Research paper

The effect of magnesium on partial sulphate removal from mine water as gypsum

Emma-Tuulia Tolonen [a], Jaakko Rämö [b], Ulla Lassi [a, c, *]

[a] University of Oulu, Research Unit of Sustainable Chemistry, University of Oulu, P.O. Box 3000, FIN-90014, Finland
[b] University of Oulu, Thule Institute, University of Oulu, P.O. Box 7300, FIN-90014, Finland
[c] Kokkola University Consortium Chydenius, P.O. Box 567, FIN-67101, Kokkola, Finland

ABSTRACT

The aim of this research was to investigate the effect of magnesium on the removal efficiency of sulphate as gypsum from mine water. The precipitation conditions were simulated with MINEQL + software and the simulation results were compared with the results from laboratory jar test experiments. Both the simulation and the laboratory results showed that magnesium in the mine water was maintaining sulphate in a soluble form as magnesium sulphate ($MgSO_4$) at pH 9.6. Thus magnesium was preventing the removal of sulphate as gypsum ($CaSO_4 \cdot 2H_2O$). However, change in the lime precipitation pH from 9.6 to 12.5 resulted in magnesium hydroxide ($Mg(OH)_2$) precipitation and improved sulphate removal. Additionally, magnesium hydroxide could act as seed crystals for gypsum precipitation or co-precipitate sulphate further enhancing the removal of sulphate from mine water.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Mine water can contain up to several thousand milligrams per litre of sulphate (Brown et al., 2002). Previously, sulphate had been considered quite harmless to the environment but this view has changed in recent years. Nowadays, more attention has been paid to the indirect environmental effects of sulphate. These include salting effect, turbidity enhancement and sedimentation (Gray, 1997). Thick layers of sediment can cause anoxic conditions and sulphate can be reduced to toxic hydrogen sulphide (Benatti et al., 2009). There is also a threat that sulphate-reducing bacteria can mediate mercury methylation (King et al., 2001). Methylmercury is the most toxic form of mercury.

Chemical precipitation with lime is the traditional treatment method for mine water although by-products as alternatives for lime have also been investigated (Mackie et al., 2010a, 2010b; Mackie and Walsh, 2012; Alakangas et al., 2013; Tolonen et al., 2014). With lime precipitation sulphate removal occurs via precipitation of gypsum. Sulphate removal efficiency of the traditional treatment is limited by the solubility of gypsum which is 1500 mg/l

when no Na^+ or Mg^{2+} ions are present (Geldenhuys et al., 2003). Mine water can contain up to thousands of milligrams per litre of sodium and magnesium. Mg^{2+} ion has been experimentally found to inhibit sulphate removal by gypsum precipitation (Maree et al., 2004). However, at high pH (10.5–11.5) magnesium has been experimentally found to improve e.g. total organic carbon (TOC) removal by $CaCO_3$ precipitation (Leentvaar and Rebhun, 1982). Tait et al. (2009) have performed gypsum crystallization laboratory experiments and aqueous equilibria simulations with and without the effects of ion activity and ion association.

Even though, lime precipitation has been used for mine water treatment for decades, the effect of solution conditions is not adequately known. There is an urgent need for more information of the effect of solution conditions on lime precipitation. The information could be used for process optimization to drastically improve material and process efficiency.

In this research the effect of Mg^{2+} ion on the removal of sulphate from mine water with precipitation by lime was investigated. MINEQL + software (Schecker and McAvoy, 2003) was used for modelling the precipitation conditions at pH values 9.6 and 12.5 and the results were compared with experimental results. Laboratory scale precipitation experiments were performed with the jar test. The inhibitive effect of magnesium on sulphate removal was investigated but also whether naturally occurring magnesium could be turned into beneficial aid in sulphate removal from the

---

material efficiency point of view by arranging the process conditions correctly.

2. Materials and methods

2.1. Mine water

Mine water was sampled from an operating gold mine, taken from neutralized process waste water from the enrichment plant. The process waste water and tailings from the enrichment plant are lead to the tailings pond where precipitation and settling occurs. In the industrial process pH is adjusted with lime to 8.7 to precipitate metals as hydroxides. Metal and anion analyses for the mine water sample were performed in an accredited laboratory. Metals were analyzed with inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES) and anions with ion chromatography (IC) according to standard SFS-EN ISO 10304-1 (Finnish Standards Association SFS, 2007). According to the metal and anion analysis data the main components of the mine water sample are sulphate and magnesium (Table 1).

Table 2 represents the balance of major cations and anions of the mine water sample. Ions are well balanced as the difference between the cation and anion sums is only 3%. 5% is an acceptable difference for analyses' correctness (Rice and Bridgewater, 2012).

2.2. Chemical equilibrium speciation calculation

Speciation calculations were carried out using MINEQL + version 4.6 (Schecker and McAvoy, 2003) which is a computer programme for chemical equilibrium modelling. Calculations were used to model magnesium and sulphate speciation at pH values 9.6 and 12.5. MINEQL + solves mass balance calculations through a Newton−Raphson method using equilibrium constants from a thermodynamic database. There are two magnesium hydroxide solids in the database from which $Mg(OH)_2$ (active) was considered in this calculation. Ionic strength was calculated with the MINEQL + programme and was 0.21 and 0.41 for system at pH values 9.6 and 12.5, respectively. The Davies equation was used for the correction of equilibrium constants for ionic strength at 25 °C (Schecker and McAvoy, 2003). The modelling parameters were the same for magnesium and sulphate in both target pH values 9.6 and 12.5 and were chosen according to Table 1. The initial values were $[Mg^{2+}] = 8.93 \cdot 10^{-2}$ M and $[SO_4^{2-}] = 9.47 \cdot 10^{-2}$ M. Due to different lime additions the initial modelling parameters for calcium were

Table 1
Metal and anion concentrations of the mine water.

Metal/Anion	Unit	Value
ICP-MS		
As	$\mu g\ L^{-1}$	190
Cd	$\mu g\ L^{-1}$	1.8×10^{-1}
Co	$\mu g\ L^{-1}$	11.6
Mn	$\mu g\ L^{-1}$	1270
Sb	$\mu g\ L^{-1}$	51.6
ICP-OES		
Al	$mg\ L^{-1}$	2.0×10^{-1}
Ca	$mg\ L^{-1}$	424
Fe	$mg\ L^{-1}$	$<5.0 \times 10^{-2}$
Mg	$mg\ L^{-1}$	2170
Na	$mg\ L^{-1}$	174
S	$mg\ L^{-1}$	3050
IC SFS-EN-ISO 10304-1		
Cl^-	$mg\ L^{-1}$	23
SO_4^{2-}	$mg\ L^{-1}$	9310
NO_3^-	$mg\ L^{-1}$	45

Table 2
The balance of major cations and anions of the mine water sample.

Cation	$(meq\ L^{-1})$	Anion	$(meq\ L^{-1})$
Ca^{2+}	21.16	SO_4^{2-}	193.8
Mg^{2+}	178.53	Cl^-	6.5×10^{-1}
Na^+	7.57	NO_3^-	7.3×10^{-1}
Total	207.26	Total	195.2

$[Ca^{2+}] = 1.06 \cdot 10^{-2}$ M at pH = 9.6 and $[Ca^{2+}] = 2.10 \cdot 10^{-1}$ M at pH = 12.5. Saturation index (SI) for brucite $(Mg(OH)_2)$ as a function of pH was also obtained with MINEQL + software. The saturation index is defined as the ion product for the solid divided by the solubility constant for the solid. When SI has a negative value the system is undersaturated with respect to the solid, compared to when SI is zero, the system is in equilibrium with the solid. When SI has a positive value the system is oversaturated with respect to the solid (Schecker and McAvoy, 2003).

2.3. Laboratory experiments

The jar test (Kemira Kemwater, Flocculator, 2000) was used for chemical precipitation experiments. The mine water sample volume was 800 ml for each jar and the experiments were conducted at room temperature (20 ± 2 °C). 10% by weight slurries were made of the hydrated lime (JT Baker min. 93% $Ca(OH)_2$) by dissolution into ultra-purified water. The appropriate amount of slurry was added to raise the sample pH to 9.6 or 12.5 depending on the experiment. The sample was then mixed rapidly at 150 rpm for 1 min, slow mixed at 50 rpm for 5 min and left to settle for 30 min. The mixing and settling parameters were chosen according to literature with minor alterations (Mackie et al., 2010b). After settling, water samples from the supernatant were taken for sulphate and magnesium analysis. All samples were identically vacuum filtered through 0.45 μm cellulose nitrate membrane filters (Sartorius) prior to sulphate and magnesium analysis. Sulphate was analyzed with ion chromatography (Metrohm 761 Compact IC) according to standard SFS-EN ISO 10304-1 (Finnish Standards Association SFS, 2007) and magnesium with an atomic absorption spectrometer (PerkinElmer AAnalyst 200) according to standard SFS 3018 (Finnish Standards Association SFS, 1982).

An additional experiment was conducted to confirm the formation of brucite crystals. The pH of 800 mL of mine water was raised to 12.5 and then rapid mixed at 150 rpm for 1 min. After that a 50 mL sample from the supernatant was taken and vacuum filtered through a 0.45 μm cellulose nitrate membrane filter (Sartorius). The filtered crystal sample was then analyzed with PANalytical X-ray diffraction (XRD) equipment with Cu Kα at 40 mA and 45 kV.

3. Results and discussion

3.1. Magnesium speciation

The treatment pH 9.6 was too low for magnesium precipitation as hydroxide since the solubility product (-logK) of brucite is 11.16 (Stumm and Morgan, 1996). According to the calculations at this pH 43% of magnesium is in the form of soluble magnesium sulphate $(MgSO_4)$ (Fig. 1). The solubility of magnesium sulphate is considerably higher than the solubility of calcium sulphate. Thus, at this pH, magnesium prevents sulphate removal by maintaining sulphate in the soluble form. Additionally, 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 and Schwartz, 1998) via the salt effect (Petrucci, 2011).