Research article

Sulfate removal from acid mine water from the deepest active European mine by precipitation and various electrocoagulation configurations

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ABSTRACT

Sulfate removal from mine or process water is a key issue in the mining industry. In this paper, precipitation with lime (calcium oxide) was integrated with electrocoagulation for sulfate removal from Pyhäsalmi/Finland mine water. Sulfate precipitation with calcium oxide decreased the sulfate concentration from 13,000 mg/L to 1600 mg/L. Various current densities were applied to the pre-treated mine water with various electrodes and aluminium and iron anodes. It was found that 25 mA/cm² was the best tested current density for both anode types. At the second stage, this current density was used for different iron and aluminium anodes in various monopolar and bipolar configurations. It was found that this hybridisation is effective for sulfate removal, and that a bipolar configuration showed better results than the monopolar configuration. The best result was gained from 25 mA/cm² with a two aluminium and two stainless steel anode–cathode configuration and calcium oxide pre-treatment to reach pH 12. The removal efficiency reached 84.4% and 63.8% with aluminium anodes in bipolar and monopolar configurations, respectively. This setup was able to decrease sulfate concentrations from 13,000 mg/L to 250 mg/L, which meets mine water discharge limits. Kinetic studies showed that iron and aluminium anodes obey pseudo-second order kinetic. Finally, the energy consumption was calculated.
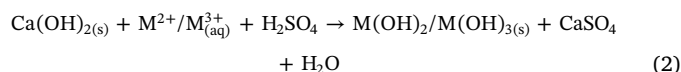
1. Introduction

Sulfate is not considered a toxic pollutant, but high concentrations result in steel and concrete corrosion as well as increasing the salinity of soil and water (Guimaraes and Leao, 2014). Depending on other parameters, 30–419 mg/L of sulfate can change the taste of water. In addition, it was reported that eating 7–8 g of sodium sulfate and magnesium sulfate could cause adult male catharsis. Sulfate concentrations of 1000–1500 mg/L can have laxative effects (World Health Organization, 2004). Restrictions for sulfate discharge are becoming tighter (Jacobs and Testa, 2014) and various regulations have been set for sulfate concentration in water (Table 1).

Sulfate concentrations in mine water range from hundreds to thousands of mg/L (Bowell, 2004; Bai et al., 2013; Tolonen et al., 2015). It is produced by (di-)sulfide oxidation, resulting from the exposure of these minerals to air and water (Stumm and Morgan, 2009). These sulfate concentrations in mine waters of working or abandoned mines are a big challenge for the mining industry (Wolkersdorfer et al., 2015), with more than 70% of mine sites in the world to be manage in regards to sulfate concentrations (Jacobs and Testa, 2014).

Various technologies have been introduced for sulfate removal, such as gypsum, ettringite or barium sulfate precipitation (Guimaraes and Leao, 2014; Silva et al., 2012; Wolkersdorfer, 2008; Pinto et al., 2016; Johnson and Hallberg, 2005). Because of its economic aspect, chemical saturation and precipitation is the first option on an industrial scale (Guimaraes and Leao, 2014; Bowell, 2004). Lime is a very efficient, cheap and common way to remove metals and sulfate from mine water, commonly resulting in the formation of gypsum (Equations (1) and (2)) (Khorasanipour et al., 2011; Lopez et al., 2009; Fernando et al., 2018; Masindi et al., 2017; Jacobs and Testa, 2014). However, sulfate concentrations by this method can only be decreased to 1200–1800 mg/L (Guimaraes and Leao, 2014; Geldenhuys et al., 2003), due to the gypsum equilibrium (Tolonen et al., 2016).

$$Ca(OH)_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2OH^-_{(aq)} \tag{1}$$

$$Ca(OH)_{2(s)} + M^{2+}/M^{3+}_{(aq)} + H_2SO_4 \rightarrow M(OH)_2/M(OH)_{3(s)} + CaSO_4 + H_2O \tag{2}$$

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Table 1
Various regulations for sulfate concentration in water.

Organisation	concentration, mg/L	reference
World Health Organisation (WHO)	500	Guimaraes and Leao (2014)
WHO and EPA (drinking water)	250	Fernando et al. (2018)
Europe (drinking water)	250	Council of the European Union (1998)
Europe (groundwater and effluent discharge)	1000	Bowell (2004)
Environmental agencies in mining countries	250 and 500	Guimaraes and Leao (2014)
Surface water discharge – Chile	1000–2000	West et al. (2011)
Ground water discharge – Chile	250–500	West et al. (2011)
Irrigation – Chile	250	West et al. (2011)
General water use and mine water – Australia	1000	West et al. (2011); Arnold et al. (2016)
Drinking water – USA	250	West et al. (2011)
USA (mine water)	10–500	Arnold et al. (2016)
Canada (mine)	65–500	Arnold et al. (2016)
South Africa (mine)	200–400	Arnold et al. (2016)
Finland (mine regulations)	2000	Arnold et al. (2016)

In the ettringite/SAVMIN process, the solution's pH is increased to pH 12 with lime and then aluminium salts are added to form ettringite (Guimaraes and Leao, 2014; Tolonen et al., 2016; Van et al., 2014; Smit, 1999). One of the disadvantages of this process is that the final pH of the solution is very high and needs pH adjustment before discharge.

Precipitation of sulfate by barium salts is expensive and not environmentally friendly (Guimaraes and Leao, 2014; Silva et al., 2012). Other sulfate removal processes, on an industrial scale not commonly used, are sorption by various sorbents such as zeolites, coconut pith or shrimp peelings (Guimaraes and Leao, 2014). Industrial scale processes include membrane-technologies such as reverse osmosis (Guimaraes and Leao, 2014), ion exchange (Guimaraes and Leao 2014; International Network for Acid Prevention (INAP, 2003), biological treatment (Bowell, 2004) and electrocoagulation (Nariyan et al., 2017b). The different processes have advantages and disadvantages: reverse osmosis is energy-intensive, prone to scaling and fouling, has a brine disposal problem (Juby, 1992) and is best used for low sulfate concentrations below 700 mg/L. Also biological sulfate treatment is mainly used for mine water from abandoned mines (Bowell, 2004).

Electrocoagulation is a comparably simple technology in which the sacrificial anodes act as flocculating and coagulating agents. The reaction in the electrocoagulation cell (EC) is more complex than a simple chemical coagulation process (Gupta and Ali, 2013). Various reactions take place inside the EC, such as cathodic reduction, coagulation, electrophoretic movement of particles and electro flocculation by the oxygen and hydrogen produced by the electrodes and other chemical and electrochemical processes. Electrocoagulation has some merits over the other processes like producing an odourless, colourless and clear water with less sludge compared to chemical coagulation. Furthermore, it produces water with lower TDS concentrations and is easy to operate. As no chemicals are used in this process, there is no secondary pollution (Gupta and Ali, 2013; Liu et al., 2010). Electrocoagulation provides neutral pH after treatment, and the sludge is more stable and easy to dewater (Liu et al., 2010). The cost of electrocoagulation (€1.98/m^3 with a current density of 50 mA/cm^2) is less than that of chemical precipitation (€4.53/m^3) for acid mine treatment (Fernando et al., 2018). Therefore, it could be considered for acid mine water treatment as it has not previously received much attention for this purpose.

The reactions of electrocoagulation at the anode and cathode have been reported before (Equations (3)–(6)) (Liu et al., 2010):

Anodic reactions:

$$M_{(s)} \rightarrow M^{n+}_{(aq)} + ne^- \qquad (3)$$

$$2H_2O_{(l)} \rightarrow ne^- \rightarrow M_{(s)} \qquad (4)$$

Cathodic reactions:

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(s)} \qquad (5)$$

$$2H_2O_{(l)} + 2e^- \rightarrow 2H_{2\,(g)} + 2OH^- \qquad (6)$$

Electrocoagulation configurations can be done in different forms of monopolar and bipolar setups. In monopolar configuration, each electrode is connected directly to the power source. This configuration is similar to a single cell consisting of several electrodes and interconnections. However, in the bipolar configuration, the sacrificial electrodes are placed between the pair of parallel electrodes and lack of an electrical connection. This cell configuration provides a simple set up and is easy to maintain (Liu et al., 2010) (Fig. 1 a and b).

In a previous study, it was found that electrocoagulation removes sulfate from mine water (Nariyan et al., 2017b). Yet, it could not
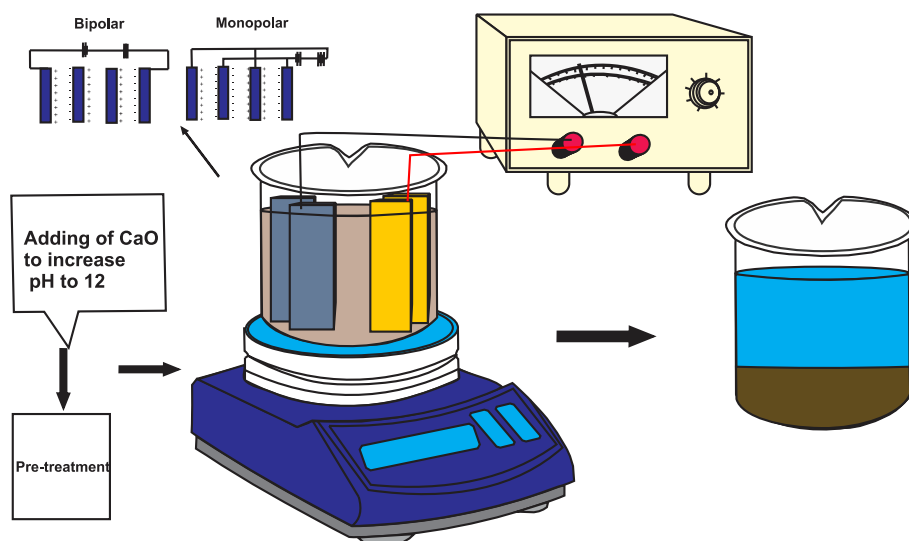
Fig. 1. Schematic diagram of the sulfate removal process with monopolar and bipolar electrocoagulation configurations (adopted from Liu et al. (2010)).