Hydrometallurgical treatment of acid mine drainage (AMD) solution

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Abstract

The purpose of this research is a treatment of acid mine drainage (AMD)-solution otherwise regarded as a waste, for recovery of some elements such as Ce, Nd. This treatment was performed through the use of sodium hydroxide for neutralization of AMD. The tests (bench-scale batch experiments) are only of an exploratory nature and, as such, will not afford sufficient data to permit a detailed cost analysis of the recovery methods. The neutralization of AMD was considered between pH-values between 3 and 11 in order to precipitate Fe, Al, Ce and Ca using sodium hydroxide. The minimal content of critical metals such as Ce (5.35 mg/l), Co (1.42 mg/l) and Nd (1.23 mg/l) in AMD-solution is new challenge for the choice of an effective selective method for their extraction. Particularly, AMD conditions (i.e. low pH, high concentration of dissolved iron species) led to natural precipitation. The filtrated iron based particles were characterized in this work.

Introduction

Acid mine drainage (AMD) formed by mining activities contain high concentration of dissolved heavy metals and sulfates, and the pH values can to be as low as 2.5. Therefore AMD with these characteristics should not been discharged into public streams [1]. Thus, assessment of AMD toxicity has been widely investigated at individual, physiological and molecular levels using various test organisms [2]. In AMD systems, natural nanoparticles such as amorphous hydroxides, ferrihydrites, and goethite seemed to be formed, which could induce lethal and sublethal toxicity toward aquatic organisms. If left untreated AMD can contaminate ground and surface water and thereby damage ecosystems and potentially impact human health. Gardic et al. [3] have studied the neutralization as the first step in the purification process of AMD in order to produce a sludge. This investigation was performed using agents such as limestone, lime and sodium hydroxide. An important disadvantage of these agents is high cost and generation of large volume of sludge that requires disposal or an additional treatment such as drying and smelting of sludge. Due to those facts, metallurgical and mining companies are always on the lookout for cheaper and effective precipitation agents for metal extraction

A joint treatment process for acid mine drainage (AMD) using coal fly ash (CFA) was developed in South Africa [4] at different CFA/AMD-ratios and pH, electrical conductivity (EC) evolution monitored over time. In a separate experiment two AMD sources with differing chemistry were treated with the same CFA to evaluate the impact of AMD chemistry on the treatment process and product water quality [4]. Treatment of such waters with flying ash resulted in no significant removal of sulfates when treated to pH less than 10. Subsequent treatment of mine water to pH greater than 11 resulted in more than 60 % sulfate removal. Treatment of mine water to pH greater than 11 with flying ash followed by seeding with gypsum crystals and the addition of amorphous $Al(OH)_3$ resulted in removal of sulfate to levels about 500 ppm. Two competing processes were observed to control the evolving pH of process water: dissolution of basic oxides (CaO, MgO) from CFA led to pH increase, but a hydrolysis of AMD species such as Al^{3+}, Fe^{2+}, Fe^{3+} and Mn^{2+} led to pH decrease.

IME, RWTH Aachen University in collaboration with the University of Belgrade in Serbia successfully completed a European Commission funded research project INTREAT (2004-2006) for the treatment of industrial wastewater produced by sulfide ore mining and metallurgical activities in the Copper Mining and Smelting Complex Bor (RTB-BOR). Similar to acid mine drainage the effluent is characterized by low pH (1.78) due to the content of sulfuric acid; heavy metals such as Cu, Fe, Ni, Mn, and Zn were precipitated. This waste stream was treated in a cascade line reactor for selective removal of heavy metals [5]. The influence of concentration and consumption of sodium hydroxide, temperature, pH value in each reactor on the degree of metal removal was investigated. The removal efficiency for copper, iron and manganese was in excess of 90%, and deemed satisfactory while the achieved removal efficiencies for Zn and Ni were lower at 72.3% and 76.3% (partially re-dissolution of these elements), respectively. Additionally electrocoagulation was used in order to improve a precipitation efficiency and decrease the operation costs [6].

Selective formation of copper nanoparticles from acid mine drainage (pH=2.67) using nanoscale zerovalent iron particles at 0.1 and 2.0 g/l was conducted in laboratory conditions [7]. HRTEM_EDS-analysis confirmed the presence of copper spherical nanoparticles (68 wt %). This precipitation might be highly useful for the selective upcycling of dissolved Cu in waste water into high value nanomaterials, which have a good protective properties and have been employed as heterogeneous catalysts for numerous environmental progressions, e.g., selective reduction in nitric oxide, oxidation of carbon monoxide and decomposition of nitrogen dioxide

The main aim of this work is a study of neutralization of AMD-solution with sodium hydroxide in order to precipitate rare earth elements such as cerium. An additional aim is characterization of the filtrated solid residue based on the iron compounds.

EXPERIMENTAL

Material

The chemical composition of AMD-solution is presented in Table 1 (ICP-OES Analysis):

Table 1: Chemical composition of the AMD-Solution from South Africa (Figure 1.a)

Species	Al	Fe	Mg	Ca	Mn	Si	Co	Cu	Zn	Ce	Nd	SO_4^{2-}
Conc, mg/L	396	4.290	474	592	93.9	47.5	1.42	0.78	14.3	5.35	1.23	12.100

As shown in Table 1 the content of valuable critical metals such as Co, Ce and Nd are very small (few milligrams per Liter). The spontaneous precipitation of iron took the place during the transport and long staying in a bottle. After filtration the AMD-solution (Figure 1.a), the solution was used for a neutralization.

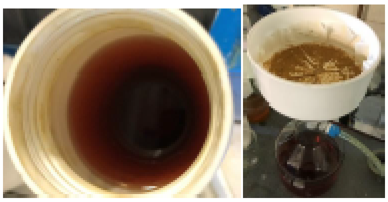

Figure 1: a. AMD-Solution and 1.b. precipitate after filtration

Characterization of solid residue after filtration (as shown at Figure 1.b) and drying at 110°C was shown at Figure 2.

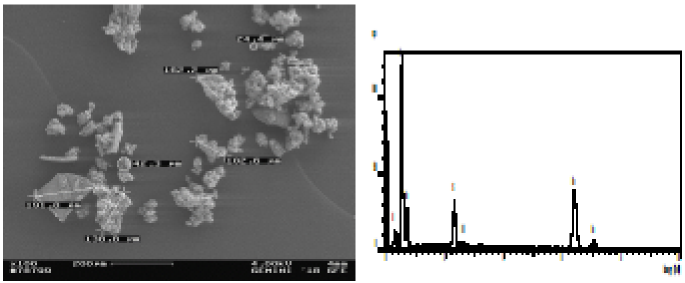

Figure 2. SEM-EDS analysis of powder after filtration (without a washing of powder)

As shown in Figure 2, the presence of iron and oxygen confirmed the iron-compounds in solid residue. The sulfur and chlorine are remained from an acidic solution, mostly sulfate. The particles are agglomerated, irregular form with sizes between 42 and 191 µm.

Neutralization behavior of AMD-solution

Neutralization of an AMD Solution was performed using sodium hydroxide at different pH-values between 1 and 11 at room temperature, in order to study a precipitation of cerium and other elements. This strategy for removal of Fe, Al and Ca was previously studied in a cascade line reactor using a wastewater from an electrolytic plant [4]. The new step is precipitation of cerium.

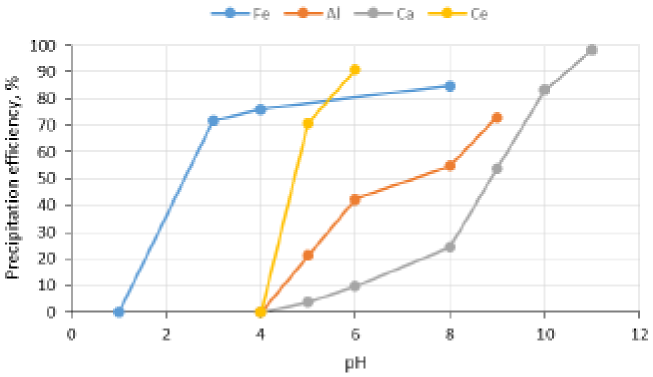

Figure 3. Precipitation efficiency during neutralization of AMD-solution with NaOH

As shown the best precipitation selectivity for iron was reached at pH-4 (at about 75 % removal degree). This is explained by the formation of $Fe(OH)_3$. A further increase of the pH-value to 6 leads to the precipitation efficiency of 85 %, more than 95 % can only be reached using an oxidation reagent such as H_2O_2 in order to oxidize $Fe^{2+}$to Fe^{3+}.
The precipitation of cerium took place between pH-value of 4 and 6 in form of sodium cerium sulfate hydrate ($NaCe(SO_4)_2 \cdot H_2O$) reaching a precipitation efficiency of about 90 %, as shown with Eqs. (1) and (2):

$$H_2SO_4 + NaOH \rightarrow Na_2SO_4 + 2\,H_2O \quad (1)$$

$$Ce_2(SO_4)_3 + Na_2SO_4 + 2\,H_2O \rightarrow 2\,NaCe(SO_4)_2 \cdot H_2O \quad (2)$$

The obtained sodium cerium sulfate hydrate might be used for winning of this metal using solvent extraction for separation of cerium and an additional treatment of obtained cleaned solution using an ultrasonic spray pyrolysis method, what is innovative and planed in our future work.
With an increase of pH-value from 4 to 9, aluminium was removed in form of $Al(OH)_3$, as shown with Eq. 3.

$$Al_2(SO_4)_3 + 6\,H_2O \rightarrow 2\,Al(OH)_3 + 3\,H_2SO_4 \quad (3)$$

This is considered and confirmed with an analysis of E –pH diagram constructed in FactSage software. An increase of pH-Value from 2 to 8 decreases the solubility of aluminium leading to his precipitation.
A further increase of pH-Value to 11, led to the removal of Calcium in form of calcium sulfate.

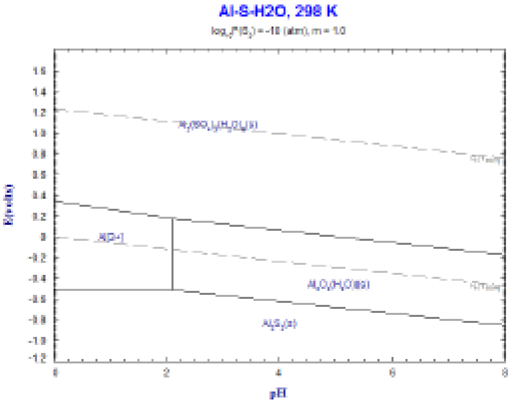

Figure 4: E-pH diagram for Al-S-H₂O system

Conclusions

Bench scale experiments were performed related to the treatment of AMD-solution Spontaneous precipitation of iron took place before the filtration and neutralization in AMD-solution (as shown at Figure 1.b). An increase of pH-Value to 6 led to the precipitation efficiency of 85 % for iron. A significant precipitation of cerium appeared as good result between pH-value of 4 and 6 with a precipitation efficiency of about 90 %. A further increase of pH-Value to 10 leads to the precipitation efficiency for aluminium and calcium, what was our target.

A future step is the use of a combined solvent extraction and precipitation in order to produce one pregnant leaching solution based on cerium. The obtained solution must be further treated aiming on metal recovery. A visional aim is the synthesis of sub-µm/nanosized particles of cerium oxide from an ultra-cleaned solution e.g. using ultrasonic spry pyrolysis.

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