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MODELLING REACTIVE TRANSPORT OF ACID MINE DRAINAGE IN GROUNDWATER:
EFFECT OF GEOCHEMICAL PROCESSES, SPATIALLY VARIABLE FLOW,
SOURCE LOCATION AND DISTRIBUTION

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Dedication

. . . To all victims of HIV/AIDS in Africa. . . .

May God rest your souls in Heaven!
Summary

Impacts from mining waste deposits on groundwater resources have been recognized in various parts of the world; though varied in scale depending on the composition of minerals being mined, the level of technology employed and environmental commitment of the developers. Mining activities usually involve milling, concentrating, and processing of ores which will result in a huge amount of waste, called tailings, usually deposited in impoundments as a slurry, composed of fine grained geological material (uneconomical minerals), chemicals utilized in the process, and water. Oxidation of these deposits, usually containing sulphide minerals, may result in generation of an acidic, metal laden leachate, called Acid Mine Drainage (AMD), which may have a devastating impact on the surrounding groundwater resources.

In this study, the stochastic LaSAR-PHREEQC reactive transport modeling approach is used in order to evaluate the coupled effect of geochemical reactions and physical heterogeneity of the subsurface in the breakthrough of acidity and metal downstream of the source while the AMD transported in the water saturated zone of an impoundment. The tailings deposit called Impoundment 1 at the Kristineberg mining site at the Skellefteå field, in northern Sweden, is used as a case study to simulate pH buffering processes and attenuation of Zn. The objectives of the study are 1) to evaluate the relevance of different possible geochemical processes in pH buffering and Zn attenuation; 2) to evaluate the effect of spatial variability of the physical processes of the groundwater system on the breakthrough of contaminants; and 3) to evaluate the effect of the location and distribution of the source zone in terms of the distance from the impoundment boundary.

Simulation results of the presented model revealed that pH buffering from calcite and chlorite are important processes capable of counteracting the acidification from AMD. Dissolution of secondary Al(OH)$_3$ is another important process capable of buffering pH. Precipitation of smithsonite, ZnCO$_3$, is an important process for attenuation of Zn$^{2+}$. Moreover, sorption of Zn$^{2+}$ on ferric iron surfaces is found to be an important process for attenuation of the metal, depending on the available sorption surface sites. Flow variability highly affects the breakthrough of the contaminants such that with increasing subsurface heterogeneity, earlier breakthrough of contaminants occurs. Moreover, increased variability results in decreased peak loads, but longer duration of the load.

Key words: Acid Mine Drainage (AMD), reactive transport, geochemical processes, flow variability, pH buffering, metal attenuation, groundwater, modelling, LaSAR-PHREEQC.
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1. Introduction

Sustainable development of the mining industry requires consideration and awareness of the long-term impact of mining activities that have been so far undertaken with little concern for the environment. Mining and milling operations together with grinding, concentrating ores and disposal of tailings, provide obvious sources of pollution in the vicinity of mines. Mining by its nature can have a serious impact on the environment as a whole and associated activities may generate sources of toxic element contamination that can damage the surface and subsurface water resources.

During extraction of metals from sulfide ore, for instance, in the ore-enrichment process, the efficiency of modern methods is approximately 90%, which implies that 10% of metals are deposited in the tailings (Salmon and Destourni, 2001), which will have a potential to contribute pollutants in the form of acidity and heavy metals and metalloids to the surrounding water bodies as Acid Mine Drainage (AMD). Additionally, all iron sulfides associated with the sulfide ore of the desired element are usually deposited in impoundments. It has been estimated that, in 1995, in Sweden, approximately 60% of all lead, cadmium, zinc and copper discharged to water in Sweden come from mining and mining waste (SCB, 2000b).

Changes in laws, technologies and attitudes can address some of the most immediate threats posed by mineral development, but there are still many areas of mining practices that should be given attention. For instance, according to the 1995 inventory of contaminated land sites in Sweden by the Swedish Environmental Protection Agency (SEPA), with the aim to assessing the need of remediation measures throughout the country, out of the 1700 sites investigated, 70 potentially contaminated sites were identified within the mining industry, and 50 of these sites were classified as a large to medium risk for health and the environment, (SEPA, 1995, 1998). Areas of abandoned mines or old operating mines that have been closed several years ago can still have a long lasting impact on the environment. Abandoned mine sites often contain un mined mineral deposits, mine dumps, and tailings that have a potential to contaminate the surrounding watershed and affect the ecosystem.
Along with advancement in mining technology, mining become more mechanized and, therefore, able to handle more rock and ore material than ever before, the amount of mine waste will be multiplied. Furthermore, as mine technologies are developed to make it more profitable to mine low-grade ore, even more waste will be generated in the future. For example, in Sweden, although the number of operating mines decreased from about 500 in 1920’s to 16 in 1999, the total ore production has increased from approximately 4 million tones in 1900 to around 45 million tones in 1999 (SGU, 2000). Mining at the current level in Sweden produces approximately half of all waste in Sweden (SCB, 2000).

Impacts from mining practices can vary depending on a variety of factors, such as the sensitivity of local terrain, the composition of minerals being mined, the type of technology employed, the skill, knowledge and environmental commitment of the developers, and our ability to monitor and enforce compliance with environmental regulations. Acid Mine Drainage (AMD) is considered to be the number one environmental problem facing the mining industry (Couturier, 1995). For instance, according to the 1993 British Colombia State of the Environment Report, mine drainage is reported to be "one of the main sources of chemical threats to groundwater quality in the province" (ECMBC, 2001).

AMD can be formed when sulphide minerals in rocks are exposed to oxidizing conditions, such as dissolved oxygen and dissolved ferric iron, in the presence of water, during mining or after the completion of mining. According to Swedish Environmental Protection Agency (SEPA), the largest Swedish environmental concern associated with mining is oxidation of sulphide wastes after closure of the mines, and in particular discharge of Hg, Cd, Pb, Cu, Zn, As, Fe, Al, and acidity (SEPA, 1995). As sulfide 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 waste as do the so called ‘gangue’ minerals, that host the ore, typically (alumino-) silicate and carbonate minerals (Salmon and Destouni, 2001). Studies showed that, in 1996, over two-thirds (35Mt) of the mining waste produced in Sweden was from mining of sulphide ores (SEPA, 1998) such as chalcopyrite (CuFeS$_2$) and sphalerite (ZnS). Due to relatively low metal concentrations in the two major types of ores mined in Sweden (ferrous and non-ferrous sulfide ores), approximately 99% of the mined volume of sulfides ores becomes waste, with the corresponding figure for iron ores being 30% (SEPA, 1998).
Geochemical reactions, which are responsible for generation of toxic chemicals that might have an adverse impact on the environment, in mine areas are more rapid than in natural weathering processes because of greater accessibility of air through mine workings; greater surface area of wastes and tailings resulted from mine workings, wastes and especially tailings; and due to different compositions of tailings as a result of mineral processing (Nordstrom and Alpers, 1999). In Sweden, mill-tailings waste products from the crushing and floatation process used to extract the economically desirable minerals have been deposited since the 1920’s. The deposits are fine-grained (e.g. 0.001- 2 mm diameter) particles, with a consequently high surface area for mineral reaction (Salmon and Destouni, 2001).

Oxidative weathering of various sulphide minerals may result in the generation of Acid Mine Drainage (AMD), characterized by net acidity, a pH as low as 2-4, and high concentration of dissolved, potentially hazardous metals such as Zn$^{2+}$ and Cu$^{2+}$, as well as sulphate, which can have a devastating environmental impact on the receiving environment, such as surface and subsurface water, over extended periods of time (Salmon, 2000; Malmström et al., 2001). In Sweden, for instance, annual deposition of Cu, Pb, Zn, and Cd in tailings is estimated to be approximately 9.2, 12, 21, and 0.06 thousand tones, respectively, and the total amount of these metals accumulated in sulfide bearing tailings is estimated to be 600,000 tonnes (Salmon and Destouni, 2001, and references there in). The presence of such heavy metals in the aquatic environment can have a serious effect on the plants and animals in an ecosystem. Furthermore, uptake of the metals by plants can result in transfer of the pollutants to animals, including human beings, through food consumption (Kelly, 1988).

Many metals are essential to life in small amounts. For instance, Zn can maintain senses of taste and smell, and healthy immune system and growth, protects liver from chemical damage. However, such metals become toxic when absorbed in excessive amounts. The fact that the level of toxicity for metals is commonly only a few to several times the level necessary to sustain life in humans demands for serious consideration of their fate of distribution in the environment. For example, while the recommended daily ingestion of zinc for humans is 12-15mg, it has been stated in literatures (see, for instance, Smith and Huyck, 1999) that the daily intake of as little as 18.5 or 25mg zinc causes decreased retention of copper (an essential metal in adult metabolism). The bioavailability of any metal, that is the fraction available to be absorbed and ready to interact in organism metabolism, is a function of geoavailability (e.g., natural abundance of the metals), their distribution in the...
environment, mobility, speciation, pathway of exposure, biological make up, and individual susceptibility of an organism (Duffus, 2001). In addition, bioavailability depends on the physicochemical properties of the metals, their ions, and their compounds (Duffus, 2001). Zn, for instance, is found in many different minerals in the world. A small quantity of zinc is present in almost every volcanic rock. It is estimated that Zn constitutes 0.013 % of earth’s crust. Fig. 1, below, shows pathways and relationships between total metal in earth material and toxicity. Toxicity of a metal will depend on each of the indicated factors and the pathways.

**Fig. 1** Pathways and relationships between total metal in earth material and toxicity (modified from Smith & Huyck, 1999).

Complex biological, geochemical and physical processes determine the mobilization and distribution of contaminants from mining wastes and from remediated waste deposits (Nordstrom and Alpers, 1999). Factors like hydrologic variability, mineralogy of waste
Modelling Reactive Transport of AMD: Effect of geochemical reactions, spatially variable flow, source location and distribution

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materials, physical structure of waste, geological structure and setting of mine site, historical evolution of mineral processing, geomorphology of terrain, and vegetation are some of the factors to be considered (Nordstrom and Alpers, 1999). Moreover, it has been stated that among the set of complex environmental factors that should be considered in the production of AMD, oxygen diffusion rate and bacterial mediation are the most important ones (Salmon, 2000 and the references therein). The timing of the potential onset and duration of acid mine drainage generation at a particular site will be a function of the physical and (bio)geochemical characteristics of the site. These, in turn, determine the rate of and the balance between sulphide oxidation and natural attenuation of contaminants such as acidity, metal and metalloid ions, within the deposit (Salmon and Malmström, 2004).

Development of effective mining, environmental prediction, mitigation, and remediation practices requires good understanding of the geochemical processes and physical environment around mineral waste deposits. In particular, reactive transport modelling of pollutants in acid mine drainage requires assessment of extensive reaction systems that involve complex geochemical conditions (Malmström et. al, 2003) and also consideration of the heterogeneity of the flow medium with other parameters like the surrounding geology and mineralogical composition of the mine wastes. In this regard, understanding and prediction of the spreading of acid mine drainage (AMD) in groundwater, in particular, and the breakthrough of acidity and heavy metals downstream of waste deposits will be very important for environmental impact assessment and evaluation of mitigation measures of acid mine drainage from mining sites.

Due to the complex geochemical characteristics of AMD and the heterogeneity of the subsurface, quantification of both multi-component reactions and spatially variable groundwater flow is required. The newly developed LaSAR-PHREEQC approach (Malmström et al., 2004; Berglund et al., 2003), which combines stochastic modelling of transport with detailed quantification of geochemical processes, seems promising for addressing these kinds of problems. In this study, the stochastic LaSAR-PHREEQC reactive transport modelling approach will be used to investigate the effect of spatially variable flow and geochemical reactions on the spreading and attenuation of pollutants within the saturated zone of a tailings deposit. The natural attenuation of acidity to limit the impact of AMD, percolating down from the unsaturated zone of a mill tailing deposit, which will be conceptualised as a source zone of AMD, and the attenuation of contaminants due to
precipitation and adsorption processes in the saturated zone will be evaluated. Special focus will be on the processes that affect spreading of Zn and relevant major ion geochemistry. Significance of the pH buffering reactions will also be evaluated in the model. For simplicity, the transport zone will be assumed anoxic, such that sulphide oxidation (primary pollutant source) can be excluded from the model.

A tailings deposit called Impoundment 1 (e.g., Malmström et al., 2001) at the Kristineberg mining site at the Skellefte field in northern Sweden will be used as a case study. This deposit contains sulphide rich tailings from base-metal mining and is one of the main study objects within the Swedish research programme “MiMi” (Mitigation of the environmental impact of mining waste, 1998-2003; funded by MISTRA; e.g. MiMi, 2002). In comparison to previous similar modelling (Malmström et al., 2003; Berglund et. al., 2003), an attempt will be made to extend the reaction model and transport mechanism to include pH buffering from aluminosilicate minerals, chlorite in particular, and assessment of effects of an elongated impoundment.

The specific objective of this study will be

1) To evaluate the relevance of different possible geochemical processes in pH buffering and attenuating Zn in the saturated zone of the mill tailing impoundment.

2) To evaluate the effect of spatial variability of the saturated tailings zone, with respect to transport properties on the resulting breakthrough concentration of the contaminants.

3) To evaluate the effect of the location of the source zone in terms of the distance from the impoundment boundary, as evaluated particularly at the downstream contact of the impoundment with the surrounding aquifer.
2. Overview of Geochemical Processes in Mill Tailing Deposits

2.1 Oxidation of sulphide minerals

A complex series of chemical weathering reactions will be initiated when mine wastes get exposed to an oxidizing environment such as potentially occurring in waste deposits. The mineral assemblages contained in the waste are not in equilibrium with the oxidizing environment and begin weathering and undergo mineral transformations. The reactions are orders of magnitude faster than in "natural" weathering systems mainly due to large surface area of the waste material. The accelerated reactions can release considerable quantities of acidity, metals, and other soluble components into the environment.

Oxidation of various sulphide minerals such as pyrite (FeS$_2$), pyrhotite (Fe$_{1-x}$S), sphalerite (ZnS), Chalcopryite (CuFeS$_2$), and Arsenopyrite (FeAsS) can result in acid mine drainage production (Nordstrom and Alpers, 1999; Nicholson and Scharer, 1994; Rimstidt et. al, 1994). Since it is the most abundant sulphide mineral in the earth and due to the fact that it has a potential to release high proton per mole of the mineral, as compared to all other sulphide minerals, pyrite oxidation is the most important to consider while dealing with environmental impacts of mining and mining wastes.

The pyrite oxidation process has been extensively studied and has been major focus of investigation by many investigators (Nordstrom, 1977 and 1982; Nordstrom et al., 1979; Ritcey, 1989; Jambor and Blowes, 1994; Alpers and Blowes, 1994; Morin and Hutt, 1997; Jambor and Blowes, 1998; Nordstrom and Alpers, 1999). The most important reactions related to weathering of sulphide minerals and, particularly pyrite, and hence generation of acidity in waste deposits is summarized below.

Pyrite oxidation initiates the AMD generation process, with ferric ion (Fe$^{3+}$) and atmospheric oxygen (O$_2$) being the major oxidants. In the low pH environment of AMD, the oxidation of pyrite by Fe$^{3+}$can become the main mechanism for acid production as the oxidation rate due to Fe$^{3+}$ is much faster than due to O$_2$ at high availability of dissolved Fe(III). Hence, the conversion of ferrous to ferric ion by dissolved oxygen (particularly in presence of microbes) and the subsequent oxidation of pyrite by ferric ion together with the release of additional ferrous ion results in a rapid AMD generation cycle.
The first reaction in the weathering of pyrite involves oxidation of pyrite by oxygen. Sulphur is oxidized to sulphate and ferrous iron is released. This reaction generates two moles of acidity for each mole of pyrite oxidized as shown in equation (1) below.

\[
2 \text{FeS}_2(s) + 7 \text{O}_2(aq) + 2 \text{H}_2\text{O} \rightarrow 2 \text{Fe}^{2+} + 4 \text{SO}_4^{2-} + 4 \text{H}^+ \quad (1)
\]

The second reaction involves the oxidation of ferrous iron to ferric iron as shown in equation (2) below. The oxidation of ferrous iron to ferric iron consumes one mole of acidity for each mole of ferrous iron. Certain bacteria increase the rate of oxidation from ferrous to ferric iron (Singer and Stumm, 1970). This reaction rate is pH dependant with the reaction proceeding slowly under acidic conditions (pH 2-3) with no bacteria present and several orders of magnitude faster at pH values near 5.

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

The third reaction, which may occur, is the hydrolysis of iron as shown below in equation (3). Three moles of acidity are generated as a by-product per each mole of ferric iron hydrolysis.

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

Equation (4) below describes further oxidation of additional pyrite by ferric iron generated in reactions (1) and (2) shown above. This is the cyclic and self propagating part of the overall reaction and takes place very rapidly, about ten to hundred times faster than by oxygen at about pH 3, and continues until either ferric iron or pyrite is depleted (Ritchie, 1994).

\[
\text{FeS}_2(s) + 14 \text{Fe}^{3+} + 8 \text{H}_2\text{O} \rightarrow 15 \text{Fe}^{2+} + 2 \text{SO}_4^{2-} + 16 \text{H}^+ \quad (4)
\]

An overall summary of the above reactions can be written as shown in equation (5) below:

\[
\text{FeS}_2 + 15/4 \text{O}_2 + 7/2 \text{H}_2\text{O} \rightarrow \text{Fe(OH)}_3(s) + 2\text{SO}_4^{2-} + 4\text{H}^+ \quad (5)
\]
As can be depicted from equation (5), net reaction of oxidation of pyrite, hydrolysis of ferric iron and precipitation of iron hydroxide produces 4H⁺ per moles of pyrite. That is the reason to consider oxidation of pyrite as the most significant acid generation processes among other common sulphide minerals. It is important to note that although reaction 5 describes the overall process, the individual reactions are spatially decoupled such that net ferrous iron oxidation (reaction 2) and subsequent precipitation of secondary Fe (III) phases (reaction 3) may not occur until mixing with oxic surface water outside the waste deposit.

2.2 Metal ions mobilization in mine waste deposits

Mobilization of heavy metal ions can result from transition to low pH due to generation of acid mine drainage and can cause transport of metal species of environmental concern. Iron, aluminium, and manganese are the most common heavy metals, which can contribute to adverse effects of mine drainage (Smith, and Huyck, 1999). Heavy metals are generally less mobile and occur in lower concentrations at circumbath neutral pH. However, below neutral pH, it is generally accepted that metal ions will become more mobile and soluble with decreasing pH. Trace metals such as zinc, cadmium, and copper, which may also be present in mine drainage, are toxic at extremely low concentrations (Hoehn and Sizemore, 1977). These metals can exist initially in tailings piles as sulphides (e.g., covellite (CuS₃) and sphalerite (ZnS)) which undergo oxidation in much the same way as pyrite, or as trace elements in the much more abundant iron sulfides, such as pyrite (FeS₂ (S₈)) and pyrrhotite (Fe₁₋ₓ S). They may also exist as carbonates or sulfates or even oxides or oxyhydroxides (Berglund et. al., 2002). These minerals may also dissolve (or, in some cases, precipitate) in conjunction with acid mine drainage. Moreover, desorption reactions involving the exchange of H⁺ ions and metal ions on mineral surfaces can also play a role in influencing the mobility of these metals in such environments.

2.3 pH buffering process in mine waste deposits

Alkalinity is the ability to consume or neutralize acidity. It is the sum of all concentrations of species able of consuming acidity, e.g., hydroxide [OH⁻], carbonate [CO₃²⁻], and bicarbonate [HCO₃⁻] (Schnoor, 1996).

\[
\text{Alkalinity} \cong [\text{OH}^-] + 2[\text{CO}_3^{2-}] + [\text{HCO}_3^-] - [\text{H}^+] \quad (6)
\]
The approximation sign in equation (6) is due to the fact that alkalinity in AMD will be affected also by other species, such as Al $^{3+}$.

An increase in the number of H$^+$ ions or a decrease in alkalinity in tailing impoundment will lower the pH of the impoundment water, sometimes drastically. However, if a chemical species that can consume or tie up H$^+$ ions is present in the water or the surrounding, drastic changes in the pH may be avoided. Thus, the interaction of this low-pH, metals and sulphate-contaminated water with tailings and aquifer minerals initiates a sequence of pH-buffering reactions. The resulting increase in pH is often accompanied by the precipitation of metal-bearing hydroxide and hydroxysulfate minerals that can remove dissolved metals from the migrating plume from mineral waste deposits and minimize contamination on the receiving water bodies. Some of the most important pH buffering mechanisms are briefly discussed below.

### 2.3.1 Buffering by Carbonates

Alkalinity can results from the dissolution of calcium carbonate (CaCO$_3$) from limestone bedrock that might be eroded during the natural processes of weathering. Carbonate (CO$_3^{2-}$) and/or bicarbonate (HCO$_3^-$) systems are the most important pH buffering systems in nature. The source of CO$_3^{2-}$ and HCO$_3^-$ is carbonate containing minerals in the earth, limestone being the most common. If sufficient limestone (CaCO$_3$) has dissolved into a system, it will contain adequate amount of carbonate (CO$_3^{2-}$) and bicarbonate (HCO$_3^-$) ions that are in turn capable of consuming hydrogen ions and maintaining a fairly constant and nearly neutral pH. Such buffering reactions protect the deposit from having low pH and can reduce the impact of AMD. However, if more H$^+$ ions enter the system or are produced within the deposit than there are carbonate and bicarbonate ions to counteract them, the buffer becomes overwhelmed and is no longer effective, resulting drop in pH.

The primary mechanism of calcite dissolution in the presence of acidity (H$^+$), forming alkalinity in the form of bicarbonate (HCO$_3^-$), is as follows:

$$\text{CaCO}_3(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{HCO}_3^-(\text{aq})$$

(7)

When bicarbonate is the predominant carbonate species and the carbon dioxide pressure is close to that in the atmosphere, the water is buffered at a pH close to 7.
As depicted in the set of reactions, shown below, carbonate (\(\text{CO}_3^{2-}\)) and bicarbonate (\(\text{HCO}_3^-\)) ions act as proton “absorbers”. The buffering capacity of bicarbonate system will enable the reactions to proceed left or right while maintaining a relatively constant pH. If protons are added to the solution, they combine with available bicarbonate or carbonate ions, causing the reactions to shift to the left and eventually liberate carbon dioxide and water molecules.

\[
\text{CO}_2 (s) + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 (aq) \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}
\]  

Once exposed to acid mine drainage, the affected carbonate buffering system is not able to control changes in pH as well. When calcite dissolves to buffer pH, it eventually gets depleted. The buffering system is completely destroyed below a pH of about 4, where all carbonate and bicarbonate ions are converted to carbonic acid. The carbonic acid readily breaks down into water and carbon dioxide.

\[
\text{H}_2\text{CO}_3 (aq) \leftrightarrow \text{H}_2\text{O} + \text{CO}_2 (g)
\]  

The presence, composition, distribution and potential depletion of carbonate minerals are important factors in determining the acid neutralizing capacity of unexploited mine deposits and mine wastes.

2.3.2 Buffering by dissolution of metallic hydroxides

Precipitation of metal hydroxides or hydroxide sulphates such as gibbsite, amorphous Al(OH)₃, amorphous Fe(OH)₃, ferrihydrite, and goethite may happen in mill tailing impoundments due to down ward increase in pH. Precipitated secondary phases may redissolve and buffer pH upon depletion of minerals that more readily buffer pH. Blowes and Ptacek, (1994) have shown that there is an ideal pH buffering sequence of gibbsite followed by ferric hydroxide and goethite after depletion of calcite (buffer to pH 6.5 - 7.5) and other carbonate minerals like siderite (pH 5.0 - 5.5). The most important buffering reactions of these phases, due to dissolution of the secondary precipitates, are shown in equations 10-12 below.
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\[ \text{Al(OH)}_3\text{(s)} + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O} \] this reaction buffers the pH to 4.0 - 4.3 \hspace{1cm} (10)

\[ \text{Fe(OH)}_3\text{(s)} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O} \] this reaction buffers the pH to below 3.5 \hspace{1cm} (11)

\[ \text{FeO(OH)}\text{(s)} + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O} \] this reaction buffers the pH to below 3.5 \hspace{1cm} (12)

2.3.3 Buffering by silicates

Dissolution of most aluminosilicate minerals can also consume H\(^{+}\) ions and contribute base cations (Ca, Mg, Fe (II)), alkali elements (Na, K), and dissolved Si and Al to the tailing pore water (Blowes and Ptacek, 1994). For instance, dissolution of chlorite (Chlinochlore) may consume acidity according to the reaction (see, for example, Malmström et. al., 2002; Salmon, 2003, and references therein)

\[ (\text{Mg}_{4.5}\text{Fe}_{0.2}^{II}\text{Fe}_{0.2}^{III}\text{Al})\text{AlSi}_3\text{O}_{10}(\text{OH})_8\text{(s)} + 16\text{H}^+ \rightarrow 4.5\text{Mg}^{2+} + 0.2\text{Fe}^{2+} + 0.2\text{Fe}^{3+} + 2\text{Al}^{3+} + 3\text{SiO}_2\text{(s)} + 12\text{H}_2\text{O} \] (13)

Though dissolution of aluminosilicate minerals is slower than of metal hydroxides and much slower than that of carbonates (Brown et. al., 1998), it will provide acid neutralising capacity through release of oxide ions from the crystal lattice of the minerals (Banwart and Malmström, 2001). Two examples of pH buffering by dissolution of feldspar minerals are shown below:

\[ 2\text{KAlSi}_3\text{O}_8 + 9\text{H}_2\text{O} + 2\text{H}^+ \rightarrow \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 + 2\text{K}^+ + 4\text{H}_4\text{SiO}_4\text{(aq)} \] \hspace{1cm} (14)

K-feldspar \hspace{1cm} kaolinite

\[ \text{NaAlSi}_2\text{O}_3\text{(s)} + \text{H}^+ + 7\text{H}_2\text{O} \rightarrow \text{Na}^+ + \text{Al(OH)}_3\text{(s)} + 3\text{H}_4\text{SiO}_4\text{(aq)} \] \hspace{1cm} (15)

Plagioclase feldspar

In these reactions, K, Na, and Si enter the solution, while protons are consumed.
2.4 Metal immobilization processes

Immobilization of metal ions in AMD affected areas can result from different geochemical processes, including precipitation of secondary phases, co-precipitation by isomorphous substitution, sorption by surface complexation and ion exchange reactions.

Precipitation of metal ions may be result when a solution is oversaturated with respect to a solid phase, due to change in chemical conditions, for instance pH and redox conditions (Berglund et. al., 2002). For instance, metals like Fe can precipitate directly from solution as the pH gets increased, as shown in reaction (16) below.

\[
Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ 
\]  

(16)

Another important process that might limit metal mobility in natural aqueous systems is sorption. Sorption is a common name for adsorption, absorption, and ion exchange. The sorption processes take place at the mineral-water interface and are controlled by the reactivity of surface functional groups.

Whether or not a mobilized element will be adsorbed depends on the redox conditions resulting from specific speciation of the metal complexes and on the pH dependent reactivity of the surface functional groups of the adsorbent. Generally, low pH conditions, reducing conditions, low particulate loads, and (or) high dissolved concentrations of a strong complexing agent cause metals to be present in the solution phase (Smith, 1999). For instance, adsorption of metal ions on Fe(III)hydroxides is a function of pH, temperature, surface area of sorbent, dissolved metal concentrations, and reaction time (see, Dzomback and Morel, 1990). A sorbent’s capacity to bind metals depends both on the number of metal- binding sites present, “binding-site density”, and on the amount of metal accessible surface (specific surface area), (see, for e.g., Smith and Huyck, 1999). The pH at which metal sorption becomes significant varies with the particular sorbent, the solid solution ratio, the specific surface area of the sorbent, the total metal-cation concentration, and the concentration of other competing or interacting species. In sorption processes, the sorbent mineral can act as a sink for metals to the surrounding solution. When the metal desorb, the sorbent mineral can act as a source of metal to the surrounding solution. (Smith and Huyck, 1999).
3. Transport of Contaminants

Reactive transport can occur, for example, in the subsurface groundwater environment, over a wide range of spatial and temporal scales. Understanding how the various subsurface processes interact to yield predictable behavior in a system with spatially variable material properties will be very important. Assessment of the hydrological conditions around tailing impoundments is important in predicting mine drainage transport mechanisms. If we assume an analogy in groundwater flow system in fine grained soils described in literature, such as in Freeze and Cherry, (1997) with that of tailing impoundments, it is most probable that the flow system is a function of the topography of the impoundment area, hydraulic gradient along the water flow direction, porosity of the impoundment materials and lithology of the rocks around the impoundment. In addition, groundwater recharge mechanisms and availability of structural discontinuities may influence the flow system. For instance, topography will influence groundwater flow in mill tailing impoundments, as it will directly influence the hydraulic gradient. Therefore, it can be said that, in general, the water table tends to reflect the overlying topography. In fact, other factors such as permeability variations and local structure will influence the orientation of the water table (see, Freeze and Cherry, 1997).

Determination of groundwater velocity is also important in mine drainage prediction because, in addition to geochemical processes, it will have a direct influence on contaminant transport rates and dispersion in groundwater. The groundwater flow velocity will be influenced by the heterogeneity of the subsurface materials, in addition to other hydrologic factors.

Impoundment heterogeneity, particularly that of the saturated zone, can be brought about due to grain size grading during milling, latter segregation while transported with the slurry, and/or, owing to the different origin of the waste. Such heterogeneity in grain size in mill tailing impoundments can be conceptualized in analogy with the heterogeneity of natural subsurface, such as explained in Dagan, (1989).

In the subsurface, and presumably in tailing impoundments, flow tend to move principally along preferential paths, isolating portion of subsurface from bulk system fluxes and resulting in non uniform flow fields (e.g., Yabusaki et. al., 1998; Berglund, 1997). Residence times for chemical components can also be spatially variable. Concentration of chemical components can be very sensitive to the spatial distribution of reactive mineral surfaces in addition to the
advective and diffusive processes. This reveals the fact that, due to complexity of the interaction between aqueous species and the geochemical environment is so complex that thermodynamic relationships and rate laws are necessarily multi component, multi species, and as a result, non linear (Yabusaki et. al., 1998; Malmström et. al., 2004).

The common way of conceptualizing contaminant transport in AMD affected areas is considering the subsurface hydrology as comprising two different zones, characterized by different water contents and availability of oxygen, see, for example, Destouni et. al, (1998). Hence, the transport problem, in this study, will be simplified by conceptualizing the flow in two contrasting zones of the impoundment. The unsaturated zone, where oxidizing conditions prevail and vertical downward transport of acidity and metal ions is assumed, will be the source zone for the contaminants. The saturated zone, where anoxic and full saturation condition prevails, will be considered as the sink. The lower boundary of the unsaturated zone, including the capillary fringe, will be conceptualized as a horizontal injection plane where contaminants enter the saturated zone subject to reactive-transport modeling in this study (see Fig. 2).

![Fig. 2 Conceptual model of unsaturated and saturated zones of mill tailing impoundments.](image)
4. Generalized conceptual Model of AMD generation

Mining activities usually involve milling, concentrating, processing of ores which will result in a waste, usually called tailings, which will be deposited in impoundments as slurry, composed of fine grained geological materials, chemicals utilized in the process, and water. After deposition of tailings biogeochemical processes may result in development of characteristic zones in the deposit. A conceptual model of an ideal tailings impoundment is shown in Fig. 3, below.

Fig. 3  Schematic representation of an idealized tailing impoundment

The primary hydrological input is coming from the precipitation in the area. The other source for the incoming water can be recharge, for instance, from the high land areas.

An ideal impoundment might consist of the following zones developed in a course of time:

i) The oxidized mine waste zone comprise the upper most part of the mine waste where oxygen diffuses with rates that vary depending mainly on water saturation
and where sulphide minerals would be effectively depleted due to extensive oxidation reactions.

ii) The **oxidation front** is a zone where sulphide minerals have not been depleted and where oxidation starts to appear. This zone is responsible for generation of acidity and mobilization of metal ions, and hence, contains large concentration of dissolved contaminants, which might have a potential threat on the environment.

iii) The unoxidized, **unsaturated zone** is the part in which molecular oxygen has been depleted, and where sulphide minerals thus can only weather through the ferric iron path.

iv) The water-**saturated zone** is a zone that normally contains unoxidized mine waste. However, due to the interaction of the groundwater with the minerals of this zone, there may be a chemical reactions acting to attenuate/retard the pollutants. This zone, as well as zone described in (iii), may be characterized by steep pH and redox gradients and the precipitation and adsorption of metals. Calcite (CaCO₃), and aluminosilicates as well as secondary mineral phases react with and neutralize acidic groundwater. Metals such as Cu, Co, Ni, and Zn may be adsorbed to Fe hydroxide, if present, and possibly other surfaces in the saturated zone because of the increase in pH.
5. Site Description

The Kristineberg mining area is situated in the western part of the Skellefteå district, about 175 km south of Luleå, in northern Sweden (see Fig. 4).

![Location map of the Kristineberg mining area](image)

**Fig. 4  Location map of the Kristineberg mining area**

The geological map of the area is shown in Fig. 5, below. The area is characterized by regionally metamorphosed metallic ore bearing volcanic rocks, which are overlain by sedimentary rocks. The metamorphosed volcano-sedimentary rocks display a marked foliation and sericitization (du Rietz, 1953, and references therein).

The central complex, of probably predominantly volcanic rocks, originally consist of sodic quartz porphyry or albite porphyry (sodic rhyolite with phenocrysts of albite). Most of this complex is now altered to quartizitic schists. The volcanic complexes have been interfolded with the overlying slates (in the west) and the Jörn granite complex (in the east). Isoclinal folding with westerly pitching axes dominate. In the South, the younger archean Revsund granite intrudes these rock complexes. There are a few small areas with dacitic rocks in the northern part of the region. These rocks are generally chloritized, though less sericitized than the surrounding rocks, evidently due to their originally more basic composition. The primary volcanics have comprised both lavas and tuffs. The least altered remnants of volcanics are
acid flows with well-developed albite phenocrysts. Within the Kristineberg area, several greenstone dykes have been observed cutting the volcanics and Jörn granite (du Rietz, 1953)

Fig. 5  Geological map of Kristinberg area (modified from Axelsson et. al., 1994)
The annual precipitation in the area varies between 400 and 800 mm/year. A large part of the precipitation is in the form of snow, which accumulates until the snowmelt season in late April and/or early May. The vegetation consists of mostly of coniferous forest with some deciduous types. Boglands are common in the area. The major soil type in the area is podzol weathered till (du Rietz, 1953, and references therein).

The area is known for its long history of mining for metal ores dating back to 19th century (Carlsson, 2000). The mine and the former enrichment plant at the site is owned and operated by Boliden Mineral AB. The Kristineberg ore body is a copper- and zinc-bearing pyritic ore and it is the first sulphide ore discovered in Sweden by electrical prospecting survey.

Kristineberg Impoundment 1, the case study site for this modelling, is one of five impoundments that were used as deposits for fine fraction of the mill tailings in Kristineberg (see Fig. 6). The impoundment is situated in a valley surrounded by steep slopes. The impoundment area is drained by Vormbäcken stream. Before remediation, it was surrounded by intercepting ditches in the south and draining ditches in the north.

Several researchers conducted geological, hydrogeological and geochemical investigations on the Kristineberg mill tailing impoundment 1 since several decades and most of the available information up to 1998 is compiled by Malmström et. al., (2001) and briefly summarized below. Since then, extensive field investigations have been conducted within the

**Fig. 6** Overview of the mill tailings impoundments in Kristineberg (modified from Werner and Salmon, 2001)
MiMi research programme (see, for example, Ebenå, 2003, Carlsson, 2002; Holmström et al., 2001). Modelling has been performed, for example, by Werner (2000) and Salmon (2000, 2003), mainly with the objective of evaluating effect of remediation measures taken.

The impoundment had been used as a deposition site for the mill tailings since 1940. It has been remediated by means of dry cover application and sealing of some intercepting and draining ditches in 1996. However, since most of the available data are on the pre-remediation condition, for this modelling work pre remediation conditions are considered.

The top of the impoundment is at an altitude of 365m above mean sea level and is bounded by earth dam. The total area of the impoundment is about 0.11km², with an average depth of about 6m, and a maximum of 10m. The total volume of the impoundment is $5.5 \times 10^5$ m³ and its catchment area is approximately 0.6 km².

The impoundment is underlain by sand to fine sand sized moraine layer that overlay the granite rocks. Presence of two layers of moraine deposits, beneath the waste, has been interpreted, but neither detailed description about the layers is provided nor confirmed by latter drilling. Lenses of peat were also reported to exist in few locations beneath the impoundment at the tailings material/moraine interface.

It has been stated that the Kristineberg mine consists of ore minerals dominated by pyrite (FeS₂), chalcopyrite (CuFeS₂), sphalerite (ZnS) and rutile (TiO₂) with relatively lower amounts of galena (PbS), arsenopyrite (FeAsS), pyrrhotite (Fe₁₋ₓ S) and magnetite (Fe₃O₄). (see, Gleisner et al., 2003) Other minerals like tetrahedrite, molybednite, limonite and scheelite are also reported to exist in subordinate amount. Quartz, sericite and chlorite are the dominant gangue minerals followed by cyanite, actinolite, tourmaline, talc and apatite with rather low amount of biotite, tremolite, epidote (zoisite), zircon, and calcite (du Rietz, 1953). However, it should be noted that, since the concentrator at Kristineberg treated ores from mines in the surrounding areas (Rävliiden, Näsliden, Holmtjärn, Rakkejavr, Kimheden and Laivijaur) the tailing mineralogy may differ from that reported by du Rietz (1953).

The saturated hydraulic conductivity, $K$, of the impoundment varies with depth from $2.4 \times 10^{-6}$ - $1.5 \times 10^{-4}$ m/sec. In this study, since the groundwater flow is supposed to be perpendicular to the vertical layering in the impoundment, a value of $3.6 \times 10^{-6}$ m/sec, which is equivalent
to the harmonic mean of the conductivity measurements at different depths, is taken as the effective hydraulic conductivity. The infiltration capacity and storage coefficient of the tailing material in impoundment is estimated to be, $5 \times 10^{-3} - 2 \times 10^{-4}$ m/sec and 0.017, respectively. The total and effective (kinematic) porosity of the impoundment is estimated to be 0.25 and 0.15 respectively. In the presented model the total porosity value is used. The tailing materials in the impoundment are well sorted and classified as silty fine sand or fine sand with relatively larger fine fractions at depth. The particle density of the materials is calculated by Malmström et al. (2001) to be 3.3 – 3.4 g/cm$^3$.

Assuming uniform infiltration rate on the whole catchment, an annual discharge of 39,000 m$^3$/year is estimated from the impoundment. The annual fluctuation of the ground water is estimated to be about 1m, related with the normal seasonal trend for the region due to the snow melt during April- May. It has also been interpreted that the impoundment probably constitute its own hydraulic unit and, hence, the water level in the impoundment might not be greatly affected by water level fluctuation in the surrounding geological formation.

Geophysical study around the impoundment revealed that there are two fracture zones in Northwest – Southeast direction that might have resulted in hydraulic conductivity of $3 \times 10^{-7} - 5 \times 10^{-5}$ m/s in bedrocks.

As described in Malmström et al., (2001), pervious investigators [Ekstav and Qvarfort (1989)] had conducted monthly groundwater sampling of impoundment 1 during the years 1983-1988, prior to remediation. They collected ground water samples at two different depths, 1.5 and 7 m below the groundwater level, at each of the sampling points. They found that the groundwater is slightly acidic, with an average pH of 4.8- 5.5 and an average acidity of 75-166 mg/l. The main dissolved components were sulphate and iron, followed by Zn, Mg, and Ca and the conductivity was on the average 375-600 mS/m. It has also been stated that the concentration of dissolved ions was found varied between the sampling locations and over the years, however, the solute concentrations differed more between sampling points than between the two sampling depths at the same location (Salmon et al., 2002). Table 1, below shows the average composition of the groundwater in impoundment 1.
**Table 1.** Field data of groundwater composition in impoundment 1, Kristineberg. 
*Modified from (Ekstav & Qvarfort, 1989) by Malmström et. al, (2001).*

<table>
<thead>
<tr>
<th>Concentrations (mol/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
</tr>
<tr>
<td>K⁺</td>
</tr>
<tr>
<td>Mg²⁺</td>
</tr>
<tr>
<td>Fe (tot) *</td>
</tr>
<tr>
<td>SO₄²⁻ **</td>
</tr>
<tr>
<td>Al³⁺</td>
</tr>
<tr>
<td>Zn²⁺</td>
</tr>
<tr>
<td>Cu²⁺</td>
</tr>
</tbody>
</table>

* In this study taken to be Fe²⁺  
** In this study taken to be total sulphur
6. Modeling Methodology

Evaluation of the impact of AMD in groundwater requires modelling of the fate of the contaminants, in this case acidity and heavy metal, coming from the unsaturated zone of the mill tailing impoundment and transported in the saturated zone. This requires adequate conceptualization of the prevailing geochemical processes and the subsurface transport mechanism.

In order to model the geochemical processes in this study, simple equilibrium condition is assumed between the minerals in the saturated zone and the aqueous phases in the groundwater system. pH buffering by calcite and chlorite will be compared independently and also in combination to evaluate the significance of each of the minerals in counteracting the adverse impact of the AMD. In addition, metal attenuation due to precipitation of secondary phases and sorption on ferric oxide surfaces in the saturated zone will be modeled, taking Zn$^{2+}$ as an example.

6.1 Simulating geochemical reactions

The well established and widely used PHREEQC (version 2) model (Parkhurst, 1995) will be used to simulate the geochemical processes along the groundwater flow direction. PHREEQC is a computer programme, written in the C programming language, capable of simulating a variety of geochemical reactions for a system including: mixing of waters, addition of net irreversible reactions to solution, dissolving and precipitating phases to achieve equilibrium with the aqueous phase, and effects of changing temperature, ion-exchange equilibria, surface-complexation equilibria, fixed-pressure gas-phase equilibria, and advective transport (Parkhurst, 1995).

The PHREEQC model requires knowledge of the type and concentration of the minerals in the receiving compartment, in this case the saturated zone, and the concentration of each of the contaminants percolating down from the source zone, the unsaturated zone in this case. The model considers the lateral extent of the impoundment as comprising a stream tube, consisting a series of boxes along which chemical reactions undergo, with different phases precipitating or dissolving and solution transferred to the next cell for each step in the
simulation to model advective transport. In this model, (bio)geochemical reactions can be simulated with various spatial resolutions and concentration of each of the contaminants can be evaluated at specified location along the water flow direction. In the specific case study investigated here, fate of the contaminant (Zn$^{2+}$) will be evaluated at the impoundment boundary in the downstream direction.

The PHREEQC modelling technique used here is in analogy with that used in pervious studies of modelling geochemical reactions and transport in AMD affected areas (see, Brown et. al., 1998; Berglund et. al., 2003, and Malmström et. al., 2004). Accordingly, geochemical reactions are simulated along a flow path, conceptualized as containing a series of sequential cells (see, Fig. 7). The water residence time in each of the cell, $\Delta \tau$, can be evaluated as $\Delta \tau = (V/Q)/n_{cell}$, where Q is the total water flow, V is the flow volume, and $n_{cell}$ is the number of cells. Since the movement along the flow path is assumed to be purely advective, the travel time along a specific path is related to the position of the cell such that $\tau_n = n \Delta \tau$, where n denotes the number and thus the location of the cell.

![Fig. 7](image)

**Fig. 7**  Schematic representation of PHREEQC model along a single stream tube, with 500 equal volume boxes in which geochemical reactions occur. Advective transport is modelled as transfer of aqueous phase (mobile) species consecutively to the next cell in line.

The PHREEQC model resulted in an array of values that depict the concentration of each of the components, $C_i$, at time, t, for each. To evaluate the breakthrough concentration of a specific species (contaminant) obtained from PHREEQC is later used in LaSAR model as input.
6.2 Simulating transport of contaminants

The LaSAR (Lagrangian Stochastic Advection Reaction) is a stochastic approach of modeling coupled transport reaction system in a heterogeneous flow media (Dagan and Cvetkovic, 1996; Destouni and Graham, 1997). The approach has been shown successful in characterizing solute transport both in surface and subsurface environments (Simic, 2001, and references there in). The main advantage of using the stochastic lagrangian travel time approach (for example, in acid mine drainage modelling) is due to the possibility of decoupling physical transport and chemical transformation processes along flow paths (Simic, 2001).

In this LaSAR modelling application a transport where the solute (contaminant) enters the transport system at an injection plane (IP) normal to the flow direction of water along a stream line of tubes to a control plane (CP) at distance X=L from the IP (Dagan and Cvetkovic, 1996) is assumed. Furthermore, uniform injection of solute at the IP is assumed such that \( C(t=0) = C_0 \). Solute transport between IP and CP is conceptualized as occurring along individual and independent flow paths (streamlines), which are non-interacting (see Fig. 8). Due to heterogeneity of the subsurface medium, some of the particles have the probability to reach the CP earlier than others. Thus, flow variability of the subsurface can be modelled by a travel time variability between individual stream tubes, where the statistics of the residence time can be represented by a pdf (Probability Density Function) that can follow one of the common statistical distributions (e.g., lognormal or bimodal), so that the over all transport equations can be formulated in terms of travel time to some control plane in space (Cvetkovic and Dagan, 1994). In this study, a lognormal travel time distribution, as commonly suggested by researchers in pervious subsurface water transport studies, e.g., Cvetkovic et. al., (1996), is used.

The water flow is assumed to be steady and unidirectional. Moreover, advection is considered to be the dominant hydrological transport mechanism and diffusion and pore scale dispersion are generally neglected (see, Dagan, 1989). Subsurface heterogeneity will cause random advection variability due to the underlying spatial variability, for instance, in hydraulic conductivity (K), regional hydraulic gradients and recharge from the unsaturated zone (Destouni and Graham, 1995).
Fig. 8 Conceptual model of AMD transport through a bundle of stream tubes from the injection plane (IP) to a control plane (CP) located at distance L from the injection plane perpendicular to the water flow direction. Each of the stream tubes will have different travel time, due to flow heterogeneity.

6.3 Coupling geochemical reaction and transport

The foregoing discussion shows how geochemical processes in AMD and transport of pollutants can be modelled independently. However, in reality the two processes occur simultaneously. Therefore, coupling of these two modelling tools will be an important step in dealing with environmental problems of AMD generation and transport. Accordingly, with the objective of understanding the breakthrough of the reacting chemical components across down gradient boundary of the problem domain, Malmström et. al, (2004) proposed the LaSAR- PHREEQC model, which combines reaction path chemistry and transport in nonuniform velocity fields using ensemble averages of advecting stream tubes.

Numerically, change in concentration of contaminant, such as due to attenuation of metals, in this case Zn$^{2+}$, for example, by precipitation or sorption reactions, as the contaminant transported from IP to CP can be calculated applying the governing equation for reactive transport, such as described in Dagan et. al., (1996) as
\[ \frac{\partial C(t, x)}{\partial t} + \frac{\partial C}{\partial \tau} + R = 0 \]  

where \( C \) = total concentration of metal in the aqueous phase  
\( t \) = time  
\( \tau \) = water residence time  
\( R \) = the rate of removal of solute from the aqueous phase, due to geochemical or other processes.

Obviously, the resulting contaminant concentration from each of the stream tubes depends on the water travel time along individual stream tubes, in addition to the encountered mineral concentrations in the receiving environment. The integrated effect of flow along each of the conceptualized stream tubes, which are characterized by a probability density function (PDF) of the travel times to the down gradient boundary of the transport domain, at a specified control plane at a time of interest can be determined by averaging of individual stream tubes concentration. Thus, the overall breakthrough of the contaminant as the plume moves between the injection plane (IP) and the control plane (CP) is obtained by summing up the resulting concentration from each of the stream tubes at the CP.

In the coupled model, the PHREEQC out put will be used as an input, to the transport model (LaSAR) and the flow variability is quantified applying the relevant pdf with different standard deviation of travel time, in order to characterize flow variability, to get time dependent concentration of each component at a given location of the CP. The concentration of a spreading contaminant, \( i \), at time \( t \), at a control plane (CP) located at distance \( x \) from the upstream boundary of the impoundment (IP) can be numerically calculated from the following equation as discussed in Malmström et. al., (2004) and references therein.

\[ \bar{C}_i(t,x) = \sum_{n=1}^{n=\text{flow}} C_i(m,n)g(\tau_n; x)\Delta \tau \]
where:

\[ C_i(t, \tau; x) = \text{the local concentration at time } t \text{ along a stream tube with water travel time, } \tau_x \text{ at CP position at distance } x \text{ along the flow direction.} \]

\[ g(\tau, x) \text{ is the probability density function (pdf) of travel time for all stream tubes in the flow system.} \]

\[ C_i(m, n) \text{ is an output from the PHREEQC simulation, where } m \text{ is the time and } n \text{ is the number of the cell.} \]
7. Site-specific Model

7.1. Geochemistry

The Kristineberg mill tailing impoundment 1 is one of the few mining sites well studied and described in Sweden. A conceptual model, describing the processes thought to be responsible for controlling the chemistry of the water as it moves through the saturated zone of the tailing impoundment is presented in Fig. 9, below. The inflow from the unsaturated zone is conceptualised as containing weathering products from oxidation of sulphide minerals. Thus, the inflowing groundwater is acidic, with pH of about 4.9, and has dissolved metals of Al, K, Mg, Cu, Zn and Fe (total) with concentrations shown in Table 2. The composition of the groundwater percolating down from the unsaturated zone is obtained from the field data by (Ekstav & Qvarfort, 1989), shown in Table 1, on page 24. Pervious modeling work, on the unsaturated zone, of the same impoundment by Salmon (2000, 2003) and, Salmon and Malmström, (2002) was targeted to model the geochemical processes assumed to be important for the proton balance and metal concentration observed in field.

![Fig 9. Conceptual model of AMD attenuation in the saturated zone of mill tailing impoundment 1; Kristineberg, Northern Sweden](image)

The available information, as described in the site description section, is used in the model, with simplification of mineralogical information on the primary and secondary minerals that were supposed to be initially present in the impoundment. The geochemical and physical parameters used in the base case model are shown in Table 2. However, due to simplification of those parameters used in the model and, more importantly, assumption of exclusively equilibrium reactions, the model should be considered as a simplified one but still considers
some of the most important parameters. Those components that may precipitate or dissolve as
the acidic mine water from the unsaturated zone percolates through the saturated zone are
assumed and, therefore, may not necessarily represent the actual conditions in the
impoundment under consideration. However, various possible geochemical scenarios, which
can be of practical importance, are simulated. In the base case model, calcite is considered to
be the major mineral responsible to buffer pH. A model scenario which considers chlorite as
additional buffering mineral will also be tested. In addition, precipitation of Al(OH)₃(s) is
included in the model with the assumption that it will be another important processes in pH
buffering with subsequent dissolution of the mineral phase. Processes assumed to be
responsible for attenuation of Zn metal, in particular, precipitation of smithsonite and sorption
on iron hydroxide surfaces are also included.

**Table 2. Input Parameters for the Base case model**

<table>
<thead>
<tr>
<th>Input parameters for the groundwater in the saturated zone</th>
<th>Input parameters for inflow coming from the unsaturated zone</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH = 5.0</td>
<td>pH = 4.9</td>
</tr>
<tr>
<td>Temperature = 4°C</td>
<td>Temperature = 1°C</td>
</tr>
<tr>
<td><strong>Equilibrium phases in the saturated zone</strong></td>
<td><strong>Equilibrium phases in the unsaturated zone</strong></td>
</tr>
<tr>
<td>Calcite (0.3 mol)/assumed originally present in the zone)</td>
<td>Partial pressure of CO₂(g) = 3 x 10⁻⁴ atm.</td>
</tr>
<tr>
<td>Smithsonite (allowed to precipitate)</td>
<td>Concentration of metals in the incoming water</td>
</tr>
<tr>
<td>Al (OH)₃(s) (allowed to precipitate)</td>
<td>(mol/kg water)</td>
</tr>
<tr>
<td>Gypsum (allowed to precipitate)</td>
<td>K⁺ = 6 x 10⁻⁵</td>
</tr>
<tr>
<td>Partial pressure of CO₂(g) = 3 x 10⁻⁴ atm.</td>
<td>Mg²⁺ = 0.011</td>
</tr>
<tr>
<td></td>
<td>Fe (tot)* = 0.080</td>
</tr>
<tr>
<td></td>
<td>SO₄²⁻** = 0.10</td>
</tr>
<tr>
<td></td>
<td>Al³⁺ = 0.002</td>
</tr>
<tr>
<td></td>
<td>Zn²⁺ = 0.006</td>
</tr>
<tr>
<td></td>
<td>Cu²⁺ = 6 x 10⁻⁵</td>
</tr>
<tr>
<td></td>
<td>* taken as Fe(II) in the model</td>
</tr>
<tr>
<td></td>
<td>** taken as S in the model</td>
</tr>
</tbody>
</table>

Water flow rate = 1.08 x 10⁻⁷ m/sec
Porosity = 0.25
Flow variability cases (σ = 1; σ = 0.3 and σ = 0.1)
Distance from the control plane (20m, 60m, 100m, 140m and 180m)

Number of cells in PHREEQC/ LaSAR- PHREEQC = 500
Number of shifts in PHREEQC/LaSAR = 2500
7.2. Water and pollutant transport

The mean groundwater flow rate, $Q$, is calculated from Darcy’s equation as $Q = k \Delta h / \Delta l$, where $k$ is the hydraulic conductivity of the deposit which is taken to be $3.6 \times 10^{-6}$ m/sec and $\Delta h / \Delta l = 6 \text{m}/200\text{m} = 0.03$ is the gradient along the flow direction (see Fig. 10) Hence, the mean water flow rate $= 1.08 \times 10^{-7}$ m/sec, which is about 3.4 m/year. The porosity of the tailing in the impoundment is taken to be 0.25 and, hence, the effective pore water velocity will be about 13.6 m/year.

![Groundwater flow direction](image)

**Fig. 10 Interpreted groundwater levels in Impoundment 1 and the surrounding moraine (modified from Axelesson and Karkvist, 1986, by Malmström et. al., 2001)**

In modeling the transport of the contaminant, the injection plane will be taken to be the lower boundary of the unsaturated zone of the impoundment and the control plane will be the contact between the impoundment boundary and the regional aquifer so that the output of the model can express the pollution load on the surrounding groundwater system. The total lateral extent of the injection plane is taken to be 200 meters, which is approximately equal to the width of the impoundment perpendicular to the water flow direction.
The flow is conceptualized as occurring in heterogeneous media, represented by several stream tubes with different variability in water travel time. Travel time variability effects will be evaluated applying pdfs with three different flow variability cases, represented by different standard deviation of water travel time distribution such as low ($\sigma = 0.1$), medium ($\sigma = 0.3$) and high ($\sigma = 1$). For each of the cases of heterogeneity, the travel time distribution is assumed to follow a unimodal lognormal pdf, such that:

$$
 g(\tau_n;\mu,\sigma) = \frac{1}{\tau_n \sigma \sqrt{2\pi}} e^{-\frac{1}{2} \left( \frac{\ln \tau_n - \mu}{\sigma} \right)^2}
$$

Where: $\mu = \ln \tau$ is the average of the log travel time

$\sigma$ = the standard deviation of the log travel time, and

$$
 \mu = \ln \tau - \frac{\sigma^2}{2}
$$

In order to evaluate the effect of source zone location and distance to the edge of the impoundment, the lateral extent of impoundment is subdivided into 5 independent sub areas, located at equal intervals (each 40m apart) from the control plane (see, Fig. 11).

**Fig 11.** Conceptual model of the impoundment. The injection of pollutants is considered to occur in independent sub areas along the center of which (along the broken lines) the contaminants enter the transport system.
The change in pH and concentration of the contaminants, due to contribution from all the ‘sub areas’ is integrated at the impoundment boundary by summing up the resultant breakthrough concentration from each of the ‘sub areas’. Fig. 12, below, shows how the transport of contaminant from each of the sub areas is conceptualized.

**Fig. 12** Conceptual model of pollutant transport in the saturated zone of mill tailings impoundment 1, Kristineberg. Flow from the center of each of the sub areas (considered as sections of the injection plane (IP) to the control plane (CP)) is conceptualized as occurring along several stream tubes with different travel time (here only two from each is shown).
8. Results

A site specific reactive transport model of AMD for tailing impoundment 1 at the Kristineberg mine site, northern Sweden, is developed to simulate the pH buffering and metal attenuation by different mineral phases, while the drainage transported through the saturated zone of the impoundment. The extent of the impoundment is about 200m along the mean water flow direction and simulation results in all settings of the model would depict the resultant contaminant concentration in the groundwater at the downstream boundary of the impoundment, just where it enters the regional groundwater system. Geochemical processes are modelled using the PHREEQC code whereas transport is by the lagrangian stochastic method (LaSAR). The coupled PHREEQC-LaSAR, proposed by Malmström et. al., (2004) and Berglund et. al., (2003), is applied to evaluate the effect of geochemical reactions and variability of the subsurface flow on the breakthrough of pollutants. In addition, effect of the aerial extent of the impoundment is analyzed by assuming the impoundment laterally comprise five independent sub areas. The unsaturated zone is the principal source of contaminant drained in to the saturated zone thus the presented model concerns natural attenuation of pollutant within the impoundment. In all settings of the model the saturated zone is assumed to be in equilibrium with atmospheric CO₂ pressure.

8.1 Evolution of the geochemistry downstream of the AMD source

As described in the site description section, the tailings impoundment 1 at the Kristineberg mining site contains a lot of minerals capable of buffering pH. Among all these mineral phases, calcite (reaction 7, on page 11) and chlorite (reaction 13, on page 13) are considered in the presented model as the principal buffering minerals. Several field investigations, for instance, Berger et. al., (2000, 2003 and Malmström, 2004), showed that calcite is the most effective mineral to buffer pH in AMD affected areas The impoundment under consideration consist of a subdued amount of calcite (less than 1% by volume). Pervious geochemical modelling works in the case study site, identified chlorite as the most important mineral of all the aluminosilicate minerals found in the impoundment (see, for example, Salmon, 2003; Salmon and Malmström, 2004). In addition, as precipitation of secondary metal oxide minerals and their subsequent dissolution will affect the geochemistry of the tailing impoundment, effect of precipitation and dissolution of Al (OH)₃(s) (reaction 10, on page 13) will also be discussed.
In all cases presented in this section, the contaminated inflow, from the unsaturated zone, is assumed to be injected at the center of the impoundment (center of sub area 3 in the model setting, see, Fig. 11). Thus, a contaminant transport distance of about 100 meters, to the downstream boundary of the impoundment, is considered. Therefore, the breakthrough curve of pH and Zn show the temporal change in groundwater pH when it just leaves the impoundment and enters the surrounding groundwater system, after transported for about 100m from the contaminant source zone.

### 8.1.1 pH buffering

An equilibrium geochemical model for pH buffering by calcite and chlorite is presented below in order to compare the significance of each of the minerals in buffering pH. A calcite content of about 0.3mol/kg of water, equivalent to 1% by volume in the impoundment, is considered to present in the saturated zone during the onset of simulation. Whereas chlorite is assumed to occur in excess amount and hence the maximum allowed amount in the model is considered to present in the saturated zone initially.

In order to show the significance of the pH buffering processes, the groundwater flow is simulated using the same setting of the model as described above but without calcite and chlorite. The resulting pH and Zn breakthrough curves are shown in Fig. 13, below.

![Breakthrough curves of (a) pH and (b) Zn for non-reactive model setting at 100 meters downstream of the AMD source ($\tau_{\text{water}} = 7.4$ years)](image-url)
As can be seen from the pH and Zn breakthrough curves, (Fig.13), in absence of both of the buffering minerals, the pH of the groundwater and the concentration of the metal leaving the impoundment will be almost the same as in the inflowing water from the unsaturated zone, just at the breakthrough time of the contaminant. This situation implies a theoretical case scenario in AMD affected areas. In such theoretical cases, the groundwater will become highly contaminated by drainage from the impoundment and may result in devastating impact on, for instance, the fauna in the surrounding water bodies. This case might be assumed to happen in areas where highly concentrated mining wastes are discarded, for instance due to low efficiency of mineral processing, where buffering minerals are completely consumed too early (such as due to low volume of the mineral) and no remediation action is taken for long period of time. Similar situation might also be assumed to happen where surface and subsurface water resources are situated very close to extremely concentrated AMD, where effect of mixing phenomena is neglected. Comparison of the buffering of calcite and chlorite minerals in the impoundment is shown by presenting breakthrough curve of pH obtained from simulation of geochemical equilibrium models containing a) only calcite b) only chlorite and c) both calcite and chlorite (see Fig. 14 (a-c)).

**Fig. 14** Breakthrough curves of pH, 100m downstream of the AMD source, obtained from the geochemical equilibrium model containing a) only calcite b) only chlorite and c) both calcite and chlorite
Fig. 14 shows that calcite is the most efficient mineral in buffering pH. Despite the relatively low amount of the mineral in the impoundment, calcite is capable of buffering the pH to about 8.1 for about 200 years. On the other hand, the chlorite, which is assumed to occur in excess, buffers pH to about 6.8 throughout the simulation period. The relatively longer period of pH buffering by chlorite, as compared to calcite, is due to its higher abundance. The effect of simultaneous presence of both of the buffering minerals (as shown in Fig. 14c) is such that slightly higher pH (7.6), as compared to 7.5 when only calcite is considered, results after depletion of calcite and, importantly, the period for which the calcite buffers pH is prolonged. For the presented model scenario, calcite-buffering time is prolonged for about 80 years due to presence of chlorite in addition to the calcite. Buffering at pH 7.5-7.6 is brought about by redissolution of the precipitated smithsonite (see section 8.1.2).

The pH buffering through dissolution of calcite and chlorite is associated with release of base cations. As an example, breakthrough curve of Mg for different cases (buffering by calcite and chlorite dissolution) is shown in Fig. 15. As can be seen from the breakthrough curves, chlorite dissolution has affected concentration of Mg, as opposed to its non-reactive character in impoundments containing only calcite. In the calcite case, Mg breaks through at $\tau = 7.4$ years at the concentration leaving the unsaturated zone (0.011M; non reactive tracer, Fig. 15a). In the chlorite case, the Mg concentration increases to 0.0003M from the start of the simulation, due to chlorite dissolution. At about $\tau = 8.5$ years, the Mg concentration increase to 0.013M.

![Fig. 15](image)

**Fig. 15** Breakthrough curve of Mg for cases buffering pH by (a) Calcite and (b) Chlorite at 100 meters downstream of the AMD source.

The higher rate of chlorite dissolution, reflecting it self in a higher Mg concentration than expected from the initial chlorite dissolution and the input Mg concentration from the
unsaturated zone, after breakthrough of the AMD is associated with consumption of the acidity of the AMD. Thus, the increased concentration of Mg in the effluent reflects the effective solubility of chlorite, and thus its buffering, at various conditions.

The comparison of the buffering capacity by the minerals showed the importance of dissolution of aluminosilicate minerals, at least chlorite, in buffering pH in AMD affected areas, in addition to the well recognized effect of carbonate minerals. In the above-discussed results, it was assumed that chlorite dissolution is fast and maintained at geochemical equilibrium. However, chlorite dissolution is generally regarded as a slow geochemical process as discussed in pervious studies, see for instance, Salmon, (2000). Thus, dissolution of chlorite should basically be quantified as a kinetic process. Alternatively, two limiting cases can be addressed; (i) Chlorite dissolution is so slow that it does not affect the geochemistry and thus can be excluded from the model (base case) and (ii) Chlorite dissolution is fast, such that equilibrium with aqueous phase is maintained. In order to be conservative, case (ii) is used to evaluate pH buffering by chlorite and case (i) is used as a base case in the following.

Simulation results of the base case model, containing calcite as a major buffering mineral, are presented below. In the model, smithsonite (ZnCO₃), Al(OH)₃ (s) and gypsum (CaSO₄.2H₂O) are allowed to precipitate. The AMD is assumed to enter the saturated zone at the center of the impoundment (center of sub area 3) and the simulation result show the groundwater composition at the downstream boundary of the impoundment, thus located at 100 meters from the AMD source. As shown in Fig. 14(a), the pH at the control plane was initially, when the solution is unaffected by the AMD, around 8.3. At \( \tau =7.4 \) years, the AMD breaks through, but the pH is maintained at a high level, pH = 8.1, through buffering by calcite. Gradually calcite is consumed and a depletion front moves forward, as shown in the mineral profile below, Fig. 16. At 200 years, all the calcite up to the control plane has been consumed and the pH drops to 7.5, now buffered by dissolution of smithsonite. After depletion of smithsonite, the pH further drops to about 5.7, as shown on breakthrough curves for source located at shorter distance (see section 8.3.2).
Fig. 16  Mineral profile at 4, 40 and 400 years for each of the buffering minerals in the base case model a) calcite b) smithsonite c) Al (OH)$_3$ (s) at a distance of 200meters (for calcite and smithsonite) and 100meters (for Al(OH)$_3$ (s)) downstream of AMD source.
Fig. 16, above shows profile of the mineral phases responsible for pH buffering for the time period of 4, 40 and 400 years. As shown on the profiles calcite is continuously dissolving in the course of buffering the pH. Both the smithsonite and Al(OH)$_3$ show initial precipitation and subsequently dissolution with time. At t= 400 years the calcite depletion front will reach about 200 meters (as shown in Fig. 14, a the calcite was depleted at about 200 years, for the distance of 100 years).

Precipitation and subsequent dissolution of secondary mineral dissolution may also be important in the geochemical modelling of AMD. The base case model shown above considers precipitation of Al(OH)$_3$ (s), as one example. To show the significance of this phase in buffering pH, simulation result of the base case model where Al(OH)$_3$ (s) precipitation is neglected and also considered, with source distance of 60 meters, is shown below in Fig. 17, below. The result revealed the fact that Al(OH)$_3$ (s) buffers pH to about 5.7 that would drop to about 4.9 otherwise. Such capacity of Al(OH)$_3$ to buffer pH in AMD affected areas was discussed in Blowes and Ptacek (1994).
Fig.17  Breakthrough curve of pH (a and c) and Zn (b and d), at 60m downstream of the AMD source, from the geochemical model where precipitation of Al(OH)$_3(s)$ is not considered (i) and (ii) included in the model.
As shown above, in Fig. 17, precipitation and redissolution of Al(OH)$_3$ (s) resulted in pH buffering to about 5.7 (fig. 16c), once the smithsonite has been consumed, which would otherwise drop to 4.9 (fig. 16a). Moreover, in absence of Al(OH)$_3$ (s) precipitation, due to drop in pH, Zn mobility will become higher with shorter peak concentration time and earlier breakthrough of the input concentration.

8.1.2 Attenuation of Zn

8.1.2.1 Attenuation of Zn due precipitation of secondary minerals

Metal attenuation, due to precipitation of secondary mineral phases has been identified to be an important processes in AMD affected areas (see Brown et. al., 1998, and elsewhere). In this modelling work, effect of precipitation of smithsonite, a mineral phase reported to be oversaturated in AMD areas (see Nordstrom et. al., 1999), is considered as the major Zn$^{2+}$ attenuating mechanism.

![Breakthrough curve of (a) SO$_4^{2-}$ (b) Fe(II) and (c) Zn from the base case model with a source zone located at 100 meters upstream of the control plane.](image-url)
Fig. 18, above, shows the breakthrough of SO\textsubscript{4}\textsuperscript{2-}, Fe (II) and Zn for a contaminant entering the transport system about 100 meters from the downstream boundary of the impoundment (from center of sub area 3). The Fe (II) concentration is, as expected, kept similar during the whole simulation period, due to the fact that no iron containing phases included in the model and thus Fe is transported non-reactively. The SO\textsubscript{4}\textsuperscript{2-} concentration is initially reduced (to about 0.09M) as compared to 0.1M (input concentration) and latter increased, after the depletion of calcite, signifying formation of gypsum (CaSO\textsubscript{4}.2H\textsubscript{2}O) during the buffering by calcite and its latter dissolution with drop in pH according to.

\[
H^+ + CaCO_{3(s)} + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O_{(s)} + HCO_3^-
\]  

(17)

\[
CaSO_4.2H_2O_{(s)} \rightarrow Ca^{2+} + SO_4^{2-} + 2 H_2O
\]  

(18)

It can be observed that the Zn has a first breakthrough at about 7.4 years, which is equivalent to the mean water travel time. The concentration at the breakthrough is about 10% of the input concentration (0.0006M), indicating immobilization of the metal ion. Attenuation of the metal was due to precipitation of smithsonite, ZnCO\textsubscript{3}, before the calcite has got completely consumed in the course of buffering the pH.

In the model, smithsonite, one of the minerals identified by Nordstrom and Alpers (1999) to occur in AMD affected area, is allowed to precipitate. The precipitation of this phase occurs due to the fact that the liberated HCO\textsubscript{3} -, during dissolution of calcite, reacted with the influent containing Zn\textsuperscript{2+} according to

\[
Zn^{2+} + HCO_3^- \rightarrow ZnCO_3(s) + H^+
\]  

(19)

After about 200 years, high concentration of Zn, which is about 160% of the input concentration (0.0095M), has occurred continuously for the remaining simulation time. Such high concentration indicates remobilisation of the metal ion due to pH drop to about 7.5, as shown above in Fig. 14 (a), which initiated subsequent dissolution of the initially precipitated smithsonite. After the available calcite has been completely consumed, the pH drops to about 7.5 and dissolution of the precipitated smithsonite is initiated, as discussed by Berglund et. al., 2003 and Malmström et. al., 2004. This results in the second breakthrough of Zn\textsuperscript{2+} at t =
200 years. It is important to note that the concentration of Zn$^{+2}$ now is higher at the CP than at the IP and that this condition remains throughout the simulation period (450 years), for a source at distance of 100m from the impoundment boundary. Thus, while smithsonite formation delayed the Zn$^{+2}$ breakthrough with several hundred years, it also resulted in an increased pollutant loading over longer times. The result shows the importance of identifying the appropriate secondary minerals phases, which would determine the temporal mobility of the respective metal ions, in modelling attenuation mechanisms.

In the base case model, precipitation of Al(OH)$_3$ (S) found to affect mobility of Zn. The breakthrough curve of Zn (Fig. 17, b), obtained after removing Al(OH)$_3$(s) precipitation from the model, showed that remobilization of Zn will occur slightly earlier and will reach too about 175% of the input concentration, as opposed to that of about 160% in the base case model. This result, due to the pH effect, on smithsonite solubility, causes the reverse of the reaction shown in reaction 19, above.

### 8.1.2.2 Attenuation of Zn by sorption

Sorption of Zn on ferric hydroxide surface is reported to be an important process capable of attenuating Zn (see, Malmström et. al., 2004). Sorption on ferric hydroxide surface with a surface site concentration of 0.006 mol/l results in Zn retardation to about 14.6 years, while the breakthrough time is about 7.4 years as shown in Fig. 19 below.

**Fig. 19** Breakthrough curves of (a) pH and (b) Zn, where sorption of the Zn on iron oxide surface (with surface concentration of 0.006) is considered, for a source at 100m upstream of CP.
Competitive sorption of Ca, Fe (II), and Mg with Zn showed similar result with the pure sorption case, indicating a higher surface affinity of Zn in sorption process as compares to the other metals.

8.2 Effect of lateral extent of the impoundment

8.2.1 “Edge effect”

The preceding discussion has shown that considerable attenuation of acidity and Zn$^{2+}$ can occur in the saturated zone of the tailings provided that the transport length from the AMD source to the boundary of the impoundment is long. This situation might be quite different for AMD source locations close to the edge of the impoundment, which thus may require special attention in remediation of the environmental impact of AMD.

In order to account for the effect of the lateral extent as well as the effect of pollutant source zones close to the edge of the impoundment on the resulting groundwater pH and concentration of Zn at the downstream boundary, the whole lateral extent of the impoundment, which is 200m, is subdivided into 5 sub areas, each 40 meter wide, and assumed to be independent of each other. AMD migration, emanating from the center of each of the areas, is simulated and the resultant breakthrough curve for pH and Zn are evaluated (see, Fig. 21).

As an example of a source zone closer to the edge of the impoundment, breakthrough of pH and Zn for the distance 1, 5 and 10 meters are compared below in Fig. 20, below. As shown in the breakthrough curves, as the AMD source is located closer to the edge of the impoundment, the impact on the groundwater quality will become rigorous, such that the contamination start earlier, due to weaker natural attenuation of the pollutants. This is due to the fact that geochemical process that would be effective to buffer pH and attenuate metal ions will become less effective, as the source zone becomes closer to the CP, due to the short water travel time. This fact is further shown in the pH drop to about 4.9, 5.7, and 7.5 (within 20 years) for sources located at 1m, 5m, and 10m distances from the impoundment boundary, respectively (Figures 20 a, c, and e). In effect, attenuation of Zn$^{2+}$ occurs for about 2 years, for the source at 1m distance, zone to about 10 and 20 years for the contaminant source distance of 5 and 10 meters, respectively (Figures 20 b, d, and f). In fact, as will be shown in more detail below, the farthest source location will have a long lasting and high metal load effect,
though immobilization of the metal may occur for appreciable time during buffering by calcite and precipitation of smithsonite.

Fig. 20  Edge effect on breakthrough pH (a, c, e) and Zn (b, d, f) for transport distances of 1m, 5m, and 10m, from the AMD source.
8.2.2 Effect of source distance on pollutant concentration

Consideration of the impoundment extent is also relevant in understanding metal mobility in AMD affected areas. Since, as discussed in previous sections, mobility of Zn in the base case model is a function of precipitation and subsequent dissolution of smithsonite, which in turn depends on the pH, the timing and duration of the Zn $^{+2}$ pollutant load from each of the sub-areas will be affected by the corresponding pH-buffering trend.

As would be expected, for the base case scenario, the resultant pH at the downstream boundary (CP) is a function of the groundwater travel time between the source and the control plane. As the source gets closer to the impoundment boundary, the resulting pH will drop progressively from about 7.5 (for the farthest, for travel distance equal to or longer than 100m) to about 5.7 (the closest, travel distance shorter or equal to 60m). The time at which the pH drops to the minimum and the length for which the highest pH sustain also depend on the position of the source, with that from nearest sub area shows several pH buffering levels, due to less amount of reactive minerals between the IP and the CP, than the farthest ones (see Fig. 21 a-e). As shown, the duration of the time period at which the pH sustain to about 8.1, due to buffering by calcite, is 364, 280, 200, 120 and 34 years for sub-areas 1, 2, 3, 4, and 5, respectively, while the corresponding mean water travel to the CP from each of the sub-areas being 13.2, 10.2, 7.4, 4.4, and, 1.4 years respectively.

One peculiar feature of the curves is that for those with source distances of 60m and 20 meters, the drop in pH is as low as 5.7, before the end of the simulation, and consequently, the breakthrough for Zn finally drops to the input value, as the mineral phase capable of attenuating Zn, smithsonite, totally dissolved before the end of the simulation. For the farthest sources, the cumulative effect from the influent and that from the dissolution of smithsonite increase the Zn concentration for longer time.
Fig. 21 Breakthrough of Zn$^{2+}$ (a-e) and the corresponding pH (f-j), for different distances from the AMD source to the control plane.
The aforementioned results, signifies the importance of the lateral extension and zones near the edge of the impoundment on buffering reactions and metal mobility. As discussed above, consideration of different contaminant sources will result in different timing, concentration levels and duration of pollutants for pH and Zn, depending on the water travel time required to reach the control plane. In order to visualize the cumulative effect of these ‘point sources’, an attempt is made to sum up the contribution from each of the sub areas, at the control plane. The resulting breakthrough curves are shown in Fig. 22, below. The cumulative breakthrough curves show a stepwise drop in pH with time and the corresponding increase in metal concentration. This stepwise behavior is due to the rough discretisation of the presented model (5 zones for 200m). Upon adding more zones to the model thereby increasing the discretisation of the model, it is expected that the curve would become smoother, at the same time, however, demanding more simulation time and computer capacity.

![Homogeneous_Cumulative](image)

**Fig. 22** Break through curves for Zn (a) and pH (b) obtained by summing up contributions from each of the sub areas at the impoundment boundary.

Although the curves are stepwise, they can be used to indicate the general trend of water composition at the CP, with monotonously decreasing pH (Fig. 20b) and on average increasing Zn $^{2+}$ concentrations over time (Fig. 22a).
8.3 Effect of flow Variability

The above results show that the PHREEQC model is efficient in modelling geochemical processes and is an easy tool to test different geochemical scenarios without considering other factors that might affect the processes. However, in reality, there are other factors that should be considered, in addition to geochemistry of the deposit, while dealing with AMD transport. One important factor that may affect the breakthrough of contaminants is flow variability of the subsurface system (see, e.g., Cvetkovic and Dagan, 1994; Berglund et. al., 2003 and Malmström et. al., 2004; and many others).

In order to appreciate the effect of variability of the flow system, breakthrough curves of Zn, for a contaminant transported from the midpoint of the impoundment, as evaluated at the impoundment boundary (after travelling for 100meters) are shown in Fig. 23 below, for three different flow variability cases. For the sake of understanding, the deterministic (homogeneous) breakthrough curve (where variability is neglected) is also shown.

From the shape of the breakthrough curves shown in Fig. 23, the effect of introducing the flow variability factor in the transport problem can be well appreciated. In the homogeneous flow case, it is not possible to observe the breakthrough concentration of Zn, before it reaches about 10% of the input concentration (at $t = \tau_{\text{water}}$). When flow heterogeneity is considered,
increasing concentration from the commencement of the simulation is observed (early breakthrough of pollutant). This is due to the fact that some of the water parcels, along stream tubes with shorter travel time, will reach the control plane soon after the commencement of the simulation. This will have relevance with respect to environmental mitigation measures, as it will enable the model users to know how early they need to take measures, particularly in situations early actions even at subdued concentration are mandatory.

Comparison of the stochastic and deterministic model (with the same discretisation and the same setting), as shown above, revealed the fact that the breakthrough curve of Zn obtained from stochastic modelling shows continuously increasing metal concentration with time. On the other hand, the deterministic breakthrough curve portrays only few concentration levels. The general effect of increasing flow heterogeneity is thus smoothening of the breakthrough curve (see also, Berglund et. al., 2003 and Malmström et. al., 2004), early arrival of the pollutants, lower Zn$^{2+}$ peak concentration and longer pollutant load. In fact, since the stochastic approach couples the effects of both geochemical processes and the spatial variability, it is difficult to understand the relevant geochemical processes, such as dissolution front, responsible for getting a certain concentration during defined time of simulation; hence, the importance of deterministic approach. However, the results shown above, as an example, show the importance of considering the combined effects of flow heterogeneity and geochemical processes for appropriate modelling of the pollutant transport. The peak concentration obtained from the deterministic (homogeneous) case is by far higher (by about 50%) than the one obtained, for example, from the high variability case.

The above result shows the breakthrough of Zn obtained from a single source located at the center of the impoundment (100 meters from the impoundment boundary). However, in the conceptual model, the source zone is considered to be multiple over the impoundment, which in the mathematical model is represented by five independent sub areas. The breakthrough curves (BTC) for Zn, for all flow variability cases, from each of the sub areas, are shown below in Fig. 24, in order to appreciate the effect of the source location on the resultant of the breakthrough curves.
Modelling Reactive Transport of AMD: Effect of geochemical reactions, spatially variable flow, source location and distribution

(a) $d = 180m$

(b) $d = 140m$

(c) $d = 100m$
**Fig. 24** BTC of Zn at the boundary of the impoundment for transport distance of (a)= 20m (b)= 60m (c)=100m (d)=140m and (e)=180m from the impoundment boundary. Three flow variability cases of high ($\sigma=1$) medium ($\sigma= 0.3$) and low ($\sigma= 0.1$) are shown for each of the transport distances considered and compared with the deterministic (homogeneous case).

Fig. 22 (a-e) shows the significance of the transport distance, in addition to the already discussed flow variability on the shape of the resulting breakthrough curve. As discussed before, for all flow variability cases, as the source gets closer, the time for the first contaminant breakthrough will be shorter and the peak concentration will be reached earlier.
Comparing the effect of the same flow variability between the distances (which is not theoretically fully correct as $\sigma$, standard deviation of the travel time, will increase with transport length), it is evident that the effect increases with increasing transport length. Thus the BTC gets smoother and smoother the farther away the CP is located from the source. Fig. 25, below, shows this fact for effect of distance on the breakthrough of Zn for different source distances.

Fig. 25. Breakthrough curves of Zn for a highly variable flow system ($\sigma=1$), with AMD source distances of a)180m b)140m c) 100m d)60m and e)20m.
While Fig. 25 shows the breakthrough curves from assuming independent source areas, in reality, the contaminant may have different source area and thus may travel from all these sources simultaneously. Therefore, for evaluation of the pollutant situation at a certain compliance boundary, such as at the impoundment boundary with the surrounding aquifer, it is important to consider the cumulative effect. Therefore, breakthrough curves of Zn obtained from each of the areas are summed up in order to get the cumulative effect and are shown below in Fig. 26.

**Fig. 26** Cumulative breakthrough curve of Zn at the impoundment boundary for different flow variability cases (high ($\sigma=1$) medium ($\sigma=0.3$) and low ($\sigma=0.1$); compared with the cumulative deterministic (homogeneous) case.

For the deterministic (homogeneous) case, as expected, the cumulative curve has a lot of steps, due to insufficient discretisation in the model. However, a general trend of metal mobilization for long period of time is indicated, provided that flow variability effects ignored. The steps would become finer if more source areas were included in the model. For the case with other flow variability cases, the curves become smoother and have similar shape to those from the individual source areas. The initial breakthrough time will be shorter and also lower peak concentration will be reached as the flow variability is increased, but with longer period of relatively high contaminant load, as compared to lower variability cases.
From the foregoing discussion, it has been shown that in both the homogeneous and heterogeneous flow cases, the position of the contaminant source and, hence, the transport distance will have influence on the shape of the breakthrough curves of Zn. Then, determining the optimal level of discretization of the source term might be of interest. That is, for instance, increasing the number of sub areas, as described in this modelling work, would be an important step in developing more relevant predictive models. Despite the resulting complexity of the model and the time of simulation required to get the results, from the very nature of the modelling approach, discretization of the system parameters may increase the reliability of the output of the model. Such work demand longer simulation period, high computer capacity and management (book-keeping) of several model outputs.

Fig. 27 shows breakthrough curves, from each of the source locations along with the cumulative one for the high variability flow case. As shown in the plot, the breakthrough curve from the sub area located at the mean distance, sub area 3, will best approximate the cumulative breakthrough curve. Hence, it can be concluded that, the mean distance can be taken as a good approximation in modelling contaminant transport in highly variable flow system (see Fig.28a).

![Comparison of Zn breakthrough curves from each of the sub areas](image)

**Fig.27** Comparison of breakthrough curve of Zn from all sub areas and the cumulative BTC for a highly variable ,($\sigma =1$), flow system(”slices” means the respective sub areas)
Fig. 28 (a), below shows how the cumulative breakthrough curve for a high variability case resembles that from sub area 3. However, it is not always possible to say that the breakthrough curve from the mean transport distance would suffice to be taken as the representative contaminant breakthrough curve for multi-source cases. As, the shape of the breakthrough curves for both the cumulative and the mean distance will be affected by the flow variability, the above shown relation may not be extended to all flow variability cases. Accordingly, in order to further appreciate what will be the effect of the flow variability in approximating the whole contaminant source area with that mean distance far from the CP, breakthrough curves of Zn for a high- and low-variability flow system are compared below in Fig. 28 (a and b).

![Breakthrough curve of Zn obtained from the mean distance (100m) and from combination of all source zone for (a) high variable flow and (b) low variable flow systems.](image)
From the comparison of the breakthrough curves shown above, in fig. 25 (a and b), it is possible to observe that approximation of the location of the contaminant source as from the mean distance from CP will be possible with reasonable deviation for a highly variable flow system. However, as the flow variability gets less variable, approximating the source location by the mean distance will not be possible.
9. Discussion and Conclusion

Modelling transport of AMD from mill tailings impoundment is essential in characterizing the impacts on groundwater resources and evaluation of mitigation measures. The resulting concentration of contaminants, as evaluated at a defined boundary of interest and as function of time, depends on the geochemical reactions involved, on transport processes and on the degree of flow heterogeneity of the subsurface system. Accordingly, a reactive transport model of AMD is presented with the objective to evaluate the significance of the geochemical reactions considered and the flow heterogeneity of the tailings impoundment.

In this study, tailings impoundment 1 at Kristineberg, northern Sweden is used as a case study and the developed model is devoted to simulate pH buffering and metal attenuation by different mineral phases, while the drainage is transported through the saturated zone of the impoundment. The extent of the impoundment is about 200m along the mean water flow direction and simulation results in all settings of the model would depict the resultant contaminant concentration in the groundwater at the downstream boundary of the impoundment, just where it enters the regional groundwater system.

A simplified geochemical model consisting few mineral phases, and where all reactions are assumed to maintain at equilibrium condition is used (compare, Berglund et. al., 2003; Malmström et. al., 2004) in order to simulate pH buffering and metal attenuation, by using Zn as an example is used. Calcite is considered as the major pH-buffering mineral and its buffering action is compared with that of chlorite, a major aluminosilicate mineral in the impoundment. Relevance of Al(OH)₃(s) precipitation and dissolution both in pH buffering and attenuation of metal is also evaluated.

A systematic approach by which geochemical processes are decoupled from transport is followed so that the complex phenomena can be understood in a better way is used. The PHREEQC model is used to simulate the geochemical processes. The effect of flow variability is modelled applying the lagrangian stochastic reactive transport (LaSAR) formulation by comparing four flow cases; high ($\sigma = 1$), moderate ($\sigma = 0.3$) and low ($\sigma = 0.1$) flow variability, assuming a lognormal pdf for the water residence time, as well as a homogeneous model ($\sigma = 0$). The PHREEQC-LASAR model proposed by Malmström et. al.,
(2004) is used in this study as the tool is proposed to be effective in handling both geochemical complexities, such as in mill tailing impoundments, and physical variability of the subsurface.

The presented geochemical base case model contains calcite as the major buffering mineral with concentration of about 0.03 mol/kg of water. Precipitation of smithsonite (ZnCO$_3$), Al(OH)$_3$ (s) and gypsum (CaSO$_4$. 2H$_2$O) is allowed in the model. Dissolution of calcite resulted in pH buffering to about 8.1, until the depletion of the mineral. The increase in pH resulted in immobilization of Zn to a subdued level, thus suggesting effective attenuation of heavy metal in areas characterized by underlying calcareous geological materials, as previously widely described in scientific literatures, (see, for instance, Berger et. al., 1999; Berglund et. al. 2003; and Malmström et. al., 2004).

After depletion of calcite, the initially precipitated secondary mineral, smithsonite, will start to dissolve and will buffer the pH to about 7.5 until the total available amount gets consumed simultaneously resulting in remobilization of Zn$^{2+}$. After all smithsonite is dissolved, the pH is buffered to about 5.7 due to dissolution of Al (OH)$_3$ (s). The sorption of Zn$^{2+}$, in the absence of smithsonite, on hydrous ferric oxide, with surface concentration of 0.006 mol/l, resulted in attenuation of the metal for about 7.2 years, equivalent to the water travel time for the considered distance, indicating effective sorption of the metal on the available sorption surface. The result is well comparable with that reported by Malmström et. al., (2004). Furthermore, it was found that competitive sorption of other metals (Ca, Mg, and Fe (II) ) did not affect the attenuation of Zn. Dissolution of the initially precipitated Al(OH)$_3$(s) resulted in pH buffering to about 5.7, without affecting mobility of Zn$^{2+}$.

The results show that Zn$^{2+}$, as one example of a heavy metal from AMD, can be substantially attenuated within the impoundment by reactions such as precipitation and sorption. They also show that Zn$^{2+}$ can be remobilised up on drop in pH. Model results, thus, indicated that contaminant transport in the saturated zone of tailing impoundments could continue for very long time, with potential threat on groundwater resources, unless mitigation measures are taken so early before the concentration of pollutants become above threshold limits. The remediation measures that would be taken need to prevent primary release of Zn$^{2+}$ from the unsaturated zone of the impoundment and/or drop in pH in the saturated zone. Both these
effects can be achieved by e.g., preventing oxygen diffusion, such as commonly aimed for, e.g. in cover techniques.

As different field situations are characterized by heterogeneity of the subsurface such as due to difference in grain size distribution in clastic sediments, variable flow pattern in karstic rocks, structural and textural variations in volcanic and metamorphic rocks, and, particularly, tailings mineralogy and grain size in tailing impoundment; consideration of flow variability will important for reliable modelling of contaminant transport.

Effect of flow variability on the timing, maximum concentration and duration of the pollution peak for Zn was shown to be important in the presented model. In all model settings the flow variability highly affect the resultant breakthrough concentration of Zn downstream of the pollutant source. Therefore, consideration of the heterogeneity of the flow media will be important in modelling contaminant transport in subsurface system as discussed in Berglund et. al., (2003) and Malmström et. al., (2004).

In general, as the flow variability increased, both pH buffering and metal attenuation capacity will be less effective at the beginning, during dissolution of calcite. This is due to early depletion of calcite along streamlines with low residence time and results in higher mobility of metals and faster drop in pH at the control plane, as compared to the homogeneous or low flow variability cases. After depletion of calcite, the peak breakthrough concentration will be lower and also the time to reach that peak will be longer for a case with high flow variability as compared to cases of homogeneous or of low flow variable system.

For representing the field condition with the contaminant source in tailing deposits, considered as non point sources, the attenuation of pollutants will depend on the travel distance from the source to the control plane, thus, the effects of zones located close to the boundary of the impoundment is different to those of the interior.

The aerial extent of the contaminant source, conceptualised as set of sub areas, was introduced in the model. Hence, breakthrough curves of Zn will differ based on the location of the source with respect to the plane of interest at which effects are monitored. Model results show that the effect from contaminant sources located far from the control plane will occur latter than those located at shorter distances. An additional effect is that up on remobilisation,
due to change in geochemical conditions, such as drop in pH, the source located at longer distance will contribute with more pollutants than that at shorter distance.

If one ignores the heterogeneity of the subsurface, the resultant breakthrough curve obtained by summing up the contribution from each the different source zones, a gradually decreasing water quality with time at the CP, and a smoother change in concentration than when only one source considered was observed. Model results indicated that representation of the whole impoundment by the center source area alone was a good approximation for cases with large flow variability. Decreasing degree of flow variability and/or transport length increased the need for considering the lateral extent of the impoundment in order to correctly quantify contaminant concentration at the CP.

Possible mitigation measures to minimize the impact of AMD on groundwater resources, thus, should start from proper site selection for tailings impoundment. Both the distance from sensitive sources and topographical position with respect to the groundwater flow direction should be properly considered. The other and may be more appropriate mitigation measure is getting rid of the contaminant generation by covering the impoundment by soil so that oxygen diffusion, which is responsible for oxidation of sulphide minerals and generation of acidity and metal ions, can be prevented. Mitigation measures that could be taken to minimize the adverse impact of AMD on the surrounding groundwater system also includes constructing a cut-off trench across the valley below the tailings impoundment and collection of the resulting water and direct it to a treatment pond where the pH can be raised by reacting with buffering minerals, such as limestone and aluminosilicate minerals. Metals can also be substantially attenuated due to precipitation in wetlands.

The above facts, namely pH buffering and metal attenuation by various geochemical processes, revealed the importance of understanding the geochemistry of the tailings in the impoundment as a whole for assessing the associated environmental impact such as metal mobility in AMD affected areas. The shortcoming of various modelling approach to characterize field condition is usually due to the difficulty to get detailed geochemical and transport data and inability to properly quantify such processes. Therefore, future development on modelling geochemical processes should look for methods where by the complex natural conditions can be conceptualized with appropriate, yet efficient, simplifications.
The presented model is simplified in terms of geochemical processes, such as for example there is no distinction of the slow and fast reactions in the system. Moreover, not all relevant reactions have been considered. Rather a few selected important pH buffering and trace metal attenuating processes have been studied in detail to show the coupled effects of flow heterogeneity, extent of the impoundment and geochemical processes. Therefore, future modelling work should include kinetic quantification of those slow processes. Improved modelling of field scale spreading of contaminants will require detailed data on subsurface variability, for instance, from tracer tests and core sampling.
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