régissent indirectement la quantité de produits d'altération obtenus, en régulant l'intensité de divers facteurs physico-

chimiques, comme le pH, la température, l'hydrologie de la halde et l'altération des minéraux. L'état physico-chimique spécifique du site et les constituants élémentaires des stériles constituent une indication générale de la forme minéralogique des précipités métalliques. En déterminant les éléments associés à divers types de gisements de minerai et en établissant leur mobilité relative, on peut obtenir une indication des éléments qui seront retenus comme constituants majeurs ou mineurs des minéraux secondaires dans les stériles oxydés. Toutefois, les minéraux secondaires renfermant du fer et du sulfate sont présents couramment dans tous les haldes de stériles oxydés riches en sulfure et exercent un effet important sur la mobilité des autres éléments moins abondants.

La stabilité subaquatique d'un minéral est régie par ses propriétés thermodynamiques et cinétiques qui dépendent elles-mêmes de caractéristiques variables, comme l'aire, la cristallinité, la chimie en solution et la température. On a étudié quatre types généraux de dissolution minérale, soit la solubilité dans l'eau, la sensibilité au pH, la réductibilité et l'oxydabilité. Les précipités hydrosolubles présents dans les haldes de stériles sont normalement des minéraux constitués de sulfate hydraté, dont bon nombre produisent une augmentation de l'acidité lors de leur dissolution. Les minéraux du groupe des carbonates et les cations adsorbés sont extrêmement sensibles au pH et sont solubles en solution acide. Les minéraux matures constitués d'oxyhydroxydes et de sulfates sont généralement insolubles dans les eaux oxygénées, mais sont susceptibles à la dissolution réductive. On a aussi étudié la matière organique et les minéraux sulfurés, qui risquent d'être oxydés, mais l'entreposage subaquatique, on le sait, réduit au minimum les risques d'oxydation des sulfures.

On a examiné un certain nombre de méthodes d'essai pour évaluer la stabilité subaquatique des stériles oxydés; parmi ces méthodes, on compte l'extraction partielle, l'extraction séquentielle, l'agitation en flacon, essai en colonne et en réservoir. L'extraction séquentielle convient surtout comme méthode de sélection initiale pour l'évaluation des espèces métalliques libérées par les stériles subaquatiques. L'agitation en flacon, les essais en colonne et en réservoir ont été utilisés pour déterminer la stabilité subaquatique des produits d'oxydation. Toutefois, ces méthodes ne permettent pas de distinguer les processus géochimiques des phases minérales responsables de la dissolution des métaux. Comme l'extraction partielle ne permet de simuler qu'une condition environnementale, on ne peut pas, avec un essai normalisé, examiner toute une gamme d'environnements récepteurs. Par contraste, l'extraction séquentielle peut servir à évaluer le dégagement d'espèces métalliques pour toute une gamme de conditions environnementales extrêmes. L'utilisation de méthodes d'extraction séquentielle pour évaluer la stabilité subaquatique des stériles oxydés est comparable à la détermination de l'équilibre acide-base pour évaluer les caractéristiques acidogènes des stériles exposés en milieu subaérien. Cependant, les méthodes par extraction sont plus avantageuses, car elles permettent d'obtenir des données sur les associations élément-phase, que ne fournit pas la détermination de l'équilibre acide-base.

On propose une méthode d'extraction à quatre étapes pour étudier le partage des espèces métalliques dans les stériles oxydés, visant les quatre phases suivantes :

- F1 : matières solubles dans l'eau (p. ex., sulfates hydratés);
- F2 : matières échangeables/adsorbées/liées aux carbonates;
- F3 : matières réductibles totales (p. ex., oxyhydroxydes); et
- F4 : matières oxydables totales (p.ex., sulfures et matière organique).

Afin de déterminer la composition élémentaire de l'échantillon avant et après l'application de la méthode d'extraction proposée, on a utilisé deux techniques d'analyse, soit la fluorescence X et la digestion acide suivie d'une analyse par SM en plasma à couplage inductif. On devrait évaluer l'applicabilité de ces techniques au cours de la phase de vérification et de normalisation de la méthode d'extraction proposée, la méthode optimale étant retenue à ce stade. Il est indispensable de déterminer la teneur en éléments de toute la roche dans les fractions initiales et résiduelles, pour interpréter les résultats de la méthode d'extraction utilisée.

Il est de la plus haute importance de noter que les méthodes d'extraction séquentielle sont définies en fonction du besoin. Ainsi, il se peut qu'une méthode d'extraction permettant de représenter fidèlement le partage des espèces métalliques dans un type d'échantillon (p. ex., un échantillon de sol) soit inefficace pour un autre type d'échantillon (p. ex., un échantillon de stérile). Il faut donc vérifier et valider la méthode envisagée avant d'utiliser directement l'extraction séquentielle pour évaluer le dégagement de métaux par des stériles oxydés.

On peut utiliser la méthode d'extraction séquentielle pour évaluer efficacement les associations métal-phase dans un stérile, lorsque les méthodes plus directes (p. ex., microscopie électronique à balayage, fluorescence X, etc.) deviennent trop coûteuses et exigent trop de temps en raison de la nature amorphe/à grains fins de nombreux minéraux secondaires. L'extraction ne peut, à elle seule, prévoir les impacts quantitatifs sur la qualité de l'eau en raison du contrôle cinétique de la dissolution des minéraux; cependant, elle constitue, lorsqu'elle est couplée à des essais cinétiques ou *in situ*, un outil efficace permettant d'évaluer les risques environnementaux associés à l'emplacement subaquatique des stériles oxydés.

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# 1. INTRODUCTION

The control and prevention of acid rock drainage (ARD) and commensurate leaching of metals is often the cornerstone of mine site waste management plans and is fundamental to the success of mine closure when reactive sulphides are exposed during mine development. While ARD prevention is always the preferred concept, in practice, environmental, geological and physical constraints may prohibit the full-scale implementation of such an approach. This can be particularly true for the management of waste rock where ARD control and prevention is largely limited to maximizing the ratio of neutralizing minerals to sulphides. Under those geological conditions where sufficient neutralization potential is not available to offset the effects of sulphide oxidation, other management strategies must be explored.

One option that has received considerable attention is that of storage of waste rock under completely saturated or submerged conditions (*e.g.,* flooded underground or placed in an abandoned, water-filled open pit). Studies performed on tailings deposits over the last 10 years by MEND indicate that the environmental effects of sulphide oxidation are obviated when fresh, reactive sulphides are placed underwater. This would certainly also hold true for fresh waste rock if submerged; however, it is not typically feasible to store potentially acid generating waste rock immediately underwater during active mining. Depending on the overall mine life, waste rock may weather and oxidize for decades before being ultimately placed in a flooded environment. The accumulation of secondary mineral assemblages during the period of subaerial exposure could have a profound influence on the geochemical behaviour of the waste material when submerged such that deleterious effects on water quality may be realized.

It has been previously documented that the submergence of oxidized waste rock in fresh water may cause significant dissolution of secondary sulphate minerals produced as by-products of ARD (Li and St-Arnaud, 1997). However, there are no standard methods available for predicting the potential impact of waste rock secondary-mineral dissolution on water quality in a range of receiving environments. In order to assess adequately the environmental implications or mitigation requirements associated with placing oxidized waste rock under water, techniques must be developed to allow proponents and government agencies to evaluate scientifically, and ultimately predict, the potential water quality impacts of this waste rock management strategy. MEND Project 2.36.3 was conceived to address these important considerations.

## *1.1 Study Objectives and Methodology*

The main objectives of the study were:

1. To establish a predictive framework to determine which secondary minerals may be present in subaerially-exposed bodies of waste rock of various compositions and age.

2. To establish the relative subaqueous stability of the various minerals that may be present in an oxidized waste rock dump.

3. To design an initial set(s) of laboratory tests to quantify the chemical stability of waste rock oxidation products in a range of subaqueous environments; data derived from these tests are to be used subsequently as an initial screening tool for evaluating the suitability of placing oxidized waste rock under a water cover as a mitigative option.

To meet the above objectives, the following tasks have been conducted:

1. A review of the mechanisms that control the formation of expected secondary minerals in waste rock dumps. Understanding such mechanisms is critical as secondary precipitates in oxidized waste rock dumps are often very fine-grained or amorphous and are difficult to identify positively and to quantify using traditional laboratory techniques. An understanding of secondary mineral formation and a general chemical knowledge of the subaerial waste rock environment can provide an indication of the minerals that may be present. To date, very few studies on secondary mineral formation and stability in waste rock dumps have been documented in the primary literature. However, broad similarities exist between the formation of gossan deposits, soils and the development of ARD and metal leaching

(Williams, 1990; Jambor, 1994). Drawing from the literature on gossan and soil formation, as well as previously documented ARD studies, the major secondary minerals that can be expected to be present in waste rock dumps and the conditions required for their continued stability are discussed.

2. The mineralogy of secondary minerals and the effects of physical and chemical processes on their solubility have been reviewed. Secondary minerals commonly observed in oxidized waste rock have been classified based on their relative solubility. This secondary mineral classification (*i.e.,* phase-solubility relationships) will aid in the interpretation of the results from the proposed testwork.

3. Various test procedures (*viz*., shake flask/barrel roll tests, subaqueous column/tank tests and partial and sequential extraction tests) developed to determine the reactivity and leaching characteristics of various solids, including tailings, landfill refuse and contaminated soils have been reviewed. The procedures have been evaluated for their applicability in assessing the subaqueous reactivity of waste rock under a range of environmental conditions (*i.e.,* pH and redox state of the receiving waters).

4. A sequential extraction method to facilitate an initial assessment of the environmental feasibility of submerging oxidized waste rock under a water cover has been recommended. The relative mobilities of contaminants (principally trace metals) derived from submerged waste rock are dependent on the solubilities of the secondary minerals to which they are bound. Therefore, determining the partitioning of metals between various mineral phases is prerequisite to establishing whether trace metals will be stable or mobilized when oxidized waste rock is placed under a water cover. A sequential extraction method can fulfill this requirement. The proposed extraction scheme was formulated by reviewing the primary soil, environmental and geochemical literature to evaluate the effectiveness of partial and sequential extraction methods previously used to extract metals from various solid phases. However, prior to utilizing the proposed extraction procedure directly, exhaustive verification of the methodology is required using waste rock of varying compositions.

## 1.2 Organization of the Report

The discussion in this report is outlined as follows. The physical and chemical conditions within a waste rock dump and the resulting zones of secondary mineral formation and accumulation are presented in Chapter 2. Chapter 3 provides an overview of the most common reaction products expected in an oxidized waste rock dump. This chapter also provides an overview of those elements which are most likely to be retained in the weathered material and the types of ore bodies with which they are most likely to be associated. Notes on their relative mobilities are also presented. Furthermore, the mineralogical forms of various elements and the conditions under which secondary minerals are stable are discussed. An evaluation of the subaqueous stability of common secondary minerals in sulphide-rich waste rock is presented in Chapter 4. Chapter 5 provides a critical review of existing laboratory methods that can be used to assess the subaqueous stability of waste rock. Based on this review, a conceptual sequential extraction scheme is proposed and verification/validation procedures that need to be conducted prior to its application to waste rock samples. Major conclusions of the study are summarized in Chapter 7.

# 2. *WASTE ROCK ENVIRONMENTS*

Brief discussions of the variable environmental conditions in a subaerially exposed waste rock dump and the potential distribution of secondary minerals are presented in this section. The discussion attempts to identify those portions of a dump for which the risk of metal release would be highest should the material be placed underwater. The discussion is not meant to provide an exhaustive description of subaerial weathering, which falls outside the scope of this study.

The primary mineralogy of waste rock and variations in climatic conditions can result in significantly different secondary mineral assemblages in waste dumps. On a smaller scale, it is the physical and chemical conditions within a waste rock dump that control the extent and type of secondary mineralization. Such conditions vary spatially within a single dump, thus the nature and extent of secondary minerals will also vary within a dump. To permit visualization of the distribution of secondary minerals within a typical dump, the zonation and the prevalent geochemical and physical processes associated with it are described below. In addition, various hydrologic controls that influence the subaqueous stability of secondary minerals and contaminant fluxes are discussed in Section 2.3.

## *2.1 Subaerial Waste Rock Dump Zonation*

Dumps are typically highly heterogeneous with respect to their physical and chemical characteristics. The resulting zonation in a dump is likely to be complex, with the relative size of each zone depending on a number of factors including mineralogy, climate, permeability, porosity and the physical structure of the waste rock pile (Ritchie, 1994).

The oxidized zone is the area of a dump with the most exposure to meteoric water and molecular oxygen. This is also the zone where primary mineral oxidation results in the depletion of sulphides and other minerals susceptible to oxidative dissolution. In most dumps, the oxidized zone will also contain the highest secondary mineral content, since this is the zone with the highest rate of sulphide oxidation accompanied by the highest rate of metal release. Iron is typically the most abundant metal released, and its low solubility in oxidizing environments at pH values greater than 3.5 results in secondary iron hydroxide precipitation very close to the reaction site. These iron precipitates often take the form of pseudomorphs after the original sulphide mineral or efflorescence on particle surfaces.

A transition zone, typified by chemical reactions (such as dissolution and precipitation) and a reduced rate of oxidation, is located inside or below the outer oxidized waste rock layer. In highly acidic environments or at sites that experience high rainfall, downward drainage of pore waters through the dump may lead to the removal of the secondary mineral constituents out of the oxidized zone and their re-precipitation in the transition zone. Thus, the secondary mineralogy of this zone will typically include a higher ratio of stable to soluble secondary precipitates than would be observed in the outer oxidized zone.

An anoxic core consisting of primary sulphide and gangue minerals may form in a dump due to limited oxygen supply to the interior and oxygen consumption by organic decomposition. Where present, such a zone will be expected to have the lowest secondary mineral content, as sulphide oxidation will be sparse. The distribution of oxidation products will therefore be limited to those reaction products that are physically transported from the outer regions of the dump.

## *2.2 Subaerial Physico-Chemical Processes*

Climate, primary mineralogy and physical characteristics of the waste rock, principally particle size and dump morphology or structure (*i.e.,* height to base ratio, exposed surface area, *etc*.), dictate the extent of zonation and secondary mineral formation within a dump by regulating, for example, pH and temperature. In addition, mechanical reworking and the release of elements into solution during weathering of non-sulphide minerals also influence the formation of secondary minerals.

### 2.2.1 Primary Sulphide Mineral Oxidation

Oxidation of primary sulphide minerals provides most of the constituents that form secondary minerals in waste dumps. Oxidative dissolution of sulphides typically yields elevated concentrations of solutes (most importantly iron, trace metals and sulphate) in pore waters, which may (depending on local microenvironments) subsequently precipitate as secondary minerals, most commonly as iron sulphates and oxyhydroxides. Thus, the sulphide oxidation rate and the chemical composition of the resulting pore waters are fundamental in determining the nature and extent of the secondary minerals.

A circular relationship exists between sulphide oxidation rates and a number of factors in a waste rock dump including:

- pH;
- oxygen concentration at the reaction site;
- pore water content and chemical composition;
- microbial population; and
- temperature.

Spatial variability amongst these factors results in localized ARD "hotspots", which in turn influence the distribution of reaction products, and ultimately, the distribution of secondary minerals. Temperature, for example, exerts a direct control on chemical reaction rates, which typically double with every 10°C increase. The proton activity similarly is of critical importance: most minerals are more soluble at low pH. Where the pH is low (<4), bacteria play an important role by catalyzing the oxidation of $Fe^{2+}$ to $Fe^{3+}(aq)$, which is a strong oxidizing agent with respect to solid-phase sulphide species (Singer and Stumm, 1970). Blowes *et al.,* (1995) suggest that the formation of secondary minerals restricts access of sulphur oxidizing bacteria to sulphide mineral surfaces and thus reduces the rate of oxidation. Note, however, that the influence of microbial activity on secondary mineral precipitation in waste rock piles is not yet well understood.

### 2.2.2 Primary Mineral Weathering

By far the most important primary minerals, due to their relative abundance, are aluminosilicate minerals (*e.g.,* feldspars). Hydrolysis of these minerals, releases aluminum and other elemental constituents, including trace metals, to solution. Trace elements commonly present in common rock forming minerals are listed in Table 2-1.

The ultimate result of weathering is the formation of products such as amorphous allophane (composed of $SiO_2$, $Al_2O_3$, and $H_2O$), gibbsite and clay minerals such as vermiculite, smectite and kaolinite (Jambor, 1994). The formation of these secondary products is important because they may coat reactive surfaces and decrease the rate of sulphide oxidation and primary mineral weathering by decreasing the amount of reactive surface area. Clay minerals form where weathering is intense and persistent for long periods. Thus, clay mineral formation will be limited in relatively immature waste rock dumps.

The high solubility of carbonate minerals (*e.g.*, calcite and dolomite) under acid conditions will contribute significantly to solution composition where such phases are present. Should the pH rise, a variety of secondary metal carbonate minerals may form (Table 2-1) and these can subsequently release bound-metals should the pH again drop.

**Table 2-1:**
**Elements that may be Leached from Minerals in Waste Rock**

| | Feldspar | Carbonate | Amphibole | Pyroxene |
|---|---|---|---|---|
| Fe | ◆ | ◆ | ◆ | ◆ |
| Cu | ◆ | ◆ | | |
| Pb | ◆ | ◆ | | |
| Zn | | ◆ | ◆ | |
| Sn | ◆ | | | |
| Mo | | ◆ | | |
| Hg | | ◆ | | |
| Ni | | ◆ | ◆ | |
| Co | | ◆ | ◆ | |
| Cr | | ◆ | ◆ | ◆ |
| Mn | | ◆ | | ◆ |
| As | | ◆ | | |
| Sb | | ◆ | | |
| Se | | ◆ | | |
| W | | ◆ | | |
| Cd | | ◆ | | |
| Ba | ◆ | ◆ | | |

### 2.2.3 pH

The pH of the pore solution in a waste rock dump is the single most important parameter controlling the behaviour of ions in solution. The pH is largely controlled by the competition between acid production (primarily from iron sulphide oxidation) and consumption (primarily from dissolution of carbonate and silicate minerals). The resulting pH governs the chemical stability of secondary mineral phases, sorptive properties of hydroxide and clay minerals, metal mobility and the binding properties of humic substances.

Changes in pH affect the thermodynamic stability of many minerals. Carbonate minerals in particular are susceptible to changes in pH. Furthermore, the pH of a system controls the charge distribution on the surface of minerals thus determining the availability of potential adsorption sites for trace metals. The negative surface charge of manganese and iron oxides, for example, increases with increasing pH and at high pH values metal cations are more strongly adsorbed. At lower pH, many of the adsorbed metals may be released into solution. In summary, the combination of increased mineral solubility and reduced cationic adsorption capacity at lower pH is manifest by higher ion activities in solution and greater ion mobility for many metals of environmental concern.

### 2.2.4 Dump Hydrology

Hydrologic environment in a waste rock dump may also contribute to the precipitation and accumulation of secondary minerals. For example, the formation of preferential flow pathways leads to highly leached zones within the dump and transport of weathering products to the lower portions of the waste pile. The formation of perched water tables in the dump may result in zones of secondary mineral accumulation above such saturated zones.

Climatic conditions may produce variable cycles of heating, drying, and cooling. Many secondary minerals, particularly many of the hydrous sulphate minerals (*e.g.*, rozenite), are sensitive to these conditions and may dehydrate or hydrate depending on the relative humidity and temperature. Thus, seasonal secondary mineralogical variability can be expected when highly soluble minerals that form during dry seasons are subsequently dissolved during rainstorms.

Seasonal cycles of infiltration, drainage, evaporation and air oxidation often result in pulsed release of acid rock drainage. This occurs in the following sequence. Meteoric water infiltrates the macropores which become temporarily saturated. Dissolution resulting from water-waste rock interaction (most importantly the dissolution of secondary minerals precipitated during the drying stages) leads to an increase in concentration of solutes in pore waters. Percolation or flow of the ion-bearing pore waters toward the water table and drainage ditches removes solutes including protons (acid). As water is drained out of pore spaces, air is introduced resulting in the evaporation of the remaining pore waters and the precipitation of secondary minerals, most commonly iron sulphate salts (*e.g.*, melanterite, siderotil).

Subsequent to the evaporation stage, the gas phase will dominate in macropores. Molecular oxygen in gaseous form and dissolved oxygen in thin water films around waste rock fragments may result in oxidation of sulphide minerals surrounding the macropores. Oxide coatings (consisting of amorphous secondary minerals) may form around grains of sulphide minerals in contact with macropores. The oxide coatings also form adjacent to neutralizing minerals (*e.g.*, carbonates) where pH conditions are more amenable to $Fe^{3+}$ and $Al^{3+}$ precipitation.

The cyclical nature of dump hydrology contributes to the aging and maturation of alteration products, many of which form as meta-stable or amorphous precipitates. With time, alteration products may dissolve and reprecipitate as a more stable form or mature into a more crystalline phase (discussed in Chapter 3).

## 2.3 Physical Controls on Subaqueous Stability

Various physical processes influence the flux of dissolution products from reactive waste rock and its effect on water quality in the receiving environment. The mode of waste rock deposition will influence the short-term chemical reactivity of solids. Hydrologic conditions at the subaqueous disposal site will influence the secondary mineral stability and subsequent contaminant flux. In particular, flow across (and through) the submerged waste rock in the host water body will affect the long-term subaqueous reactivity.

### 2.3.1 Short Term

The two main modes of subaqueous deposition of waste rock include:

1. placement of waste rock in an existing water body (*e.g.*, flooded open pit, tailings impoundment, lake); and
2. flooding of an existing subaerial pile/dump or flooding of underground workings containing backfill.

During the rehandling and placement of waste rock in an existing water body, the physical disturbance and mechanical breakup of rock can lead to an increase in surface area of oxidized material. This deposition mode will also lead to sediment segregation based on grain size and density. Should the waste rock contain a significant amount of fine material, high levels of suspended solids may result. Due to rapid dissolution kinetics of soluble phases, waste rock sinking through a water column may also result in an initial pulse of metal release to the water body. Less physical disturbance would be expected during the flooding of waste rock or underground workings, which may result in a lower initial release of metals to solution. The principal impact of the mode of deposition on water quality is therefore its effect on the short-term dissolution rates as waste rock is submerged. Laboratory based column experiments have documented an initial release of sulphate and acidity while establishing a water cover (Davé *et al.*, 1997)

### 2.3.2 Long Term

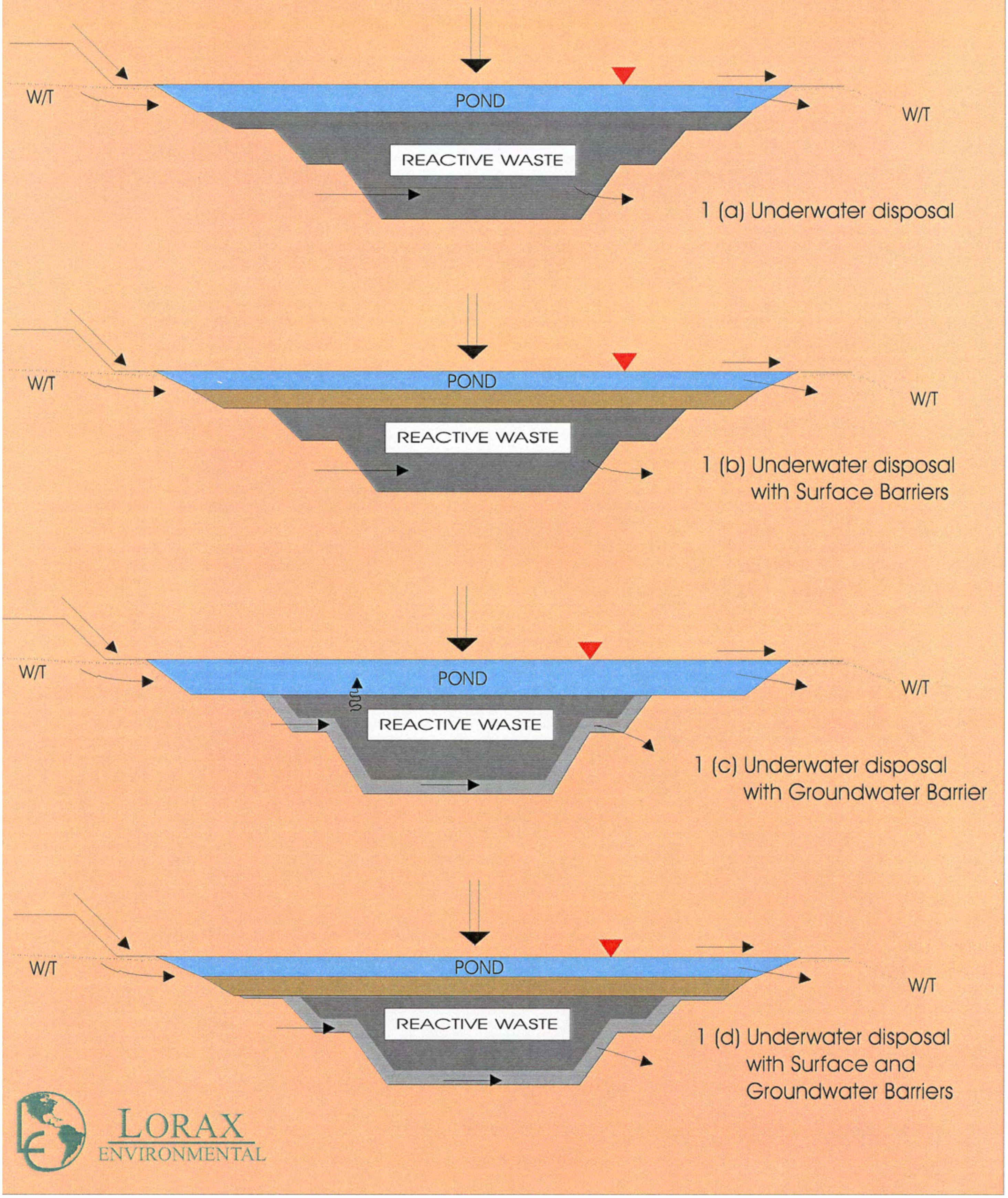
Various in-pit disposal methods have previously been examined (MEND, 1995b), including the subaqueous disposal scenario. Subaqueous disposal may be modified to incorporate barriers that may reduce diffusive or advective fluxes into the overlying water or into groundwater (Figure 2-1). After deposition and submergence, the long-term impact on water quality due to soluble secondary minerals is largely dependent on flow rates in groundwater and in the water cover and secondarily dependent on the rate of addition via diffusion of dissolved solutes from the waste material.

Flow in the water cover (induced by wind action or thermal advection) will influence the rate of chemical reaction at the solid-liquid interface. High flow rates would be expected to enhance exchange between the solid and liquid phases by controlling the rate of dissolution. Molecular diffusion, which is usually much slower than turbulent diffusion, will dominate in small pore spaces and across the diffusive boundary layer or DBL (a zone of laminar flow between a solid and a liquid in which molecular diffusion dominates). The thickness of the DBL is dependent on the shear velocity of flowing water at the solid-liquid interface. The greater the flow, the thinner the DBL, and therefore the greater the effective diffusion rate to and from the solid surface. A positive correlation between water flow and dissolution rates is therefore expected for subaqueous waste rock.

High rates of advective flow through the tailings may increase the transport of dissolution products to the receiving environment. The rate of flow is dependent on waste rock parameters (porosity, permeability, and compaction) and the hydrologic setting of the open pit/underground workings. Grain size controls the reactive surface area of the waste as well as porosity and hence determines the volume of porewater. Permeability of the waste will partially control the advective flux through the waste rock because the hydraulic gradient also affects the advective flux. In certain instances, permeability may be reduced due to mineral precipitation or compaction; in other cases the permeability may increase due to dissolution.

The hydrogeology of the disposal site must be considered. Although the essential issue that will determine the amount of groundwater flow through the waste rock is the permeability of the material compared to the permeability of the surrounding country rock, factors such as the presence of faults, a high degree of fracturing and jointing around the disposal site, or thick deposits of overburden are important. Where present, such features may allow the majority of groundwater to pass around the waste rock which would result in a much slower release of metals to receiving waters. The preferred disposal site, however would have a low hydraulic gradient surrounded by relatively impermeable bedrock. This situation would effectively minimize the flux of contaminants out of the waste into groundwater. Installation of a low-permeability barrier prior to disposal of waste rock may reduce the addition of metals to groundwater where the predicted contaminant flux out of the waste is unacceptable (Figure 2-1).

Figure 2-1 Subaqueous Pit Disposal Concepts



1 (a) Underwater disposal

1 (b) Underwater disposal
with Surface Barriers

1 (c) Underwater disposal
with Groundwater Barrier

1 (d) Underwater disposal
with Surface and
Groundwater Barriers

LORAX
ENVIRONMENTAL

[Modified from MEND, 19953

# 3. WEATHERED WASTE ROCK REACTION PRODUCTS

This chapter provides an overview of the reaction products of sulphide oxidation and includes a summary of the various elemental associations observed in the weathered zone of several types of ore deposits. In addition, the major secondary minerals that may precipitate in a waste rock dump are described. The observations related in this section pertain to the subaerial processes that occur in waste dumps prior to being submerged in a pit or lake. The ability to understand element affiliations and the presence of various mineralogical phases in oxidized waste rock is critical for meaningful interpretation of the extraction results. As detailed in section 5.1.3, a sequential extraction scheme targets particular phases, and the list of associated minerals that may be present can be constrained by such experimental results.

Direct correlations between the primary mineral precursors and secondary mineral products can rarely be made due to the variety of controls on secondary mineral precipitation outlined in Chapter 2. Thus the discussion in this chapter is centered on the elements rather than the minerals typically associated with ore deposits and associated waste rock. A summary is provided of the geochemical behaviour of these elements subsequent to being released via the oxidation of sulphides (Section 3.1) and their subsequent role in the formation of secondary minerals (Section 3.2). This information can be used to predict the secondary mineral assemblages that may occur in waste rock derived from a variety of ore deposits.

## 3.1 Element Affiliations and Relative Mobilities

Iron, copper and zinc are the metals that are retained in the widest range of oxidized ore bodies, while lead is typically retained in a lesser number of weathered ores (Table 3-1). The associations provided in Table 3-1 are those typically reported in geochemical exploration when prospecting for ore bodies. Similar associations would also be expected in oxidized waste rock dumps derived from the listed deposit types (Table 3-1).

## Table 3-1:
## Elemental Affiliation in Different Types of Oxidized Sulphide Deposits

| | Volcanogenic Cu-Pb-Zn | Porphyry Cu (Mo) | Iron Formation | Skarn | Carbonate Replacement (Cu-Zn) | Epithermal (Au-Ag) | Mesothermal (Au-Ag) | Sedex (Pb-Zn) | Au- Bearing Stockworks | Ultramafic (Ni-Cu) | Black Shale Hosted Cu | Barren Pyrite and/or Pyrrhotite | False Gossans | Kimberlite |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Fe | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ |
| Cu | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ |
| Pb | ◆ | | | ◆ | ◆ | ◆ | ◆ | ◆ | | | ◆ | ◆ | | |
| Zn | ◆ | ◆ | | ◆ | ◆ | ◆ | ◆ | ◆ | | | ◆ | ◆ | ◆ | |
| Sn | ◆ | | | ◆ | ◆ | | | | | | | | | |
| Ag | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | ◆ | | | | | |
| Au | ◆ | ◆ | ◆ | ◆ | | ◆ | ◆ | ◆ | ◆ | | | ◆ | | |
| Mo | ◆ | ◆ | | ◆ | | ◆ | ◆ | | | | | | | |
| Hg | ◆ | ◆ | | | ◆ | ◆ | ◆ | | ◆ | | ◆ | | | |
| Ni | | | | | | | | | | ◆ | | | | ◆ |
| Co | ◆ | ◆ | ◆ | | | | | | ◆ | ◆ | | | | ◆ |
| Cr | | | | | | | | | | ◆ | | | | ◆ |
| Mn | | | | ◆ | ◆ | ◆ | | | | | | | | |
| As | ◆ | ◆ | ◆ | ◆ | | ◆ | | ◆ | ◆ | | ◆ | | | |
| Sb | ◆ | ◆ | | ◆ | | ◆ | | ◆ | ◆ | | ◆ | | | |
| Bi | ◆ | ◆ | | | | ◆ | | | | | ◆ | | | |
| Se | ◆ | | | ◆ | | ◆ | | | | | | | | |
| Te | ◆ | ◆ | | | | | | | ◆ | | | | | |
| W | | | | ◆ | | | | | ◆ | | | | | |
| Cd | ◆ | | | ◆ | ◆ | | | ◆ | | | | | | |
| Ba | ◆ | ◆ | | | | | | | | | | | | |

Modified from Nickel and Daniels (1985)

The relative mobilities of elements released as a result of the oxidation of the mineral deposits are listed in Table 3-2 (after Nickel and Daniels, 1985). This information can be used in association with Table 3-1 to provide a rudimentary indication of which elements are likely to form an essential component of major secondary minerals, coprecipitate with major secondary minerals, or leach from the waste rock dumps.

Elements listed as "relatively mobile" in Table 3-2, are those that are most likely to be released from waste rock or form highly soluble minerals that will be unstable in a subaqueous setting. Those elements that are listed as "relatively immobile" will likely form stable secondary minerals that will be retained in a waste rock dump and will remain stable under oxidizing conditions. Similarly, those elements that are listed as being a minor component of stable secondary minerals will likely be retained in the waste rock through adsorption or coprecipitation with the major secondary minerals. It must be noted that the elements listed as "major components of stable secondary minerals" include those that are retained in relatively insoluble primary minerals. For example, barium is concentrated in weathered material because it occurs as the relatively insoluble primary mineral barite.

## *3.2 Secondary Mineral Formation*

The discussion that follows regarding secondary mineral formation in waste rock is focused on elements that are typically released from primary minerals. The ultimate form possible for each of the reaction products is then discussed based on the range of physical and chemical conditions that may be present in a specific waste rock dump or portion of a dump.

Due to the paucity of published information on secondary mineral formation in waste rock piles, it is necessary to draw on mineralogical and geochemical studies conducted in analogous environments. The difference between such analogues and waste rock dumps is outlined in Section 3.2.1.

Iron and sulphur are the most significant products that are common to essentially all waste rock types, due to the relative abundance of iron sulphide minerals in acid

**Table 3-2:**
**Mobility of Elements in Oxidized Sulphide Gossan Deposits**

| | **Relatively Mobile** | **Relatively Immobile** | |
|---|---|---|---|
| | | Major Component of Stable Secondary Minerals | Minor Component of Stable Secondary Minerals |
| Fe | $Fe^{2+}$ | $Fe^{3+}$ | |
| S | ◆ | ◆ | |
| Cu | ◆ | ◆ | ◆ |
| Pb | | ◆ | ◆ |
| Zn | ◆ | | |
| Sn | | | ◆ |
| Ag | ◆ | | |
| Ba | | ◆ | |
| Mo | | ◆ | ◆ |
| Hg | | | ◆ |
| Ni | ◆ | | |
| Co | ◆ | | |
| Cr | | | ◆ |
| Mn | $Mn^{2+}$ | $Mn^{4+}$ | |
| As | | ◆ | ◆ |
| Sb | | ◆ | ◆ |
| Bi | | ◆ | ◆ |
| Se | | | ◆ |
| Te | | | ◆ |
| W | | ◆ | |
| K | ◆ | | |
| Na | ◆ | | |
| Ca | ◆ | | |
| Mg | ◆ | | |
| Si | ◆ | ◆ | |
| Al | | ◆ | |
| Cd | ◆ | | |

After Nickel and Daniels (1985)

generating waste rock. The common reaction products from these two elements are discussed in detail below in Section 3.2.2 and Section 3.2.3. The occurrence of secondary minerals containing elements other than iron and sulphur is not universal and will be primarily determined by the site-specific mineralogy of the waste rock. For example, waste rock from a lode gold deposit and a copper porphyry deposit exposed to the same environmental conditions would contain iron-bearing secondary minerals, but copper-bearing secondary phases such as malachite would only be expected to form in waste rock from the porphyry deposit. The geochemical behaviours of elements that will form secondary minerals with a more restricted occurrence or less environmental impact, including Mg, Ca, Al, Si, Mn, Cu, Pb, Co, Ni, Zn, Cd, Cr, Ti, V, Mo, W, Ba, Ag, Bi, Sb, As, Se, Te and Hg are summarized in Appendix A. A list of all minerals discussed in this document along with their chemical formula is provided in Appendix B.

### 3.2.1 Source and Limitations of the Reviewed Literature

There is limited published information on the development and stability of secondary minerals in waste rock. The most germane sources are recent studies on tailings impoundments or mine drainage, gossan deposits and oxide formation in soils. A number of papers have been published recently on the geochemical evolution of water percolating through and out of tailings impoundments (*e.g.,* Blowes and Jambor, 1990; Jambor, 1994; Ribet *et al*., 1995); an important component of many of these studies was the identification of secondary minerals that precipitated in tailings. A much more extensive body of literature is available for the oxidized mineralogy observed in gossan deposits (*e.g.,* Nickel and Daniels, 1985; Thornber, 1985; Williams, 1990). The formation and behavior of iron oxides and hydroxides in soils has also been investigated (Borggard, 1983; Schwertmann 1985; Taylor, 1987).

It must be recognized that there are certain limitations in drawing from these sources. Although waste rock dumps share many physical and chemical characteristics with soils, gossans and tailings solids, there are critical differences in key factors that influence secondary mineral formation. These include length of formation time, air entry rate, hydrologic conditions and rock type, as summarized in Table 3-3. The differences among the environments have been taken into consideration as much as possible by presenting processes and mineral occurrences in situations that are analogous to those expected in waste rock. Nevertheless, many of the mineral associations have not yet been documented in waste rock dumps constructed in temperate and arctic climates. The results herein present general mineral assemblages that are likely to occur but should continually be verified and updated as additional mineralogical studies are undertaken in waste rock dumps in settings applicable to Canada.

**Table 3-3:**
**Critical Differences Between Waste Rock, Gossans, Soil and Tailings**

| | Waste Rock | Gossan | Soil | Tailings |
|---|---|---|---|---|
| Time of Formation (yrs) | $10^1$-$10^2$ | $10^2$-$10^6$ | $10^2$-$10^5$ | $10^1 – 10^2$ |
| Primary Sulphide Mineralogy | iron sulphide | multi-metal sulphide | high organic<br>low % of sulphide | iron sulphide |
| Particle Size | $D_{50}$ > 20 cm | non-particulate | < 2 mm | < 0.2 mm |
| Air Entry Rate | high | low | low | low |
| Hydrologic Characteristics | unsaturated, high permeability | unsaturated, low permeability | unsaturated/saturated, high-moderate permeability | unsaturated/saturated, moderate permeability |

$D_{50}$ - 50 percentile grain size diameter

### 3.2.2 Secondary Iron Minerals

Secondary iron oxide and oxyhydroxide minerals that precipitate so commonly in waste dumps are significant not only in volume terms, but also because they exert a control on the mobility of other ions through sorption processes. Furthermore, iron is important because the hydrolysis of ferrous iron influences the pH, and this in turn influences secondary mineral precipitation. In reducing environments, iron remains stable in solution as $Fe^{2+}$, but under oxidizing conditions, $Fe^{2+}$ is oxidized to $Fe^{3+}$. At neutral pH, $Fe^{3+}$ quickly hydrolyzes and precipitates as insoluble ferric oxides (typically ferrihydrite) releasing acidity (Section 3.2.2.1). The equilibrium relationship between the predominant aqueous ferric iron species and the solid hydroxide phase is graphically presented in Figure 3-1. As illustrated, the solubility of iron is strongly pH dependent. At low pH values, aqueous forms of ferric iron are stable in solution allowing iron to be transported away from the reaction site. Furthermore, because $Fe^{3+}$(aq) is a strong oxidant, its presence abiogenically accelerates the dissolution of solid-phase iron sulphides.

Iron has a solubility minimum, under oxidizing conditions, at a pH of 8.5 to 9.0. As a result, significant accumulations of solid phase iron hydroxide can be expected immediately adjacent to a reaction site if the pH of a solution is buffered by the dissolution of other minerals such as carbonates. Iron hydroxides may then undergo, upon aging, subsequent dehydration and re-crystallization. Alternatively, if a solution contains high concentrations of other ligands ($SO_4^{2}$ , $CO_3^{2}$ , $PO_4^{3}$ , $AsO_4^{3}$ ), iron may react with these ions, rather than hydroxide, and precipitate as iron sulphates, carbonates, phosphates or arsenates.

The biochemical model (Bigham, 1994) discussed in the following sections was developed from field observations and physical data of precipitates formed in sulphate-rich mine drainage (Table 3-2). This model illustrates that a variety of secondary iron minerals may precipitate depending on solution pH and ion activity. However, all the minerals are metastable with respect to goethite (Figure 3-2). It should be noted that other less stable minerals also form in the waste rock dumps (*i.e.*, soluble iron sulphates such as rozenite and melanterite, which are discussed in Section 3.2.2.7). However, these less stable minerals, under most conditions, will ultimately dissolve and re-precipitate to form ferrihydrite, goethite, lepidocrocite, schwertmannite, or jarosite.

#### *3.2.2.1 Ferrihydrite*

In oxic conditions, the reaction path followed by $Fe^{2+}$ after being released from sulphide minerals is that of rapid oxidation to $Fe^{3+}$ and hydrolysis according to the following equations:

$$Fe^{2+} \leftrightarrow Fe^{3+} + e^{-}$$

$$Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_{3\,(S)} + 3H^{+}$$

Ferrihydrite ($5Fe_2O_3.9H_2O$), a poorly ordered $Fe^{3+}$ mineral that has been referred to as “amorphous ferric hydroxide” in the early literature, is often expressed by the nominal formula $Fe(OH)_3$. It has a red color intermediate between that of goethite and hematite. Ferrihydrite forms most readily when the $Fe^{2+}$ is oxidized quickly, in slightly acidic to neutral water ($pH<8.5$).

Although ferrihydrite is metastable with respect to goethite and hematite, it may persist at disequilibrium for significant periods of time particularly when physico-chemical conditions inhibit crystal growth. High concentrations of $Al^{3+}$ decrease the rate of

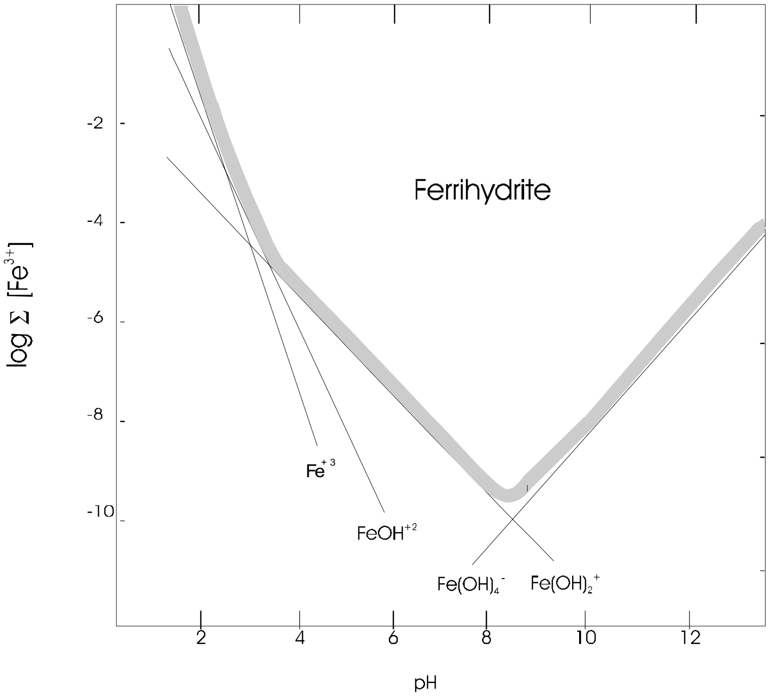


**Figure 3-1: Solubility of Ferric Iron (Stumm & Morgan, 1981)**

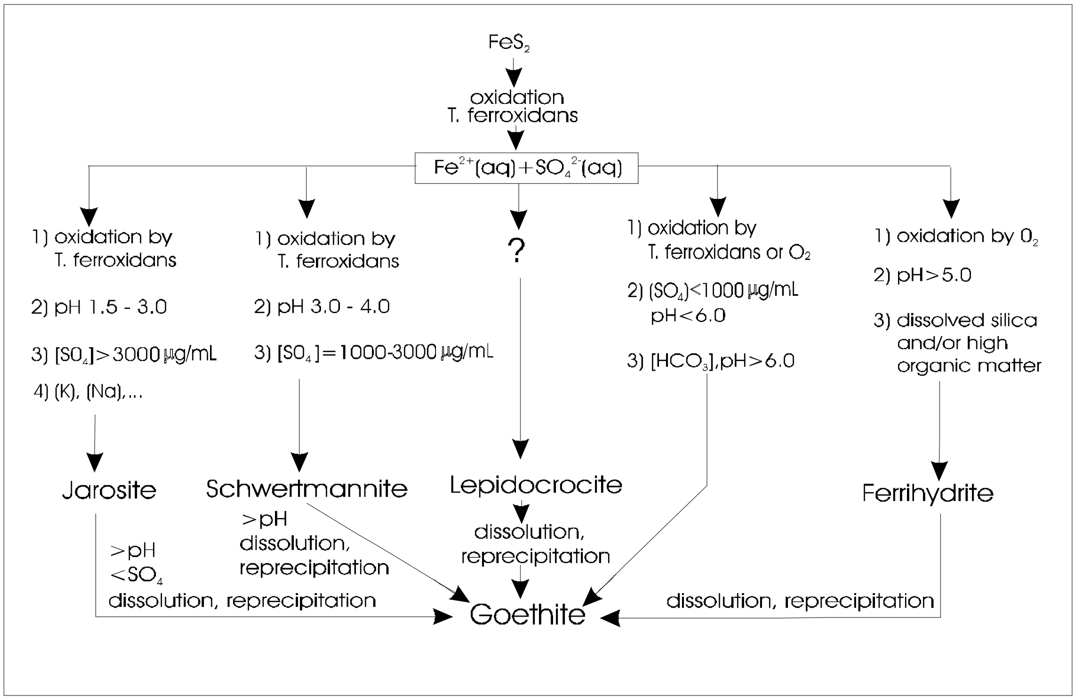


**Figure3-2: Biochemical Model for mineral Precipitation in**

**Mine Drainage Ochres (Bigham, 1994)**

ferrihydrite conversion to goethite and instead favour the crystallization of hematite (Williams, 1990). Transformation to goethite can be temporarily delayed when silica or organic matter is present as a coating on the surface of the ferrihydrite structure. It has also been determined that the presence of phosphate and manganese oxides stabilizes the ferrihydrite structure (Schwertmann & Fitzpatrick, 1992). Similarly, high concentrations of $Co^{2+}$, $Ni^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ stabilize the ferrihydrite structure relative to goethite and reduce the rate of crystallization at pH 12 (Giovanoli and Cornell, 1992).

The transformation of ferrihydrite to goethite proceeds via a dissolution recrystallization process during which elements other than iron may be incorporated into the goethite structure. Laboratory studies also indicate the rate of ferrihydrite conversion to crystalline iron hydroxides/oxides (goethite and hematite) decreases with decreasing pH. Transformation of ferrihydrite to a crystalline phase is favored between $pH < 6$ and $pH > 9$. Schwertmann & Murad (1983) demonstrated that after 441 days at 24°C, 62% to 85% of the initial ferrihydrite converted to crystalline phases at $pH < 6$. At $pH > 7$, more than 96% of the ferrihydrite crystallized to form one of the more stable phases. These results indicate that under optimal conditions, ferrihydrite, once formed, will be converted to a crystalline phase within one year. However, the optimal rate of the transformation may be reduced by the rate inhibiting processes related in the previous paragraph, which likely explains the widespread coexistence of ferrihydrite goethite in oxidizing environments.

#### *3.2.2.2 Goethite*

Goethite ($\alpha$ -FeOOH), a yellowish brown mineral, is the most common mineral found in gossans (Nickel and Daniels, 1985) and is also one of the most abundant oxy-hydroxide alteration products in waste rock piles. The abundance of goethite reflects the dominance of iron-bearing sulphide minerals in waste rock. In addition, its stability over a wide pH range under oxidizing conditions allows it to persist when other minerals become unstable. Figure 3-3 illustrates thermodynamic stability range of the mineral. Other common secondary iron minerals are transient to goethite, which reinforces widespread distribution in oxidizing environments (Section 3.3).

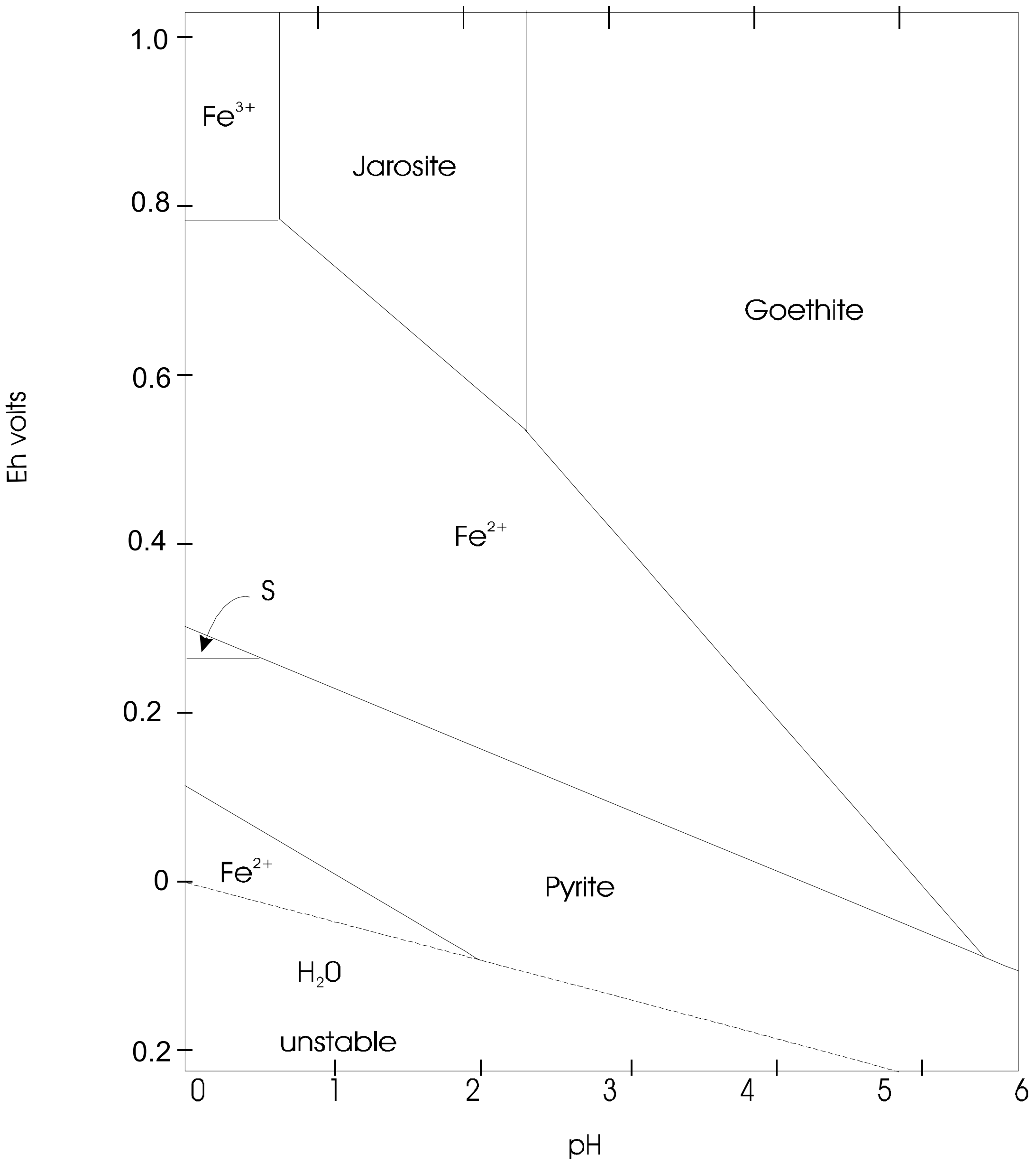


**Figure 3-3: Iron-Sulphur Eh-pH Diagram (Nickel & Daniels, 1985)**
**T 25°C, Fe $10^{-4}$, K $10^{-3}$, S $10^{-2}$**

Goethite can be formed by two mechanisms: 1) direct precipitation from solution; and 2) transformation of poorly ordered ferrihydrite. Direct precipitation proceeds via a nucleation crystal growth process, which is favored under conditions of slow oxidation, low temperatures, pH values >6 and high carbonate ion activity (Figure 3-2). During this process, primary iron minerals may supply nucleation sites that encourage crystal growth from solution. Under these conditions, goethite is often seen forming pseudomorphs after the original pyrite grain. Goethite formation through the transformation of the ferrihydrite structure takes place by a dissolution-reprecipitation mechanism as discussed in Section 3.2.2.1.

### *3.2.2.3 Lepidocrocite*

Lepidocrocite (γ-FeOOH) is a polymorph of goethite that is commonly recognizable by its bright orange color. This mineral is commonly found in weathered soils, gossan deposits and tailings waste but the exact set of field conditions that favor its formation over other minerals is not clear. However, when synthesizing this mineral the solution is required to be buffered in the 5 to 7.5 pH range. Its formation is also believed to be favored in solutions with low concentrations of $Al^{3+}$, $SO_4^{2}$ and $HCO_3$ .

### *3.2.2.4 Schwertmannite*

Schwertmannite ($Fe_8O_8(OH)_6SO_4$) is a recently identified mineral associated with precipitates from acid drainage waters with a bright yellow color. It is very poorly crystallized and its exact chemical formula is unclear due to the fact that a significant fraction of the sulphate associated with the mineral is specifically adsorbed to the mineral surface. This surface-sorbed sulphate cannot be discounted because it stabilizes the high surface-area mineral particles. This is particularly abundant in mine drainage with pH values of 3 to 4.5 and sulphate concentrations between 1000 to 3000 mg/L. Schwertmannite coprecipitates with jarosite between pH 2 to 3 and with ferrihydrite between pH 4.5 to 6. However, it is metastable with respect to goethite (Bigham *et al.,* 1996) via the hydrolysis reaction:

$$Fe_8O_8(OH)_{5.5}(SO_4)_{1.25(S)} + 2.5\ H_2O \rightarrow 8\ FeOOH_{(S)} + 2.5\ H^+ + 1.25\ SO_4^{2-}.$$

The hydroloysis of schwertmannite occurs gradually. Laboratory studies indicate the transformation to goethite in distilled water is initiated within 65 days and total transformation is complete within 543 days (Bigham *et al.*, 1996).

### *3.2.2.5 Jarosite*

Jarosite ($KFe_3(OH)_6(SO_4)_2$) is a well-crystallized mineral that is the most commonly referred to end-member of a family of basic iron sulphates formed by the replacement of $K^+$ with other cations. Other end-member forms of the jarosite group include: natrojarosite ($NaFe_3(OH)_6(SO_4)_2$); hydroniumjarosite ($H_3OFe_3(OH)_6(SO_4)_2$); ammoniumjarosite ($NH_4Fe_3(OH)_6(SO_4)_2$); argentojarosite ($AgFe_3(OH)_6(SO_4)_2$); and plumbojarosite ($PbFe_{0.5}(OH)_6(SO_4)_2$. Intermediate forms in the solid solution series are likely more stable; it has been shown that 10 to 20 mole percent $H_3O^+$ is commonly incorporated into the cation site in the jarosite group (Alpers *et al.*, 1994). Therefore, it must be recognized that assuming an end-member composition may lead to erroneous saturation index calculations due to the prevalence of solid solution in naturally occurring jarosite group minerals.

In gossan deposits, sulphur is commonly retained in alunite-jarosite group minerals. When looking at the thermodynamic stability of iron minerals in a $Fe_2O_3$-$H_2O$-$SO_3$ system, it is apparent that jarosite is stable over a wide range of solution composition. However, chemical speciation modelling conducted on mine drainage waters often indicates supersaturation with respect to alunite and jarosite. The models indicate that other minerals such as ferrihydrite, ferric hydroxides, gibbsite, less crystalline oxyhydroxysulphates (possibly schwertmannite) and gypsum often control aqueous iron, aluminum and sulphate concentrations, suggesting the presence of a kinetic barrier to jarosite precipitation (Stromberg and Banwart, 1994; Karathanasis and Thompson, 1995). Poorly crystalline oxyhydroxysulphate minerals may therefore initially form from acidic discharges and eventually revert to jarosite, which is common in mature gossan deposits and tailings impoundments.

Bigham's (1994) model indicates that jarosite can be expected to precipitate from solutions with sulphate concentrations greater than 3,000 mg/L and low pH values (1.5 to 3). At high pH and low sulphate concentrations, jarosite becomes unstable and will dissolve and re-precipitate to form goethite. In addition, the formation of jarosite may be inhibited by the presence of organic matter (Karathanasis and Thompson, 1995).

#### *3.2.2.6 Hematite*

Hematite ($Fe_2O_3$) is a bright red mineral formed via the dehydration and internal rearrangement of the ferrihydrite structure, not by the dehydration of goethite as is often assumed (Schwertmann, 1985). Hematite is preferentially formed over goethite at higher temperatures and would likely be absent under cool humid conditions. Similarly, hematite formation is favoured over goethite with increasing aluminum activity and in environments containing low organic matter content. The pH dependence of hematite formation from ferrihydrite was discussed previously in Section 3.2.2.1.

#### *3.2.2.7 Hydrated Iron Sulphate Minerals*

The most soluble secondary minerals found in waste rock piles are likely formed during dry periods as evaporation promotes the rise of water in the waste dump through capillary action. As these waters reach the upper portions of the dump, they become progressively more concentrated and become supersaturated with respect to various salts. These salts may precipitate in an efflorescence, a process similar to that associated with closed basin lakes in arid environments (Nordstrom, 1982). Many of the hydrated sulphate minerals form as a result of the dehydration of other hydrated minerals (Bayless & Olyphant 1993). The hydrate that forms depends on subtle fluctuations of temperature, ionic strength and water vapor pressure. A rough dehydration sequence of hydrated iron sulphate mineral formation with increasing temperature and decreasing vapor pressure is:

melanterite → siderotil ~ rozenite ~ szomolnokite → coquimbite → copiapite.

These hydrated minerals may also form during periods of dry weather immediately adjacent to oxidizing sulphide minerals (such as pyrite and marcasite) under unsaturated conditions. Under optimal conditions, formation kinetics allow these minerals to form very rapidly (< 1 hour). However, large accumulations of these soluble minerals are unlikely to persist in waste rock, except in arid climates, due to seasonal dissolution by rainwater or melt-water percolating through the dump. The formation of soluble hydrated iron sulphate minerals is an important intermediate step preceding the precipitation of fully oxidized minerals such as ferrihydrite or goethite. The overall sequence of mineral formation is presented in Figure 3-4. Goethite and jarosite are thermodynamically stable over a much wider range of pH and Eh conditions, and as a result, have a greater spatial distribution in the oxidizing environment than hydrated iron sulphate minerals.

Melanterite ($FeSO_4{\cdot}7H_2O$), a white or blue hydrated iron sulphate mineral, is formed via the precipitation of ferrous iron and sulphate. These ions are readily available in highly acidic conditions (pH < 4) and are liberated during the oxidation of iron-sulphides in the reaction:

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

The hydrous iron sulphate, rozenite ($FeSO_4{\cdot}4H_2O$), a white vitreous mineral, and the iron-copper sulphate, siderotil ($(Fe,Cu)SO_4{\cdot}5H_2O$), a pale green mineral, have been observed to form at room temperature as a result of the reaction of fine-grained iron sulfides and atmospheric moisture (Huggins *et al.,* 1983; Jambor, 1994). They have also been reported to form as dehydration products of melanterite (Jambor and Traill, 1963; Ehlers and Stiles, 1965; Nordstrom, 1982) as a result of increasing temperature or lower relative humidity. In gossan deposits, siderotil occurs adjacent to oxidizing sulphides where there is enough acidity to prevent hydrolysis of the transition metals to basic double salts and inhibit the oxidation of iron to higher valence states. A mineral suite composed of melanterite-rozenite-szomolnokite has been observed to form on pyrite grain surfaces as white or pale green filamentous needles in pyritic coal spoils (Bayless and Olyphant, 1993). Szomolnokite ($FeSO_4{\cdot}4H_2O$) along with the ferric mineral kornelite ($Fe_2(SO_4)_3{\cdot}7H_2O$) are most stable at elevated temperatures of +45 to +50$^0$C, which may be realized in actively oxidizing waste rock dumps (Alpers *et al*., 1994).

Copiapite ($Fe^{2+}(Fe^{3+})_4(SO_4)_6(OH)_2{\cdot}20H_2O$), a golden yellow mineral, may form from the further oxidation of szomolnokite, rozenite or siderotil if these minerals remain in contact with pore waters or humid air. Copiapite requires warm temperatures, oxidizing conditions and low pH to form and may incorporate several other divalent and trivalent metals into the ferrous and ferric sites (Nordstrom, 1982); this phase has been documented forming in the unsaturated zone of pyritic coal spoils (Bayless and Olyphant, 1993). A faint rose-pink to tan yellow mineral, coquimbite ($Fe_2(SO_4)_3{\cdot}9H_2O$), has been observed to be intimately associated with copiapite in gossan deposits and mine workings (Blanchard, 1968; Alpers, 1994). Blanchard's observation of these two minerals coexisting in underground workings indicate that coquimbite may persist for a few hours

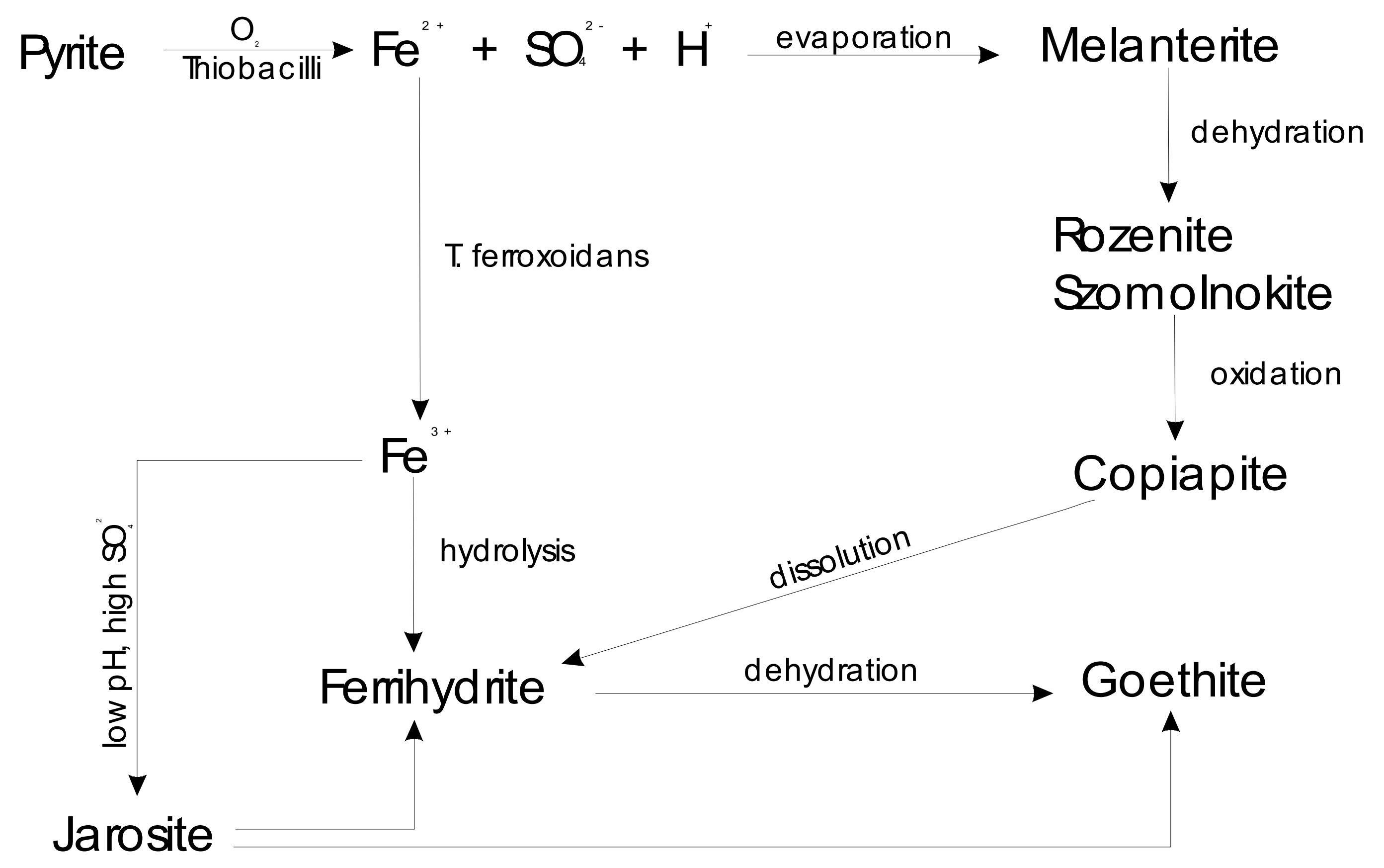


Figure 3-4: Reaction Sequence of Mineral Products from Pyrite Oxidation (Modified for Nordstrom, 1985

to several weeks before altering to copiapite. Blanchard (1968) observed copiapite was stable from several days to several years or more before being fully oxidized to “limonite”. The relative period of stability of the former was shown to be dependent on the temperature, degree of ventilation and humidity.

The amount of ferrous iron contained in these soluble minerals is significant because it represents stored acidity that can be released when the iron is ultimately oxidized to ferric iron. For example, melanterite, rozenite and szomolnokite theoretically contain only divalent iron, which could upon dissolution, oxidation and re-precipitation, produce acidity. Copiapite, on the other hand, theoretically contains 80% trivalent iron and only 20% divalent iron.

Alpers *et al.,* (1994) has illustrated that the known occurrence of rhomboclase ($(H_3O)Fe(SO_4)_2 \cdot 3H_2O$) in waste rock dumps and mine workings is limited but suggests that this mineral could be formed when acid-sulphate solutions are evaporated to dryness and act as a sink for acidity. Romerite ($Fe^{2}+Fe_3^{+2}(SO_4)_4 \cdot 14H_2O$), a mixed valence iron sulfate mineral, may form directly from evaporating mine water as a fine-grained pink alteration product or as brown crystals.

### *3.2.2.8 Iron Arsenates and Carbonates*

In gossans derived from arsenide-bearing assemblages, iron arsenates are common. Arsenic is also commonly adsorbed onto goethite under acidic pH conditions (Appendix A). The green arsenate, scorodite ($FeAsO_4 \cdot 2H_2O$), may also form in oxidized waste dumps and is highly insoluble under mildly acidic and neutral conditions (Kwong and Ferguson, 1990). In carbonate-rich environments, secondary siderite ($FeCO_3$) may form. However, limited siderite is expected to form as a consequence of limited ferrous iron availability at circum-neutral pH in oxic waste rock dumps.

## 3.2.3 Secondary Sulphur Minerals

Sulphide mineral oxidation results in the release of sulphur species to solution. The most stable aqueous form of oxidized sulphur is sulphate ($SO_4^{2}$); however, the oxidation of sulphur may proceed in many steps forming several intermediate metastable dimers such as thiosulphates. Much of the sulphate produced from sulphide oxidation will be transported away from the reaction site in an aqueous state; however, as the sulphate activity of a solution increases, secondary sulphate minerals may precipitate preferentially over oxyhydroxide minerals. The precipitation of secondary sulphate minerals allows a significant quantity of sulphate to be retained as sulphur minerals which are commonly reported in gossans, tailings impoundments and mine drainage.

#### *3.2.3.1 Elemental Sulphur*

Elemental sulphur has also been observed in oxidized tailings impoundments (Blowes and Jambor, 1990) but is typically seen only immediately adjacent to oxidizing sulphide grains in gossan deposits. Marcasite and sulphur are closely associated, occurring as the initial alteration products of pyrrhotite and are often seen forming pseudomorphs after the primary sulphide (Kwong and Ferguson, 1990; Jambor, 1994; Janzen *et al.,* 1997). The production of elemental sulphur from oxidizing pyrite is favored at low pH and in the presence of ferric iron. The presence of organic substances may prevent further oxidation of sulphur to sulphate; this is supported by the presence of elemental sulphur in many oxidized coal seams (Nordstrom, 1982). Although elemental sulphur is relatively insoluble, the oxidation of elemental sulphur to sulphate is an acid generating process, as shown by the chemical equation:

$$2S^{0}_{(S)} + 3O_2 + 2H_2O \rightarrow 2SO_4^{2} + 4H^{+}$$

#### *3.2.3.2 Gypsum*

Gypsum ($CaSO_4{\cdot}2H_2O$) is typically the most abundant sulphate mineral in waste rock. Calcium and sulphate ions are typically released into mine drainage waters in sufficient concentrations to exceed saturation with respect to gypsum. Calcium is predominately obtained from the dissolution of carbonate minerals which are extremely soluble at acidic pH and to a lesser extent silicate minerals such as plagioclase feldspar, epidote, augite and hornblende. Unlike many of the base metal sulphates, the precipitation of gypsum is not inhibited by high concentrations of ferrous iron often observed in low pH mine drainage. Unlike many other secondary sulphate minerals, gypsum is relatively pure with negligible incorporation of trace elements into the crystal structure (Williams, 1990).

### 3.2.3.3 *Jarosite*

Jarosite ($KFe_3(OH)_6(SO_4)_2$) has a widespread occurrence in oxidized tailings impoundments. However, the extent to which it may be present in waste rock dumps has not been fully documented. The potassium is likely released from the primary minerals biotite and stilpnomelane with the more stable minerals, K-feldspar and muscovite, available as supplementary sources. Jarosite may be absent or scarce in the at-surface leached zone but content typically increases with depth in a mature tailings profile (Jambor, 1994). The conditions favouring jarosite formation were described in Section 3.2.2.5.

### 3.2.3.4 *Additional Hydrated Sulphate Minerals*

The simple hydrated sulphates of divalent metal ions such as siderotil $(Fe,Cu)SO_4\cdot 5H_2O$ or epsomite ($MgSO_4\cdot 7H_2O$) may be present in waste rock dumps. Numerous other hydrated sulphates have been documented in oxidized zones (Williams, 1990), including hydrated species of simple sulphates ($MSO_4$, where M represents a divalent metal cation), sulphates in various stages of hydration ($MSO_4\cdot ?H_2O$), and complex sulphates ($M_2M(SO_4)_2\cdot ?H_2O$). The number of possible minerals is overwhelming and therefore the list is not presented here. These minerals form and dissolve in a similar way to the hydrated iron sulphate minerals described in Section 3.2.2.7. It must be noted, however, that these minerals are rarely "pure". Substantial substitution of various metals into divalent hydrated sulphates has been documented (Williams 1990 and contained references). In fact, many of the hydrated sulphate mineral structures are only stabilized by such substitution. In addition, mineral suites commonly crystallize together with the proportions of the various phases being determined by the relative activities of the competing ions in the evaporating solution.

## 3.3 *Mineral Aging and Maturation*

The timing of secondary mineral formation and crystallization that can be expected in oxidized waste rock is outlined below. As indicated elsewhere in the report, maturation and crystallization stabilize the secondary products in the oxidized zone. This discussion summarizes the information provided in Section 3.2.

The minerals that have the highest rate of kinetic formation are the hydrated sulphates. The majority of these, with the notable exception of gypsum, are extremely soluble. Provided with the optimal conditions of high ionic strength, warm temperature and low pH, hydrated sulphate minerals may form in a matter of hours or days, typically as effloresences on the surface of mine spoils or mine walls, or from evaporating mine water.

Many of the hydrated minerals will dehydrate, with age, to lower hydration states if conditions of high temperature and low relative humidity persist. However, due to their high solubility they are unlikely to accumulate in waste rock dumps. Instead, these minerals are likely to be dissolved during precipitation or melting events and contribute to metal loading in mine drainage. Alternatively, they may reprecipitate as one of the more stable iron mineral phases discussed below.

A number of relatively stable iron-bearing minerals may form in waste rock dumps, all of which mature to form goethite. For example, ferrihydrite, schwertmannite, jarosite and to a lesser extent lepidocrocite commonly form in waste rock dumps, but they are metastable and with age dissolve and reprecipitate as goethite. Because such progressive alteration is inhibited by various physico-chemical conditions , these precursor minerals often coexist in nature with goethite, which is stable over a wide pH range and persistent in oxidizing environments.

Crystallinity is related to the age of the secondary mineral and the concentration of the solution it precipitates from, particularly for hydroxides. Finely crystalline precipitates with disordered lattices are generally formed from strongly supersaturated solutions whilst well-ordered crystalline phases are more likely to precipitate directly from solutions that are only slightly over-saturated. The poorly crystalline precipitates may persist for significant periods of time, but slowly convert to the more stable crystalline forms through internal structural modification or dehydration.

# *4. SUBAQUEOUS STABILITY OF SECONDARY MINERALS*

The subaqueous chemical stability of oxidized waste rock, or more specifically, the dissolution characteristics of secondary minerals and the potential for release of trace metals are discussed in this chapter. Chemical processes and rate-controlling factors on the dissolution of secondary minerals in oxidized waste rock are described in Section 4.1. In addition, the solubilities of various phases that roughly correspond to the proposed sequential extraction scheme (Chapter 6) are discussed in Section 4.2.

## *4.1 Geochemical Controls on Subaqueous Stability*

Processes that may affect the stability of submerged waste rock include the oxidation of primary sulphide minerals, the precipitation of secondary minerals and the dissolution of secondary minerals formed during subaerial storage.

Dissolution in a subaqueous environment involves diffusion of solutes in water-filled pore spaces and across the diffusive boundary layer (DBL); adsorption onto the mineral surface; transport of reactants to reactive sites on mineral surfaces; chemical reactions; desorption of reaction products from mineral surfaces; and diffusion of products across the DBL into pore spaces and ultimately to the bulk solution. Key factors controlling the extent and rate of dissolution are:

- the surface area of secondary minerals exposed to solution;
- the degree of crystallinity of the secondary minerals;
- the temperature, and to a lesser extent, pressure in the receiving environment;
- the chemical composition of the receiving water (including ambient pH and Eh); and
- the thermodynamic and kinetic properties of the minerals.

The applicability of these factors to mineral dissolution is discussed in the following subsections.

### 4.1.1 Surface Area

The amount of exposed surface area of previously oxidized material will influence the mass transfer of elements and substances from the solid to the liquid phase (*i.e.*, the larger the surface area, the greater the potential for dissolution to occur, and the greater likely impact to water chemistry in the receiving environment).

### 4.1.2 Crystallinity

The degree of crystallinity also controls solubility. As noted earlier, finely crystalline-precipitates with disordered lattices are generally formed from strongly supersaturated solutions while well-ordered crystalline phases are more likely to precipitate directly from solutions that are only slightly over-saturated. The poorly crystalline precipitates may persist for significant periods of time, only slowly converting to the more stable crystalline forms through internal structural modification or dehydration. However, the poorly crystalline phases are typically more soluble than the crystalline phases. In addition, it has been suggested that the solubility product (Ksp) of a specific mineral phase varies with particle size. The Ksp of iron oxide particles less than 1 μm in diameter, for example, appears to increase by several orders of magnitude with decreasing particle size (Schwertmann, 1991). Technically, this view is not correct and is chemically misleading. This is because there is a phase transformation at the surface of iron oxyhydroxide surfaces which produces protoferrihydrite (amorphous $Fe(OH)_3$) via reaction between $Fe00H.2H_2O$ and water (S.Bradley, Dept. Chemistry, UBC, Personal communication). Protoferrihydrite is more soluble than goethite; thus, the apparent increase in Ksp is an artifact of the phase change at the particle surface. The effect of such a transformation on overall solubility will be more evident for finer particles which have more reactive surface area.

### 4.1.3 Temperature and Pressure

Temperature (T) and to a lesser extent pressure in receiving waters will influence ambient molecular diffusion rates for solutes (diffusion rates increase with increasing temperature). Temperature will also influence chemical equilibria between solid and liquid phases, and will therefore affect dissolution of the solid phase. The solubility of many inorganic salts increases with increasing temperature but the solubility of compounds that are often of interest in mine waters such as $CaCO_3$ and $CaSO_4$ actually decreases at higher T. The pressure dependence of solubility is slight except at extreme pressures not anticipated in a subaqueous in-pit disposal or flooded workings scenario.

A key control on the solubility of calcium carbonate which may be important in confined backfill situations is the partial pressure of carbon dioxide ($pCO_2$) since increasing partial pressure increases the solubility of $CaCO_3$. The increase in solubility occurs mainly as a result of moderate pH depression associated with higher $pCO_2$. For example, under atmospheric conditions, as the $pCO_2$ increases from its atmospheric value ($10^{3.5}$) to $10^{1}$, the solubility of calcite increases from about 0.5 mmol/L to 4 mmol/L (at $25^{o}$C).

### 4.1.4 Thermodynamic and Kinetic Effects

The ionic strength and chemical composition of receiving waters will affect chemical equilibria in subaqueous settings and therefore influence the rate and extent of mineral dissolution, as will the pH and Eh (redox state) of the solution. Typically, oxidized secondary minerals become more soluble at lower pH and Eh.

Comparison of solubility constants ($K_{sp}$) for secondary minerals provides an accurate indication of their relative solubility only if the dissolving solution is dilute, the aqueous products do not form complexes and the dissolution kinetics are relatively rapid. In addition to the physical factors outlined in Section 2.2, the actual solubility of a mineral is dependent on the ionic strength of a solution, the relative activity of the reaction products, aqueous complexation, and the kinetics of mineral formation and dissolution. The relative solubility of a solid can therefore rarely be assessed from the solubility product alone. A more detailed discussion on the limitations of comparing $K_{sp}$ is provided in Appendix C. Dissolution kinetics has a strong influence on mineral stability and to date dissolution rates have only been examined for a limited number of secondary minerals that prevail in oxidized waste rock.

The importance of the kinetics of dissolution compared to solubility (as indicated by $K_{sp}$) can be exemplified by the dissolution of an alumino-silicate mineral such as potassium feldspar, *according to the chemical reaction*:

$$KAlSi_3O_8 + 8H_2O \leftrightarrow K^+ + Al^{3+} + 3H_4SiO_4 + 4OH^-$$

In this case, the reaction proceeds extremely slowly, because although the rate-controlling step for the dissolution of soluble mineral phases is diffusion across the DBL, for relatively insoluble minerals such as feldspars and many metal hydroxides, the dissolution rate is governed by reaction at the mineral surface. Such reactions occur in two steps: (i) reactants (*e.g.,* protons) attach to the mineral surface (fast); and (ii) metal ions detach (slow). The latter is rate-limiting. Thus, the release of ions to solution may not be related to the thermodynamic $K_{sp}$ of the mineral.

## 4.2 Mineral and Metal Solubility

In the following discussion, secondary minerals that may form in waste rock dumps are placed in general solubility categories that roughly correspond to the sequential extraction fractions described in Chapter 5. It must be emphasized that sequential extractions are operationally defined and are not phase-specific. In addition, many mineral phases that are present in waste rock are either not present or are present in very low concentrations compared to soils or sediments typically submitted for sequential extraction analyses. Thus, the following discussion must only be used as a general guide to assist in the interpretation of the extraction results. Highly soluble secondary minerals that dissolve readily in oxic waters are presented in Section 4.2.1. Phases highly sensitive to pH, such as carbonates and adsorbed phases are discussed in Section 4.2.2. Secondary mineral phases that are relatively insoluble under oxic conditions but are susceptible to reductive dissolution are presented in Section 4.2.3. Finally, phases susceptible to dissolution under strongly oxidizing conditions such as sulphide minerals and organic matter are discussed in Section 4.2.4.

### 4.2.1 Water Soluble Minerals

Highly soluble secondary minerals in subaerially-exposed waste rock dumps form from evaporating supersaturated solutions. These minerals will be relatively unstable in the more dilute waters that would be present in a flooded open pit. The most abundant and soluble secondary minerals expected in a waste rock dump are hydrated iron sulphate minerals (Blowes and Jambor, 1990; Bayless and Olyphant, 1993; Alpers *et al.,* 1994); the most common of the hydrated iron sulphates are the ferrous sulphates listed in Table 4-1. The mixed ferrous/ferric sulphate minerals and ferric sulphate minerals are less common, with the most frequently observed being copiapite and coquimbite. Melanterite, rozenite and szomolnokite theoretically contain only divalent iron which could produce acidity, upon dissolution, oxidation and reprecipitation as ferric hydroxides.

In extraction studies on oxidized tailings, water-soluble sulphate is released primarily from minerals with the stoichiometry $CaSO_4 \cdot nH_2O$ such as gypsum (Blowes and Jambor, 1990). However, a variety of other highly soluble salts may be present including such minerals as epsomite, bianchite or chalcanthite (Table 4-1).

### 4.2.2 Ion Adsorption and Carbonate Minerals

The sorption of metals onto particle surfaces and carbonate mineral solubility are both extremely pH dependent. Sorbed cations are typically more mobile at low pH and anions at high pH. Carbonate minerals that may be present in waste rock are relatively insoluble at near-neutral pH but may increase their solubility by several orders of magnitude at lower pH. The solubility controls of these metal binding phases are examined below.

#### *4.2.2.1 Sorbed Ions*

The processes of metal adsorption onto solid surfaces and coprecipitation with secondary minerals are important mechanisms in the cycling of trace metals in waste rock dumps. Concentrations of trace elements in natural porewaters are often much lower than would be expected based on either equilibrium solubility calculations or source water concentrations. The most common reason for this is adsorption of the element onto a solid phase (or phases). Sorption processes involve coordination or ion-exchange reactions at the solid-liquid interface that allow ions in solution to bind to solid surfaces, whereas the process of coprecipitation involves inclusion of ions from solution into the secondary mineral lattice as the phases precipitate. The extent of dissolved metal adsorption onto solid surfaces and coprecipitation with secondary minerals depend on the solution characteristics including pH, Eh, ionic strength, and relative concentrations of competing cations and ligands. At a given pH, adsorption of a specific ion increases as

**Table 4-1:**
**Secondary Minerals / High Solubility**

| Mineral | Formula | Color |
|---|---|---|
| **$Fe^{II}$** | | |
| melanterite | $Fe^{II}SO_4 \cdot 7H_2O$ | pale blue-green |
| ferrohexahydrite | $Fe^{II}SO_4 \cdot 6H_2O$ | white |
| siderotil | $(Fe^{II},Cu^{II})SO_4 \cdot 5H_2O$ | white |
| rozenite | $Fe^{II}SO_4 \cdot 4H_2O$ | white |
| szomolnokite | $Fe^{II}SO_4 \cdot H_2O$ | white, green |
| halotrichite | $(Fe^{II})Al_2(SO_4)_4 \cdot 22H_2O$ | white, green |
| **Mixed $Fe^{II}$-$Fe^{III}$** | | |
| copiapite | $Fe^{II}Fe_4^{III}(SO_4)6(OH)_2 \cdot 20H_2O$ | yellow |
| bilinite | $Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 22H_2O$ | orange |
| romerite | $Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 14H_2O$ | brown, pink |
| voltaite | $K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12} \cdot 18H_2O$ | black, green |
| **$Fe^{III}$** | | |
| coquimbite | $Fe_2^{III}(SO_4)_3 \cdot 9H_2O$ | purple, white |
| kornelite | $Fe_2^{III}(SO_4)_3 \cdot 7H_2O$ | pink |
| rhomboclase | $HFe_2^{III}(SO_4)_2 \cdot 4H_2O$ | cream |
| ferricopiapite | $Fe_5^{III}(SO_4)_6O(OH) \cdot 20H_2O$ | yellow, orange |
| **Other Sulphates** | | |
| epsomite | $MgSO_4 \cdot 7H_2O$ | |
| hexahydrite | $MgSO_4 \cdot 6H_2O$ | |
| goslarite | $ZnSO_4 \cdot 7H_2O$ | |
| bianchite | $ZnSO_4 \cdot 6H_2O$ | |
| gunningite | $ZnSO_4 \cdot H_2O$ | |
| gypsum | $CaSO_4 \cdot 2H_2O$ | |
| anhydrite | $CaSO_4$ | |
| retgersite | $NiSO_4 \cdot 6H_2O$ | |
| chalcanthite | $CuSO_4 \cdot 5H_2O$ | |
| alunogen | $Al_2(SO_4)_3 \cdot 17H_2O$ | |
| mirabilite | $Na_2(SO_4) \cdot 10H_2O$ | |
| thenardite | $Na_2(SO_4)$ | |

After Alpers *et al.,* (1994)

its activity increases in the equilibrium solution. Similarly, ion adsorption increases as the overall ionic strength of the solution increases.

Many metals have a strong affinity for iron, aluminum and manganese oxides and oxyhydroxides. However, due to the higher solubility of manganese in acidic waters, iron oxides will be the major oxide component of secondary mineral assemblages in acidic waste rock dumps. Substantial incorporation of many trace elements (*e.g.,* Al, As, Cd, Co, Cu, Pb, Ni and Zn) has been documented in iron oxides (Schultz *et al.,* 1987; Schwertmann & Taylor, 1989; Giovanoli and Cornell, 1992; Alpers *et al*., 1994; Jambor, 1994), although the exact mechanism responsible for the metal association (*i.e.,* coprecipitaion/isomorphic substitution or adsorption) is often unclear. Regardless of the association mechanism, precipitation and/or dissolution (including reductive dissolution) of iron oxides and hydroxides have the potential to strongly influence aqueous metal concentrations.

The surfaces of sulphide minerals have a strong affinity for dissolved metals (Al *et al*., 1997 and references cited within) and thus may play an important role in controlling the concentrations of dissolved metals in waste rock submerged under water. Similar to hydroxide minerals, ions in solution may react with the sulphide mineral surface through coprecipitation, chemical adsorption to hydroxyl and thio functional groups, electrostatic adsorption, or alternatively by ionic replacement or redox reactions with ferrous iron.

### *Cations*

Iron oxides such as hematite, goethite, lepidocrocite, and ferrihydrite commonly adsorb cations, under alkaline pH conditions the cations may subsequently be released in acidic environments. The adsorption capacity of an oxide/oxyhydroxide mineral is also dependent on its reactive surface area and the adsorptive behavior of a specific cation. These various effects are discussed below.

Poorly crystalline iron phases are typically characterized by loosely hydrated structures which are permeable to ions (Davison, 1993). The permeability does not restrict sorption reactions to external sites, as is the case for more crystalline solids. Thus, poorly-ordered phases such as ferrihydrite or schwertmannite, have a higher reactive surface area than crystalline iron oxides. The incorporation or adsorption of foreign ions to these phases appear to restrict crystal development, thus contributing to random growth (Taylor, 1987).

The dependence of the degree of adsorption on pH and ionic strength has been attributed to variations in surface charge that result from changes in the degree of protonation of the oxide/oxyhydroxide surface (Schwertmann and Taylor, 1989). As the metal oxide is immersed in solution, water molecules orient and bind to the surface, offsetting the inherent surface charge. Variation in the protonation of bound water molecules, resulting from variations in pH, changes the surface charge of the oxide/oxyhydroxide mineral, and affects its affinity for dissolved metals.

The pH of the solution is therefore an important factor in determining whether cations or anions will be preferentially adsorbed and retained on iron oxyhydroxides. A rough adsorption sequence (from the most to least strongly adsorbed) for the principal metal cations of environmental concern is: Al > Cu > Pb > Zn > Co > Ni > Cd > Mn (Thornber, 1985; Davis *et al.,* 1991). However, Schwertmann and Taylor (1989) report a slightly different sequence specifically for goethite where cadmium is positioned between cobalt and zinc. The sequence indicates that cations such as copper and lead are more likely to be retained on the goethite surface at lower pH while cations such as manganese and cadmium would be released. The adsorption behaviour of various metals at 20 $\mu$mol/g of goethite is presented in Figure 4-1.

In contrast to adsorption, desorption processes are relatively unstudied. However, an effect commonly observed in desorption experiments is that of a hysteresis effect. That is, a portion of the adsorbed ions is not subsequently desorbed simply by reducing the pH to a range where sorption is not normally observed. In a series of short-term tests ($t < 1$ day), Schultz *et al.,* (1987) illustrated that in aging ferrihydrite, (prior to reducing the pH to a level where the metal would be expected to desorb), the amount of adsorbed/coprecipitated metal that was subsequently released at pH 4.5 was less than previously adsorbed. This was shown to be true for copper, lead, nickel and zinc, but not cadmium.

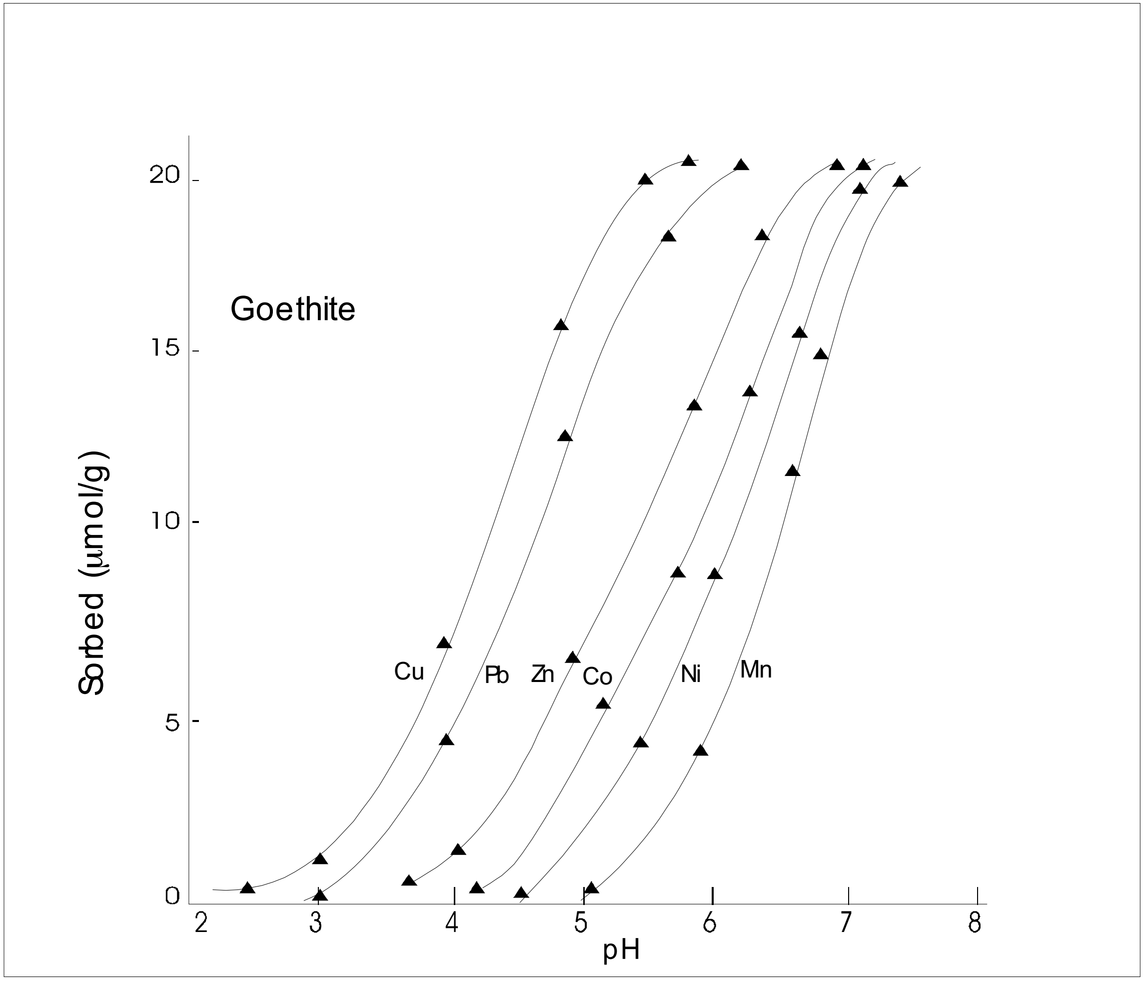


**Figure 4-1: The Effect of pH on Adsorption of Various Metals by Synthetic Goethite (Schwertmann and Taylor, 1989)**

*Anions*

Iron hydroxides adsorb anionic complexes which, unlike cation adsorption, is favoured at low pH when mineral surfaces exhibit positive surface charge. The metals that typically form anionic complexes in solution include: selenium, tellurium, molybdenum and arsenic. The adsorptive capacity of iron oxyhydroxides for arsenic is particularly high (Pierce and Moore, 1982) and is mediated by both redox conditions and solution pH. Adsorption of arsenate onto iron oxyhydroxides occurs via simple electrostatic attraction and through the formation of more stable inner-sphere complexes (Hsia *et al.,* 1994). The amount of adsorption is highest when the charge differences between the oxyanion and the surfaces of the oxyhydroxides are greatest. As discussed earlier, many oxide surfaces, including those of goethite and amorphous iron hydroxide, change from being positively charged at low pH to negatively charged at high pH (Bowell, 1994). The pH at which the change occurs (*i.e.,* the isoelectric point, at which the net surface charge is zero) lies between pH 7.6 and 8.1 (Parks and DeBruyn, 1962). Therefore, above pH 8, the surfaces of iron oxyhydroxides are expected to become, for the most part, negatively charged. While the ability to adsorb cations (Cu, Pb, Hg, *etc*.) would be enhanced under such conditions, the opposite would be true for anion (*e.g*., arsenate) adsorption.

#### *4.2.2.2 Carbonates*

Carbonate minerals are often more stable than oxides or hydroxides. However, their solubility is strongly pH dependent, increasing with decreasing pH (Section 4.1.3). At neutral pH, the solubility of calcium carbonate (the most soluble carbonate species) exceeds that of strontium, iron, magnesium, cadmium, and lead carbonates. The hydroxyl carbonates such as malachite, azurite and hydrozincite are typically persistent in mature waste rock (Williams, 1990), and are relatively insoluble at alkaline pH. Various carbonate minerals that may be present in waste rock are listed in Table 4-2.

### 4.2.3 Sparingly Soluble Minerals

Secondary minerals that are typically insoluble in oxic waters include mature (aged) oxyhydroxide and sulphate minerals that form in subaerially-exposed waste rock dumps. The most common of these are iron oxides and oxyhydroxides such as hematite and goethite, sulphate minerals from the jarosite and alunite groups, and copper, lead and strontium sulphate minerals. In addition to the major cations essential to the mineral structure, these minerals often contain isomorphically substituted metals that will be released when the mineral is dissolved.

Although many of these minerals are susceptible to reductive dissolution, a strong kinetic effect controls the rate of dissolution and hence the potential impacts on water quality. To date, the kinetic controls on the dissolution of the various secondary minerals that may form in oxidized waste dumps is incomplete. Thus, in the absence of site-specific studies, quantification of the impact associated with kinetically-controlled dissolution is not presently possible.

**Table 4-2:**
**Carbonate Minerals**

| Mineral | Formula | Mineral | Formula |
|---|---|---|---|
| **Rhombohedral** | | **Orthorhombic** | |
| calcite | $CaCO_3$ | aragonite | $CaCO_3$ |
| magnesite | $MgCO_3$ | strontianite | $SrCO_3$ |
| siderite | $FeCO_3$ | witherite | $BaCO_3$ |
| rhodochrosite | $MnCO_3$ | cerussite | $PbCO_3$ |
| smithsonite | $ZnCO_3$ | **Double** | |
| otavite | $CdCO_3$ | dolomite | $CaMg(CO_3)_2$ |
| gaspeite | $NiCO_3$ | kutnohorite | $CaMn(CO_3)_2$ |
| sphaerocobaltite | $CoCO_3$ | ankerite | $Ca(Fe,Mg)(CO_3)_2$ |
| **Hydroxyl** | | minrecordite | $CaZn(CO_3)_2$ |
| malachite | $Cu_2(CO_3)(OH)_2$ | | |
| azurite | $Cu_3(CO_3)_2(OH)_2$ | hydrozincite | $Zn_4(CO_3)_2(OH)_2$ |
| hydrocerussite | $Pb_3(CO_3)_2(OH)_2$ | aurichalcite | $(Zn,Cu)(CO_3)_2(OH)_6$ |

After Alpers *et al.,* 1994

#### *4.2.3.1 Implications of Reductive Dissolution*

The dissolution of certain oxidation products may be induced by changing Eh, in addition to the solubility considerations discussed above. Specifically, iron oxides, manganese oxides (and to a lesser degree, sulphate-bearing solids such as jarosites) will be sensitive to changes in the redox conditions to which they are subjected. Following is a brief discussion of the salient issues.

When sulphide-rich waste rock is placed underwater, it will continue to consume oxygen; however, both the availability and rate of supply of oxygen to reaction sites in subaqueous settings is markedly limited compared to the subaerial setting (Pedersen *et al*., 1993; MEND, 1995c; MEND, 1996). This factor enhances the stability of unoxidized sulphides. As oxygen is progressively consumed (at a greater rate than it can be replaced), interstitial solution becomes dysaerobic and alternate (secondary) oxidants are consumed in place of oxygen. Table 4-3 lists the available redox couples. The environmental issue that may arise concerns the role that oxide minerals play in such redox cycling.

**Table 4-3:**
**Redox Couples**

| Oxidant | Reductant |
|---|---|
| $O_2$ | |
| $NO_3$ | $NH_4^+$ |
| $MnO_2$ | $Mn^{2+}$ |
| $Fe(OH)_3$ | $Fe^{2+}$ |
| $SO_4^2$ | HS |
| | Organic C |

In oxic environments, iron and manganese exist in their highest oxidation states of +3 and +4, respectively. However, as the redox potential in subaqueous environment decreases through the oxidation of sulphides (or possibly through the oxidation of organic matter), Fe(III) and Mn(IV) act as secondary oxidants. These phases may accept electrons from residual sulphide minerals in the waste rock or organic matter, and may be reduced to their lowest oxidation states of Fe(II) and Mn(II). In their reduced forms, iron and manganese are soluble and thus the dissolving oxides release associated trace metals to the interstitial solution. Depending on the nature of transport, these metals may be available to proximal surface of groundwaters. Note that manganese oxides are more soluble than iron by six or seven orders of magnitude at any given pH or Eh (Nickel and Daniels, 1985) and are particularly soluble at acidic pH values.

In cases where reductive dissolution is driven by sulphide oxidation (*i.e.*, trace oxidation of the waste rock), the solublization of oxides may continue (albeit at a slow rate) because the redox potential will never be sufficiently low to foster sulphate reduction. However, if the trend towards reducing conditions is fueled by the oxidation of organic matter, sulphate reduction may occur commensurate with oxide reduction such that free sulphide is produced in close proximity to the release of metals. This mechanism will have the effect of mitigating metal release, as most trace metals will instantaneously precipitate as their respective sulphides in such environments. Providing that anoxia persisted, such a mechanism would enhance the long-term stability of alteration products by converting sparingly soluble oxides to comparatively insoluble sulphides.

Solid organic matter that may be buried in the waste rock sediment may act as a complexing agent for metals and can lead to the removal of metals from solution as observed in groundwater seeping from coal seams (Drever, 1988). Buried organic matter may partially decompose to form dissolved organic matter (DOM), which influences trace metal mobility and toxicity through the formation of metal-ligand complexes. The presence of organic ligands may either accelerate or retard dissolution of iron oxides. For example, DOM in pore water promotes reducing conditions that may change the oxidation state of metals such as Fe, Mn, Mo, U, Cr and V and directly increase their mobility by reductive dissolution. Furthermore, such reducing conditions enhance the complexing characteristics of ligand atoms that have multiple oxidation states, such as sulphur and nitrogen. The formation of metal complexes lowers the toxicity of the mobile elements and enhances metal-sulphide precipitation. Note that metals that may not be subject to direct changes in oxidation state may experience increased mobility as oxide phases (*e.g.,* Fe, Mn, *etc*.) release adsorped or coprecipitated metals (Section 4.2.2). Alternatively, at low pH, organic ligands may block adsorption sites and reduce the rate of protonation-induced dissolution (Schwertmann, 1991).

An additional but less-well understood phenomenon involves the potential reductive dissolution of sulphate-based solids (*i.e.,* jarosite). It is conceivable that under sufficiently reducing conditions, the reduction of sulphate could further destabilize such solids thereby releasing sulphur and any associated trace metals to the water cover.

#### *4.2.3.2 Minerals with Low Solubility*

Several sparingly soluble minerals are discussed in this section and listed in Table 4-4. Many of these phases including the iron and manganese oxides will be susceptible to the F3 extraction fraction discussed in Section 6.1. However, the extraction susceptibility of the sulphate minerals and aluminum oxides has not been established.

As discussed in Section 4.1, dissolution is controlled by a number of processes that occur

**Table 4-4:**
**Sparingly Soluble Secondary Minerals**

| Mineral | Formula | Mineral | Formula |
|---|---|---|---|
| **Jarosite Group** | | **Alunite Group** | |
| jarosite | $KFe_3^{III}(SO_4)_2(OH)_6$ | alunite | $KAl_3(SO_4)_2(OH)_6$ |
| natrojarosite | $NaFe_3^{III}(SO_4)_2(OH)_6$ | natroalunite | $NaAl_3(SO_4)_2(OH)_6$ |
| hydronium jarosite | $(H_3O)Fe_3^{III}(SO_4)_2(OH)_6$ | ammonioalunite | $(NH_4)Al_3(SO_4)_2(OH)_6$ |
| ammoniojarosite | $(NH4)Fe_3^{III}(SO_4)_2(OH)_6$ | osarizawaite | $PbCuAl_2(SO_4)_2(OH)_6$ |
| argentojarosite | $AgFe_3^{III}(SO_4)_2(OH)_6$ | beaverite | $PbCuFe_2^{III}(SO_4)_2(OH)_6$ |
| plumbojarosite | $Pb_{0.5}Fe_3^{III}(SO_4)_2(OH)_6$ | | |
| **Other Iron Sulphates** | | **Hydrated Aluminum Sulphates** | |
| fibroferrite | $Fe^{III}(SO_4)(OH).5H_2O$ | jurbanite | $Al(SO_4)(OH).5H_2O$ |
| amarantite | $Fe^{III}(SO_4)(OH).3H_2O$ | hydrobasaluminite | Al4(SO4)(OH)10.12-$36H_2O$ |
| schwertmannite | $Fe_8^{III}O_8(SO_4)(OH)_6$ | basaluminite | $Al_4(SO_4)(OH)_{10}.H_2O$ |
| **Other Sulphates** | | | |
| celestite | $SrSO_4$ | brochantite | $Cu_4(SO_4)(OH)_6$ |
| anglesite | $PbSO_4$ | langite | $Cu_4(SO_4)(OH)_6.2H_2O$ |
| barite | $BaSO_4$ | posnjakite | $Cu_4(SO_4)(OH)_6.H_2O$ |
| antlerite | $Cu_3(SO_4)(OH)_4$ | | |
| **Iron Oxides** | | **Aluminum Oxides** | |
| hematite | $\alpha$-$Fe_2O_3$ | corundum | $Al_2O_3$ |
| maghemite | $\gamma$-$Fe_2O_3$ | diaspore | AlO(OH) |
| magnetite | $FeO.Fe_2O_3$ | boehmite | AlO(OH) |
| goethite | $\alpha$-FeO(OH) | gibbsite | $Al(OH)_3$ |
| akaganeite | $\beta$-FeO(OH,Cl) | bayerite | $Al(OH)_3$ |
| lepidocrocite | $\gamma$ -FeO(OH) | doyleite | $Al(OH)_3$ |
| ferroxyhyte | $\delta$-FeO(OH) | nordstrandite | $Al(OH)_3$ |
| ferrihydrite | $5Fe_2O_3.9H_2O$ | | |
| **Manganese Oxides** | | | |

| | | | |
|---|---|---|---|
| binessite | δ-$MnO_2$ | feitknechtite | β-MnOOH |
| hausmannite | $Mn_3O_4$ | manganite | γ -MnO(OH) |

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at or near the mineral surface. A detailed discussion of surface-controlled dissolution processes is presented in Hering and Stumm (1990). The dissolution of many iron oxyhydroxides can occur directly in the presence of a complexing agent or agents. In the absence of complexing ligands, many $Fe^{3+}$ phases are essentially insoluble above pH 4 (Zinder *et al.*, 1986). The rate of goethite dissolution in the presence of inorganic ions Cl , $SO_4^{2}$ , $ClO_4$ or organics such as oxalate, humic acid and fulvic acid has been summarized (MEND, 1995); the rate of dissolution is dependent on both the ligand concentration and the pH. The rate of dissolution is increased by the presence of the ligand; however, the presence of the ligand (*e.g*., Cl) alone without a strongly acidic medium is not enough to initiate goethite dissolution (Cornell *et al.*, 1976).

Reductive dissolution can markedly enhance the dissolution rate of goethite (Torrent *et al*., 1987; LaKind and Stone, 1989). Zinder *et al.,* (1986) indicates that at pH 4 the presence of a reducing agent (oxalate) increases the dissolution rate of goethite by an order of magnitude. The reductive dissolution rate of iron hydroxides has been shown to be proportional to the concentration of the surface-bound reductant (Stumm and Wollast, 1990). Like non-reductive dissolution, reductive dissolution is enhanced by the presence of complexing ligands and pH. Conversely, the rate of reductive dissolution decreases in sulphate-laden solutions (LaKind and Stone, 1989).

Manganese oxides are more susceptible to reductive dissolution than iron oxides and may be reduced by ferrous or sulphide ions in addition to organic matter. Like iron oxides the rate of reductive dissolution is proportional to the concentration of the reductant and pH, with the rate increasing as the proton activity increases. However, the kinetics of dissolution are much slower for manganese oxides than for iron oxides (Davison, 1993). Thus, manganese oxides are not expected to have a strong influence on metal mobility initially after the flooding of oxidized waste rock due to the relative abundance of other secondary minerals. However, subsequent enrichment of manganese in the submerged waste rock may be significant in controlling long-term metal mobility.

The sulphate minerals jarosite, alunite and schwertmannite all exhibit low solubility. Both jarosite and schwertmannite are believed to be metastable with respect to goethite and under circum-neutral conditions are likely to dissolve and reprecipitate as goethite over an extended period. However, the solid phase sulphate contained in jarosite is retained in the solid phase after being subjected to water-soluble extractions (Blowes and Jambor, 1990).

The lead(II) sulphate mineral (anglesite) is relatively insoluble, nevertheless it is much more soluble than galena, PbS (Williams, 1990). Copper hydroxy-sulphate minerals, such as antlerite and brochantite, are of intermediate solubility and will remain in the solid phase in dilute waters but may slowly release metals over time. Although the various sulphate minerals discussed above are relatively insoluble under oxic conditions, their dissolution rates have not been established. Many of the non-ferrous sulphate minerals are less susceptible to reductive dissolution than iron oxide minerals, which reflects the difference in the redox potentials for sulphate reduction (low) and iron (higher).

Aluminum hydroxides such as gibbsite are extremely insoluble at circum-neutral pH. Unlike iron or manganese, aluminum only has one oxidation state, +3. Therefore aluminum oxides are not susceptible to reductive dissolution. At pH values < 4.5 aluminum hydroxides are increasingly soluble. Indeed, their dissolution rate is reported to be seven times greater than that of goethite at pH 3 (Mogollon *et al.*, 1996).

### 4.2.4 Phases Susceptible to Dissolution Under Strongly Oxidizing Conditions

Both sulphide minerals and organic matter are present in many natural environments. Although large quantities of organic matter are not typically associated with mine waste, introduction of organic matter to a water cover subsequent to subaqueous disposal may affect trace metal mobility. The behaviour of sulphides and organic matter in subaqueous settings is discussed below.

#### *4.2.4.1 Sulphide Minerals*

Extensive research (principally under the MEND program) during the last 10 years has shown that oxidation of sulphides and subsequent oxidative dissolution of these minerals is negligible in subaqueous settings. This is because maximum oxygen concentrations and the molecular diffusion coefficient for oxygen in water are several orders of magnitude less than those in air. In addition, the mineralization of even small quantities of dissolved organic ligands, ubiquitous in the aquatic environment, effectively competes for oxygen thereby further reducing the availability of oxygen for sulphide oxidation. Precipitation of secondary minerals will also be less significant under water than in subaerial regimes (pore spaces remain saturated in the former and therefore there is no drainage, evaporation or air-oxidation).

In addition to the metals contained in the primary sulphide mineral structure, the surfaces of sulphide minerals may accumulate high concentrations or various metal species. Dissolved metal may attach to sulphide minerals through various mechanisms including: coprecipitation, chemical adsorption, or alternatively by ionic replacement or redox reactions with ferrous iron in the sulphide structure. Metal accumulation on the surface of sulphides is pH sensitive following relationships established for adsorption of metals to hydroxide minerals. Metal cations such as Cd, Pb and Zn have been shown to be abundant at circum-neutral pH and arsenic, which forms anionic complexes, being relatively more abundant at $pH < 4.5$ (Al *et al.*, 1997). Should the pH decrease, it is likely that accumulated cations will be released to solution or conversely increasing pH will allow the sulphide mineral surfaces to act as a sink for dissolved metals.

As for primary sulphide minerals in waste rock, authigenic sulphides that may form in the anoxic zone of waste rock dumps are insoluble relative to the secondary minerals listed in Table 4-2. The relative solubility of the sulphide minerals follows the order (from most to least soluble): $MnS > FeS > NiS \sim ZnS > CdS \sim PbS > CuS > HgS$ (Alpers *et al.*, 1994).

### *4.2.4.2 Organic Matter*

Organis matter is not always present in large quantities in subaerially exposed waste rock. However, organic matter plays a critical role in controlling metal behaviour in subaerial and subaqueous environments. Organic compounds may increase the rate of metal release during weathering of silicate and sulphide minerals, affect the rate of secondary mineral precipitation and act as a sink for adsorbed metals in sediments. Organic matter in waste rock may also affect the extent of reductive dissolution and sulphide precipitation, as discussed in Section 4.2.3.

Humic substances are the most important organic compounds present in the surface and near-surface waters, and consist of complex heterogeneous polymers that are defined by their molecular weight and solubility (Hall *et al*., 1995). Humic substances include humins, humic acids and fulvic acids (Table 4-5).

Although hydrolysis is typically the primary mechanism of mineral dissolution, metals may also be removed by chelating acids. Iron and aluminum are among the metals that form the strongest complexes with humic acids and compete for coordination sites. This strong affinity for humic and fulvic acids is believed to assist in the decomposition of silicate minerals via the complexation of metals from the silicate structure (Birkeland, 1984) to form hydroxo- and chelating-type bonds. The complexation is pH dependent, with higher pH favoring a greater degree of metal bonding with humic substances in the following order: $Fe^{3+}$ > Hg > Cu > Pb > Cd > Zn > $Fe^{2+}$ > Ni > Co > Mn > Mg and Ca. Humic complexation becomes less significant in controlling solution chemistry when solutions have high ionic strength, as is often observed in drainage from sulphide-rich waste rock dumps (Thornber, 1985). However, organic matter will still be a significant sink for trace metals. For example, Filipek *et al*., (1981) documented that high concentrations of trace metals were bound to organic manner in boulder coatings and sediments from streams impacted by acidic mine drainage.

**Table 4-5:**
**Humic Substances**

| | **Molecular Weight** | **Solubility** |
|---|---|---|
| Humins | $> 10^6$ | acid & alkaline insoluble |
| Humic Acid | $10^4$ $10^6$ | alkaline soluble |
| Fulvic Acid | $10^3$ $10^5$ | acid & alkaline soluble |

The presence of humic substances may promote the crystallization of aluminum oxides and iron oxyhydroxides (Pavlova and Sigg, 1988; Williams, 1990). In addition, humic acid has been shown to accelerate the breakdown of minerals such as galena and sphalerite.

# 5. LABORATORY TEST METHODS

In this chapter, existing laboratory methods, and their applicability to assessing metal release from subaqueous oxidized waste rock are discussed. A sequential extraction method is recommended as an initial screening tool for assessing the suitability of waste rock for subaqueous disposal in a range of receiving environments.

## *5.1 Summary of Existing Laboratory Methods*

Several laboratory techniques used for determining the subaqueous reactivity of tailings and waste rock have been reviewed for their applicability in assessing the release of metals from previously oxidized waste rock when placed under a water cover. These methods included shake flask/barrel roll tests, subaqueous column/tank tests and partial and sequential extraction tests.

### 5.1.1 Shake Flask Extraction Tests

Shake flask (or barrel roll) extraction tests are typically used in the initial phase of water quality prediction studies. These two tests essentially follow the same procedures, with the main difference being one of scale; barrel roll tests generally employ larger sample sizes and larger volumes of extractants than shake flask tests. Such procedures may be used to assess the short-term (days) leaching characteristics of the solid phase (*i.e.,* acidity/metal release due to dissolution). This technique provides a rapid initial screen to identify potential environmental impacts (*e.g.,* dissolved metal concentration or pH in the supernatant) associated with solid-liquid interactions.

Shake flask tests involve agitation of a solid-liquid slurry for a prescribed period of time. Supernatant water is sampled and analyzed at time zero prior to the start of the experiment and at designated intervals during the test. A suite of parameters is typically measured (*e.g.,* pH, dissolved metals, sulphate, *etc.*). There are a number of standard shake flask extraction tests which are used to provide initial predictions of dissolution rates, and in which the main variables are the nature of the extractant and the duration of the test. Some of the most commonly used extraction tests are:

- ASTM D3987 distilled water extraction;
- B.C. Special Waste Extraction Procedure (SWEP), using an acetic acid extractant;
- USEPA 1312 procedure using nitric/sulphuric acid extractant; and
- USEPA 1311 or TCLP leach test, using an acetic acid-based extractant.

Shake flask tests are most applicable for predicting dissolution products in agitated slurries. For example, a common application in mining-related environmental studies is the prediction of water quality in the supernatant fraction of a tailings slurry at the point of discharge (end of pipe). Although variables such as the solid to liquid ratio, nature of the extractant and *in situ* temperatures may be regulated to best represent field conditions, variations in environmental conditions (*e.g.*, oxic versus anoxic water column) are not simulated in these tests.

### 5.1.2 Subaqueous Column/Tank Tests

Subaqueous column or tank tests are used to predict the quality of surface water and ground water seepage from tailings/waste rock deposits. A known volume or weight of material is placed in the column or tank and covered with a solution (most commonly distilled water or site water). The overlying water is usually circulated to eliminate physical and chemical stratification in the supernatant fraction. Samples are drawn from the supernatant (representing surface water quality) and at the base of the column/tank (representing ground water quality) and analyzed for a suite of physical and chemical parameters (*e.g.*, pH, alkalinity, conductivity, sulphate and trace metals). Additional water may be added to the column/tank supernatant after sampling to simulate flushing/turnover rates at the study site (*e.g.*, in an open pit). These tests are often employed to assess the intermediate (months) to long-term (years) reactivity of sulphide-rich material under a water cover.

Data derived from subaqueous columns/tank tests provide information regarding the evolution of water quality but do not discriminate between the geochemical processes responsible for observed changes. These processes would be primarily dissolution of secondary minerals, reductive dissolution of iron and manganese oxyhydroxides and oxidation of organic matter and sulphides. For example, increases in sulphate concentrations in the column/tank supernatant could be due to oxidation of sulphides or to dissolution of sulphate minerals (*e.g.*, secondary gypsum); it is not possible to differentiate between these sources using the column/tank methods.

### 5.1.3 Partial and Sequential Extraction

In order to elucidate the solid phase partitioning of trace metals in sediment and soils, several investigators have adopted partial (Chao, 1972; Slavek and Pickering, 1986; Kheboian and Bauer, 1987; Belzile *et al.,* 1989; Bendell-Young *et al.*, 1992), and sequential extraction procedures (*e.g.,* Tessier *et al.*, 1979; 1989; 1996; Filipek *et al.*, 1981; Ribet *et al.*, 1995). Such techniques involve the leaching of sediments and soils by various extractants, and the chemical composition of the leachate is used to infer metal associations with various solid phases.

Partial extraction procedures involve the treatment of a solid sample by a single extractant to determine the metal content of specifically-targeted phases. The choice of the extractant is dependent on the phases of interest and the inherent characteristics of the various chemical reagents available *(i.e.,* degree of contamination, reaction kinetics, *etc*.). Conversely, sequential extraction procedures use a series of successive chemical treatments administered to a single sample, each being more aggressive or of a different nature than its predecessor. Various adaptations of this procedure are presently being used in several fields of research including marine and fresh water sediment studies, geochemical exploration, and soil science.

Marine and fresh water extraction methods (*e.g.,* Tessier, 1979; McKee *et al.*, 1989; Harrington *et al.*, 1998) are used to shed light on the origin, mode of occurrence, biological and physico-chemical availability, and post-depositional mobility of metals. Extractions methods in geochemical exploration (*e.g.,* Chao, 1972; Gatehouse *et al.*, 1977; Paterson *et al.*, 1993; Hall *et al.*, 1996a) are designed for application to soil, till and surficial sediment samples. The rationale behind these techniques is that ore and pathfinder elements are transported from the ore body to surface deposits where they are held in relatively labile forms. Soil science extraction methods (*e.g.,* McKeague and Day, 1965; Paterson *et al.,* 1993; Hong *et al*., 1995) are used to assess the bioavailability of metals, assess impact and remediation methods in contaminated soils, and differentiate various classes of soils.

Extraction techniques concentrate on trace metals associated with organic matter and iron and manganese oxyhydroxides, otherwise referred to as “scavenger” phases. In general, extraction procedures examine metal distribution in the following sediment/soil fractions:

- exchangeable;
- bound to carbonates or specifically adsorbed;
- bound to Mn oxides;
- bound to amorphous Fe oxides;
- bound to crystalline Fe oxides;
- bound to organic matter and sulphides; and
- trace metals typically associated with silicate minerals and residual oxides.

The extraction steps listed above are “operationally-defined" (Tessier *et al*., 1989), which means that the fractions to some degree reflect the experimental conditions employed, rather than true geochemical partitioning. Results derived from sequential extractions can therefore provide an indication of the solid phase partitioning of metals in waste rock (and by inference, environmental conditions under which the metals may be released), but may not be used to predict water quality impacts to the receiving environment.

## *5.2 Applicability to Subaqueous Waste Rock Assessment*

The present study represents the first detailed assessment of available laboratory techniques to evaluate the metal-release potential of oxidized waste rock when placed under a water cover. The main aim of the study has been to identify a laboratory method that provides initial information on how environmental conditions in the receiving water body will affect the stability of the various solid phases. It is envisaged that information derived from such tests will aid in identifying potentially problematic environmental conditions (*e.g.,* low pH), and therefore facilitate sound management decisions regarding the subaqueous disposal of oxidized waste rock on a site-specific basis.

Shake flask and column/tank tests described above provide information on release rates of metals, acidity and other constituents from subaqueous waste rock. However, as discussed above, information regarding the source of metals, processes responsible for the release of these metals and how release rates would be affected under different environmental conditions cannot be derived from such tests. Data from these tests may be used in conjunction with predicted or known information regarding the disposal scenario (*e.g.*, mass/surface area of rock, volume and residence time of the receiving water body) to make water quality impact predictions. Shake flask and column/tank tests may therefore be useful for prediction when the waste rock, the potential receiving waters and the disposal scenario have been well-defined.

The main drawback of these techniques with respect to the present study is that only metals released under the environmental conditions of the experiment are accounted for, which may result in erroneous water quality impact predictions. For example, all standard tests described in the previous section are conducted under oxic conditions. These tests do not account for metals which may be released from iron and manganese oxyhydroxides under reducing conditions (reductive dissolution). Furthermore, conditions in the receiving environment are subject to change with time due to diagenetic and seasonal influences. For example, the water column in a lake or open pit may alternate seasonally between oxia and anoxia. This has been extensively documented in several studies in basins where restricted vertical mixing during under-ice conditions results in the development of anoxic bottom waters (*e.g.*, MEND, 1994; Martin, 1996).

Partial extraction procedures will provide information on the potential release of metals from various phases under one specified environmental condition. For example, the shake flask tests described earlier are essentially partial extractions which can be used to assess the relative amounts of metals bound to selected solid phases. However, this one-step extraction procedure is best suited to determining metals bound to the most available phases (*i.e.,* water soluble and exchangeable) rather than more refractory phases such as the reducible fraction. This is because acidic and strongly-reducing extractants used to attack oxides will also extract water soluble (hydrated sulphate minerals) and acid soluble (*e.g.*, carbonates) phases within the waste rock. This extraction will therefore give a bulk estimate of metals released from water soluble, acid soluble and reducible phases, with no indication of the specific hosts(s) or the relative mobility of the released metals. Partial extractions cannot therefore provide information on the relative mobility of trace metals under a range of environmental conditions.

Sequential extraction schemes have been developed to determine the solid phase partitioning of trace metals in sediment and soils using a myriad of chemical reagents (*e.g.,* Beckett, 1989). This method may be used as a tool to determine all potentially available trace metals in oxidized waste rock that may be mobilized under a range of environmental conditions. Development of a sequential extraction scheme for assessing the relative release of metals under different environmental conditions would facilitate evaluation of the suitability of proposed receiving waters and would represent the first phase of environmental impact prediction for subaqueous disposal schemes.

The extraction methodologies used to assess phase-specific metal associations have been extensively researched by several investigators (Gatehouse *et al.*, 1977; Tessier *et al.*, 1979; Hall *et al.*, 1996a) and as a result, there is sufficient information available to recommend appropriate procedures for testing of subaqueous waste rock. In particular, existing techniques have attempted to isolate various metal fractions including water soluble, exchangeable/specifically absorbed, carbonate-hosted, reducible phases (*e.g.,* oxides and oxyhydroxides) and phases susceptible to oxidative dissolution (*viz*., organic matter and sulphide minerals). A proposed sequential extraction scheme for assessing subaqueous oxidized waste rock reactivity is presented and discussed in Chapter 6. The proposed technique is a modified version of the Tessier sequential extraction scheme (Tessier *et al.*, 1979; 1988; 1996) and would require extensive testing and validation prior to its application in assessing solid phase partitioning of elements in waste rock.

Criticisms and limitations of sequential extraction procedures are discussed in detail in the following section. The principal flaw in the proposed technique is that a small proportion of a non-targetted phase may be released in a particular extraction step due to the non-specific nature of extractants and the subsequent misinterpretation of results by researchers, as pointed out by Nirel and Morel (1990) and Pedersen (1996). In the context of the present study however, the non-specific nature of extractants is not problematic as it is the simulation of extreme environmental conditions rather than extraction of the various phases that are of primary concern. For example, differentiating between manganese oxides, crystalline iron oxides and amorphous iron oxides is often difficult due to the continuum that exists in their compositions. However, it is the metal release from all reducible phases, rather than the specific partitioning of metals between manganese and iron oxyhydroxides, that is most germane to the objectives of this study.

## *5.3 Potential Pitfalls of Sequential Extraction Procedures*

Sequential extraction schemes involve relatively laborious laboratory procedures and require a high degree of care and attention to produce meaningful and scientifically defensible results. The main criticisms of sequential extraction techniques have been:

- unrealistic physico-chemical conditions;
- non-specificity of extractants;
- lack of standard techniques;
- post extraction re-adsorption; and
- over- or misinterpretation of results.

One of the major concerns associated with the application of extraction techniques is the degree to which the method simulates natural processes. Martin *et al.,* (1987) and Nirel and Morel (1990) note that the strong reagents and fast reactions inherent to the approach differ drastically from the weak reagents and slow kinetics typically found in nature. The extreme environments inherent to the extraction technique therefore provide a worst-case estimate of trace metal release from the various fractions.

Reagents used in extraction schemes typically mobilize elements from phases other than the targeted fraction (Nirel and Morel, 1990; M$^{c}$Carty *et al.,* 1998). This is particularly true for weakly adsorbed metals (*e.g.*, calcium) which may be mobilized by low pH conditions in the test without dissolution of the associated phase (Tipping *et al.*, 1985). Thus, the extracts are termed "operationally-defined" (Tessier *et al.*, 1989), which means that the fractions to some degree reflect the experimental conditions employed, rather than true geochemical partitioning.

The amount of metal or other species extracted at each step is a complex function of the extraction reagent type and concentration, the sequence of application, temperature, exposure time, extent of re-adsorption, mineralogical composition of the solid phase and the solid to solution ratio. In addition, sequential extraction is a labour-intensive technique where careful manipulations and sample handling protocols are crucial if meaningful results are to be obtained. Standardization of techniques and full documentation of all laboratory and analytical protocols are therefore critical to facilitate defensible interpretation of results and inter-study comparisons.

Subsequent to the mobilization of metals by an extractant, strongly absorbed metals such as lead may become re-adsorbed onto other existing solid phases. For example, Tipping *et al.,* (1985) noted significant re-adsorption of lead (liberated from the "manganese oxide fraction") onto residual iron oxides due to the high pH of the extractant. Re-adsorption of trace metals at each step in the sequential process may therefore result in erroneous interpretation of the solid phase partitioning of strongly adsorbed trace metals. However, re-adsorption effects are minimized in the recommended extraction procedure (Tessier *et al.*, 1979; Belize, 1989).

There are examples in the scientific literature of the improper use of chemical extraction techniques, and these have lead to serious misinterpretations of geochemical partitioning in systems where sediments have been contaminated by mining activities. For example, Horowitz *et al.,* (1992; 1993) adopted two steps of Tessier's five-step extraction scheme without full consideration of the effect of the modification on the operationally-defined fractions. Conclusions derived by these authors regarding the partitioning of trace metals were therefore misleading, and probably wrong (Pedersen, 1996). This conclusion has been supported by recent revaluation of the Horowitz *et al.,* work (Harrington *et al*., 1998).

In summary, the scientific danger of extraction schemes lies in their indiscriminant use and in over-interpretation of the results. Sequential extraction schemes must therefore be applied with proper scientific rigour, without which, little interpretative gain can be realized. Nevertheless, sequential extraction schemes can be used pragmatically in geochemical studies if they are applied with discrimination, care, and circumspection.

# 6. *PROPOSED SEQUENTIAL EXTRACTION SCHEME*

Since the relative mobility of trace metals in subaqueous settings is dependent on the solubility of the mineral phases to which they are bound, determining the partitioning of metals between various phases is a prerequisite to establishing whether trace metals will be stable or mobilized when placed under a water cover. Based on the findings and the objective of the present study, it is proposed that a sequential extraction is the most appropriate initial screening method for evaluating the suitability of oxidized waste rock for subaqueous disposal.

The main advantage of sequential extraction over shake flask, column/tank tests and partial extractions is that a standard method can be developed to assess mobility of metals in oxidized waste rock under a range of receiving environments. This is an important consideration as temporal variations in environmental conditions in potential receiving water bodies (*e.g.*, open pit) are common. For example, under ice cover, anoxic conditions could result from the consumption of dissolved oxygen resulting from organic matter degradation and the elimination of air-water exchange. Water bodies may therefore become seasonally anoxic under ice, yet be fully oxygenated during ice-free periods. A standard method to evaluate the suitability of waste rock for subaqueous disposal must therefore provide information on metal releases associated with environmentally-sensitive phases (*i.e.,* pH and redox driven metal releases) as well as immediate impacts to water quality caused by the dissolution of water soluble phases. A sequential extraction procedure fulfills this mandate.

A conceptual sequential extraction scheme for oxidized waste rock is proposed and described in this chapter. Recommended protocols for the validation/verification of the methodology and a discussion on the interpretation of data derived from the proposed extraction test is also included.

## *6.1 Four-Step Sequential Extraction Scheme*

The proposed scheme has been based on a thorough review of recent literature on well characterized extractants (Chao, 1972; 1984; Rendell *et al.*, 1980; Beckett, 1989; Patterson *et al.*, 1993; Hall *et al.*, 1995) and sequential extraction schemes (Gatehouse *et al.*, 1997; Tessier *et al.*, 1979; 1989; Filipek *et al.*, 1981; Hall *et al.*, 1996a). The four-step scheme described in this section is a hybrid of sequential extraction procedures used in two well-established extraction schemes, in addition to a water soluble extraction. The final and last steps in the complete extraction procedure involve the determination of elemental abundances in the whole rock and residual fraction, respectively.

In designing the four-step extraction scheme, steps developed by Gwendy Hall and co-workers at the Geological Survey of Canada and André Tessier and others at the INRS-Eau, Université du Québec have been adopted. This approach yields a scientifically defensible sequential extraction scheme since all extractants, sequence of application and operational variables have been well characterized through rigorous scientific examination. Operational variables and considerations that have to be accounted for in the detailed methodological development of the scheme and recommended quality assurance/quality control (QA/QC) procedures for the validation of the proposed technique are presented in Section 6.2. Uses and application of the chemical data derived from the proposed extraction scheme in relation to the assessment of the subaqueous disposal of waste rock is discussed in Section 6.3. A schematic representation of the proposed four-step sequential extraction scheme is presented in Figure 6-1. The following are the four targeted phases (nominally identified as F1, F2, F3 and F4):

- F1: water soluble;
- F2: exchangeable/adsorbed/bound to carbonates;
- F3: total reducible; and
- F4: total oxidizable.

The first three extraction steps roughly correspond to environmental conditions that could be realized should oxidized waste rock be submerged under a water cover (*i.e.*, dilute pit water, acidic pit water and strongly reducing). The fourth extraction step (strongly oxidizing) is designed to extract trace metals associated with primary sulphides and organic

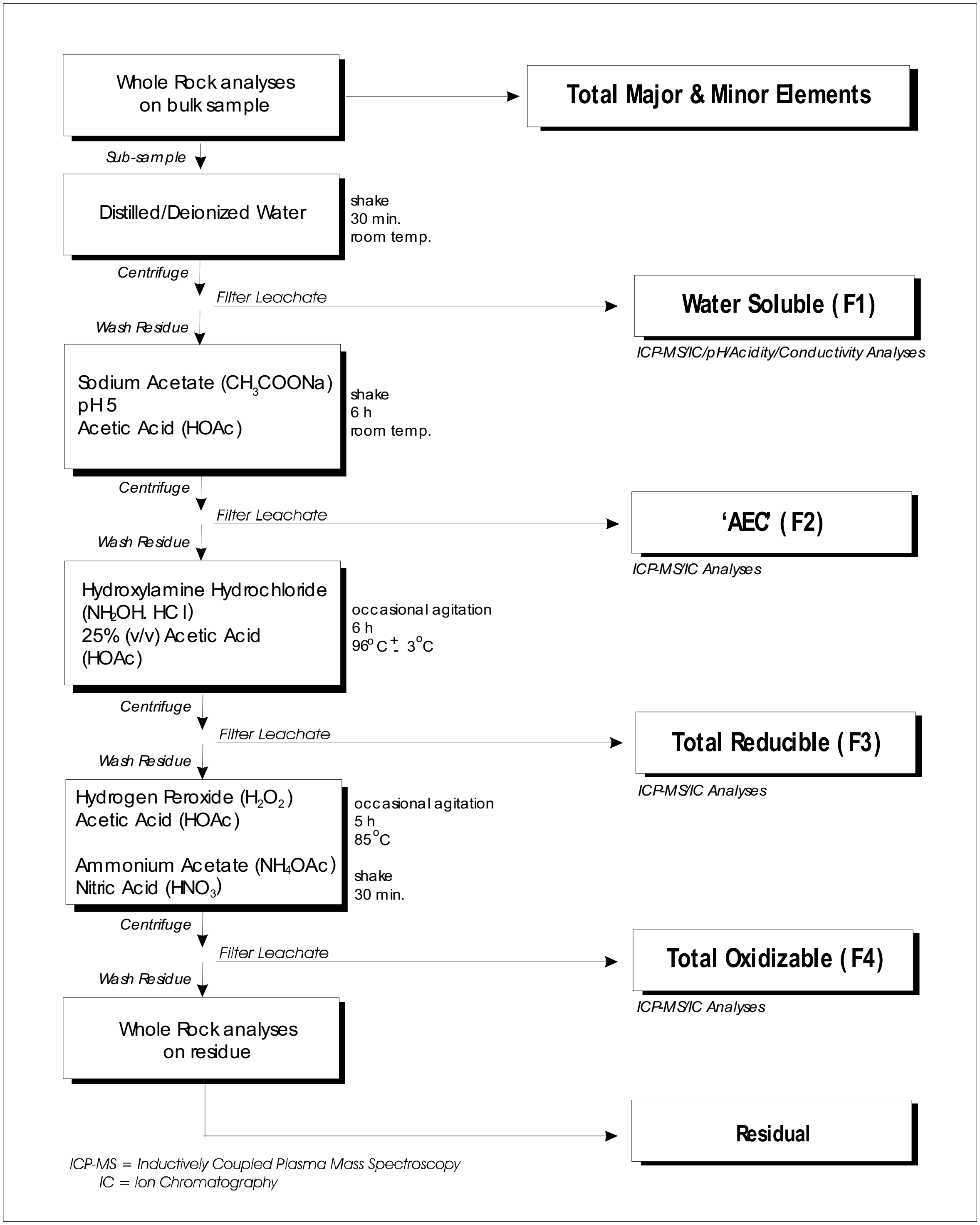

**Figure 6-1: Conceptual Sequential Extraction Scheme for**

## Oxidized Waste Rock

matter. Although it is acknowledged that metals liberated in this fraction would likely not be significant in the natural environment (due to low sulphide oxidation rates under water and relatively low organic matter content of waste rock), the data derived from this fourth step are useful in interpretation of results derived from the preceding trio of extractions (for details see Section 6.3 and Appendix D).

Each extraction is aggressive and will bring into solution most to all of the material available in each targeted phase. With the exception of the water soluble fraction (F1), direct application of the extraction results to predict water quality is not possible because the extractions do not take into account chemical reaction rates that will take place in the field. However, metal partitioning data from subsequent extraction steps (*i.e.,* F2 and F3) may be used as a tool for the initial assessment of environmental risk associated with the dissolution of pH- and redox-sensitive phases within the waste rock (Section 6.3 and Appendix D).

Although trace metal partitioning obtained from extractions is operationally-defined, the mineralogical phases that are conceptually targeted by each extraction step is outlined below.

- F1: highly soluble hydrated sulphate minerals such as melanterite and copiapite.
- F2: exchangeable ions, specifically adsorbed ions and carbonates (such as calcite, dolomite, siderite and magnesite).
- F3: amorphous and crystalline oxide and hydroxide minerals (ferrihydrite, goethite, hausmannite, and gibbsite).
- F4: metals associated with sulphide minerals and organic matter.

A description of each extraction step and the rationale for their selection are presented below. Between every step described below, the residue is to be washed using distilled/deionized water.

### *F1 Fraction*

A distilled/deionized water extraction will be conducted for the water soluble fraction. This is a classical procedure for soils (*e.g.,* Gatehouse *et al.*, 1977) and consists of a slurry (typically at a solid:liquid ratio of 1:5 by weight) vigorously shaken at room temperature for approximately 30 minutes. This fraction represents the short-term release of available metals from oxidized waste rock when placed under a water cover. The mixture would then be centrifuged and the leachate removed, filtered and analyzed for pH, alkalinity, acidity and a suite of dissolved metals and anions. The residue would be rinsed with distilled/deionized water. Significant pH depression may be associated with this step depending on the nature of the sample and may remove a significant portion of metals associated with the F2 fraction. To reduce the pH effect the liquid:solid ratio should be maximized to reduce the impingement on the F2 fraction while still ensuring that metal levels are sufficiently above analytical detection limits. For oxidized waste rock, a solid:liquid ratio of 1:10 to 1:50 by weight will likely be most appropriate.

An alternative approach that would curtail the potential impingment of the F1 on the F2 fraction is to use a buffered (at near-neutral pH) water extractant. This approach would eliminate the effect of pH variability in different types of waste rock on the partitioning of metals between the F1 and F2 fractions. The applicability of the buffered and unbuffered water extraction on waste rock should be assessed during the verification and standardization of the proposed sequential extraction scheme. If buffered water is selected as the preferred extractant of the F1 fraction, a classical water extraction (as described above) should be conducted in conjunction with the proposed sequential extraction procedure to determine the pH, alkalinity and acidity of the water soluble fraction.

### *F2 Fraction*

The F1 residue will be treated with sodium acetate ($CH_3COONa$) buffered at pH 5 for 6 hours at room temperature (20 mL of extractant for 1 g dry weight of sample). This fraction consists of metals that are exchangeable, adsorbed and bound to carbonates; called "AEC" after Hall *et al.,* (1996a). Exchangeable metals are held by predominantly electrostatic forces on negatively charged surface sites (*e.g.*, clays, organic matter, amorphous materials at high pH, *etc.*) and may be displaced by other cations. Specifically-adsorbed metals are held on sites predominantly by covalent and coordinate forces. Specifically-adsorbed metals are held more strongly than exchangeable metals, typically resulting in a slower release than the latter fraction. The low pH of this extraction will also dissolve carbonates and release metals coprecipitated with the carbonate phases in the waste rock. In addition, the acetate buffer treatment has been shown not to attack iron and manganese oxide minerals and leaves the lattice structure of silicate minerals intact (Chao, 1984). Subsequent to the prescribed reaction time, the mixture would be centrifuged and the leachate removed, filtered and analyzed for a suite of dissolved metals and anions. The residue will be rinsed with distilled/deionized water.

Although soil samples immersed in sodium acetate at pH 5 for nine weeks do not release organic carbon or iron, pH levels lower than this lead to a partial attack on iron and manganese oxides (Tessier *et al.*, 1979). These results suggest that if samples have high carbonate contents the extraction time can be lengthened to ensure that the carbonates dissolve without danger of leaching subsequent fractions. The optimal extraction time should be investigated during the verification phase. XRD studies indicate that this extraction procedure effectively removes calcite and the relatively insoluble carbonate mineral dolomite (Tessier *et al.*, 1979). However, its effectiveness in removing other carbonates such as malachite has not been documented in the primary literature.

### *F3 Fraction*

The F2 residue from the previous step will be treated with 0.5 M hydroxylamine hydrochloride ($NH_2OH{\cdot}HCl$) in 25% (v/v) acetic acid (resultant pH of 2-3) at 96°C ±3°C for 6 hours (30 mL for 1 g dry weight of sample) after Tessier *et al.*, (1989). Hydroxylamine hydrochloride is a highly reducing extractant, the efficiency of which increases with acidity and temperature. This step extracts metals bound in reducible phases including iron and manganese oxides over a wide range of crystallinity and a significant fraction of aluminum oxides (Harrison *et al.*, 1981; Hickey and Kittrick, 1984) but does not attack sulphides or organic matter (Tessier *et al.*, 1979). Subsequent to the prescribed reaction time, the mixture would be centrifuged and the leachate removed, filtered and analyzed for a suite of dissolved metals. The residue will be rinsed with distilled/deionized water.

Several reducing reagents were reviewed for their applicability to the present study and were rejected. For example, sodium dithionite-citrate is an extractant often used to leach iron and manganese oxides. However, the use of this extractant was rejected due to high levels of zinc in the reagent and trace metal precipitation as sulphides due to the disproportionation of dithionite (Chao, 1984), resulting in an underestimation of trace metals bound in reduced phases. Sulphide precipitation resulting from the disproportionation of dithionite is supported by Gupta and Chen (1975) who conducted parallel experiments with hydroxlamine hydrochloride and dithionite citrate. Their results indicated that the leachate from the latter contained significantly lower amounts of trace metals than the former, due to sulphide precipitation. In addition, the dithionite-citrate extraction does not fully dissolve hematite and goethite while iron-rich layer silicate minerals may dissolve easily (Hall *et al.*, 1996a).

Another reducing agent previously used is ammonium oxalate, commonly referred to as Tamm's reagent. The extraction method typically used was 0.175 M ammonium oxalate ($(NH_4)_2C_2O_4$) in oxalic acid in the dark at pH 3.2. However, this extraction is selective only in the absence of magnetite and organic matter (Hall *et al.*, 1996a) and this method "in the dark" is thought to be impractical if applied in a large laboratory setting.

Various published extraction schemes use HCl at concentrations up to 0.25 M to extract or dissolve adsorbed, carbonate and easily reducible phases. This concentration of acid removes significant quantities of sulphide minerals especially sphalerite and galena (Hall *et al.*, 1996a), attacks the clay mineral lattice (Van Valin and Morse, 1982) and may bring amorphous allophanic materials into solution. Correspondingly, these extraction schemes were excluded from consideration. Hall *et al.,* (1996a) state that the hydroxylamine hydrochloride extraction removes significant quantities of labile organic matter (humates and fulvates) regardless of the concentration of the reagent. Although organic matter may play a significant role in subaqueous cycling of metals it is not a major sink for metals in most subaerially-exposed waste dumps. Therefore, the non-specificity of this leach with respect to organic matter should not be a concern.

### *F 4 Fraction*

The residue from the previous step will be treated with 30% hydrogen peroxide ($H_2O_2$) adjusted to pH 2 with nitric acid and occasionally agitated at 85°C for 5 hours and then continuously agitated for 30 minutes in 3.2 M ammonium acetate ($NH_4OAc$) in 20% (v/v) nitric acid at room temperature. The addition of $NH_4OAc$ is designed to prevent the readsorption of extracted metals onto oxidized sediments. Subsequent to the prescribed reaction time, the mixture is centrifuged and the leachate is removed, filtered and analyzed for a suite of dissolved metals and anions. This step extracts metals bound to organic matter and primary sulphides. It is recognized that oxidation of organic matter and sulphides by acidified hydrogen peroxide, although extensive, is incomplete. The remaining organic matter should consist of paraffin-like material and resistant structural organic matter residues (Tessier *et al.*, 1979).

### *Initial Whole Rock/Residual Fraction Analyses*

Prior to the extraction procedure, a representative initial split of the sample will be obtained, and total carbon, nitrogen and sulphur will be determined by an elemental analyser. Two techniques have been considered as possible methods for the determination of elemental abundances within the initial and residual fractions of the proposed extraction scheme (Figure 6-1). They are X-ray fluorescence (XRF) and inductively coupled plasma mass spectrometry (ICP-MS) following total acid digestion. The techniques are fundamentally different in their approach to determining elemental abundance, and accordingly, have different advantages and disadvantages. Following is a brief discussion of each technique as it pertains to the requirements of the proposed methodology.

The main advantage of XRF is the ease and therefore the relatively low cost of sample preparation. Preparation for XRF is straight-forward and involves the fabrication of pressed-powder pellets and fused glass discs, which are analyzed directly through bombardment with X-rays. Conversely, preparation of sample for analysis by ICP-MS involves a labour-intensive total (quantitative) acid digestion. Many so-called “quantitative digestions” are in actuality, semi-quantitative. For example, the aqua-regia procedure is not capable of digesting most aluminosilicate minerals. Rather, the most effective digestion "recipes" are material-specific and involve the use of several concentrated acids under conditions of high temperature and pressure *(i.e.,* microwave digestion). The most likely combination for quantitative digestion of waste rock would include hydrochloric, nitric, hydrofluoric and boric acids. However, even under these conditions, care must be taken to ensure that digestion is complete.

Assuming quantitative acid digestion, the primary advantage of the digestion/ICP-MS method is its superior detection limits compared to XRF. Solid-phase concentrations of trace constituents are typically in the low ppm range. This presents no limitation to the ICP-MS which has detection limits many orders of magnitude below this, however, XRF detection limits for the same elements are in the low ppm range. Thus, the primary disadvantage of XRF arises for some elements where the instrument is insufficiently sensitive to differentiate changes in concentration from analytical noise.

It is recommended that as part of the validation/verification of the proposed extraction scheme, XRF and acid digestion/ICP-MS methods be evaluated for their applicability to determining the solid phase elemental abundance in waste rock prior to and at the end of the extraction scheme. Should detection limits achieved by XRF be sufficient to determine variations in trace elements before and after the extraction, this more cost-effective method should be adopted. However, if XRF detection limits are insufficient to resolve minor concentration changes, which prove to be critical to the interpretation of the sequential extraction results, the more labour-intensive quantitative acid digestion/ICP-MS should be used to determine solid phase element abundances.

*Leachate Analyses*

Since the proposed extraction scheme represents the first assessment of the solid phase partitioning of metals in oxidized waste rock, a full assessment of all metals and major anions liberated in the various extraction fractions is desirable. For this reason, it is proposed that the leachates from the proposed four-step sequential extraction procedure be analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC). The ICP-MS and IC analyses provide data on a comprehensive suite of elements with low detection limits (Table 6-1). The IC provides data on major anions in the leachate at sub-ppm detection levels (Table 6-1). Dilution of the leachates will however be necessary prior to ICP-MS and IC analyses as the high ionic strength matrix of the undiluted F2, F3 and F4 fractions may not be suitable for these analytical instruments.

The conceptual extraction scheme outlined above needs detailed development and validation prior to use. Although some operational parameters (*e.g.*, extract concentration, extraction time, *etc*.) have been suggested in this section as a “starting point” for the proposed extraction scheme, the final extract concentrations, time of extraction, sample handling procedures and a host of other operational variables need to be defined in the context of oxidized waste rock samples. Detailed development of the waste rock sequential extraction method and resulting standardization are critical to interpreting the data generated and in facilitating inter-study comparisons. Key operational variables and proposed testing and validation protocols for the conceptual sequential extraction scheme are outlined in the following section.

## *6.2 Development and Validation of the Proposed Extraction Procedure*

The basic requirement for an extraction procedure is the selective extraction of specific weathering products. However, different media contain different weathering products and/or different proportions of the various phases. Due to the operationally-defined nature of the extraction procedures, a technique that provides an accurate picture of the partitioning in one type of sample (*e.g.,* sediment) may not be effective in another (*i.e.,* waste rock). As noted above, although various extraction techniques have been devised to investigate the association of trace metals in many different media including soils, marine sediments and lake sediments, no well-characterized extraction procedure has been developed to date and tested for oxidized waste rock.

The proposed extraction scheme has been selected because it has been well characterized on sediment and soil samples by previous workers, uses clean reagents and the procedure minimizes post-extraction reactions such as readsorption onto residual phases. However, soil and sediment samples do not contain minerals that may be present in oxidized waste rock such as malachite or schwertmannite and they typically contain significantly lower concentrations of iron hydroxides. Therefore, the effectiveness of the extraction technique has not been established for waste rock and must be verified.

**Table 6-1:**
**ICP-MS and IC Analytes and Analytical Detection Limits**

| ***ICP-MS*** | ***Units*** | ***Detection Limit*** |
|---|---|---|
| Aluminum | µg/L | 1 |
| Antimony | µg/L | 0.05 |
| Arsenic | µg/L | 1 |
| Barium | µg/L | 0.05 |
| Beryllium | µg/L | 0.5 |
| Bismuth | µg/L | 0.5 |
| Boron | µg/L | 1 |
| Cadmium | µg/L | 0.05 |
| Calcium | µg/L | 50 |
| Chromium | µg/L | 0.5 |
| Cobalt | µg/L | 0.1 |
| Copper | µg/L | 0.1 |
| Iron | µg/L | 10 |
| Lead | µg/L | 0.05 |
| Lithium | µg/L | 1 |
| Magnesium | µg/L | 50 |
| Manganese | µg/L | 0.05 |
| Molybdenum | µg/L | 0.05 |
| Nickel | µg/L | 0.1 |
| Phosphate | µg/L | 300 |
| Potassium | µg/L | 2000 |
| Selenium | µg/L | 1 |
| Silicon | µg/L | 50 |
| Silver | µg/L | 0.01 |
| Sodium | µg/L | 2000 |
| Strontium | µg/L | 0.1 |
| Thallium | µg/L | 0.05 |
| Tin | µg/L | 0.1 |
| Titanium | µg/L | 10 |
| Uranium | µg/L | 0.01 |
| Vanadium | µg/L | 1 |
| Zinc | µg/L | 1 |
| ***IC*** | ***Units*** | ***Detection Limits*** |

| | | |
|---|---|---|
| Nitrate | mg/L | 0.01 |
| Phosphate | mg/L | 0.01 |
| Sulphate | mg/L | 0.1 |
| Chloride | mg/L | 0.05 |

Key consideration during such development and evaluation of the proposed scheme are:

- sample particle size;
- solid:liquid ratio;
- suitability of chemical reagents;
- sample and leachate handling procedures;
- extraction efficiency;
- precision and reproducibility; and
- waste rock variability.

Waste rock is typified by a wide range of particle sizes (ranging from less than 10 microns to several metres in diameter). The increasing surface area to volume ratio with decreasing particle size is expected to result in a higher proportion of secondary oxidation products in the fine fraction. Consequently, the compositional variability of oxidized waste rock with particle size necessitates the use of well-defined particle size fractions in the evaluation of the proposed extraction scheme. It is proposed that the “fine fraction”, defined here as particle size less than 177 $\mu$m (80 mesh), be initially used for the development and validation of the proposed scheme. Subsequently, a range of grain sizes up to 2 cm should be used to establish the relationship between waste rock particle size and chemistry of the various extracted fractions. Compared to larger oxidized waste rock particles, the fine fraction will host greater amounts of secondary minerals (due to the higher surface area to volume ratio) to which available trace metals may be bound, making it particularly well-suited to the evaluation of the proposed technique.

The solid (fine fraction of oxidized waste rock) to liquid (extractant) ratio is a critical variable in designing the waste rock extraction test. The ratio must be high enough to result in measurable changes in the chemical composition of the leachate. The solid:liquid ratio is particularly critical in the F1 fraction due to potential pH depression and impingement on the F2 fractions. However, the ratio must also be low enough so as to not produce chemical equilibria restrictions (*i.e.*, saturation of the leachate) on the solubility of metal-bearing phases in the sample. Initially, it is proposed that the solid:liquid ratios be those specified in previous studies (Tessier *et al*., 1979; Hall *et al*., 1996a). However, modifications to these ratios may be incorporated during the development of the detailed experimental protocols.

In order to avoid contamination from impure chemicals, analytical grade reagents and ultra-pure Seastar™ acids should be used in the extraction procedure. It is recommended that a method blank (reagents only) be run through the complete proposed extraction scheme to determine trace element and anion concentrations in the test reagents and assess whether contamination is occurring during the procedure. If the data from the blank run show high concentrations of trace elements, reagents should be cleaned prior to use in the extraction procedure. For example, sodium acetate (F2 extractant) may be cleaned of trace metals by passing through a Chelex 100 column (Hall *et al.*, 1996a).

The fine fraction of the waste rock should be separated by dry sieving (80 mesh). It is recommended that the extractions and subsequent washing and centrifugation be conducted in acid-washed Teflon or polypropylene centrifuge tubes. Extreme care must be taken during centrifugation and washing of the sample and filtering of the leachate to avoid sample loss and contamination. In some previous studies of sequential extraction methods, loss of elements such as manganese and compounds such as organic matter have been observed during sample washing in between the various extraction steps (Bendall-Young *et al.,* 1992). However, it has been demonstrated that careful sample manipulation during the washing stage (*i.e.,* minimize readsorption and suspended material in the decant which is discarded after centrifugation) will result in negligible loss of constituents during the washing stages (Belzile, 1989; Piper and Wadless, 1992; Hall *et al.*, 1996a; Hall and Pelchat, 1998).

The efficiency of each proposed extraction step in mobilizing trace elements and anions must be assessed. This should be done by running an experiment in which each extraction is conducted twice on one sample or by assessing the continued release of metals over an extended period of time. Trace metal and major anion data from the second leachate may be used to re-evaluate the extraction conditions (*i.e.,* duration, temperature, reagent strength *etc.*). The experimental conditions under which the fractions are extracted (*i.e.,* temperature or reagent strength) in the proposed sequential extraction procedure may therefore be modified based on the findings of the extraction efficiency experiments.

The precision and reproducibility of the proposed extraction scheme must be assessed through a rigorous QA/QC procedure during the validation of the methodology. A minimum of four replicate extractions must be conducted on certified reference materials and waste rock samples to facilitate a statistical assessment of the precision and reproducibility of each extraction step.

Laboratory experiments designed to optimize the solid:liquid ratio, extraction efficiency and to assess the precision of the proposed extraction method should be conducted on waste rock with a range of compositions (*i.e*., various degrees of oxidation). This will aid in developing a standard extraction procedure that can be applied to all types of waste rock, irrespective of the degree of oxidation and their primary mineralogy.

## *6.3 Uses and Application of Sequential Extraction Data*

The use of sequential extraction testwork to assess subaqueous stability of oxidized waste rock is comparable to the use of the common acid base accounting (ABA) methods for assessing the acid generating characteristics of subaerially-exposed waste rock. However, the proposed extraction is more powerful because it provides data on the elemental associations which are lacking in ABA testing. Chemical data derived from the proposed sequential extraction scheme subsequent to its validation will facilitate quantitative prediction of immediate water quality impacts, as well as a qualitative evaluation of pH- and redox-sensitive phases and their metal-release potential. Similar to ABA testing, kinetic studies may be required subsequent to the initial extraction testwork to assess metal release rates from the pH- and redox-sensitive phases if significant amounts of metals have been identified in the F2 and F3 fractions.

The first and most important use of the sequential extraction data is a relative assessment of the potential impacts associated with metal release from each fraction. The total extractable metal content (the sum of all four fractions) can be contrasted with the metal content from each individual fraction to assess the relative risk (metal release) associated with each fraction. The "total available metals" per unit of submerged waste rock can be determined from the sum of the first three fractions. The relative environmental risk associated with metal release can then be assessed to assist regulating government agencies and mine operators to determine:

- if kinetic testing is required and the most appropriate kinetic test method;
- the most appropriate disposal method; and
- additional treatment requirements or contingencies.

As discussed previously, metals bound to the primary sulphides and organic matter (metals in the F4 fraction) are unlikely to be environmentally significant when waste rock is placed under a water cover. However, data from the F4 fraction will allow the available metals data from the first three steps of the sequential extraction to be expressed as a ratio to the metals bound to the unoxidized sulphides. In this way, concentrations of available metals bound to the various fractions (*i.e.*, F1, F2 and F3) can be normalized to their precursor sulphide content. This is an important consideration since the degree of waste rock oxidation influences the relative partitioning of metals between the precursor sulphides and the secondary minerals extracted during the first three steps of the proposed extraction procedure. For example, should the extraction results show that 95% of the metals are associated with the F4 fraction, a significantly greater risk of metals release and treatment costs would be expected for subaerial storage than with subaqueous disposal. Appendix D provides two examples of how to present and interpret the data derived from the extractions.

A flow chart showing the uses of the sequential extraction data in the decision making process pertaining to subaerial versus subaqueous storage of oxidized waste rock is presented in Figure 6-2. In reviewing data from the sequential extractions, should a high percentage of metals be associated with the F1 fraction, impacts to the water cover can be assessed from the results of the F1 leachate. The mass of each metal released combined with water cover volume at the disposal site can be used to estimate increases in metal concentrations in the water cover. In addition, acidity stored in soluble oxidation products and residual moisture can be quantified to determine lime treatment requirements. However, to provide an accurate assessment, the overall particle surface area in the dump must be characterized.

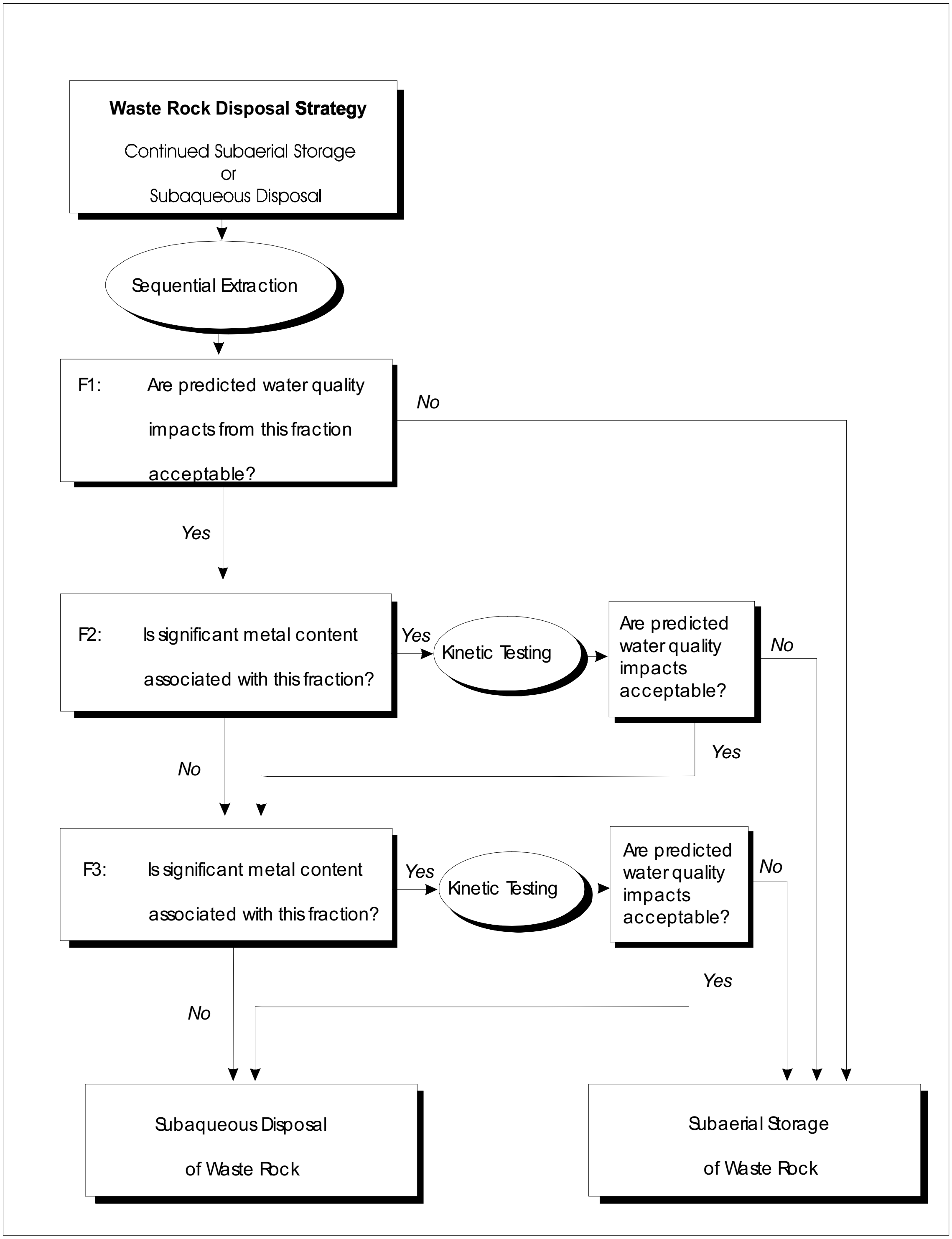

**Figure 6-2: The Use of Sequential Extraction Results to Determine Appropriate Waste Rock Disposal Strategies**

Oxidation products are typically amorphous or finely crystalline and will be concentrated in the fine grain size fractions in waste rock. Hence, to extrapolate the extraction results to make predictions of water chemistry, sample particle size and the overall particle size distribution in the waste rock dump must be characterized.

As shown by the flow chart (Figure 6-2), the mass of metals (expressed as a percentage of available metals) associated with the F2 and F3 fractions can be compared to the metals bound to the F1 fraction to determine their relative impact on water quality. For example, if 80% of available metals are bound in the F1 fraction and this fraction is shown to have no discernible impact on water quality, the release of metals from the F2 and F3 fractions, containing 10% of available metals each, would also result in no significant impacts. Alternatively, if the mass of metals bound to the F2 and F3 fraction is significant with respect to the F1 fraction, site-specific kinetic tests should be developed to predict water quality impacts from these environmentally sensitive phases.

The results of the extractions can also be used to assess relative oxidation zonation in a dump. When combined with a methodical sampling program, the extraction results can quantify the risk of metal release associated with highly oxidized, transition and anoxic zones in a waste rock dump. Zonation depths in a dump may vary significantly depending on variable oxygen and water penetration (discussed in Chapter 2). Trenches excavated in a waste rock dump often reveal readily visible zonation. Tabulation of the zone depths and extent can be used to quantify the volume of waste associated with each oxidation zone. These data combined with the extraction results should yield an indication of the total metal mass susceptible to release under the varying environmental conditions targeted by the extraction procedure. These data can assist in the calculation of sludge volumes and associated treatment and storage costs.

An alternative use of the extraction results that may be extremely effective in the future is the combined use of extractions, mineralogical studies and geochemical modelling. Dissolution rates and themodynamic data for many of the minerals commonly found in oxidized waste rock dumps is presently limited. However, this is an area of active research and it is envisaged that sufficient empirical data may soon be available to construct models that will use kinetically-controlled dissolution of secondary minerals (using sequential extraction data as input) to predict water quality impacts.

The proposed sequential extraction method therefore provides a powerful tool to assess metal-phase associations in waste rock when other sophisticated methods (*e.g.,* SEM, XRD *etc.*) become too expensive and time consuming due to the fine grained/amorphous nature of the secondary minerals. Although the extraction alone cannot predict quantitative water quality impacts due to kinetic controls on mineral dissolution, when combined with kinetic or *in-situ* testing it can be an effective tool with which to assess environmental risk associated with the subaqueous disposal of oxidized waste rock.

# 7. CONCLUSIONS

The most salient conclusions of MEND project 2.36.3 are listed below:

1. The extent of oxidation is spatially variable in a subaerial waste rock dump; hence the distribution of weathering products is heterogeneous.

2. The climate and physical characteristics of a waste rock dump indirectly control the formation of secondary minerals by regulating the intensity of various physico-chemical conditions such as pH, temperature, dump hydrology and mineral weathering.

3. There are various physical controls on the magnitude of impact on water quality. Physical controls on the short-term impact may vary with the method employed to submerge the waste (*e.g.,* end dumping or flooding). Long-term impact may be increased due to turbulent diffusion in the water cover or high advective flow through the waste.

4. An indication of which elements will be retained as major or minor components of secondary minerals in oxidized waste rock can be obtained by determining the elements associated with various types of ore deposits and their relative mobilities. The mineralogical form taken by metal precipitates can be predicted or inferred from site-specific physico-chemical conditions.

5. Iron and sulphate secondary minerals are common in all oxidized waste rock dumps and exert a major control on the mobility of other less abundant elements.

6. Surface area, crystallinity, temperature, thermodynamic properties and kinetic properties of a secondary mineral control its subaqueous stability.

7. Water soluble precipitates found in waste rock dumps are typically hydrated sulphate minerals. Carbonate minerals and adsorbed cations are soluble in acidic solutions. Mature oxyhydroxide and sulphate minerals are typically insoluble in oxic waters but are susceptible to reductive dissolution. If sulphate reduction is

induced by the oxidation of organic matter the sulphur and metals released may reprecipitate as sulphide minerals.

8. Shake flask, column and tank tests have been used to determine the subaqueous stability of oxidation products. However, they do not discriminate between the geochemical processes or mineral phases responsible for the release of metals to solution.

9. Partial extraction tests are limited to simulating one environmental condition and are extremely non-selective which can lead to misinterpretation of the results.

10. Sequential extraction tests are the most appropriate initial screening tool to evaluate metal release from subaqueous waste rock.

11. Sequential extraction test results can be used to evaluate the subaqueous metal release potential of oxidized waste rock under a range of extreme environmental conditions.

12. A four step sequential extraction scheme is proposed to examine metal partitioning in oxidized waste rock by targeting the following four phases:

    - F1: water soluble (*e.g.,* hydrated sulphates);
    - F2: exchangeable/adsorbed/bound to carbonates;
    - F3: total reducible (*e.g.,* oxyhydroxides); and
    - F4: total oxidizable (*e.g.,* sulphides and organic matter).

    The initial whole rock elemental composition would be determined on a sample split. The residual solid phase would also be analyzed for its major and minor element composition subsequent to conducting the extraction procedure. Determination of whole rock elemental abundances in the initial and residual solids is critical for the interpretation of results from the proposed sequential extraction procedure.

13. Sequential extractions are "operationally defined", therefore an extraction procedure that provides an accurate representation of metal partitioning in one type of sample

(*i.e.*, soil) may not be effective in another (*i.e.*, waste rock). Thus, prior to utilizing sequential extractions directly for assessing metal release from oxidized waste rock, verification and validation of the proposed procedure is required.

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# APPENDIX A

## ELEMENT GEOCHEMISTRY & SECONDARY MINERAL FORMATION

The geochemical behaviors of magnesium, calcium, aluminum, silicon, manganese, copper, lead, cobalt, nickel, zinc, cadmium, chromium, titanium, vanadium, molybdenum, tungsten, barium, silver, bismuth, antimony, arsenic, selenium, tellurium and mercury are summarized below. In addition to iron and sulphur discussed in Chapter 3, these elements may be released from oxidizing sulphide minerals in a waste rock pile and may form essential or significant components of the secondary minerals.

*Magnesium, Calcium, Potassium and Sodium*

Magnesium and calcium are often essential components of major rock forming minerals. These elements have low ionic potentials, are highly soluble, and are therefore readily leached from waste rock under acidic conditions. Gypsum ($CaSO_4 \cdot 2H_2O$) is a common secondary sulphate mineral, and is typically the major control on aqueous calcium concentrations in mine drainage (see Section 3.2.2). Epsomite ($MgSO_4 \cdot 7H_2O$) and hexahydrite ($MgSO_4 \cdot 6H_2O$) may act as sinks for magnesium in waste rock containing abundant dolomite (Jambor, 1994). In alkaline conditions double-salt minerals are preferentially stabilized; calcium hydroxide may also crystallize under hyperalkaline conditions. In addition, magnesium may be incorporated directly into the hydroxide mineral structures. Up to 0.9 mol% magnesium for iron replacement in goethite has been documented (Bobkovskii and Yalovoi, 1987).

Major sources of potassium and sodium are the alkali feldspar minerals. Potassium is abundant in biotite and its release is pH dependent. The release rate would likely be high and variable in the unsaturated zone. Major sinks for sodium and potassium are phyllosilicate minerals, or under extreme acidic conditions, sulphate minerals from the alunite and jarosite groups.

*Aluminum*

Aluminum is a major constituent in most primary rock forming minerals. As such, its geochemical behavior may play an important role in the cycling of metals in certain situations. In particular, scaveging of metal ions by freshly precipitated aluminum oxides may provide a significant control on metal mobility in waste rock.

Aluminum may be released from weathered aluminosilicate minerals such as biotite or amphiboles and, to a lesser extent, from more resistant minerals such as muscovite and feldspar. Aluiminum is often retained in clay minerals, which are typical alteration products of aluminosilicate minerals. However, aluminum is soluble at extreme pH levels. Below pH 5, $Al^{3+}$ is the major species in solution and aluminum sulphate mineral precipitation controls the aqueous aluminum concentration. Above pH 9, the aqueous species $Al(OH)_4$ predominates. Between these two extremes aluminum is relatively insoluble and the aqueous aluminum concentrations are dictated by the kinetic controls of diaspore ($AlO(OH)$) and gibbsite ($Al(OH)_3$) formation (Nordstrom and Ball, 1986; Karlsson *et al*., 1988).

Various clay minerals resulting from the weathering of aluminosilicates have been identified in oxidized tailings impoundments including vermiculite, smectite and kaolinite (Jambor, 1994). However, the intensity and length of the weathering process will limit the extent of clay mineral formation in relatively immature waste rock dumps. The ability of clay minerals to adsorb cations at circum-neutral pH is well documented. This process may immobilize many metals in subaerially exposed dumps or subsequently if the rock is submerged. Similarly, aluminum hydroxides may provide a sink for various ionic complexes. Pavola & Sigg (1988) indicate that freshly precipitated aluminum oxides effectively remove Zn, Cu, Pb and Cd from solution. However, aqueous Co and Ni concentrations were not affected by aluminum oxide precipitation.

The minerals jurbanite ($Al(SO_4)(OH)^{\cdot}5H_2O$), basaluminite ($Al_4(SO_4)(OH)_{10}{}^{\cdot}H_2O$) and amorphous basaluminte are typically observed in mine drainage where an acidic stream ($pH < 5$) is mixed with a buffered stream producing a solution having a $pH > 5$.

However, non-aluminum bearing components in a solution alter the relative stability of secondary aluminum minerals by inhibiting precipitation and recrystallization pathways. For example, the presence of fulvic acid at moderate and high pH prevents the nucleation of aluminum hydroxides (Williams, 1990; Karlsson *et al*., 1988). Also high ionic strength, high sulphate concentration, and low pH may favor aluminum precipitation in the form of alunite ($KAl_3(SO_4)_2(OH)_6$). However, kinetic controls on the precipitation of alunite may restrict its widespread production as a weathering product (Davis *et al*., 1991; Alpers, 1994).

Aluminum may be adsorbed onto iron oxyhydroxides and subsequently released into solution at pH values less than 6.8 (Davis *et al.,* 1991). Aluminum has been observed to substitute in goethite and hematite to a maximum concentration of 33 mole% AlO(OH) and 14 mole% $Al_2O_3$, respectively. However, substantial aluminum substitution into iron oxide minerals has not been directly observed in mine drainage waters (Alpers *et al*., 1994).

*Silicon*

Primary quartz is relatively insoluble and its dissolution will contribute only a minor amount to available silica in the relatively short flow paths through waste rock. However, dissolution of other silicate minerals proceeds under acidic conditions. Soluble silica in gossan deposits often precipitates as an amorphous silica gel or quartz. Precipitation of silica is relatively insensitive to pH and will precipitate over a wide pH range. Silicon also occurs as highly stable secondary ore minerals such as chrysocolla (an amorphous hydrated copper silicate) commonly found in copper gossans and hemimorphite (a hydrous zinc silicate) present in some zinc gossans under strongly neutralizing conditions.

Silicon has been observed to be associated with or forms goethite, clay minerals and cristobalite. Silicon released during weathering is often homogeneously associated with goethite in significant amounts. The association between the two is a spatial relationship rather than structural incorporation. The implications of this relationship on goethite stability are not fully understood. Silicon may also be retained in residual clay minerals such as vermiculite, kaolinite or smectite. Formation of the secondary silicon mineral cristobalite ($SiO_2$) has also been documented in oxidized tailings impoundments.

### *Manganese*

Manganese is not a major component of sulphide assemblages but may be released from primary silicate minerals such as pyroxenes, amphiboles, garnets, biotite, chlorite or epidote where it is present as Mn(II). The formation of secondary manganese oxides is not expected to be as abundant in waste rock as iron oxides. However, if formed, manganese oxides are still significant due to their ability to “scavenge” metal ions. Characteristics of manganese oxides include fine-grain size, poor crystallinity and black color.

The geochemistry of manganese oxides is much more complex then iron oxides due to the numerous valance states possible for manganese. The $Mn^{2+}$ valence is often observed in the early stages of gossan formation, when it is quite soluble. $Mn^{3+}$ and $Mn^{4+}$ oxides and hydroxides precipitate at higher oxidation potentials, and high pH values. Manganese oxides are typically associated with high quantities of barium, cobalt, copper and lead. In mine drainage waters, the mixed valence mineral hausmannite ($Mn_3O_4$) or feitknechtite.

($\beta$-MnOOH) are the first phases formed. These phases age to manganite ($\gamma$-MnOOH) over a period of several months or manganite may precipitate directly in the presence of sulphate (Davis *et al.,* 1991). These forms may be expected in waste rock under high pH and Eh conditions. The most common manganese oxides in soils are birnessite ($\delta$-$MnO_2$) and lithiophorite $(Al,Li)MnO_2(OH)_2$ (Nickel and Daniels, 1985).

### *Copper*

Chalcopyrite and bornite, typical primary copper sulphide minerals, may break down to form iron oxide and an acidic solution of cupric sulphate, according to the reaction:

$$2CuFeS_2 + 8.5O_2 + 2H_2O \rightarrow Fe_2O_3 + 2Cu^{2+} + 4SO_4^{2-} + 4H^+$$

The acid generated in these reactions or by iron sulphide oxidation may keep copper in solution and transport it away from the reaction site.

Selective formation of copper sulphate minerals could result from variations in pH and sulphate ion activities. Antlerite ($Cu_3SO_4(OH)_4$) would be expected to be favored over brochantite ($Cu_4SO_4(OH)_6$) under acidic conditions, and its presence in oxide zones in arid desert environments supports these relationships (Williams, 1990). Calcanthite ($CuSO_4 \cdot 5H_2O$) is another secondary mineral that may form from solutions rich in copper but only at high sulphate concentrations and low pH values. Chalcoalumite ($CuAl_4SO_4(OH)_{12} \cdot 3H_2O$) has been observed associated with hydrated iron minerals and aluminum hydroxide in surface pools.

The most widespread secondary copper mineral associated with ore deposits is the double salt malachite ($Cu_2CO_3(OH)_2$). Malachite and broncantite form at near neutral pH. Malachite is formed preferentially over the copper oxide tenorite (CuO) in solutions containing carbonate alkalinity. Malachite is significantly less soluble than calcium carbonate minerals and is frequently retained in surface gossans. In solutions with high copper concentrations and extremely high $pCO_2$, which may be observed in dehydrating systems, the formation of azurite ($Cu_3(CO_3)_2(OH)_2$) may be favored over malachite (Williams, 1990; Guilbert and Park, 1986). Broncanthite in addition to malachite has been observed forming in waste piles in coastal British Columbia (Kwong & Ferguson 1990).

Copper ions may also be removed from solution through replacement reactions on sulphide mineral surfaces. Replacement of metals in sulphides is favoured when the reactant sulphide mineral is more soluble than the product mineral and the $K_{sp}$ of CuS is lower than Fe, Zn, Pb and Cd sulphides. Covellite (CuS) precipitation at the surface iron sulphides may be a mechanism responsible for relatively high Cu abundance on the surface of pyrite in the oxic zone (Al *et al.*, 1997).

### *Lead*

Lead is released into solution as a result of the weathering of galena (PbS) or lead-containing sulphosalts. Lead is relatively insoluble in natural waters, but may have significant solubility at low and high levels of pH due to the formation of soluble complexes with sulphate, carbonate, chloride and hydroxyl ions. The major lead secondary minerals anglesite and cerussite are both relatively stable. Under moderately acidic pH conditions lead readily precipitates as anglesite ($PbSO_4$). Anglesite is formed when high concentrations of $Pb^{2+}$ ions are released into sulphate containing solutions and thermodynamic equilibrium models suggests that its precipitation controls maximum lead concentrations observed in leachate collected from waste rock column experiments (Li and St-Arnaud, 1997). Anglesite becomes more stable at circum-neutral conditions when the mineralizing solution contains high sulphate concentrations. At circum-neutral conditions, cerussite ($PbCO_3$) or hydrocerussite $Pb_3(CO_3)_2(OH)_2$ are likely to form. Aqueous lead is also adsorbed to hydroxide minerals and is most strongly attenuated at lower pH (3.1 - 6.5) than other metal cations.

### *Cobalt and Nickel*

Nickel and cobalt may be contained in the pyrite and pyrrhotite structure. When present, they are soluble and are most readily released at low pH and may be depleted in acidic waste rock. At intermediate to high pH, however, they are increasingly adsorbed by iron oxides such as goethite (Blowes and Jambor, 1990). Secondary minerals are readily precipitated at higher pH values, but these tend to be dissolved during subsequent weathering and are rarely found in surface gossans.

Cobalt has a special affinity for manganese and enrichments are commonly found in precipitates of manganese oxides. Cobalt forms asbolan (mixtures of Mn oxide and other phases), grading into heterogenite (CoOOH) which typically incorporates nickel in its structure. These forms have been observed resulting from the weathering of cobalt-nickel sulphide ores and mafic rocks rich in cobalt and nickel.

The formation of distinct secondary nickel-bearing minerals in sulphate-rich mine drainage has not yet been documented. The most common secondary nickel mineral in gossan deposits is the sulphide mineral violarite ($Ni_2FeS_4$). Other nickel minerals that form in the weathering environment include the sulphate minerals morenosite ($NiSO_4 \cdot 7H_2O$), regersite ($NiSO_4 \cdot 6H_2O$) and nickel-hexahydrite. Although no discrete nickel hydroxide has been observed in oxidized mine waste, in the lab three oxide minerals have been characterized: bunsenite (NiO), theophrastite ($Ni(OH)_2$), and jamborite $(Ni,Fe)(OH)_2(OH,S,H_2O)$. The majority of nickel that is retained in oxidizing mine waste is believed to be adsorbed/co-precipitated with goethite and minor amounts being taken up by phyllosillicate minerals and possibly violarite precipitation. Cornell (1991) has observed coprecipitation of nickel in freshly precipitated goethite.

### *Zinc and Cadmium*

The behavior of zinc is generally similar to that of nickel and cobalt, being very soluble at low pH. Zinc is generally not retained in gossan deposits and is a relatively mobile metal (Andrew, 1984). However, zinc may co-precipitate or adsorb with iron oxides at pH values greater than 5.5 (Blowes and Jambor, 1990) or be attenuated on the surface of pyrite grains (Al *et al*., 1997). Zinc may also co-precipitate with other secondary minerals such as ferrous sulphates. Up to 2.5% zinc has been documented in goethite formed in gossans and appreciable zinc contents have also been reported in a variety of secondary minerals in gossan (Nickel and Daniels, 1985).

Secondary zinc minerals, such as the carbonates smithsonite ($ZnCO_3$), hydrozincite ($Zn_5(CO_3)_2(OH)_6$) and hemimorphite ($Zn_4Si_2O_7(OH)_2 \cdot H_2O$) are readily precipitated at neutral and higher pH but will be retained only in arid conditions (Guilbert and Park, 1986). Of the zinc carbonates, hydrozincite is likely to be the most common found in oxidized portions of waste rock dumps. Zinc hydroxides ($Zn(OH)_2$) may form as intermediate products, however, the most common secondary zinc(II) minerals in gossan deposits are the double salts. Goslarite ($ZnSO_4 \cdot 7H_2O$) is a soluble sulphate mineral that has been observed to form in shallow portions of oxidized tailings profiles.

The zinc sulphide mineral sphalerite typically contains cadmium which may be released when the mineral oxidizes. Cadmium is geochemically similar to zinc, but is more soluble at higher pH values. Secondary cadmium minerals which may form include otavite ($CdCO_3$) or amorphous cadmium hydroxide ($Cd(OH)_2$). Cadmium may also be retained on the surface of sulphide minerals or oxyhydroxides in a similar pH range as zinc.

### *Chromium, Titanium and Vanadium*

Chromium in nickel sulphide deposits commonly occurs as chromite, which is resistant to weathering, and can often be found as residual grains in nickel gossans. Significant quantities of chromium may also be present in magnetite. Titanium, which is not necessarily associated with sulphide deposits, usually occurs as ilmenite or rutile, both of which are resistant to weathering, and therefore retained as residual minerals. In silicate minerals, chromium, titanium and vanadium are frequently present as minor constituents. When such minerals decompose during weathering, these elements are released into solution where they are rapidly oxidized to their higher oxidation states. In this form they hydrolyze readily, and may be precipitated with the iron oxides (Nickel and Daniels, 1985). Chemical equilibrium modeling in tailings pore waters suggests that amorphous $Cr(OH)_3$ may control chromium concentrations in this environment (Blowes and Jambor, 1990). Vanadium and chromium may also occur as secondary minerals in combination with ore-forming elements, most notably lead and copper.

### *Molybdenum and Tungsten*

Molybdenite ($MoS_2$), is a common constituent of porphyry copper deposits and, to a lesser extent, of polymetallic sulphide deposits. Molybdenum is also contained as an impurity in sphalerite which upon weathering, may be released into solution and is often observed hydrolyzed at the base of the weathering zone in gossan deposits as the sulphur-yellow secondary mineral, ferrimolybdite ($Fe_2(MoO_4)_3 \cdot 15H_2O$).

Tungsten is not generally associated with sulphide deposits. The primary tungsten minerals are scheelite and wolframite, both of which are resistant to weathering, and are retained in secondary mineral assemblages. Although molybdenum and tungsten have similar geochemical weathering behavior, molybdenum is the more soluble of the two.

### *Barium*

This element occurs primarily in the form of barite ($BaSO_4$). Some polymetallic sulphide deposits of the Kuroko type contain barite as a primary mineral. Barite is resistant to weathering and is generally retained in gossans as a residual primary mineral (Andrew, 1984). Barium is also a common minor constituent of feldspars that upon weathering release barium into solution. However, reported occurrences of secondary barite in gossan deposits are limited which suggest that it is unlikely to form in oxidizing waste rock.

### *Silver*

This element is often a minor constituent of polymetallic sulphide deposits as the silver sulphide mineral acanthite or as silver sulphosalts. Silver behaves like copper under oxidizing conditions except that it has fewer stable oxidation products. In gossan deposits native silver is common which forms as a result of the reduction of $Ag^+$ probably by ferrous iron (Guilbert and Park, 1986). Silver is not likely to form oxides or carbonates but may form weakly soluble halogenated salts in arid climates if chlorine, bromine and/or iodine are present in solution. The chloride salt, chlorargyrite (AgCl) is the most soluble of these halides.

### *Bismuth, Antimony and Arsenic*

These elements are frequently found in polymetallic sulphide deposits and gold deposits where they may occur as stibnite or arsenopyrite. The minerals decompose readily during weathering to release the elements into solution. Although bismuth, antimony and arsenic have chemical similarities, they exhibit rather variable behavior because their hydrolysis properties are transitional between those of cations and anions. Below pH 7.5, bismuth forms the large cationic molecule $Bi_6(OH)_{22}^{5+}$, whereas at higher pH zero-charged species such as $Bi(OH)_3$ dominate. Antimony, on the other hand, is predominately in the aqueous form of $Sb(OH)_2^+$ at all pH values between 2 and 11.

Antimony forms stable minerals valentinite ($Sb_2O_3$) and stibiconite ($Sb_3O_6(OH)$) which are easily mistaken for iron oxyhydroxides. Bismuth and antimony associate readily with iron oxides over most of the pH range, and tend to be retained near the reaction site throughout the weathering process.

Arsenic is relatively soluble, but arsenic, in contrast to antimony, is present in solution predominately as anionic aqueous complexes. Under oxidizing conditions, arsenate ($H_2AsO_4$ ) is the most thermodynamically stable species in acidic mine waters at pH 2 - 6 and the complex $HAsO_4^2$ predominates at higher pH values. However, arsenic concentrations are often lower in oxygenated waters than its solubility would suggest due to its strong affinity for iron oxides and are most strongly sorbed in the pH range of 4 - 8. Arsenic has a much stronger affiliation to amorphous iron oxyhydroxides than crystalline iron minerals such as hematite due to the higher reactive surface area of the poorly crystaline phases such as ferrihydrite. Masscheleyn *et al.,* (1991), working with arsenic contaminated soils, observed significantly higher arsenic concentrations in solution under alkaline (pH 8.0) and oxidizing conditions as compared to lower pH conditions (5.0 to 7.0). These workers attributed the higher arsenic concentrations in solution to greater arsenic desorption from the decreasing positive charge on the surface of iron oxides with increasing pH. Similarly, Al *et al*., (1997) documented relatively high abundance of arsenic on the surface of iron sulphide minerals in a low pH environment (pH ~ 4).

The presence of fulvic acid reduces the ability of the arsenic anion to sorb to the iron oxyhydroxides. Fulvic acid acts as an anion and competes with arsenic for sorption sites. The green alteration product, scorodite ($FeAsO_4 \cdot 2H_2O$), may also form in oxidized waste dumps and is highly insoluble under mildly acidic and neutral conditions (Kwong and Ferguson, 1990). Mansfieldite ($AlAsO_4 \cdot 2H_2O$) is an analogue to scorodite and can be found in advanced argillitic alteration zones.

### *Selenium and Tellurium*

These elements are commonly present as minor constituents in volcanogenic sulphide deposits and are also present in many uranium ore deposits. In solution, both elements form anionic species, mainly $HTeO_3$ in the case of tellurium, and $HSeO_3$ and $SeO_3^{2}$ in the case of selenium. They are both rapidly adsorbed onto or co-precipitated with iron oxides and tend to be retained in gossans. However, unlike metal cations these anionic complexes are adsorbed more readily under acidic conditions. Selnate competes with other anions such as phosphate, molybdate, silicate and sulphate for adsorption sites onto the iron oxide precipitates.

Selenium can occur in three different oxidation states: -2, +4 and +6. In oxidizing solutions it occurs as selenite ($SeO_3{}^{2}$) or selenate ($SeO_4{}^{2}$) (ie. an oxidation state of +4 or +6, respectively). In the presence of iron it may be co-precipitated or may form the mineral ferroselite, $FeSe_2$. Selenate competes with other anions such as phosphate, molybdate, silicate and sulphate for adsorption sites onto the iron oxide precipitates. The more oxidized forms (particularly selenite) may be adsorbed onto ferric oxyhydroxides (Hem, 1985). Under reducing conditions (*e.g.* oxygen depletion in lake hypolimnions, pore waters of anaerobic sediments or groundwater), selenate is reduced to selenite which is further reduced to elemental selenium (Se0). Elemental selenium is relatively insoluble and may precipitate. However, adsorption, rather than precipitation, is the major geochemical control on concentrations of selenium in solution. Under oxidizing conditions, dissolved organic selenides are oxidized to selenite, which in turn is slowly oxidized to selenate. Under fully oxidized conditions (high redox potential) and circum-neutral pH, selenate is the thermodynamically stable form of selenium.

Both chemical and biological processes limit the concentration of dissolved selenium in water. Adsorption, precipitation and co-precipitation all remove selenium to the sediments. Biological uptake and the subsequent settling of selenium-containing organic detritus also contributes selenium to the sediments. Thus, sediments form a major repository for selenium in aquatic ecosystems.

### *Mercury*

Although mercury can occur as the sulphide cinnabar, this mineral oxidizes very slowly and for practical purposes it can be considered stable in surface outcrops. In most sulphide deposits the mercury content can be largely accounted for by minor amounts of the element in sphalerite, pyrite and sulphosalts. Upon weathering, mercury is released into solution and is often absorbed by clay, iron oxides and organic matter. Mercury adsorption is inhibited by the presence of chloride, especially at low pH.

# *APPENDIX B*

## *SECONDARY MINERAL NAMES & CHEMICAL FORMULAE*

### Table B1 - Secondary Mineral Alphabetic Listing

| Mineral | Formula |
|---|---|
| akaganeite | $\beta\text{-}FeO(OH,Cl)$ |
| alunite | $KAl_3(SO_4)_2(OH)_6$ |
| alunogen | $Al_2(SO_4)_3 \cdot 17H_2O$ |
| amarantite | $Fe^{III}(SO_4)(OH)\ 3H_2O$ |
| ammonioalunite | $(NH_4)Al_3(SO_4)2(OH)_6$ |
| ammoniumjarosite | $NH_4Fe_3(OH)_6(SO_4)_2$ |
| anglesite | $Pb^{II}SO_4$ |
| anhydrite | $CaSO_4$ |
| antlerite | $Cu_3^{II}(SO_4)(OH)_4$ |
| argentojarosite | $AgFe_3^{III}(SO_4)_2(OH)_6$ |
| azurite | $Cu_3^{II}(CO_3)_2(OH)_2$ |
| barite | $BaSO_4$ |
| basaluminite | $Al_4(OH)10SO_4$ |
| bayerite | $Al(OH)_3$ |
| beaverite | $Pb^{II}Cu^{II}Fe_2^{III}(SO_4)_2(OH)_6$ |
| bianchite | $ZnSO_4 \cdot 6H_2O$ |
| bilinite | $Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 22H_2O$ |
| birnessite | $\delta\text{-}Mn^{IV}O_2$ |
| boehmite | $AlO(OH)$ |
| brochantite | $Cu_4^{II}(SO_4)(OH)_6$ |
| cadmium hydroxide (am) | $CdOH_2$ |
| calcite | $CaCO_3$ |
| celestite | $SrSO_4$ |

| | |
|---|---|
| cerussite | $PbCO_3$ |
| chalcanthite | $Cu^{II}SO_4 \cdot 5H_2O$ |
| chalcocite | $Cu_2{}^{I}S$ |
| chalcophanite | $ZnMn_3O_7 \cdot 3H_2O$ |
| chlorargyrite | $AgCl$ |
| chromium hydroxide (am) | $Cr^{III}(OH)_3$ |
| copiapite | $Fe^{II}Fe_4{}^{III}(SO_4)_6(OH)_2 \cdot 20H_2O$ |
| coquimbite | $Fe_2{}^{III}(SO_4)_3 \cdot 9H_2O$ |
| coronadite | $PbMn_8O_{16}$ |
| corundum | $Al_2O_3$ |
| cryptomelane | $KMn_8O_{16}$ |
| diaspore | $AlO(OH)$ |
| dolomite | $CaMg(CO_3)_2$ |
| doyleite | $Al(OH)_3$ |
| epsomite | $MgSO_4 \cdot 7H_2O$ |
| feitknechtite | $(\beta\text{-}Mn^{III}OOH)$ |
| ferricopiapite | $Fe_5{}^{III}(SO_4)_6O(OH) \cdot 20H_2O$ |
| ferrihydrite | $5Fe_2{}^{III}O_3 \cdot 9H_2O$ |
| ferrimolybdite | $Fe_2(MoO_4)_3 \cdot 15H_2O$ |
| ferrohexahydrite | $Fe^{II}SO_4 \cdot 6H_2O$ |
| ferroxyhyte | $\delta\text{-}Fe^{III}O(OH)$ |
| fibroferrite | $Fe^{III}(SO_4)(OH) \cdot 5H_2O$ |
| gibbsite | $Al(OH)_3$ |
| goethite | $\alpha\text{-}Fe^{III}OOH$ |
| goslarite | $ZnSO_4 \cdot 7H_2O$ |
| gunningite | $ZnSO_4 \cdot H_2O$ |
| gypsum | $CaSO_4 \cdot 2H_2O$ |
| halite | $NaCl$ |

| | |
|---|---|
| halotrichite | $(Fe^{II})Al_2(SO_4)_4{\cdot}22H_2O$ |
| hausmannite | $Mn_3O_4$ |
| hematite | $\alpha\text{-}Fe_2^{III}O_3$ |
| hemimorphite | $Zn_4Si_2O_7(OH)_2{\cdot}H_2O$ |
| heterogenite | $Co^{III}OOH$ |
| hexahydrite | $MgSO_4{\cdot}6H_2O$ |
| hollandite | $BaMn_8O_{16}$ |
| hydrobasaluminite | $Al_4(SO_4)(OH)_{10}{\cdot}12\text{-}36H_2O$ |
| hydrocerussite | $Pb_3^{II}(CO_3)_2(OH)_2$ |
| hydronium jarosite | $(H_3O)Fe_3^{III}(SO_4)_2(OH)_6$ |
| hydrozincite | $Zn_5(CO_3)_2(OH)_6$ |
| jarosite | $KFe_3^{III}(SO_4)_2(OH)_6$ |
| jurbanite | $Al(SO_4)(OH)\ 5H_2O$ |
| kornelite | $Fe_2^{III}(SO_4)_3{\cdot}7H_2O$ |
| lanarkite | $Pb_2^{II}OSO_4$ |
| langite | $Cu_4^{IV}(SO_4)(OH)_6{\cdot}2H_2O$ |
| lepidocrocite | $\gamma\text{-}Fe^{III}O(OH)$ |
| lithiophorite | $(Al\ Li)MnO_2(OH)_2$ |
| maghemite | $\gamma\text{-}Fe_2^{III}O_3$ |
| magnesite | $MgCO_3$ |
| magnetite | $Fe^{II}O{\cdot}Fe_2^{III}O_3$ |
| malachite | $Cu_2^{IV}CO_3(OH)_2$ |
| manganite | $\gamma\text{-}Mn^{III}OOH$ |
| melanterite | $Fe^{II}SO_4{\cdot}7H_2O$ |
| mirabilite | $Na_2(SO_4)\ 10H_2O$ |
| natroalunite | $NaAl_3(SO_4)_2(OH)_6$ |
| natrojarosite | $NaFe_3^{III}(SO_4)_2(OH)_6$ |
| nordstrandite | $Al(OH)_3$ |

| | |
|---|---|
| osarizawaite | $PbCu^{II}Al_2(SO_4)_2(OH)_6$ |
| otavite | $CdCO_3$ |
| plumbojarosite | $PbFe_{0.5}(OH)_6(SO_4)_2$ |
| posnjakite | $Cu_4^{II}(SO_4)(OH)_6 \cdot H_2O$ |
| pyrolusite | $Mn^{IV}O_2$ |
| retgersite | $NiSO_4 \cdot 6H_2O$ |
| rhodochrosite | $MnCO_3$ |
| rhomboclase | $HFe_2^{III}(SO_4)_2 \cdot 4H_2O$ |
| romerite | $Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 14H_2O$ |
| rozenite | $Fe^{II}SO_4 \cdot 4H_2O$ |
| schwertmannite | $Fe_8^{(III,II)}O_8(OH)_6SO_4$ |
| scorodite | $Fe^{III}AsO_4 \cdot 2H_2O$ |
| siderite | $Fe^{II}CO_3$ |
| siderotil | $(Fe^{II},Cu^{II})SO_4 \cdot 5H_2O$ |
| smithsonite | $ZnCO_3$ |
| stibiconite | $Sb_3O_6(OH)$ |
| sulphur | $S$ |
| szomolnokite | $Fe^{II}SO_4 \cdot H_2O$ |
| tenorite | $Cu^{II}O$ |
| thenardite | $Na_2(SO_4)$ |
| valentinite | $Sb_2O_3$ |
| voltaite | $K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12} \cdot 18H_2O$ |
| witherite | $BaCO_3$ |
| zinc hydroxide | $Zn(OH)_2$ |

## Table B2 - Secondary Mineral Metal Association Listing

| Metal | Mineral | Formula |
|---|---|---|
| Aluminum | alunite | $KAl_3(SO_4)_2(OH)_6$ |
| | alunogen | $Al_2(SO_4)_3 \cdot 17H_2O$ |
| | ammonioalunite | $(NH_4)Al_3(SO_4)2(OH)_6$ |
| | ammoniumjarosite | $NH_4Fe_3(OH)_6(SO_4)_2$ |
| | basaluminite | $Al_4(OH)10SO_4$ |
| | bayerite | $Al(OH)_3$ |
| | boehmite | $AlO(OH)$ |
| | diaspore | $AlO(OH)$ |
| | doyleite | $Al(OH)_3$ |
| | gibbsite | $Al(OH)_3$ |
| | halotrichite | $(Fe^{II})Al_2(SO_4)_4 \cdot 22H_2O$ |
| | hydrobasaluminite | $Al_4(SO_4)(OH)_{10} \cdot 12\text{-}36H_2O$ |
| | jurbanite | $Al(SO_4)(OH)\ 5H_2O$ |
| | lithiophorite | $(Al\ Li)MnO_2(OH)_2$ |
| | nordstrandite | $Al(OH)_3$ |
| | osarizawaite | $PbCu^{II}Al_2(SO_4)_2(OH)_6$ |
| Antimony | stibiconite | $Sb_3O_6(OH)$ |
| | valentinite | $Sb_2O_3$ |
| Arsenic | scorodite | $Fe^{III}AsO_4 \cdot 2H_2O$ |
| Barium | barite | $BaSO_4$ |
| | hollandite | $BaMn_8O_{16}$ |
| | witherite | $BaCO_3$ |
| Cadmium | cadmium hydroxide (am) | $CdOH_2$ |
| | otavite | $CdCO_3$ |
| Calcium | anhydrite | $CaSO_4$ |
| | calcite | $CaCO_3$ |

| | | |
|---|---|---|
| | dolomite | $CaMg(CO_3)_2$ |
| | gypsum | $CaSO_4\cdot 2H_2O$ |
| Cobalt | heterogenite | $Co^{III}OOH$ |
| Copper | antlerite | $Cu_3^{II}(SO_4)(OH)_4$ |
| | langite | $Cu_4^{IV}(SO_4)(OH)_6\cdot 2H_2O$ |
| | azurite | $Cu_3^{II}(CO_3)_2(OH)_2$ |
| | beaverite | $Pb^{II}Cu^{II}Fe_2^{III}(SO_4)_2(OH)_6$ |
| | brochantite | $Cu_4^{II}(SO_4)(OH)_6$ |
| | chalcanthite | $Cu^{II}SO_4\cdot 5H_2O$ |
| | chalcocite | $Cu_2^{I}S$ |
| | malachite | $Cu_2^{IV}CO_3(OH)_2$ |
| | osarizawaite | $PbCu^{II}Al_2(SO_4)_2(OH)_6$ |
| | posnjakite | $Cu_4^{II}(SO_4)(OH)_6.H_2O$ |
| | siderotil | $(Fe^{II},Cu^{II})SO_4\cdot 5H_2O$ |
| | tenorite | $Cu^{II}O$ |
| Chromium | chromium hydroxide (am) | $Cr^{III}(OH)_3$ |
| Iron | akaganeite | $\beta$-FeO(OH,Cl) |
| | amarantite | $Fe^{III}(SO_4)(OH)\ 3H_2O$ |
| | bilinite | $Fe^{II}Fe_2^{III}(SO_4)_4\cdot 22H_2O$ |
| | copiapite | $Fe^{II}Fe_4^{III}(SO_4)_6(OH)_2\cdot 20H_2O$ |
| | coquimbite | $Fe_2^{III}(SO_4)_3\cdot 9H_2O$ |
| | ferricopiapite | $Fe_5^{III}(SO_4)_6O(OH)\cdot 20H_2O$ |
| | ferrihydrite | $5Fe_2^{III}O_3\cdot 9H_2O$ |
| | ferrimolybdite | $Fe_2(MoO_4)_3\cdot 15H_2O$ |
| | ferrohexahydrite | $Fe^{II}SO_4\cdot 6H_2O$ |
| | ferroxyhyte | $\delta Fe^{III}O(OH)$ |
| | fibroferrite | $Fe^{III}(SO_4)(OH)\ 5H_2O$ |
| | goethite | $\alpha$-$Fe^{III}OOH$ |

| | | |
|---|---|---|
| | halotrichite | $(Fe^{II})Al_2(SO_4)_4 \cdot 22H_2O$ |
| | hematite | $\alpha\text{-}Fe_2^{III}O_3$ |
| | hydronium jarosite | $(H_3O)Fe_3^{III}(SO_4)_2(OH)_6$ |
| | jarosite | $KFe_3^{III}(SO_4)_2(OH)_6$ |
| | kornelite | $Fe_2^{III}(SO_4)_3 \cdot 7H_2O$ |
| | lepidocrocite | $\gamma\text{-}Fe^{III}O(OH)$ |
| | maghemite | $\gamma\text{-}Fe_2^{III}O_3$ |
| | magnetite | $Fe^{II}O.Fe_2^{III}O_3$ |
| | melanterite | $Fe^{II}SO_4 \cdot 7H_2O$ |
| | plumbojarosite | $PbFe_{0.5}(OH)_6(SO_4)_2$ |
| | rhomboclase | $HFe_2^{III}(SO_4)_2 \cdot 4H_2O$ |
| | romerite | $Fe^{II}Fe_2^{III}(SO_4)_4 \cdot 14H_2O$ |
| | rozenite | $Fe^{II}SO_4 \cdot 4H_2O$ |
| | schwertmannite | $Fe_8^{(III,II)}O_8(OH)_6SO_4$ |
| | scorodite | $Fe^{III}AsO_4 \cdot 2H_2O$ |
| | siderite | $Fe^{II}CO_3$ |
| | siderotil | $(Fe^{II},Cu^{II})SO_4 \cdot 5H_2O$ |
| | szomolnokite | $Fe^{II}SO_4 \cdot H_2O$ |
| | voltaite | $K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12} \cdot 18H_2O$ |
| Lead | anglesite | $Pb^{II}SO_4$ |
| | beaverite | $Pb^{II}Cu^{II}Fe_2^{III}(SO_4)_2(OH)_6$ |
| | cerussite | $PbCO_3$ |
| | coronadite | $PbMn_8O_{16}$ |
| | hydrocerussite | $Pb_3^{II}(CO_3)_2(OH)_2$ |
| | lanarkite | $Pb_2^{II}OSO_4$ |
| | osarizawaite | $PbCu^{II}Al_2(SO_4)_2(OH)_6$ |
| | plumbojarosite | $PbFe_{0.5}(OH)_6(SO_4)_2$ |
| Lithium | lithiophorite | $(Al\ Li)MnO_2(OH)_2$ |

| | | |
|---|---|---|
| Magnesium | dolomite | $CaMg(CO_3)_2$ |
| | epsomite | $MgSO_4 \cdot 7H_2O$ |
| | hexahydrite | $MgSO_4 \cdot 6H_2O$ |
| | magnesite | $MgCO_3$ |
| Manganese | birnessite | $\delta\text{-}Mn^{IV}O_2$ |
| | chalcophanite | $ZnMn_3O_7 \cdot 3H_2O$ |
| | coronadite | $PbMn_8O_{16}$ |
| | cryptomelane | $KMn_8O_{16}$ |
| | feitknechtite | $\beta\text{-}Mn^{III}OOH$ |
| | hausmannite | $Mn_3O_4$ |
| | hollandite | $BaMn_8O_{16}$ |
| | lithiophorite | $(Al\ Li)MnO_2(OH)_2$ |
| | manganite | $\gamma\text{-}Mn^{III}OOH$ |
| | pyrolusite | $Mn^{IV}O_2$ |
| | rhodochrosite | $MnCO_3$ |
| Nickle | morenosite | $NiSO_4 \cdot 7H_2O$ |
| | retgersite | $NiSO_4 \cdot 6H_2O$ |
| Potassium | alunite | $KAl_3(SO_4)_2(OH)_6$ |
| | cryptomelane | $KMn_8O_{16}$ |
| | jarosite | $KFe_3^{III}(SO_4)_2(OH)_6$ |
| | voltaite | $K_2Fe_5^{II}Fe_4^{III}(SO_4)_{12} \cdot 18H_2O$ |
| Silver | argentojarosite | $AgFe_3^{III}(SO_4)_2(OH)_6$ |
| | chlorargyrite | $AgCl$ |
| Sodium | halite | $NaCl$ |
| | mirabilite | $Na_2(SO_4)\ 10H_2O$ |
| | natroalunite | $NaAl_3(SO_4)_2(OH)_6$ |
| | natrojarosite | $NaFe_3^{III}(SO_4)_2(OH)_6$ |
| | thenardite | $Na_2(SO_4)$ |

| | | |
|---|---|---|
| Strontium | celestite | $SrSO_4$ |
| Zinc | bianchite | $ZnSO_4 \cdot 6H_2O$ |
| | chalcophanite | $ZnMn_3O_7 \cdot 3H_2O$ |
| | goslarite | $ZnSO_4 \cdot 7H_2O$ |
| | gunningite | $ZnSO_4 \cdot H_2O$ |
| | hemimorphite | $Zn_4Si_2O_7(OH)_2 \cdot H_2O$ |
| | hydrozincite | $Zn_5(CO_3)_2(OH)_6$ |
| | smithsonite | $ZnCO_3$ |
| | zinc hydroxide | $Zn(OH)_2$ |

# APPENDIX C

## LIMITATIONS OF Ksp COMPARISON

The comparison of solubility constants ($K_{sp}$) for secondary minerals cannot be used to provide an accurate indication of their relative solubility. As indicated in Section 4.3, the actual solubility of a mineral is dependent on the ionic strength of a solution, relative activity of the reaction products in solution, aqueous complexation, kinetics of mineral formation and dissolution, in addition to the environmental factors outlined in Section 4.2. Several secondary minerals that have been discussed in this report are ranked based on Log $K_{sp}$ values obtained primarily from Ball *et al.,* (1991). Many of the reaction equations and corresponding Log $K_{sp}$ values have been modified (marked with an "*") to remove the $H^+$ component from the left side of the equation. This modification allows a more valid comparison at circum-neutral pH. However, even with this modification a valid quantifiable comparison is not warranted as discussed below.

The first limitation of determining relative mineral solubility using $K_{sp}$ is that $K_{sp}$ is an equilibrium concept. It is well recognized that equilibrium conditions are often not met in waste dumps, mine drainage or groundwater. Reaction kinetics cannot be quantitatively determined from thermodynamically-derived solubility constants although the further a solution is from equilibrium the faster dissolution and precipitation reactions will occur. The main problem is that minerals form and dissolve at a different rates and the relative difference between rates associated with various minerals may be very significant. To illustrate how reaction kinetics limit the applicability of a $K_{sp}$ comparison, various common minerals have been highlighted in Table C-1. According to this ranking quartz is one of the most soluble minerals when in actuality it is very insoluble.

The ionic strength of a solution affects the order of the water molecules around many of the ions in solution, as such the activity of many ions may not be accurately represented by the measured concentration. Thus, the relative solubilities may only be compared in dilute solutions, a condition that is typically not met in mine-water solutions. In addition, the $K_{sp}$ is dependent on which aqueous dissociation product is stable at specific pH and Eh conditions. Therefore, the $K_{sp}$ must be modified to reflect the stable aqueous complex at the pH and Eh of the solution (not represented in Table C-1). In summary, $K_{sp}$ values cannot be used as a routine indicator of solid phase solubility due to variations in stoichiometry and speciation of minerals. Relative solubility can therefore only be inferred from $K_{sp}$ values when similar species are compared.

| **Mineral Name** | **Chemical Reaction** | **Solubility Constant** | **Revised** |
|---|---|---|---|
| basaluminite | $Al_4(OH)10SO_4 = 4Al^{3+} + SO_4^{2-} + 10OH-$ | -117.3 | * |
| jarosite | $KFe_3(OH)_6(SO_4)_2 = K+ + 3Fe + 2SO_4 + 6OH^-$ | -98.8 | |
| natrojarosite | $(NaFe_3(OH)_6(SO_4)_2 = Na^+ + 3Fe + 2SO_4 + 6OH^-$ | -95.2 | |
| brochantite | $Cu_4SO_4(OH)_6 = 4Cu^{2+} + SO_4^{2-} + 6OH$ | -68.66 | * |
| azurite | $Cu_3(CO_3)_2(OH)_2 + 2H_2O = 3Cu^{2+} + 4OH^- + 2HCO^{3-}$ | -52.25 | * |
| alunite | $KAl_3(SO_4)_2(OH)_6 = K_+ + 3Al^{3+} + 2SO_4^{2-} + 6OH^-$ | -50.25 | |
| chalcocite | $Cu_2S + H_2O = 2Cu + HS^- + OH^-$ | -48.619 | * |
| antlerite | $Cu_3SO_4(OH)_4 = 3Cu^{2+} + SO_4^{2-} + 4OH^-$ | -47.7 | * |
| hematite | $Fe_2O_3 + 3H_20 = 2Fe^{3+} + 6OH^-$ | -46.008 | * |
| **goethite** | $\boldsymbol{\alpha}$ **-** $\mathbf{FeOOH + H_2O = Fe^{3+} + 30H^-}$ | **-42.7** ‘ | |
| ferrihydrite | $Fe(OH)_3 = Fe^{3+} + 3OH^-$ | -37.11 | * |
| malachite | $Cu_2CO_3(OH)_2 + H_2O = 2Cu^{2+} + 3OH^- + HCO_3^-$ | -36.85 | * |
| diaspore | $AlO(OH) + H_2O = Al^{3+} + OH^-$ | -35.12 | * |
| gibbsite | $Al(OH)_3 = Al^{3+} + 3OH^-$ | -33.89 | * |
| boehmite | $AlOOH + H_2O = Al^{3+} + 3OH^-$ | -33.42 | * |
| tenorite | $CuO + H_2O = Cu^{2+} + 2OH^-$ | -20.38 | * |
| scorodite | $FeAsO_4.2H_2O = Fe^{3+} + AsO_4^{3-} + 2H_2O$ | -20.249 | |
| dolomite | $CaMg(CO_3)_2 = Ca^{2+} + Mg^{2+} + 2CO_3{}^{2-}$ | -17.02 ‘ | |
| zinc hydroxide (am) | $Zn(OH)_2 = Zn^{2+} + 2OH^-$ | -15.55 | * |
| cadmium hydroxide | $CdOH_2 = Cd^{2+} + 2OH^-$ | -14.27 | * |
| cerussite | $PbCO_3 = Pb^{2+} + CO_3^{2-}$ | -13.13 | |
| otavite | $CdCO_3 = Cd^{2+} + CO_3^{2-}$ | -12.1 | |
| siderite | $FeCO_3 = Fe^{2+} + CO3{}^{2-}$ | -10.55 ‘ | |
| rhodochrosite | $MnCO_3 = Mn^{2+} + CO_3^{2-}$ | -10.41 ‘ | |
| smithsonite | $ZnCO_3 = Zn^{2+} + CO_3^{2-}$ | -10 | |
| barite | $BaSO_4 = Ba^{2+} + SO_4^{2-}$ | -9.97 | |
| witherite | $BaCO_3 = Ba^{2+} + CO_3^{2-}$ | -8.56 | |
| **calcite** | $\mathbf{CaCO_3 = Ca^{2+} + CO_3^{2-}}$ | **-8.48** ‘ | |
| magnesite | $MgCO_3 = Mg^{2+} + CO_3^{2-}$ | -8.029 | |
| anglesite | $PbSO^4 = Pb^{2+} + SO_4^{2-}$ | -7.79 | |
| gypsum | $CaSO_4.2H_2O = Ca^{2+} + SO_4{}^{2-} + 2H_2O$ | -4.58 | |
| **quartz** | $\mathbf{SiO_2 + 2H_2O = H_4SiO_4}$ | **-3.98** | |
| cristobalite | $SiO_2 + 2H_2O = H_4SiO_4$ | -3.59 | |
| silica (am) | $SiO_2$ | -2.71 | |
| chalcanthite | $CuSO_4.5H_2O = Cu^{2+} + SO_4^{2-} + 5H_2O$ | -2.64 | |
| melanterite | $FeSO_4.7H_2O = Fe^{2+} + SO_4^{2-} + 7 H_2O$ | -2.209 | |
| epsomite | $MgSO_4.7H_2O + Mg^{2+} + SO_4^{2-} + 7H_2O$ | -2.14 | |
| goslarite | $ZnSO_4.7H_2O = Zn^{2+} + SO_4^{2-} + 7H_2O$ | -1.96 | |
| **halite** | $\mathbf{NaCl = Na^+ + Cl^-}$ | **1.58** | |

‘ after Drever 1988

* reaction adjusted for no acid on right side of reaction

# *APPENDIX D*

## *EXAMPLES OF SEQUENTIAL EXTRACTION INTERPRETATION*

The primary use of the sequential extraction data is discussed below referring specifically to two hypothetical data sets, a strongly oxidized sample (X1) and a weakly oxidized sample (X2). Metal concentrations from each fraction and the total metal concentrations (whole rock analysis) from the two samples are listed in Table D-1. Table D-2 lists ratios that can be used to facilitate data interpretation using the total available and total extractable concepts.

Ion concentrations are expressed as molar concentrations per unit mass of sample (μmol/g) in Table D-1. Normalizing the data in this way allows comparisons of the relative metal release between extraction fractions regardless of the leachate volume or sample size. Metals expressed as molar concentrations may provide insight into the susceptible mineral phases associated with each fraction. Should the dissolution of a single mineral phase with an ideal stoichiometry be dissolved in a fraction, the concentrations of this mineral's essential elements will be proportional to the mineral's chemical formula. These relationships, should they exist, would not be readily apparent if the concentrations are expressed as mass per unit mass (mg/g) or mass per leachate volume (mg/l). The overall accuracy of an extraction can be assessed from the % recovery, which is the sum of all fractions for each metal and expressed as a percentage of the metal content obtained from the whole rock analysis.

Total available metals and total extractable metals are calculated from the sum of the first three and four fractions, respectively. The % of available metal (total available / total extractable x 100%) can be used to assess the relative risk of metal release between subaqueous disposal and continued subaerial exposure. For example, Table D-2 lists the percent of available metals for samples X1 and X2. Most of the metals examined in sample X1 are > 70% available, indicating that a higher percentage of metals may be susceptible to release underwater than in a subaerial dump. A closer examination of the data indicates that the majority of the Zn and Cd are released in the water-soluble F1 fraction along with considerable acidity. The mass of these metals can be combined with site specific data on dilution capability and grain size/surface area constraints to estimate water quality impact. If such an assessment indicate that this level metal release is unacceptable and cannot be treated economically, subaerial waste management alternatives should be pursued. A significant concentration of Cu is present in the reducible F3 fraction. If sediments at the disposal site are suspected to become reducing, kinetic testing may be warranted to examine the metal release rate from this phase to establish water quality impact. Conversely, the majority of metals are not available in sample X2 and have low relative concentrations, particularly in the F1 and F2 fractions. This indicates that this material will have significantly less impact if submerged, although the specific impact will again be dependent on dilution characteristics of the disposal site.

Sample X1 contained a significant quantity of metal bound in the F1 fraction. However, a risk assessment may indicate that short-term treatment of the water cover is more beneficial than long term treatment of drainage from a subaerial waste dump. In such a case, the extraction results can be used to estimate sludge volumes produced from the effluent treatment plant and assist in the cost evaluation. In this hypothetical scenario, kinetic testing indicated that kinetic constraints on F3 fraction dissolution would not have significant impact on water quality. Thus, only the combined metal mass associated with the F1 and F2 fractions would require treatment. The total metal mass associated with these two fractions (including major cations not shown in Table D-1) can be adjusted to account for grain size constraints. These data can then be used with the total waste mass and achievable sludge densities to estimate the sludge volume, which will be produced through the treatment of the water cover.

## Table D-1:
## Hypthetical Data Set Illustrating Metal Partitioning

| | F1<br>μmol/g | F2<br>μmol/g | F3<br>μmol/g | F4<br>μmol/g | Residual<br>μmol/g | Sum<br>μmol/g | Whole Rock<br>μmol/g | % Recovery |
|---|---|---|---|---|---|---|---|---|
| **Sample X1** | | | | | | | | |
| Cu | 2.12 | 0.96 | 3.57 | 3.42 | 5.74 | 15.81 | 15.7 | 101 |
| Pb | 0.0008 | 0.184 | 0.531 | 0.156 | 0.043 | 0.915 | 0.92 | 99 |
| Zn | 4.6 | 0.117 | 0.219 | 0.168 | 0.93 | 6.03 | 6.35 | 95 |
| Cd | 0.15 | 0.004 | 0.031 | 0.002 | 0.026 | 0.213 | 0.215 | 99 |
| Ni | 0.002 | 0.24 | 0.39 | 0.55 | 17.70 | 18.88 | 19.3 | 98 |
| Fe | 0.05 | 22.22 | 1107.4 | 174.0 | 980.0 | 2283.7 | 2375 | 96 |
| Mn | 0.005 | 0.282 | 1.073 | 0.353 | 2.35 | 4.063 | 4.05 | 101 |
| Al | 0.01 | 4.2 | 354.3 | 0.2 | 409.3 | 768.0 | 772 | 99 |
| $SO_4$ | 257.6 | 41.6 | 420.3 | 320.5 | 1.43 | 1041.43 | 1006 | 104 |
| Acidity | 10 | | | | | | | |
| pH | 4.2 | 5.0 | 3.0 | 2.0 | | | | |
| **Sample X2** | | | | | | | | |
| Cu | 0.0001 | 0.12 | 0.43 | 3.42 | 7.63 | 11.60 | 11.9 | 97 |
| Pb | 0.00 | 0.03 | 0.098 | 0.356 | 0.092 | 0.576 | 0.58 | 99 |
| Zn | 0.00 | 0.015 | 0.002 | 0.168 | 1.48 | 1.67 | 1.79 | 93 |
| Cd | 0.00001 | 0.0004 | 0.0009 | 0.0028 | 0.043 | 0.047 | 0.048 | 98 |
| Ni | 0.0002 | 0.002 | 0.22 | 0.55 | 19.2 | 19.97 | 19.3 | 103 |
| Fe | 0.001 | 1.2 | 297.3 | 1483 | 1050 | 2831.5 | 2910 | 97 |
| Mn | 0.001 | 0.043 | 0.12 | 0.231 | 2.67 | 3.065 | 3.07 | 100 |
| Al | 0.001 | 0.005 | 4.78 | 0.11 | 510 | 514.9 | 524 | 98 |
| $SO_4$ | 0.82 | 0.23 | 87.4 | 720.4 | 1.57 | 810.42 | 795.3 | 102 |
| Acidity | 0.001 | | | | | | | |
| pH | 5.3 | 5.0 | 3.0 | 2.0 | | | | |

Sum = F1+F2+F3+F4+Residual
% Recovery = Sum / Whole Rock

## Table D-2:
## Analysis of Hypothetical Data Set

| | **Total Available** µmol/g | **Total Extractable** µmol/g | **% Available** | **F1** % | **F2** % | **F3** % | **F4** % |
|---|---|---|---|---|---|---|---|
| **Sample X1** | | | | | | | |
| Cu | 6.65 | 10.07 | 66 | 21.0 | 9.5 | 35.5 | 34.0 |
| Pb | 0.7158 | 0.8718 | 82 | 0.1 | 21.1 | 60.9 | 17.9 |
| Zn | 4.936 | 5.104 | 97 | 90.1 | 2.3 | 4.3 | 3.3 |
| Cd | 0.185 | 0.187 | 99 | 80.2 | 2.1 | 16.6 | 1.1 |
| Ni | 0.632 | 1.182 | 53 | 0.2 | 20.3 | 33.0 | 46.5 |
| Fe | 1129.7 | 1303.7 | 87 | 0.0 | 1.7 | 84.9 | 13.3 |
| Mn | 1.360 | 1.713 | 79 | 0.3 | 16.5 | 62.6 | 20.6 |
| Al | 358.5 | 358.7 | 100 | 0.0 | 1.2 | 98.8 | 0.1 |
| $SO_4$ | 719.5 | 1040 | 69 | 24.8 | 4.0 | 40.4 | 30.8 |
| **Sample X2** | | | | | | | |
| Cu | 0.550 | 3.970 | 14 | 0.0 | 3.0 | 10.8 | 86.1 |
| Pb | 0.128 | 0.484 | 26 | 0.0 | 6.2 | 20.2 | 73.6 |
| Zn | 0.017 | 0.185 | 9 | 0.0 | 8.1 | 1.1 | 90.8 |
| Cd | 0.0013 | 0.0041 | 32 | 0.2 | 9.7 | 21.9 | 68.1 |
| Ni | 0.222 | 0.772 | 29 | 0.0 | 0.3 | 28.5 | 71.2 |
| Fe | 298.5 | 1781.5 | 17 | 0.0 | 0.1 | 16.7 | 83.2 |
| Mn | 0.164 | 0.395 | 42 | 0.3 | 10.9 | 30.4 | 58.5 |
| Al | 4.786 | 4.896 | 98 | 0.0 | 0.1 | 97.6 | 2.2 |
| $SO_4$ | 88.45 | 808.85 | 11 | 0.1 | 0.0 | 10.8 | 89.1 |

Total Available = F1+F2+F3
Total Extractable = F1+F2+F3+F4
% Available = Total Available / Total Extractable x 100%
% F1 = F1 / Total Extractable x 100%