Emma-Tuulia Nurmesniemi

EXPERIMENTAL AND COMPUTATIONAL STUDIES ON SULPHATE REMOVAL FROM MINE WATER BY IMPROVED LIME PRECIPITATION
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UNIVERSITY OF OULU, OULU 2018
Abstract

Lime precipitation has been used for the treatment of mine water for decades; however, the impact of precipitation conditions is not adequately known. In this thesis, four aspects related to the removal of sulphate from mine water by lime precipitation are considered: the effect of magnesium on lime precipitation, the utilisation of by-products in lime precipitation, enhancement of lime precipitation, and utilisation of the precipitate.

Sulphate removal in the presence of magnesium at the commonly used lime precipitation treatment pH of 9.6 was found inefficient as magnesium was keeping the sulphate soluble in the form of magnesium sulphate. At higher treatment pH of 11.5, magnesium that was naturally present in the mine water was shown to precipitate as magnesium hydroxide, which could serve as seed crystals for gypsum or co-precipitate sulphate thus enhancing sulphate removal.

Quicklime manufacturing generates by-products that, currently, have few applications. The by-products examined in this study were successfully applied for mine water neutralization replacing commercial lime products. These by-products were found to remove sulphate equally well from the mine water. However, differences between by-products were observed in the consumption, and produced sludge quantities and qualities.

An enhanced lime precipitation method is the precipitation as ettringite, which was used to reduce the sulphate content in mine water to less than the value set as the drinking water guideline in Finland. Furthermore, the formed precipitate was found to remove arsenate from the model solution.

Keywords: arsenate sorption, ettringite, gypsum, industrial wastewater treatment, mine water, sulphate removal, waste utilisation

Tiivistelmä

Vaikka kalkkisaostusta on käytetty kaivosten vesienkäsittelyyn useiden vuosikymmenen ajan, tieto olosuhteiden vaikutuksesta käsittelyyn saaatin sultaatin poistoa on puutteellista. Tämä väitöskirja käsittelee sulfaatinpoistoa kaivosvesistä kalkkisaostuksen avulla neljällä eri osa-alueella: magnesiumin vaikutus kalkkisaostukseen, kalkinpolton sivutuotteiden hyödyntäminen kalkkisaostuksessa, kalkkisaostuksen tehostaminen ja muodostuvan saostuman hyödyntäminen.

Magnesiumin todettiin kokeellisesti ja laskennallisesti haittaavan sulfaatin poistoa kaivosvesistä kalkkisaostuksessa yleisesti käytettyssä pH:ssä 9.6 pitämällä sulfaattia liukoisessa muodossa magnesiumsulfaattina. Korkeammassa pH:ssa 11.5 puolestaan kaivosveden luontaisesti sisältämän magnesiumin havaittiin kokonaisesti ja laskennallisesti saostuvan magnesiumhydroksidiä, joka voi toimia siemenkiteinä kipsille tai keraasiaotaa sulfaattia ja siten tehostaa sulfaatin poistoa.


Saostuksella ertrangiittinä, joka on tehostettu versio perinteisestä kalkkisaostuksesta, saavutettiin sulfaattipitoisuuden lasku alle Suomessa juomavedelle käytetyn suositusarvon. Lisäksi havaittiin muodostuneen ertrangiittisaaostuman olevan potentiaalinen materiaali arsenaatin poisoon vedestä.

Asiasanat: arsenaatin sorptio, ettringiitti, kaivosvesi, kiertoalous, kipsi, sulfaatin poisto, teollisuuden jäteveden käsittely
To my family
Acknowledgement

This thesis work was conducted in the Research unit of Sustainable chemistry at the University of Oulu during years 2012-2018.
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Oulu, September 2018

Emma-Tuulia Nurmesniemi
### Abbreviations and symbols

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AMD</td>
<td>Acid mine drainage</td>
</tr>
<tr>
<td>b</td>
<td>Isotherm constant related to energy of sorption</td>
</tr>
<tr>
<td>c&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Equilibrium solution concentration</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EPMA</td>
<td>Electron probe microanalysis</td>
</tr>
<tr>
<td>HDS</td>
<td>High density sludge</td>
</tr>
<tr>
<td>IC</td>
<td>Ion chromatography</td>
</tr>
<tr>
<td>ICP-OES</td>
<td>Inductively coupled plasma optical emission spectrometry</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>K</td>
<td>Isotherm constant related to intensity of sorption</td>
</tr>
<tr>
<td>k&lt;sub&gt;1&lt;/sub&gt;</td>
<td>Pseudo-first order rate constant</td>
</tr>
<tr>
<td>k&lt;sub&gt;2&lt;/sub&gt;</td>
<td>Pseudo-second order rate constant</td>
</tr>
<tr>
<td>n</td>
<td>Isotherm constant related to intensity of sorption</td>
</tr>
<tr>
<td>q&lt;sub&gt;e&lt;/sub&gt;</td>
<td>Amount of arsenate sorbed on ettringite at equilibrium</td>
</tr>
<tr>
<td>q&lt;sub&gt;m&lt;/sub&gt;</td>
<td>Maximum sorption capacity</td>
</tr>
<tr>
<td>q&lt;sub&gt;t&lt;/sub&gt;</td>
<td>Amount of arsenate sorbed on ettringite at time t</td>
</tr>
<tr>
<td>R&lt;sup&gt;2&lt;/sup&gt;_{adj}</td>
<td>Adjusted correlation coefficient</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SI</td>
<td>Saturation index</td>
</tr>
<tr>
<td>SRB</td>
<td>Sulphate reducing bacteria</td>
</tr>
<tr>
<td>UHLA</td>
<td>Ultra high lime with aluminium</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>XRF</td>
<td>X-ray fluorescence</td>
</tr>
<tr>
<td>-logK</td>
<td>Solubility product</td>
</tr>
</tbody>
</table>
List of original publications

This thesis is based on the following publications, which are referred throughout the text by the corresponding Roman numerals:


Emma-Tuulia Nurmesniemi (née Tolonen) was the main author of Papers II-V. In Paper I Nurmesniemi’s main contribution was writing the section dealing with precipitation.
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1 Introduction

1.1 Sulphate in mine waters

Exposure of sulphide minerals in rocks to oxygen and water results in the production of environmentally harmful mine water that is acidic and has high concentrations of sulphate and metals (Akcil & Koldas, 2006; Bowell, 2004; Brown, Barley, & Wood, 2002). Such mine water is termed acid mine drainage (AMD). Gray (1997) has summarised the main polluting effects of AMD as acidity, salinisation, metal toxicity and sedimentation processes. Reactions for the oxidation of the sulphide mineral pyrite (FeS₂) are the most well-known (Fernando, Ilankoon, I M S K, Syed, & Yellishetty, 2018). When pyrite is exposed to oxygen and water, iron leaches out of pyrite in the ferrous state and sulphidic sulphur becomes oxidized to sulphate (eq. 1) (Nordstrom & Alpers, 1999). The sulphur present in pyrite oxidises more rapidly than iron (Nordstrom & Alpers, 1999). The formation of elemental sulphur is a possible side reaction of pyrite oxidation, but the yield is low at ambient temperature (Nordstrom & Alpers, 1999). The formation of intermediate sulpho-oxyanions such as thiosulphate (S₂O₃²⁻), polythionates (S₆O₃²⁻), and sulphite (SO₃⁻), which will oxidise into sulphate, is also possible (Nordstrom & Alpers, 1999).

\[
FeS_2(s) + \frac{1}{2} O_2(aq) + H_2O(l) \rightleftharpoons Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 2H^+(aq) \tag{1}
\]

Ferrous iron can subsequently be oxidised to ferric iron (eq. 2) (Lottermoser, 2010). At pH values above 4, the oxidation reaction can be mediated by iron-oxidising bacteria (Lottermoser, 2010).

\[
4Fe^{2+}(aq) + O_2(g) + 4H^+(aq) \rightleftharpoons 4Fe^{3+} + 2H_2O(l) \tag{2}
\]

The rate of pyrite oxidation is influenced by the pH value of the solution in contact with the pyrite (Lottermoser, 2010). Under low to neutral pH conditions ferric iron acts as an oxidiser and oxidises pyrite indirectly (eq. 3) (Lottermoser, 2010). Usually, the main oxidant in pyrite oxidation is ferric iron (Johnson & Hallberg, 2005). The oxidation of pyrite with ferric iron is significantly faster than that with oxygen as the oxidant (Nordstrom & Alpers, 1999).

\[
FeS_2(s) + 14Fe^{3+}(aq) + 8H_2O(l) \rightleftharpoons 15Fe^{2+}(aq) + 2SO_4^{2-}(aq) + 16H^+(aq) \tag{3}
\]
At pH values above 3, ferric iron can precipitate as ferric hydroxide through hydrolysis producing hydrogen acidity (eq. 4) (Lottermoser, 2010).

\[Fe^{3+}(aq) + 3H_2O(l) \rightleftharpoons Fe(OH)_3(s) + 3H^+(aq) \quad (4)\]

AMD is produced both in active mines and after mine closure (Johnson & Hallberg, 2005) and may contain > 10 000 mgL\(^{-1}\) of sulphate (Bowell, 2004; Brown et al., 2002).

Sulphate affects aquatic ecosystems directly and indirectly (Gray, 1997). It causes freshwater salinisation which is detrimental to freshwater organisms that can tolerate only certain levels of water salinity (Cañedo-Argüelles et al., 2013). Sulphate can cause laxative effects when drinking water with high levels of sulphate is ingested (Backer, Esteban, Rubin, Kieszak, & McGeehin, 2001). In addition, dense, sulphate-rich mine discharge water can result in permanent stratification i.e. meromixis of receiving lake which influences aspects such as the nutrient and oxygen transfer within the lake (Boehrer & Schultze, 2008; Moncur, Ptacek, Blowes, & Jambor, 2006). Sulphate can be microbially reduced to sulphide by sulphate reducing bacteria (SRB). There is also a threat that SRB can mediate mercury methylation producing methylmercury which is the most toxic form of mercury (Åkerblom et al., 2013; Jeremiasen et al., 2006; King, Kostka, Frischer, Saunders, & Jahnke, 2001). Sulphide causes toxicity via the formation of hydrogen sulphide (Benatti, Tavares, & Lenzi, 2009). Sulphides can also accumulate in sediments and affect the environment via sedimentation processes (Gray, 1997). Anoxic sulphate-rich environments are also corrosive due to the corrosive hydrogen sulphide formed by action of SRB (Enning & Garrels, 2014). Certain SRB strains can also corrode iron by direct electron uptake (Enning & Garrels, 2014). Eh and pH conditions control the hydrolysis speciation of sulphate and sulphide (Fig. 1). Sulphate is the dominant form in oxidising conditions (positive redox potential values), while sulphide is dominant in reducing conditions (negative redox potential values). Fig. 2 presents sulphate hydrolysis speciation as a function of the pH. At pH > 2, SO\(_4^{2-}\) is the dominant species while at pH < 2 the dominant species is HSO\(_4^-\).

The first step in protecting the environment from the aqueous sulphate emissions should be the prevention of formation of AMD and sulphate-containing process waste water through the management of rock waste and tailings, and optimising process conditions (Kefeni, Msagati, & Mamba, 2017). Once formed, the sulphate-containing mine waters should be managed and treated properly (Kefeni et al., 2017). The treatment of sulphate-containing mine waters should
focus on the recovery of valuable materials in addition to sulphate removal (Nleya, Simate, & Ndlovu, 2016).

Fig. 1. Eh/pH diagram of hydrolysis speciation of sulphate and sulphide at 25 °C (HSC Chemistry software).
1.2 Sulphate discharge from mine sites

More attention has been paid to limiting metal containing water emissions than sulphate emissions (Bowell, 2004; Silva, Lima, & Leão, 2012). Not until recent decades have authorities in Finland set limits for sulphate emissions in mine discharge water. In Finland, these limits are specific to each mine and are defined in the relevant environmental permissions. At present, the limits for sulphate discharge vary between 1000 and 4000 mg L$^{-1}$. However, there are still currently operational sulphide ore mines in Finland without sulphate emission limits. The amount of sulphate is also limited indirectly by regulating the amount of total dissolved solids in which, being usually the dominant anion in mine waters, sulphate is as a major contributor (Alpers & Nordstrom, 1999; Lorax Environmental, 2003).
1.3 Sulphate removal technologies

Sulphate removal technologies can be classified as active or passive. Active technologies require continuous addition of chemicals, as well as maintenance and monitoring whereas passive technologies utilise natural water flow along with natural chemical and biological processes (Lottermoser, 2010). Active methods for sulphate removal from mine waters include precipitation as gypsum (Aubé & Lee, 2015; Geldenhuyys, Maree, De Beer, & Hlabela, 2003; Maree, De Beer, Strydom, Christie, & Waanders, 2004), ettringite (Dou et al., 2017; Madzivire, Petrik, Gitari, Ojumu, & Balfour, 2010; Sapsford & Tufvesson, 2017; Smit, 1999) or barite (Bologo, Maree, & Carlsson, 2012; Hlabela, Maree, & Bruinsma, 2007; Kefeni, Msagati, Maree, & Mamba, 2015; Maila, Maree, & Cele, 2014; Maree et al., 2004), adsorption (various materials have been studied but no commercial adsorbents available yet), ion-exchange (GYP-CIX and Sulf-IX processes (Fernando et al., 2018; Lorax Environmental, 2003)), active biological treatment processes (sulphidogenic bioreactors (Nancucheo et al., 2017)) and membrane technologies (Bódalo, Gómez, Gómez, León, & Tejera, 2004; Buzzi, Viegas, Rodrigues, Bernardes, & Tenório, 2013; Visser, Modise, Krieg, & Keizer, 2001).

Constructed or natural wetlands, and bioreactors are passive sulphate removal technologies (Skousen et al., 2017). However, all these technologies have drawbacks and in some cases a combination of technologies is needed to reach the target sulphate limit. In many cases mine water treatment with lime is suitable at least as a pre-treatment. Sulphate removal technologies are described in more detail in Paper I.
1.4 Objectives and scope

The main scope of this thesis was to enhance the available knowledge regarding sulphate removal by lime based chemical precipitation. The main objectives of this research were:

1. to study the effect of magnesium on partial sulphate removal from mine water as gypsum (Paper II)
2. to investigate the replacement of lime with by-products from quicklime manufacturing as neutralising agents in AMD treatment (Paper III)
3. to study sulphate removal from mine water as ettringite with enhanced lime treatment (Paper IV)
4. to study the utilisation of the formed ettringite precipitate as an arsenate sorbent (Paper V)
2 Chemical precipitation with lime

Chemical precipitation with quicklime (CaO) or hydrated lime (Ca(OH)\(_2\)) for neutralisation, removal of metals, and partial removal of sulphates (eq. 5-7 respectively (Lottermoser, 2010)) has been used for decades for the treatment of mine waters (Aubé & Lee, 2015; Bosman, 1983; Brown et al., 2002; Chen Ming et al., 2009; Geldenhuys et al., 2003; Throop, 1981). Alkaline slurry, which is typically made of quicklime slaked with water is added to raise the pH of water to approximately 9.5 and the metals precipitate primarily as hydroxides according to their specific pH values. Limestone (CaCO\(_3\)) is also used for minewater neutralization but it can raise the pH of mine water only up to a value of approximately 7 (Maree & Du Plessis, 1994; Maree et al., 2004). Partial sulphate removal occurs through the precipitation of gypsum (CaSO\(_4\cdot2\)H\(_2\)O) (Geldenhuys et al., 2003). However, mine water can contain up to thousands of milligrams per litre of sodium and magnesium. Metals precipitate as hydroxides rapidly while the precipitation of gypsum is slow (Aubé & Lee, 2015).

\[
\begin{align*}
Ca(OH)_2(s) + 2H^+(aq) & \rightarrow Ca^{2+}(aq) + 2H_2O(l) \\
Ca(OH)_2(s) + Me^{2+}(aq) & \rightarrow Me(OH)_2(s) + Ca^{2+}(aq) \\
Ca^{2+}(aq) + SO_4^{2-}(aq) + 2H_2O(l) & \rightarrow CaSO_4 \cdot 2H_2O(s)
\end{align*}
\] (5) (6) (7)

Precipitation with quicklime or hydrated lime is effective for the treatment of highly acidic mine waters, barely affected by temperature fluctuations and the process is relatively simple (Brown et al., 2002). However, lime precipitation produces a large amount of sludge with limited utilisation possibilities, high water content and difficulties in dewatering, high sludge disposal costs and plugging of equipment and pipelines (Chen Ming et al., 2009; Lorax Environmental, 2003; Matlock, Howerton, & Atwood, 2002). Dewatering of the sludge and floc strength can be improved using polymers such as polyacrylamides and polyamines. Mine water precipitation with lime typically produces sludge that has a solids content of only 2-6% (Throop, 1981). The high density sludge (HDS) process has been developed for obtaining sludges with 15-50% solids contents (Aubé & Lee, 2015; Kalin, Fyson, & Wheeler, 2006; Kostenbader & Haines, 1970). In the HDS process, a part of the sludge is recycled and mixed with lime slurry prior to neutralization (Kostenbader & Haines, 1970). In the HDS process, the precipitates form on the recycled particles creating larger and denser particles that can be more easily settled and dewatered (Aubé & Lee, 2015).
2.1 Effect of magnesium on lime precipitation

Even though, lime precipitation has been used for mine water treatment for decades, the effect of solution conditions on the process is not adequately known. In addition, more attention has been paid to the efficient removal of metals rather than sulphate with lime precipitation. There is an urgent need for more information regarding the effect of solution conditions on lime precipitation to facilitate process optimization that could drastically improve material and process efficiency.

It has been found that by gypsum crystallisation, in the presence of Mg$^{2+}$, more sulphate remains in solution due to high solubility of MgSO$_4$ (Maree et al., 2004). Geldenhuys et al. (2003) have reported the solubility of gypsum as 1500 mg L$^{-1}$ when no Na$^+$ or Mg$^{2+}$ ions were present. Tait et al. (2009) have performed gypsum crystallisation laboratory experiments and aqueous equilibria simulations with and without the effects of ion activity and ion association. They found the specific ion association of sulphate with magnesium to be more influential than the interaction with sodium. Other ions in a solution usually increase the solubility of a solid by reducing the activity of the ions contributing to the dissolution-precipitation reaction (Domenico & Schwartz, 1998) via the salt effect (Petrucci, 2011). Tait et al. (2009) have experimentally observed that impurities in wastewater inhibit gypsum nucleation and increase the solubility of gypsum.

Geldenhuys et al. (2003) have reported the reduction of sulphate concentration to less than 1500 mg L$^{-1}$ with high pH (>11) lime treatment due to the precipitation of magnesium and removal of the associated sulphate fraction. Particulate contaminants can have a catalytic effect on nucleation owing to a decrease in the energy barrier to nucleation (Myerson, Myerson, & Myerson, 2002). Rashad et al. (2004) have studied the effect of Al$^{3+}$ and Mg$^{2+}$ ions on gypsum crystallisation under simulated conditions of phosphoric acid manufacturing. They have observed a higher nucleation rate in the presence of 1% MgO (Rashad et al., 2004). van Vuuren et al. (1967) have reported that magnesium hydroxide acted as nuclei for suspended CaCO$_3$ and that the magnesium hydroxide floc structure was suitable for the adsorption of CaCO$_3$ that would otherwise remain in suspension. Mg(OH)$_2$ precipitate has a large adsorptive surface area and a positive superficial charge (Leentvaar & Rehun, 1982; Semerjian & Ayoub, 2003). The isolectric point (point of zero charge) of magnesium hydroxide is at pH > 12 (Ferguson & Vrale, 1984). Donnert and Salecker (1999) have studied phosphorus removal from waste water by precipitation as calcium phosphate using MgO as seeding material. At pH > 10.5 magnesium has been experimentally found to improve total organic carbon
removal by lime treatment as well (Leentvaar & Rebhun, 1982). In Paper II the effect of magnesium on the removal of sulphate from mine water with precipitation as gypsum was investigated both experimentally and computationally.

2.2 Replacing lime with industrial by-products

The emergence of circular economy thinking has sparked interest towards the utilisation of industrial by-products that would otherwise be treated as waste. The underlying idea here is that the waste from one industry or process could be a valuable resource in another. European Union waste legislation guides to prevent waste as prioritised waste management followed by reuse, recycling, other recovery, and as a last option disposal (Directive 2008/98/EC, Article 4). Reuse of waste is both ecological and economical due to reduced amount of waste and reduced chemical and waste disposal costs. Different alkaline by-products have been studied for potential application to mine water treatment including alkaline waste materials from the alumina refining industry (Kaur, Couperthwaite, Hatton-Jones, & Millar, 2018), coal fly ash (Gitari et al., 2006; Kumar Vadapalli et al., 2008; Madzivire, Gitari, Vadapalli, Ojumu, & Petrik, 2011), wood ash (Heviánková, Bestová, & Kyncl, 2014), metallurgical slag (Name & Sheridan, 2014), and cement kiln dust (A. Mackie, Farmer, & Walsh, 2010; A. Mackie, Boilard, Walsh, & Lake, 2010; A. L. Mackie & Walsh, 2012; A. L. Mackie & Walsh, 2015). The use of by-products from quicklime manufacturing for the neutralisation of mine water was studied in Paper III.

2.3 Enhanced lime precipitation

Sulphate precipitation as ettringite \([\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_12\cdot26\text{H}_2\text{O}]\) (eq. 8) (Myneni, Traina, & Logan, 1998a) is a modification of the high pH (> 11) lime precipitation process (Geldenhuys et al., 2003). With precipitation as ettringite, sulphate concentration in mine water can be reduced to less than 200 mg L\(^{-1}\) i.e. less than the drinking water guideline in Finland which is 250 mg L\(^{-1}\) sulphate (Asetus 683/2017, 4 § ; Council directive 98/83/EC, Article 5). A decrease in sulphate removal efficiency by precipitation as ettringite in the presence of Mg\(^{2+}\) has been reported (Dou et al., 2017). This is due to Mg\(^{2+}\) competing with Ca\(^{2+}\) and hydrotalcite-type compounds \([\text{Mg}_6\text{Al}_2\text{SO}_4(\text{OH})_{16}\cdot\text{nH}_2\text{O}]\) rather than ettringite is formed. When precipitation as ettringite is used for waters with high sulphate concentration (>3000 mg L\(^{-1}\)), it may be economical to use traditional lime
precipitation (a pH of approximately 9.5) as a pre-treatment. In the pre-treatment step, a part of the sulphate and metals are precipitated as gypsum and metal hydroxides, respectively. Pre-treated mine waters require only a smaller dosage of aluminium salt in the ettringite precipitation step, improving process economy as aluminium chemicals are considerably more expensive than lime.

\[
6Ca^{2+}(aq) + 2Al^{3+}(aq) + 3SO_4^{2-}(aq) + 12OH^- (aq) + 26H_2O(l) \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O(s)
\]  

(8)

The basic idea is that the pH of the water is raised to approximately 12 using lime. Ettringite is stable at pH values of approximately 10.7-12.5 (Myneni, Traina, & Logan, 1998b). Thereafter, aluminium salt is added, leading to the precipitation of ettringite. Sodium aluminate, aluminium hydroxide, aluminium chloride, aluminium nitrate and polyaluminium chloride have been used for ettringite precipitation (Sapsford & Tufvesson, 2017). Additionally, the applicability of industrial aluminium containing wastewaters has been studied (Álvarez-Ayuso & Nugteren, 2005). Electrocoagulation as well can be used to produce aluminium ions in the ettringite precipitation process (AU20170201329 20170227, 2017). The applied aluminium salt has been found to affect sludge volume and sludge settling velocity (Sapsford & Tufvesson, 2017). The ettringite sludges produced are voluminous but denser sludges can be obtained by recycling some of the sludge by methods such as using the HDS process (Sapsford & Tufvesson, 2017). Polymers, such as polyacrylamides and polyamines, can also be used to dewater and improve the floc strength of the precipitate. The purified water can be treated with CO₂ to lower the pH into discharge limits precipitating calcite (CaCO₃). Different versions of the process of precipitation as ettringite have been patented (FI20120005884 20120827, 2014; ZA19980004724 19980602, 1999). Additionally, several similar processes, such as ultra-high lime with aluminium (UHLA) (Abdel-Wahab & Batchelor, 2011), SAVMIN (Smit, 1999) and alumina-lime-soda process (Nebgen, Weatherman, Valentine, & Shea, 1976) have been documented. In Papers IV and V, the removal of sulphate from mine water by precipitation as ettringite using sodium aluminate was studied and the results were compared with computational results.

2.4 Utilisation of the sludge formed

In the traditional lime treatment of mine water, large amounts of gypsum sludge are formed with only limited options for usage. Usually, the sludge is stored in settling ponds (Keefer & Sack, 1983). However, a preferable disposal approach would be
its utilisation for the manufacture of paste backfill (Rakotonimaro, Neculita, Bussière, Benzaazoua, & Zagury, 2017). Reuse as substitute materials in cement manufacturing could also be an option, but the metal content limits the possibilities for utilisation of the sludge (Rakotonimaro et al., 2017). Mine water typically contains metals and the metals precipitate into the sludge during mine water treatment with lime. Still, the metal recovery from the gypsum sludge is not usually economically feasible (Rakotonimaro et al., 2017).

The recycling of ettringite sludge is more cost-effective as aluminium reagents are more expensive than lime. The precipitated ettringite can be decomposed to regenerate aluminium (Smit, 1999). Another possibility could be the usage of the precipitated ettringite as a sorbent for pollutants such as arsenic, which could offer savings in waste disposal, and a source of income. More information regarding arsenic as a pollutant can be found in Papers IV and V.

Myneni et al. (1998b) investigated the sorption of arsenate to ettringite. Ettringite can sorb arsenate by two mechanisms: through interactions with the surface functional groups by ligand exchange or by substitution into ettringite channels with the displacement of sulphate by anion exchange (Myneni, Traina, Logan, & Waychunas, 1997). Figure 3. shows the ettringite structure that consists of \{Ca₆[Al(OH₆)]₂·2₄H₂O\} columns with channels between them, which are occupied by sulphate and water molecules (Myneni, Traina, Waychunas, & Logan, 1998). Sulphate removal from mine water with precipitation as ettringite and further utilisation of the precipitate as arsenate sorbent was investigated in Papers IV and V.

**Fig. 3.** Ettringite structure projection along the c axis the needle axis illustrated using Vesta software based on X-ray diffraction (XRD) data documented by Moore and Taylor (1968). Calcium-coordinated water molecules are unlabelled.
3 Materials and methods

3.1 Samples

3.1.1 Neutralised enrichment plant process waste water

The mine water used for studies concerning the effect of magnesium on the partial removal of sulphate as gypsum was sampled from the neutralised process waste water from the enrichment plant of an operational gold mine (Paper II). At the mine site pH is adjusted to 8.7 using lime to precipitate most metals as hydroxides. The balance of major cations and anions of the neutralised enrichment plant process waste water is presented in Table 1. The water contained mainly sulphate and magnesium which made it suitable for investigating the effect of magnesium on the partial removal of sulphate as gypsum.

Table 1. Balance of major cations and anions in the neutralised enrichment plant process waste water.

<table>
<thead>
<tr>
<th>Cation</th>
<th>[meq·L⁻¹]</th>
<th>Anion</th>
<th>[meq·L⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca²⁺</td>
<td>21.16</td>
<td>SO₄²⁻</td>
<td>193.8</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>178.53</td>
<td>Cl⁻</td>
<td>6.5x10⁻¹</td>
</tr>
<tr>
<td>Na⁺</td>
<td>7.57</td>
<td>NO₃⁻</td>
<td>7.3x10⁻¹</td>
</tr>
<tr>
<td>Total</td>
<td>207.26</td>
<td>Total</td>
<td>195.2</td>
</tr>
</tbody>
</table>

3.1.2 AMD from copper-zinc mine

The mine water sample for the precipitation experiments using by-products, quicklime, and hydrated lime, was AMD which was pumped from the underground workings of an operational copper-zinc mine located in Finland (Paper III). The pH of the AMD sample was 2.6. Table 2 shows the balance of major cations and anions of the AMD sample.
Table 2. Balance of major cations and anions in the AMD sample.

<table>
<thead>
<tr>
<th>Cation</th>
<th>[meqL⁻¹]</th>
<th>Anion</th>
<th>[meqL⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al³⁺</td>
<td>40</td>
<td>SO⁴⁻</td>
<td>155.9</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>25</td>
<td>Cl⁻</td>
<td>13.0</td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>23.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>63.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>6.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>12.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>171.6</td>
<td>Total</td>
<td>168.9</td>
</tr>
</tbody>
</table>

3.1.3 Drainage water from gold mine

The mine effluent sample used in the ettringite precipitation experiments was drainage water from an underground gold mine with pH approximately 7.9 (Papers IV and V). The drainage water was treated with ferric sulphate at the mine site and sampled after allowing it to settle in a settling pond. The initial sulphate concentration of the mine drainage water was 1400 mg L⁻¹.

3.1.4 By-products from quicklime manufacturing

Samples of four by-products denoted as BP A to BP D from quicklime manufacturing were collected from two lime plants located in Finland (Paper III). BP A was partly burnt lime stored outdoors while BP B was also partly burnt lime but that was stored in a silo. Partly burnt lime, which is a mixture of limestone and quicklime, is produced in fault situations and during kiln power-up. BP C was kiln dust, which is the dust collected using a fabric filter during quicklime manufacturing, whereas BP D was a mixture of BP A and dolomite. Present application options for these by-products are limited, and they are mainly stored onsite. Table 3 shows the amounts of total lime and free lime in the by-products, quicklime, and hydrated lime as reported by the manufacturer. Free lime is the amount of CaO available for reaction and is measured by titration according to the standard ASTM C-25 (ASTM International, 2011). Total lime includes free lime and also CaO that is bonded to calcium carbonate (CaCO₃) and was determined with X-ray fluorescence (XRF).
Table 3. Percentages of total lime and free lime in by-products, quicklime, and hydrated lime as reported by the manufacturer.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total lime (%)</th>
<th>Free lime (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP A</td>
<td>54</td>
<td>14</td>
</tr>
<tr>
<td>BP B</td>
<td>87</td>
<td>75</td>
</tr>
<tr>
<td>BP C</td>
<td>48</td>
<td>10</td>
</tr>
<tr>
<td>BP D</td>
<td>not reported</td>
<td>not reported</td>
</tr>
<tr>
<td>Quicklime</td>
<td>94</td>
<td>91</td>
</tr>
<tr>
<td>Hydrated lime</td>
<td>73</td>
<td>71</td>
</tr>
</tbody>
</table>

3.2 Analytical methods

3.2.1 Water samples

Anions were analysed with ion chromatography (IC) according to standard SFS-EN ISO 10304-1 (Finnish standards association, 2007a). Elements were analysed with inductively coupled plasma optical emission spectrometry (ICP-OES) according to the standard SFS-EN ISO 11885 (Finnish standards association, 2007b), inductively coupled plasma mass spectrometry (ICP-MS) (Paper II), and atomic absorption spectrometry according to SFS 3018 (Finnish standards association, 1982) (Paper II).

3.2.2 Solid samples

The sludge samples were analysed with PANanalytical X-ray diffraction (XRD) equipment with Cu Kα at 40 mA and 45 kV (Papers II-V), and electron probe microanalysis (EPMA) (Paper IV). Scanning electron microscopy (SEM) images of by-products, quicklime, hydrated lime, and sludges were obtained using a Zeiss Ultra plus field emission SEM equipment at the Centre of Microscopy and Nanotechnology in the University of Oulu operated at 5 kV (Papers III-IV). The amount of sludge was estimated from the graduation marks on the test jars (Paper III). Particle size distributions of by-products, quicklime and hydrated lime were determined using an Alpine Air Jet Sieve e200LS (Paper III).
3.3 Precipitation experiments

Experiments were performed using jar test equipment (Kemira Flocculator 2000) in which an AMD sample volume of 800 mL was used for each jar (Fig. 4). Experiments were conducted at room temperature (20 ± 2 °C). Slurries that were 10% by weight were made for each of the by-products, quicklime and hydrated lime by dissolution into ultra-purified water. The appropriate amount of slurry was then added to raise the pH of the AMD sample to the desired value. Sodium aluminate and polymers were added experiment-dependently. Next, the sample was mixed at predetermined speeds and durations and then left to settle for a predetermined time. Water samples from the effluent were taken for analysis and the precipitates were filtered by vacuum filtration. Subsequently, the precipitate samples were air-dried, weighed, crushed, sieved, and stored in a desiccator prior to analysis. A more detailed description of the precipitation experiments can be found in Papers II-V.

3.4 Sorption experiments

3.4.1 Batch experiments

The effect of the sorbent dosage and initial arsenate concentration on arsenate removal from a synthetic arsenate solution was studied via 24 h batch sorption tests using a reciprocal shaker at room temperature (20 ± 2 °C) (Papers IV and V). An arsenate model solution was prepared by dissolving arsenic(V) oxide (Acros Organics 99.9+ %) in ultrapure water. Then, an appropriate amount of the
synthesised ettringite was dosed into the arsenate model solution having a predetermined initial arsenate concentration and agitated at 250 rpm for 24 h in a reciprocal shaker (POL-EKO LS 700). After shaking, the samples were centrifuged at 4000 rpm for 5 min in a Thermo Scientific SL 8 Centrifuge, after which the supernatant pH was measured. The supernatant was saved for arsenic analysis. The used sorbent was filtered with a Sartorius Stedim Biotech cellulose nitrate membrane filter with 0.45 µm pore size by vacuum filtration, and then it was air-dried and stored in a desiccator before analysis.

The effect of contact time on arsenate removal by sorption on ettringite was also studied (Paper V). One litre of the 1.8 mgL\(^{-1}\) arsenate model solution was stirred at 250 rpm in a 2 L glass beaker with a magnetic stirrer, and 1 gL\(^{-1}\) of ettringite was dosed into the solution. Samples were taken at 0, 1, 3, 5, 7, 10, 30 minutes, as well as 1, 2, and 5 hours after ettringite addition. The samples were centrifuged for 1 min at 4000 rpm, and the supernatant was saved for arsenic analysis.

### 3.4.2 Isotherms

Langmuir (1918), Freundlich (1906), and Langmuir-Freundlich (Sips, 1948) isotherm models were fitted using OriginPro software to the experimental data. The Langmuir, Freundlich, and Langmuir-Freundlich isotherms are represented by equations 9-11, respectively. The Langmuir isotherm model assumes monolayer sorption that occurs on a homogenous surface with no interactions between sorbates. The Freundlich isotherm model is empirical and assumes that sorption occurs on a heterogeneous surface. The Langmuir-Freundlich isotherm is a combined form of the Langmuir and Freundlich isotherms. At low adsorbate concentrations it reduces to the Freundlich isotherm, and at high adsorbate concentrations it reduces to the Langmuir isotherm.

\[
qe = \frac{qm b c_e}{1 + b c_e} \quad (9)
\]

\[
qe = K c_e^n \quad (10)
\]

\[
qe = \frac{qm (b c_e)^n}{1 + (b c_e)^n} \quad (11)
\]

where \(q_e\) (mgg\(^{-1}\)) is the amount of arsenate sorbed on ettringite at equilibrium, \(q_m\) (mgg\(^{-1}\)) the isotherm constant relating to maximum sorption capacity, \(b\) (Lmg\(^{-1}\)) the isotherm constant related to energy of sorption, \(c_e\) (mgL\(^{-1}\)) equilibrium solution concentration.
concentration, \( K \) ((mg g\(^{-1}\))/(mg L\(^{-1}\))\(^{n-1}\)) the isotherm constant related to sorption capacity, and \( n^{-1} \) the isotherm constant related to intensity of sorption. The fit of each isotherm model to experimental data was compared according to the adjusted correlation coefficient \( R_{adj}^2 \) values.

### 3.4.3 Kinetics

The pseudo-first order kinetic model (Lagergren, 1898) and the pseudo-second order kinetic model (Ho & McKay, 1999) are represented by equations 12 and 13, respectively.

\[
q_t = q_e(1 - e^{-k_1 t}) \tag{12}
\]

\[
q_t = \frac{k_2 q_e^2 t}{1+k_2 q_e t} \tag{13}
\]

where \( k_1 \) (min\(^{-1}\)) is the pseudo-first order rate constant, \( k_2 \) (g(mg min\(^{-1}\))\(^{-1}\)) the pseudo-second order rate constant, \( q_e \) (mg g\(^{-1}\)) the amount of arsenate sorbed on ettringite at equilibrium and \( q_t \) (mg g\(^{-1}\)) the amount of arsenate sorbed on ettringite at time \( t \) (min). The fit of the models to experimental data was evaluated by comparing the adjusted correlation coefficient \( R_{adj}^2 \) values.

### 3.5 Chemical equilibrium calculations

Speciation calculations were performed using MINEQL+ version 4.5 and HSC Chemistry version 7.1 (Outotec 2011) which are computer programs for thermodynamic calculations. MINEQL+ solves mass balance calculations by the Newton-Raphson method using equilibrium constants from a thermodynamic database. HSC Chemistry program calculates equilibrium composition in isothermal and isobaric conditions utilising the Gibbs energy minimisation method. The temperature used in the calculations was 25 °C. Calculations were used to model magnesium and sulphate speciation at pH values of 9.6 and 12.5 (Paper II). The saturation index (SI) for brucite (Mg(OH)\(_2\)) as a function of the pH was also obtained using the MINEQL+ software (Paper II). In Paper II, the ionic strength was calculated with MINEQL+ program and the Davies equation was used for the correction of equilibrium constants for ionic strength. Calculations using HSC Chemistry software were used to model the dependence of sulphate and sulphide as well as arsenate and arsenite hydrolysis speciation on Eh and pH conditions.
(Paper IV). Sulphate and arsenate hydrolysis speciation were calculated without ionic strength correction as a function of pH using MINEQL+ software (Paper IV). In addition, calculations without ionic strength correction using MINEQL+ were used to model sulphate, nitrate, aluminium, sodium and calcium speciation (Paper IV).
4 Results

4.1 Effect of magnesium on sulphate removal (Paper II)

The effect of magnesium on sulphate removal from mine water with lime treatment was investigated by conducting batch precipitation experiments and modelling the precipitation conditions. The effect of magnesium on sulphate removal with lime was studied, and the influence of treatment pH was found to be of critical importance.

According to the calculations at pH 9.6 19% of magnesium was in the form of magnesium sulphate (MgSO₄) (Fig. 5) which has considerably higher solubility than calcium sulphate (–logK values for MgSO₄·7H₂O and CaSO₄·2H₂O are 2.127 and 4.610 respectively) (MINEQL+ v. 4.6). At pH 9.6, sulphate removal was ineffective due to magnesium that was maintaining sulphate in the soluble form as magnesium sulphate and probably also by increasing the solubility of gypsum via the salt effect. At pH 9.6, calculations indicated that 99% of the sulphate was in a soluble form (Fig. 6).
At pH 12.5, modelling predicted all the magnesium being precipitated as brucite (Fig. 5), no longer keeping sulphate in a soluble form as magnesium sulphate. The XRD analysis of a sample taken after 1 min of rapid mixing at pH 12.5 confirmed the formation of brucite crystals (Fig. 7). From the XRD spectrum gypsum (ICDD 04-009-3817) and brucite (ICDD 04-015-9383) peaks were identified. Brucite crystals were smaller than gypsum crystals, which were observed as wider peaks in
the XRD pattern. At pH 12.5, 84% of the sulphate had precipitated as gypsum according to the speciation calculation (Fig. 6).

Fig. 7. XRD spectrum of a sample taken after 1 min rapid mixing at pH 12.5.

The computational results corresponded well with the experimental results (Fig. 8) with the difference being 20% or less for sulphate and 1.4% or less for magnesium. The measurement error of sulphate analysis was estimated to be 10% as reported by an accredited laboratory for IC analysis according to standard SFS-EN ISO 10304-1 (Finnish standards association, 2007a). Both experimental and computational studies showed that sulphate removal from the tested mine water was efficient at pH 12.5. However, at pH 9.6 the sulphate removal was inefficient probably due to the magnesium originally present in the mine water.
4.2 Replacing lime with industrial by-products (Paper III)

The possibility of using alkaline by-products (defined in section 3.1.4) from quicklime manufacturing instead of commercial quicklime and hydrated lime for mine water neutralisation was studied using batch precipitation tests. The efficiency of the by-products was evaluated based on required dosage as well as metal and sulphate removal compared with quicklime and hydrated lime. For predicting the suitability of the by-products for mine water neutralisation the sludge quality was also taken into account.

The by-product dosage varied from 1.2 (BP A) to 7.3 (BP C) times the amount of quicklime and 1 (BP A) to 6.5 (BP C) times the amount of hydrated lime needed (Table 4). Although the required dosages of BP A and BP D were slightly higher than those of quicklime and hydrated lime, sludge properties turned out to be more beneficial. The by-products A and B produced less sludge by volume and mass than quicklime or hydrated lime. Despite the highest dosage, the smallest volume of sludge was gained by using BP C. The sludge dry mass of BP C was almost three times that of the sludge of quicklime and hydrated lime. The high solids content of sludge BP C could be an advantage because of cost savings in sludge dewatering. The sludge volume of BP D was the highest and the sludge dry mass was almost 2.5 times the sludge of quicklime and hydrated lime.
Table 4. Added 10% slurry volumes to 800 mL of AMD to raise the pH from 2.6 to 9.5 and sludge volumes, dry masses, solids contents and densities after settling.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added slurry volume (mL)</th>
<th>Sludge volume (mL)</th>
<th>Sludge dry mass (g)</th>
<th>Sludge solids content (g L⁻¹)</th>
<th>Sludge density (g L⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BP A</td>
<td>28.5</td>
<td>250</td>
<td>7.9</td>
<td>31.6</td>
<td>1032</td>
</tr>
<tr>
<td>BP B</td>
<td>32.5</td>
<td>225</td>
<td>8</td>
<td>35.6</td>
<td>1036</td>
</tr>
<tr>
<td>BP C</td>
<td>180</td>
<td>180</td>
<td>22.6</td>
<td>125.6</td>
<td>1126</td>
</tr>
<tr>
<td>BP D</td>
<td>110</td>
<td>400</td>
<td>19.3</td>
<td>48.3</td>
<td>1048</td>
</tr>
<tr>
<td>Quicklime</td>
<td>24.5</td>
<td>375</td>
<td>8.6</td>
<td>22.9</td>
<td>1023</td>
</tr>
</tbody>
</table>

All tested by-products as well as quicklime and hydrated lime removed over 99% of Al, As, Cd, Co, Cu, Fe, Mn, Ni and Zn but increased the amount of Ca (Table 5). By-product C which had the highest dosage added 2.5 times more Ca into the AMD than quicklime and hydrated lime. On average 46% of Mg was removed with the by-products, quicklime and hydrated lime. The adjustment of pH to 9.5 was too low to achieve complete Mg precipitation as hydroxide since the solubility product (\(-\log K_s\)) of brucite (Mg(OH)₂) is 11.16 (Stumm & Morgan, 1996). Na removal was very limited. All the tested by-products removed approximately 60% sulphate from the AMD (Fig. 9).

Table 5. Concentrations of elements of AMD before (pH 2.6) and after (pH 9.5) treatment with by-products (BP A-D), quicklime, and hydrated lime.

<table>
<thead>
<tr>
<th>Element</th>
<th>AMD (mg L⁻¹)</th>
<th>BP A</th>
<th>BP B</th>
<th>BP C</th>
<th>BP D</th>
<th>Quicklime</th>
<th>Hydrated lime</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>360</td>
<td>6.6 x 10⁻¹</td>
<td>8.8 x 10⁻¹</td>
<td>5.2 x 10⁻¹</td>
<td>6.6 x 10⁻¹</td>
<td>5.2 x 10⁻¹</td>
<td>5.3 x 10⁻¹</td>
</tr>
<tr>
<td>As</td>
<td>2.1 x 10⁻²</td>
<td>&lt; 1.5 x 10⁻³</td>
<td>&lt; 1.5 x 10⁻³</td>
<td>&lt; 1.5 x 10⁻³</td>
<td>&lt; 1.5 x 10⁻³</td>
<td>&lt; 1.5 x 10⁻³</td>
<td>&lt; 1.5 x 10⁻³</td>
</tr>
<tr>
<td>Ca</td>
<td>500</td>
<td>593</td>
<td>609</td>
<td>785</td>
<td>645</td>
<td>609</td>
<td>616</td>
</tr>
<tr>
<td>Cd</td>
<td>8.1 x 10⁻¹</td>
<td>6.0 x 10⁻¹</td>
<td>3.0 x 10⁻¹</td>
<td>&lt; 2.0 x 10⁻²</td>
<td>4.0 x 10⁻²</td>
<td>5.0 x 10⁻³</td>
<td>5.0 x 10⁻³</td>
</tr>
<tr>
<td>Co</td>
<td>5.3 x 10⁻¹</td>
<td>&lt; 3.0 x 10⁻³</td>
<td>&lt; 3.0 x 10⁻³</td>
<td>&lt; 3.0 x 10⁻³</td>
<td>&lt; 3.0 x 10⁻³</td>
<td>&lt; 3.0 x 10⁻³</td>
<td>&lt; 3.0 x 10⁻³</td>
</tr>
<tr>
<td>Cu</td>
<td>35.3</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
</tr>
<tr>
<td>Fe</td>
<td>443</td>
<td>&lt; 1.5 x 10⁻²</td>
<td>2.5 x 10⁻²</td>
<td>&lt; 1.5 x 10⁻²</td>
<td>&lt; 1.5 x 10⁻²</td>
<td>2.0 x 10⁻²</td>
<td>&lt; 1.5 x 10⁻²</td>
</tr>
<tr>
<td>Mg</td>
<td>771</td>
<td>478</td>
<td>359</td>
<td>401</td>
<td>387</td>
<td>446</td>
<td>419</td>
</tr>
<tr>
<td>Mn</td>
<td>29.3</td>
<td>2.1 x 10⁻¹</td>
<td>6.2 x 10⁻²</td>
<td>1.0 x 10⁻¹</td>
<td>1.4 x 10⁻¹</td>
<td>1.0 x 10⁻¹</td>
<td>1.2 x 10⁻¹</td>
</tr>
<tr>
<td>Na</td>
<td>158</td>
<td>151</td>
<td>150</td>
<td>152</td>
<td>138</td>
<td>152</td>
<td>152</td>
</tr>
<tr>
<td>Ni</td>
<td>1.26</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
<td>&lt; 5.0 x 10⁻³</td>
</tr>
<tr>
<td>Zn</td>
<td>410</td>
<td>1.1 x 10⁻²</td>
<td>&lt; 1.0 x 10⁻²</td>
<td>&lt; 1.0 x 10⁻²</td>
<td>1.3 x 10⁻²</td>
<td>1.8 x 10⁻²</td>
<td>1.2 x 10⁻²</td>
</tr>
</tbody>
</table>
4.3 Enhanced lime precipitation (Paper IV)

Sulphate removal from mine water with precipitation as ettringite with the purpose of further utilising the produced sludge was investigated using batch precipitation tests and modelling. Characterisation of the sludge was also done.

In the precipitation experiments, sulphate reduced by 85-90% from the 1400 mg/L initial concentration of mine water through the precipitation of ettringite (Fig. 10). This was even a higher amount than the 71% indicated by the modelling results (Fig. 11). Sodium and aluminum concentrations increased during treatment. In all precipitation experiments, the aqueous residual sodium and aluminum concentrations were below 285 mgL⁻¹ and 11 mgL⁻¹ respectively. Calcium concentration remained the same or even decreased during treatment from the initial value of 312 mgL⁻¹. Nitrate concentration decreased moderately during the treatment.

Extending the settling time from 1 h to overnight had no significant effect on water quality. However, the longer settling time resulted in denser sludge. Polymers improved the settling characteristics of the produced sludges. Ettringite (ICDD 00-041-1451) and calcite (ICDD 04-012-8072) peaks were identified from the XRD spectra of the precipitated solids. Full pattern quantitative Rietveld analysis showed
that the solids were 89-91% ettringite and 9-11% calcite (Fig. 12). Unidentified peaks were probably impurities from the mine water from which the solids precipitated. The presence of 9-11% calcite in the precipitates could have enhanced the settling by increasing the densities of the precipitates (Leentvaar & Rebhun, 1982).

Fig. 10. Sulphate removal from mine water by precipitation as ettringite. Error bars represent standard deviation (n = 2).
Fig. 11. Calcium, aluminum, sodium, sulphate, and nitrate speciation at pH 12.5 calculated with MINEQL+.
4.4 Utilisation of the sludge formed (Papers IV and V)

Arsenate sorption on the ettringite formed during sulphate removal from mine water by precipitation as ettringite was investigated with the aim of lowering waste disposal costs and the possibility of extracting value from mine water. Batch sorption experiments for studying the effect of ettringite dosage and contact time were conducted using arsenate model solutions and isotherm and kinetic models were fitted to the results data.
The precipitated solids from the treatment of mine water by precipitation as ettringite, which contained mainly (89-91%) ettringite, were further used as sorbents for arsenate removal. SEM analysis confirmed no change in the morphology of the sorbent before and after sorption, indicating that the sorbent was stable under the sorption experiment conditions (Fig. 13).

**Fig. 13.** SEM analysis of the sorbent before and after sorption.
The effect of ettringite dosage on arsenate removal was investigated and it was noted that the percentage of arsenate removal increased as the dosage of ettringite increased from 0 to 4 gL\(^{-1}\), and then stabilised. With an ettringite dosage of 4 gL\(^{-1}\), an arsenic concentration below the drinking water limit was obtained. However, the increase in sorption efficiency after a dosage of 1 gL\(^{-1}\) was quite moderate. Thus, the best arsenate removal from techno-economical point of view (90%) was obtained with an ettringite dosage of 1 gL\(^{-1}\). Langmuir and Freundlich isotherm models were fitted to the data obtained from the experiments on the effect of ettringite dosage on arsenate removal, and were found to fit equally well. The fit of the models was evaluated according to the adjusted correlation coefficient \(R_{adj}^2\) values (Table 6). The maximum sorption capacity obtained from the Langmuir isotherm was 1.8 ± 0.1 mgg\(^{-1}\), which was comparable to the maximum experimental sorption capacity 1.9 mgg\(^{-1}\).

### Table 6. Isotherm parameters from the experiments on the effect of ettringite dosage on arsenate removal.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Langmuir</th>
<th>Parameter</th>
<th>Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Q_{max})</td>
<td>1.835</td>
<td>(K)</td>
<td>1.844</td>
</tr>
<tr>
<td>Standard error of (Q_{max})</td>
<td>0.109</td>
<td>Standard error of (K)</td>
<td>0.101</td>
</tr>
<tr>
<td>(b)</td>
<td>17.616</td>
<td>(n)</td>
<td>2.914</td>
</tr>
<tr>
<td>Standard error of (b)</td>
<td>3.619</td>
<td>Standard error of (n)</td>
<td>0.249</td>
</tr>
<tr>
<td>(R^2)</td>
<td>0.943</td>
<td>(R^2)</td>
<td>0.937</td>
</tr>
<tr>
<td>(R_{adj}^2)</td>
<td>0.938</td>
<td>(R_{adj}^2)</td>
<td>0.932</td>
</tr>
<tr>
<td>reduced chi-square</td>
<td>0.022</td>
<td>reduced chi-square</td>
<td>0.024</td>
</tr>
<tr>
<td>residual sum of squares</td>
<td>0.259</td>
<td>residual sum of squares</td>
<td>0.284</td>
</tr>
<tr>
<td>root mean square error</td>
<td>0.147</td>
<td>root mean square error</td>
<td>0.154</td>
</tr>
</tbody>
</table>

Additionally, the effect of the initial arsenate concentration on the sorption of arsenate on the precipitate was studied. The percentage of arsenate removal decreased as the initial arsenate concentration increased because of the saturation of the sorption sites on the surface of the precipitate. However, the sorption capacity increased as the initial arsenate concentration increased owing to the increase of the driving force for mass transfer due to the concentration gradient. The Freundlich and Langmuir-Freundlich isotherms were found to fit the experimental sorption data the best. The maximum arsenate sorption capacity \((q_{max} = 11.2 ± 4.7 \text{ mgg}^{-1})\) of the precipitate was obtained from the Langmuir-Freundlich isotherm and was in accordance with the experimental maximum sorption capacity value 6.6 mgg\(^{-1}\). The isotherm parameters are shown in Table 7.
Table 7. Isotherm parameters from the experiments on the effect of initial arsenate solution concentration on the sorption of arsenate on ettringite.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Freundlich</th>
<th>Langmuir-Freundlich</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K$</td>
<td>3.156</td>
<td>11.241</td>
</tr>
<tr>
<td>Standard error of $K$</td>
<td>0.188</td>
<td>4.701</td>
</tr>
<tr>
<td>$n$</td>
<td>2.906</td>
<td>0.211</td>
</tr>
<tr>
<td>Standard error of $n$</td>
<td>0.260</td>
<td>0.352</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.971</td>
<td>0.527</td>
</tr>
<tr>
<td>$R_{adj}^2$</td>
<td>0.967</td>
<td>0.126</td>
</tr>
<tr>
<td>reduced chi-square</td>
<td>0.188</td>
<td>0.981</td>
</tr>
<tr>
<td>residual sum of squares</td>
<td>1.318</td>
<td>0.974</td>
</tr>
<tr>
<td>root mean square error</td>
<td>0.434</td>
<td>0.148</td>
</tr>
</tbody>
</table>

The effect of contact time on the removal of arsenate from a 1.8 mgL$^{-1}$ model solution was also studied. At first the uptake of arsenate on ettringite was rapid owing to the many available sorption sites on the surface of the ettringite for arsenate sorption. Later, the sorption proceeded at a slower rate and reached equilibrium within 10 minutes of contact. Probably the saturation of the sorption sites on the surface of ettringite led to the slower rate of arsenate sorption as time passed. The pseudo-first order and the pseudo-second order kinetic models were fitted to the experimental data, and the pseudo-second order model was found to fit the best (Fig. 16). The parameters of the kinetic models are presented in Table 8.

Table 8. Parameters from the kinetic models.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pseudo-first order</th>
<th>Pseudo-second order</th>
</tr>
</thead>
<tbody>
<tr>
<td>$q_e$</td>
<td>1.467</td>
<td>1.530</td>
</tr>
<tr>
<td>Standard error of $q_e$</td>
<td>0.030</td>
<td>0.014</td>
</tr>
<tr>
<td>$k_1$</td>
<td>1.257</td>
<td>1.437</td>
</tr>
<tr>
<td>Standard error of $k_1$</td>
<td>0.206</td>
<td>0.146</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.972</td>
<td>0.996</td>
</tr>
<tr>
<td>$R_{adj}^2$</td>
<td>0.969</td>
<td>0.996</td>
</tr>
<tr>
<td>reduced chi-square</td>
<td>0.007</td>
<td>0.001</td>
</tr>
<tr>
<td>residual sum of squares</td>
<td>0.056</td>
<td>0.008</td>
</tr>
<tr>
<td>root mean square error</td>
<td>0.083</td>
<td>0.031</td>
</tr>
</tbody>
</table>
5 Discussion

5.1 Effect of magnesium on sulphate removal (Paper II)

The treatment pH of 9.6 was found to be too low for magnesium precipitation as hydroxide which was expected since the solubility product (-logK) of brucite is 11.16 (Stumm & Morgan, 1996). This was also in accordance with the fact that magnesium hydroxide precipitation becomes significant at pH 10.5 and almost complete at pH 11-11.5 as reported by Semerjian and Ayoub (2003). Despite magnesium decreased sulphate removal by gypsum precipitation at pH 9.6, it could have had an opposite effect at pH 12.5. Brucite could have acted as seed crystals for gypsum inducing secondary nucleation (Myerson et al., 2002). The fact that MgO has been used as a seeding material for calcium phosphate precipitation supports this (Donnert & Salecker, 1999). Brucite could also have had a catalytic effect on gypsum nucleation via heterogeneous nucleation (Myerson et al., 2002). Similarly, a higher nucleation rate indicating heterogeneous nucleation for gypsum in the presence of 1 % MgO was reported by Rashad et al. (2004). Mg(OH)\textsubscript{2} could have also co-precipitated sulphate by e.g. adsorption enhancing its removal. Similar observations have been made by van Vuuren et al. (1967) who reported the suitability of magnesium hydroxide floc for the adsorption of CaCO\textsubscript{3} that would otherwise remain in suspension. Thus, by arranging the process conditions correctly, naturally occurring magnesium could be turned into a beneficial aid in the removal of sulphate, thus enhancing the material efficiency.

5.2 Replacing lime with industrial by-products (Paper III)

The amount of by-products A (partly burnt lime stored outdoors), and B (partly burnt lime stored in a silo) needed for the AMD neutralisation, the removal of >99% of Al, As, Cd, Co, Cu, Fe, Mn, Ni and Zn, as well as the 60% removal of sulphate, and the amount of sludge produced in the treatment were in the same range as those for quicklime and hydrated lime. This indicated the possibility that these, by-products A and B, could be used instead of commercial lime. This could offer a cost saving alternative to commercial lime used for AMD neutralisation at the mine site, and also lead to savings in waste disposal costs at the lime plant. However, the particle sizes of the studied by-products varied which could have affected the neutralisation rate. Smaller particles have more surface area and, in
general, an increase in surface area results in an increase in neutralisation rate (Potgieter-Vermaak, Potgieter, Monama, & van Grieken, 2006). An interesting observation was that the densest sludge was obtained by using by-product C, kiln dust. The high solids content of the sludge could offer cost savings in sludge dewatering. Similarly, Mackie and Walsh (2015) have obtained denser sludge with the use of cement kiln dust instead of lime in the HDS treatment of AMD.

5.3 Enhanced lime precipitation (Paper IV)

Sulphate concentration below the drinking water guideline in Finland (250 mgL$^{-1}$) (Asetus 683/2017, 4 §; Council directive 98/83/EC, Article 5) was achieved in experiments that used precipitation as ettringite. The modelling underestimated the amount of sulphate removed compared to the experimental results, which could have been due to co-precipitation that the calculation did not take into account. Additionally, there is variation in the solubility product values reported for ettringite in the literature and the value used in the calculations has effect on the modeling results (Chrysochoou & Dermatas, 2006). The precipitates formed were mostly (89-91%) ettringite which was beneficial considering the further utilisation of the precipitates as arsenate sorbents. The precipitates contained 9-11% calcite which could have also contributed to the arsenate sorption (Alexandratos, Elzinga, & Reeder, 2007; Sø, Postma, Jakobsen, & Larsen, 2008).

5.4 Utilisation of the sludge formed (Papers IV and V)

The results indicated that the ettringite formed during sulphate removal from mine water could further serve as an arsenate sorbent. A part of the mine water treatment expenses could be covered by the utilisation of the formed ettringite as this would reduce waste disposal costs, and possibly, also become a source of income. A 90% reduction in arsenate was achieved with an ettringite dosage of 1 gL$^{-1}$. The maximum arsenate sorption capacities of ettringite determined by varying the dosage of ettringite and the initial arsenate concentration deviated with values $q_m = 1.8 \pm 0.1$ mgg$^{-1}$ and $q_m = 11.2 \pm 4.7$ mgg$^{-1}$, respectively. The low initial arsenate concentration chosen to model the arsenate concentration in mine waters in the experiments where ettringite dosage was varied could cause the relatively low sorption capacity. In precipitation as ettringite the stability of the produced sludge should be verified in case of storage in settling ponds. In addition, if the ettringite
sludge is reused for example as arsenate sorbent, the stability of the used sorbent needs to be ensured in order to avoid toxic arsenate leaching out.

5.5 Recommendations for further research

As concerns regarding the environmental effects of sulphate increase and the mine discharge limits for sulphate continue to become more stringent, optimization of the traditional lime precipitation is essential, in some cases, combining it with advanced sulphate removal methods such as precipitation as ettringite. This requires more research on the factors affecting lime precipitation and precipitation as ettringite. Furthermore, research especially focusing on the stability and possibilities for utilisation of the formed sludge is needed.
6 Conclusions

Sulphate removal from mine water using lime was studied with four focus areas: the effect of magnesium on lime precipitation, utilisation of by-products in lime precipitation, enhancement of lime precipitation, and utilisation of the precipitate. The following main conclusions can be made based on this work:

- Using the traditional mine water treatment with lime (at the pH 9.6) magnesium decreased sulphate removal by keeping the sulphate in aqueous form as magnesium sulphate and also via the salt effect.
- On the contrary, at high pH (>11) lime treatment magnesium precipitated as magnesium hydroxide which could enhance sulphate removal by acting as seed crystals for gypsum, by lowering the activation energy of nucleation, or via co-precipitation.
- By-products from quicklime manufacturing (partly burnt lime stored outdoors and partly burnt lime stored in a silo) were used successfully for replacing lime in mine water neutralisation.
- A treatment procedure, consisting of sulphate removal from mine water by precipitation as ettringite, followed by the utilisation of the ettringite as a sorbent for arsenate removal from water, was suggested as a promising less polluting solution for mine water treatment.
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Original publications


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Emma-Tuulia Nurmesniemi

EXPERIMENTAL AND COMPUTATIONAL STUDIES ON SULPHATE REMOVAL FROM MINE WATER BY IMPROVED LIME PRECIPITATION