Lead removal in zinc leach residues from Kabwe, Zambia by carrier-in-pulp method using zero-valent iron

M. Silwamba^{1,2*}, M. Ito³, T. Fukushima¹, I. Park³, S. Jeon³, C. B. Tabelin⁴, N. Hiroyoshi³

1) Division of Sustainable Resources Engineering, Graduate School of Engineering, Hokkaido University, Sapporo, 060-8628, JAPAN

2) Department of Metallurgy and Mineral Processing, School of Mines, The University of Zambia, P.O. Box 32379, Lusaka, ZAMBIA

3) Division of Sustainable Resources Engineering, Faculty of Engineering, Hokkaido University, Kita-Ku, Sapporo 060-8628, JAPAN

4) School of Minerals and Energy Resources Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

* corresponding author: smarthias11@gmail.com

Abstract: Zinc leach residues (ZLRs) are hazardous materials because they contain toxic heavy metals such as lead (Pb) and pose serious risks to the ecosystem and people living nearby. This study investigated Pb removal from ZLRs collected from Kabwe (Zambia), one of the most Pb-polluted towns in the world, using carrier-in-pulp method. ZLRs and zero-valent iron (ZVI), which was used as the carrier, were simultaneously mixed in NaCl solution. Pb was extracted from ZLRs and formed Pb-chloride complexes, which was reductively precipitated as Pb⁰ on ZVI. The Pb-loaded ZVI was then separated from the leach pulp by magnetic separation. Pb removal was evaluated under various conditions such as leaching time, ZVI dosage and solution composition. The maximum Pb removal from ZLRs (about 78 wt% Pb) was collated with Pb bound to acid leachable solid phases determined by sequential extraction. Comparing Pb removal when ZLRs were leached with and without the addition of ZVI, it was found that the addition of ZVI significantly improved the removal of Pb at low concentrations of NaCl.

Keywords: lead, zero-valent iron, zinc leach residues

1. INTRODUCTION

Zinc (Zn) is a widely utilized metal owing to its application in cosmetics, healthcare, dry batteries, corrosion protection as a sacrificial anode, and construction¹. Zinc extraction processes depend on the mineralogy of the ore. For example, roasting-leaching-electrowinning processes is used for zinc sulfide minerals while direct leaching-electrowinning processes are typically applied to zinc oxide minerals. Zinc sulfide or oxide minerals usually occur with ‘sister’ lead minerals. During the leaching stage, enormous amounts of solid wastes called zinc leach residues (ZLRs) are generated that contain significant amounts of lead (Pb) and Zn. The high amounts of valuable metals in ZLRs make these solid waste materials to have an economic importance especially recently when high-grade ores have depleted. However, these materials pose serious environmental threats to ecosystem and human beings owing to the amounts of toxic metal, Pb, that causes numerous disorders and diseases.

Hydrometallurgical processes have been applied to recover or remove Pb from ZLRs for the detoxification of these materials as well as for the Pb metal sustainability as it is still used in acid batteries². These hydrometallurgical processes usually start with leaching followed by filtration, and the recovery of dissolved metals from the filtrate after

purification. The disadvantages of this traditional approach of Pb removal from ZLRs are the use of highly concentrated leaching solutions, the very long process flow and above all, the generation of residues that contain residual solutions of toxic Pb due to the inherently incomplete solid-liquid separation encountered with very fine particles. To overcome this, extensive washing or stabilization of residues before disposal should be carried out. These challenges can be addressed by the addition of a ‘carrier’ during leaching that can sequester extracted Pb from leach pulp directly and separated from the suspension before filtration. Our laboratory has developed this new approach called carrier-in-pulp (CIP) method³. One good carrier for Pb²⁺ is zero-valent iron (ZVI) because of its lower standard redox potential than Pb that allows this material to sequester dissolved Pb via reductively precipitation (i.e., cementation). Pb-loaded ZVI, which is magnetic, can then be separated from the leach pulp using a magnet. CIP has been previously applied to remove Pb from municipal solid waste (MSW) molten fly ash. This solid waste contains lower concentration of Pb, which is found in easier to dissolve phases compared with those found in ZLRs.

This study investigated the removal of Pb from ZLRs obtained Kabwe, Zambia, one of the most highly Pb-polluted town in the world, using the CIP approach. To understand the solid-phase partitioning of Pb and Zn in

ZLRs, sequential extraction was carried out to supplement the mineralogical characteristics obtained by X-ray powder diffraction (XRD). The effects of ZVI dosage, time and solution composition on Pb removal were also elucidated.

2. MATERIALS AND METHODS

2.1. Materials

ZLRs composed were air-dried for 30 days in the laboratory before being dry-sieved using stainless steel sieves to obtain $-106\ \mu\text{m}$ fraction. The elemental compositions of ZLR samples were determined by X-ray fluorescence spectroscopy (XRF, EDXL 300, Rigaku Corporation, Japan) and inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPE-9820, Shimadzu Corporation, Japan) after aqua regia ($3\ \text{HCl}: 1\ \text{HNO}_3\ \text{v/v}$) digestion using a microwave-assisted acid digestion system. XRD (MultiFlex, Rigaku Corporation, Japan) was used to analyze the mineralogical composition of the samples. Reagent grade sodium chloride and hydrochloric acid (Wako Pure Chemical Industries, Ltd., Japan) were used to prepare the leaching solutions of different compositions. Ultrapure ZVI ($>99.9\%$, $-150\ \mu\text{m}$, Wako Pure Chemical Industries, Ltd., Japan) was selected to sequester Pb^{2+} from the pulp via reductive precipitation.

2.2 Methods

2.2.1 Sequential extraction

The solid-phase partitioning of Pb, Zn and iron (Fe) in ZLRs was investigated by sequential extraction based on the procedure adapted from Dold⁴). This was done to understand solid-phase partitioning of Pb, Zn and Fe amenable to acid leaching. Table 1 shows the details of the different lixiviants and experimental conditions used at each extraction stage as well as their target phases. In the first stage, 3 g of ZLRs were mixed with 120 mL of deionized (DI) in 300 mL Erlenmeyer flask placed in a thermostat water bath shaker and shaken at 200 rpm for 4 h. After shaking, solid-liquid separation was done by centrifugation at 3000 rpm for 20 minutes. The supernatant was filtered through syringe-driven membrane filters with a pore size of $0.20\ \mu\text{m}$. The filtrate was analyzed for its Pb, Zn and Fe concentrations using ICP-EAS. The residue was washed with 10 mL of DI water before the next extraction stage step. The same procedure was applied to all the extraction stages except for the last one (5th stage). In the 5th stage, the residue was dissolved in aqua regia using a microwave-assisted acid digestion system (Ethos Advanced Microwave Lab station, Milestone Inc., USA).

2.2.2 Leaching experiments with and without the addition of zero-valent iron

Batch leaching experiments for Pb extraction from ZLRs were carried out using 200 mL Erlenmeyer flasks and the solution volume was fixed to 50 mL for all experiments. NaCl solutions of varying concentrations (0–5.13 M) and HCl of different concentrations (0.01–0.1 M) were added in

the flasks and purged with ultrapure N_2 for 10 minutes prior to the addition of ZLRs only or addition of both ZLRs and ZVI addition. 2.5 g of ZLRs with and without ZVI were added in the flasks containing the leaching solution. N_2 purging of the pulp after sample addition was carried out for 5 minutes before sealing the flasks with silicon stoppers. The flasks were then shaken in a thermostat water bath shaker at 25°C at a shaking speed of 125 strokes/min and amplitude of 40 mm. At the end of each shaking experiment, the leach pulp was collected, filtered through syringe-driven membrane filter (pore size, $0.20\ \mu\text{m}$) and analyzed for its Pb concentration using ICP-AES. When ZLRs and ZVI were simultaneously leached together, separation of magnetic fractions (Pb-loaded ZVI) from the pulp was carried out using a handheld 0.6 T magnet. The magnetic fractions were then thoroughly washed with DI water and dried in a vacuum drying oven at 40°C for 24 h. After drying, the magnetic fractions were digested in aqua regia and the concentrations of Pb, Zn and Fe were quantified. The magnetic fractions were also analyzed by scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (SEM-EDX; JSM-IT200, JEOL Ltd., Japan).

Table 1. Procedure and lixiviants applied for targeted solid-phase in sequential extraction.

Stage	Target phase(s)	Extracting reagent(s)/condition
1	Water-soluble	Deionized water (200 rpm, 4 h and 25°C).
2	Carbonates	1 M sodium acetate pH 5 (200 rpm, 4 h and 25°C).
3	Amorphous Fe/Mn oxyhydroxides	0.12 M oxalic acid + 0.13 M ammonium oxalate (200 rpm, 6 h, 25°C in the dark).
4	Crystalline Fe-oxides	0.3 M trisodium citrate + 0.2 M sodium hydrogen carbonate + sodium dithionite (200 rpm, 85°C , until the brownish color disappears).
5	Residual	Aqua regia (heat to 220°C for 20 min and hold for 30 min).

3. RESULTS AND DISCUSSION

3.1 Elemental and mineralogical characteristics of zinc leach residues

Results of elemental composition analyses by ICP-AES after aqua regia digestion and XRF (Table 2) showed that ZLRs sample contains high amounts of Pb (6.19 wt%), Zn (2.53 wt%), Fe (17.02 wt%), Ca (7.3 wt%), and SiO_2 (31.43 wt%). The residues also contain small amounts of Cu (0.21

wt %), Al₂O₃ (2.9 wt %), and other elements.

Table 2. Chemical composition of zinc leach residues.

Metal composition by ICP-AES analysis		Elemental oxide composition by XRF analysis	
Metal	%	Element oxide	%
Pb	6.19	PbO	6.48
Zn	2.53	ZnO	3.28
Fe	17.02	Fe ₂ O ₃	24.3
Cu	0.21	CuO	0.25
Ca	7.3	CaO	10.57
		SiO ₂	31.43
		Al ₂ O ₃	2.89
		SO ₃	18.17
		V ₂ O ₅	0.72
		MnO	0.25
		P ₂ O ₅	0.54
		ZrO ₂	0.59

Minerals such as gypsum (CaSO₄·2H₂O), anglesite (PbSO₄), zinc sulfate dihydrate (ZnSO₄·2H₂O), quartz (SiO₂), and goethite (FeO(OH)) were detected by XRD analysis (results not shown). During sulfuric acid leaching, dissolved Pb²⁺ from lead oxide minerals precipitated as PbSO₄, which explains why anglesite was present in the ZLRs. Additionally, PbSO₄ could also be formed via the weathering of galena (PbS) to lead oxide and further converted to anglesite⁵. Similar to PbS weathering, ZnS in the residues could have weathered and transformed to ZnSO₄·2H₂O. Physical entrapment of solution (ZnSO₄) during filtration of zinc leach pulp may also have contributed to the formation of ZnSO₄·2H₂O⁶.

3.2 Solid-phase partitioning of lead, zinc and iron

The solid-phase partitioning of Pb, Zn and Fe in the ZLRs sample is shown in Fig. 1. Pb was mostly associated with two fractions: 66% of Pb was partitioned with the acid-soluble fraction (i.e., exchangeable and carbonates), and 33% of Pb was associated with the residual phases, which in this study denotes those found with sulfides and silicates). High amounts of acid soluble Pb fraction in ZLRs may be attributed to PbSO₄ mineral which was detected by XRD. Previous research on Pb speciation from PbSO₄ showed that Pb fractionated in huge amounts at the acid-soluble stage with very low amounts in preceding and succeeding extraction stages which is in agreement with results obtained in this study⁷.

Unlike Pb that was mainly partitioned with two of the five operationally defined solid-phases, Zn was associated in all

solid-phases in the following in order of abundance: crystalline Fe/Mn-oxides > amorphous Fe/Mn-oxyhydroxides ≈ carbonates > residual > water-soluble phases. High fractions of Zn extracted under reducing conditions were obtained (, i.e., 27% at amorphous Fe-oxide and 33% crystalline Fe-oxide stage), which is similar to those reported by Sethurajan et al.⁸) using ZLRs from Brazil. The association of Zn with reducible fractions could be attributed to co-precipitation or encapsulation within Fe-oxide/oxyhydroxide phases.

Fig. 1. Solid-phase partitioning of lead, zinc and iron in ZLRs.

From the solid-phase partitioning results, it was shown that ZLRs contain significant amounts of Pb and Zn in the acid-leachable fraction, indicating that ZLRs should be regarded as environmentally hazardous materials. Looking at it from another perspective, the results also show that ZLRs can be considered as secondary sources of Pb and Zn as they contain significant amounts of these metals in easily extractable fractions.

3.3 Lead removal from zinc leach residues

Fig. 2 illustrates the concentration of Pb in solution as a function of time when 2.5 g of ZLRs was leached in a 50 mL solution containing 5.13 M (300 g/L) NaCl and 0.05 M HCl with and without the addition of 0.5 g ZVI. When ZLRs were leached in the absence of ZVI, the concentration of Pb in solution increased with time and stabilized at around 10.4 mM after 2 h, suggesting that apparent equilibrium was reached. When ZLRs were leached with ZVI, the concentration of Pb in solution initially increased with time up to 8.8 mM, but after this, Pb concentration decreased drastically below 0.5×10^{-6} mM (0.01 mg/L) after 12 h. Pb extraction from ZLRs likely occurred via chemical reaction (1) while chemical reaction (2) might explain why Pb concentration decreased in the presence of ZVI.

Here $x = 1, 2, 3, 4$ and $\text{PbCl}_x^{-(x-2)}$ is lead chloride complexes.

Fig. 2. Fig. 2. Effects of time on Pb dissolution from ZLRs with and without ZVI.

Figure 3. Fig. 3. SEM microphotograph and EDX elemental maps of the magnetic fraction after the carrier in pulp technique.

Because the drastic decrease of Pb concentration occurred only after 2 h, there is a lag time prior to the start of reductive precipitation (reaction 2). This lag time may be related to the removal of the oxide film on ZVI and the need to attain a critically large cathodic area (deposit of Pb on the surface of Fe) for reductive precipitation ⁹⁾.

To confirm that reductive precipitation of Pb^{2+} occurred on the surface of ZVI, the magnetic fractions obtained after 12 h of leaching ZLRs with ZVI were analyzed by SEM-EDX (Fig. 3). The elemental maps illustrate that Pb as well as Cu were extracted from ZLRs and cemented on the surface of ZVI.

Fig. 4 shows the effects of ZVI dosage on the Pb distribution to three different fractions (solution, ZVI (magnetic fraction), and residues (non-magnetic fraction or un-leached Pb in ZLRs)) when ZLRs were leached together with ZVI in solution containing 5.13 M and 0.05 M HCl for 12 h. Substantial amounts of Pb remained in solution when 0.05 g ZVI was added. This may be attributed to insufficient ZVI to reduce Pb^{2+} to metallic Pb. Although the mole ratio of ZVI to total Pb in 2.5 g ZLRs was stoichiometry sufficient to reduce all Pb^{2+} , unnecessary ZVI consumption may have occurred via side chemical reactions. These side reactions may involve oxide film removal on ZVI (Eq. 3), consumption of ZVI via reactions with ferric ions (Eq. 4), oxidation of cemented Pb to Pb^{2+} by the ferric ions (Eq. 5), and dissolution of ZVI through proton-promoted attack (Eq. 6).

Fig. 4. Effects of ZVI dosage on the distributions of Pb in solution, ZVI (magnetic fraction), and residues after 12 h of leaching.

Fig. 5 shows the effects of solution composition on Pb removal when 2.5 g ZLRs were leached together with 0.35 g ZVI for 12 h. The amount of ZVI used in this series of experiments was decided based on the results shown in Fig. 4. Here, Pb removal when ZLRs were leached without the

addition of ZVI is referred to in percentage of total Pb in ZLRs that dissolved in solution, whereas when ZLRs and ZVI were added together, Pb removal corresponds to the amount of Pb cemented on ZVI because almost 100% of dissolved Pb was recovered as metal deposited on ZVI after 12 h.

Fig. 5. Effects of solution composition on Pb removal when ZLRs were leached with and without 0.35 g ZVI for 12 h.

Fig. 5 shows that Pb removal increased with increasing concentration of HCl and NaCl, regardless of whether or not ZVI was present in the system. The highest Pb removal reached around 78% of the total Pb in ZLRs at 0.1 M HCl and NaCl concentration of over 3.4 M. The higher amounts of Pb extracted in comparison to that determined by sequential extraction (66%) may be attributed to the dissolution of Pb associated with sulfide/organic at high H^+ and Cl^- concentration.

The relationship between increasing NaCl concentration and Pb removal could be explained by the formation of soluble lead chloride complexes as the concentration of chloride (Cl^-) increases (Eq. 1). Increasing the HCl concentration in NaCl solution not only increased the concentration of Cl^- but also that of H^+ , which enhanced the dissolution of $PbSO_4$ and $CaSO_4 \cdot 2H_2O$ minerals. ZLRs

contain significant amounts of $CaSO_4 \cdot 2H_2O$ (from XRD analysis) which may have covered the surface of $PbSO_4$. The solubility of $CaSO_4 \cdot 2H_2O$ in NaCl solution has been found to increase with increase not only Cl^- but also H^+ . However, there is an optimum Cl^- concentration beyond which dissolution of $CaSO_4 \cdot 2H_2O$ starts to decrease again¹⁰.

It is noteworthy that the addition of ZVI promoted Pb extraction even at low concentrations of NaCl. Without ZVI, the solution becomes saturated with dissolved Pb and once this threshold is reached, further Pb dissolution from ZLRs becomes negligible. When ZVI is present, however, the recovery from the solution of dissolved Pb^{2+} as elemental Pb prevents the solution from reaching saturation, a condition that promoted the dissolution of Pb from ZLRs.

4. CONCLUSIONS

This study investigated Pb removal from ZLRs by extracting Pb into solution, recovering the extracted Pb^{2+} by reductive precipitation on ZVI, and separation from the leach pulp by a magnet. A summary of the findings are as follows:

1. The addition of ZVI during leaching of ZLRs increased Pb removal even at a low concentration of NaCl. This increase was attributed to the recovery of dissolved Pb by ZVI that prevented the leach solution from attaining saturation.
2. The generated leach solution contains less than 0.01 mg/L of dissolved Pb when ZLRs were leached in the presence of ZVI. This approach to detoxification of ZLRs removes the need for extensive washing of the generated residues to remove this toxic heavy metal.
3. At higher HCl addition, Pb removal increased by 12%, which was higher than the determined labile Pb in ZLRs by sequential extraction. This increase is ascribed to the H^+ -promoted and Cl^- -enhanced dissolution Pb-containing sulfide/organic phases.

References

1. Graedel TE, Beers D van, Bertram M, et al. The Multilevel Cycle of Anthropogenic Zinc. *Journal of Industrial Ecology*. 2005;9(3):67-90.
2. Turan MD, Altundoğan HS, Tümen F. Recovery of zinc and lead from zinc plant residue. *Hydrometallurgy*. 2004;75(1):169-176.
3. Alorro RD, Mitani S, Hiroyoshi N, Ito M, Tsunekawa M. Recovery of heavy metals from MSW molten fly ash by carrier-in-pulp method: Fe powder as carrier. *Minerals Engineering*. 2008;21(15):1094-1101.

4. Dold B. Speciation of the most soluble phases in a sequential extraction procedure adapted for geochemical studies of copper sulfide mine waste. *Journal of Geochemical Exploration*. 2003;80(1):55-68.
5. Heidel C, Tichomirowa M. Galena oxidation investigations on oxygen and sulphur isotopes. *Isotopes in Environmental and Health Studies*. 2011;47(2):169-188.
6. Ru Z, Pan C, Liu G, Wang X, Dou G, Zhu K. Leaching and recovery of zinc from leaching residue of zinc calcine based on membrane filter press. *Transactions of Nonferrous Metals Society of China*. 2015;25(2):622-627.
7. Leinz R., Sutley S., Desborough G., Briggs P. An Investigation of the Partitioning of Metals in Mine Wastes Using Sequential Extractions. In: *Proceedings from the Fifth International Conference on Acid Rock Drainage*. Vol 2. Colorado USA: Society for Mining, Metallurgy, and Exploration; 2000:1489-1499.
8. Sethurajan M, Huguenot D, Lens PNL, Horn HA, Figueiredo LHA, van Hullebusch ED. Fractionation and leachability of heavy metals from aged and recent Zn metallurgical leach residues from the Três Marias zinc plant (Minas Gerais, Brazil). *Environ Sci Pollut Res*. 2016;23(8):7504-7516.
9. Chen HJ, Lee C. Effects of the type of chelating agent and deposit morphology on the kinetics of the copper-aluminum cementation system. *Langmuir*. 1994;10(10):3880-3886.
10. Shukla J, Mohandas VP, Kumar A. Effect of pH on the Solubility of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ in Aqueous NaCl Solutions and Physicochemical Solution Properties at 35 °C. *J Chem Eng Data*. 2008;53(12):2797-2800.