学　位　論　文　内　容　の　要　旨

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学　位　論　文　題　名

Development of the detoxification method for zinc plant leach residues by removing heavy metals using coupled extraction-cementation (CEC) process
(同時浸出-析出法に基づいた亜鉛浸出残渣からの毒性重金属の除去法の開発)

Enormous amounts of solid wastes are generated annually as the result of extensive mining, mineral processing, and metal extraction operations. For example, zinc (Zn) metal extractions via hydrometallurgical processes—leaching of calcine or zinc oxide minerals followed by electrowinning of Zn—generate huge amounts of zinc plant leach residues (ZPLRs) which are often stockpiled, and in many instances abandoned after closure of mining/metallurgical processing operations. With the rapid depletion of high-grade geogenic ores, ZPLRs are now considered as secondary resource because they contain significant amounts of valuable metals such as Zn, copper (Cu), lead (Pb), and silver (Ag) depending on the original ores processed. From an environmental point of view, however, ZPLRs are considered as toxic wastes because they contain hazardous heavy metals such as Pb, Zn, and cadmium (Cd) among others. The environmental and the resource's concerns of the ZPLRs could be addressed by removing/recovering heavy/valuable metals. In this study, an innovative method, a coupled extraction-cementation (CEC) process that combines two stages (i.e., extraction and recovery of extracted valuable/heavy metals thereby minimizing the operation stages and amounts of lixiviant) is investigated to detoxify high-Pb and Zn ZPLRs obtained from Kabwe, Zambia. The outline and abstract of each chapter are as below:

In Chapter 1, background, problem description, and objectives of the study was presented.

In Chapter 2, a review of previous studies on methods and techniques used in the concentration of valuable minerals and recovery of valuable and critical metals from ZPLRs and other Zn hydrometallurgical solid wastes such as iron removal purification residues and metal cementation filter cake was conducted.

Chapter 3 reported on the detoxification of ZPLRs by the Fe-based CEC process using micro-scale zero-valent iron (mZVI) and acidified chloride solution. For the Fe-based CEC process, only Pb (the most toxic) was targeted for cementation in leaching pulp before solid-liquid separation. Lead and Zn removal was evaluated in different solution compositions with and without the addition of mZVI. The addition of mZVI during ZPLRs leaching (i.e., Fe-based CEC) increased Pb removal from 3% to 24%, 1.3% to 27.5%, 5.2% to 34.9%, and 6.5% to 55.8% when NaCl concentration was fixed at 0.86 M and HCl concentrations were 0 M, 0.01 M, 0.05 M and 0.1 M, respectively, after 12 h. Meanwhile, Zn removal was not affected by NaCl concentration and addition of mZVI but increased with increasing the HCl concentration. In fact, extracted Zn remained in solution because it is thermodynamically unfavorable to be cemented by mZVI. Analysis of the Pb-loaded mZVI (magnetic fraction) by scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDX) and X-ray photoelectron spectroscopy (XPS) revealed that Pb was recovered during leaching via cementation as zero-valent Pb. The toxicity characteristic leaching procedure (TCLP) for Pb of ZPLRs before and after treatment decreased from 12.9 to 3.5 mg/L (below 5 mg/L threshold).

In Chapter 4, selective agglomeration of zero-valent Pb, Zn, and Al was investigated. This was necessary to evaluate the applicability of the Al-based CEC process for ZPLRs because the hypothesized cementation product (Pb-Zn-Al) cannot be separated physically from the leaching pulp using magnet which is the case for Fe-based CEC process. When Zn, Al, and Pb metal powders were shaken in 0.1 M HCl, only Pb agglomerated. Further investigation showed that Pb agglomeration occurred in acidified chloride (HCl-NaCl) solution, but not in non-acidified chloride (NaCl) solution. Agglomeration was proposed to be as a result of the removal of the brittle oxide film and metallurgical bond formation (‘solid state cold welding’) between Pb particles because Pb is a soft metal whose crystallization occurs even at room temperature. To investigate selective agglomeration of fine Pb metal particles in presence of other fine particles, fixed amounts of Pb metal powder were mixed with various amounts of fine quartz particles (-53 microns). Aluminum metal powder to cement dissolved Pb ions. Separation of agglomerated Pb from quartz was done by sieving. Around 98% of Pb metal powder was selectively agglomerated and could be separated effectively from quartz even in as high mass ratio of quartz to Pb metal as 24 g to 0.15 g. This implied that Al-based CEC could be applied to ZPLRs because cementation product could agglomerate and separated from the leaching pulp by sieving.

Chapter 5 investigated the removal of both Pb and Zn from ZPLRs by Al-based CEC process using zero-valent aluminum (ZVAl) in acidified chloride solution. The reasons for using ZVAl were (1) to cement both Pb and Zn since they both thermodynamically feasible to be reductively precipitated by Al metal, and (2) to use stronger reducing agent metal so as to increase the rate of the electrochemical reaction of cementation of Pb and Zn. The fact that ZVAl and cemented metals (i.e., Pb and Zn) are non-ferromagnetic, separation of cementation product from the leaching pulp was achieved via sieving since the cemented product agglomerated. The results showed that Pb removal, for 2 h, significantly increased when ZVAl was added at a low chloride concentration (e.g., for 0.1 M HCl, the addition of ZVAl increased Pb removal from 3% to 69% and 9% to 72% for 0.5 M and 1 M NaCl). The dramatic increase of Pb removal at low NaCl concentration was attributed to the leaching solution not attaining saturated with dissolved Pb ions and Pb-Cl complexes. However, Zn removal, which was independent of NaCl concentration and addition of ZVAl, was not cemented out of the leaching pulp despite its cementation reaction being thermodynamic favorable. The suppression of cementation of Zn by ZVAl was attributed to proton competition for electrons from ZVAl. The leachability test results using TCLP protocol for detoxified residues showed that Pb and Zn in solution were as low as 0.12 mg/L (below 5 mg/L threshold) and 21.5 mg/L, respectively. Treatment flowchart for detoxification of ZPLRs using Al-based CEC was proposed.

And finally, Chapter 6 summarized important findings of this dissertation and proposed a possible application.