Geochemical processes in mine waste subjected to a changing chemical environment: Fe speciation in leachate water from column experiments

Paula Lundberg

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Luleå University of Technology
Department of Civil, Environmental and Natural Resources Engineering
Preface
This master's thesis is the final step of a Master Degree in Natural Resources Engineering which hereby ends five wonderful years at Luleå University of Technology. This thesis is written in the area of geochemistry and poses part of the larger ongoing project StopOx, in collaboration with the division of Geosciences and Environmental Engineering LTU, Boliden Mineral AB and Nordkalk.

I would like to express my sincere gratitude to my advisor Hanna Kaasalainen for introducing me to this project and for constant support during the supervision of my thesis work. Your enthusiasm and knowledge in the area of geochemistry have been most appreciated.

Moreover, I would like to thank Elsa Nyström for literary references and Desiree Nordmark for introducing me to the Environmental Laboratory at Luleå University of Technology.

Finally, I would like to thank all of my friends and family for your love and encouragement.

Paula Lundberg
Luleå, June 2017
Abstract

Oxidation of sulfidic mine waste is of significant environmental concern due to the consequent formation of acid rock drainage (ARD), deteriorating the water quality of natural water systems. Iron (Fe) and sulfur (S) are two major redox elements involved in these reactions and typically the major redox-sensitive elements (whose solubility, speciation, and mobility are affected by pH and Eh) in water affected by ARD. Measurements of Fe and S species concentrations may reveal valuable information about geochemical processes in mine waste but are typically included when analyzing the chemical composition of ARD.

In this study, robust and portable methods for the determination of Fe and S species concentrations in leachate water affected by sulfidic mine waste were tested and evaluated. The leachate water resulting from interaction with high- and low-sulfide waste rock was collected from three leaching columns, each reflecting different geochemical environments that could occur during mine waste management: (1) fully oxidized conditions (reference column), (2) gradual oxygen depletion from atmospheric level to <1% (anoxic column), (3) treatment with alkaline industrial residual material (alkaline column). The leachate water was analyzed for its pH, Eh, electric conductivity (EC), and major and trace elements.

UV-Vis spectrophotometric ferrozine method was tested and applied for Fe speciation and concentration analysis, allowing determination of Fe(II) and Fe$_{\text{tot}}$ and further calculation of Fe(III) as a difference. The method was found to achieve accurate and reliable results. Turbidimetry was tested and evaluated for dissolved sulfate analysis, and even though the analytical precision was poorer, ca. ±20%, the method provides useful semi-quantitative estimations of dissolved sulfate concentrations. Both spectrophotometry and turbidimetry are easy to perform and utilizes robust, cheap and portable instrumentation.

Leachate water from the high and low sulfide experiments had pH and Eh in the range of pH 2.6 – 12 and Eh 200 – 720 mV and pH 3.5 – 4 and Eh 550 – 700 mV, respectively. Measurements of iron species and sulfate concentrations revealed that sulfate was the dominating S species and during the background leachate Fe(II) was the predominant Fe oxidation state. Upon decreasing oxygen saturation and pH in the anoxic column, Fe speciation in the reference and anoxic column differed, with the relative importance of Fe(III) increasing in the anoxic column. Total Fe, pH and Eh potential measured in the leachate water did not respond to decreasing oxygen saturation, but changes in the Fe redox speciation coincided with this decrease. Under alkaline conditions, total Fe and sulfate concentrations decreased in the alkaline environment, indicating their immobilization in the solid phase.

Geochemical calculations were carried out to gain further understanding of the dominant reactions in the columns. Theoretical values of Fe(II) and Fe(III) concentrations were calculated from the measured redox potential, and these were found to deviate from the measured concentrations. Therefore, estimation of Fe species distribution from redox measurements using a Pt-electrode is not considered sufficient in these systems. Mineral saturation indices of common
secondary minerals associated with ARD indicated dissolution of ferrihydrite, jarosite and schwertmannite in the leachate water from the anoxic column. This suggests that these minerals are the probable source of the Fe and sulfate, as well as As and Cu released to the leachate water.

**Keywords:** Sulfidic mine waste, sulfide oxidation, water quality, environmental analytical chemistry, iron redox speciation
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<td>Ag</td>
<td>Silver</td>
<td>Hg</td>
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<td>Mg</td>
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<tr>
<td>Fe(OH)₃</td>
<td>Ferrihydrite</td>
</tr>
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<td>FeOOH</td>
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<td>KFe₃(SO₄)₂(OH)₆</td>
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<td>SO₄²⁻</td>
<td>Sulfate (referred to as SO₄)</td>
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<tr>
<td>H₂S</td>
<td>Dissolved sulfide</td>
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<tr>
<td>S₂O₃²⁻</td>
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<tr>
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<tr>
<td>ARD</td>
<td>Acid rock drainage</td>
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<tr>
<td>(UV-Vis)</td>
<td>(Ultraviolet-visible) spectrophotometry</td>
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<tr>
<td>ICP-OES</td>
<td>Inductively-coupled plasma optical emission spectrometry</td>
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1. Introduction
The mining industry is one of the largest industries in the world today and except producing highly valuable metals, it produces large amounts of waste such as waste rock and tailings. In 2015, 35.9 Mt waste rock was produced in Sweden during mining of 0.915 Mt ore concentrates (Cu, Pb, Zn and Au) from non-ferrous ore mines (Geological Survey of Sweden, 2016). The composition and amount of waste produced vary depending on the ore-deposit and host-rock mineralogy but also because of differences in ore-processing techniques (Blowes, et al., 2014). Waste rock is often deposited into waste rock dumps close to the mine site without further treatment, or if possible, it is backfilled into the mine after closure.

Sulfidic waste rock by definition contains sulfide minerals that tend to undergo oxidative weathering upon exposure to air and water. Sulfide oxidation and further the release and transport of oxidation products in mine drainage is an environmental problem of international scale (Blowes, et al., 2014) and the main environmental problem of contemporary mining activity (Dold, 2014). Pyrite is the most abundant sulfide mineral in the earth’s crust and also one of the sulfides producing the most acidity (free H⁺ ions) during oxidation, besides releasing sulfate, Fe and metal(loid)s to the water. The products released from sulfide oxidation follow water percolating through the waste rock, giving the water the main characteristics of ARD: low pH and elevated concentrations of sulfate, Fe and other metal(loid)s (Salomons, 1994). The prerequisite for ARD is that the acid generation rate is faster than the neutralization capacity of the material (The International Network for Acid Prevention (INAP), 2009). When pH decreases, the solubility of metals like Cu, Pb, Zn, Cd, Co and Ni increases, therefore ARD is also characterized by a high metal content (INAP, 2009). The solutes released upon sulfide weathering are either transported away or incorporated into secondary minerals by precipitation, coprecipitation or surface adsorption (Smith, 2007). The main problem arises when the ARD reaches natural aqueous systems where it can harm ecosystems. Most potentially harmful metal(loid)s associated with ARD can cause toxic responses to ecosystems, but the toxicity varies depending on the metal content and their redox state (Blowes, et al., 2014).

Among the most common secondary minerals associated with mine waste in an oxidizing environment are Fe(III)-oxides, -oxyhydroxides or oxyhydroxide sulfate minerals such as ferrihydrite, schwertmannite, goethite and jarosite (Dold, 2010). Their stability depends on the pH-Eh conditions and availability of elements like K and sulfate (e.g. Bigham, 1996; Dold, 2010). Figure 1, modified from Dold (2010), shows a stability diagram of these common Fe-bearing minerals and can be used to evaluate the behavior of Fe in different geochemical environments. The formation of secondary minerals is also time-dependent: schwertmannite, ferrihydrite and jarosite may gradually transform into goethite (Dold, 2014). These secondary minerals play an important role in the fate and transport of metal(loid)s due to their large specific surface area and reactivity (Smith, 2007; Majzlan, et al., 2004). Because of their ability to adsorb many metals and metalloids present in ARD, such as As, Mn, Cu and Zn (Dold, 2014), the secondary Fe minerals affect their mobility and distribution between the solid and dissolved phase. As
mentioned earlier, the formation of secondary Fe minerals are highly dependent on water pH and redox conditions, but also the iron chemistry affects the water pH. Precipitation and hydrolysis of secondary Fe(III)-oxy(hydr)oxide minerals produces acid, while the reverse reaction (i.e. upon their dissolution) consumes acid. These processes may occur both inside and outside waste rock deposits. Creation of acidity upon Fe(II) oxidation, hydrolysis and precipitation outside waste rock deposits is often called latent acidity and is a consequence of changing pH or redox conditions after the mine drainage has left the deposit (INAP, 2009; Höglund, et al., 2004). Moreover, iron is not only important for the water pH and metal(loid) distribution, but Fe(III) may also act as an oxidant. If dissolved Fe(III) is present, it has been demonstrated to be the primary oxidant in acid waters (pH<4) (Nordstrom, et al., 1979).

The formation and dissolution of secondary minerals in different chemical environments of mine waste have been widely studied (Höglund, et al., 2004). However, there still is a lack of knowledge regarding the rates and conditions of secondary minerals dissolution. Therefore, the effect of dissolution of secondary minerals in the waste rock and the potential remobilization of the associated metal(loids) on the water quality upon changing chemical conditions is still uncertain.

![Figure 1. pe-pH diagram](image)

**Figure 1. pe-pH diagram** for Fe-S-K-O-H system at 25°C, originating from Bigham et al. (1996) and modified from Dold (2010). The diagram has been drawn with total log activities of $\text{Fe}^{3+} = -3.47$, $\text{Fe}^{3+} = 3.36$ or $-2.27$, $\text{SO}_4 = -2.32$, $K^+ = -3.78$, the log $K_v$ values for goethite, $K$-jarosite, ferricydrite and schwertmannite 1.40, -12.51, 4.5 and 18.0, respectively and schwertmannite having composition of $\text{Fe}_{8}\text{O}_{8}\text{(OH)}_{4.8}\text{(SO}_4)_{1.6}$. The stability fields have to be interpreted as indicative since the thermodynamic data published from schwertmannite and ferricydrite show high variability (Nordstrom, 1990; Majzlan et al. 2004).

The primary goal in remediation attempts involving sulfidic mine waste is to prevent the process of sulfide oxidation generating ARD and to stop the generated ARD from leaving the mine site (INAP, 2009; Kefeni, et al., 2017). Prevention of sulfide oxidation is performed by minimizing the supply of primary reactants, namely oxygen and water. Maximizing the availability of acid neutralization
reactants is another measure, not to prevent oxidation, but to decrease the oxidation rate and create favorable conditions for secondary mineral precipitation. Dry- and wet covers and flooding are common techniques used during the decommissioning of a mine. Dry covers are usually constructed by single or multiple layers of soil or till limiting the transport of oxygen, or gravel, limiting the transport of water to the waste (Höglund, et al., 2004). Dry covers can be used together with the addition of pH controlling alkaline materials such as lime or industrial waste products as well as oxygen consuming materials like sludge and peat (Höglund, et al., 2004). Water covers limits the oxygen availability due to the low diffusivity and solubility of oxygen in the water and may be obtained by underwater disposal in natural lakes or by flooding waste rock backfilled to an open pit (Höglund, et al., 2004; Villain, 2014). When determining cover design, an impact analysis is performed to quantify the relationship between cover system performance criteria of oxygen ingress and net percolation and the key environmental impacts like surface water quality. This requires an integrated analysis of the geochemical reactions and the transport processes occurring in the waste and along the flow path (O’Kane & Wels, 2003). Sulfide oxidation may also be prevented at the particle scale by encapsulation with inert material or by accelerated oxidation on the surface of sulfide particles creating a protective armor layer of secondary precipitates like Fe-oxyhydroxides (Nyström, et al., 2017; Kefeni, et al., 2017). If promoting the formation of secondary minerals, it is important to understand the stability of these phases and associated metal(loids) in the conditions that will prevail.

As a treatment of ARD alkaline materials can be added to the ARD at the drainage outlet of the deposit neutralizing the drainage pH and enhances the removal of metals by precipitation of metal hydroxides and sulfate by precipitation of gypsum sludge (Kefeni, et al., 2017). Using alkaline additives, carefulness is needed as some metal(loids) may show enhanced mobility if the alkalinity grows high enough.
2. Issue
The complex microbiological, hydrological, mineralogical and geochemical processes occurring after deposition of mine waste are not fully understood at the present. In order to effectively prevent the formation of ARD by sulfide oxidation, knowledge about the underlying mineralogical and geochemical processes that take place in the waste rock dumps is essential (Dold, 2010). As the ultimate aim of prevention measures is to reach acceptable water quality, there is a further need to address the geochemical effect on secondary minerals during changing of their geochemical environment, as such a change is often associated with remediation measures.

3. Purpose
This master thesis was performed with the general aim to examine the geochemistry in leachate water affected by ongoing sulfide oxidation and dissolution of secondary minerals in sulfide-containing waste rock. As Fe and S are the dominating major elements and the main redox-sensitive elements in water affected by sulfide oxidation processes and ARD, the focus of this study was to analyze the speciation of these elements in the leachate water. Therefore, the main purpose of this work was to evaluate the convenience of Fe speciation measurements. To reach this purpose, this master thesis included the following tasks:

- The instrumental implementation of spectrophotometric measurements for Fe redox speciation and S determinations in the Environmental Laboratory at Luleå University of Technology.
- Assessing the application of UV-Vis spectrophotometry for Fe and turbidimetry for S determination on samples with different types of chemistries over a wide range of pH and elemental composition
- Demonstrate the usefulness of simple, cheap and accessible methods to determine Fe and S species concentrations for the applied and environmental studies on mine waste.
- Characterization of redox conditions in the leachate water from unsaturated leaching-type column experiments on previously weathered waste rock subjected to different changing geochemical environments. These chemical conditions were:

1. Fully oxidized geochemical environment
2. Transition from oxic to anoxic conditions that may occur during coverage or backfilling of waste rock
3. Increased alkalinity due to surface application of alkaline industrial residue, relevant to the prevention techniques by covering and inhibition.

The expectation is to obtain information that may constrain when dissolution of secondary minerals and remobilization of metal(loid)s may occur and how it might affect the water quality.
4. Limitations
The column leaching experiment started in October 2016 and will continue at least until the end of the year 2017. This master thesis focuses on the experimental progress from the start of the experiment until the 13th of April 2017.

This master thesis is part of a larger ongoing project, Utilization of Industrial Residuals for Prevention of Sulfide Oxidation in Mine Wastes (StopOx) that is funded by Vinnova and Boliden Mineral AB. Within the larger project, careful mineral characterization and sequential chemical extraction of the examined waste rock are in progress, but this data has not been available for this thesis. Therefore, limited mineralogical information was available at the time of writing this report.
5. Theory
In this chapter, the theory behind the central topics of this thesis is described, including oxidative weathering of sulfide minerals, redox conditions and measurement of redox potential and redox sensitive elements, determination of Fe species concentrations by UV-Vis spectrophotometric ferrozine method and sulfate by turbidimetry, and geochemical calculations and modeling.

5.1 Sulfide weathering
Oxidation of sulfide minerals is a chemical and microbial process that takes place when exposed to an oxidant and water (Nordstrom, 2011; Blowes, et al., 2014). The most common oxidant is oxygen, and reaction (1) shows the oxidation of one mole pyrite by atmospheric oxygen, producing one mole Fe(II), two moles SO\(_4^{2-}\) and two moles of H\(^+\) (Blowes, et al., 2014).

\[
\text{FeS}_2(s) + \frac{7}{2} \text{O}_2(g) + \text{H}_2\text{O}(l) = \text{Fe}^{2+}_{(aq)} + 2\text{SO}_4^{2-}_{(aq)} + 2\text{H}^+_{(aq)} \tag{1}
\]

Further, the Fe(II) formed in this reaction tends to oxidize to Fe(III), consuming one mole H\(^+\) according to reaction (2).

\[
\text{Fe}^{2+}_{(aq)} + \frac{1}{4} \text{O}_2(g) + \text{H}^+ = \text{Fe}^{3+}_{(aq)} + \frac{1}{2} \text{H}_2\text{O}(l) \tag{2}
\]

The aqueous speciation and solubility of Fe(III) is highly dependent on pH, reactions 3 – 8. Iron(III) hydrolyzes according to reactions (3) – (6), and due to solubility constrains this results in precipitation of Fe(III)-containing minerals such as ferrihydrite (referred to as Fe(OH)\(_3\)), reaction (7) or goethite (FeOOH\(_\text{(s)}\)) reaction 8, these having low solubility in neutral to alkaline pH range but are highly soluble in acid conditions. The formation of solid Fe(III) (hydr)oxides by hydrolysis of Fe(III) therefore has a large effect on the water pH (Kefeni, et al., 2017): the formation of one mole solid Fe(OH)\(_3\) or Fe(OOH) will produce three moles of H\(^+\) (reactions 7 and 8), therefore resulting in a pH decrease.

Hydrolysis:
\[
\text{Fe}^{3+}_{(aq)} + \text{H}_2\text{O}(l) = \text{FeOH}^{2+}_{(aq)} + \text{H}^+_{(aq)} \tag{3}
\]
\[
\text{Fe}^{3+}_{(aq)} + 2\text{H}_2\text{O}(l) = \text{Fe(OH)}^+_{2(aq)} + 2\text{H}^+_{(aq)} \tag{4}
\]
\[
\text{Fe}^{3+}_{(aq)} + \text{H}_2\text{O}(l) = \text{Fe(OH)}^+_{3(aq)} + 3\text{H}^+_{(aq)} \tag{5}
\]
\[
\text{Fe}^{3+}_{(aq)} + 4\text{H}_2\text{O}(l) = \text{Fe(OH)}^+_{4(aq)} + 4\text{H}^+_{(aq)} \tag{6}
\]

Precipitation:
\[
\text{Fe}^{3+}_{(aq)} + 3\text{H}_2\text{O}(l) = \text{Fe(OH)}^+_{3(s)} + 3\text{H}^+_{(aq)} \tag{7}
\]
\[
\text{Fe}^{3+}_{(aq)} + 2\text{H}_2\text{O}(l) = \text{FeOOH}_{(s)} + 3\text{H}^+_{(aq)} \tag{8}
\]
According to overall reactions (1) – (2) and (7), one mole of pyrite may produce two moles of SO₄, one mole of Fe(OH)₃(s) and four moles of H⁺ during oxidation by oxygen, see reaction (9).

\[
FeS_2(s) + \frac{15}{4} O_2(g) + \frac{7}{2} H_2 O(l) = Fe(OH)_3(s) + 2SO_4^{2-}(aq) + 4H^+(aq)
\]  

(9)

In addition to oxygen, other catalysts such as Fe(III) can drive the chemical oxidation, see reaction (10) (Blowes, et al., 2014). Due to a more efficient electron transfer for Fe, the oxidation rate is more rapid with Fe(III) as the main oxidant (Luther, 1987).

\[
FeS_2(s) + 14Fe^{3+}(aq) + 8H_2 O(l) = 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq)
\]  

(10)

Which oxidizing agent that is dominating sulfide oxidation is determined by (bio)geochemical conditions. Oxygen is the main oxidant at circumneutral pH, but in acidic environments, Fe(III) becomes the main oxidant and the oxidation rate is fastest (Blowes, et al., 2014; Dold, 2010; Maest & Nordstrom, 2017). Oxidation of Fe(II) may be catalyzed by Fe-oxidizing bacterium that can grow in the absence of light and with minimal oxygen available (Nordstrom, et al., 1979). The Fe-oxidizing bacterium also affects the oxidation rate and may increase the rate by 5 or 6 orders of magnitude over abiotic rate (Nordstrom, et al., 1979). In partially oxidized waste rock, Fe(III) is present in the material as secondary minerals and the dissolution of these phases therefore providing a source for Fe(III).

High sulfate concentrations are found in most ARD due to its formation during sulfide oxidation. Its presence is often correlated with environmental issues and measuring sulfate is useful when assessing redox state of an aquatic environment (Reisman, et al., 2006). In low Ca environment, sulfate is considered as a good indicator of sulfide oxidation rates. A mass balance of sulfate released from sulfidic mine waste compared to the sulfate transported in surface water shows that sulfate is rather conservative (Alakangas, et al., 2009). If Ca is present, gypsum tends to precipitate and limit sulfate concentrations in the leachate.

Sulfide mineral oxidation is a major source of metal(loid)s in natural waters (Nordstrom, 2011; Blowes, et al., 2014). Metal(loid)s may be incorporated in the major or accessory sulfide minerals, thus becoming released through the oxidation of the respective sulfide mineral, or be associated with the gangue minerals and become released upon dissolution of buffering minerals. For example, increasing concentrations of As, Cu, Zn, Pb, Co, Ni and Cd correlated to increasing sulfate concentration indicate their release from sulfide minerals including pyrite, sphalerite, chalcopyrite, galena, arsenopyrite and tetrahedrite-tennantite (Sánchez Espana, et al., 2005).

The released metal(loid)s can be transported away or taken up by precipitation, coprecipitation or adsorption reactions (Blowes, et al., 2014; Smith, 2007; Hudson-Edwards, et al., 1999). As discussed previously, secondary Fe-hydroxide minerals can precipitate, either on the sulfide mineral surface or in the leachate water.
The importance of secondary minerals precipitating in ARD as a consequence of sulfide weathering has been widely studied (Sánchez Espana, et al., 2005; Villain, 2014; Hudson-Edwards, et al., 1999). For example, jarosite, a typical secondary mineral formed under acidic conditions, can incorporate Pb, Hg, Cu, Zn, Ag and Ra by adsorption, substituting for structural K and Fe and anions such as chromate, arsenate and selenite by substituting for sulfate (Smith, 2007). Schwertmannite, another common secondary mineral formed under acidic and sulfate-rich conditions is known to accumulate metal(loids) such as Cu, Zn, Ni, Se and As by substitution or adsorption (Smith, 2007). It is important to note that depending on the environmental conditions and stability of the secondary minerals, metals may become remobilized by dissolution or desorption upon changes in the pH, local redox condition or transport and burial (Smith, 2007).

5.2 Estimating redox potential in an aqueous system
A reduction-oxidation (redox) reaction (11) is characterized by the electron transfer between two ions:

\[ \text{Red} = \text{Ox} + e^- \]  

Red = Reduced species  
Ox = Oxidized species  
e\(^-\) = Electron

The equilibrium constant \( K \), defined according to equation (12), represents a product of activities at equilibrium.

\[ K = \frac{[\text{Ox}] [\text{e}^-]}{[\text{Red}]} \]  

(12)

The electron activity of a solution is often expressed as \( pe \), defined according to equation (13), where \([e^-]\) stands for the activity of an electron, and can be solved from the logarithmic expression of equation (12) according to equation (14).

\[ pe = -log[e^-] \]  

(13)

\[ -log[e^-] = log[\text{Ox}] - logK - log[\text{Red}] \]  

(14)

According equations (13) and (14), \( pe \) can be calculated from the activities of the aqueous species Red and Ox and the known equilibrium constant of reaction (12). Using Nernst equation (15), redox potential (Eh) for the redox pair Red/Ox relative to the standard hydrogen electrode (SHE) can be calculated and expressed in volts or millivolts (V, mV) (Nordstrom, 2000).

\[ E_r = E^0 - 2.303 \frac{RT}{F} \log \frac{[\text{Red}]}{[\text{Ox}]} \]  

(15)
\[ E_h = \text{Electrode potential relative to the standard hydrogen electrode for a redox couple (Red/Ox)} \]

\[ E^0 = \text{Standard electrode potential for the redox couple based on the standard hydrogen electrode} \]

\[ R = \text{Gas constant} \]

\[ T = \text{Temperature in Kelvin} \]

\[ F = \text{Faraday constant} \]

This potential is the driving force of the redox reaction, measuring the difference in electric potential needed to move an electric charge between two points.

The concept of electron activity and redox potential might be confusing as electrons never occur as free species in nature. This is because oxidation half-cell reactions, releasing electrons are always coupled with and occurs simultaneously as reduction half-cell reactions, consuming electrons. By other means, electrons are only released if they can be accepted by another species in the environment (Misra, 2012). The difference between the pH and pe concepts is that acidity expressed as \(-\log[H^+]\) actually is measurable while the activity of free electrons is not (Nordstrom, 2000).

The way to determine the redox conditions prevailing in water is to analyze all relevant redox species (Red and Ox activities) and calculate the Eh potential from their activities (Nordstrom, 2000). General observation is the redox potential calculated for different redox pairs does not agree, meaning that there is overall redox disequilibrium with respect to redox reactions in natural open system and can’t be described by one overall redox potential (Nordstrom, 2000; Stefánsson, et al., 2005; Stumm & Morgan, 1996). However, to estimate the oxidizing or reducing potential of a solution, redox (ORP) measurements are often performed with a platinum electrode and reference electrode (typically Ag/AgCl), presented in millivolts (mV), and converted to correspond to the standard hydrogen electrode system. When measuring ORP, it is the combined potential of the solution that is measured (Nordstrom, 2000) which may be a mix of potentials of various redox pairs (O₂/H₂O, NO(II)/N₂, MnO₂/Mn(II), Fe(III)/Fe(II), SO₄²⁻/H₂S, CO₂/CH₄ and H₂O/ H₂ among others) resulting from several ongoing electrochemical reactions that are not at equilibrium (Nordstrom, 2000; Stefánsson, et al., 2005; Stumm & Morgan, 1996). However, if Fe(II)/Fe(III) and S(II)/S(0) are present in concentrations over 10⁻⁵ M, the Pt-electrode have been shown to respond to these couples (Nordstrom, 2000). Note that in addition to the dissolved species, several solid phases are present in the natural system and may be take part in these reactions.

### 5.3 Redox potential and the Fe system

If the Eh potential measured with Pt-electrode is controlled by the Fe(II)/Fe(III) redox couple according to reaction (16), and the electrode-solution system is at equilibrium, the electrode potential relative to the standard hydrogen electrode according to Nernst equation will follow equation (17).

\[ Fe^{2+}_{(aq)} = Fe^{3+}_{(aq)} + e^- \quad (16) \]
As many solid Fe phases are associated with mine waste, these may also be involved in the redox reactions and control the solubility and speciation of Fe(II) and Fe(III). If the concentration of Fe(III) is in equilibrium with solid Fe(III), for example ferrihydrite referred to as Fe(OH)$_3$ (s) (18), the $-\log[Fe^{3+}]$ can be deduced from the pH of the solution and the solubility product of ferrihydrite according to equations (19) and (20).

$$Fe(OH)_3(s) + 3H^+_{(aq)} = Fe^{3+}_{(aq)} + 6H_2O_{(l)}$$ (18)

$$\log K_{s,F} = \log[Fe^{3+}] - 3 \log[H^+]$$ (19)

$$-\log[Fe^{3+}] = 3pH - \log K_{s,F}$$ (20)

Substitution of the $-\log[Fe^{3+}]$ and the solubility product into equation (17) allows Eh calculation results in reaction (21), describing the Eh potential for the overall redox reaction (22).

$$E_h = E^0 - 2.303 \frac{RT}{F} \cdot (3pH - \log K_{s,F} + [Fe^{2+}])$$ (21)

$$Fe^{2+}_{(aq)} + 3H_2O_{(l)} = Fe(OH)_3(s) + 3H^+_{(aq)} + e^-$$ (22)

If the solution is in equilibrium with other minerals like schwertmannite, goethite or jarosite, the Nernst equation can be solved with respect to these minerals in the same way as for ferrihydrite, according to reactions 23 to 26:

Schwertmannite (different compositions and solubility reactions have been reported (Bigham, et al., 1996)):

$$Fe_8O_8(OH)_6SO_4(s) + 22H^+ = 8Fe^{3+}_{(aq)} + SO_{4}^{2-}_{(aq)} + 14H_2O_{(l)}$$ (23)

$$Fe_8O_8(OH)_{4.5}(SO_4)_{1.75}(s) + 20.5H^+ = 8Fe^{3+}_{(aq)} + 1.75SO_{4}^{2-}_{(aq)} + 12.5H_2O_{(l)}$$ (24)

Goethite
$$FeOOH_{(s)} + 3H^+ = Fe^{3+}_{(aq)} + 3H_2O_{(l)}$$ (25)

Jarosite
$$KFe_3(SO_4)_2(OH)_6(s) + 6H^+ = 3Fe^{3+}_{(aq)} + 2SO_{4}^{2-}_{(aq)} + K^+_{(aq)} + 6H_2O_{(l)}$$ (26)

Previous studies involving measurements of Fe redox speciation and Eh measurements have shown a good agreement between the Eh calculated from the Fe(II) and Fe(III) species concentrations, and Eh measurements in ARD and receiving streams (Nordstrom, 2011; Sánchez Espana, et al., 2005). Relying on this relationship, redox measurements have been used to quantitatively estimate the
Fe speciation and to evaluate the redox state of the system (Maest & Nordstrom, 2017).

As summarized above, the redox speciation of Fe(II) and Fe(III) have been demonstrated to govern the redox state of many acid mine waters (Villain, et al., 2017; Sánchez Espana, et al., 2005; Nordstrom, 2000). It might then seem like a simple and useful approach estimating Fe speciation in this way. Taking a closer look at the findings it is evident that there are some difficulties that need to be considered. A systematic deviation between Eh measured with Pt-electrode and the Eh potential estimated by Fe speciation has often been observed (Sanchez-Espana et al., 2005; Villain et al., 2017). The concentration of measured Fe(III) tends to be higher than what is expected considering the measured Eh potential, resulting in a systematically higher Eh potential calculated for the Fe(II)/Fe(III) pair. This deviation was also observed in this study on leachate water from previously weathered sulfidic waste rock, having a range of pH, redox conditions and Fe and S concentrations (see sections 6.2 and 7). The reason has not been thoroughly demonstrated and could originate from difficulties obtaining accurate potential measurements due to long stabilization times or disequilibrium between the Pt-electrode and the Fe system, or be a consequence of difficulties determining Fe species concentrations. The magnitude of the deviation between the Eh based on the measurements using Pt-electrode and Fe redox speciation ranges between ca. 50-100 mV (Sánchez Espana, et al., 2005) which results in large differences in the predicted Fe concentrations. According to Espana et al. (2005), the range within which Fe(II)/Fe_{tot} changes from >95 % to <5 % is ca. 150 mV, that is narrow compared to the uncertainty of redox measurements. Nordstrom (1979) talks about ±30 mV as the anticipated uncertainty of Eh measurements in the case of careful measurements using a closed flow through cell supplying large volumes of water to the surface of the Eh electrode and careful readings.

Knowing whether Fe(II)/Fe(III) is in equilibrium in leachate water in different geochemical environments is not trivial. The equilibrium between Fe(II) solid Fe(III)-minerals has been discussed by the several authors previously (e.g. Villain et al. 2017), but this was not carefully examined in this study. Iron species distribution may depend on the dissolution and precipitation of different Fe-bearing primary and secondary minerals, reactions rates and microbial activity. As many solid Fe phases are associated with mine waste, there may indeed be in a partial equilibrium between dissolved Fe(II). Knowing the absolute and relative Fe(II) and Fe(III) concentrations and their development in different geochemical environments may provide useful information about ongoing (bio)geochemical reactions. As Fe(III) may work as an oxidant in addition to O_2, it is important to identify in which conditions it may occur.

5.4 Determination of species concentrations in water
Standard analytical procedure to determine the chemical composition of leachate water does not include determination of species concentrations, such as Fe(II) or Fe(III) or various sulfur species (Eaton, Clesceri, Rice, & Greenberg, 2005). This information, however, is required to assess the possible redox equilibrium as well as to reliably assess the water-rock interaction such as calculation of mineral
saturation state. Compared to the determination of total element concentrations by methods like ICP-OES and ICP-MS, determination of species concentrations tends to be more challenging. Difficulties include preserving the true speciation through the sampling procedure, sample treatment, storage and analytical steps (Pekhonen, 1995). Challenges when measuring Fe speciation may be because of the complex chemistry of the element affected by pH, redox, organic complexation and biological activity (Kaasalainen, et al., 2016). Fe is found in various physical forms that may be affected by the procedure of sampling collection, storage, preparation and analysis as well as possible contamination (Kaasalainen, et al., 2016). Studies have also reported that Fe(III) colloids may pass through standard filtration equipment, using standard 0.2 µm filter pore, size causing results of unreasonable oversaturation of Fe(III) (Nordstrom, 2011; Kaasalainen, et al., 2016). Distinguishing the complex variety of truly dissolved, colloidal and particulate Fe phases are one of the major challenges among Fe determinations, and may create large uncertainties in speciation analyses of Fe(II) and Fe(III).

Spectrophotometry is a common method used to determine Fe speciation and often relies on measuring Fe_{tot} and Fe(II), and calculating Fe(III) as the difference between the two (To, et al., 1999). It is relatively simple and cheap method enabling determination of Fe_{tot} and Fe(II) with a simple instrumentation that is found in most laboratories. Also, several portable models exist. A large number of dissolved elements, in particular transition metals such as Cu, Zn, Cd, may also be determined by spectrophotometric methods. Other methods used to determine Fe speciation include voltammetry, ion chromatography (IC) and chemiluminescence, among others (Pekhonen, 1995; Eaton, et al., 2005)

In water associated with sulfidic mine waste, dissolved sulfur is predominantly found as sulfate. Other species may also be found in addition to sulfate, including intermediates from sulfide oxidation as from S(I-) in pyrite to S(V) in sulfate.

Turbidimetry is a widely used laboratory and field technique for sulfate quantification in aquatic environments (Reisman, et al., 2006). It is applicable to ground water, drinking and surface waters as well as domestic and industrial waste waters. The method works for a wide range of concentrations of sulfate, with the detection limit of approximately 1 ppm (U.S. Environmental Protection Agency (EPA), 1986). The method only analyses sulfate but by oxidizing a sample it is also possible to determine the presence of other sulfur species as well. If a sample is analyzed for sulfate before and after oxidation, it is the difference between those concentrations that may be interpreted as other sulfur species. The other common method used to analyze sulfate is the IC, but also the determination of total S by ICP-AES is often used, assuming S to be in the form of sulfate (Reisman, et al., 2006). Therefore, comparing the turbidimetric method or IC with ICP-AES gives an indication of the potential presence of other sulfur species than sulfate.

5.4.1 Principles of spectrophotometry
Spectrophotometry utilizes the ultraviolet-visible (UV-Vis) light to measure elemental and compound concentrations in a solution. It uses the fact that a chemical compound in solution absorbs energy when a light of a given wavelength
is passed through the sample. The energy absorbed (not transmitted) by the sample is used to determine the quantity of a molecular species absorbing the radiation. The relationship between the absorbance and concentration is described by Beer’s law (27). It states that, for a specific instrumental set up using a certain path length, there is a linear relationship between the absorbance and the concentration:

\[ A = \varepsilon \cdot l \cdot c \]  

(27)

\( A \) = absorbance  
\( \varepsilon \) = molar absorptivity coefficient, \( \text{cm}^{-1}\text{mole}^{-1} \)  
\( l \) = optical path length, cm  
\( c \) = concentration, mole/l

The color responsible for the absorbance usually appears due to the formation of stable colored compounds, produced by adding a color reagent to form complexes with the ions and compounds of interest. As a light source, spectrophotometric analysis uses the ultraviolet and visible region of the spectrum. Spectrophotometric measurements are performed with a spectrophotometer which measures the quantity of transmitted radiation at selected wavelengths from incident electromagnetic radiation (Jeffery, et al., 1989). Transmitted radiation is inversely related to absorbance, therefore the absorbance can be determined as the difference between incident and transmitted radiation (Jeffery, et al., 1989).

5.4.2 Ferrozine method, \( \text{Fe(II)} \) and \( \text{Fe}_{\text{tot}} \) determination

The ferrozine method was developed in 1970 by Stookey (Stookey, 1970) and is commonly used for geochemical characterization of AMD (Ball & Nordstrom, 1985). Ferrozine is an organic compound that reacts with \( \text{Fe(II)} \) and forms a stable magenta-colored complex species with high solubility in water at \( \text{pH} \) between 4 and 7. In order to determine the concentration of \( \text{Fe(II)} \) in a solution, spectrophotometry can be used by analyzing the color of this stable magenta complex. Over time the method has been developed and modified by several authors in order to increase the precision and application of the method. These methods involve \( \text{Fe(II)} \) determination directly in the sample after addition of ferrozine and \( \text{pH} \) buffer solution, and determination of \( \text{Fe}_{\text{tot}} \) by adding a reducing agent before the ferrozine addition, this subsequently reducing all \( \text{Fe(III)} \) to \( \text{Fe(II)} \) allowing measurement of \( \text{Fe}_{\text{tot}} \). The concentration of \( \text{Fe(III)} \) can then be calculated as the difference between \( \text{Fe}_{\text{tot}} \) and \( \text{Fe(II)} \). Among the most common references cited in the context of water associated with sulfidic mine wastes is To et al. (1999), who describe the analytical procedure in detail although focus of the publication is the further development of the method by addition of direct measurement of \( \text{Fe(III)} \) instead of calculating \( \text{Fe(III)} \) from \( \text{Fe}_{\text{tot}} \) and \( \text{Fe(II)} \). In this study, their procedure for determining \( \text{Fe(II)} \) and \( \text{Fe}_{\text{tot}} \) has been followed, and \( \text{Fe(III)} \) calculated as the difference.

The ferrozine complex has the highest absorption capacity of light at a wavelength of 562 nm. That means that this is the wavelength at which spectrophotometric should be performed in order to achieve the highest sensitivity of the
measurements (Stookey, 1970). The magenta complex has a purple color directly proportional to the concentration of the complex due to its specific molar absorption capacity, 27900 mole⁻¹cm⁻¹ (Stookey, 1970).

The spectrophotometric ferrozine method used here has a limited concentration range up to 1.6 ppm (To et al., 1999). It can be difficult to target as most waters affected by AMD and sulfide oxidation tend to contain dissolved Fe in much higher concentrations. This range can be extended by selection of optical path length (cuvette size), but in most cases, significant dilution is required as implied by To et al (1999). It is therefore, important to consider the potential redistribution of Fe redox species upon dilution.

Another limitation with the ferrozine method is the interference of other elements like Cu(II) in concentrations above 20 ppm, Cd (II) if its molar ratio exceeds 24 and Cr(III) if its molar ratio exceeds 5 compared to Fe(III) (To, et al., 1999). The interference of these other elements may result in an overestimated concentration of Fe(II). The ferrozine method is also limited by the Fe concentration itself. It has been demonstrated that high Fe(III) concentration can increase the inaccuracy of the measurements. The reason is due to incomplete reduction of Fe(III) or that Fe(III) also might react with the ferrozine, interfering the coloration of the Fe(II) complex (Giokas, et al., 2002). At very high and low Fe(II)/Fe(III) ratios, inaccuracy of the Fe(III) calculated as the difference between Fe(II) and Fe_{tot} increases (To, et al., 1999).

5.4.3 Turbidimetric sulfate determination

Turbidimetry measures the attenuation of incident light at selected wavelengths by scattering, caused by suspended particles, rather than absorption as in spectrophotometry. The intensity decrease of the incident light is measured and related to the particle concentration. The concentration is obtained by comparing the turbidity of a suspension of unknown concentration to the turbidity of a suspension with known concentration. The method uses either a turbidimeter or the same spectrophotometric instrumentation as the ferrozine method. (Jeffery, et al., 1989)

The analysis is performed by converting the sulfate ion into a barium sulfate (BaSO₄) suspension under controlled conditions and measuring the resulting turbidity with a spectrophotometer or turbidimeter at a wavelength of 420 nm. The solid BaSO₄ is formed by the addition of BaCl₂ to the sample (U.S. Environmental Protection Agency (EPA), 1986). The solid is amorphous in the targeted pH range, between 3 and 7. The turbidimetric method is limited by the formation of the BaSO₄ complex. It is important that each solution is shaken at the same rate and the same number of times, and also the time between precipitation and measurements must be kept constant (Jeffery, et al., 1989). Interferences have been detected by Si in concentrations over 500 ppm (U.S. Environmental Protection Agency (EPA), 1986). Moreover, the sulfate concentrations determined by the method have been observed to be highly affected by sample dilution and acidification (Reisman, et al., 2006).
The stability of samples for sulfate analysis also needs to be considered, as depending on the water composition, the sulfate concentrations may change upon storage. For example, precipitation of secondary sulfate minerals might occur. Samples collected in anoxic conditions might initially contain S species with lower oxidation states, such as thiosulfate, sulfide or elemental sulfur. If oxygen is introduced into the sample (as happens upon sample storage) these might oxidize to sulfate upon long time storage.
6. Materials and methods
In this project, leachate water from column leaching experiments on partially oxidized sulfidic waste rock subjected to various geochemical conditions was sampled and studied for its chemical composition. Implementing Fe redox measurements for the leachate water and testing the Fe speciation as a tool to trace geochemical processes in the columns was the main focus. In the following, the waste rock material, leaching experiments, as well as the methods used for leachate sampling, chemical analyses and data interpretation are described.

6.1 Sulfidic waste rock materials
Waste rock for this study originates from two active mine sites in northern Sweden and was supplied by Boliden Mineral AB. The constituents of the waste rock differ in terms of the deposit type, sulfide content and the time during which they have been exposed to oxidative weathering prior to the column leaching experiments. The material with high S content (ca. 20% S) originates from Maurliden open pit mine, a volcanic associated massive sulfide deposit in the Skellefteå area (fig. 2), whereas the material with low S content (1.15 % S) is from the Aitik open pit mine, a porphyry-related Cu deposit in Northern Sweden (fig. 3). For both materials, sulfur is predominantly in sulfidic form (Table 1).

The waste rock with high sulfur content was originally selected for experimentation due to its high sulfide content and is therefore not representative of the majority of the waste rock dumped at the site. The material used as a start material in this study is a mixture of waste rock collected from four pilot-scale experiments. In these experiments the material was exposed to weathering under unsaturated, partially saturated and water saturated conditions for approximately 5 years prior to the sampling for this study. An unpublished mineralogical characterization of the material has been made after its sampling in the field and prior to its use in the pilot-scale experiments. This showed that the dominating minerals are pyrite and quartz with traces of muscovite, chlorite and calcite. Also chalcopyrite, bournonite, sphalerite and arsenopyrite were found (Nyström, et al., 2017). The potential of the high-sulfur waste rock to generate acid was evaluated using the total S and total C as carbonate (table 1) from which the net neutralization potential (NNP) was calculated to -448 kg CaCO$_3$ per ton waste rock and the neutralization potential ratio (NPR) to 0.3 indicating that the material is acid producing (CEN - European Comittee for Standardization, 2013). Particle surfaces of the material used for the experiments discussed in this study were coated with oxidation products as can be observed in figure 2. No detailed mineralogical or geochemical characterization of the weathered material has been available for this study but is on-going within the larger StopOx-project. The preliminary microscopic, XRD and SEM analyses suggest the presence weathering products such as ferric (hydr)oxide phases and gypsum.
The low-sulfur waste rock material comes from the Aitik Cu-Au mine in the north of Sweden. Waste rock from three different places in the oldest waste rock dump (T5) was sampled and supplied by Boliden Mineral AB for the experiments performed in this thesis. The waste rock dump T5 contains the oldest waste rock from the area but has also been used to dump marginal ore, therefore not being representative of the bulk waste rock from the site (O’Kane consultants inc. (OKC), 2015). The material has been exposed to surface conditions over several decades and the particles were coated with secondary minerals as may be observed in figure 3. The typical mineralogy of the Aitik waste rock has been studied by several authors in the past (Strömberg and Banwart, 1999) and includes quartz, plagioclase, K-feldspar, biotite, muscovite, chlorite, and minor amphiboles, pyroxides, calcite, epidote, apatite ilmenite, Fe-oxides (hematite, magnetite), barite, as well as the sulfides pyrite, chalcopyrite, pyrrhotite, molybdenite, and bornite. Secondary mineralogy has not been systematically studied but the secondary minerals reported in association with the Aitik waste rock include jarosite and schwertmannite-type minerals, ferric (hydr)oxide and various clays including illite, kaolinite and serpentine (OKC, 2015; Strömberg and Banwart, 1999; Kaasalainen unpublished data). The potential of the low-sulfur waste rock to generate acid was evaluated in the same way as the high-sulfur waste rock, using the total S and total C as carbonate (table 1). The NNP was calculated to -3 kg CaCO₃ per ton waste rock and the NPR to 0.9 indicating that the material is potentially acid producing (CEN - European Comittee for Standardization, 2013).
Figure 3. Partially oxidized low-sulfide waste rock material from Aitik that was used in the column experiments considered in this thesis.

The material used in the column experiments had a particle size in the cm-range and was loaded to the columns uncrushed in order to avoid creating fresh surfaces for sulfide oxidation. For the material with high-sulfur content, 56% and 44% of the material passed the 31.5 and 45 mm sieve sizes respectively whereas the corresponding values were 42% and 31% for the low-sulfur material, with the remaining 27% being larger than 45 mm but smaller than 90 mm.

For geochemical characterization, the samples were sent to ALS Piteå for crushing and pulverization (85 % <75 µm). A complete geochemical characterization has been performed on the material at ALS global, Loughlin Ireland. The characterization was done according to the ALS package CCP-PKG01 including whole rock analyses by lithium-borate fusion followed by quantification of major elements in the sample (table 1) by ICP-determination (ME-ICP06). Three digestions were used followed by either ICP-AES or ICP-MS analyses to report trace elements. Resistive elements were reported from a lithium borate fusion (ME-MS81), base metals from a four acid digestion (ME-4ACD81) and volatile gold related trace elements were reported from an aqua regia digestion (ME-MS42). Combustion furnace analysis (ME-IR08) were used to analyze total sulfur and carbon.

Additional analyses of the sulfur, C, F and Cl content of the solid material were also requested and performed at ALS Vancouver and Loughlin, Ireland. In order to constrain the relative amounts of sulfidic and sulfate S, S was analyzed after digestion of sulfate by 15 % HCl (S-GRA06a) and Na₂CO₃ (S-GRA06) digestion. The HCl digestion, only little or no dissolution of BaSO₄ and SrSO₄ is expected, whereas digestion with Na₂CO₃ is expected to completely digest various sulfates compounds including BaSO₄ and SrSO₄. Pyrite and sulfide minerals are expected to dominate the material, but sulfate minerals like gypsum and secondary sulfate minerals and salts might be present as well as affect the leachate composition. By analyzing both total S and solid phase sulfate, the sulfide content was estimated as the difference between those. To estimate inorganic C contents in the samples, carbonate-C was analyzed after HClO₄-digestion as total carbonate by colorimetric analyses coulometer (C-GAS05). Chlorine and F were analyzed by KOH-fusion and ion chromatography (IC881).
Table 1. Chemical composition of the high-sulfur waste rock used in the column experiments considered in this thesis compared to average concentrations of the earth’s crust from (Smith & Huyck, 1999).

<table>
<thead>
<tr>
<th>Element</th>
<th>unit</th>
<th>Method</th>
<th>Low-sulfidic material</th>
<th>High-sulfidic material</th>
<th>Earth crust</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Average(^a)</td>
<td>Rel.error (^a)</td>
<td>Average</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>concentration  %</td>
<td></td>
<td>percent</td>
</tr>
<tr>
<td>SiO(_2)</td>
<td>%</td>
<td>ME-ICP06</td>
<td>61.8</td>
<td>0.40</td>
<td>42.9</td>
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<tr>
<td>Al(_2)O(_3)</td>
<td>%</td>
<td>ME-ICP06</td>
<td>16.6</td>
<td>0.15</td>
<td>11.9</td>
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<tr>
<td>Fe(_2)O(_3)</td>
<td>%</td>
<td>ME-ICP06</td>
<td>6.86</td>
<td>0.66</td>
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<td>CaO</td>
<td>%</td>
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<tr>
<td>MgO</td>
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<td>ME-ICP06</td>
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<td>Na(_2)O</td>
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<td>0.00</td>
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<td>MnO</td>
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<tr>
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<td>0.04</td>
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<td>Total S</td>
<td>%</td>
<td>S-IR08</td>
<td>1.15</td>
<td>0.87</td>
<td>20.2</td>
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<td>Sulfate S(^b)</td>
<td>%</td>
<td>S-GRA06a</td>
<td>0.02</td>
<td>33.33</td>
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<td>Sulfate S(^c)</td>
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<td>S-GRA06</td>
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<td></td>
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<tr>
<td>Total C</td>
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<td>Carbonate C</td>
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<td>LOI</td>
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<td>0.00</td>
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<tr>
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<tr>
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<td>ppm</td>
<td>ME-4ACD81</td>
<td>1135</td>
<td>0.44</td>
<td>19.0</td>
</tr>
</tbody>
</table>

\(^a\) Average of two samples.
\(^b\) 15% HCI digestion of sulfates - little to no dissolution of BaSO\(_4\) and SrSO\(_4\).
\(^c\) Sodium carbonate digestion of sulfates - complete dissolution of BaSO\(_4\) and SrSO\(_4\).

6.2 Column experiments

The leachate water considered in this study originates from the unsaturated leaching-type column experiments on the previously weathered sulfide waste rock materials described in section 6.1. For both materials, with waste rock of high and low sulfide contents, three columns were prepared. One column, referred to as reference column (C1, C4), was prepared to mimic fully oxidized environment, the second mimicking the transition from oxic to anoxic conditions, referred to as the anoxic column (C2, C5) and the third, the alkaline column (C3, C6), mimics the transition from acid to alkaline conditions.

The design of the columns can be seen in figure 4. The columns are made of Perspex glass and caps are polypropylene. Each column has two inlets on the top. One inlet is used for irrigation with Milli-Q water. The water enters the columns from the top through 6 holes drilled into the caps. The other inlet works as an air inlet in order to maintain constant air pressure and oxygen saturation. In the bottom of the columns is the water outlet used for sampling. Perforated plate (polypropylene) holds the material ca. 2.5 cm above the bottom of the column.
Prior to loading of the columns, the columns and all column materials were acid washed (1 M nitric acid, analytical grade) and thoroughly cleaned with deionized water. A polypropylene filter (105 µm mesh size) was placed on the perforated plate in the bottom of the columns to prevent clogging of the outlet by small particles. System blanks were collected prior to column loading with waste rock material, following the same watering and leachate collection procedure as used in the experiments later. After system blank sampling, the columns were left to dry and loaded with the uncrushed waste rock materials.

During each leaching cycle, the columns were irrigated approximately once per week with 430 ml of Milli-Q water, except for the background leaching for which watering was done twice per week. The water entering the column drains through the waste rock and is gathered at the bottom of the column below the material held by the perforated plate. Therefore, the water has no contact with the material after it has drained through the column, simulating free-drainage conditions. The leachate from each column was collected through the sample outlet in the bottom part of the column 4-5 hours after irrigation.

The amount of input water was based on the estimated future precipitation and oxygen transported in the water at the Aitik mine (O’Kane consultants inc. (OKC), 2015), see table 2 below, assuming each leaching cycle to represent one week during a year. The oxygen transported by the water to the anoxic cell is of the same order of magnitude as estimated to enter through the cover system at the Aitik mine assuming the future net percolation rates (Boliden, 2015) and relevant to what has been suggested for dry and wet cover systems (Höglund, et al., 2004; Öhlander, et al., 2012).

Oxygen sensors (Presens oxygen sensor spots, PreSens Precision Sensing Gmbh) were installed in the columns, calibrated against fully oxygen-saturated and oxygen-free water. They were used to track the oxygen concentration/saturation on an hourly basis during the whole experiment. As humidity largely affects the oxygen saturation conditions, the results are only interpreted in a qualitative sense.
For the material with high-sulfur contents, the first 11 cycles of the experiment were considered as background leaching as all columns were fully air saturated without additives. After the 11th cycle, the anoxic column was sealed from the atmosphere to establish anoxic conditions and alkaline material was added on the surface of the waste rock in the third column, referred to as the alkaline column. The sampling procedure continued as before but extra caution was taken concerning the anoxic column. This included flushing input water first through a 3-way valve and use of gas bag during irrigation and leachate collection to avoid pressure changes. The leachate was also collected directly through a filtration system and the water was never completely drained from the column (a few ml
were left in the tubing) in order to prevent air from seeping into the column. When sealing the anoxic column, it mimics the geochemical environment that may occur during coverage of mine waste. The cover prevents oxygen ingress but the oxygen that will be buried with the material still enables sulfide oxidation. As long as oxygen is present it will be consumed by the sulfide oxidation establishing anoxic conditions. However, the water used for the irrigation is higher than expected through a dry cover but is required to allow leachate sampling from the experiment. The relevant remediation options include backfilling and flooding. Before the water table reaches its permanent level, flooding the waste rock, it might fluctuate. Also, seasonal fluctuations of the water table might occur (Villain, 2014). Both situations make the amount of water used for irrigation of the column relevant.

The alkaline material added to the high-sulfidic waste rock corresponded to 2 wt. % of the total waste rock in the column and consisted of the alkaline industrial residual material Lime Kiln Dust (LKD) (fig. 5). The LKD consists of partially calcined material mixed with finely crushed limestone, primarily finely crushed calcium carbonate, quicklime and traces of portlandite and gypsum. It originates from combustion gasses formed in the production of quicklime by Nordkalk (Nyström, et al., 2017). The water flow in the alkaline column is unsaturated as in the other columns, but the LKD absorbs large amounts of water keeping the material damp. The selection of the material was based on its promising performance in inhibition of sulfide oxidation, and consequently, the interest in using it for that purpose on previously unoxidized material (Nyström, et al., 2017). The experiments performed in this project are of interest in order to understand the possible effects of applying it on previously weathered material. As the scope of this thesis project was to focus on the transition from acid to alkaline conditions of the waste rock, no further evaluation was made on the LKD material itself, that belonging to the larger project.

![Figure 5. Surface addition of LKD.](image)

The leachate water from the experiments on the material with low sulfur content was set up in the same way as described for the high-sulfur material. It was
sampled for this study only during the background leaching period (7 weeks) in order to test the analytical methods for Fe and S determinations on leachate with different chemical properties. Therefore, no detailed information on the column experiments is given here.

### 6.3 Leachate Sampling and Analyses

Leachate water was sampled from each column 4-5 hours after irrigation. The total mass of the collected leachate was determined by weight. Leachate water pH, oxidation-reduction potential (ORP) and electric conductivity (EC) were measured in the unfiltered leachate water immediately upon sampling. In case the leachate pH exceeded 4.5, alkalinity samples were collected into amber-glass bottles that were top-filled and analyzed with modified alkalinity titration. For anion and cation samples, the leachate was vacuum filtered through 0.2 μm cellulose nitrate membrane filters (Whatman, 47 mm diameter) that had been previously cleaned with acetic acid (5 %) and thoroughly rinsed and soaked in Milli-Q water. Filtered samples for anion, cation and Fe determinations were collected into PP or LDPE flasks. The samples for anion analyses were not further treated. The samples for Fe speciation were acidified with hydrochloric acid (0.3 ml HCl, 30%, Merck Suprapur® per 60 ml sample), whereas for cation and trace element analyses, the samples were acidified with nitric acid (0.6 ml 65 % HNO₃, Merck Suprapur®, per 60 ml sample). Additionally, unfiltered samples were collected for Fe and cation determinations. The samples were stored cold (4°C) and dark until analysis. Figure 6 shows a simplified scheme over the sampling procedure.

![Figure 6. Simplified sampling procedure.](image)

### 6.4 Analytical Methods

pH measurements were performed using a glass-electrode (SenTix® 82) calibrated before each measurement with standard buffer solutions at pH 4 and 7, and checked for pH 2, 10 and/or 11 buffer solutions. ORP measurements were performed using a platinum electrode (SenTix® ORP) checked against known ORP
standard solution (228 mV at 20°C). Redox potential (Eh) with respect to the standard hydrogen electrode (SHE) was calculated by adding 210 mV to the measured potential corrected for the offset determined by the check standard solution. EC was measured in all samples using a WTW Multi 3420 multimeter equipped with TetraCon® 925 (EC) electrodes, checked against conductivity standard solution.

The cation samples were analyzed at the accredited ALS Scandinavia in Luleå Sweden (accredited in accordance with ISO/IEC 17025:2005; Swedish Board for Accreditation and Conformity Assessment – SWEDAC). The cation samples were screened for major, minor, trace and ultra-trace element concentrations, including S, Si, Na, K, Ca, Mg, Fe, Al, Ag, As, Au, Ba, Cd, Co, Cr, Cs, Cu, Fe\textsubscript{tot}, Hg, Mn, Mo, P, Pb, Sb, Sr, Zn and large number of other elements, by ICP-MS. The anion samples were analyzed for F, Cl and sulfate at ALS Czech Republic using ion chromatography (IC) (method CZ_SOP_D06_02_068, CSN ISO 10304-1, CSN EN 16192), potentiometric titration (CZ_SOP_D06_07_023.A (CSN 03 8526:2003, CSN 83 0530:2000 part 20, SM 4500-Cl D) and gravimetry (CZ_SOP_D06_07_N36), respectively. The determination of Fe redox speciation was carried out using the spectrophotometric ferrozine method and sulfate by turbidimetric method at the Luleå University of Technology. Section 6.4.1 gives a more detailed description of the Fe measurements by UV-vis spectrophotometry and 6.4.2 about the turbidimetry that was performed at the university.

6.4.1 Ferrozine method for Fe(II) and Fe\textsubscript{tot} determination

All filtered leachate samples collected from the columns were analyzed for their Fe\textsubscript{tot} and Fe(II) concentrations, referred to as Fe\textsubscript{tot} <0.2µm and Fe(II)<0.2µm, with Hach DR™ 2800 portable spectrophotometer using a modified version of the ferrozine method described by To et al. (1999). The concentration of Fe(III)<0.2µm was calculated as the difference between Fe\textsubscript{tot} <0.2µm and Fe(II)<0.2µm. The detailed analytical procedure is described in appendix 1 and the instrumentation is shown in figure 38.

An adequate amount of each sample was determined based on the chemistry of the sample, namely pH and redox conditions, and added to a 10 ml vessel. To analyze concentrations of Fe\textsubscript{tot} <0.2µm, Fe(III) was reduced to Fe(II) by addition of 0.1 ml hydroxylamine hydrochloric acid (10 % w/v), analyzing Fe(II)<0.2µm, this step was excluded. 0.2 ml ferrozine reagent was added to produce the color complex, and 0.5 ml ammonium acetate pH buffer solution was added to buffer the sample to pH 7 – 7.5. If the sample was discolored by a brick or rust red color, 0.6 M HCl (6 M Merck Suprapur®) was added to the sample after the color development. If interference was suspected but not visibly noticeable, duplicates was prepared, one with HCl and one without. Dilution with Milli-Q water was performed when all chemicals had been added into the vessel, and the final sample volume was always 10 ml. The prepared sample was pipetted into one of the two cuvettes (1- or 2.5 cm) and absorbance of the solution measured at wavelength 562 nm within 2 hours.

Before sample analysis was performed, standard solutions and a linear calibration curve were prepared. The method performance was also evaluated according to
several tests. The standard solutions of 1000 ppm Fe were prepared by dissolving Fe(III)Cl₃ or Fe(II)SO₄ in 0.1 M HCl, prepared by dilution of concentrated HCl (Merck Suprapur®) in Milli-Q water. Both Fe(II) and Fe(III) salts were used in the calibration. The working standards, covering the concentration range 0.02 – 1.4 ppm were prepared gravimetrically by stepwise dilution of the stock solutions using 0.1 M HCl. The individual steps did not exceed 10 times dilution. The analysis of the standards followed the same procedure as for the samples but all the standards were treated with hydroxylamine to reduce all Fe(III) to Fe(II) prior to analysis.

Quality assurance was performed by measuring the absorbance of the standards using optical path length of 1 cm to check the agreement with the reported molar absorptivity coefficient according to Beer’s law. The calculated coefficient was then compared to 27900 mole⁻¹cm⁻¹ which according to Stookey (1970) is the molar absorptivity coefficient of the ferrozine complex.

The linear range of the method using 1 cm cuvette size is limited compared to the range of Fe concentrations in the acidic leachate water, approximately 1 to 1200 ppm, and that expected in the alkaline conditions relevant to the leachate water from the column treated with alkaline material. According to the Beer’s law, one possibility to extend this range is to decrease and increase the path length (cuvette size). In the analysis, two cuvettes of different sizes were used in order to expand the application of the method. These two cuvette sizes were separately calibrated and tested to verify that the effect of the variable optical path length was as expected from Beer’s law using nine randomly collected samples with unknown Fe concentrations that were analyzed for Feₜₒₜ <0.2µm and Fe(II) <0.2µm in the two different cuvettes. The corresponding concentrations were calculated for each sample and cuvette with the equations obtained from the standard curves and compared to each other.

According to To, et al (1999), a sample discolored by a brick or rust red color or a sample where the color is masked needs to be treated with HCl to enable Fe determination. Such coloration was observed in some of the samples in this study, and therefore it was checked if the HCl itself has an effect on the absorbance in the sample. This was done by comparing the absorbance of the prepared standard solutions with and without addition of HCl, performed by measuring the absorbance of the standards within the interval of 0.05 to 1.4 ppm Fe(III) and calculating the resultant linear calibration curve.

To target the linear range of the ferrozine method, a significant dilution might be needed considering the typical Fe concentrations in water affected by ARD may be in the range from zero up to thousands of ppm. This could be a critical step in the sample preparation and may affect the distribution of Fe(II) and Fe(III) in the samples. In order to rule out the redistribution of Fe(II) and Fe(III) upon dilution, the method accuracy was tested by spiking. Two samples were chosen and analyzed for Feₜₒₜ<0.2µm and Fe(II)<0.2µm eight times with an increasing sample volume each time. First 10 µl sample was added to a 10 ml vessel and diluted with reagents and Milli-Q water before analyzed. Then the sample volume was
increased to 20, 30, 40, 50, 100, 200, 300 and 400 µl respectively. If the sample volume and dilution factor is insignificant, the concentration calculated from the absorbance should be equal for all the volumes studied.

The stability of Fe(II) and Fe(III) upon storage have been studied and contrasting findings have been reported. To et al. (1999) states that samples of ARD that are filtered (0.1 µm) and acidified (2 ml of 6 M HCl/250 ml sample) immediately after collection can be stored up to 6 months in acid-washed opaque plastic bottles without significant changes in Fe redox distribution as determined by the same ferrozine method as used here. The reason this works, according to To et al. (1999), is because the pH is low enough to keep metals solubilized, microbial catalysts are removed and the Fe oxidation rate is negligible. Other studies have however reported time-dependent Fe(II) and Fe(III) concentrations during longer sample storage when using methods such as ion chromatography (Kaasalainen, et al., 2016; Moses, et al., 1988). As different methods might differ in their sensitivity to different species, sample pretreatment with various chemicals, the filtration processes and the presence of colloids, it is important to evaluate the application of chosen method to the solution concerned.

The samples analyzed for Fe in this experiment were filtered (0.2µm), acidified (0.3 ml of 6 M HCl/60 ml sample) and stored in acid washed bottles. In order to examine any time-dependent change in the Fe redox species distribution, samples collected from all columns from cycle 20 (high-sulfide waste rock) and cycle 005 (low-sulfide waste rock) were chosen and repeatedly analyzed for their Fe<sub>tot</sub> <0.2µm and Fe(II) <0.2µm concentrations. The analysis was performed directly after sampling (within one hour), after one- and three days and after one-, two- and five weeks.

In addition to determining Fe redox speciation in the filtered leachate water, the ferrozine method was also used to analyze Fe<sub>tot</sub> in the unfiltered leachate from cycle 21 from the column with high-sulfur waste rock and compared to Fe<sub>tot</sub><0.2µm. The difference should reveal the presence of particulate Fe in the collected leachate.

The Fe concentrations in the filtered leachate water were also determined with ICP-MS which is a standard method for determining Fe concentrations in water. The accuracy of the spectrophotometric analysis was evaluated by comparison with the results from ICP-MS and calculation of the relative error between the methods.

6.4.2 Turbidimetric sulfate determination

Quantification of sulfate in the collected leachate was performed by turbidimetry using the same spectrophotometer as in the Fe analysis, Hach DR™ 2800 portable spectrophotometer (appendix 1, fig. 38), following the standard method 9038 Sulfate (Turbidimetric) (U.S. Environmental Protection Agency (EPA), 1986).

An adequate amount of filtered sample, determined based on pH and redox conditions, was pipetted into 5 ml cuvettes with 1 cm diameter and treated with 0.5 ml conditioning reagent. The reagent had been prepared by mixing 30 ml concentrated HCl, 300 ml Milli-Q water, 100 ml 95% ethanol or isopropanol, 75 g
NaCl in solution and 50 ml glycerol. If needed, the sample was diluted to the 5 ml mark with Milli-Q water. After addition of conditioning reagent and dilution, the turbidity was measured in the cuvette as a blank with the spectrophotometer at wavelength 420 nm. After such blank measurement, BaCl₂ was added to the sample and it was stirred immediately for 1 min at constant speed using a vortex mixer (Fisons Whirlimixer). The turbidity in the samples were analyzed in the cuvette instantly after stirring. The measurements were taken at 30-second intervals over a 4-minute period, and the maximum reading during the 4-minute period was recorded.

Before analysis, a calibration curve was prepared from HACH Sulfate Standard Solution 100 ppm SO₄. The standard was diluted with Milli-Q water to make a series of standards with the concentration range within 5 ppm to 100 ppm. The dilution was performed stepwise and never exceeded a factor of 10. As for the ferrozine method, the calibration curve was prepared in order to calculate the linear relation between absorbance and concentration. Analysis of standard solutions was carried out in the same way as the leachate samples in the cuvette.

The leachate water samples for sulfate determinations are filtered but no chemicals are added to ensure preservation of the sulfate speciation. Depending on the leachate composition, the sulfate concentrations may change upon storage as was discussed in section 5.4.3. To study if there is a time dependent change in sulfate concentration in the leachate samples, selected samples from all three columns were collected (cycle 24) and analyzed repeatedly directly after sampling (within 1 hour), after one-, four- and eight days storage and after two weeks.

Depending on the pH and redox conditions, other species than sulfate may be present in the leachate. In an oxidized and acidic environment sulfate is the dominating dissolved sulfur species. In alkaline conditions S₂O₅²⁻ may also be present. In an anoxic environment sulfide (referred to as H₂S), the lowest oxidation state of S, is stable. To evaluate if sulfur species other than sulfate may be important in the leachate samples, additional anion samples were collected (cycle 24) from the high-sulfur experiments. These samples were treated with hydrogen peroxide, and allowed to oxidize for three days prior to analysis in order to oxidize all the possible S species present to SO₄. If other sulfur species than sulfate are present in the samples, the oxidized sample should contain higher sulfate concentration than the untreated original sample.

Difficulties regarding dilution and acidification have been noticed during turbidimetric measurements that would introduce uncertainties in the analysis and results with a large deviation from the other methods (Reisman, et al., 2006). To evaluate the accuracy of the turbidimetric sulfate determination, the sulfate concentrations determined by turbidimetry were compared to sulfate determined by gravimetry and total S (calculated as SO₄) by ICP-MS. The samples for gravimetric analyses were filtered and analyzed at ALS in the Zech Republic, whereas filtered and acidified (65% Suprapur HNO₃, 1 ml per 100 ml sample) samples were analyzed for total sulfur concentrations by ICP-MS at ALS Luleå, Sweden.
6.5 Calculations and geochemical modeling

Speciation-solubility models are created to provide easily assessed information about concentrations, activities and distribution of ionic and molecular species in an aqueous solution at equilibrium. It may also provide the saturation index of different minerals in the system and hence in what direction reactions in the system is expected to occur (Zhu & Anderson, 2002). In this project geochemical modeling was used to calculate species activities, theoretical Eh values based on measured Fe(II) and Fe(III) concentration and pH, activities of Fe(II) and Fe(III) based on measured Eh and pH, and to calculate saturation indexes of minerals that may control the Fe solubility and speciation in the leachate. Saturation indices were calculated with Fe(II), Fe(III), pH as well as major elements obtained from ICP-MS as input data. The following calculations and geochemical modeling were performed with PHREEQC version 3.3.2 (Parkhurst & Appelo, 1999) using the wateq4f.dat database (Ball & Nordstrom, 1991). Thermodynamic data for schwertmannite presented by Bigham et al. (1996) was also used as it is not included in the wateq4f.dat -database. The results obtained from geochemical modeling are presented and discussed in the discussion of this report in section 8.2 and 8.3.

As the concentration of Fe in the leachate exceeds $10^{-5}$ M in most samples, the redox controlling couple may be assumed to be Fe(III)/Fe(II) (Nordstrom, 2000). To evaluate if that was true, the theoretical Eh potential was calculated with the Nernst equation based on the activities of Fe(II)<0.2µm and Fe(III)<0.2µm in the leachate (see sections 5.2-5.3). The activities of Fe(II) and Fe(III) were calculated using the concentrations of Fe(II)<0.2µm and Fe(III)<0.2µm measured with the ferrozine method and pH in the leachate. Reversed, the theoretical activities of Fe(II)<0.2µm and Fe(III)<0.2µm were calculated with Nernst equation using the Eh potential measured with the Pt-electrode and pH of the leachate.

The saturation indexes of selected minerals including ferrihydrite, jarosite, goethite and schwertmannite were calculated using the concentration of Fe(II)<0.2µm and Fe(III)<0.2µm obtained from the ferrozine method, concentrations of major elements obtained from ICP-MS, pH and the Eh potential measured with the Pt-electrode.
7. Results
Sections 7.1 and 7.2 present the results of the methodological evaluation of the ferrozine and turbidimetric method. In section 7.3, the results from Fe and sulfate analysis of the leachate water and the chemical characteristics and the elemental composition of the leachate water are presented.

7.1 Determination of Fe concentrations and speciation in leachate water
The collected leachate water was analyzed for Fe with two methods, spectrophotometry and ICP-MS. The methodological evaluation of the ferrozine method is presented in this section including standard curve preparation and sample stability tests. It also includes a comparison between the Fe obtained from spectrophotometric and from the standard method ICP-MS.

7.1.1 Calibration and quality control
Calibration curves were prepared based on the measurements of standard solutions made from FeCl$_3$ and FeSO$_4$ stock solutions. The different salts resulted in identical calibration curves. Figure 7 shows an example of a calibration curve measured using the 1 cm cuvette. The linear range of the calibration curve is 0.016 – 1.4 ppm (absorbance 0.02 to 0.66). The detection limit was determined by adding the standard deviation of 9 blank samples multiplied by six, to the average absorbance of those blanks. The upper limit was determined by measuring standards and studying the linearity of the calibration curve. Measurements were also made with the 2.5 cm cuvette and the resultant concentration was identical to measurements in the 1 cm cuvette.

The result indicates that as expected, the standard calibration curve is unaffected of the stock solution that is used and within the range of 0.016-1.4 ppm, the linearity of the calibration is fulfilled. The equation obtained from the calibration curve presented in figure 7 and has been used for all following Fe measurements. The 1 cm cuvette has been used as the standard choice, but when necessary, the 2.5 cm cuvette has been used to extend the range.

In figure 8, a comparison is made between the standard curve in figure 7 and the standard curve prepared with the addition of HCl before analysis, recommended by To et al. (1999) to prevent masking of the magenta color due to Fe(III). The relative error between absorbance with and without HCl was on average 3.2 %, based on the absolute error between the measurements divided by the absorbance without HCl.

Based on the standard measurements and Beers law, the molar absorptivity coefficient was calculated, corresponding to 27070±555 cm$^{-1}$mole$^{-1}$. The coefficient is in excellent agreement with the molar absorptivity of ferrozine presented by Stookey (1970) which is 27900 cm$^{-1}$mole$^{-1}$. 
Figure 7. Calibration curve for the ferrozine Fe determinations with optical path length 1 cm. The linear equation is also presented in the figure.

Figure 8. Comparison between the two calibration curves: one prepared as in fig. 7, and the other for standards additionally treated with HCl as suggested by To et al. (1999) for samples where the magenta color is masked.

The absorbance of every sample was measured three times for each analysis, and duplicates were performed to selected samples to test the precision of the method. Additional quality control included analyzing a check standard approximately every 10th sample. Also, blank samples were analyzed regularly. Table 3 shows the results of 5 repeated analyses of one check standard with concentration 1.502 ppm Fe. The relative error calculated based on the average of all measurements compared to the known concentration was at maximum 1.64 %.
Table 3. Repetitive analysis of a check standard containing 1.502 ppm of Fe. The measured absorbance and the calculated concentration of Fe are listed as well as the relative error of calculated concentration compared to the known standard concentration.

<table>
<thead>
<tr>
<th>Check Standard ppm</th>
<th>Absorbance</th>
<th>Fe ppm</th>
<th>Rel.error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.502</td>
<td>0.290</td>
<td>1.521</td>
<td>1.28</td>
</tr>
<tr>
<td>1.502</td>
<td>0.291</td>
<td>1.527</td>
<td>1.64</td>
</tr>
<tr>
<td>1.502</td>
<td>0.289</td>
<td>1.516</td>
<td>0.93</td>
</tr>
<tr>
<td>1.502</td>
<td>0.291</td>
<td>1.527</td>
<td>1.64</td>
</tr>
<tr>
<td>1.502</td>
<td>0.291</td>
<td>1.527</td>
<td>1.64</td>
</tr>
</tbody>
</table>

Average 1.524

7.1.2 Sample stability

In table 4, \( \text{Fe}_{\text{tot}<0.2\mu m} \) concentration for nine leachate water samples from the experiments on the low-sulfur waste rock measured using both 1 cm and 2.5 cm cuvettes are listed. The relative error of the two calculated concentrations is presented as well, calculated based on the absolute error between the measurements divided the average of the two concentrations obtained from the different cuvettes. In figure 9, the absorbance of the samples in table 4 is plotted against the concentration. As expected from the Beers law, the calculated concentrations are independent on the cuvette used during the analysis and the measurements made with optical path lengths of 1- and 2.5 cm are directly comparable.

Table 4. Absorbance and calculated concentrations of \( \text{Fe}_{\text{tot}<0.2\mu m} \) in nine leachate water samples from experiments on the low-sulfur waste rock. Also reported is the relative error calculated based on the absolute error between the measurements divided the average of the two concentrations obtained from the different cuvettes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Absorbance 2.5 cm</th>
<th>Concentration 1 cm</th>
<th>Concentration 2.5 cm</th>
<th>Average</th>
<th>Rel. error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>C4-001</td>
<td>0.332</td>
<td>1.60</td>
<td>1.59</td>
<td>1.59</td>
<td>0.55</td>
</tr>
<tr>
<td>C4-002</td>
<td>1.164</td>
<td>5.62</td>
<td>5.60</td>
<td>5.61</td>
<td>0.23</td>
</tr>
<tr>
<td>C4-003</td>
<td>0.963</td>
<td>4.65</td>
<td>4.63</td>
<td>4.64</td>
<td>0.33</td>
</tr>
<tr>
<td>C5-001</td>
<td>0.325</td>
<td>1.56</td>
<td>1.55</td>
<td>1.56</td>
<td>0.68</td>
</tr>
<tr>
<td>C5-002</td>
<td>1.132</td>
<td>5.47</td>
<td>5.45</td>
<td>5.46</td>
<td>0.34</td>
</tr>
<tr>
<td>C5-003</td>
<td>0.948</td>
<td>4.57</td>
<td>4.56</td>
<td>4.57</td>
<td>0.29</td>
</tr>
<tr>
<td>C6-001</td>
<td>0.246</td>
<td>1.18</td>
<td>1.17</td>
<td>1.18</td>
<td>0.77</td>
</tr>
<tr>
<td>C6-002</td>
<td>0.904</td>
<td>4.36</td>
<td>4.35</td>
<td>4.36</td>
<td>0.30</td>
</tr>
<tr>
<td>C6-003</td>
<td>0.563</td>
<td>2.72</td>
<td>2.70</td>
<td>2.71</td>
<td>0.78</td>
</tr>
</tbody>
</table>
Figure 9. Absorbance measured in nine leachate water samples using two different cuvettes sizes (1 cm and 2.5 cm indicated by the symbol color).

By using the standard cuvette sizes and instrumental set up, basically every sample affected by ARD has to be diluted prior to analysis due to the high Fe concentrations compared to the linear range of the method. This might result in the redistribution of Fe species and compromise the accuracy of the analysis. The analytical procedure includes the addition of reducing, complexing and buffering chemicals, and the sample is left to stabilize for 5 to 10 minutes after reagent addition but before dilution. Spiking was performed to evaluate if dilution resulted in Fe species redistribution in two samples representing both the high- (C2-019) and low- (C5-008) sulfide waste rock. In table 5, the different samples volumes are presented that were diluted to a 10 ml final volume with chemicals and Milli-Q water using a range of dilution factors, the measured absorbance in the diluted samples, and the corresponding concentration of Fe$_{\text{tot}<0.2\mu m}$ and Fe(II)$_{<0.2\mu m}$ in the original sample. In figure 10, the sample absorbance is plotted against the sample volume. A clear linear relationship can be seen, where the absorbance increases directly proportional to the sample volume in both samples. The absorbance of the low-sulfide sample is close to detection limit for all Fe(II)$_{<0.2\mu m}$ analysis and three of the Fe$_{\text{tot}<0.2\mu m}$ analysis. Those samples therefore, provide a poorer fit to the calculated concentration. When dilution with Milli-Q water is performed after addition of reagents and the sample is left to stand for 5 minutes before analysis, the results show no sign of dilution having an effect on the measured Fe redox speciation. The dilution of the sample seems to preserve the Fe speciation and the selection of sample volume does not matter as long as the measured concentration stays in the acceptable range of the method.
Table 5. Dilution test. Sample volume (µl), absorbance and the corresponding calculated concentration of the sample (ppm).

<table>
<thead>
<tr>
<th>V sample (µl)</th>
<th>Fe_{tot&lt;0.2µm}</th>
<th>Fe(II)&lt;0.2µm</th>
<th>Concentration calculated (ppm)</th>
<th>Fe_{tot&lt;0.2µm}</th>
<th>Fe(II)&lt;0.2µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>High-sulfide</td>
<td>Absorbance</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.029</td>
<td>0.017</td>
<td>53</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>0.054</td>
<td>0.029</td>
<td>53</td>
<td>27</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>0.087</td>
<td>0.043</td>
<td>59</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0.142</td>
<td>0.071</td>
<td>59</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0.287</td>
<td>0.139</td>
<td>60</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>0.422</td>
<td>0.203</td>
<td>59</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>0.565</td>
<td>0.271</td>
<td>60</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>58</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

Low-sulfide

<table>
<thead>
<tr>
<th>V sample (µl)</th>
<th>Fe_{tot&lt;0.2µm}</th>
<th>Fe(II)&lt;0.2µm</th>
<th>Concentration calculated (ppm)</th>
<th>Fe_{tot&lt;0.2µm}</th>
<th>Fe(II)&lt;0.2µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>0.008</td>
<td>0.003</td>
<td>0.09</td>
<td>-0.003</td>
<td></td>
</tr>
<tr>
<td>2000</td>
<td>0.014</td>
<td>0.006</td>
<td>0.11</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>3000</td>
<td>0.020</td>
<td>0.009</td>
<td>0.11</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>4000</td>
<td>0.027</td>
<td>0.011</td>
<td>0.12</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>5000</td>
<td>0.032</td>
<td>0.014</td>
<td>0.12</td>
<td>0.021</td>
<td></td>
</tr>
<tr>
<td>6000</td>
<td>0.039</td>
<td>0.015</td>
<td>0.12</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>7000</td>
<td>0.044</td>
<td>0.017</td>
<td>0.12</td>
<td>0.019</td>
<td></td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td>0.11</td>
<td>0.015</td>
<td></td>
</tr>
</tbody>
</table>

Figure 10. Absorbance based on sample volume (spiking).
Another critical aspect of the Fe species determination may be the sample stability upon storage. To study the sample stability upon storage, six samples were collected on the 14th of February 2017 from both the high- and low-sulfide materials. These samples were analyzed for $\text{Fe}_{\text{tot}<0.2\mu m}$ and $\text{Fe(II)<0.2\mu m}$ immediately after sampling (within one hour) as well as after one and three days and after one-, two- and five weeks from the sampling. The measured pH, Eh and EC in the samples are shown in table 6. The results are presented in figures 11 to 12, showing that no systematic change in the measured $\text{Fe(II)<0.2\mu m}$ and $\text{Fe}_{\text{tot}<0.2\mu m}$ concentrations can be seen upon storage for this time interval. Only on the 21st of February $\text{Fe(II)<0.2\mu m}$ shows an increase in the anoxic column. The results obtained from the sample collected in the high-sulfide alkaline column were excluded due to too low Fe concentrations. Only one sample from the low sulfide reference column is presented in figure 12 due to the similar redox conditions in all low sulfide samples during background leaching. Based on these results, it can be said that the Fe redox distribution is preserved in the type of samples considered here, having a wide range of pH and redox conditions and Fe concentrations when filtered through 0.2 µm and acidified.

Table 6. pH, Eh and EC of samples analyzed in the time series.

<table>
<thead>
<tr>
<th>High-sulfide C-20</th>
<th>pH</th>
<th>Eh mV</th>
<th>EC mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>2.97</td>
<td>599</td>
<td>1.19</td>
</tr>
<tr>
<td>Anox.</td>
<td>2.69</td>
<td>642</td>
<td>2.37</td>
</tr>
<tr>
<td>Alk.</td>
<td>11.67</td>
<td>343</td>
<td>1.33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Low-sulfide C-5</th>
<th>pH</th>
<th>Eh mV</th>
<th>EC mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>3.50</td>
<td>630</td>
<td>0.532</td>
</tr>
<tr>
<td>Anox.</td>
<td>3.70</td>
<td>640</td>
<td>0.364</td>
</tr>
<tr>
<td>Alk.</td>
<td>3.76</td>
<td>596</td>
<td>0.253</td>
</tr>
</tbody>
</table>

Figure 11. Time series of $\text{Fe}_{\text{tot}<0.2\mu m}$ and $\text{Fe(II)<0.2\mu m}$ concentrations in the samples from the high-sulfide material (C1-020 and C2-020) collected the 14th of February.
7.1.3 Comparison of Fe analyzed with spectrophotometry and ICP-MS

The $\text{Fe}_{\text{tot}<0.2\mu m}$ concentration analyzed with ICP-MS is plotted against the $\text{Fe}_{\text{tot}<0.2\mu m}$ analyzed with spectrophotometry in figure 13. The analyses compare very well to each other in all column systems. The relative error between the methods, calculated based on the absolute error of each sample between both methods divided by the average of those, was on average 10% in all high-sulfide columns.
Figure 13. Comparison of the concentration of Fe_{tot<0.2µm} measured with spectrophotometry and ICP-MS in leachate water samples. Results from the high-sulfide waste rock are presented to the left and low-sulfide to the right. The 1:1 line (solid) is plotted in the figures. Notice the different scales.
7.2 Determination of sulfate concentration in leachate water
The collected leachate water was analyzed for sulfate with two different methods; turbidimetry and gravimetry. Additionally, total sulfur concentrations (reported as sulfate) were analyzed by ICP-MS. This section presents the results of the methodological evaluation of the turbidimetric method including standard curve preparation and sample stability tests. It also includes a comparison between the sulfate obtained from turbidimetry and from the standard method ICP-MS.

7.2.1 Calibration and quality control
Figure 14 shows the relationship between the absorbance and sulfate concentrations prepared with 7 standard solutions with the concentrations 5, 10, 20, 30, 40, 50 and 100 ppm sulfate. The linear equation obtained, as the calibration curve is shown in figure 14, and was used for calculating the sulfate concentrations in the analyzed samples. The linear range of the method is 5 to 100 ppm (absorbance 0.05 to 0.63), but the detection limit, determined by adding the standard deviation of 30 blank samples multiplied by six, to the average absorbance of those blanks, was 14 ppm.

![Figure 14. Calibration curve for the turbidimetric sulfate determination measured at wavelength 420 nm and using 1 cm cuvette.](image)

Before analysis, a blank sample was prepared for each sample by adding the conditioning reagent and measuring the absorbance at 420 nm. A check standard solution was analyzed every 10th sample. In table 7, 11 absorbance measurements of two different check standard solutions and the respective blank sample absorbance, analyzed repeatedly, are presented. The average absorbance for the first and the second check standard are 0.0814 and 0.0738 with relative standard deviation of 18.6% and 16.4%, respectively. It is evident that the method precision is lower than what is typically desired for laboratory analyses. The reason for this is considered to be the nature of the analyses (formation of a solid suspension, mixing etc.). The method is still considered of interest as it allows quick, simple, and cheap determination of sulfate, the major product of sulfide oxidation, and can be easily carried out in the field with a variety of portable instruments available on the market. Such prompt analyses are especially required if S species other
than sulfate are expected to be present. The sulfate concentrations by turbidimetry are compared to other methods in section 7.2.3.

Table 7. Repeated analyses of sulfate check standards.

<table>
<thead>
<tr>
<th>Check standard</th>
<th>Blank absorbance at 462 nm</th>
<th>Max. absorbance at 462 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>0.002</td>
<td>0.065</td>
</tr>
<tr>
<td>#1</td>
<td>-0.001</td>
<td>0.096</td>
</tr>
<tr>
<td>#1</td>
<td>-0.001</td>
<td>0.083</td>
</tr>
<tr>
<td>#1</td>
<td>0.001</td>
<td>0.107</td>
</tr>
<tr>
<td>#1</td>
<td>-0.001</td>
<td>0.077</td>
</tr>
<tr>
<td>#1</td>
<td>-0.001</td>
<td>0.071</td>
</tr>
<tr>
<td>#1</td>
<td>-0.003</td>
<td>0.071</td>
</tr>
<tr>
<td>#2</td>
<td>-0.001</td>
<td>0.073</td>
</tr>
<tr>
<td>#2</td>
<td>-0.001</td>
<td>0.091</td>
</tr>
<tr>
<td>#2</td>
<td>-0.001</td>
<td>0.067</td>
</tr>
<tr>
<td>#2</td>
<td>-0.001</td>
<td>0.064</td>
</tr>
</tbody>
</table>

7.2.2 Sample stability

In figure 15 the three samples analyzed to study the time dependent variation of sulfate in the collected leachate water is presented. The leachate water originates from the three columns with the high-sulfide waste rock under different conditions. The concentration measured in sample C1-024 from reference column collected from the experiment on the high-sulfide waste rock, indicates somewhat increasing trend with time, but this variation is of the same order as the error associated with the turbidimetric method (ca. 20%). The sulfate concentrations in the sample from the anoxic column (C2-024) shows a variation between 539 ppm and 466 ppm. That is also within the error of the turbidimetric method. The sample from the alkaline column (C3-024) shows a stable sulfate concentration with an average of 68 ppm over the time-interval studied. Notice that the first two analyses are missing for this sample, due to too high dilution factor used for these samples. The results presented in figure 15 are the concentrations corrected for dilution. The result presented from the analysis performed on the 20th March is calculated as an average of two duplicates. The measured absorbances for the duplicate samples are also reported in table 8.

![Figure 15. Time series of samples C1-024, C2-024 and C3-024 collected the 16th of March. Notice that the two first measurements for C3-024 are missing due to mistakes during sample preparation.](image)
Table 8. Duplicates of three samples analyzed the 20th March.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Dilution X</th>
<th>Absorbance Blank</th>
<th>Absorbance Sample</th>
<th>SO₄ ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td>5</td>
<td>0.008</td>
<td>0.621</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.008</td>
<td>0.644</td>
<td>497</td>
</tr>
<tr>
<td>Anox.</td>
<td>5</td>
<td>0.006</td>
<td>0.687</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.004</td>
<td>0.633</td>
<td>489</td>
</tr>
<tr>
<td>Alk.</td>
<td>1</td>
<td>0.002</td>
<td>0.471</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>0.000</td>
<td>0.462</td>
<td>71</td>
</tr>
</tbody>
</table>

Figure 16 shows the sulfate concentration determined in the oxidized and unoxidized samples collected 16th March. The sulfate concentration in the unoxidized sample was analyzed directly. The sulfate concentration in the oxidized samples was calculated from an average of two duplicates measured the 21st of March when the samples have oxidized for three days. In all three samples, the oxidized sample indicates higher sulfate concentration than the unoxidized sample, but the difference is close to the analytical error. Therefore, it is not possible to conclude whether this actually suggests that some S species other than sulfate may be present in the systems and further tests and analyses should be carried out to confirm this.

Figure 16. Comparison between sulfate concentrations determined using the turbidimetric method filtered but otherwise untreated samples (“unoxidized”) and samples treated with hydrogen peroxide (“oxidized”) prior to sulfate determination.

7.2.3 Comparison of sulfate from various methods

Figures 17 and 18 show the sulfate concentrations analyzed by turbidimetry in comparison to the sulfate concentrations analyzed using gravimetry and calculated from the total S concentrations determined by ICP-MS, carried out at ALS. These results are also presented in section 7.3, table 9. In figure 17, the comparison is presented for the high-sulfide systems, whereas in figure 18, the comparison is presented for the low-sulfide waste rock. In general, the ICP-MS reports higher concentrations than the turbidimetric method. This is reasonable as ICP-MS determines total sulfur rather than sulfate, and in the case that other S species than sulfate are present in the leachate water, these would be included in the ICP-MS determinations but not in turbidimetric analyses. The gravimetric method appears to report higher concentrations than the turbidimetric method. Both
gravimetry and turbidimetry include precipitation of the sulfate in the sample as BaSO$_4$. Similarly, to the turbidimetric sulfate determination, the analytical error is relatively high in the range of 20%.

*Figure 17. Comparison between the sulfate concentrations measured using the turbidimetric method and the ICP-MS and gravimetry in the leachate water from the reference, anoxic-, and alkaline column experiments on the high-sulfide waste rock. Note the different scales of the y-axis. 1:1 line (solid) is plotted for comparison.*
Figure 18. Comparison between the sulfate concentrations measured using the turbidimetric method and ICP-MS and gravimetry in the reference, anoxic-, and alkaline column in the leachate water from column experiment on the low-sulfide waste rock. Note that gravimetric measurements are only presented for the reference column and that the scales are different. 1:1 line (solid) is plotted for comparison.
Considering the analytical uncertainty, the turbidimetric method shows fairly good agreement with the results of the two other analytical methods and correlates well both in concentration and trend in all systems. Reisman, et al studied the effect of dilution using dilution factors 40, 80 and 100 and stated that increased dilution decreases the measured sulfate of a sample. In this thesis, the dilution factor was kept under 20 and no systematic effect of dilution could be detected.

7.3 Leachate water composition
The results of all Fe and S analyses performed with spectrophotometry, turbidimetry, gravimetry and ICP-MS are presented in table 9. They are presented by the sample name and measured pH, EC and Eh in all collected leachate water samples from the columns experiments on the high- and low-sulfide waste rock systems.
Table 9. The chemical composition of leachate water from the column experiments. The different experiments are indicated in the sample name (leachate water from experiments on high-sulfide waste rock: C1-oxic conditions, reference column; C2-anoxic column, C3-alkaline column, and leachate water from experiments on low-sulfide waste rock: C4-oxic conditions, reference column; C5-anoxic column, C6-alkaline column). The anoxic columns C2 and C4 were sealed off and alkaline material added to columns C3 and C6 after sample number 011 and 007, for the material with high- and low-sulfide content, respectively.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Base Parameters</th>
<th>UV-Vis Spectrophotometric</th>
<th>Turb.(^b)</th>
<th>Gravimetric(^b)</th>
<th>ICP-MS(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH/°C(^a)</td>
<td>EC(^a)</td>
<td>Eh(^a)</td>
<td>Fe(^{ii})(^d)</td>
<td>Fe(^{ii})(^d)</td>
</tr>
<tr>
<td></td>
<td>20°C±1</td>
<td>20°C±1</td>
<td>20°C±1</td>
<td>0.2µm</td>
<td>0.2µm</td>
</tr>
<tr>
<td>C1_004</td>
<td>3.07</td>
<td>3.85</td>
<td>624</td>
<td>1109</td>
<td>1047</td>
</tr>
<tr>
<td>C1_008</td>
<td>3.31</td>
<td>1.923</td>
<td>530</td>
<td>613</td>
<td>543</td>
</tr>
<tr>
<td>C1_011</td>
<td>3.40</td>
<td>1.421</td>
<td>543</td>
<td>379</td>
<td>353</td>
</tr>
<tr>
<td>C1_012</td>
<td>3.31</td>
<td>1.688</td>
<td>540</td>
<td>428</td>
<td>415</td>
</tr>
<tr>
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<td>3.26</td>
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<td>616</td>
<td>181</td>
<td>172</td>
</tr>
<tr>
<td>C1_016</td>
<td>3.25</td>
<td>0.69</td>
<td>675</td>
<td>87</td>
<td>72</td>
</tr>
<tr>
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<td>3.03</td>
<td>1.12</td>
<td>648</td>
<td>140</td>
<td>121</td>
</tr>
<tr>
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<td>2.90</td>
<td>1.13</td>
<td>635</td>
<td>94</td>
<td>64</td>
</tr>
<tr>
<td>C1_023</td>
<td>2.90</td>
<td>1.01</td>
<td>663</td>
<td>60</td>
<td>29</td>
</tr>
<tr>
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<td>728</td>
<td>683</td>
</tr>
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<td>1.42</td>
<td>544</td>
<td>366</td>
<td>338</td>
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<td>187</td>
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<tr>
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<td>73</td>
<td></td>
</tr>
<tr>
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<td>615</td>
<td>72</td>
<td>57</td>
</tr>
<tr>
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<td>690</td>
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</tr>
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<td>693</td>
<td>59</td>
<td>27</td>
</tr>
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<td>642</td>
<td>181</td>
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</tr>
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<td>C2_021</td>
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<td>659</td>
<td>149</td>
<td>63</td>
</tr>
<tr>
<td>C2_022</td>
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<td>2.54</td>
<td>719</td>
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</tr>
<tr>
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<td>1.92</td>
<td>707</td>
<td>34</td>
<td>16</td>
</tr>
<tr>
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<td>3.69</td>
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<td>749</td>
<td></td>
</tr>
<tr>
<td>C3_008</td>
<td>3.28</td>
<td>1.72</td>
<td>544</td>
<td>565</td>
<td>552</td>
</tr>
</tbody>
</table>

\(^a\) Values are reported as means of triplicates. 
\(^\text{b}\) Turbidity, Gravimetric, and ICP-MS measurements are reported as means of duplicate samples.
<p>| | | | | | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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<th></th>
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<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C3_011</td>
<td>3.27</td>
<td>1.236</td>
<td>568</td>
<td>217</td>
<td>203</td>
<td>14</td>
<td>512</td>
<td>597</td>
<td>672</td>
<td>250</td>
<td></td>
</tr>
<tr>
<td>C3_012</td>
<td>12.48</td>
<td>6.06</td>
<td>207</td>
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<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>509</td>
<td>502</td>
<td>574</td>
<td>0.555</td>
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</tr>
<tr>
<td>C3_013</td>
<td>12.37</td>
<td>4.74</td>
<td>232</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
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<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>140</td>
<td>198</td>
<td>173</td>
<td>0.015</td>
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</tr>
<tr>
<td>C3_016</td>
<td>11.84</td>
<td>2.27</td>
<td>200</td>
<td>0.062</td>
<td>0.060</td>
<td>0.002</td>
<td>94</td>
<td>126</td>
<td>107</td>
<td>0.044</td>
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</tr>
<tr>
<td>C3_019</td>
<td>11.98</td>
<td>1.22</td>
<td>359</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>60</td>
<td>62</td>
<td>74</td>
<td>0.006</td>
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</tr>
<tr>
<td>C3_021</td>
<td>11.85</td>
<td>1.19</td>
<td>339</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>&lt;0.016</td>
<td>0.17</td>
<td>83</td>
<td>62</td>
<td>59</td>
<td>0.008</td>
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<td>82</td>
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</table>

aUnfiltered
bFiltered through 0.2 µm cellulose membrane filter
cCalculated as a difference between Fe_{tot<0.2} and Fe(II)<0.2 µm
dAcidified with HCl Merck Suprapur®
eAcidified with HNO₃ Merck Suprapur®
The high-sulfide column experiments were started earlier than the low-sulfide experiments. Having a longer experimental duration only the high-sulfide experiments will be further discussed in this report.

During the first cycles of background leaching, the measured EC, pH and Eh in all columns were very similar (fig. 19). At the start of the experiments, the conductivity of the leachate water was around 3 to 4 mS/cm but decreased to 1 mS/cm during background leaching that lasted until cycle 11 (sample numbers C1-011, C2-011, C3-011, marked with an arrow in fig. 19). Leachate water pH was around 2.8 after which it increased up to 3.4, before starting to slowly decrease again. The Eh was near 600 mV and showed a decreasing trend that continued to the end of the background leaching. After the anoxic column was sealed from the atmosphere, oxygen was consumed in the column and the EC increased from near 1 mS/cm up to at highest 2.54 mS/cm. In the reference column, EC also increased with experimental duration but the increase was much slower than in the anoxic column. Leachate pH and Eh measured in the anoxic and reference columns seem to follow the same trend throughout the whole time but there are some systematic differences. The decreasing trend in pH in the anoxic column starts somewhat earlier and the minimum pH is lower than that in the reference column. The lowest pH measured in the anoxic column was observed during cycle 22 and 23 (9 kg H₂O input) where it reached 2.66 after which it started to increase. It increased continuously until the end of the experiment duration considered here. In the reference column, the lowest pH value (2.72) was measured during cycle 27 (11 kg H₂O input), which is the last measured cycle. The Eh measurements in both columns show more scatter but follows an overall increasing trend from cycle 1 until cycle 25 and 26.
Figure 19. Leachate water EC, pH and Eh measurements plotted against the sample name in the reference, the anoxic and alkaline column experiments on the high-sulfide waste rock. Notice the different pH scales. The arrows indicate the end of background leaching.

Figure 20, 22 and 24 visualize the Fe$_{\text{tot}}<0.2$, Fe(II)$_{\text{tot}}<0.2$ and Fe(III)$_{\text{tot}}<0.2$ concentrations in the leachate water from the reference, anoxic and alkaline column respectively. Concentrations of Fe$_{\text{tot}}$, analyzed in unfiltered samples, are also shown in the last eight samples. Only the results obtained with the spectrophotometric method are shown. Each cycle is represented by the column name and the number of the leaching cycle. The first cycle 002 was performed 28$^{\text{th}}$ October 2016 and the last 028 was performed 13$^{\text{th}}$ April 2017. The time between each cycle varied between 3 to 14 days depending on the moisture level in the column. If data is missing from one cycle it is because no sample was collected during that cycle. If Fe(II)$_{\text{tot}}<0.2$ was equal to Fe$_{\text{tot}}<0.2$ no data was reported for Fe(III)$_{\text{tot}}<0.2$. 
During the background leaching period, the Fe concentration in the leachate water from reference column is very high, around 700-1000 ppm (fig. 20). The dominating Fe species is Fe(II)<0.2µm, contributing to around 90 % of total Fe (fig. 21). With time, the total Fe concentration decreases, ending up in the range 50 – 150 ppm in. The decreasing Fe concentration in the reference column is associated with the change in the species distribution: Fe(III)<0.2µm shows an increasing trend, from 5.6 % in cycle 4 all the way up to 55.3 % in cycle 25. In figure 20 and 22, three lines are drawn that represent the oxygen conditions in the anoxic columns: The dotted line represents the end of background leaching, the straight line shows when the oxygen saturation has decreased to 50 % (mid-January), and the dashed line when the oxygen saturation is down at 0.9 % (early February) in the anoxic column. After cycle 20, unfiltered samples were also collected, in addition to the filtered samples, and analyzed for Fe<sub>TOT</sub>. The Fe concentration in the unfiltered leachate water resulted in nearly exactly the same concentration as in the filtered leachate water, suggesting that dissolved iron species are dominating the leachate.

**Figure 20.** Fe concentration in leachate collected from the reference column. End of background leaching in column C2 and C3 is indicated by the dotted line, and the solid and dashed lines represent 50 %- and <1 % oxygen saturation respectively in the anoxic column to allow comparison with fig. 22.

**Figure 21.** Relative distribution of Fe(II)<0.2µm and Fe(III)<0.2µm in the filtered leachate water collected from the reference column. The solid and dashed lines represent 50 %- and <1 % oxygen saturation respectively in the anoxic column to allow comparison with fig. 23.
During the background leaching and prior to the sealing of the column from atmospheric oxygen, total Fe concentration in the leachate water from anoxic column shows similar concentrations and trend as the reference column (fig. 22). At the start, the relationship between Fe(II)<0.2µm and Fe(III)<0.2µm also show a similar trend in the anoxic column compared to the reference column with predominantly Fe(II)<0.2µm present, around 80 to 90 % of total Fe. But a few cycles after sealing the column from atmospheric oxygen (cycle 16), an abrupt change can be seen where the contribution of Fe(III)<0.2µm increases from around 10 to 20 % up to 66 % and then very slowly it decreases, reaching 33 % in sample C2-026 (fig. 23). The largest change in species distribution between Fe(II) and Fe(III) takes place when the oxygen saturation has decreased to 50 % and 0 %. As in the reference column, after cycle 20, unfiltered samples were also collected, in addition to the filtered samples, and analyzed for Fe$_{tot}$. In cycles 21 to 25, the concentration of Fe in filtered and unfiltered samples were more or less equal. After cycle 25 the Fe concentration in unfiltered samples increased compared to filtered samples indicating that some Fe may be mobilized from the columns in particulate form. If the particulate Fe have been mobilized from the solid waste rock material or have precipitated in the leachate prior to sampling is though uncertain.

![Figure 22. Fe concentration in leachate collected from the reference column. End of background leaching is indicated by the dotted line, and the solid and dashed lines represent 50 %- and <1 % oxygen saturation respectively.](image-url)
During the background leaching and prior to addition of alkaline material, the concentration of Fe\textsubscript{tot}\textless0.2 in leachate water from to the alkaline column is high (fig. 24) and similar to the other columns (figs. 20, 22). After surface application of alkaline material LKD, the Fe concentration in leachate water rapidly decreases under the detection limit (0.016 ppm), with only one exception (C3\_016) during the experimental progress considered here. The addition of LKD to the column is marked by a dotted line in figure 24. Unfiltered samples analyzed for Fe\textsubscript{tot} after cycle 20 contained Fe in the 0.1-1 ppm range, indicating that some Fe may be mobilized from the columns in particulate form. However, the total mass of Fe mobilized in the particulate form is low.

Sulfate concentrations measured with turbidimetry, gravimetry and ICP-MS are presented for all columns in figure 25. During the first cycles of background leaching, the concentration is very high, in the range of 2000-3000 ppm as determined using the turbidimetric method. At the end of the background leaching,
the concentration has decreased to 764 ppm in the reference column, 413 ppm in the anoxic column and 512 ppm in the alkaline column. The trend is similar in all columns, but the sulfate concentrations still show some differences. When the oxygen saturation reached low levels in the anoxic column, around 20 %, an increase of sulfate content in the leachate is detected. A similar increase can also be seen in the reference column but is lesser in magnitude and does not occur at the same time as in the anoxic column. After addition of LKD to the alkaline column, the sulfate concentration decreases rapidly and stays on a low level, around 70 ppm.

Figure 25. Sulfate concentrations in the leachate water measured with turbidity, ICP-MS and gravimetry. The solid line indicates 50 % air saturation in the anoxic column and the dotted line indicates the end of background leaching when LKD was added to the alkaline column and the anoxic column sealed.

To get a preliminary idea about the effect of different geochemical conditions to the metal(loid) mobility, arsenic and copper concentrations in the filtered leachate are shortly presented here. The concentration of these elements (µg/l) is presented in table 10. Figures 27 and 28 present the elemental ratios of these elements and the \( \text{Fe}_{\text{tot}<0.2\text{µm}} \) (mg/l) in the leachate water. The concentrations of \( \text{Fe}_{\text{tot}<0.2\text{µm}} \) used to calculate the ratios were those obtained using the spectrophotometric method for all samples above the detection limit. If concentration was under detection limit for spectrophotometry, data from ICP-MS was used.
The Cu/Fe-ratio in the leachate increases continuously in both the reference column and the anoxic column throughout the time period studied. In the leachate water from the anoxic column, As deviates from Cu: the As/Fe-ratio increases up until sample 16 and starts decreasing when fully anoxic conditions have been established, marked in figures 26 and 27 by solid lines. For comparison, the As/Fe-ratio in the reference column shows continuous increase similarly to the Cu/Fe-ratio. Concentrations of As and Cu in table 10 show a difference between the leachate from the reference and the anoxic column. In samples 16 to 21, both As and Cu from the anoxic column are relatively higher than from the reference. In the alkaline column, the Cu/Fe-ratio follows the same pattern as in the leachate water in the other columns until LKD was added, where the ratio peaked. It increased from 0.1 up to 1124. The same is true for As, where the ratio increased from 0.03 to 324. Note that the increase in the ratio does not indicate the mobilization of Cu and As after LKD addition, but rather the almost complete immobilization of dissolved Fe.

Figure 26. Elemental ratios between As and Cu (µg/l) and Fe\textsubscript{tot<0.2µm} (mg/l) in the leachate water from all columns containing high-sulfide waste rock. Note the different scales and that they are logarithmic. The solid and dashed lines represent 50 % and <1 % oxygen saturation respectively in the anoxic column.
Figure 27. Elemental ratios between As and Cu (µg/l) and Fe_{tot<0.2µm} in the leachate water from the reference, anoxic and alkaline column respectively. Note the different scales. The solid and dashed lines represent 50 % and <1 % oxygen saturation respectively in the anoxic column and the dotted line represents the addition of LKD in the alkaline column.

Table 10. Concentrations of Cu and As in selected leachate water samples.

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8. Discussion
The results presented in chapter 7 are discussed in this section, concentrating on the speciation analyses, comparison of measured Eh and Fe redox speciation, as well as the use of Fe redox speciation in tracing the geochemical processes occurring during changing chemical environment.

8.1 Speciation analyses in leachate water

8.1.1 Ferrozine method
Performing spectrophotometric analysis using the ferrozine method is a simple way to determine the Fe concentration and speciation in a solution. It requires a spectrophotometer that can be found in most laboratories and portable instruments are available at low prices. A spectrophotometer suitable for these analyses costs from ca. 20000 to 100000 SEK, depending on its features (HACH, 2017). The same instrumentation can also be used to determine other chemical components of environmental interest like dissolved SO$_4$, SiO$_2$ and N compounds.

The reagents used in the ferrozine method are reasonable easy to prepare and handle for personnel with a moderate background in water sampling and analyses. The various steps in the analyses, including acidification, dilution, pipetting, reagent addition, and the use of the spectrophotometer, require carefulness and precision but are not more difficult than any standard laboratory work. There are also commercial test kits for various solutes including ferrozine iron test kits available for order from Hach simplifying the procedure. In that sense, the ferrozine method can be considered as an accessible and useful method that relatively easily may be adopted in the work of an environmental consultant, researcher, mining company or another actor who is in need of simple and fast Fe speciation analysis.

The standard curve preparation is crucial to obtain reliable results and a part of the standard analytical procedure. The correlation between absorbance and concentration within the absorbance range 0.02 to 0.66 showed a clear linearity and was unaffected by the addition of HCl prior to analysis. The quality control including blanks, duplicates and analysis of standards showed low blank levels and very good accuracy and precision of the method. The relative error between an average of five measurements of one standard solution compared to the true value of the standard was 1.4 %. Time series studied in six samples with differentiating redox and chemical composition revealed no systematic change in Fe species distribution with time during a five-week period, indicating that samples may be stored for at least five weeks prior to analysis if treated with HCl. Only one sample, collected from the reference column of the low-sulfide material could be considered as unstable. The reason for this is unclear and was not further studied in this thesis work, but the presence of ppm-level concentrations of Cu, known to interfere with the ferrozine Fe analyses, could be one reason (To et al. 1999). Also, as it is known that colloidal and particulate Fe phases may pass through standard filtration equipment that could be another reason. It has been observed that in case any colloidal Fe are present in the samples they will be effectively dissolved
by the ferrozine reagents, overestimating the concentration of dissolved Fe. The presence of colloidal Fe that may have passed the 0.2 µm filter pore size was not addressed here, and can therefore not be ruled out.

The results of Fe<sub>tot<0.2µm</sub> from spectrophotometry agrees well with the results from ICP-MS. These findings suggest that determination of Fe redox species concentrations by the ferrozine method using a portable spectrophotometer provides accurate and reliable results.

8.1.2 Turbidimetric method
Sulfate determination by the turbidimetric method is very similar to the ferrozine method considering the analytical procedure and the instrumentation. The treatment of samples for sulfate analyses is though different as no acid or other chemical is added to ensure the preservation of the sulfate speciation. Difficulties regarding preservation of sulfur species have been observed and depend largely on the presence of sulfide (Kaasalainen & Stefánsson, 2011). One reason for testing the turbidimetric method is the need for easily available, quick and portable analytical methods allowing immediate analyses in the field or in laboratory conditions of the major compounds in water affected by sulfidic mine waste.

The calibration curve that was prepared showed a good linear fit to the concentration range 5 to 100 ppm. The detection limit was determined to 14 ppm by the analysis of blanks and duplicates samples showed low reproducibility for the samples with a concentration less than 14 ppm. Overall, the precision of the method (16%) is not as good as typically desired for an analytical method in the laboratory. Determination of sulfate concentrations in selected samples in a time series showed variable concentration variation during the two-week period, but the observed variation fell within the range of analytical uncertainty. Despite the large uncertainties observed during the quality controls and stability tests, the results obtained by turbidimetry agree reasonably well with the result from gravimetric sulfate determinations and sulfate concentrations calculated based on the total S determined by ICP-MS carried out at ALS in the Zech Republic and Luleå. ICP-MS reported generally higher concentrations than the turbidimetric method, but as ICP-MS includes all S species that may have been present, not only sulfate, this result is realistic. The reasonable agreement of these methods indicates that most S is actually present as sulfate, but the difference might be due to the presence of other species as well. This was also indicated by the analysis when three samples were analyzed before and after treated with hydrogen peroxide, oxidizing all S to sulfate. All three samples suggested increasing concentrations after oxidation, but the increase was of the similar magnitude with the analytical uncertainty (20%) and therefore a matter of more detailed study.
8.2 Comparison between the Fe species concentrations and redox measurements by Pt-electrode

With the assumption that Fe(II)/Fe(III) is the redox controlling couple, measured concentrations of Fe(II)\(<0.2\,\mu m\) and Fe(III)\(<0.2\,\mu m\) obtained from spectrophotometry were used to calculate the expected Eh potential in PHREEQC. The results are presented in figure 28, where also the measured Eh potential is shown.

The general trend in the Eh calculated based on the Fe redox species concentrations follows the measured potential, but is systematically somewhat higher compared to the Eh measured with the Pt-electrode. This is true in all three columns. After addition of LKD in the alkaline column, the measured potential rapidly decreases to 207 mV and it stays low until cycle 20 where it starts to increase. Because the concentration of dissolved Fe was under detection limit after addition of LKD in the alkaline column, it was not possible to calculate the Eh potential to allow comparison.
Figure 28. Eh potential (Eh meas) measured using Pt-electrode and Eh potential calculated (Eh mod) using the measured the Fe(II) <0.2µm and Fe(III) <0.2µm concentrations in the leachate water from spectrophotometry in the reference, anoxic and alkaline column respectively. Dotted line represents the end of background leaching (addition of LKD to the alkaline column and sealing of anoxic column), the solid line 50 % and the dashed line 0.9 % oxygen saturation.
The time-dependent variation of the measured Eh in the reference and anoxic column is plotted in figure 29. The overall trends in these two columns are relatively similar with some scatter, but it appears that Eh of the leachate water from the reference column is slightly but systematically lower, in particular after oxygen level decreases below 50% saturation in the anoxic column.

![Figure 29. Measured Eh potential in leachate water from the reference column (C1) and the anoxic column (C2). Dotted line represents the end of background leaching (sealing of anoxic column), the solid line 50 % and the dashed line 0.9 % oxygen saturation.](image)

The Eh potential measured with Pt-electrode and calculated based on Fe redox speciation in all columns are plotted against each other in figure 30. This figure clearly shows that the Eh potential based on the Fe redox speciation provides a systematically higher value compared to that measured with the Pt-electrode, especially in the anoxic column. The difference between measured and calculated Eh in comparison to the measured concentration of Fe_{tot<0.2µm} in each sample is presented in figure 31. No systematic relationship can be observed between the deviation and Fe concentrations. The largest relative error between measured and calculated Eh in all columns is 19 %, based on the absolute error between measured and calculated potential divided by the average of those two. This level of disagreement is similar to that observed by previous authors, such as Espana et al. (2005). Earlier research has indicated that the difference between measured and calculated Eh potentials increases if the species of Fe(II) or Fe(III) reaches 95 % or more (Sánchez Espana, et al., 2005). This agrees with an increased inaccuracy of Fe(III) concentrations, at very high or low Fe(II)/Fe(III) ratios, when Fe(III) is calculated as a difference between the Fe_{tot} and Fe(II) concentrations (To et al., 1999). The speciation is not shown in figure 31, however, there is no trend showing that samples dominated by Fe(II) (>95%) would represent a larger deviation between calculated and measured Eh potential more than any other sample. No samples analyzed within this thesis project were dominated by Fe(III) (>95%) and the error cannot be evaluated.
Figure 3. Comparison between \( \text{Eh} \) measured using Pt-electrode and \( \text{Eh} \) calculated with Fe(II) \(<0.2\mu m\) and Fe(III) \(<0.2\mu m\) concentrations from spectrophotometry in all columns. Dashed lines represent \( \pm 50 \text{ mV} \) error.

Based on the Nernst equation, the \( \text{Eh} \) potential is expected to increase as a response to increasing activity of Fe(III) as a consequence of increasingly oxidized conditions, whereas \( \text{Eh} \) should decrease if the opposite was true. The relative importance of Fe(II) \(<0.2\mu m\) of dissolved \( \text{Fe}_{\text{tot}}<0.2\mu m\) compared to \( \text{Eh} \) potential measured with the Pt-electrode is plotted in figure 32. As expected, when Fe(II) is decreasing compared to Fe(III), the measured \( \text{Eh} \) potential increases although scatter associated with the data complicates the interpretation of this relationship. Important is not to forget that plots like shown in figure 32 do not acknowledge the pH and the connection between different pH values, total iron concentrations and Fe speciation. The Fe speciation including the relative importance of the simple Fe(III) ion and various hydrolysis species, as it is only the activity of the simple Fe(III) ion that goes into the Nernst equation. It can be seen in figure 32 that samples with similar Fe speciation determined by spectrophotometry can have an \( \text{Eh} \) potential deviating by over 100 mV and that large variation of the Fe speciation measures the same \( \text{Eh} \) potential. The interpretation of figure 32 may therefore not be as simple as implied by Espana et al (2005), who implied that
higher Eh values are indicative of more oxidizing conditions and lower Eh of less oxidizing conditions (Sánchez Espana, et al., 2005), separated by the Eh value of approximately 640 mV. Such conclusion does not acknowledge that the Eh value appears to be a result of Fe(III)-mineral-water reactions, Fe hydrolysis reactions and their interactions with the Pt-electrode, and leachate water pH, rather than an indication of the presence or absence of oxygen. As an example, the highest measured Eh potential in the anoxic column during this thesis work was measured in cycle 22 (719 mV) when oxygen saturation was <1%, in other words, one could state that fully anoxic conditions prevailed and Fe(II)<0.2µm contributed to 52 % of Fe_{tot}<0.2µm. That is very similar to the highest Eh measurement (696 mV) in the reference column (open to atmosphere, with 100% O2 saturation) with 45 % of the Fe_{tot}<0.2µm being Fe(II)<0.2µm. These examples demonstrate that a high measured Eh potential with similar Fe speciation does not directly indicate if the overall system is under oxic or anoxic conditions. When deciding which analysis are to be performed to answer specific questions related to a system, for example Eh or redox speciation measurements, this is important to have in mind. This, as well as the difficulty of achieving accurate Eh measurements due to the time needed for Eh (ORP) measurements to stabilize as too rapid measurements, may result in erroneous interpretation of the redox conditions in the respective system. Coatings on the electrode measuring surface decrease the sensitivity and increase the electrode response time even further.

![Figure 32. A comparison between leachate water Fe(II)<0.2µm /Fe_{tot}<0.2µm measured with spectrophotometric and the Eh values measured using Pt-electrode. The solid line represents Eh equal 640 mV, suggested to separate acid mine drainages dominated by Fe(II) and Fe(III).](image)

In the same way that concentrations of Fe(II)<0.2µm and Fe(III)<0.2µm were used to calculate the Eh potential for the Fe(II)/Fe(III) redox pair, the measured Eh potential was used to calculate the expected speciation of Fe(II) <0.2µm and Fe(III) <0.2µm in PHREEQC. The measured pH and Eh potential and the Fe_{tot}<0.2µm obtained from spectrophotometry were used as input. In figures 33 and 34 the relationship between measured and calculated concentrations of Fe(II)<0.2µm and Fe(III)<0.2µm are shown.
Figure 33. Concentrations of Fe(II)<0.2µm analyzed with spectrophotometric and calculated based on measured Eh potential. Notice that both plots display the same data but using a different scale. The 1:1 line (solid) is plotted in both figures.

Figure 34. Concentrations of Fe(III)<0.2µm in the leachate water analyzed with spectrophotometry and calculated based on the measured Eh potential. The 1:1 line (solid) is plotted in the figure.

The calculated and measured concentration of Fe(II)<0.2µm compare well in the concentration range between 0.06 and 800 ppm, even though the Fe(II) concentrations expected based on the Eh measurements were somewhat higher than what was measured. For Fe(III)<0.2µm however, such relationship is not observed and the measured concentration is in general much higher than that expected based on the Eh measured with the Pt-electrode (fig. 30). Therefore, the Eh measurements approach is not able to reproduce the observed Fe(III)<0.2µm concentrations in the system. The largest differences in the measured and predicted Fe(III) concentrations are found in the beginning of the experiment (up to 200 ppm) when the measured Fe(III)<0.2µm concentrations are high but the measured Eh potential is relatively low. What explains the difference was not further studied within this thesis work but may be due to several reasons including...
insensitive Eh (ORP) measurements and disequilibrium between the Pt-electrode and the Fe(II)/Fe(III) redox couple. Overestimation of Fe(III)<0.2µm as a result of Fe(III) colloids passing through the filter or by the calculation as a difference between Fe_{tot}<0.2µm and Fe(II)<0.2µm concentrations may be another reason. Partial equilibrium of Fe(II) with a solid phase (e.g. Fe(OH)_3) may still be true and is a matter of further studies.

8.3 Leachate water composition – Fe redox speciation as a tracer of geochemical reactions

The leachate water composition from the different columns is presented in section 7.3. In this section, these results are further discussed concentrating on the basic water quality parameters EC, Eh, and pH and the concentrations and speciation of Fe and S.

Electric conductivity can be used as a quick measure of dissolved solids and ions in a solution and is often correlated with the dissolved sulfate content as the major anion in water affected by sulfide oxidation (Jeffery, et al., 1989). A systematic trend between the measured EC and dissolved sulfate concentrations may be observed in the leachate water from the reference column and during background leaching in the anoxic and alkaline column (fig. 35). When anoxic and alkaline conditions are established, the EC does no longer follow the trend of measured sulfate. In the alkaline column the relatively high EC in the sample seems to be due to increase in dissolved Ca, Na and K concentrations in the leachate (data not reported here). In the anoxic column, increase in the leachate EC is associated with the decrease of O_2 saturation (starting at ca. 50 % O_2), even though the dissolved sulfate decreases. Therefore, also other solutes in addition to sulfate appear to be important for such elevated EC. The highest elevated EC in the leachate from the anoxic column also coincides with the lowest measured pH. In the following, the behavior of Fe, another major element present in the leachate water is discussed.
High concentrations of Fe were measured in the leachate water from all columns during background leaching and the dominating Fe species was Fe(II). After addition of alkaline material, dissolved iron concentrations dropped to ppb-level, and determination of Fe redox speciation in the dissolved phase was not possible with the cuvette sizes and the ferrozine method used here. It may though be expected that the reactions of dissolved Fe are of lesser importance in these conditions.

The speciation between Fe(II) and Fe(III) in the reference and anoxic column starts to deviate in the beginning of the second period presented in figure 21 and 23 that is a few cycles after sealing the column from the atmosphere. With experimental progress, the Fe(III) contribution in the leachate from the reference column
increased continuously. At the same time in the anoxic column, Fe(III) first increases, and then steadily decreases. The increase in Fe(III) contribution is well correlated with the oxygen saturation in the anoxic column reaching 50%. It peaks just before 50% is reached and then slowly decreases. This is associated with somewhat elevated leachate EC. Also, the leachate pH in the anoxic column decreases faster and to a lower value than in the reference column. These observations regarding O₂, EC, pH and Fe concentrations and redox speciation may be a result of complex interactions involving the sulfides and Fe(III) containing secondary minerals, Fe-hydrolysis reactions and their effect on the pH.

To get insights into the mineral-water interactions in the columns, the mineral saturation with respect to common Fe(III) minerals were calculated using PHREEQC. Several Fe-containing minerals have been identified associated with mine waste environments. Some of these are also present in the experimental columns, as indicated by the visual observations of and the previous and preliminary mineralogical observations of the material. Still, the mineralogical characterization of the material has not been completed and available for this study. These minerals likely to play an important role to the Fe concentration and speciation in the leachate. The saturation index of goethite, ferrihydrite, jarosite and schwertmannite (only one stoichiometry considered, Fe₈O₈(OH)₈SO₄) are presented (fig. 36, table 11) and discussed here. The saturation index in the alkaline column is not discussed in this thesis work after the addition of alkaline material when the Fe redox species concentrations in the leachate water were below the detection limit of the ferrozine method.

Goethite, jarosite and schwertmannite are supersaturated in all columns during background leaching and goethite continuous to be supersaturated during the whole experiment. In all three columns the SI of ferrihydrite is close to zero (±2) during background leaching, indicating that this is the mineral that may control Fe(III) solubility in the leachate, taking into consideration the large variation associated with the reported solubility constants due to the varying crystallinity and aging effects (Majzlan, et al., 2004; Nordstrom, et al., 1990). With experimental progress, the SI of ferrihydrite, jarosite and schwertmannite show decreasing trends and in anoxic conditions established after sample 21 the SI indicates dissolution of jarosite and schwertmannite. Goethite on the other hand, is supersaturated during the whole experimental progress. These results are in qualitative agreement with what is expected based on the leachate water pH and Eh and in the pe-pH diagram (fig. 1).
Table 11. Saturation indexes for selected Fe-minerals calculated in the leachate water. For schwertmannite, stoichiometry Fe₈O₈(OH)₆SO₄ was considered

<table>
<thead>
<tr>
<th>Sample</th>
<th>Goethite</th>
<th>Ferrihydrite</th>
<th>Jarosite</th>
<th>Schwertmannite</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1_004</td>
<td>5.00</td>
<td>-0.71</td>
<td>2.48</td>
<td>7.14</td>
</tr>
<tr>
<td>C1_008</td>
<td>5.81</td>
<td>0.10</td>
<td>3.86</td>
<td>13.03</td>
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<tr>
<td>C1_011</td>
<td>5.71</td>
<td>0.00</td>
<td>3.12</td>
<td>11.96</td>
</tr>
<tr>
<td>C1_012</td>
<td>5.14</td>
<td>-0.57</td>
<td>1.83</td>
<td>7.59</td>
</tr>
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<td>C1_014</td>
<td>5.08</td>
<td>-0.63</td>
<td>0.94</td>
<td>6.96</td>
</tr>
<tr>
<td>C1_016</td>
<td>5.32</td>
<td>-0.39</td>
<td>1.97</td>
<td>8.80</td>
</tr>
<tr>
<td>C1_019</td>
<td>4.70</td>
<td>-1.01</td>
<td>0.91</td>
<td>4.45</td>
</tr>
<tr>
<td>C1_020</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-1.08</td>
<td>0.33</td>
<td>4.06</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
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<td>-0.96</td>
<td>0.47</td>
<td>4.90</td>
</tr>
<tr>
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<td>2.80</td>
<td>8.87</td>
</tr>
<tr>
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<td>5.63</td>
<td>-0.08</td>
<td>3.08</td>
<td>11.43</td>
</tr>
<tr>
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<td>5.37</td>
<td>-0.34</td>
<td>2.28</td>
<td>9.37</td>
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<tr>
<td>C2_012</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C2_014</td>
<td>5.15</td>
<td>-0.56</td>
<td>1.31</td>
<td>7.54</td>
</tr>
<tr>
<td>C2_016</td>
<td>4.91</td>
<td>-0.80</td>
<td>1.75</td>
<td>6.29</td>
</tr>
<tr>
<td>C2_019</td>
<td>4.57</td>
<td>-1.14</td>
<td>0.69</td>
<td>3.57</td>
</tr>
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<td>C2_020</td>
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<td>0.68</td>
<td>3.19</td>
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<td>C2_021</td>
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</tr>
<tr>
<td>C2_023</td>
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<td>-1.43</td>
<td>-0.97</td>
</tr>
<tr>
<td>C3_004</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C3_008</td>
<td>5.00</td>
<td>-0.71</td>
<td>1.68</td>
<td>6.64</td>
</tr>
<tr>
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<td>5.23</td>
<td>-0.48</td>
<td>1.89</td>
<td>8.21</td>
</tr>
</tbody>
</table>
The development of the saturation index in the leachate water during the experimental progress. Solid line indicates 0.9 % oxygen saturation in the anoxic column.

The behavior of Cu and As in the leachate water from the reference and anoxic columns coincide with the changes in the SI of the Fe(III)-(hydroxy) sulfates, jarosite, schwertmannite and ferrihydrite. As both jarosite and schwertmannite are capable of accumulating Cu and As during their formation, As and Cu may become released to the solution upon their dissolution. However, longer experimental duration, further data on the mineralogy and sequential extractions are needed for further interpretations on the As and Cu association and processes in these experiments.

Summarizing all analytical results obtained within this thesis work it is evident that the different geochemical environments studied affect the leachate water quality. In order to further conclude about the exact reactions or the magnitude of metalloid mobilization upon transition from oxic to anoxic conditions, longer experimental duration and additional data are required and is not the scope of this thesis work.
9. Conclusions

9.1 Speciation analysis
Iron speciation analysis by spectrophotometry using the modified ferrozine method fulfills the criteria of simple cheap and accessible speciation measurements for the applied geochemistry and for environmental studies with mine waste. The conclusion is based on the following:

- The absorbance of the ferrozine complex at 562 nm is linear within the concentration range 0.016 to 1.4 ppm Fe with 1 cm cuvette
- Acidification with HCl before analysis to prevent discoloration did not affect the results.
- Filtration, acidification with HCl and storage in a dark and cold (<4ºC) place enables preservation of the Fe redox distribution.
- The Fe speciation is unaffected by dilution as long as the final concentration stays within the applicable range of the method.
- The method shows high reproducibility
- Analysis of Fe$_{\text{tot}}$ by spectrophotometry is comparable to ICP-MS

Turbidimetry by the sulfate method 9038 provides simple and cheap analysis, but with a precision lower than normally expected from laboratory analyses. It may however still be useful for estimation of the sulfate concentration based on the following and in particular due to the possibility to carry out field measurements with portable instruments:

- Linearity of the calibration curve within the concentration range 10 to 100 ppm sulfate with 1 cm cuvette
- Analysis of sulfate by turbidimetry is comparable to gravimetry and ICP-MS and reproduces the observed trends.
- The method shows somewhat lower low reproducibility, but may still be considered acceptable for field analyses.
- Dilution up to a maximum factor 20 did not affect the results.

9.2 Iron speciation and redox conditions
The transition from oxic to anoxic and from acid to alkaline conditions affects the geochemistry and Fe speciation and concentration in leachate water. During the transition from oxic to anoxic conditions the Fe redox speciation changes, increasing the relative importance of Fe(III). The transition was also associated with an increase in leachate EC but not clearly indicated by pH, Eh, total Fe and sulfate in the leachate water. To understand the ongoing processes additional information (e.g. oxygen concentrations) is needed. Fe redox species measurements may therefore provide valuable information about the geochemistry and processes occurring in leachate water.

The concentration of Fe(II) calculated based on the Eh potential measured with the Pt-electrode was relatively well related to the Fe(II) determined by spectrophotometry. The measured concentrations of Fe(III) however was not
reproduced by these calculations, being in general highly underestimated by the calculation. This is considered to be due to the relatively narrow range in which distribution of Fe(II)/Fe(III) changes dramatically. That means small differences in Eh will result in a large change of Fe(II)/Fe(III). Considering the error of the measurements and difficulty in achieving good Eh readings with a Pt-electrode, estimating the Fe speciation from Eh measurements can be misleading.

Iron concentrations drop to ppb-level in the alkaline environment established by LKD and determination of Fe redox speciation in the dissolved phase is not possible using the cuvette sizes and the ferrozine method used here. It may though be expected that the dissolved Fe redox species are not that important for the leachate chemistry in that environment.
10. Future research
In this thesis the Fe species concentrations measured with the ferrozine method were not quantitatively reproduced by the Eh potential measured with the Pt-electrode. As many solid Fe phases are associated with mine waste, these may control the solubility and speciation of Fe(II) and Fe(III). Assuming the Eh potential is a result of Fe(III)-mineral-water reactions, hydrolysis and pH, to continue this research it would be interesting to study mineral-water reactions of Fe(II) with Fe(III)-oxy(hydroxides) as described in section 5.3 for ferrihydrite. The aim would be to calculate the Eh potential responding to selected secondary minerals like jarosite, schwertmannite and goethite, that might provide a better fit to the Eh potential measured with the Pt-electrode.

Colloids passing through the filter membrane used in this study (having pore size 0.2µm) might be a reason for the large deviation between Fe(III) measured with spectrophotometry and Fe(III) calculated from redox measurements using a Pt-electrode. Studying the presence of colloids may provide useful information about the ongoing processes in the leachate water.

The column experiments discussed in this thesis have been running for six months. To be able to allow conclusions about the exact processes occurring within the columns, the magnitude of secondary mineral mobilization and remobilization of metal(loid)s and how that affects the leachate water, six months is not enough time. To further study these processes the experimental duration needs to continue for a much longer time.
11. Literature


Appendix I.
Spectrophotometry

Preparation of Standard Solutions
a. Prepare chemicals needed:
   - Fe(III)Cl₃ 1000 ppm
   - 6 M hydrochloric acid (HCl)
   - Hydroxylamine hydrochloride (NH₂OH·H₂O) 10 % w/v
   - Ammonium acetate buffer solution (CH₃COONH₄) pH 7.4 (7 – 7.5)
   - 0.25 % ferrozine reagent (C₂₀H₁₃N₄S₂O₆Na·H₂O) Hach 95.2 % pure
   - Milli-Q water.
b. Determine an adequate amount of standard solutions to be prepared and analyzed, between 6 and 8 is sufficient. This to reveal the linear correlation between absorbance and concentration. The concentration range for which the calibration curve is linear is 0.016 – 1.4 ppm. After 1.4 ppm the line starts to bend and the absorbance is no longer dependent on the concentration.
c. Prepare standard solutions for the calibration curve by stepwise dilution of Fe(III)Cl₃ stock solution (1000 ppm) with 0.1 M HCl, prepared by dilution of concentrated HCl in Milli-Q water, into acid washed plastic bottles
d. Determine the size of the bottles based on the volume of sample that is needed for analysis and further dilution, between 60 and 250 ml should be sufficient.
e. Dilution is performed stepwise from high to low concentration and should never exceed 10x initial volume. In order to achieve precise concentrations, use a scale when measuring the solutions.

Analysis
This procedure is a modified version of the ferrozine method described by To et al. (1999). The instrumentation and chemical reagents are shown in figure 37.
a. Pipette an adequate amount of sample into a 10 ml vessel. Make sure not to fill the vessel completely, always leave space for the reagents.
b. If the solution is a standard or blank, add 0.1 ml hydroxylamine hydrochloride. It reduces Fe(III) to Fe(II) enabling total Fe measurements.
c. Add 0.2 ml ferrozine reagent and mix.
d. Add 0.5 ml ammonium acetate buffer solution to neutralize the sample. Shake the sample well and let it stand for five minutes for full-color development.
e. If the sample is discolored by a brick or rust red color, add 0.6 ml of 6 M HCl sample after color development. The red color appears due to high Fe(III) concentrations. If interference is suspected but not visibly noticeable, prepare duplicates, one with HCl and one without.
f. Dilute the sample to 10 ml mark with Milli-Q water if needed and shake well.
g. Pipette into cuvette and measure absorbance at 562 nm within 2 hours.
h. For Fe₉₀₉ measurements, follow the procedure with the addition of step c. in all samples.
Comment: As the absorbance depends on the optical path length the size of the cuvette is important. Concentrated solutions should be measured in a cuvette with a short optical path length (1 cm), dilute solutions should be measured in a cuvette with longer optical path length (2.5 cm). This in order to target the absorbance interval between 0.02 and 0.66 independently on which cuvette that is used, representing the concentration range of 0.016 to 1.4 ppm Fe. E.g. if a 1 cm cuvette is used and the absorbance is less than 0.02, change to a larger. 2.5 cm cuvette and re-measure to fit the interval, and the other way round.

Figure 37. Instrumentation needed to perform spectrophotometric Fe speciation analysis using the ferrozine method: spectrophotometer, 1- and 2.5 cm cuvettes, chemical reagents, 10 ml sample vessels and pipettes. This spectrophotometer was also used for the turbidimetric sulfate analysis.
Appendix II.

**Oxygen Saturation**

Oxygen saturation was measured in the anoxic column. In figure 39 the $O_2$ saturation from the 21st December 2016 until 7th March 2017 is presented. The 2nd March the concentration reached 0.9 % and the system is assumed to be anoxic.

*Figure 39. Oxygen saturation anoxic column.*