Summary

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学 位 論 文 題 名

Title of dissertation submitted for the degree

< Enhanced cementation for heavy metal removal and recovery using aluminum as electron donor and electro-conductive particles as electron mediator>

<summary>

Cementation, which is an electrochemical reduction reaction, is generally used to remove and recover metal ions from aqueous solutions using more noble metal. As a more noble metal, aluminum (Al) is considered a promising electron donor for environmental remediation because of its very low standard electrode potential (i.e., $E^0_{Al3+/Al} = -1.67$ V vs. SHE) and less toxicity. However, its practical use is limited due to the tight and dense insulating Al oxide layer (Al_2O_3 layer) on Al^0 surface. Because of this, many researchers have been studied the removal of Al_2O_3 layer for cementation using Al by operating at high temperature, strongly acid/alkaline pH, and the addition of chloride ions. These factors can enhance the cementation efficiency using Al^0, but make it difficult to use Al for environmental remediation. Recently, it was reported that cementation efficiency using Al^0 was enhanced even without Al_2O_3 layer removal by using activated carbon (AC), which acts as an electron mediator from Al^0 to gold ions in ammonium thiosulfate solutions. This AC/Al-cementation can successfully recover gold ions, but there is no investigation in the removal and recovery of heavy metal ions not gold ions from sulfate and chloride solutions using AC/Al-mixture, and no investigation alternative electron mediator to AC. In this study, the applicability of AC/Al-mixture and alternative electron mediators to replace AC were investigated by batch-type cementation experiments, surface analyses, and electrochemical measurements.

Sulfate and chloride solutions containing 1 mM metal ions were prepared by dissolving reagent grade chemicals in DI water. The initial pH was adjusted to 1–5, the total concentration of SO_4^{2-} and Cl^- was adjusted to 0.1 M to normalize the effects of these anions during cementation experiments. Prepared 10 mL of solutions were added to a 50-mL Erlenmeyer flask, then ultra-pure N_2 gas was

introduced to remove dissolved oxygen in solutions for 15 min. After this, the designated amount of Al powder and/or AC (or SiO_2, TiO_2, and Fe_3O_4) were added to the sulfate/chloride solutions, N_2 gas was further introduced for 5 min, and then the flask was tightly sealed with a rubber cap and parafilm. The flasks were shaken at 25 °C in a thermostat water bath shaker with 40 mm of shaking amplitude and 120 min^{-1} of shaking frequency. After predetermined time periods, the filtrates were collected using a syringe-driven membrane filter, measured the final pH, diluted, and analyzed the metal concentration by ICP-AES. The cementation products were collected by vacuum filtration, washed several times with DI water, and dried in a vacuum oven at 40 °C for 24 h, and then analyzed by SEM-EDS, XPS, and AES. To understand the mechanisms of cementation, OCP, LSV, and EIS were carried out using a potentiostat in a conventional three-electrode system (working electrodes: Al, AC/Al, Fe_3O_4/Al, and metals (e.g., Pb, Cd, Co, Ni, and Zn) electrodes; reference electrode: Ag/AgCl electrode filled with saturated KCl; counter electrode: platinum electrode). Ultra-pure N_2 gas was introduced for 30 min to remove dissolved oxygen, three electrodes were immersed, then electrochemical experiments were measured at 25 °C under the determined conditions.

When using only Al, cementation efficiency of metal ions (e.g., Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}) was 0 at initial pH over 4 in sulfate solutions. The XPS results of cementation products using only Al showed that the Al and Al_2O_3 peaks were detected, which indicates Al_2O_3 layer was not removed and inhibited electron transfer from Al to metal ions. With AC, cementation efficiency of whole metal ions was higher than using only Al and only AC. The results of SEM-EDS, XPS, and AES of cementation products obtained by using AC/Al-mixture showed that cemented metals were deposited as an elemental form on AC attached Al surface. Linear sweep voltammograms for Al and AC/Al electrodes showed that the reduction reaction was more active when AC was attached on Al electrode surface, which suggests that AC acts as an electron mediator from Al to metal ions even without Al_2O_3 layer removal.

In chloride solutions, insulating Al_2O_3 layer was removed from Al^0 surface at initial pH 4 because of the formation of soluble aluminum chloride complexes, so cementation efficiency of Pb^{2+} and Cd^{2+} was around 99% while the cementation efficiency of Co^{2+}, Ni^{2+}, and Zn^{2+} was almost 0. The results of OCP and LSV showed that the cementation of Co^{2+} and Ni^{2+} was inhibited by hydrogen competition and Zn^{2+} was suppressed by a slow cementation rate. With AC, the cementation efficiency was depending on the metal ions: cementation efficiency of Pb^{2+} and Cd^{2+} was suppressed and of Co^{2+}, Ni^{2+}, and Zn^{2+} was enhanced. These results may be due to the high specific area of AC attached on Al surface.

To investigate alternative electron mediators to AC, semi-conductor TiO_2 and non-conductor SiO_2 were used as candidates for electron mediator on cementation using Al. When SiO_2 was used on cementation using Al, cementation efficiency was not enhanced even without Al_2O_3 layer in chloride solutions, which indicates non-conductivity materials can not used as electron mediator from Al to metal ions. In the case of using TiO_2, enhanced cementation was observed with/without Al_2O_3 layer. Based on the AES analysis, Co and Ni were deposited as an elemental form together with small TiO_2 particles attached on Al surface, which suggests electro-conductivity particles can be used as electron mediators from Al to metal ions even without Al_2O_3 layer removal.

To apply physical separation such as magnetic separation, magnetite (Fe_3O_4), a ferromagnetic material, was used as an electron mediator for cementation of Cd^{2+} and Zn^{2+} from sulfate solutions using Al. When Fe_3O_4 was used as an electron mediator, cementation efficiencies were enhanced even with insulating Al_2O_3 layer. The SEM-EDS results for cementation products using Fe_3O_4/Al-mixture showed that Cd and Zn were reductively cemented on the Fe_3O_4 attached on Al surface. To understand the cementation mechanisms when Fe_3O_4 was attached on Al surface, EIS measurements were carried out for Al and Fe_3O_4/Al electrodes. The EIS results showed that the charge transfer resistance was significantly decreased from 120 to 2 kΩ when Fe3O4 was attached on Al surface, which indicates that Fe_3O_4 acts as an electron mediator and cementation reaction occurs due to the low resistance on Fe_3O_4 surface attached on Al surface. After cementation, cementation products were ultrasonicated for 10 min in 400 mL DI water, and then the suspension was agitated at 400 rpm to disperse the cementation products. After this, magnetic separation was conducted for 1 min by attached a rare earth tube magnet to the outer surface of the beaker. To minimize the entrapment of non-magnetic particles in magnetic fraction and of magnetic particles in non-magnetic fraction, magnetic separation was conducted at least 2 times. After magnetic separation, the magnetic and non-magnetic fractions were filtered by a vacuum pump with a membrane filter, thoroughly washed with DI water, and dried in a vacuum oven at 40 °C for 24 h. The dried non-magnetic and magnetic fractions were analyzed by SEM-EDS and dissolved in aqua regia to determine the effects of magnetic separation. The distribution results of magnetic separation for Cd- and Zn- cementation products showed that a significant portion of cemented Cd and Zn were concentrated together with Fe_3O_4 in magnetic fraction, and used Al was concentrated in non-magnetic fractions. These results showed that magnetic separation could be used as a post-cementation process using Al as an electron donor and electro-conductive materials as an electron mediator.

This dissertation showed that electro-conductive materials as an electron mediator enhance the cementation efficiency using Al as an electron donor even without Al_2O_3 layer removal. This suggests that cementation technique using Al and electro-conductive materials provides a practical way to use Al with a very low standard electrode potential for environmental remediation because it does not require extreme operating conditions to remove Al_2O_3 layer such as strongly acid/alkaline pH, high temperature, and with chloride ions. Moreover, if Fe_3O_4 was used as an electron mediator, magnetic separation could be considered as a post cementation process.