Synthesis of Iron/Aluminium Substrate for Copper Cementation

Arunwan Tottippumiruk, Pongthon Roongcharoen, Dawan Wiwattanadate*

Department of Mining and Petroleum Engineering, Chulalongkorn University,
254 Phayathai Road, Pathumwan, Bangkok 10330, Thailand
*dawancu@gmail.com; dawan.w@chula.ac.th

ABSTRACT

The present study was performed on synthesis of iron/aluminium substrate for copper cementation by mixing aluminium powder with FeCl$_2$ or FeCl$_3$ in various concentrations of HCl solution. The adsorbed amount of Fe on aluminium powder was investigated by ICP in order to achieve an optimum condition. Characteristics of iron/aluminium substrate were also investigated by XRD. Cementation of copper using the iron/aluminium substrate was also studied.

KEY WORDS: Iron/Aluminium substrate, bimetallic particles, Copper cementation

1. INTRODUCTION

Nowadays, various manufacturing processes play an important role in waste generation and environmental impacts. Hydrometallurgical cementation has been broadly used for metal recovery in waste water treatment, ore treatment, resource recycling, electrolyte purification, etc. In general, hydrometallurgical methods consist of three main processes namely leaching; solid-liquid separation; and washing-collecting, that is metal ions are recovered from pregnant solutions and then processed to provide valuable metals, and valences of the noble and reductant metals turn into ions by dissolving in solutions; solid-liquid separation, that is solid residues are separated from pregnant solutions; and washing-collecting, that is metal ions are recovered from pregnant solutions [1]. Cementation is an electrochemical process in which a metal is precipitated or melted from the solution and replaced by a metal having more active in the electromotive series [2-8].

A cementation process occurs according to the following reaction:

$$nA^{m+} + mB^{0} \rightarrow nA^{0} + mB^{b+}$$  \hspace{1cm} (1)

Where $n$, $m$, $A$, $B$, $a+$ and $b+$ represent the stoichiometric coefficients, the noble and reductant metals, and valences of the noble and reductant metal, respectively [9,10].

Copper is one of the most valuable and widespread metals used in industry; therefore, a number of copper has been widely spread as industrial wastes. Researchers continuously study on removal of copper by cementation on various substrate materials like aluminium, iron, and zinc. Due to effective electron donor in such substrate materials, especially aluminium, it has been widely used as a substrate to remove different kinds of heavy metals. While iron has a magnetic property, it is easy to separate iron from whatsoever processes which are related to the cementation on account of its characteristic. Therefore, integration of effective electron donor property of aluminium and magnetic property of iron has been widely studied.

Bimetallic iron/aluminium particles were synthesized on many previous studies in order to taste their reactivity toward different heavy metals and its application. According to standard electromotive series, aluminium has evidently seen lower reductive potential than iron. Therefore, aluminium exhibits electron donor property more effective than iron. While iron provides easier and better separation in the recovery process when it is formed together with aluminium in terms of bimetallic iron/aluminium substrate.

In this study, bimetallic iron/aluminium particles were synthesized to provide substrate having both strong reducing ability and magnetic property. Ferrous (Fe$^{2+}$) or ferric (Fe$^{3+}$) was reduced and adsorbed on the aluminium surface as favorable zero-charge iron (Fe). Adsorption experiments of copper ions on the bimetallic substrate by cementation technique were carried out in acidic solutions.

2. MATERIALS AND METHODS

2.1 Materials

Analytical grade iron (II) chloride tetrahydrate, iron (III) chloride anhydrous and copper (II) chloride dehydrated were procured from Merck, Germany. Zinc chloride (97.8%) was purchased from Ajex Finechem Pty Ltd., New Zealand and fine aluminium powder (D$_{50}$ = 90μm) was supported by Mining Engineering Laboratory, Chulalongkorn University, Thailand.
2.2 Analytical measurement

The iron/aluminium substrate was stirred at room temperature (Clifton CERASTIR), filtrated by using a filter paper (Whatman No.42) and washed in acetone. The solids were characterized with X-ray Diffraction (XRD BRUKER, model D8 advance) to confirm its nature of the composite. While metal concentrations in the solutions were measured with Inductively Coupled Plasma (ICP) optical emission spectrometer (JOBIN YVON, HORIBA, model JY 2000).

2.3 Adsorption experiments

Adsorption experiments were carried out by adding 1 gram of substrate into 10 ml of copper and zinc solutions containing in a 50 ml Erlenmeyer flask. In this phase, HCl did not play a crucial role in reaction acceleration because copper and zinc solutions have already acidic property. The solution has been slowly stirred for 3 hours and filtered via a filter paper. After that, the concentrations of metal ion left in the solution were measured ICP optical emission spectrometer.

3. RESULT AND DISCUSSION

3.1 Preparation of the iron/aluminium substrate

In this experiment, a green solution of ferrous (Fe²⁺) ion was prepared by adding 19.88 grams of 1 M FeCl₂•4H₂O, 1.6 M NaCl and 0.04 M HCl in 100 ml volumetric flask. Pipetted 50 ml of the green solution into an Erlenmeyer flask containing 5 grams of fine aluminium powder in a fume hood. After that, the solution was consistently stirred for 3 hours in order to mix well. An adsorption process occurs according to the following reaction:

\[ 3\text{Fe}^{2+} + 2\text{Al} \rightarrow 3\text{Fe} + 2\text{Al}^{3+} \]  

(2)

A concentration of 0.04 M HCl was chosen from different circumstances to be an optimal condition for 7.73% Fe adsorption. At this level, aluminium rarely dissolved in an acidic solution. Generally, an oxide layer will cover on aluminium surface causing the process to be an obstruction [1]. The calculation method of percent adsorption shown as the following equation:

\[ \text{adsorbed Fe(\%)} = \frac{\text{Fe}_{\text{initial}} - \text{Fe}_{\text{final}}}{\text{Fe}_{\text{initial}}} \times 100 \]  

(3)

Where adsorbed Fe, Fe_{initial}, Fe_{final} represent adsorbed ferric or ferrous (%), initial concentration of Fe (g), and final concentration of Fe (g) respectively. The H² of HCl and the Cl of NaCl were added into the reaction in order to support iron adsorption onto the aluminium surface effectively.

The XRD patterns demonstrate that both forms of the aluminium particle and the iron/aluminium substrate differ from each other, especially in the range of intensity from 20 to 23. At this range, the iron peaks are higher and more identical intensity than any other discrepancy. As a result, the synthesized particle was confirmed as the bimetallic system consisting of a core metal (Al) and a second metal (Fe) [12]. Furthermore, the synthesized particle also shows a brown reddish color which is different from the original color of aluminium. Comparing the highest aluminium peak of the aluminium particle (320) in figure 1a with the Al particle (320) in figure 1a with the Al particle (320) in figure 1b showed significantly decreasing. This confirmed that there were the Fe particles adsorbed onto the Al surface, even though quite low concentration (7.73%). The aluminium peak intensity was found to decrease with the increasing of Fe absorption onto the aluminium surface. Under this condition, the mixed solution of 1 M FeCl₂•4H₂O, 1.4 M NaCl, and 0.4 M HCl, with contact time 1.5 and 3.0 hours, was found not to be an optimal condition for synthesizing the iron/aluminium substrate.

Figure 1: XRD patterns of (a) the aluminium particle, (b) the iron/aluminium substrate. When compared (a) with (b), iron particles were coated on aluminium surface making the pattern in which the range of intensity from 20 to 23 more smoothly.

Resources Recycling 17
In case of the solution mixed with 0.01 M HCl, it was found that the Fe could adsorb onto the aluminium surface effectively; however, some ferrous ions was transformed into ferric ions so that the green solution turned into brown reddish color instead. Hence, the 0.01 M HCl was not an optimal condition as well. Whereas, the solution mixed with 0.04 M HCl was found to be a suitable condition so that the condition was used for the adsorption experiments of copper ion in this study.

3.2 Adsorption experiments of copper ion using the iron/aluminium substrate

Cementation of copper ion using the iron/aluminium substrate was investigated under acidic condition (pH 3.65). CuCl$_2$.2H$_2$O 1 g/L was measured and poured in 50 mL volumetric flask. Pipetted 10 ml of the solution into 50 ml Enlemayer flask containing 1 gram of aluminium powder and the iron/aluminium substrate. Prior to ICP-OES analysis, The solutions were filtered through filter papers (Whatman No.42). The cementation process occurs according to the following reaction:

$$3\text{Cu}^{2+} + 2\text{Al} \rightarrow 3\text{Cu} + 2\text{Al}^{3+}$$ \hspace{1cm} (4)

The adsorbed amount of copper on aluminium powder and the iron/aluminium substrate was found to be 98.6 and 99.1%, respectively (Fig. 3). It was assumed that iron has no significant impact on the cementation process. Mechanism of the cementation process was also monitored by switching the solution from CuCl$_2$.2H$_2$O to ZnCl$_2$ with aluminium powder and the iron/aluminium substrate in order to find out the ability of iron whether it enchances the percenteate of metal recovery or not.

Figure 2: Standard Electrode Potential (E$^0$) of copper, ferric, ferrous, zinc and aluminium.

According to figure 2, Zn cannot reduce copper and iron (either Fe$^{2+}$ or Fe$^{3+}$) to metal form adsorbed on the surface of the iron/aluminium substrate. While, Al can reduce either copper, ferrous, ferric or zinc to recover metal on the Al surface.

ACKNOWLEDGEMENTS

The author would like to thank the Department of Mining and Petroleum Engineering, Faculty of Engineering, Chulalongkorn University for analytical instruments and chemicals support in this study. Thanks are also expressed to Mr. Utit Thongkueng and Mr. Pongthon Roongcharoen for kind advising on analytical instruments.
REFERENCES


