



Selective Recovery of Dissolved Metals from Mine Drainage Using Electrochemical Reactions



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ABSTRACT

Heavy metal contamination caused by abandoned mines is a serious environmental problem in Korea. Acid mine drainage (AMD) contains various toxic heavy metals as well as dissolved iron and aluminum that contaminate downstream areas. Recent research on the removal and recovery of metals in AMD has attempted to solve environmental problems related to AMD. In a previous study, we reported that dissolved Fe, Al, Cu, and Zn/Ni can be recovered from AMD via selective precipitation. However, the recovery process consumed too many chemicals, both neutralizing and oxidizing agents. To solve this problem, the current intensity study investigated the potential of electrochemical methods to produce oxidizing and neutralizing agents that will decrease the need for chemicals. Fe(II) in anolyte was directly oxidized to Fe(III) on the electrode surface, not by oxidants. Anode material and current intensity influence oxidation reaction rate. Graphite anode resulted in the highest oxidation rate, and higher current intensity enhanced oxidation rate. In the connecting media experiments, the cation exchange membrane (CEM) and anion exchange membrane (AEM) demonstrated high loss of Fe (about 40–50%) caused by precipitation on the membrane surface and in the catholyte. The Fe loss used for salt bridge (SB) was about 10%. The catholyte contained a high concentration of hydroxide generated by the cathodic reaction that can be used as a neutralizing agent. The neutralizing agent produced by electrochemical reactions can be used to selectively recover dissolved metals. Additionally, the use of solar cell reduced energy consumption. Based on the results, it is possible to oxidize Fe(II) to Fe(III) while producing neutralizing agents for selective recovery of dissolved metals from AMD.

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1. Introduction

Mining activities have contaminated the surrounding forest, downstream areas, and farmland through acid mine drainage (AMD), mine tailing, and waste rocks [1,2]. In particular, AMD is generated by the oxidation of metals sulfides such as pyrite and generates the sulfate and acid [3]. AMD has contaminated the soil, ground water, and surface water located downstream from mines. Because of its low pH, AMD attracts various dissolved metals including Fe, Al, Mn, Cu, Zn, Pb, Ni, and Cd and is very mobile [4,5]. Both active and passive techniques have been used for AMD treatment [6–9], but these treatment methods involve

re-dissolution and sludge [10,11]. Many research groups have recently studied the recovery of dissolved metals in AMD in an attempt to solve these problems [12–17]. A previous study investigated the selective recovery of dissolved metals via simple pH control, but too many chemicals were used, including oxidizing and neutralizing agents [17,18]. Therefore, it is not cost-effective to recover metals from AMD. Additional studies should be carried out to reduce the number or cost of chemicals used in oxidation and neutralization processes. An electrochemical method was expected to solve this problem. Some research groups have studied electrochemical methods to recover and remove metals. Wang et al. (2003) reported the removal of arsenic by co-precipitation with iron hydroxide using electrochemical pH adjustment [19]. Aji et al. (2012) removed heavy metals (Cu, Zn, Ni, and Mn) from wastewater using electrocoagulation with monopolar iron electrodes [20]. Subbaiah et al. (2002) used electrochemical precipitation to remove Ni [21]. However, these studies did not

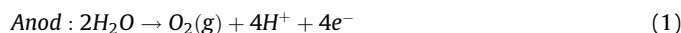
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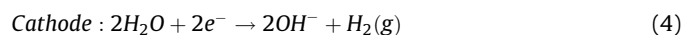
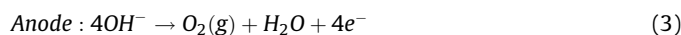
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consider selective recovery of metals dissolved in solutions. They also did not consider the simultaneous oxidation of Fe(II) and neutralization of dissolved metals. In solutions, Fe(III) and Fe(II) generally precipitates at pH range of 3~4 and 7~8, and the pH range of Fe(II) is similar to Zn, therefore, Fe(II) should be oxidized to Fe(III) to prevent the co-precipitation of Zn and Fe [22].

We hypothesized that oxidizing and neutralizing agents are produced by electrolysis of water. Theoretically, the electrochemical reaction in acidic condition is as follows [23].



The reaction in basic conditions is as follows.



Fe(II) was expected to oxidize to Fe(III) due to dissolved oxygen generated by anodic reaction. Fe(III) could then be precipitated with increase in the pH, and the neutralizing agent could be generated by cathodic reaction. We hypothesized that oxidizing and neutralizing agents could be generated for use instead of chemicals.

This study investigated how Fe(II) is oxidized to Fe(III) in the anolyte while the catholyte simultaneously generates a neutralizing agent via electrochemical reactions. The anolyte and catholyte produced by electrochemical reactions were expected to selectively recover dissolved metals from AMD.

2. Experimental

2.1. Materials

All the reagents used in this study were analytical grade, and ferrozine (monosodium salt hydrate of 3-(2-pyridyl)-5,6-diphenyl-1,2,4-triazine-*p,p'*-disulfonic acid) was used to analyze speciation of Fe by ferrozine analysis method. The actual AMD used in precipitation experiments was obtained from the Il-Kwang mine located in Busan, Korea. The initial concentrations of Fe, Al, Cu, Zn, Ca, and Mg in actual AMD were 226.4 ± 12.1 , 34.8 ± 2.0 , 25.1 ± 1.2 , 18.3 ± 2.2 , 92.4 ± 1.3 , and $18.0 \pm 0.2 \text{ mg L}^{-1}$, respectively. And the pH, ORP, and concentration of sulfate were 2.4, 424 mV, and $1,299.7 \text{ mg L}^{-1}$. Titanium, boron doped diamond (BDD), and graphite electrodes were used as anodes, and a titanium electrode was used as the cathode. The cation exchange membrane (CEM, Nafion[®] 117, Dupont, USA), anion exchange membrane (AEM, Neosepta[®] ACS, ASTOM, Japan), and salt bridge (SB) were used as connecting media to allow migration of ions between the anolyte and catholyte (Table 1). CEM pre-treatment was sequentially carried out as follows: the membrane was boiled in 30% v/v H₂O₂ and deionized water and then soaked in 0.5 M H₂SO₄ and deionized water for 1 hour each [24].

2.2. Reactors

Experiments were carried out in a Pyrex glass electrolysis reactor to evaluate the oxidizing and neutralizing capacity of electrolytes. The reactor was composed of two identical 500 mL bottles connected by Pyrex glass tubing. Electrolytes in the reactor underwent indirect oxidation by the connecting media.

The experimental reactors were designed as two types of reactors (Fig. 1). The direct oxidation reactor directly oxidizes Fe(II) to Fe(III) in the anolyte while the catholyte is injected toward the anolyte for selective precipitation. In the indirect oxidation reactor, oxidizing and neutralizing agents are first generated in the anolyte and catholyte and then injected to another reactor that contains AMD.

2.3. Experiments

Direct and indirect oxidation test used the artificial AMD. In experiments with the direct oxidation reactor, 200 mg L⁻¹ of Fe(II) was used for the anolyte while 0.3 M NaHCO₃ was used as catholyte. The influences of anode material and current intensity (0, 60, 120, and 160 mA L⁻¹) were investigated to evaluate oxidizing capacity. The influence of connecting media on minimizing the loss of Fe through precipitation and migration was also evaluated (Table 1). The ferrozine method was used to determine the amount of oxidized Fe [25,26]. Fe(III) was analyzed as Fe(II) after reduction by a 10% hydroxylamine solution. The amount of oxidized Fe was analyzed by spectrophotometer (HS 3300, Humas, Korea). Other metals were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES, Agilent 720ES, USA).

In the indirect oxidation reactor, 0.01 M NaHCO₃ was used as the electrolyte. Normal direct current (DC) power supply (P6015, ADVANTEK, Korea) or solar cell power (10 W, Yingli Solar, China) was used to supply electricity to the system (Table 1). Oxidizing and neutralizing solutions were prepared electrochemically for oxidation and neutralization of Fe(II) in the other bottle. An air blower was used to confirm oxidation by oxygen. The oxidation potential was evaluated as follows: 10, 20, 50, and 100 mL of a prepared anolyte were mixed with a 100-mL solution of 200 mg Fe (II) L⁻¹ for 24 hours at room temperature. The prepared neutralizing solution was used for selective precipitation experiments used in actual AMD using a Masterflex L/S pump (Cole Parmer 7524-45, USA).

Table 1

Experimental conditions: direct oxidation reactor (Exp. 1~8) and indirect oxidation reactor (Exp. 9 and 10).

Exp. No.	Current intensity (mA L ⁻¹)	Electrode		Electrolyte		Connecting media
		Anode	Cathode	Anolyte	Catholyte	
Exp. 1	0	-	-			-
Exp. 2	60	Graphite				
Exp. 3	120	Titanium				
Exp. 4	120	BDD		200 mg Fe(II) L ⁻¹	0.3 M NaHCO ₃	CEM
Exp. 5	120	Graphite				
Exp. 6	160	Graphite	Titanium			
Exp. 7	120	Graphite				AEM
Exp. 8	120	Graphite				SB
Exp. 9	120	Graphite		0.01 M NaHCO ₃		CEM
Exp. 10	Solar-cell	Graphite				

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