Recovery of Fe, Al and Mn in acid coal mine drainage by sequential selective precipitation with control of pH

E.Y. Seo [a], Y.W. Cheong [b,*], G.J. Yim [b], K.W. Min [a], J.N. Geroni [c]

[a] Department of Energy & Resources Engineering at the College of Engineering of Kangwon National University kangwondegil, Chuncheon, South Korea
[b] Earth and Environmental Research Division, Korea Institute of Geoscience and Mineral Resources, 92 Gwahang-no, Daejeon, South Korea
[c] Research Development Officer Research, Innovation and Enterprise Services, Cardiff University, Cardiff, UK

ARTICLE INFO

ABSTRACT

This study was carried out to develop a process for recovering dissolved metals from acid mine drainages (AMD). AMD sludge normally consists of a heterogeneous mixture of many elements that are thrown out due to a lack of low purity. However, purified Fe, Al and Mn hydroxides would be potential resources. The AMD from Samma-Taejeong coal mine, Samcheok, Gangwon province in Korea was neutralized by adding neutralizing agents and oxidant, hydrogen peroxide to evaluate recovery of the metals and purity of their precipitates. The metals in AMD were recovered individually according to two process schemes: (i) only neutralization, and (ii) neutralization after addition of hydrogen peroxide. The result shows that using only neutralizing agents, both dissolved Al and Fe were concurrently precipitated around at pH 4.5 so that caused the purity of each precipitate to be lowered. In the case of oxidation and then neutralization of AMD, sequence of metal removal was Fe > Al > Mn in order. Recovery ratios of dissolved Fe and Al reached 99.2–99.3% at pH 4.5 and 70.4–82.2% at pH 5.5, respectively. Recovery of Mn reached 37.8–87.5% at pH 8.5. Based on the results, oxidation before neutralization increased the recovery of dissolved Fe and Al in AMD with high purity of precipitates.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Acid mine drainages (AMD) causes water systems pollution around the mine, and they require water treatment through active or passive treatment method. The active treatment methods use neutralizing agents to raise the pH up to the effluent water quality standards, precipitate dissolved metals into insoluble sludge and then discharge overlying water. At this time, sludge with a very high water content occurs, and since it consists of a variety of chemical compositions of Fe, Al, Mn, Ca, Mg, S and so on, dehydration and disposal costs are required. As Fe hydroxide has a large specific surface area and characteristics of strong absorption with metal ions (Younger et al., 2002), researches on the sludge utilizations, including absorbent of dyes and pigments have progressed (Hedin, 2003; Wei and Viadero, 2007), but pure single component will be more appropriate in terms of utilization (Marcello et al., 2008). Provided that major pollution sources of mine drainage such as Fe, Al and Mn, etc. can be recovered in a pure state, it would maximize the utilization of each pure precipitate, thereby helping to offset the costs of water treatment.

In this context, physical, chemical and biological methods have been studied to recover dissolved metals from mine drainage. First, Deorkar and Tavlarides (1998) conducted a research to recover Fe^{3+}, Cu^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+} dissolved in mine drainage selectively using an absorbent as a physical method. In addition, there are selective recovery practices, including studies of selective absorption of Fe^{3+} from sulfuric acid solution using acrylic resin and uranium recovery research by ion exchange (Riveros, 2004; Nascimento et al., 2004).

A chemical method is a process to precipitate/recover metal components in the form of hydroxide or sulfides using specific solubility characteristics of each dissolved metal. Jenke and Diebold (1983) succeeded in forming Cu, Al, Zn and Fe into hydroxide and sulfide precipitates by injecting lime and hydrogen sulfide. Rao et al. (1996) studied a 3-step selective precipitation process of recovering Fe in the form of iron hydroxide $(Fe(OH)_3)$ at pH 3.5 by inputting lime and hydrogen peroxide before recovery of zinc as zinc sulfide (ZnS) through injection of Na_2S and removing residual metals by increasing pH to 9.5. Meanwhile, Sheremata and Kuyucak (1996) conducted a study of recovering copper at pH 3.5, obtaining Fe in the form of $FePO_4 \cdot H_2O$ at pH 1.6 using H_3PO_4 and recovering zinc in the form of zinc hydroxide. Wei et al. (2005) reported the effects of neutralizers on the recovery of Fe and Al in mine drainages.

In recent years, bioreactor research has been actively conducted to obtain sulfide source that induces sulfide precipitation from microorganisms and to improve economic efficiency of chemical methods. In a

* Corresponding author.
E-mail address: ywc@kigam.re.kr (Y.W. Cheong).

related move, Ucar et al. (2011) performed a research on the selective precipitation of Cu and Fe into sulfide precipitates using hydrogen sulfide generated from sulfate reduction reactor as a sulfide source. Tabak et al. (2003) conducted a research to recover Cd, Co, Cu, Fe, Mn, Ni and Zn into sulfide precipitates through biological treatment. In addition, Foucher et al. (2001) performed selective recovery of Cu and Zn at pH 2.8 and 3.5, respectively, using sulfate-reducing bacteria and removal of Ni and Fe with sulfide at pH 6.

The common contaminants from AMD of abandoned coal and metal mine are Fe, Al and Mn. Since these components are finally turned into sludge through active treatment or passive treatment systems, they are disposed at the outside of facilities or accumulated in the inside of passive treatment facilities. In this study, we examined the chemical proper conditions that can selectively precipitate and recovered the dissolved Fe, Al and Mn in AMD under consideration that the pure components would be potential resources. Toward this end, AMD of an abandoned coal mine were selected to evaluate ratios of recovery and purity of precipitates considering injection of an oxidant while neutralizing AMD.

2. Materials and methods

2.1. Acid mine drainage

The AMD used in the test has been discharging from an adit of the Samma-Taejeong coal mine which is located in Dogye-eup, Samcheok, Gangwon province about 300 km away from Seoul, the capital of the Republic of Korea. Table 1 shows the results of water quality analyzed by ICP (Ultima 2C, Horiba-Yuvon, France) and by IC (ICS-3000, Dionex, USA) just before the experiment. From these results, the AMD was highly acidic with pH 3.28, and concentration of Fe, Al, Mn and SO_4^{2-} was also very high with 186, 40, 13 and 1950 mg/L, respectively. The experiments were performed within 12 h as quickly as possible to minimize change in water quality due to oxidation over time.

2.2. Evaluation of sludge characteristics

Two clean beakers with volume of 2 L were prepared, and 1 L of AMD was added to each. The two beakers were stirred at 60 to 80 rpm in a Jar test (J-6S, Jisico, Korea), and the pH increased to 7 using 0.5 M Na_2CO_3 (DC Chemical, Korea). The initial suspended solid (SS) concentration was calculated by taking 100 mL of AMD from beaker 1 at the just end of jar test and by using weight loss of SS on 0.45 μm filters (Membranfilter, Macherey-Nagel, Germany) after drying at 105 °C in an oven.

Settling rate was determined by transferring the entire contents of beaker 2 into a 1 L measuring cylinder and recording the height of the boundary between overlying water and suspended solid at 2-minute intervals for the first 30 min and a 10-minute interval for the next 60 min to obtain suspended solid settling rate.

Since the solid content of the final sludge sedimentation is equal to the value multiplied by the sample volume and the initial SS concentration (Eq. (1)), the rate of sludge production (volume of precipitated

sludge/volume of neutralized sample) calculated by below Eq. (1) (USEPA, 1983).

$$V_i \times S_i = V_s \times S_s$$
$$S_s = \frac{V_i \times S_i}{V_s} \tag{1}$$

where,

V_i = sample volume (mL)
S_i = the initial SS concentration before sedimentation (mg/L)
V_s = volume of the final precipitated sludge (mL)
S_s = solid content of the precipitated sludge

2.3. Selective neutralization precipitation tests and performance evaluation

Three neutralizing agents, sodium hydroxide (10 M NaOH, Junsei, Japan), calcium hydroxide (0.5 M $Ca(OH)_2$, Fluka, Germany) and sodium carbonate (1 M Na_2CO_3, DC Chemical, Korea) were used and the concentration range of the agents was determined by referring to case studies (Wei et al., 2005; Lenter et al., 2002).

For neutralization precipitation tests, the AMD was collected and analyzed for Fe, Al and Mn whenever the pH was increased in 1 unit by adding each a small amount of neutralizing agent, while stirring AMD samples at 200 rpm in the jar test.

In order to evaluate the effects of oxidation, another neutralization test was carried out in the same way as above after putting 30 mL of 30% H_2O_2 into 1 L AMD.

Iron, Al and Mn were analyzed by means of ICP (Ultima 2C, Horiba-Yuvon, France). The samples were collected and analyzed for Fe, Al and Mn after filtration with a 0.45 μm syringe (Whatman, Cat. No. 6872-2504).

The recovery (γ) and purity (p) of metal components (Al, Fe and Mn) in the AMD according to various pH levels were obtained through following Eqs. (2) and (3) (Wei et al., 2005).

$$\gamma = \frac{C_{in} - C_{out}}{C_0} \times 100\% \tag{2}$$

where,

C_0: the concentration of the specific metal in the raw AMD (mg/L)
C_{in}: the concentration of the metal in aqueous phase before pH adjustment (mg/L)
C_{out}: the concentration of the metal in aqueous phase after pH adjustment (mg/L)

$$P = \frac{C_i}{\sum_{i=1}^{n} C_j} \times 100\% \tag{3}$$

where,

C_i: the concentration of the individual desired metal in the digested solution (mg/L)
n: the Number of metal measured
C_j: the concentration of jth metal species (mg/L)

2.4. Mineral identification and physical characteristics of selective neutralization precipitates

Particle size and its distribution curves using Fe and Al precipitate without any pretreatment were measured by a particle size analyzer (Mastersizer 2000, Malvern, UK).

The Fe and Al precipitates produced by adjusting to specific pH after oxidation were filtered with 0.45 μm filters under vacuum and then dried at a temperature of 105 °C for 1 day for XRD analysis (Philips MPD, Netherlands).

Table 1
Chemical analysis of acid mine water used for this study.

pH	Al (mg/L)	Ca	Fe	K	Mg	Mn	Na	SO_4^{2-}
3.28	40	1070	186	9	272	13	14	1950