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 Cu, Ni. This treatment was performed through the use of sodium hydroxide for neutralization of AMD. The tests (batch-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 1 and 11 in order to precipitate Fe, Al, Cu and Cd using sodium hydroxide. The minimum content of critical metals such as Cu (1.54 mg/l), Co (1.41 mg/l) and Ni (1.75 mg/l) in AMD-solution is now 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 concentrations of dissolved heavy metals and sulfates, and the pH values can be as low as 2.5. Therefore AMD with these characteristics should not be discharged into public streams [1]. Thus, neutralization of AMD toxicity has been widely investigated at individual, physiological and molecular levels using various test organisms [2]. In AMD systems, natural aerosol particles such as dust, cloud water, and gas-phase nitrate are 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. Garcia et al. [2] have studied the neutralization at the first step in the purification process of AMD in order to produce a sludge. This investigation was performed using agents such as lime, 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 these 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 soda ash (SFA) was developed in South Africa [3] 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 waste quality [4]. Treatment of such waters with flying ash resulted in no significant removal of metals that was treated to pH less than 10. Subsequent treatment that water to pH greater than 11 resulted in more than 90% sulfide 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 sulfide to levels about 100 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 hydrolysis of AMD species such as Al(OH)+, Fe(OH)+, Fe(OH)2 and Mn2+ led to pH decrease.
The University of Belgrade and RWTH Aachen University in collaboration with the University of Belgrade in Serbia successfully completed a European Commission funded research project TREAT (2004-2009) for the treatment of industrial wastewater produced by sulfide ore mining and metallurgical activities in the Copper Mining and Smelting Complex Bar (RTB-BGR). Similar to acid mine drainage the effluent is characterized by low pH (1-1.5) 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 series reactor for selective precipitation 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 desired satisfactory while the achieved removal efficiencies for zinc and nickel were lower at 72.3% and 76.3% (partially re-dissolution of these elements), respectively. Additionally electrowinning 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 monocoal ascorbic acid particles at 0.1 and 1.0 g/l was conducted in laboratory conditions [1]. HRTEM-EDS analysis confirmed the presence of copper spherical nanoparticles (98 wt%). The 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 processes, e.g., selective reduction in nitric acid, oxidation of carbon monoxide and decomposition of nitrogen oxides.

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 filtered solid residue based on the iron compounds.

EXPERIMENTAL

Material

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

<table>
<thead>
<tr>
<th>Species</th>
<th>Al</th>
<th>Fe</th>
<th>Mg</th>
<th>Cu</th>
<th>Mn</th>
<th>Si</th>
<th>Ca</th>
<th>Na</th>
<th>Mg</th>
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<tr>
<td>Conc. mg/L</td>
<td>305</td>
<td>4.200</td>
<td>474</td>
<td>500</td>
<td>63.6</td>
<td>47.5</td>
<td>1.42</td>
<td>0.78</td>
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</table>

As shown in Table 1 the content of valuable critical metals such as Ce, Co and Nd are very small (few milligrams per Liter). The spontaneous precipitation of iron took the place during the transport and long standing 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](image-url)
Characterization of solid residue after filtration (as shown at Figure 1b) and drying at 110°C was shown at Figure 2.

![SEM-EDS analysis of powder after filtration (without a washing of powder)](image_url)

As shown in Figure 2, the presence of iron and oxygen confirmed the iron compounds in solid residue. The sulfur and chlorine are removed from an acidic solution, mostly sulfates. The particles are agglomerated, irregular form with sizes between 42 and 101 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.

![Precipitation efficiency during neutralisation of AMD-solution with NaOH](image_url)
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 H₂O₂ in order to oxidize Fe²⁺ to Fe³⁺.

The precipitation of cerium took place between pH-value of 7 and 8 in form of sodium cerium sulfate hydrate (Na₂Ce₂(SO₄)₃·H₂O) reaching a precipitation efficiency of about 98 %, as shown with Eq. (1) and (2).

\[ \text{H}_2\text{SO}_₄ + \text{NaOH} \rightarrow \text{Na}_2\text{SO}_₄ + 2 \text{H}_₂\text{O} \]  
\[ \text{CeSO}_₄ + \text{Na}_2\text{SO}_₄ + 1 \text{H}_₂\text{O} \rightarrow 1 \text{Na}_2\text{Ce}_2\text{(SO}_₄)_₃ \cdot \text{H}_₂\text{O} \]  

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 planned 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.

\[ \text{Al}_2\text{(SO}_₄)_₃ \cdot 6 \text{H}_₂\text{O} \rightarrow 2 \text{Al(OH)}₃ + 3 \text{H}_₂\text{SO}_₄ \]  

This is considered and confirmed with an analysis of E-pH diagram constructed in FactSage software. An increase of pH-Value from 1 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 5: E-pH diagram for Al-S-H₂O system**

**Conclusion:**

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 in 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 amending an ion exchange resin column to achieve a final clear solution of cerium oxide from the ultra-cleaned solution e.g. using ultrasonic spray pyrolysis.

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References