Summary

Development of the detoxification method for zinc plant leach residues by removing heavy metals using coupled extraction-cementation (CEC) process

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Introduction

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 extraction 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 (Gutiérrez et al., 2016).

With the rapid depletion of high-grade geogenic ores, ZPLRs are now considered as secondary resources 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 toxic wastes because they contain hazardous heavy metals such as Pb, Zn, and cadmium (Cd), among others. Among the heavy metals of concern, Pb and Cd are ones of the most problematic because of their deleterious effects on human health even at very low amounts (i.e., 0.01 mg/L levels) (Tabelin et al., 2018). For example, the Kabwe town, Zambia (Fig. 1), is one of the most Pb-polluted areas where the topsoil of residential area has alarming high Pb content of over 2000 mg/kg (Kříbek et al., 2019) and children with blood Pb level as high as 4.28 mg/L (Yabe et al., 2019) and all these are attributed to the mining solid wastes that were generated and dumped between 1902 and 1994 when the area had a large lead-zinc (Pb-Zn) mining and processing industry (Tembo et al., 2006).

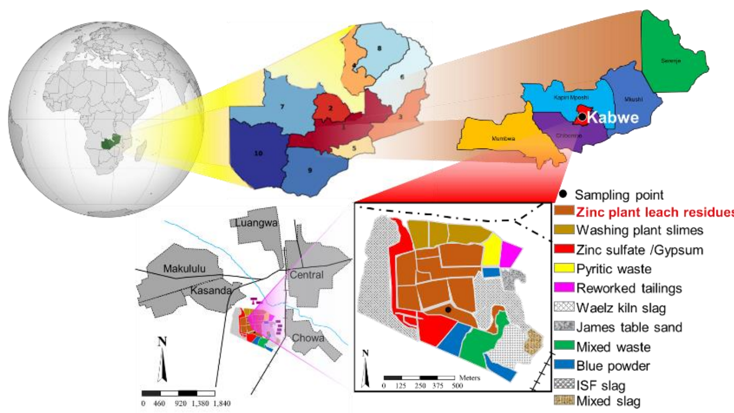

Figure 1. Schematic geographic map of Africa superimposed with the map of Zambia superimposed and the location of Kabwe and residential areas as well as different types of historic Pb-Zn mine wastes.

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. This approach would innovatively solve the environmental and resource concerns of the ZPLRs altogether. The main objectives of this study are (1) to detoxify ZPLRs by removal of Pb via Fe-based CEC process using micro-scale zero-valent iron (mZVI) as the

Pb^{2+} cementation agent in acidified chloride solution, and (2) to investigate the removal of both Pb and Zn from ZPLRs by Al-based CEC process using zero-valent aluminum (ZVAl) in acidified chloride solution.

Lead removal from zinc plant leach residues by coupled extraction-cementation using micro-scale zero-valent iron in an acidified brine solution

In Chapter 3, an innovative approach to achieve the rapid and permanent detoxification of ZPLRs via coupled extraction-cementation (CEC) process—a process whereby Pb (most toxic metal in the studied ZPLRs) from the pulp is recovered/captured as soon as it is extracted during the leaching stage via cementation onto magnetic materials (micro-scale zero-valent iron (mZVI))—prior to solid-liquid separation was reported. This process is referred to as the Fe-based CEC process because mZVI was used as the reductant of extracted Pb^{2+} while leaving co-dissolved Zn^{2+} in solution. Besides, using mZVI made it easy for the physical separation of reductively precipitated Pb on the surface of mZVI from the leaching pulp using a magnet. 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 (Fig. 2). 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).

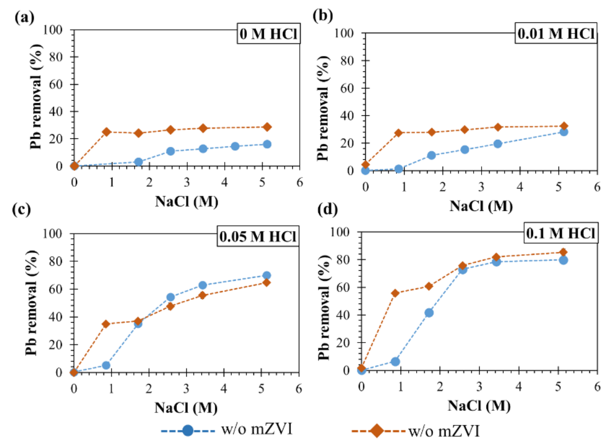

Figure 2. Effects of solution composition on Pb removal from ZPLRs with and without addition of mZVI: (a) 0 M HCl and 0–5.13 M NaCl, (b) 0.01 M HCl and 0–5.13 M NaCl, (c) 0.05 M HCl and 0–5.13 M NaCl, and (d) 0.1 M HCl and 0–5.13 M NaCl

Lead and zinc removal from zinc plant leach residues by coupled extraction-cementation using zero-valent aluminum in an acidified brine solution

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 the removal of Pb and Zn from ZPLRs because the hypothesized cementation product (Pb-Zn-Al) cannot be separated physically from the leaching pulp using a magnet as the case for the 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 (0.15 g) of Pb metal powder were mixed with various amounts of fine quartz particles (-53 microns). The aluminum metal powder was added 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 a 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 the cementation product could agglomerate and be 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 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 (which was shorter than 12 h required for Fe-based in chapter 3), 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) (Fig. 3 (a)). 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 (Fig. 3 (b)). 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. A treatment flowchart for detoxification of ZPLRs using Al-based CEC was proposed (Fig. 4).

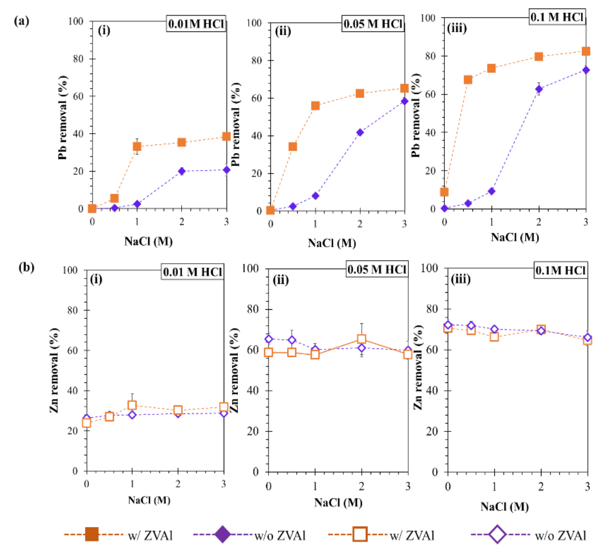

Figure 3. Effects of solution compositions on (a) Pb and (b) removal from ZPLRs with and without ZVAl addition: (i) 0.01 M HCl and 0–3 M NaCl, (ii) 0.05 M HCl and 0–3 M NaCl, and (iii) 0.1 M HCl and 0–3 M NaCl.

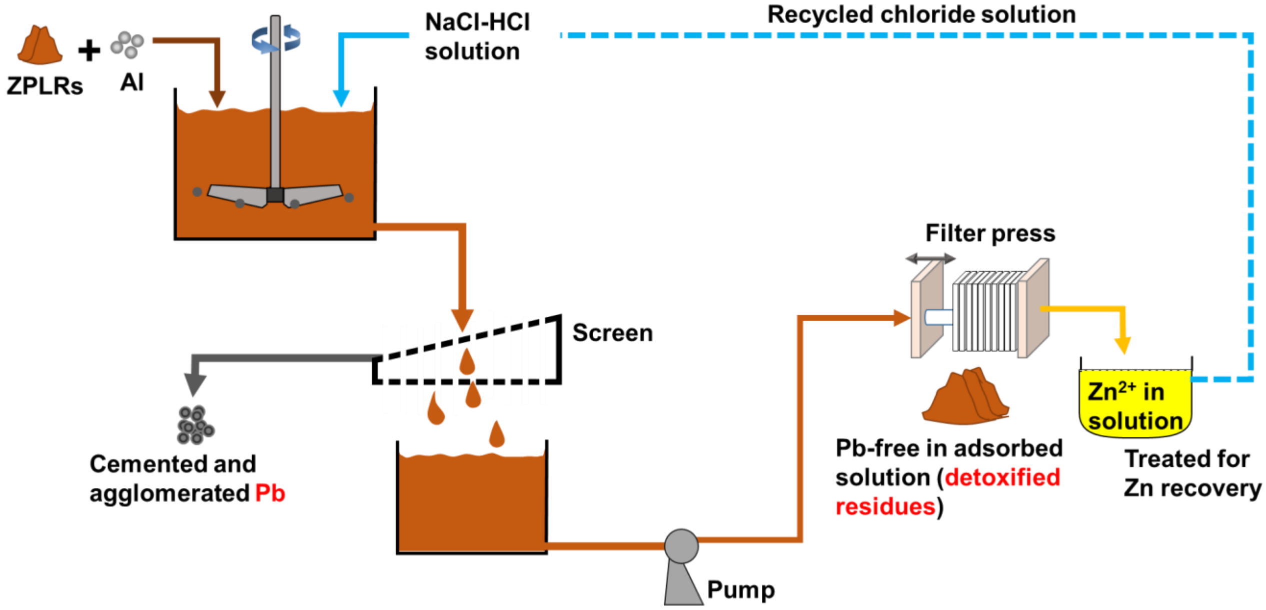

Figure 4. A conceptual flowsheet of the treatment of ZPLRs using Al in the concurrent extraction-cementation (CEC) technique.

References

Gutiérrez, M., Mickus, K., Camacho, L.M., 2016. Abandoned PbZn mining wastes and their mobility as proxy to toxicity: A review. Science of The Total Environment 565, 392–400. https://doi.org/10.1016/j.scitotenv.2016.04.143

Kříbek, B., Nyambe, I., Majer, V., Knésl, I., Mihaljevič, M., Ettler, V., Vaněk, A., Penížek, V., Sracek, O., 2019. Soil contamination near the Kabwe Pb-Zn smelter in Zambia: Environmental impacts and remediation measures proposal. Journal of Geochemical Exploration 197, 159–173. https://doi.org/10.1016/j.gexplo.2018.11.018

Tabelin, C.B., Igarashi, T., Villacorte-Tabelin, M., Park, I., Opiso, E.M., Ito, M., Hiroyoshi, N., 2018. Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies. Science of The Total Environment 645, 1522–1553. https://doi.org/10.1016/j.scitotenv.2018.07.103

Tembo, B.D., Sichilongo, K., Cernak, J., 2006. Distribution of copper, lead, cadmium and zinc concentrations in soils around Kabwe town in Zambia. Chemosphere 63, 497–501. https://doi.org/10.1016/j.chemosphere.2005.08.002

Yabe, J., Nakayama, S.MM., Nakata, H., Toyomaki, H., Yohannes, Y.B., Muzandu, K., Kataba, A., Zyambo, G., Hiwatari, M., Narita, D., Yamada, D., Hangoma, P., Munyinda, N.S., Mufune, T., Ikenaka, Y., Choongo, K., Ishizuka, M., 2019. Current Trends of Blood Lead Levels, Distribution Patterns and Exposure Variations among Household Members in Kabwe, Zambia. Chemosphere 125412. https://doi.org/10.1016/j.chemosphere.2019.125412