Pollution control and metal resource recovery for acid mine drainage

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ARTICLE INFO

ABSTRACT

Although the metals contained in acid mine drainage (AMD) are considered environmental pollutants, they may also be valuable resources. The traditional chemical precipitation processes for AMD not only produce large amounts of sludge, but also make it difficult to recycle the waste metals. This study comprehensively investigated the recycling of Fe, Cu, Zn and Mn from AMD. Ferrous ions were first oxidised by 0.15 ml/L 30% H_2O_2, and then a four-step fractional precipitation was applied with the selective addition of $Ca(OH)_2$ and Na_2S solutions. The Fe, Cu, Zn and Mn contents of particular sludges were 45.91%, 11.58%, 31.06% and 7.95% respectively, and the recovery efficiencies of Fe, Cu, Zn and Mn from AMD reached 99.51%, 86.09%, 87.87% and 79.71%, respectively. The metals contained in the effluent were below the Code of Federal Regulations (CFR) limits after the Mn precipitation process. Technology for the complete reuse of the sludge was also tested. Fe oxide red was obtained by roasting the Fe sludge for 30 min at a temperature of 500 °C, resulting in a Fe_2O_3 content of 85.18%. Cu and Zn crude concentrates were generated by a flotation process; the Cu and Zn contents of these concentrates were 35.72% and 55.13% respectively, and the recovery efficiencies of the Cu and Zn were 72.66% and 76.18%, respectively. The Mn sludge obtained can be used in cement mixes to replace 45% of ordinary Portland cement (OPC). Based on the technology tested, a comprehensive metal recovery process is proposed here for the control of metal pollution and metal recovery from AMD.

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1. Introduction

Acid mine drainage (AMD) causes severe environmental pollution because of its high heavy metal content and strong acidity (Gray, 1998). Heavy metals, including Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn, have the potential to become major contamination sources and are often extremely detrimental to aquatic and soil environments (Anju and Banerjee, 2010; Kim et al., 2009). As a typical poly-metallic mine, and one of the biggest opencast mines in Southern China, the Dabaoshan Mine region in northern Guangdong province was one of the largest copper mining and refining centres during the Song Dynasty (960–1279 AD) (Chen et al., 2007). The Liwu mud-retaining dam (LWMRD), with a capacity of 20 million cubic metres, was constructed in 1979 to retain the waste rock produced by the mine. However, large quantities of mine tailings have been dumped by illegal miners, and illegal pits have been connected to the LWMRD. Approximately 15,000 m³/day of AMD has been produced by the LWMRD, contaminating surface water, groundwater and soil downstream from the mine. The heavy metal levels detected have been above the limits set in the Chinese National Standards for Drinking Water (Chen et al., 2007), and the average concentrations of Cu, Zn, Cd and Pb in the surrounding soil have all been above the natural soil background levels (Zhao et al., 2012). Zhuang et al. (2009) found that the heavy metals accumulated in the food crops (rice and vegetables) grown around the mine posed a serious health risk to the local population.

There are currently several methods used to treat AMD, including chemical precipitation, solvent extraction, reverse osmosis, ultrafiltration, electrodialysis, ion exchange/adsorption and wetland treatments (Bruggen and Vandecasteele, 2002; Kongsricharoern and Polprasert, 1995; Lazaridis et al., 2004; USEPA, 2000; Ujang and Anderson, 1996; Mitsch and Wise, 1998). Lime has commonly been used in AMD treatment as a neutraliser and precipitator in chemical precipitation methodology (Pepe et al., 2007). However, metal precipitation investigations have only been carried out in attempts to reduce the metal concentrations to below those of the waste water emission standard requirements. A 15,000 m³/day AMD treatment plant with chemical precipitation technology was constructed downstream of the LWMRD in 2010. The sludge level reached 100 t/day (with a water content of 80 wt.%), and disposing of it became extremely difficult. The sludge was transported back to the LWMRD, introducing secondary pollution through the dissolution of metal hydroxides and the release of heavy metals from the sludge in the low pH environment. It then became worth considering the recovery of these metals. Selective precipitation has been tested for the recovery of the metal from the industrial waste water (Mauchauffée and Meux, 2007), the waste leaching solution (Innocenzi and Vegliò, 2012) and the mine waste water

(Hammack and Edenborn, 1992; Hammack et al., 1994). Mechanisms for selective precipitation are based on the difference between the metal compounds' solubility products (Mauchauffée and Meux, 2007). Precipitators commonly used include sodium hydroxide, sodium sulphide and sodium decanoate (Jameson et al., 2010; Mauchauffée et al., 2008; Michalkova et al., 2007; Tokuda et al., 2008). Sampaio et al. (2010) studied the sludge generated in the Zn selective precipitation process, and found that, with the addition of sodium sulphide, sphalerite could be detected in the sludge. This method reduced the overall volume of sludge by 70% compared to the chemical precipitation treatment with no metal recovery process (Silva et al., 2012). Furthermore, the optimization of the precipitation and sludge refinement processes allows the refined sludge to be sold to smelters, which can either recover the metals or use them in paint production (Cibati et al., 2013; Silva et al., 2012). The sludge volume would then be significantly reduced, and the metals could be effectively recycled. The metal recovery efficiencies and the refined products are similar to those reported in studies that have used solvent extraction (Bertuol et al., 2009). The method is easy, economical and does not pose the same environmental threats as those of solvent extraction. Metal recovery efficiencies and the metal contents of the sludge are affected by the metal concentration, pH value and molar ratio between the precipitator and the targeted metal during the selective precipitation process. The metal concentration is, however, lower than that of the leaching solution and the industrial waste water, which is why research into metal recovery from the AMD has been limited (Johnson and Hallberg, 2005). Furthermore, the refining of the precipitate has not been previously investigated. A fractional precipitation process and the precipitate refining process for metal resource recovery from the AMD of the LWMRD were thus investigated in this study.

Nomenclature

REM_M	removal rate of metal from aqueous phase [%]
RES_M	residual M in the aqueous phase after precipitation process [%]
REC_M	recovery rate of metal from the aqueous phase [%]
CON_M	metal content of sludge [%]
MOR_M	ratio of the molar precipitant added to the total molar content of a specific metal
Subscript M	denotes a specific metal

2. Materials and methods

2.1. Water sampling and materials used

Water samples were taken periodically from the LWMRD at a rate of approximately 4 times per month from March 2010 to April 2011. As shown in Fig. 1, all of the samples were collected at the exit of the LWMRD and were then filtered through the 0.45 μm membrane to remove any debris or suspended solids. The samples were stored in closed high-density polyethylene bottles and kept at 4 °C. All of the chemical reagents used were analytical reagent (AR) grade chemicals.

2.2. Precipitation and sludge recovery tests

Precipitation tests were performed within a 2500 ml beaker. The actual liquid volume was 2000 ml, and a mechanical agitator (JJ-1, AoHua) was used for the precipitation chemical reaction, with an agitation rate of 100 rpm used to enhance the precipitation. The precipitator
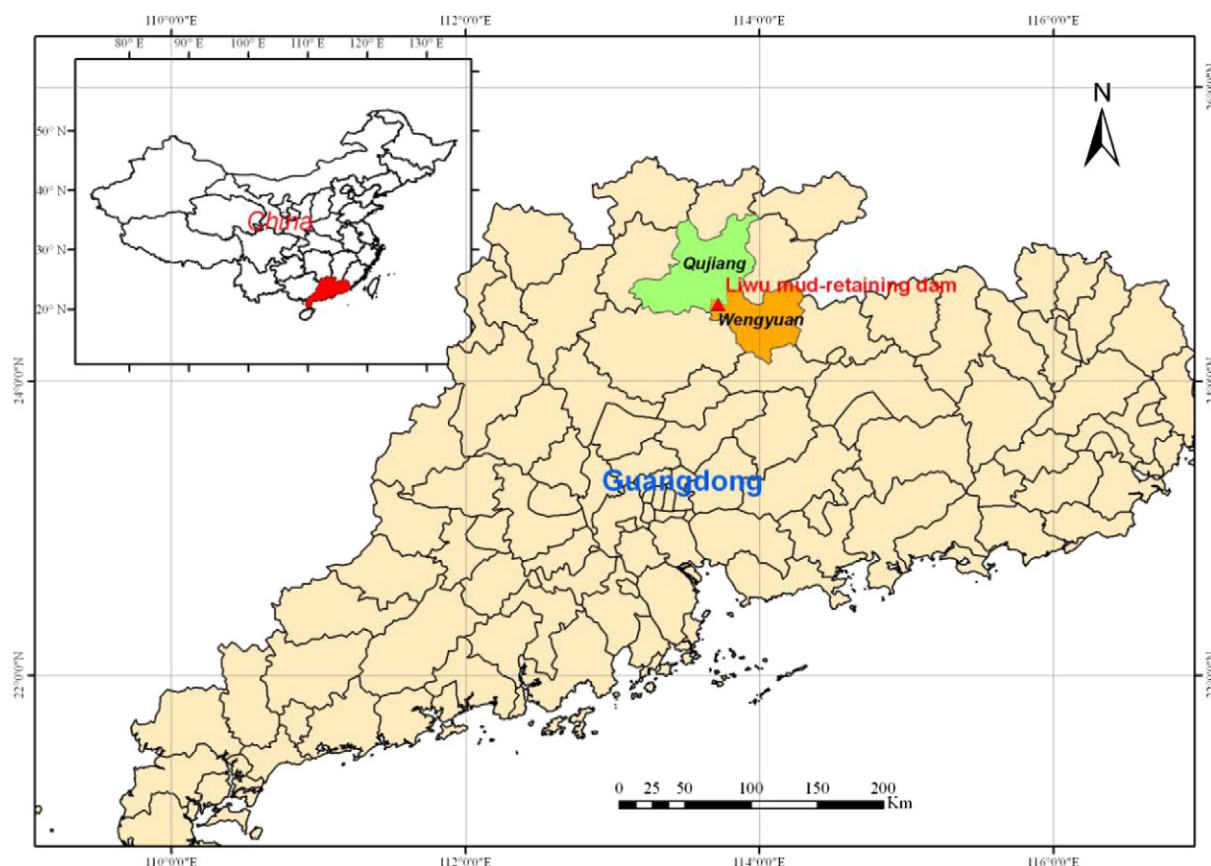

Fig. 1. Sampling location.