学 位 論 文 内 容 の 要 旨

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学 位 論 文 題 名

Enhanced cementation for heavy metal removal and recovery using aluminum as electron donor and electro-conductive particles as electron mediator
(電子供与体アルミニウムと電子媒介粒子を用いた重金属回収・除去のための高効率セメンテーション)

Cementation is a method to recover and remove metal ions from aqueous solutions by reductive deposition of the metals using another elemental metal acting as an electron donor or reducing agent. Cementation has been used in hydrometallurgical processes as well as in environmental remediation to remove toxic heavy metals from contaminated solutions. Aluminum (Al) has been considered as a promising electron donor for environmental remediation, because of its less toxicity and low standard electrode potential, allowing it to use for reducing most other metal ions without secondary contamination. Practical application of Al in cementation is, however, limited due to the presence of surface Al oxide layer(Al_2O_3), which inhibits electron transfer from Al to metal ions. Recently, a new cementation technique using the mixture of Al and activated carbon (AC) has been proposed for recovering gold ions from ammonium thiosulfate solution. In this technique, AC attached on Al surface act as an electron mediator, and electrons are transferred from Al to gold ions even without removing Al oxide layer. In this study, applicability of the cementation method using Al as an electron donor and AC as an electron mediator was investigated for removing heavy metal ions from sulfate and chloride solutions, and alternative electron mediators to AC was also studied.

Chapter 1 describes the background and objectives of this study, and a literature review on cementation using Al.

In Chapter 2, effects of AC addition on the cementation of Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} from sulfate solutions were investigated using Al powder as an electron donor. The results of solution analysis showed that at pH over 4, efficiencies of metal ion removal from solutions were higher when using both AC and Al than that with only AC or Al. The results of surface analysis for the cementation products by SEM-EDX, XPS, and AES showed that the metals were deposited as an elemental form on AC attached on Al surface. The result of linear sweep voltammetry (LSV) for Al electrode in cadmium sulfate solution at pH 5 showed that current for reducing Cd ions increased by attaching AC on Al electrode surface. These results suggested that AC act as an electron mediator to enhance electron transfer from Al to heavy metal ions even in the presence of insulating surface aluminum oxide layer, and that cementation technique using AC/Al mixture can be applied to remove a wide variety of heavy metal ions from sulfate solution.

In Chapter 3, the effects of AC addition on the cementation of Pb^{2+}, Cd^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} from chloride solutions at initial pH 4 were investigated using Al as an electron donor. In chloride solutions, insulating Al oxide layer was removed from Al surface due to formation of soluble aluminum

chloride complexes, and this caused high cementation efficiency (99%) for Pb^{2+} and Cd^{2+} while the cementation efficiencies for Co^{2+}, Ni^{2+}, and Zn^{2+} were almost zero, mainly because of competition of metal deposition and hydrogen evolution (for Co^{2+} and Ni^{2+}), and slow metal deposition rate (for Zn^{2+}). With AC/Al, cementation of Pb^{2+} and Cd^{2+} was suppressed and cementation of Co^{2+}, Ni^{2+}, and Zn^{2+} was enhanced. Based on the results of electrochemical experiments and SEM-EDX analysis for cementation products, a possible mechanism for the suppression and enhancement of the cementation of different metal species in chloride solutions was discussed.

In Chapter 4, alternative electron mediators to AC were studied. Using fine particles of Ti oxide (TiO_2, rutile) and Si oxide (SiO_2) as an alternative to AC, cementation of Co^{2+} and Ni^{2+} from sulfate and chloride solutions were investigated with Al as an electron donor. No cementation occurred when non-conductive SiO_2 was used. When semi-conductor TiO_2 was used, enhanced cementation of Co and Ni occurred: the results showed that elemental Co and Ni were deposited on TiO_2 particles attached on Al surface, and that cementation efficiencies increased with increasing the dosage of TiO_2. These results suggest that electro-conductive particles like TiO_2 can be used as an alternative electron mediator for enhanced cementation using Al as an electron donor.

In Chapter 5, using Al particles as an electron donor and magnetite (Fe_3O_4) particles as an electron mediator, cementation of Cd^{2+} and Zn^{2+} from sulfate solutions were investigated. The results of cementation experiments showed that Cd and Zn were deposited on Fe_3O_4 particles attached on Al surface, and that the cementation efficiencies of these metals increased with increasing Fe_3O_4 dosage. The results of electrochemical impedance spectroscopy for Al electrode confirmed that charge transfer resistance was reduced when Fe_3O_4 was attached on the surface. By applying ultra-sonification and magnetic separation for cementation products, a significant portion of cemented Cd and Zn were recovered together with Fe_3O_4 in a magnetic fraction, and Al were separated to a non-magnetic fraction.

Chapter 6 summarized the important findings of this dissertation.