GEOCHEMICAL MODELLING OF ACID MINE DRAINAGE IN MILL TAILINGS: QUANTIFICATION OF KINETIC PROCESSES FROM LABORATORY TO FIELD SCALE

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ABSTRACT

Assessment of the potentially acidic, heavy metal–laden leachates that leave deposits of sulfide ore mill tailings and evaluation of various possible options for mill tailing remediation are scientific problems of increasing practical importance. High costs may be associated with the mill tailing remediation, not least after recent changes in Swedish and European environmental legislation. This thesis presents a methodology for studying and quantifying geochemical processes that contribute to generation of so-called acid mine drainage (AMD). The methodology builds from first principles regarding geochemical processes, and is based on geochemical characterisation of the mill tailings combined with explicit model quantification of the effect of factors, such as temperature, pH, and mineral (BET) surface area, that influence mineral weathering rates. Application of the modelling methodology to a case study site, Impoundment 1, Kristineberg, northern Sweden, including quantification of slow processes through literature rate laws, successfully reproduced the pH and relative concentrations of major ions in the impoundment groundwater. Absolute concentrations of most major ions, with the exception of Zn, were 1-2 orders of magnitude higher in the model than in the field, which is consistent with the commonly observed scale dependence of mineral weathering rates; however, application of a single calibration factor, $X_r=10^{-2}$, to all weathering rate expressions, sufficed to account for this apparent scale dependence.

Subsequent laboratory determination of mineral weathering rates in Impoundment 1 tailings indicated that rates for the major minerals pyrite ($\text{FeS}_2$) and aluminosilicates were in fact 1-2 orders of magnitude lower in the ~50-year-old tailings than rates reported in the literature. Weathering rates of chalcopyrite ($\text{CuFeS}_2$) and sphalerite ($\text{ZnS}$) were by contrast 1-3 orders of magnitude greater than predicted by the literature rate laws that were used in the modelling study. While the mechanism of Zn release requires further investigation for improved forward model prediction, the underestimation of Zn concentration in Impoundment 1 by the model was resolved. The laboratory study furthermore indicated that the weathering rates of most major minerals exhibited the same dependence on pH, temperature and surface area as reported in the literature, and thereby supported the use of literature rate laws for model assessment of dominant geochemical processes in tailings deposits, once allowance is made for lower rates in older tailings material.

Analysis of the dominant geochemical processes in the model of Impoundment 1 indicated that slow weathering of aluminosilicate minerals provided the bulk of proton attenuation and, as a result, considerably affected the rate of depletion of fast-reacting pH-buffering minerals. Inclusion of the kinetics of aluminosilicate dissolution and of the feedbacks between slow and fast processes is thus potentially crucial for prediction of pH and its long-term evolution. The sensitivity of modelled groundwater composition and pH to iron redox reactions, such as may be accelerated by acidophilic bacteria, indicated that, while iron redox cycling was low at the present case study site, quantification of microbial mediation of these reactions may be necessary for predicting AMD quality under other conditions. The laboratory studies also indicated that application of common sterilisation techniques, such as is necessary for study of relative contributions of abiotic and biotic weathering processes, had little effect on the long-term (>30 days) abiotic element release rates in the tailings.

This study suggests that within certain limits, which appear narrower than currently recognised in industrial prediction practices, it is possible to predict the weathering behaviour of major minerals, and hence proton release and attenuation, in base metal tailings under field conditions.
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Peer-reviewed publications:


MiMi-reports:
Salmon, S., Malmström, M., 2002. Steady state, geochemical box model of a tailings impoundment: Application to Impoundment 1, Kristineberg, Sweden, and prediction of effect of remediation. MiMi 2002:2, Mitigation of the environmental impact from mining waste programme (MiMi), Stockholm, Sweden.


Licentiate thesis:

International conference abstracts:


1 INTRODUCTION

The history of mining in Sweden stretches back over 1000 years; Swedish mines were for many centuries one of the major suppliers of steel, copper and silver to central Europe (Gustafsson et al., 1999). Although the number of operating mines has decreased from approximately 500 in the early 20th century to 16 in 1999, prospecting has also increased after changes in ownership laws in the early 1990s, indicating that there is both the resource potential and the will of the mining industry for new mines to open (see also further discussion on mining conditions in Sweden in Paper VII and references therein).

Fine mill tailings and waste rock are waste products from mining and ore enrichment processes. Mining at the current level in Sweden produces approximately half of all waste in Sweden (SCB, 2000a); in 1996, over two thirds of the mining waste produced, or 35Mt, was from mining of sulfide ores (SEPA, 1998), such as chalcopyrite (CuFeS$_2$) and sphalerite (ZnS). As sulfide ore minerals are generally associated with large quantities of economically undesirable iron sulfides, such as pyrite (FeS$_2$), the iron sulfides often comprise a large fraction of the waste, as do the so-called “gangue” minerals that host the ore, typically (alumino-)silicate and carbonate minerals. Oxidation of the iron sulfide minerals upon exposure to dissolved molecular oxygen, e.g.,

$$FeS_2(s) + H_2O + \frac{7}{2}O_2(aq) \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+$$  \(1\),

by abiotic or microbially mediated processes, combined with reactions of the other minerals in the waste, can lead to release of acidic leachate with high concentrations in metals and sulfate (referred to as acid mine drainage, AMD) over hundreds to thousands of years (SEPA, 1986).

The largest Swedish environmental concern associated with mining, according the Swedish Environmental Protection Agency (here referred to as SEPA), is oxidation of sulfidic wastes after closure of the mines, and in particular, discharge of Hg, Cd, Pb, Cu, Zn, As, Fe, Al, and acidity (SEPA, 1995). In 1995, it was estimated that over 60% of all Pb, Cd, Zn and Cu discharge to Swedish waters came from mining and mining waste, with the majority originating from waste (SCB 2000b). The main environmental impact of AMD is generally considered to be associated with the heavy metal content, with effects such as acute and chronic toxicity and bioaccumulation, where the low pH of the mine waste leachate enhances metal mobility (SEPA, 1995). However, AMD is also often characterised by high concentrations of Fe(II), aluminium, and sulfate, where these components are mobile even under non-acidic conditions (e.g., Smith and Huyck, 1999). Oxidation of Fe(II) upon exposure to oxygen and precipitation of characteristically yellow-red Fe(III) phases, as well as precipitation of Al$_3^+$ phases, both release further acidity and may physically impair biological function (e.g., Pentreath, 1994). Also dissolved Al$_3^+$ may be harmful at high concentrations (e.g., Wachtmeister and Sundström, 1986; Pentreath, 1994). In addition, in countries where water is in short supply, even high concentrations of sulfate may be critically detrimental to water resources (Pulles, 2003).

The focus of regulation of water polluting activities in Sweden and the E.U. has recently changed, from placement of limits on individual discharges, to regulation of the integrated impact of many different pollution sources within a catchment on the receiving water body (see also more detailed legislation discussion in Paper VII). Relatively new Swedish and EU legislation has introduced concepts such as Environmental Quality Standards, which will specify limits, for example, of concentrations of metals that may not be exceeded in surface or ground water bodies. Inability to fulfil these criteria, or to demonstrate the capability to do so, may thus have serious consequences for the future of the mining industry; while the impact of the new legislation on AMD regulation is largely untried, the Swedish mining industry is
concerned for its viability (Paper VII). At the same time, societies will for the foreseeable future continue to depend upon mining to meet resource needs (Plumlee and Logsdon, 1999). Sustainable regulatory decisions on mining require means to accurately assess the long-term environmental impact of mining, the associated waste material, and the outcome of any remedial measures.

Remediation measures are commonly applied with the intention of limiting generation of AMD through reduction of oxygen availability, for example through application of water or soil covers. The large quantities of generated mining waste leads to such remediation being a costly undertaking (e.g., SEPA, 1998). Despite the considerable financial burden of remediation, remediation measures are often based on reproducing at any mine waste site similar practices as have applied elsewhere, rather than linked to the actual, site-specific downstream effect of the remediation measure (O’Kane and Wels, 2003). In order to quantify and predict such downstream effects, accurate source term quantification and prediction is necessary. Such quantification and prediction is also necessary for optimisation of remediation measures with respect to individual mine waste sites (O’Kane and Wels, 2003), or the total number of mine waste sites within a water catchment (Baresel et al., 2003); optimisation is required for economic efficiency in environmental preservation and reduced costs to the mining industry and to society as a whole.

Methods that have been used for prediction of AMD generation in tailings are both laboratory and model based, with standardised methods of static and kinetic laboratory testing being often applied (e.g., White et al., 1999; MEND, 2000). However, static tests can at best only predict whether leachate pH will become acidic at some (unknown) point in time (Parker and Robertson, 1999), and typical application of kinetic laboratory testing to prediction of field scale leachate quality is associated with a high degree of uncertainty (Salomons, 1995). Furthermore, these methods assume geochemical control of AMD quality (Salomons, 1995), and thereby largely neglect the crucial interaction with oxygen availability.

A number of modelling studies of AMD generation from mill tailings exist in the literature (e.g., Scharer et al., 1994; Wunderley et al., 1996; see also review in Alpers and Nordstrom, 1999) where models have been produced as tools to examine effects of dominant processes and compare different tailings remediation measures. However, the predictive capability of many of these models is limited (MEND, 2000; Parker and Robertson, 1999), due to, for example, oversimplification or neglect of some important geochemical processes. Recent model developments open for better consideration of kinetic processes (Lichtner, 1996; Mayer et al., 2003), with application of such models to field data including model calibration to field observations (Mayer et al., 2003).

In parallel lines of investigation, focussed on weathering of aluminosilicate minerals, independently determined weathering rate laws for monomineralic samples on laboratory scale have been applied to field-scale prediction of, for instance, acidification and mineral weathering impact on global climate (White and Brantley, 1995), or AMD generation in waste rock (Strömberg and Banwart, 1994). It is then commonly observed that weathering rates determined on the laboratory scale overestimate apparent field rates by orders of magnitude (e.g., Schnoor, 1990; White and Peterson, 1990; Strömberg and Banwart, 1994). The study by Malmström et al. (2000) indicates that such discrepancies between apparent field and laboratory rates may be resolved through relevant, explicit consideration of the influence of factors, such as temperature, pH, and water flow conditions, which may be quite different on different scales.

This thesis presents a modelling methodology that is based on fundamental geochemical principles and is adapted to field conditions of a mill tailings impoundment case study, Impoundment 1, Kristineberg, northern Sweden, in analogy
with earlier modelling of mining waste rock deposits (Strömberg and Banwart, 1994). In particular, this thesis addresses the importance of aluminosilicate weathering and iron redox cycling for the groundwater composition and pH in mill tailings deposits. Furthermore, laboratory studies are performed to test model assumptions made in the application of literature rate laws to the modelling of field-scale AMD generation. These laboratory studies investigate the dependence of mineral weathering rates on pH, temperature, and BET surface area under conditions relevant for mill tailings. In addition, the laboratory studies include investigation of sterilisation techniques that are required to investigate abiotic vs biotic weathering processes.

Specific objectives of this thesis can be summarised as:

1. To develop a modelling methodology for quantifying leachate composition and pH in pyritic base metal tailings impoundments, which include kinetic reactions and their feedbacks with equilibrium processes.

2. To apply this modelling methodology to a specific case study, Impoundment 1, Kristineberg, using independently reported mineral weathering rate laws, and particularly investigate the site-specific importance of slow aluminosilicate dissolution and iron redox cycling coupled with fast geochemical processes and oxygen availability.

3. To test various model assumptions through systematic laboratory studies of site-specific tailings material from Impoundment 1 and separated sulfide phases, and through comparison of weathering rates determined on different experimental/observation scales.
2 GENERATION OF ACID MINE DRAINAGE IN SULFIDIC MILL TAILINGS

Mill tailings are the finely ground waste product from ore enrichment by flotation. As mentioned in the introduction, common minerals in base metal pyritic mill tailings are iron sulfides and gangue minerals from the ore body host rock, such as aluminosilicate and carbonate minerals, as well as lesser amounts of ore minerals. The focus of this work is geochemical processes contributing to the major ion composition and pH in tailings impoundment groundwater. Below is an overview of major physical and geochemical processes (see also detailed reviews in Evangelou and Zhang, 1995; Nordstrom and Southam, 1997; Nordstrom and Alpers, 1999) and general means of quantification of kinetic geochemical processes, such as is applied in the modelling study in Chapter 3. In Chapter 2.2, earlier approaches to modelling the aqueous geochemistry of AMD are briefly reviewed.

2.1 Processes in mill tailings

2.1.1 Oxygen availability and solute transport

Fine tailings are often deposited as a slurry in a containing dam and allowed to sediment. Tailings impoundment dams can contain vast volumes of material, for example, the tailings dam at the Aitik open cut porphyry copper mine in northern Sweden, which has been in operation for approximately 35 years, covers up to 11 km², and is up to 40 m in depth (Lindvall and Eriksson, 2003). As diffusion of oxygen in air is approximately 4 times greater than in water (e.g., Nicholson et al., 1998), ingress of oxygen into tailings is relatively slow under water-saturated conditions. After closure of an impoundment, or even during use, decrease in the water level may lead to formation of an unsaturated zone, thereby opening the way for oxygen diffusion in pore spaces, and hence faster oxidation processes such as in Equation 1.

The dependence the overall reaction rate on the availability of oxygen implies that oxidation, and hence proton production, will predominantly occur in the unsaturated zone of tailings deposits. This is consistent with the commonly reported field observations of depletion of sulfides above the water table in tailings deposits (e.g., Holmström et al., 2001). The partial pressure of oxygen, \( P_o_2 \), in the impoundment is a result of the balance between the rate of transport into pore spaces, by diffusion and advection, and the rate of oxygen consumption. If the rate of transport is relatively fast, the overall reaction rate is controlled by the surface reaction, and the \( P_o_2 \) will be equal to the atmospheric \( P_o_2 \) (0.2 atm). If the rate of transport is of a similar order of magnitude as the rate of consumption, or slower, the overall reaction rate will be mixed kinetic or transport controlled, and \( P_o_2 \) will decrease.

Transport of reaction products from the reaction site to downstream environment depends upon inflow of precipitation, groundwater and/or surface water. The aqueous composition and pH of the groundwater in tailings deposits thus depends upon the relative rates of geochemical processes occurring in the tailings, as well as physical processes such as gas and solute transport, and feedbacks between these processes.

2.1.2 Oxidation processes

The slow oxidation of sulfide minerals leads to release of sulfate, \( Fe(II) \), protons and heavy metals and metalloids, as exemplified by Equations 1-6 in Table 1 (see also, e.g., reviews Nordstrom and Southam, 1997, and Nordstrom and Alpers, 1999). Under most conditions in the presence of dissolved molecular oxygen, \( Fe(III) \) is the thermodynamically more stable specie of the iron redox couple; however, kinetic limitation on the oxidation of \( Fe(II) \) results in a relatively slow abiotic rate of oxidation to \( Fe(III) \) (Equation 10 in Table 1), particularly at low pH. The produced \( Fe(III) \)
**Table 1. Typical slow geochemical processes in base metal ore/pyritic tailings, as exemplified by the weathering reactions used in the modelling of the unsaturated zone of Impoundment 1 in this study, and rate expressions.**

<table>
<thead>
<tr>
<th>Process and reaction stoichiometry</th>
<th>Rate law a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pyrite oxidation (oxygen path):</td>
<td>[ r_{pyo} = k_{pyo} \left[ O_2 (aq) \right]^{0.3} \left[ H^+ \right]^{-0.11} ]</td>
</tr>
<tr>
<td>(FeS_2(s) + H_2O + \frac{7}{2} O_2(aq) \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+)</td>
<td></td>
</tr>
<tr>
<td>2 Pyrite oxidation (ferric iron path):</td>
<td>[ r_{pyf} = k_{pyf} \left[ Fe^{3+} \right]^{0.62} ]</td>
</tr>
<tr>
<td>(FeS_2(aq) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+)</td>
<td></td>
</tr>
<tr>
<td>3 Chalcopyrite oxidation (oxygen path):</td>
<td>-</td>
</tr>
<tr>
<td>(CuFeS_2(s) + 4O_2(aq) \rightarrow Fe^{2+} + Cu^{2+} + 2SO_4^{2-})</td>
<td></td>
</tr>
<tr>
<td>4 Chalcopyrite oxidation (ferric iron path):</td>
<td>[ r_{cyp} = k_{cyp} \left[ Fe^{3+} \right]^{0.43} ]</td>
</tr>
<tr>
<td>(CuFeS_2(s) + 16Fe^{3+} + 8H_2O \rightarrow 17Fe^{2+} + Cu^{2+} + 2SO_4^{2-} + 16H^+)</td>
<td></td>
</tr>
<tr>
<td>5 Sphalerite oxidation (oxygen path):</td>
<td>-</td>
</tr>
<tr>
<td>(ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-})</td>
<td></td>
</tr>
<tr>
<td>6 Sphalerite oxidation (ferric iron path):</td>
<td>[ r_{spf} = k_{spf} \left[ Fe^{3+} \right]^{0.58} ]</td>
</tr>
<tr>
<td>(ZnS(s) + 8Fe^{3+} + 4H_2O \rightarrow Zn^{2+} + SO_4^{2-} + 8Fe^{2+} + 8H^+)</td>
<td></td>
</tr>
<tr>
<td>7 Chlorite (chlinochlore) b weathering:</td>
<td>[ r_{ch} = k_{ch} \left[ H^+ \right]^{0.50} + k_{ch2} ]</td>
</tr>
<tr>
<td>((Mg_{4.5}Fe_{0.5}Fe_{0.1}Al_{0.1})AlSi_3O_{10}(OH)_8(s) + 16H^+ \rightarrow 4.5Mg^{2+} + 0.2Fe^{2+} + 0.2Fe^{3+} + 2Al^{3+} + 3SiO_2(s) + 12H_2O)</td>
<td></td>
</tr>
<tr>
<td>8 Muscovite c weathering:</td>
<td>[ r_{ma} = k_{mal} \left[ H^+ \right]^{0.40} + k_{ma2} ]</td>
</tr>
<tr>
<td>(K_{0.8}Na_{0.2}(Fe_{0.1}Al_{1.9})AlSi_3O_{10}(OH)_2(s) + 10H^+ \rightarrow 0.8K^+ + 0.2Na^+ + 0.1Fe^{3+} + 2.9Al^{3+} + 3SiO_2(s) + 6H_2O)</td>
<td></td>
</tr>
<tr>
<td>9 Plagioclase c weathering:</td>
<td>[ r_{pl} = k_{pl1} \left[ H^+ \right]^{0.45} + k_{pl2} ]</td>
</tr>
<tr>
<td>(Na_{0.25}Ca_{0.25}Al_{1.2}Si_{2.2}O_8(s) + 5H^+ \rightarrow 0.75Na^+ + 0.25Ca^{2+} + 1.25Al^{3+} + 2.75SiO_2(s) + 2.5H_2O)</td>
<td></td>
</tr>
<tr>
<td>10 Ferrous iron oxidation:</td>
<td>[ r_{fe} = k_{fe}\left[ O_2 (aq) \right]k_{fe}\left[ Fe^{2+} \right] + k_{fe2}\left[ FeOH^+ \right] + k_{fe3}\left[ Fe(OH)_2 \right] ]</td>
</tr>
<tr>
<td>(Fe^{2+} + \frac{1}{4} O_2(aq) + H^+ \rightarrow Fe^{3+} + \frac{1}{2} H_2O)</td>
<td></td>
</tr>
</tbody>
</table>

*a References given in Table 4 in Paper I. Rate laws were not found in the literature for oxidation of chalcopyrite and sphalerite by oxygen; in the modelling study, analogy was made with pyrite oxidation and rate constants were derived from reported rates (see Paper I).

*b Composition based on reported mineralogy of aluminosilicates in the Kristineberg mine (du Rietz, 1953).

*c Oligoclase; use of this plagioclase composition resulted in a solid phase chemical composition that most closely resembled that in Impoundment 1.
is also a powerful oxidant for sulfides (Equations 2, 4, and 6 in Table 1) and is itself reduced to Fe(II), leading to iron redox cycling (Fig. 1). The availability of aqueous Fe(III) for reaction is potentially limited by relatively fast precipitation of secondary Fe(III) phases, such as amorphous ferric hydroxide:

\[ \text{Fe}^{3+} + 3\text{H}_2\text{O} \leftrightarrow \text{Fe(OH)}_3(s) + 3\text{H}^+ \quad (2) \]

where the final position of equilibrium is a function of, and may also affect, solution pH. Availability of ferrous and ferric iron for slow reactions and equilibria, such as Equation 2, will also depend upon aqueous speciation of these components and amounts of complexing agents present. Table 3 in Paper I gives examples of aqueous speciation reactions for components released by reactions such as those in Table 1. Modelling of pH and aqueous component concentrations thus clearly requires consideration of coupling between slow kinetic and fast equilibrium processes.

The slow oxidation of sulfide minerals is accelerated by mediation by acidophilic bacteria. Optimal conditions for microbial mediation have been reported to be ~30 °C, \( \text{Po}_2 = 0.2 \text{ atm} \), acidic pH, and with nutrients such as phosphate, nitrate, and carbon readily available (e.g., Ehrlich, 1996). In laboratory studies under such favourable conditions, pyrite oxidation by oxygen has been reported to be up to a factor 35 greater in microbial experiments than in abiotic controls (Olson, 1991; Fowler et al., 2001, Yu et al., 2001). The acceleration of sulfide oxidation by microorganisms is even utilised in industrial hydrometallurgical metal extraction (e.g., Rossi, 1990). Observations made on the field (Elberling et al., 2000) and near-field (large columns; Strömberg and Banwart, 1999) scales at low temperature also indicate higher rates of oxidation, by a factor 1.5-5, prior to addition of bactericides.

Figure 1. Iron redox cycling. Pyrite oxidation by 1) dissolved molecular oxygen and 2) aqueous ferric iron; 3) Oxidation of aqueous ferrous iron by oxygen. Reaction stoichiometry and abiotic rate laws are given in Table 1. 4) Solubility equilibrium between aqueous solution and Fe(OH)\(_{3(s)}\), as represented in Equation 2.

Nordstrom and Southam, 1997; and Nemati et al., 1998), particularly at low pH where the abiotic oxidation rate is relatively low. It has even been suggested that the overall rate of pyrite oxidation is limited by the rate of generation of ferric iron (e.g., Singer and Stumm, 1970); particularly in microbial studies, this is still a topic of debate and investigation (Fowler et al., 2001, Yu et al., 2001; Sand et al., 2001). Oxidation of aqueous Fe(II) and sulfide minerals may also be increased by abiotic factors; for example, acceleration of aqueous Fe(II) oxidation has been reported subsequent to adsorption of Fe(II) on to surfaces of iron oxy-hydroxides (Tamura et al., 1976; Wehrli, 1990), and contact between two sulfide minerals can lead to accelerated dissolution of the sulfide with lower electrochemical rest potential (e.g., Kwong, 1993, 2001).

Rate laws quantifying the dependence of reaction rates, \( r \), upon various key factors are given in Table 1 for slow, abiotic reactions of common minerals in mill tailings and aqueous Fe(II). The rate laws are selected, where available, from studies reported in the literature, where they have been determined from systematic laboratory experiments. As can be seen, reaction rates [mol s\(^{-1}\)] depend
on factors such as the value of the temperature-dependent rate constant, the availability of oxidant and protons, and mineral surface area.

Although acceleration of oxidation reactions in Table 1 by various mechanisms as described above is widely reported in the literature, these alternative reaction pathways are seldom quantified in a way that is useful for modelling (e.g., Edwards et al., 2000); additionally, there is no consensus as to which of the few rates laws that are available is best (Kirby et al., 1999). In the modelling study presented in Papers I and II (see also Chapters 4-5), abiotic rate laws are applied and the sensitivity of model results to acceleration of rates is tested. Furthermore, systematic study of the relative contribution of abiotic and biotic processes in tailings, such as is required for determination of rate laws, requires sterilisation. However, the effect on mineral weathering rates of exposure to extreme chemical or physical conditions usually associated with sterilisation has not been reported; this is investigated in Paper IV.

2.1.3 pH-buffering processes

As described above, processes such as oxidation of sulfides and precipitation of Fe(III) phases leads to release of protons in tailings impoundments. Natural attenuation of the released protons and, thus, the final pH in the tailings impoundment groundwater, is dependent upon the reactions of minerals that dissolve and consume protons, which in turn depend on the quantity of the mineral available for reaction and the reaction rate. Acid-neutralising process rates are expected to be higher in the unsaturated zone, where the rate of protons production is higher, as a result of greater oxygen availability (e.g., Banwart and Malmström, 2001; Banwart et al., 2002).

Carbonate minerals, such as calcite, are generally considered to dissolve sufficiently quickly to maintain solubility equilibrium with aqueous solution and buffer pH at around neutral, e.g.:

$$
\text{CaCO}_3(s) + \text{H}^+ \leftrightarrow \text{Ca}^{2+} + \text{HCO}_3^- \quad (3)
$$

Maintenance of pH at high levels, combined with release of components such as iron and aluminium, leads to precipitation of secondary carbonates and hydroxides such as amorphous Fe(OH)$_{x_0}$ and Al(OH)$_{y_0}$. After depletion of calcite, pH is buffered at successively lower levels by the dissolution sequence of the secondary minerals (Blowes and Ptacek, 1994). Acid neutralisation by dissolution of aluminosilicate minerals (e.g., Equations 7-9 in Table 1) is relatively slow, but as these minerals are often present in large quantities, the contribution to acid attenuation may be significant, as has been suggested in a number of field studies (e.g., Nesbitt and Jambor, 1998; Johnson et al., 2000) and in a recent water saturated column study with tailings (Jurjovec et al., 2002). Decrease of proton production with time, due to, for example, eventual depletion of sulfide minerals in the unsaturated zone, will lead to return of pH to higher levels (e.g., Banwart and Malmström, 2001).

Selected rate laws for aluminosilicate minerals are given in Table 1. There is a wealth of literature on the weathering rates of aluminosilicate minerals under laboratory conditions, including the dependence of different mineral weathering rates on factors such as pH and temperature (see e.g., review in White and Brantley, 1995).

2.2 Prediction of AMD on field scale

A number of previous modelling studies of AMD from tailings deposits presented in the scientific literature focus on detailed modelling of oxygen diffusion, coupled to limited description of geochemical processes (e.g., Jaynes et al., 1984; Elberling et al., 1994; Scharer et al., 1994; Wunderly et al., 1996; Werner and Berglund, 1999; Bain et al., 2000; Romano et al., 2003). These models provide valuable insight into the coupling of, and feedback mechanisms between, different physical processes and
oxidation of iron sulfide minerals. Other geochemical reactions, such as pH-buffering processes, have often been simplified or neglected (e.g., MEND, 2000; Parker and Robertson, 1999), thus limiting the possibility to investigate geochemical processes that contribute to the master geochemical variable pH.

Detailed representations of kinetic limitations on slow geochemical processes are presented in Lichtner (1996) and Mayer et al. (2003). Both studies use AMD generation as one case study and, by fitting to field observations, Mayer et al. (2003) determined diffusion constants for a shrinking core model of sulfide dissolution, aluminosilicate mineral surface areas, and the reaction order of the rate of pyrite oxidation by Fe(III) with respect to ferric iron. The thus calibrated model reproduced pH and aqueous concentration profiles and furthermore simulated attenuation of Cu below the groundwater level due to covellite formation. As calcite was depleted, aluminosilicates were found to attenuate acidity. Geometric surface areas were calculated for aluminosilicates, based on an average grain size of the tailings, and compared with the surface areas obtained by calibration; while some discrepancies were observed, the authors concluded that laboratory-derived rate expressions for aluminosilicate minerals may be applicable in tailings.

In the work of Lichtner (1996) and Mayer et al. (2003), oxidation of aqueous Fe(II) was represented by equilibrium rather than a kinetic processes; Lichtner (1996) explained this as an approximation to microbial mediation leading to a rates that approach equilibrium conditions. However, as discussed in the previous section, the degree of microbial activity in the field may be limited by various environmental conditions, such as low temperature, high pH, and limited availability of nutrients.

In parallel developments, a large number of laboratory studies have been performed on aluminosilicate dissolution in order to investigate processes such as acidification of soils and watersheds and long-term global climate change (see e.g., White and Brantley, 1995, and references therein). Comparison of rates obtained from laboratory experiments with field observations typically yields rates in the laboratory that are up to 2 orders of magnitude greater than in the field (e.g., Schnoor, 1990; White and Peterson, 1990; Strömberg and Banwart, 1994; Malmström et al., 2000). For example, application of rate laws obtained from the literature for weathering of aluminosilicates and sulfides at the Aitik waste rock site in northern Sweden required a scaling down of ~2 orders of magnitude to reproduce absolute field rates (Strömberg and Banwart, 1994). Orders of magnitude differences were also observed in weathering rates in Aitik waste rock on laboratory, large column, and field scales; these differences were resolved by explicit account of independently quantified differences in temperature, pH-dependence, mineral content, and water flow conditions between different experimental/observation scales (Malmström et al., 2000).

Previous studies that have been briefly outlined in this chapter have increased our understanding of dominant geochemical processes that may occur in mill tailings and proposed different modelling tools for quantitative reproduction of these processes. A number of qualitative and quantitative issues with regard to field scale prediction, however, have also been opened and remain open, thus requiring further investigation in order to be resolved. The specific investigation objectives of this thesis, which have been summarised in Objectives 1-3 in the Introduction, include some of these open issues:

- the applicability of literature monomineralic weathering rates laws for reproduction of mineral weathering rates in tailings;
- the importance of aluminosilicate weathering and abiotic or microbially mediated iron redox cycling for tailings deposit groundwater composition and pH, and
- whether sterilisation of tailings samples, such as is required to investigate abiotic vs biotic weathering processes, affects mineral weathering rates.
3 MILL TAILINGS CASE STUDY: KRISTINEBERG IMPOUNDMENT 1

The case study used for model application is a mill tailings deposit called "Impoundment 1" in Kristineberg, which is also the special case study site of the Swedish multidisciplinary research program "Mitigation of the environmental impact from mining waste" (MiMi), funded by the Swedish Foundation for Strategic Environmental Research (MISTRA; see, e.g., MiMi, 2002). Papers I-VI have been produced within the framework of the MiMi research program.

The underground Kristineberg mine, owned and still operated by Boliden Mineral AB, is based on a massive sulfide Zn-Cu ore body located in the Skellefte district 175 km south-west of Luleå, Sweden (Fig. 2). The average annual air temperature at the site is 1 °C with 5 months of average temperature below 0 °C. The tailings deposit referred to as “Impoundment 1” was in use from the 1940s to the 1950s for deposition of tailings from the enrichment plant at Kristineberg, which processed ore from other mines in the area as well. The geology of the Kristineberg mine is described in du Rietz (1953); field data for pre-remediation conditions in Impoundment 1 from sampling campaigns in the 1980s and early 1990s (e.g., Qvarfort, 1983; Axelsson et al., 1986, 1991; Ekstav and Qvarfort, 1989) have been compiled and interpreted by Malmström et al. (2001) and form the basis of the case study used in the modelling application in Chapters 4 and 5 of this thesis. A summary of field data relevant for the modelling study is also given in Paper I.

Impoundment 1 was remediated in 1997 by combined dry cover application and raised groundwater level. The remediation programme for the site is summarised in Lindvall et al. (1999) and Werner and Salmon (2000). Post-remediation characterisation of the deposit to date is summarised in Holmström et al. (2001), Werner et al. (2001), Corrège et al., (2001), and Carlsson et al. (2002, 2003).

As part of the present work, the BET surface area for tailings in Impoundment 1 (Papers I, III-V) and saturation indices for both pre- (e.g., Paper I) and post- (Holmström et al., 2001) remediation conditions were determined. These quantities provide missing key parameter values and contribute to the conceptual model of geochemical processes occurring in Impoundment 1, which in turn is the basis for the desktop modelling study described in Chapters 4 and 5 (Papers I, II) and scaling of laboratory rates to field conditions in Chapter 7 (see also Paper V). Detailed characterisation of the specific Impoundment 1 tailings used in weathering experiments was also performed; see Chapter 6 and Papers III-V.

Impoundment 1 covers an area of approximately 0.11 km² and is on average 5 m deep. The extent of the unsaturated

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**Figure 2. Location and overview of the Kristineberg site.**
zone, that is, the average depth to the
groundwater, was 1 m prior to remediation. 
The total water flow through the deposit, 
consisting of effective infiltration and 
recharge from moraine slopes surrounding 
the deposit, was ~47 000 m$^3$ year$^{-1}$. Figure 3 
summarises the main attributes of the water 
balance over the deposit, along with the 
position of the groundwater table and the 
water sampling plane.

Neither concentrations of individual pore 
gases, the influx of oxygen, the water 
content of the unsaturated zone, nor the 
oxygen diffusivity are reported for the pre-
remediation conditions.

The specific surface area of the tailings was 
determined using five-point, nitrogen gas 
adsorption data evaluated through the BET 
equation, a method commonly used in 
kinetic mineral weathering studies. The 
specific surface area of eight samples from 
seven locations within the deposit ranged 
from 0.2 to 10.1 m$^2$ g$^{-1}$, with an average 
value of 2.96 m$^2$ g$^{-1}$. The large variability in 
specific surface area is consistent with the 
reported highly variable particle size 
distribution (see Paper I and Malmström et 
al., 2001).

The tailings within the deposit are pyritic 
and carbonate-depleted; the main minerals 
are chlorite, talc, muscovite, plagioclase, 
quartz, and pyrite. Sphalerite and 
chalcopyrite are also present. More detailed 
post-remediation characterisations of the 
tailings confirmed this mineralogy and also 
indicated the presence of feldspars and 
minor amounts of pyrrhotite, galena, and 
arsonopyrite (e.g., Holmström et al., 2001).

The tailings in the upper part of the deposit, 
on average down to the groundwater table, 
had been partly depleted in S, Fe, Zn, and 
Cu, suggesting weathering of sulfides in the 
water unsaturated zone. Volumetric 
fractions of major minerals in the 
unsaturated zone are given in Table 2.

The groundwater, which had been sampled 
1.5 m below the groundwater table, had an 
average pH of 4.9; redox potentials are not 
available in the literature. The groundwater 
contained high concentrations of dissolved 
SO$_4^{2-}$, Fe, Mg$^{2+}$, Zn$^{2+}$, Ca$^{2+}$, and Al$^{3+}$, as well 
as lower concentrations of Na$^+$, Cu$^{2+}$, and 
K$^+$ (see Table 3). In order to investigate 
whether aqueous concentrations were 
controlled by fast dissolution or 
precipitation of secondary phases at 
solubility equilibrium with solution,
Table 2. Mineralogy of the unsaturated zone of Impoundment 1 as estimated for the modelling study (see Paper I).

<table>
<thead>
<tr>
<th>Sulfides</th>
<th>Silicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>Chlorite</td>
</tr>
<tr>
<td>Pyrrhotite</td>
<td>Talc</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>Talc</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>Talc</td>
</tr>
</tbody>
</table>

Table 3. Average concentrations (mol l⁻¹) and pH reported for Impoundment 1 (see Paper I and Malmström et al., 2001).

<table>
<thead>
<tr>
<th>Average field values</th>
<th>Range of values</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>4.87</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.10</td>
</tr>
<tr>
<td>Fe(tot)</td>
<td>0.080</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>0.011</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>0.006</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>0.005</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>0.002</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>6 x 10⁻⁵</td>
</tr>
<tr>
<td>K⁺</td>
<td>6 x 10⁻⁵</td>
</tr>
<tr>
<td>Na⁺</td>
<td>4 x 10⁻⁴</td>
</tr>
</tbody>
</table>
4 MODELLING OF PRE-REMEDIATION IMPOUNDMENT 1

Based on analysis of the available data from pre-remediation conditions in Impoundment 1, BET surface determinations, and saturation index calculations for potential sources and sinks for the aqueous components in Impoundment 1, a conceptual model was formed, as is describe in this chapter. Solid phase data and the total water flow through the impoundment were used as model input data; process rates and equilibria were quantified using rate laws and thermodynamic data obtained from the literature. In Paper I (and this chapter), the resulting simulated aqueous component concentrations and pH were compared with those reported for Impoundment 1, and results were interpreted with respect to dominant geochemical processes.

4.1 Conceptual model

In the modelling study of Impoundment 1, the unsaturated zone was considered to be the major reactive zone in the tailings deposits and the dominant source of dissolved constituents in the groundwater. For sulfide minerals, this was supported by depletion above the groundwater level in Impoundment 1. Given the low spatial and temporal resolution of the available field data, as a first approximation the groundwater composition was modelled by assessing the unsaturated zone only; this zone was conceptualised as a single, completely-mixed flow-through reactor (box). The modelled leachate leaving the unsaturated zone was compared with the available data for groundwater quality from 1.5 m below the groundwater level (see Fig. 1).

The site-specific conceptual model for the geochemical processes occurring in the unsaturated zone of Impoundment 1 is shown in Figure 4. Based on the reported mineral abundance in Impoundment 1 (Table 2) and the composition of the aqueous phase, the main primary sources of groundwater solutes were considered to be the slow oxidation of sulfide minerals (pyrite, sphalerite, and chalcopyrite) by dissolved molecular oxygen and ferric iron and the slow weathering of aluminosilicates (chlorite, muscovite, and plagioclase) (reactions presented in Table 1). Although ferric iron is the thermodynamically favoured iron redox specie in the presence of dissolved molecular oxygen, the high Fe concentrations in the groundwater suggested dominance of Fe(II), as Fe(III) is highly insoluble at the impoundment groundwater pH of 4.9. This implied a kinetic limitation on the oxidation of Fe(II) to Fe(III). Aquiferous ferrous iron oxidation by dissolved molecular oxygen was thus also conceptualised as a relatively slow, kinetic process (cf. Strömberg and Banwart, 1994). Relatively fast, reversible geochemical processes included aqueous speciation, solubility equilibrium between the aqueous solution and secondary mineral phases (gypsum, ferrihydrite, and amorphous silicate), and Henry's law equilibrium between aqueous solution and oxygen and carbon dioxide in the gaseous phase in the unsaturated zone (see Table 3 in Paper I).

The yearly average of the total water flow rate through the deposit was used and all physico-chemical properties, such as the water content, pore gas composition, and mineral abundance, were assumed constant over the modelled zone and in time. This approach is consistent with the limited spatial and temporal resolution of available site data for Impoundment 1 (Malmström et al., 2001) and for mine waste sites in general (cf. Banwart and Malmström, 2001). The geochemistry was furthermore assumed to be at quasi-steady state (cf. Furrer et al., 1989), as was later justified by the water residence time in the saturated and unsaturated zones (0.5-1 years; Malmström et al., 2001) being much greater than the mineral turnover time (see Chapter 4.3).
4.2 Process quantification

For each simulation, the partial pressure of oxygen (\(P_{O_2}\)) was held constant, and the resulting flux (\(F_{O_2}\)) determined by mass balances. Simulations were performed over a range of oxygen partial pressures; results are presented for i) surface reaction control (\(P_{O_2}=0.2\) atm) and ii) mixed or transport controlled, \(P_{O_2} < 0.2\) atm (see Chapter 2.1). Fast processes in the conceptual model were quantified through mass action equations (see Table 3 in Paper I); Fe(II) and Fe(III) were specifically considered as separate components, to allow investigation of slow iron redox processes. The abiotic, kinetic rate laws used were those given in Table 1, that is, the basis for quantification of all kinetic processes was independent of site observations. Rate laws were not found in the literature for oxidation of chalcopyrite and sphalerite by dissolved molecular oxygen; analogy was thus made with the rate law for oxidation of pyrite and rate constants were calculated from reported (Scharer et al., 1994) abiotic rates of oxidation of these minerals by dissolved molecular oxygen.

Through consideration of the site specific properties of the unsaturated zone, the rate laws were converted to rate expressions, \(R_i\) [mol dm\(^{-2}\)s\(^{-1}\)], normalised to the surface area of the deposit; for heterogeneous reactions:

\[
R_i = h \delta A_i r_i
\]  

(4)

where \(h\) and \(\delta\) are the height and density of the unsaturated zone. For homogeneous reactions:

\[
R_i = h \theta r_i
\]  

(5)

where \(\theta\) is the water content. Table 4 in Paper 1 lists the final rate expressions, together with associated rate constants that have been adjusted for site temperature using published activation energies. Additional parameter values for Impoundment 1 used in the rate expressions are given in Table 2 in Paper I.

The specific mineral surface area, \(A_s\), to be used in conjunction with surface area normalised empirical rate laws in quantification of weathering rates (see Table 4 in Paper I), was for the \(i^{th}\) mineral estimated by allocation of a fraction of the total specific surface area of the tailings (\(A_{s,\text{tot}}\)) in proportion to the volumetric fraction, \(\gamma_i\), of the mineral:

Figure 4. Conceptual model for geochemical processes in the unsaturated zone of a mill tailings deposit. Kinetically controlled processes (single headed arrows) include weathering of aluminosilicate minerals (chlorite, muscovite, and plagioclase), oxidation of sulfide minerals (pyrite, sphalerite, and chalcopyrite) by both dissolved molecular oxygen and Fe(III), and oxidation of aqueous Fe(II). Fast, equilibrium controlled processes (double headed arrows) include aqueous speciation, Henry’s law equilibrium between the aqueous solution and pore gases, and dissolution/precipitation of secondary minerals.
\[ A_i = \gamma_i A_{i,in} \quad (6). \]

This modelling approach is based on the assumptions that weathering rate laws for monomineralic samples can be applied to mixtures of minerals, such as in tailings, that minerals are evenly distributed over all the particle size fractions, and that the specific surface area is constant between the minerals for a given particle size. Volumetric fractions (\(\gamma\)) for the case study are given in Table 2.

The mathematical model was implemented through STEADYQL (Furrer et al., 1989), which allows a numerical, geochemical quasi-steady state box modelling approach that previously has been successfully applied to waste rock dumps and underground mines (Strömberg and Banwart, 1994; Brown and Lowson, 1997; Brown et al., 2000). Processes such as depletion and accumulation of minerals that are much slower than the residence time of water can be considered through successive steady state simulations (see, e.g., Salmon, 2000, and Chapter 5).

### 4.3 Model results

#### 4.3.1 Comparison with field observations

Simulated concentrations in the impoundment groundwater were assessed in Papers I and II and are shown in Figure 5 vs concentrations observed in the field; the solid diagonal line indicates “perfect prediction”. Uncalibrated results of the model described in the previous section (\(P_{O_2}=0.2\) atm) are shown in Figure 5a, with the exception that solubility equilibrium with gypsum is not assumed. The model successfully reproduced the pH in the impoundment and the relative release rates, with the exception of \(Zn^{2+}\) and \(Ca^{2+}\).

Absolute rates were, however, one to two orders of magnitude higher in the model than in the field, despite accounting for field relevant temperature, pH, mineral content, and tailings surface area. This is consistent with the commonly observed scale-dependence of mineral weathering rates from laboratory to the field scale (e.g., White and Peterson, 1990; see also Malmström et al., 2000, and references therein). Release of Fe, \(SO_4^{2-}\), \(Zn^{2+}\), \(Cu^{2+}\), and pH were sensitive to \(P_{O_2}\). Decreased \(P_{O_2}\) implied decreased concentrations of these components, however, components from aluminosilicate weathering still remained high, and pH increased above the range of values reported for the field.

In order to account for the scale dependence of mineral weathering rates from laboratory values reported in the literature to field relevant rate values, a single calibration factor, \(X_r=10^{-2}\), was applied to all weathering rate expressions (i.e., multiplying the right hand side of Equation 4). In the quantification of \(X_r\), the concentration of \(Mg^{2+}\) was used as a tracer for the field weathering rates, as \(Mg^{2+}\) originates from the dominant (alumino)silicates, the weathering rates of which do not depend (directly) upon the dissolved molecular oxygen concentration. A value of \(X_r=10^{-2}\) thus resulted in a \(Mg^{2+}\) concentration corresponding to that reported for the field.

For all major components, the single calibration factor \(X_r=10^{-2}\) sufficed to account for the scale-dependence of mineral weathering rates, and resulted in modelled concentrations and pH that were close to those reported for the field (Fig. 5b). The possible physical reason for the difference between absolute literature values of weathering rates, used in the model, and the field weathering rates were further investigated in the laboratory study in Papers III-VI (Chapters 6-7). With regards to the field model, assumption of solubility equilibrium between solution and gypsum lead to improved reproduction of field \(Ca^{2+}\) and \(SO_4^{2-}\) concentrations (triangles in Fig. 5b), thereby supporting the inclusion of this process in the conceptual model. Remaining discrepancies between model results and field observations are considered small, given the uncertainty associated with, for example, the limited availability of data from only a small number of observation points.
The only major exception to the good agreement between results of the calibrated model and field observations was the Zn$^{2+}$ concentration, where the modelled concentration was approximately three orders of magnitude lower than the field concentration (Fig. 5a and b). This suggested that Zn$^{2+}$ release in the field was controlled by processes other than oxidation of sphalerite by oxygen or Fe(III), or that, for example, dissolution of sphalerite is accelerated by galvanic interactions with other sulfide minerals (e.g., Kwong, 2001, and references therein; see also Chapter 2.2.1 and Chapters 6 and 7).

4.3.2 Dominant processes and turnover times

The calibrated model was analysed for dominant processes that contributed to the proton balance, oxygen consumption, redox cycling of iron, and composition of the groundwater in the deposit. For full oxygen availability, the major processes contributing to the proton balance were pyrite oxidation by dissolved molecular oxygen (proton release) and chlorite dissolution (proton...
consumption; Fig. 6a, filled bars). This explains why the pH was not greatly affected by application of $X_r$ (compare Figures 5a and b); the rates of the reactions dominating proton production and consumption were scaled by the same factor. As well as being the major source of protons, oxidation of pyrite by dissolved molecular oxygen was found to be the major source of Fe(II) and $SO_4^{2-}$ and the major sink of dissolved molecular oxygen (Fig. 6). Pyrite oxidation by ferric iron was relatively low (Fig. 6), due to low solubility of $Fe^{3+}$ at pH ~5. Ferrous iron oxidation was also low; Fe(II) was found to be the dominant redox form of iron.

As well as being a major sink for protons (Fig. 6), chlorite dissolution was also the source of $Mg^{2+}$, the main source of $Al^{3+}$ and Si, and a minor source of Fe(II) and Fe(III). Dissolution of muscovite and plagioclase had only a minor effect on the proton balance (not shown), but were sources of $K^+$, $Na^+$, and $Ca^{2+}$, as well as of $Al^{3+}$ and Si. Evolution of groundwater impoundment geochemistry will depend on factor such as decrease in mineral content with time. Nonetheless, first-hand estimates of turnover times for primary minerals in the unsaturated zone of the deposit can be made by division of the amount of each mineral (Table 2) by their respective, modelled dissolution rate (see e.g., Strömberg and Banwart, 1994; Banwart and Malmström, 2001) after application of $X_r$. For full oxygen availability ($Po_2 = 0.2$ atm), pyrite had the shortest turnover time of in the order of 100 years. As pyrite is the major source of protons, the characteristic turnover time of pyrite also provides a first-hand estimate of the expected duration of AMD production (e.g., Banwart and Malmström, 2001). The characteristic turnover times for the other primary minerals in the model, that is, sphalerite, chalcopyrite, and aluminosilicates, were in the order of $10^3$-$10^4$ years. As Zn$^{2+}$

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**Fig. 6. Modelled fluxes of components from different processes normalised to the deposit surface area [µmol m$^{-2}$s$^{-1}$], of a) $H^+$; b) $SO_4^{2-}$; c) Fe(II); d) Fe(III); and e) $O_2$(aq) for a fixed $Po_2$ of 0.2 atm (filled bars) and 0.002 atm (open bars). Processes are i) ferrous iron oxidation, ii) pyrite oxidation by oxygen, ii) pyrite oxidation by Fe(III), iv) chlorite dissolution. Processes vii)-vii) show the effect of solubility equilibrium between aqueous solution and the given secondary phase.**
release in the model underestimated \( \text{Zn}^{2+} \) release in the impoundment by approximately 3 orders of magnitude, the turnover time of sphalerite is potentially much lower.
5 Model sensitivity and remediation implications

The sensitivity of model results to uncertainties such as may arise from natural variability in physico-chemical characteristics of the deposit and individual minerals, uncertainty in the experimentally determined kinetic parameters, and possible unquantified parallel reaction pathways, is presented in the following Chapter 5.1 (see also Paper I, as well as Salmon, 2000, and Salmon and Malmström, 2002). In Chapter 5.2, the model is used to approximate the evolution of the impoundment groundwater geochemistry with time under unremediated and remediated conditions (e.g., see Paper II); implications of this for Impoundment 1, and modelling of tailings AMD in general, are highlighted.

5.1 Sensitivity analysis

5.1.1 Oxidation processes

Abiotic rate expressions were applied in the model for pyrite oxidation by O$_2$(aq) ($R_{pyo}$) and Fe(III) ($R_{pyf}$), as well as Fe(II) oxidation ($R_{feo}$); see Reactions 1, 2, and 10 in Table 1; see also Fig. 1). However, as discussed in Chapter 2, these oxidation processes may be accelerated by a variety of processes; in the absence of rate laws explicitly defining the rates of such parallel reactions, the sensitivity of model results to such mediation was tested by application of factors $\alpha_{py}$, $\alpha_{fe}$, and $\beta$ to $R_{pyo}$, $R_{pyf}$, and $R_{feo}$, respectively. The values of $\alpha_{py}$, $\alpha_{fe}$, and $\beta$ were varied over a range of values that corresponds to the effect of microbial mediation under favourable laboratory conditions, as reported in the literature (see Chapter 2.1.1). Testing in this manner also reveals sensitivity to uncertainty in rate expressions, for example due to choice of rate law (Salmon and Malmström, 2002), mineral surface area (mineral content and tailings specific surface area, cf. Equation 6), rate constant, and activation energy ($E_a$).

Model results indicated that the overall rate of pyrite oxidation is the result of complex interactions between the processes depicted in Figure 1, pH, and O$_2$ availability, and also depends upon the presence/absence of Fe(OH)$_3$(s). For example, acceleration of pyrite oxidation by Fe(III) (i.e., $R_{pyf}$ with $\alpha_{fe}$ > 1) alone had almost no effect (not shown). However, acceleration of Fe(II) oxidation ($\beta$ > 1; Fig. 7a-b, $P_{O_2}$=0.2 atm) lead to an increase in $R_{pyf}$ (compare Fig. 8a and b) and a decrease in the overall pH (Fig. 7b). For $\beta$ in the order of $10^3$, $R_{pyf}$ was the dominant source of protons (Fig. 8b).

The rate of pyrite oxidation by Fe(III) was also increased with an increase in $R_{pyo}$. The higher rate of proton production associated with a value of $\alpha_{py}$ as small as 3.5 was not compensated by an increase in the kinetically limited chlorite dissolution rate, but by increased Fe(OH)$_3$(s) dissolution to maintain solubility equilibrium with solution (Fig. 8c). Dissolution of Fe(OH)$_3$(s) also released Fe$^{3+}$, and by this means lead to increased importance of $R_{pyf}$, which then contributed up to $\sim$ 40% and $\sim$ 50% of the total proton (Fig. 8c) and Fe(II) release, respectively. For a given value of $\alpha_{py}$ > 1, removal of the condition of solubility equilibrium between Fe(OH)$_3$(s) and solution led to lower pH (e.g., $\times$ in Fig. 5b; $\alpha_{py}$ = 3.5), as then determined by the balance between pyrite oxidation and aluminosilicate dissolution only. Under these conditions, the contribution by the ferric iron pathway for pyrite oxidation was insignificant, as there was no readily available source of ferric iron.

All simulation results in Figure 7a-d are plotted in Figures 7e and f as a function of $P_{O_2}$. Irrespective of the values of $\alpha_{py}$, $\alpha_{fe}$ and $\beta$ and dominance of $R_{pyo}$ or $R_{pyf}$, SO$_4^{2-}$ concentrations are determined by $P_{O_2}$ (Fig. 7e), as is consistent with conclusions of, e.g., Elberling and Nicholson (1996). However at low $P_{O_2}$, SO$_4^{2-}$ release is determined by gypsum dissolution. The pH, on the other hand, was sensitive to buffering processes, for example, whether solution was at
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Figure 7. Modelled \(SO_4^{2-}\) concentrations and pH as function of \(\beta\) (panel a-d) and \(F_{O_2}\) [mol m\(^{-2}\)s\(^{-1}\)] (panel e and f) with \(a_{Fe}^{\alpha} = 1\), where \(\beta\) and \(a_{Fe}^{\alpha}\) represent the magnitude of acceleration of ferrous iron oxidation and the ferric iron pathway for pyrite oxidation, respectively. Filled symbols indicate \(P_{O_2} = 0.2\) atm, open symbols indicate \(P_{O_2} = 0.002\) atm. Symbol shapes indicate the value of \(a_{Fe}^{\alpha}\) : \(\bigcirc = 1\), \(\square = 3.5\), \(\diamond = 10\), \(\Delta = 35\). Black crosses indicate simulations without solubility equilibrium between aqueous solution and Fe(OH)\(_3\) \(a_{Fe}^{\alpha} = 3.5\), \(P_{O_2} = 0.2\) atm).

solubility equilibrium with Fe(OH)\(_3\)\(_{\infty}\), and to values of \(a_{Fe}^{\alpha}\) and \(\beta\), even at low \(F_{O_2}\) (Fig. 7f).

Model results, and in particular, the proton balance and pH, are thus sensitive to relatively small changes in the rate of pyrite oxidation, irrespective of whether the changes are due to, for example, microbial mediation or uncertainty in mineral surface area. This implies that more detailed quantification of microbial processes on the field scale, and the surface area of the sulfide minerals available for reaction, is important for prediction of impoundment groundwater composition and pH.

5.1.2 pH-buffering processes

Given the importance of pH for the environmental impact of AMD, model results were tested for sensitivity to uncertainty in pH-buffering processes, namely, chlorite dissolution and the condition of solubility equilibrium between aqueous solution and Fe(OH)\(_{\infty}\). To start with, simulation of pH-buffering by aluminosilicate weathering alone, by removal of the forced solubility equilibrium between
Fe(OH)$_{3(s)}$ and the aqueous phase, had little effect on pH and component concentrations, as Fe(OH)$_{3(s)}$ dissolution was not a major process (cf. Fig. 6a).

The sensitivity of the groundwater composition and pH to uncertainty in the chlorite rate constant and/or chlorite content was tested by increasing or decreasing the rate expression for chlorite weathering, $R_{\text{ch}}$, by a factor $\alpha_{\text{ch}}$, the magnitude of which was varied by up to an order of magnitude. The impact of this on the proton balance and pH is shown in Figure 9. Increase in $R_{\text{ch}}$ by as little as a factor of two led to an increase in pH to around neutral (Fig. 9f). Further increase in $R_{\text{ch}}$ lead, as expected as a result of the associated increase in proton consumption, to further increase in pH (Fig. 9e and f), and correspondingly higher concentrations of Mg$^{2+}$ and Al$^{3+}$.

A decrease in $R_{\text{ch}}$ by a factor of two led to a drop in pH by about half a unit (Fig. 9f). With further decrease in $R_{\text{ch}}$, the influence of the chlorite weathering rate on the proton balance became insignificant (Fig. 9a). As for increased $\alpha_{\text{O}_2}$ in Chapter 5.1.1, the expected decrease in pH was mitigated to an extent by increased dissolution of Fe(OH)$_{3(s)}$. This maintained the pH at ~4.3, but also implied faster depletion of Fe(OH)$_{3(s)}$ (compare Fig. 9a-c).

Removal of both aluminosilicate weathering and Fe(OH)$_{3(s)}$ dissolution from the model, that is, simulation of the conditions after the depletion of Fe(OH)$_{3(s)}$ without consideration of aluminosilicate weathering, resulted in a pH below 2.

These simulations indicated that, while Fe and SO$_4^{2-}$ concentrations and pH in Impoundment 1 could be reproduced without aluminosilicate dissolution as long as fast-dissolving minerals were present in the model, accurate representation of a) the proton balance, and thus the rate of dissolution of Fe(OH)$_{3(s)}$ and duration of pH-buffering by this phase, and b) the pH after depletion of Fe(OH)$_{3(s)}$, required consideration of aluminosilicate dissolution. Furthermore, neglect of aluminosilicate weathering reactions excluded the possibility to quantify the primary sources of components, such as Al$^{3+}$, Mg$^{2+}$, Na$^+$, K$^+$, and Ca$^{2+}$, which are released by these processes, and which may participate in other geochemical reactions subsequent to release.
5.2 Implications for Impoundment 1

The box model presented in Chapter 4 was used to provide a first hand approximation of the temporal evolution of the impoundment geochemistry, in terms of processes that have occurred since deposition and potential future evolution of a tailings impoundment under continued unremediated conditions (Chapter 5.2.1 and Salmon, 2000), as well as potential effects of changed conditions such as may be caused by remediation (Chapter 5.2.2 and Paper II).

5.2.1 Geochemical evolution of Impoundment 1

Indications from saturation index calculations on field data (Chapter 3) were that Fe(OH)$_3$(s) and gypsum exerted solubility control on aqueous solution; the modelling study presented in Chapter 4 indicated that these phases were dissolving to maintain solubility equilibrium with aqueous solution, raising questions with regards to where these phases could have originated from.

The temporal evolution of the impoundment geochemistry was therefore approximated by considering consecutive steady-state periods, or stages. Initial conditions of mineral content were 16 vol-% pyrite, which was the pyrite content of the saturated zone of Impoundment 1, 10 vol-% calcite, as was reported for the Kristineberg mine (Qvarfort, 1983), and other minerals in the same proportions as given in Table 2. Conditions were kept constant for each steady-state period; if solution was oversaturated with respect to a phase likely to be at solubility equilibrium with aqueous solution in AMD environments (Nordstrom and Alpers, 1999), or if such a phase had precipitated at an earlier stage, solubility equilibrium between this phase and aqueous solution was assumed. The duration of each stage was determined by the turnover time of the mineral that mass balances indicated would be the first to be consumed. After each stage, remaining or accumulated amounts of minerals were calculated and used as input conditions for the next steady-state period (for mathematical formulation, see Salmon, 2000).

It is not implied that accurate predictions of the temporal evolution of the impoundment geochemistry can be made with these simple calculations; however, this approach provides a qualitative insight into the time
Geochemical modelling of acid mine drainage in mill tailings: Quantification of kinetic processes from laboratory to field scale

Simulations resulted in a sequence of precipitation and dissolution reactions and associated consecutive drops in pH (Fig. 10) similar to that which has previously been described in the literature (e.g., Blowes and Ptacek, 1994). Buffering of the pH was due to the fast dissolution of, in order of succession, calcite, siderite (FeCO$_3$) and aluminium and ferric iron hydroxides. After depletion of ferric iron hydroxide, the pyrite content was 11 vol-%; the pH was controlled only by the relative rates of pyrite oxidation and aluminosilicate dissolution, resulting in a pH below three. The lifetime of the pyrite in this simulation, and hence the duration of the acidic pH, was in the order of 1000 years. After depletion of pyrite, the modelled pH returned to above neutral (not shown).

As indicated in Chapter 5.1.2, the rate of dissolution of fast-reacting minerals, such as carbonates and hydroxides, required to maintain solubility equilibrium with solution would be greater in the absence of proton attenuation by aluminosilicates. Modelling without consideration of aluminosilicates would in a scenario such as that depicted in Figure 10 lead to underestimation of the time to reach acid pH, and furthermore, the simulated final low pH, as determined only by pyrite oxidation and iron redox processes, would be lower. Implications for the geochemical modelling of the groundwater composition of Impoundment 1 include that it may be plausible that a sufficient amount of Fe(OH)$_3$ and gypsum accumulated in Impoundment 1 to be the dissolving at the point in time represented by the case study, ~30 years after deposition.

5.2.2 Effect of remediation

Following a post-remediation investigation of the performance of a composite soil cover applied on parts of Impoundment 1, Werner et al. (2001) reported an oxygen flux of $\sim 1 \times 10^8$ mol m$^{-2}$ s$^{-1}$ and a water infiltration rate of $<1 \times 10^9$ m s$^{-1}$. These values correspond, compared to the pre-
remediation situation assessed in the case study, to a 1-2 order of magnitude decrease in both the oxygen and water fluxes.

As shown in Figure 7e and f, such a dramatic decrease in the oxygen influx would be sufficient to slow down pyrite oxidation to a level where the resulting pH is above 7. Inclusion of the kinetic representation of Fe redox processes allowed testing of the hypothesis that, with decreasing oxygen availability, the oxidation of pyrite by ferric iron would dominate over the oxygen path; however, this hypothesis was not supported by the model results, even in simulations with the maximum degree of acceleration that is reportedly possible due to microbial mediation \((\alpha_\alpha = \alpha_\beta = 35, \beta = 10^4 - 10^6)\). Simulations with low \(F_\text{O}_2\) and in the absence of aluminosilicate dissolution resulted in lower predicted pH, of \(~5\), as controlled by solubility equilibrium with \(\text{Fe(OH)}_3(s)\). Decrease in the water flux alone, with the fixed partial pressure of oxygen of 0.2 atm, had little effect on the pH, but did, however, result in higher concentrations of dissolved components (Paper II). As the impoundment has only relatively recently been remediated, the long-term efficiency of the applied techniques has not been assessed. However, comparison of release rates in saturated column experiments with Impoundment 1 tailings (Paper VI) with pre-remediation release rates (see Chapter 7) indicated that sulfide oxidation rates do decrease under saturated conditions.

Holmström et al. (2001) and Corrège et al. (2001) also report positive trends in the impoundment water quality a few years after remediation.
6 QUANTIFICATION OF ELEMENT RELEASE RATES FROM BATCH EXPERIMENTS

The modelling study of Impoundment 1 indicated that mineral weathering rates from literature, based on experiments on freshly prepared, monomineralic samples, overestimated rates observed in the field by 1-2 orders of magnitude, despite consideration of dependence of rates on pH, temperature, mineral content, and (BET) surface area of tailings, and differences in these physico-chemical conditions between the laboratory and the field. This chapter presents results of weathering experiments that were then performed on different tailings samples and sulfide minerals in order to test whether literature rates and rate dependencies were applicable for weathering of minerals in tailings (Papers III-V). In addition, the effect of application of various sterilisation techniques, as is necessary to obtain abiotic weathering rates in tailings samples, on the weathering characteristics of tailings were tested (Paper IV). The experimental method is only briefly described below; Papers III-V are referred to for details.

6.1 Materials and methods

Tailings were obtained from Impoundment 1 in August 1999 from near the original tailings dam wall, far from the original tailings slurry discharge point (“fine tailings” sample) and in August 2000 from near the original discharge point (“coarse tailings” sample); this distribution of fine and coarse particles is typical for tailings impoundments (e.g., Robertson, 1994). A sulfide concentrate was obtained from the coarse tailings by decanting of fine particles, gravimetric separation of the heavy fraction, and sieving to 0.035-0.5 mm size. Pyrite crystals were purchased (geographic origin unknown), crushed in a ceramic mortar and pestle and sieved to obtain a 0.125-0.25 mm fraction. Both sulfide concentrate and pyrite crystals were treated briefly with ultrasound in order to remove fine particles, which may otherwise result in unrepresentative high initial release rates (e.g., Nicholson, 1994).

The mineralogy of the 2 tailings samples, the sulfide ore concentrate, and the pure pyrite was determined by X-ray diffraction (XRD), and samples were analysed for total chemical composition. Tailings samples were further characterised by infrared spectroscopy (IR) and optical microscopy (including point counting of opaque minerals in thin sections). The particle size distribution of the tailings was determined with a laser granulometer, and the specific surface area of all samples was determined by evaluation of 5- and/or 1-pt N\textsubscript{2} adsorption data. The results of the mineralogical determinations were consistent with other determinations for the major minerals in Impoundment 1 as reported in Malmström et al. (2001), Holmström et al. (2001), and Carlsson et al., 2002; based on the mineralogy and total chemical composition, the mineral content of the tailings samples was estimated (Table 4; see Paper V).

Table 4. Estimated mineral content and BET surface area

<table>
<thead>
<tr>
<th></th>
<th>Fine tailings</th>
<th>Coarse tailings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrite</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>Chalcopyrite</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>Sphalerite</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>Quartz</td>
<td>28</td>
<td>40</td>
</tr>
<tr>
<td>Chlorite\textsuperscript{a}</td>
<td>26</td>
<td>25</td>
</tr>
<tr>
<td>Muscovite\textsuperscript{b}</td>
<td>14</td>
<td>7</td>
</tr>
<tr>
<td>Plagioclase\textsuperscript{c}</td>
<td>12</td>
<td>6</td>
</tr>
<tr>
<td>Surface area</td>
<td>10.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Chlorite and talc represented as chlinochlore, \(\text{Mg}_2\text{Al}_3\text{Si}_3\text{AlO}_{10}(\text{OH})_8\)

\textsuperscript{b}\(\text{KAl}_3(\text{AlSi}_3\text{O}_10)(\text{OH})_2\)

\textsuperscript{c}\(\text{Na}_{0.55}\text{Ca}_{0.45}\text{Al}_{1.45}\text{Si}_{2.55}\text{O}_8\)
The higher pyrite content in the tailings samples (~18 vol-%; Table 4), which were collected from the saturated zone, than was estimated for the unsaturated zone (~4 vol%; Table 2) is consistent with other reported solid phase characterisation of the saturated zone (e.g., Malmström et al., 2001; Holmström et al., 2001). The difference in mineral contents between the water saturated and unsaturated zone is likely due to partial depletion of sulfides in the upper part of the impoundment (see Chapter 3 and 4.1).

The XRD analyses confirmed that the pyrite sample was pure within the detection limits of the XRD (~5 %). The sulfide concentrate was found to consist predominantly of pyrite with some traces of feldspar, pyrrhotite, and possibly sphalerite.

### 6.2 Effect of pH, temperature, and surface area

#### 6.2.1 Weathering experiments

Weathering experiments were performed on fine and coarse tailings, sulfide concentrate, and pure pyrite over 89-480 days, at different conditions of pH, temperature, and acid medium; selected conditions are given in Table 5. Approximately two to six grams of samples were placed in 200 or 400 mL solution. Reactors were continually agitated and air-sparged. The pH and (in all but B4) redox potential were measured either in filtered samples or in reactors. Direct measurement of redox potential in fine tailings reactors with H$_2$SO$_4$ (C1, C7, C8), and on last 2 sampling occasions in the pure pyrite reactor (C12) lead to influx of the redox electrode electrolyte (KNO$_3$) to the reactor solution. Redox measurement over an extended period of time on Day 74 in C7 and Day 94 in C1 directly preceded an increase in the SO$_4^{2-}$ release rate in these reactors, as is discussed in the results section below (see also Paper V). For the C-series experiments, the solid phase was collected after closure of the experiments for mineralogical analysis using XRD and IR.

Samples were analysed for concentrations of SO$_4^{2-}$ and major cations (see Papers III-V for analysis techniques). Calculation of saturation indices indicated that, for the majority of components during the period of time over which release rates are derived, aqueous concentrations were generally not controlled by solubility equilibrium with typical phases for AMD, with the major exception of iron.

### Table 5: Experimental conditions

<table>
<thead>
<tr>
<th>Reactor</th>
<th>B4$^b$</th>
<th>C-series</th>
<th>G-series$^d$</th>
<th>E-series</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Fine tailings</td>
<td>Fine tailings</td>
<td>Coarse tailings</td>
<td>Sulfide conc.</td>
</tr>
<tr>
<td>pH</td>
<td>~3</td>
<td>~3</td>
<td>~3</td>
<td>~3</td>
</tr>
<tr>
<td>Acid medium</td>
<td>HNO$_3$</td>
<td>H$_2$SO$_4$</td>
<td>H$_2$SO$_4$</td>
<td>H$_2$SO$_4$</td>
</tr>
<tr>
<td>Start</td>
<td>Dec'99</td>
<td>Nov'00</td>
<td>Dec'00</td>
<td>Nov'01</td>
</tr>
<tr>
<td>Duration [day]</td>
<td>89</td>
<td>480</td>
<td>480</td>
<td>343</td>
</tr>
</tbody>
</table>

$^a$See also Table 4, Paper V
$^b$Preliminary results reported in Salmon and Malmström (2001; Paper III)
$^c$5°C; other experiments at ~23±1 °C.
$^d$Preliminary results reported in Salmon and Malmström (2003; Paper IV)
6.2.2 Results

Sulfate release in fine tailings under different conditions of pH, acid medium, and temperature are shown in Figure 11a. For fine tailings at 25 °C, two release rate regimes were observed. In the experiment with pH ~3 in HNO₃, performed soon after collection of tailings, a typical pattern for bacterial leaching (e.g., Rossi, 1990) was observed, with a fast release rate, or “accelerated” release, after a lag phase of ~8 days (Fig. 11a). By contrast, in later experiments with the same tailings and pH, but in H₂SO₄ medium, the SO₄²⁻ release rate remained approximately constant until ~Day 96, after which a similarly accelerated release was observed. A similar pattern was also observed in the pH 2 H₂SO₄ reactor (Fig. 11a). After the period of high release rate in all reactors, approximately 70-90% of the S initially present in the solid phase in each reactor had been released to solution, suggesting that the main S-source, pyrite, was completely or effectively depleted at this point or soon after. The greater delay before the accelerated rate in the H₂SO₄ reactors may be due to an extended lag phase after approximately a year of storage, and/or addition of K⁺ and NO₃⁻, possibly acting as nutrients for the micro-organisms, on the preceding sampling occasion (see above). The similar release rates at pH ~2 and pH ~3 in both the accelerated and non-accelerated period suggests low to negligible pH-dependence of the dominant S-releasing process.

In the reactor with coarse tailings in HNO₃ (not shown; see Paper V), the final SO₄²⁻ release rate was by contrast somewhat lower than the initial rate; the mass-normalised release rate [mol g⁻¹ day⁻¹] was also lower

Figure 11. a) Accumulated release of SO₄²⁻ in fine tailings experiments, and b) Mg²⁺ and c) Zn²⁺ in fine and coarse tailings experiments.
than the “non-accelerated” rate in the fine tailings. The coarse tailings did not exhibit a period of accelerated SO$_4^{2-}$ release in either HNO$_3$ or H$_2$SO$_4$ medium. A possible explanation for the accelerated release period in the fine tailings but not in the coarse is that in the absence of other nitrogen sources, the low levels of nitrate in the fine tailings reactors were utilised as a N source (Erlich, 1996, and references therein). At higher concentrations, however, nitrate has been reported to inhibit microbial activity (e.g., Harahuc et al., 2000); it is also reported to have greater toxicity at lower pH (Alexander et al., 1987), and may therefore have had an inhibiting effect on microbial activity in the coarse tailings reactor with HNO$_3$. Over the course of the coarse tailings experiment (~100 days), less than 10% of the S in the coarse tailings was released to solution.

In the reactor with fine tailings (H$_2$SO$_4$) at 5°C (Fig. 11a), the SO$_4^{2-}$ release rate was lower than that at 25°C, and constant over the ~340 days of the experiment. Sulfate release rates in the sulfide concentrate reactors (not shown, see Paper V) were constant with time, over the ~40 days of experiments. Release in the pure pyrite reactors was constant for the first ~150 days, and also for the latter 300 days of the experiments, but at a lower rate.

The increase in SO$_4^{2-}$ release in all fine tailings reactors was accompanied by a drop in pH, by up to 1 pH unit in reactors at pH 3, and an increase in redox potentials (not shown). In reactors where pH decreased by up to one pH unit over the experiments, an increase in the release rate of base cations was observed (e.g., Fig. 11b; see also Fig.3 in Paper V). However, in reactors at pH ~2, where the pH remained relatively constant, base cation release generally decreased with time (Fig. 11b), a phenomenon commonly observed in aluminosilicate weathering experiments (e.g., Malmström and Banwart, 1997; Brandt et al., 2003; Gustafsson and Puigomenech, 2003), and suggested to be due to processes such as preferential leaching of metal ions, weathering and depletion of fine particles and/or more reactive sites on freshly exposed mineral surfaces (e.g., White and Brantley, 1995). Indications were that initial Ca$^{2+}$ release in coarse tailings was affected by gypsum dissolution (see Paper V); if this process occurred in the fine tailings, it did not appear to affect Ca$^{2+}$ release rates.

For fine and coarse tailings and the sulfide concentrate, Zn$^{2+}$ and Cu$^{2+}$ release was initially fast, then decreased to level off before 100% was released to solution (e.g., Zn$^{2+}$ in Fig. 11c), irrespective of SO$_4^{2-}$ release pattern, acid medium (HNO$_3$/H$_2$SO$_4$), or temperature (5/25°C). In the reactors with fine tailings at 25°C, the remaining Zn$^{2+}$ was released to solution at the same time as the accelerated SO$_4^{2-}$ release rate; the accumulated Cu$^{2+}$ release was not affected. Both Zn$^{2+}$ and Cu$^{2+}$ release rates displayed low dependence on pH but high dependence on temperature. A decrease in leaching rates with time is commonly observed in leaching experiments of chalcopyrite and sphalerite, and is suggested to be due to, for example, decrease in surface area due to reduction of particle size, or formation of a leached layer on the mineral surface such that dissolution becomes transport-limited. A shrinking radius model relatively successfully explained the Zn$^{2+}$ and Cu$^{2+}$ release (Papers III and V).

In summary, release rates of base cations and Al$^{3+}$ and Si were affected by pH, which was not the case for release of SO$_4^{2-}$, Zn$^{2+}$, or Cu$^{2+}$. Some fine tailings reactors exhibited periods of accelerated sulfate release, which was tentatively assigned to microbial mediation. In experiments with relatively constant pH, initial release rates of, for example, Mg$^{2+}$ were higher than final release rates. Release rates [mol/g/day] were generally lower in coarse tailings than in fine tailings, and at low temperature than at high temperature.
6.3 Effect of sterilisation

6.3.1 Experimental method

Weathering experiments and BET surface area determinations were performed on coarse tailings sub-samples that had been subjected to various traditional and novel methods of sterilisation (see Table 6, Paper IV and Herbert et al., 2003). Sterilisation was found to have little effect on the bulk mineralogy or total chemical composition; however, oxidised sulfur surface species and non-hydrocarbon surface C, as well as ascorbate-extractable metals, increased as a result of some treatments (see Herbert et al., 2003).

Procedures for weathering experiments were similar to in the other experiments (Chapter 6.2.1) with the exception that measures were taken (see Paper IV) to prevent microbial contamination of reactors. Extra samples were also collected from all reactors for staining with 4′6-diamidino-2-phenylidylole (DAPI). This process leads to fluorescence of DNA and organic material under UV light, and is generally used for total count of viable bacteria in aqueous solution.

6.3.2 Results

In the sterilisation experiments, the BET surface area of the sterilised samples was found to be on average slightly lower than in the untreated samples, possibly due to, e.g., loss of fine particles during the sterilisation treatments. However, the mineralogical and chemical analysis of the tailings, as mentioned above, indicated that the bulk composition did not vary more between treated and untreated samples than between untreated controls. Release rates in the sterilisation experiments generally followed the same pattern as in the untreated controls (coarse tailings reactors G1 and G2, see Chapter 6.2), with the exception of reactors where inspection by fluorescent microscopy revealed the presence of large amounts of organic filaments, probably fungal.

Final and initial element release rates, obtained from linear regression on element release data in the reactors containing sterilised (G3-9) and untreated controls and normalised to the BET-surface area of each sample, are given in Figure 12. In both treated and untreated samples, initial rates

<table>
<thead>
<tr>
<th>Phase</th>
<th>Reactor</th>
<th>Tailings treatment</th>
<th>Degree of microbial activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>G1</td>
<td>Phase I control - untreated</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>G2</td>
<td>Phase I control - untreated</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>G3</td>
<td>autoclave</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>G4</td>
<td>repeated heating to 70°C</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>G5</td>
<td>ethanol</td>
<td>none</td>
</tr>
<tr>
<td>II</td>
<td>G6</td>
<td>antibiotics mixture</td>
<td>medium</td>
</tr>
<tr>
<td></td>
<td>G7</td>
<td>γ-irradiation – 10 kGy</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>G8</td>
<td>γ-irradiation – 25 kGy</td>
<td>none</td>
</tr>
<tr>
<td></td>
<td>G9</td>
<td>rinsed with distilled water</td>
<td>high</td>
</tr>
<tr>
<td></td>
<td>G10</td>
<td>Phase II control- untreated</td>
<td>high</td>
</tr>
</tbody>
</table>

*Reactor name in weathering experiments.

*bSolution was 0.05 M H$_2$SO$_4$, as opposed to 0.1 M HNO$_3$ as used in the other reactors.

*cDetected after 30 days (Herbert et al., 2003).
exceeded final rates by up to a factor of 35. Higher initial release rates may be due to, for example, dissolution and depletion of fine particles with high specific surface area or of secondary minerals present in the tailings.

Final release rates of all elements were similar in most of the reactors (Fig. 12), irrespective of the presence/absence of filaments and which/whether a sterilisation technique had been applied (cf. Table 6), with the exception of reactors where large amounts of filaments were observed, that is, G6, G9 and final Cu$^{2+}$ release rate in G10 (see Paper IV). The similarity of final release rates from the majority of reactors suggested that the sterilisation methods, other than treatment with antibiotics, do not mechanically or chemically affect the long-term weathering of the tailings, given the experimental conditions. Normalisation to sample weight instead of the BET-surface area of each sample does not affect this conclusion (compare Fig. 12 with Fig. 2 in Paper IV). An implication of the decline in release rates with time is that long-term experiments (> 30 days) are to be recommended for establishment of weathering rates in untreated and sterilised mill tailings samples.

The results also indicated similar release rates of elements between sterilised and untreated samples at the end of the experiments. While other explanations were possible (see Paper IV), these results indicate that biological mediation of sulphide oxidation is not favoured at the experimental conditions, possibly due to, e.g., nutrient limitation or inhibition due to high nitrate concentration at low pH (e.g., Alexander et al., 1987), and that abiotic processes dominate the release of elements.
7 MODELLING WEATHERING RATES ON BATCH, COLUMN, AND FIELD SCALE

7.1 Model interpretation of element release rates

Conceptual understanding of element release rates, as is important for interpretation of impoundment groundwater composition and prediction of its evolution with time, relies on identification of source processes. In Papers III and V, element release from tailings samples were thus attributed to, and interpreted in terms of, specific mineral weathering reactions. Element release rates \( R_j \) from batch experiments were used as tracers for mineral weathering reactions (Reactions 1, 3, 5, and 7-9 in Table 1). Copper and Zn\(^{2+} \) were used as tracers for the chalcopyrite and sphalerite weathering, respectively, and Mg\(^{2+} \), K\(^{+} \) and Ca\(^{2+} \) (or Na\(^{+} \)) as tracers for chlorite, muscovite and plagioclase weathering, respectively. The pyrite weathering rates was obtained from release of SO\(_4^{2-} \) after correction for contribution of ZnS and CuFeS\(_2 \) weathering. (see Papers III and V). From the obtained rates [mol g\(^{-1} \) s\(^{-1} \)] and the mineral surface area as estimated by Equation 6, the surface-area normalised weathering rate of the \( i^{th} \) mineral, \( r_i \) [mol m\(^{-2} \) s\(^{-1} \)] was obtained from:

\[
r_i = \frac{R'_j}{A_i \eta_{i,j}} \text{ [mol m}^{-2} \text{s}^{-1}] \quad (7)
\]

where \( \eta_{i,j} \) is the stoichiometric coefficient of tracer \( j \) in the weathering reaction of mineral \( i \). This approach, combined with check of solubility equilibrium control of tracer concentrations, correction for multiple source minerals where possible, and estimation of surface area through Equation 6, is also applied in consideration of rates from column experiments (see Chapter 7.3) and the field study (Chapter 3 and 7.3).

For comparison of results from experiments at different temperatures, rates were converted to 23 °C using the Arrhenius equation and the activation energies, \( E_a \), given in Table 4 in Paper I, with the exception of chlorite, where \( E_a \approx 60 \) kJ/mol was used, in keeping with recent chlorite weathering studies (Brandt et al., 2003, and references therein).

7.2 Mineral weathering rates in tailings compared to monomineralic samples

7.2.1 Pyrite

Figure 13 shows the obtained pyrite weathering rates vs the average pH for the time interval over which the rate was determined. Despite a decrease in rate with time, both initial and final rates of pyrite weathering in the pure pyrite reactor (crosses in Fig. 13b) were within the range of reported abiotic pyrite weathering rates in the literature. This indicates that the applied experimental method can achieve comparative rates to those reported in the literature.

Determination of the pyrite weathering rate using Equation 7 lead to rates from the coarse tailings, the non-accelerated release period of the fine tailings, and the sulfide concentrate that agreed internally within a factor ~4 (Fig. 13a). In addition, the rate in the fine tailings reactor at low temperature (squares in Fig. 13a), when scaled up to room temperature, was in the same range. However, these “non-accelerated” rates (Fig. 13a) were up to an order of magnitude lower than the lowest abiotic rates reported in the literature. Possible explanations may include that the pyrite weathering rates in the literature are generally performed on freshly exposed mineral surfaces, whereas the reactivity of the pyrite in the tailings had decreased after 40 years of exposure in the tailings impoundment, resulting in slower dissolution rates in the laboratory experiments. Lower weathering rates in aged samples has been reported in a number of weathering studies (e.g., Anbeek, 1993, for feldspar), and is further supported by the decrease in the pure pyrite weathering rate with time in this study.
The fact that pyrite weathering rates in the sulfide concentrate, which was a relatively well-defined size fraction, also were low compared to the reported abiotic literature rates, suggests that the relatively lower rates in the batch tailings experiments are not due to overestimation of the pyrite surface area by Equation 6, which for example may be the case if pyrite was predominantly present in coarse size fractions. A further possibility is that the surface area normalised release rate is not constant over the different particle size fractions, as is assumed in application of literature rate laws, determined on one particle size, to a particle size distribution such as in tailings.

Figure 13 highlights that the pyrite weathering in the tailings and its sulfide concentrate exhibited low to negligible pH-dependence for 2 < pH < 4.5, as has previously been reported in the literature for monomineralic weathering studies of pyrite (e.g., Nicholson, 1994; Williamson and Rimstidt, 1994). The accelerated rates observed in fine tailings reactors (Fig. 13b) at 25 °C may be due to microbial mediation. However, rates are lower than reported microbially mediated rates (e.g., Olson, 1991; surface area normalisation reported in Nordstrom and Alpers, 1999); it is possible that the rates are limited by the same factor as limiting abiotic rates, by low concentrations of nutrients, or by another, unknown factor. The low rates relative to reported biotic rates are consistent with the findings described in Chapter 6.3 and Paper IV, where similar element release rates were observed in sterilised and untreated tailings samples, leading to the conclusion that microbial mediation was not favoured under the experimental conditions.

7.2.2 Sphalerite and chalcopyrite

As for pyrite, utilisation of Equation 7 gave weathering rates from all samples that were the same to within a factor of approximately 10 for sphalerite (Fig. 14a). Figure 14 also highlights the low pH-dependence of the weathering rates of these minerals and that conversion of sphalerite release from 5 °C using reported activation energies gave similar rates to those at 25 °C (squares in Fig. 14). For chalcopyrite, rates agree within a factor 14, and rates for coarse tailings and fine reactors in H₂SO₄ at 25 °C agree within a factor 8 (Fig. 14b). The lower rate for chalcopyrite at 5 °C may indicate that the
employed literature value of $E_a$ is not representative of chalcopyrite oxidation in tailings, or that another process, with a higher $E_a$, controls Cu$^{2+}$ release. Release was also higher in the reactor with fine tailings in HNO$_3$ (circle in Fig. 14b); of note may be that this greater release rate occurred at the same time as the accelerated SO$_4^{2-}$ release in this reactor.

In contrast to the pyrite rates, the chalcopyrite and sphalerite weathering rates determined in the batch experiments were orders of magnitude higher than reported abiotic rates in the literature, although lower than reported biotic (Fig. 14). The observed rates were close to reported abiotic rates for mineral dissolution in a mixture with pyrite. As mentioned in Section 2, it was observed that opaque minerals in the tailings (i.e., predominantly sulfides) are often intergrown; accelerated dissolution of sphalerite, and other minerals with lower rest potentials than pyrite in the electrochemical series, has been reported in the presence of pyrite (e.g., Kwong, 1993, 2001), and may be the cause of the relatively higher rates. Further possibilities may include oxidation of these minerals by aqueous Fe(III), or predominance of these minerals in the fine tailings fraction, which would lead to underestimation of surface area by Equation 6 and therefore overestimation of the rate in Equation 7.

### 7.2.3 Aluminosilicate minerals

Normalisation of aluminosilicate weathering rates to the BET surface area using Equation 6 and 7 lead to generally higher initial rates for coarse tailings for chlorite (Fig. 15a) and plagioclase (Fig. 15c), whereas rates of muscovite dissolution were similar in coarse and fine tailings (Fig. 15e,f). For the plagioclase rate, which is derived from the Ca$^{2+}$ release rate, this would appear to be due to gypsum dissolution in the initial stages of the coarse experiments, and is resolved only by considering later rates of Ca$^{2+}$ release or plagioclase weathering based on Na release (Figure 15c,d). Higher chloride weathering was also found in the fine tailings reactor at pH ~2; this suggests that the higher release is a function of preferential leaching at low pH (e.g., Schnoor, 1990; Malmström and Banwart, 1997; Gustafsson and Puigdomenech, 2003), and that Mg$^{2+}$ release at low pH does not necessarily reflect chlorite weathering.

While final weathering rates were generally 1-2 orders of magnitude lower than those reported in the literature, the pH-dependence of mineral weathering in general displays the same trends as reported in the
Fig 15: Initial (left panel) and final (right panel) weathering rates \([\text{mol m}^{-2} \text{s}^{-1}]\) (23 °C) vs pH. a, b) chlorite; c, d) plagioclase; and e, f) muscovite; Markers denote fine tailings (HNO₃, pH ~3-3; H₂SO₄, at pH~3-2) and coarse tailings (HNO₃ - ◻, pH~3-0). Additional symbols in panel c and d indicate weathering rates derived from Na release for coarse tailings (HNO₃ - ◼; H₂SO₄ - ◼) and fine tailings (H₂SO₄, pH~2 - ▲). Dashed lines indicate rates from literature rate laws (chlorite – Malmström et al., 1995; plagioclase, Oxburgh et al., 1994; muscovite – Knauss and Wolery, 1989). Solid line in b: regression on fine tailings points. Error bars indicate uncertainty due to unknown tracer stoichiometry (see Table 1 in Paper V).
7.3 Comparison: Batch, column and field rates

In order to further assess the 1-2 orders of magnitude discrepancy between field and laboratory weathering rates observed in Papers I and III, experimental mineral weathering rates obtained on different scales were compared directly, before and after correction for field conditions (Papers III and V). Element release rates determined on a mesoscale in water saturated columns (Table 2 in Paper VI), using similar coarse and fine tailings as used in the batch experiments, were preliminarily interpreted in terms of weathering rates and utilised in the comparison between different scales. As the tailings surface area-normalised element release rates obtained for the two columns agreed within a factor 3, results from the coarse tailings column are used here. The effluent pH from the column over 11 month-experiment was similar to that in the field, ~5.

Element release rates from the field and column experiment were assessed as concentration x flowrate and were normalised to the mass of material present (see Papers V and VI). For Impoundment 1, the mass of tailings in the unsaturated zone was used, assuming, as in the modelling study, that the unsaturated zone is the major source of solutes in the impoundment groundwater (see also Banwart and Malmström, 2001).

Comparison of data in Figure 16, where laboratory rates for batch experiments on fine tailings at 25 and 5 °C and coarse tailings, as well as rates in columns, are normalised to field rates, indicates that for most components, rates determined in batch experiments overestimate field rates by 1-5 orders of magnitude, which is consistent with the commonly observed scale dependence of mineral weathering rates. In contrast, rates from columns underestimated the majority of components.

7.4 Prediction of field weathering rates from laboratory experiments

In order to predict field element release rates, kinetic data from the laboratory experiments were scaled with factors accounting for the effect of differences in temperature, mineral surface area (as estimated by Equation 6), and, where appropriate, pH and Po2, between the scales on the weathering rates, in an approach similar to that proposed by Malmström et al. (2000):

\[ R_j^{B-F} = \eta_{i,j} A_j^{F} r_i^{B-F} = \eta_{i,j} A_j^{F} r_i^{B} \beta_j^T \beta_j^T \beta_j^T \beta_j^T \]

(8)

![Figure 16. Comparison of element release rates [mol g^-1 day^-1] in batch reactors (fine tailings, 25 °C, HNO\textsubscript{3}, pH~3, ◊; fine tailings, 5 °C, H\textsubscript{2}SO\textsubscript{4}, pH~3, ▲; coarse tailings, 25 °C, HNO\textsubscript{3}, pH~2 ©) and coarse tailings column (△), normalised to field rates.](image)
where $\beta_i^{T}$ is the correction factor for temperature based on the Arrhenius equation, $\beta_i^{pH}$ and $\beta_i^{P_{O_2}}$ are correction for pH and Po$_2$ based on the dependencies given in rate laws in Table 1 (see Paper V for details), and superscripts B, F, and B-F denote batch, field, and batch scaled to field. The quantification of scaling factors for Po$_2$, pH, and temperature are thus independent of the laboratory experiments presented in this thesis. An analogous approach was applied for adjustment of the column rates, with the exception for the correction for field Po$_2$. Given the sensitivity of the release rate of S, Fe, Cu$^{2+}$ and Zn$^{2+}$ to the partial pressure of oxygen (e.g., Table 1) and that this quantity was not measured in the columns, release rates of these elements were not corrected for field Po$_2$ (i.e. $\beta_i^{P_{O_2}}=1$ for all minerals). The predicted field rates from the column studies thus applies to water saturated conditions in the field, such as was aimed for with the applied remediation measures at the site, rather than prevailing partly water-unsaturated conditions at the time of field sampling. Aluminium release was predicted from aluminosilicate mineral weathering rates and stoichiometry (i.e., the aluminium model applied in Papers III and V, see, e.g., Equation 8 and Figure 8 in Paper V); as the modelling study indicated a low degree of iron oxidation or immobilisation in Impoundment 1, Fe release was predicted from SO$_4^{2-}$ release and pyrite stoichiometry. Adjustment for field conditions (Fig. 17a-c) brought batch experiment-derived rates for all elements, except Ca$^{2+}$, closer to those observed in the field, particularly for those derived at low temperature (Fig. 17b) and from the coarse tailings (Fig. 17c), which agreed with field rates to within a factor 10, except for Cu$^{2+}$, K$^+$ and Ca$^{2+}$. Sulfate release (and thus, Fe release) is overestimated by the accelerated SO$_4^{2-}$ release rate observed in the 25 °C fine batch reactor in HNO$_3$ medium (Fig. 17a; cf. Fig. 11a). This result is consistent with conclusions of the earlier modelling study (Chapters 4-5) that
microbial processes do not contribute greatly to the geochemical processes occurring in Impoundment 1. Consideration of microbial conditions when deriving laboratory sulfide oxidation rates to extrapolate to other scales is thus of importance, particularly as model results were sensitive to small changes in the pyrite weathering rate (Chapter 5.5.1).

Calcium release is underestimated by the adjusted plagioclase rates in all reactors; this is consistent with control of calcium release in the field by dissolution of gypsum rather than plagioclase weathering, as was also concluded from the modelling study (cf. Figure 5). The prediction based on batch experiments for Cu\(^{2+}\), Zn\(^{2+}\), K\(^{+}\) and Al\(^{3+}\), and, from coarse tailings, Mg\(^{2+}\), overestimated the field release rates, indicating a remaining unresolved difference between the laboratory results and field rates. Possible reasons for remaining discrepancies include that additional processes affect the component discharge rate at the somewhat higher pH in the field. This suggests a need for experiments at pH values that are similar to those that will occur in the field, long term experiments so that mineral weathering reaches steady state, and further investigation and quantification of potential immobilising processes in the field.

Lower rates of SO\(_4^{2-}\), Fe, Cu\(^{2+}\) and Zn\(^{2+}\) as predicted from columns-derived rates are due to the low oxygen availability in these experiments; low aluminosilicate dissolution may be due to the decreased proton release (e.g., Banwart et al., 2002), or greater preferential flow in the column than in the field. This implies that rates of contaminant release will be lower at water saturated conditions, which is consistent with modelling studies and reported preliminary post-remediation studies of Impoundment 1 (Chapter 5.2.2). However, it also indicates that prediction of unremediated conditions (i.e. with the presence of an unsaturated zone) from saturated columns will be difficult without consideration of the dependence of aluminosilicate weathering rates on acid production rather than just pH.

Field rates were also predicted from mineral weathering rate laws from the literature (Paper V, Figure 9d). However, in general, prediction using kinetic data of the site specific tailings resulted in better prediction of element release rates in the field. This indicates that factors that contribute to discrepancies between laboratory weathering rates of minerals in the tailings and in monomineralic museum specimens (see Chapter 7.2) also are important in the field.
8 CONCLUSIONS AND IMPLICATIONS

A methodology is presented for studying and quantifying geochemical processes that contribute to AMD generation in base metal sulfide ore mill tailings. The methodology builds on first principles regarding geochemical processes, using site-specific quantification of factors that are commonly observed to exert a large influence on mineral weathering rates, such as temperature, pH, and mineral surface area. Similar modelling approaches have been applied to waste rock and other geochemical systems in the past, however the bulk of literature on prediction of AMD from mill tailings currently focuses on static and kinetic laboratory testing. Such testing is reported to be associated with a high degree of uncertainty, and furthermore largely neglects coupling between geochemical processes and oxygen availability. The transparent modelling methodology and results presented in this thesis will hopefully contribute to increased general understanding of dominant processes affecting AMD generation, increased capacity to quantify these processes, and wider application of such quantification, with improved mitigation of the environmental impact of mining as the ultimate result.

Application of the modelling methodology to the case study site, Impoundment 1 of the Kristineberg mine site in northern Sweden, involved consideration of site-specific tailings mineralogy, quantification of slow weathering processes using rate laws obtained from the literature, and coupling to fast equilibrium processes, such as aqueous speciation and precipitation/dissolution of secondary phases. This approach successfully reproduced the pH at the site; the major processes contributing to the balance of proton production and consumption were found to be pyrite oxidation and aluminosilicate and Fe(OH)$_3$ dissolution. Relative release rates of most major ions were also the same as in the impoundment. Uncalibrated, absolute weathering rates and thereby also resulting model concentrations were however 1-2 orders of magnitude higher than observed in the field. For all major components, a single calibration factor, $X_{i} = 10^{-2}$, applied similarly to all weathering rate expressions, sufficed to account for this (commonly observed) apparent scale dependence of mineral weathering rates, from laboratory values reported in the literature (uncalibrated model) to field relevant rate values (calibrated model).

Subsequent laboratory studies of mineral weathering rates in site-specific tailings material taken from the field indicated that weathering rates for pyrite and aluminosilicates, normalised to mineral surface area, were in fact 1-2 orders of magnitude lower in the ~50-year-old tailings than the rates reported in the literature, which are usually determined on freshly exposed mineral surfaces. Observations of similarly low, surface area-normalised weathering rates in a sulfide concentrate (where extraction of this fraction from the tailings removed a number of assumptions otherwise required for determination of mineral surface area in tailings) indicated that the applied method of sulfide surface area estimation in the experimental tailings material was a reasonable approximation, and that the observed difference in weathering rates was likely due to differences in mineral properties between freshly exposed minerals and old tailings material. Exact reasons for the observed decrease with time of weathering rates normalised to mineral surface area is a topic of ongoing scientific discussion (e.g., White and Brantley, 1995; Hodson and Langan, 1999), and remains yet to be explicitly quantified in predictive geochemical models. The results of the present laboratory study, however, indicated that model results of dominant processes in tailings impoundments were valid after the scaling down of all weathering rates in the model by the single factor $\sim 10^2$. Furthermore, the laboratory study indicated that pyrite and aluminosilicate minerals exhibited the same
dependence on pH and temperature, and for some minerals, also on surface area, as reported in the literature. This observation further supported the hypothesis that literature weathering rate laws, obtained from monomineralic samples, are applicable for tailings, once allowance is made for the scale dependence in absolute rate values.

The modelling study demonstrated the importance of kinetic representation of aluminosilicate dissolution and iron redox reactions for prediction of pH, which results from the balance of proton production and attenuation, and major ion composition of the impoundment groundwater. At the case study site, kinetic aluminosilicate dissolution was found to provide the bulk of proton attenuation and, as a result, considerably affect the rate of depletion of fast-reacting pH-buffering minerals, such as calcite, which are able to keep pH at a circum neutral level. Inclusion of the kinetics of aluminosilicate dissolution and of the feedbacks between slow and fast processes is thus potentially crucial for prediction of the proton balance and the long-term evolution of pH in general.

Simulations further indicated that the iron redox cycling, which may be accelerated by acidophilic bacteria, was low at the case study site, where conditions of low temperature and near-neutral pH prevail. However, the sensitivity of the modelled groundwater composition and pH to sulfide and iron redox reactions indicated that quantification of microbial mediation of these reactions at other sites may be necessary for predicting the overall oxidation rate. Limited oxygen availability has in previous modelling studies been assumed to be the overall limiting factor on AMD quality; however, even for a given, low oxygen flux, the modelled pH was sensitive to the balance between pyrite oxidation pathways. Consideration of the possibility of microbial mediation and other factors that lead to uncertainty in the iron redox cycling therefore require closer investigation. Comparison of rates in the field and in the laboratory studies, however, also indicated that further investigation is also needed of other factors, such as nutrient availability, which may limit microbial mediation in the field. To this end, the present laboratory experiments indicate that commonly applied sterilisation methods do not affect long-term (>30 days) abiotic element release rates in tailings.

In contrast to findings for pyrite and aluminosilicate weathering rates, heavy metal (Zn$^{2+}$, Cu$^{2+}$) release rates derived here from batch laboratory experiments exceeded reported literature rates for oxidation of sphalerite and chalcopyrite by 1-3 orders of magnitude. For Zn$^{2+}$, uncalibrated extrapolation of this batch rate from laboratory to field conditions lead to reproduction of the field rate within a factor 10; for Cu$^{2+}$ release, however, the corresponding field rate was overestimated by 2-4 orders of magnitude. Possible differences in the mechanisms of release and immobilisation of Zn$^{2+}$ and Cu$^{2+}$ (and also Al$^{3+}$ and K$^+$) between the laboratory and the field require further investigation.

This study suggests that within certain limits, which appear narrower than recognised in current prediction practices in industry, it is possible to predict the weathering behaviour of major minerals, and hence proton release and attenuation, in base metal tailings under relevant field environmental conditions. Remaining issues to resolve for further improved confidence in predictive modelling of leachate composition from tailings impoundment include changes in mineral weathering rates with time and the mechanisms controlling heavy metal release and retention. The herein proposed methodology of integrating model quantification, geochemical characterisation and observations on different scales may considerably aid in such issue resolution. Furthermore, more sophisticated mathematical-numerical models than used in this thesis provide means to couple more detailed representations of transport and mass transfer processes with the geochemical processes and principles focussed upon here. Important
complementary studies to those presented in this thesis include prediction of AMD potential already during the mining exploration stage (e.g., Kwong, 1993, 2003), and assessment of the effect of subsurface heterogeneity on soil cover remediation of mine wastes (e.g., Werner, 2000) and on downstream contaminant transport (e.g., Berglund et al., 2003), which all indicate that the improved source term quantification attempted here will contribute to improved prediction reliability of the environmental impacts of AMD. Such improved reliability will in turn assist in optimisation of remediation expenditure on both site (O’Kane and Wels, 2003) and water catchment (Baresel et al., 2003) scales, and thereby facilitate efficient attainment of environmental water quality goals.
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