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Article

Recovery of Lead and Zinc from Zinc Plant Leach Residues by Concurrent Dissolution-Cementation Using Zero-Valent Aluminum in Chloride Medium

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Abstract: Zinc plant leach residues (ZPLRs) contain significant amounts of metal compounds of lead (Pb), zinc (Zn), iron (Fe), etc., hence, they are considered as a secondary source of metals. On the other hand, ZPLRs are regarded as hazardous materials because they contain heavy metals that pollute the environment. Resources and environmental concerns of ZPLRs were addressed in this study by removing/recovering Pb and Zn using a concurrent dissolution and cementation technique. To cement the dissolved Pb and Zn in leaching pulp, zero-valent aluminum (ZVAl) was added during ZPLRs leaching in the hydrochloric (HCl)–sodium chloride (NaCl) solution. The resulting cemented metals were agglomerated and separated by sieving. Lead removal increased with increasing both NaCl and HCl concentrations. However, when ZVAl was added, significant Pb removal was achieved at a low concentration. Zinc was not cemented out of the pulp using ZVAl and its recovery from ZPLRs was dependent on the HCl concentration only. By applying a concurrent dissolution and cementation technique, both Pb and Zn were removed using a low concentration of NaCl, and most importantly Pb—the most toxic metal in ZPLRs—was captured and separated before the solid-liquid separation, hence, eliminating the need for extensive washing of the generated residues to remove the inherent residual solution.

Keywords: lead; zinc; zinc plant leach residues; zero-valent aluminum; leaching; cementation

1. Introduction

Explosive population growth and its associated economic activities such as massive construction projects to modernize and improve communication, transportation, and agricultural sectors have in recent years led to high demands for metals [1–4]. To keep up with demands, mining and metals production have also increased at unprecedented levels. Enormous amounts of solid wastes are also generated as a result of more extensive mining, mineral processing, and metal extraction operations by metallurgical processes [5–7]. For example, zinc (Zn) metal production via hydrometallurgical processes (i.e., leaching of calcine or zinc oxide minerals followed by electrowinning of Zn) generates huge amounts of zinc plant leach residues (ZPLRs) [8,9], which are stockpiled and often abandoned after closure of mining/processing operations.

With the rapid depletion of high-grade ores, ZPLRs are now considered as secondary resources because they still contain substantial amounts of residual Zn, copper (Cu), lead (Pb), and iron (Fe) [10–13]. From an environmental point of view, ZPLRs are considered hazardous wastes because they contain hazardous heavy metals such as Pb, Cu, and Zn. Pb, for example, is extremely toxic to babies and children and is known to cause various disorders of the reproductive organs, central nervous system, and kidneys [14–16]. Therefore, the reprocessing of ZPLRs for metal removal/recovery could address both environmental and resource concerns associated with these waste materials.

Pyrometallurgical [17,18] and hydrometallurgical [19,20] techniques can be employed to recover valuable metals from ZPLRs. When appropriate, the latter approach is preferred because it is less energy-intensive and generates wastes (e.g., solid residues) that may cause less or no secondary environmental pollution. Numerous studies have been published to process metallurgical wastes using conventional hydrometallurgical processes that follow the sequence of leaching, solid-liquid separation, and recovery of dissolved metals (usually Cu, Pb, and Zn) from pregnant leach solutions [9,11,20–23]. Although effective, there are two serious drawbacks of conventional approaches for Pb and Zn extraction-recovery from ZPLRs. Firstly, leaching approaches require highly concentrated reagents to extract the target metals [10,20]. Secondly, leaching residues contain a heavy metal-rich residual solution due to difficulties and inherently incomplete solid-liquid separation partly exacerbated by silica gel formation and the presence of very fine particles in ZPLRs [24,25]. To remove residual solutions from generated solid residues after solid-liquid separation, extensive washing or stabilization before disposal should be carried out, requiring complex treatment processes that increase operating costs.

To address these limitations of conventional hydrometallurgical techniques for Pb and Zn recovery from ZPLRs, this study used a technique combining Pb and Zn dissolution from ZPLRs with the recovery of these metals directly in one reaction reactor without solid-liquid separation (i.e., concurrent dissolution-cementation). Since dissolved metals are sequestered (i.e., recovered) in the leaching pulp, it follows that a low concentrated solution can be used to achieve high removal/recovery as the solution would not be saturated with dissolved metals. Additionally, heavy metals are removed before solid-liquid separation, so the need for extensive washing to remove the residual heavy metal-rich solution is eliminated.

In this study, concurrent dissolution-cementation was applied to extract and recover Pb and Zn removal from historic abandoned ZPLRs obtained from Kabwe, Zambia. To dissolve Pb and Zn from ZPLRs, acidified chloride (HCl–NaCl) solutions of various concentrations were used. The chloride solution was used due to the complexation capability of chloride with Pb. The dissolved amounts Pb and Zn were quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The recovery of dissolved Pb and Zn from leaching pulp was achieved by cementation using the zero-valent aluminum (ZVAl) powder. Cementation products were characterized by the scanning electron microscopy equipped with an energy dispersive X-ray spectroscopy (SEM-EDX) and X-ray powder diffraction (XRD). To evaluate whether the solid residues generated by concurrent dissolution-cementation meets environmental standards, the toxicity characteristic leaching procedure (TCLP) was carried out.

2. Materials and Methods

2.1. Materials

ZPLR samples were collected from the historic dumpsite of Pb-Zn mine wastes in Kabwe, Zambia (Figure 1). The samples were air-dried for 30 days in the laboratory, lightly pulverized with an agate mortar and pestle, and then dry-sieved using stainless steel sieves to obtain sample with particles passing 106 µm fraction. Chemical characterization of the ZPLR samples was carried out using both X-ray fluorescence spectroscopy (XRF, EDXL 300, Rigaku Corporation, Tokyo, Japan) and ICP-AES (ICPE-9820, Shimadzu Corporation, Kyoto, Japan) after aqua regia (3 HCl:1 HNO_3 v/v) digestion in a microwave-assisted acid digestion system (Ethos Advanced Microwave Lab station, Milestone Inc., Sorisole, Italy). The amounts of Pb and Zn in ZPLR samples were as high as 6.19% and 2.53%, respectively (Table 1). ZPLR samples also contained significant amounts of other elements such as Si, Fe, Ca, S, Cu, and other elements, as shown in Table 1. The mineralogical composition of ZPLRs was determined by XRD (MultiFlex, Rigaku Corporation, Tokyo, Japan) and crystalline minerals were identified using a full package of the Crystallography Open Database (COD) and MATCH 3.4. The crystalline Pb and Zn minerals in ZPLRs that were detected included anglesite ($PbSO_4$), cerussite ($PbCO_3$), esperite ($PbCa_2Zn_3(SiO_4)_3$), and zinkosite ($ZnSO_4$), as illustrated in Figure 2. Other minerals detected in the samples are quartz (SiO_2), gypsum ($CaSO_4{\cdot}2H_2O$), hematite (Fe_2O_3), and goethite (FeOOH). The particle size distributions of lightly pulverized ZPLRs were analyzed using Laser diffraction (Microtrac® MT3300SX, Nikkiso Co. Ltd., Osaka, Japan) and were found to have a median size (D_{50}) of around 9.6 µm (Figure 3a).

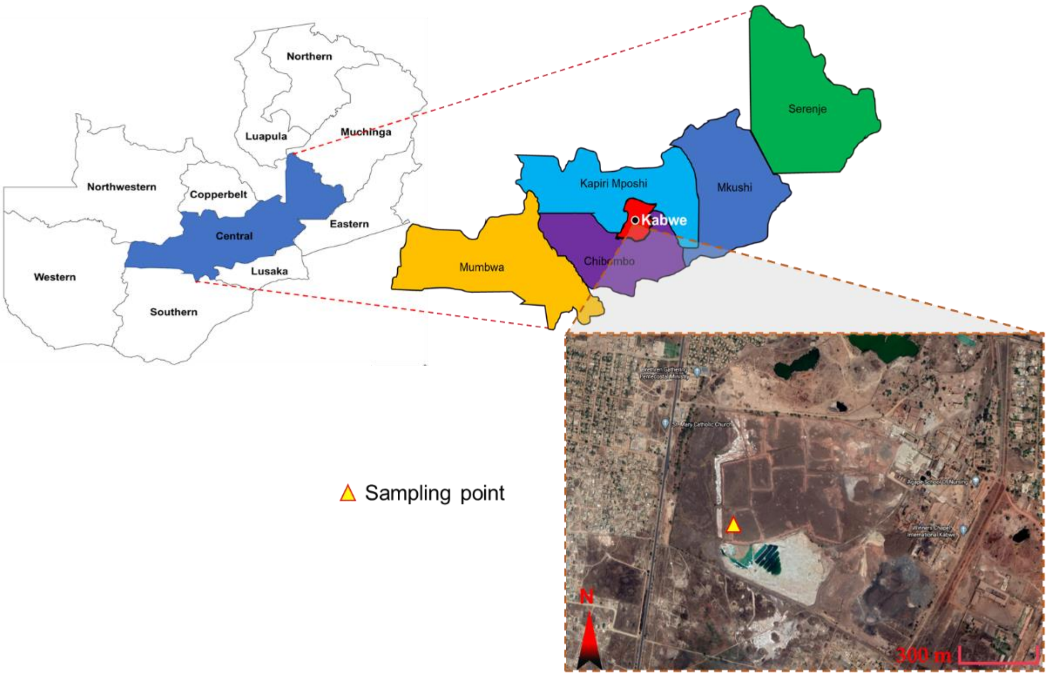

Figure 1. Schematic geographic map of Zambia superimposed with the location of Kabwe and historic Pb-Zn mine wastes.

Table 1. Chemical composition of zinc plant leach residues from Pb-Zn mine wastes from Kabwe, Zambia.

Elements/Oxides	**Pb ***	**Zn ***	**Fe ***	**Cu ***	**CaO**	**SiO_2**	**Al_2O_3**	**SO_3**	**V_2O_5**	**MnO**	**Others**
Mass %	6.2	2.5	17.0	0.2	10.6	31.4	2.9	18.2	0.7	0.3	1.1

* Elemental composition was determined by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) after aqua regia digestion. Elemental oxides were determined by XRF.

Reagent grade NaCl and HCl (Wako Pure Chemical Industries, Ltd., Osaka, Japan) were used to prepare the leaching solutions of different concentrations by dissolution and dilution using deionized (DI) water (18 MΩ·cm, Milli-Q® Integral Water Purification System, Merck Millipore, Burlington, Vermont, USA). To simultaneously precipitate reductively (cement) the dissolved Pb^{2+} and Zn^{2+} in leaching pulp, ultra-pure ZVAl powder (>99.99%, 50–150 µm, Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used (the median particle size (D_{50}) of ZVAl was 126.8 μm). The particle size distribution is shown in Figure 3b. A stainless steel sieve with 150 μm aperture size was used to separate cemented and agglomerated Pb and Zn from the leaching pulp. The sieve size was selected by taking into consideration the particles size ranges of both ZPLRs and ZVAl. In other words, this sieve could only retain cemented and agglomerated particles while passing particles of unreacted ZVAl and particles of undissolved minerals particles of ZPLRs.

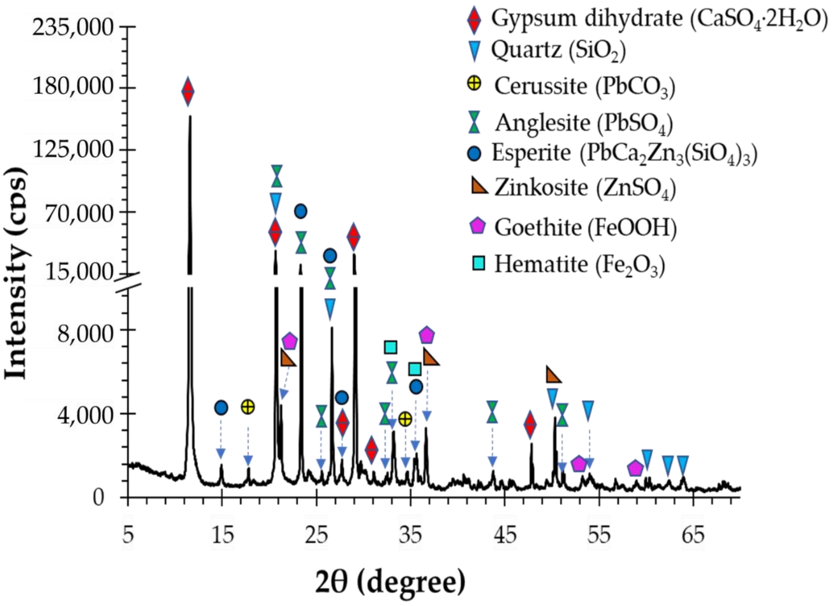

Figure 2. XRD pattern of the zinc plant leach residues from Kabwe, Zambia.

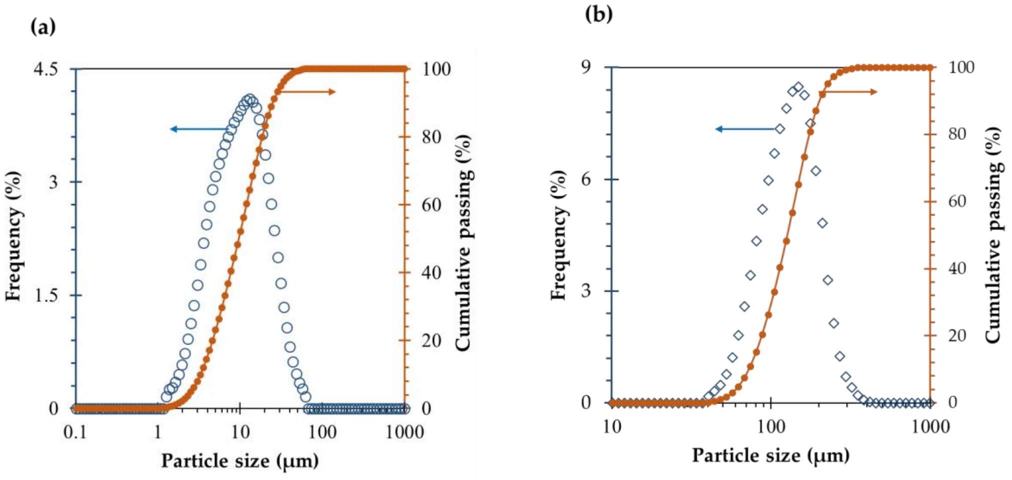

Figure 3. The particle size distribution of (**a**) zinc plant leach residues and (**b**) zero-valent aluminum.

2.2. Methods

2.2.1. Leaching-Cementation Experiments in Chloride Solution

Batch leaching experiments for the extraction of Pb and Zn from ZPLRs with and without ZVAl additions were conducted using a 200-mL Erlenmeyer flask. The volume of the leaching solution was at 50 mL for all experiments. Concentrations of NaCl (0–3 M) were varied and acidified with different HCl concentrations (0–0.1 M) to obtain required leaching solutions. Fifty milliliters (50 mL) of leaching solution of a given concentration was initially poured in an Erlenmeyer flask and nitrogen (N_2) was purged for 10 min to remove dissolved oxygen (DO). Nitrogen gas (N_2) purging was again carried out for 2 min after the addition of 2.5 g ZPLRs with and without 0.1 g ZVAl that were added before sealing the flask using silicon stoppers and parafilm®. The flask was then shaken at 4 cm amplitude and 120 min^{-1} shaking frequency in a water-bath shaker maintained at 25 °C for a predetermined length of time. At the end of the predetermined shaking time, the leaching pulp was carefully collected, and solid-liquid separation was carried out by filtering the collected leaching pulp using a syringe-driven membrane filter—pore size of 0.20 µm— (LMS Co., Ltd. Tokyo, Japan). The filtrate was then analyzed for dissolved Pb and Zn using ICP-AES. In the case where ZVAl was added during ZPLR leaching, additional steps—the separation of cemented and agglomerated product from the leaching pulp by screening using a sieve of aperture size of 150 µm—were carried out. The +150 µm particles (cemented and agglomerated) were thoroughly washed with deionized (DI) water before drying in a vacuum oven at 40 °C for 24 h. Dried +150 µm particles were then digested in aqua regia using a microwave-assisted acid digestion system and the leachate was analyzed for Pb and Zn using ICP-EAS. Furthermore, the +150 µm particles obtained were examined by both XRD and SEM-EDX (JSM-IT200, JEOL Ltd., Tokyo, Japan). All the experimental tests were carried out twice and the average was reported here.

The Pb and Zn removal ($R_{Pb,Zn}$) from ZPLRs without and with ZVAl were quantified using Equations (1) and (2), respectively.

$$R_{Pb,Zn} = \frac{V * C_{Pb,Zn}}{W_S * M_s} * 100 \tag{1}$$

$$R_{Pb,Zn} = \frac{\left(V * C_{Pb,Zn}\right) + \left(W_{cg} * M_{cg}\right)}{W_S * M_s} * 100 \tag{2}$$

where $C_{Pb,Zn}$ is the concentration (g/L) of Pb and Zn, V is the volume (L) of leaching solution, W_S is the weight percent (%) of either Pb and Zn, M_s is the mass (g) of leached ZPLRs, M_{cg} is the mass (g) of cemented and agglomerated particles, and W_{cg} is the weight percent (%) of cemented and agglomerated particles calculated based on the digested fraction of M_{cg} in aqua regia and analysis of the solution by ICP-AES.

2.2.2. Leachability of Lead and Zinc after Concurrent Dissolution-Cementation

To evaluate the leachability of Pb and Zn from before and after concurrent dissolution-cementation, leachability experiments were conducted according to the toxicity characteristic leaching procedure (TCLP) [26]. For TCLP, 1 g of vacuum-dried treated and untreated residues were equilibrated with 20 mL of acetic acid solution (pH 2.89) in a centrifuge tube shaken at 30 rpm on a rotary tumbler for 18 h. After the predetermined leaching time, the leachate was filtered through 0.20 µm syringe-driven membrane filters and the filtrate was analyzed for dissolved Pb and Zn using ICP-AES.

3. Results and Discussion

3.1. Concurrent Dissolution-Cementation of Pb and Zn from Zinc Plant Leach Residues

The concentrations of Pb and Zn as a function of time when 2.5 g of ZPLRs were leached in a solution composed of 3 M NaCl and 0.05 M HCl with and without the addition of 0.1 g ZVAl is shown in Figure 4a,b. The concentration of Pb when ZPLRs were leached without ZVAl reached an apparent equilibrium of around 8.5 mM (which represents 59% of total Pb) after just 15 min (Figure 4a). Pb dissolution from ZPLRs involves the formation of lead-chloride complexes as explained by Equations (3) and (4) [20,27–29]:

$$\text{PbSO}_4 + x\text{Cl}^- = \text{PbCl}_x^{(2-x)} + \text{SO}_4^{2-} \tag{3}$$

$$\text{PbCO}_3 + 2\text{H}^+ + x\text{Cl}^- = \text{PbCl}_x^{(2-x)} + \text{CO}_2 + \text{H}_2\text{O} \tag{4}$$

where $PbCl_x^{(2-x)}$ and x are lead-chloride complex(es) and integers from 1 to 4, respectively, all of which depended on the chloride concentration.

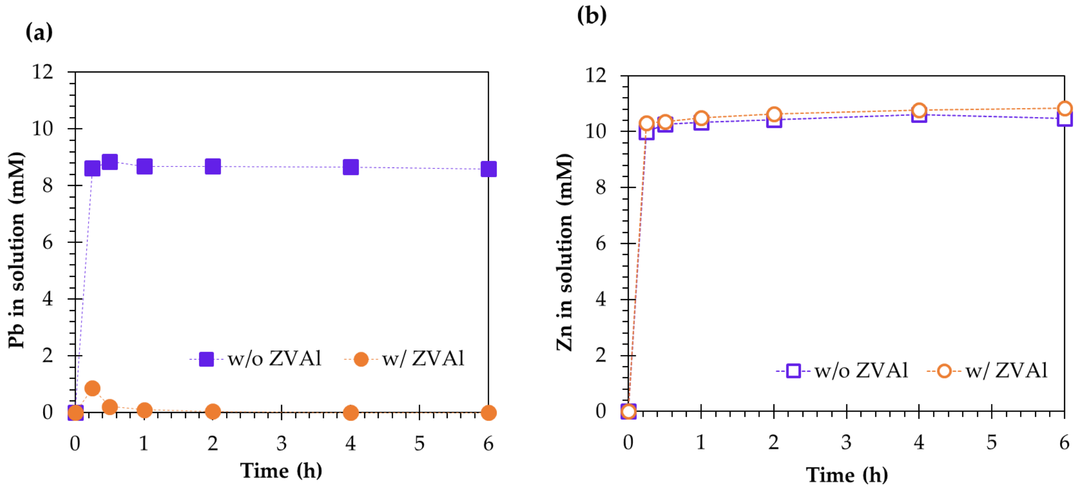

Figure 4. Concentration of (**a**) Pb and (**b**) Zn dissolved in the leaching solution as a function of time when zinc plant leach residues (ZPLRs) were leached without and with zero-valent aluminum (ZVAl).

The concentration of dissolved Pb when ZVAl was added was 10-fold lower than when only ZPLRs were leached in the same solution. The dissolved concentration of Pb decreased further with increasing the treatment time and reached below 0.048 mM (i.e., 0.1 mg/L) with ZVAl after 4 h. The dramatically lower dissolved concentration of Pb after 15 min and its continued decrease to below 0.1 mg/L with ZVAl could be attributed to its sequestration from the solution via cementation. In other words, an additional chemical reaction—cementation described by the overall reaction (Equation (7)) which is the sum of two half-reactions (i.e., Equations (5) and (6))—occurred concurrently with dissolution reactions, as previously described.

$$Al^{3+} + 3e^- = Al^0 E^0 = -1.66\ V \tag{5}$$

$$Pb^{2+} + 2e^- = Pb^0 \quad E^0 = -0.126\ V \tag{6}$$

$$3Pb^{2+} + 2Al^0 = 3Pb^0 + 2Al^{3+} \tag{7}$$

The overall reaction potential, ΔE^0, is calculated by subtracting the standard electrode potential of Equation (5) from Equation (6), that is, $\Delta E^0 - 0.126 - (-1.66) = 1.534\ V$. The standard Gibbs free energy change, ΔG^0 (i.e., $\Delta G^0 = -nF\Delta E^0$, n number of electrons transferred, F is Faraday's constant, and ΔE^0 is the galvanic cell potential), of Equation (7) is negative (−888.047 kJ/mol) because ΔE^0 is positive indicating that cementation of dissolved Pb^{2+} from ZPLRs by ZVAl is thermodynamically spontaneous. In addition, the Al_2O_3 layer which was inherently present on the surface of ZVAl and passivated the cementation is removed at the acidified chloride solution [30,31]. Hence, simultaneous cementation of dissolved Pb^{2+} from ZPLRs occurred, which could explain why Pb^{2+} was comparatively lower and was even below 0.1 mg/L with ZVAl during ZPLRs leaching.

Meanwhile, the concentration of dissolved Zn reached an apparent equilibrium after 15 min at around 10.3 mM (i.e., equivalent to around 52% of total Zn) for without and with ZVAl (Figure 4b). This implied that dissolved Zn from ZPLRs was not cemented on ZVAl as described by Equation (10) (i.e., the summation of two half-cell reactions Equations (8) and (9)) though it is thermodynamically feasible due to negative ΔG^0 (i.e., −519.282 kJ/mol).

$$Al^{3+} + 3e^- = Al^0 \quad E^0 = -1.660\ V \tag{8}$$

$$Zn^{2+} + 2e^- = Zn^0 \quad E^0 = -0.763\ V \tag{9}$$

$$3Zn^{2+} + 2Al^0 = 3Zn^0 + 2Al^{3+} \tag{10}$$

The cementation product that was obtained as +150 µm particles were characterized by SEM-EDX and XRD. Figure 5 shows that Pb was cemented on ZVAl and agglomerated. However, Zn was not detected, which confirms that dissolved Zn was not cemented by ZVAl. Further characterization of the cementation product by XRD (Figure 6) showed that cemented Pb was mainly in a zero-valent Pb (metallic Pb) form and a small amount of oxidized metallic Pb as PbO, which supports the chemical reaction expressed in Equation (7).

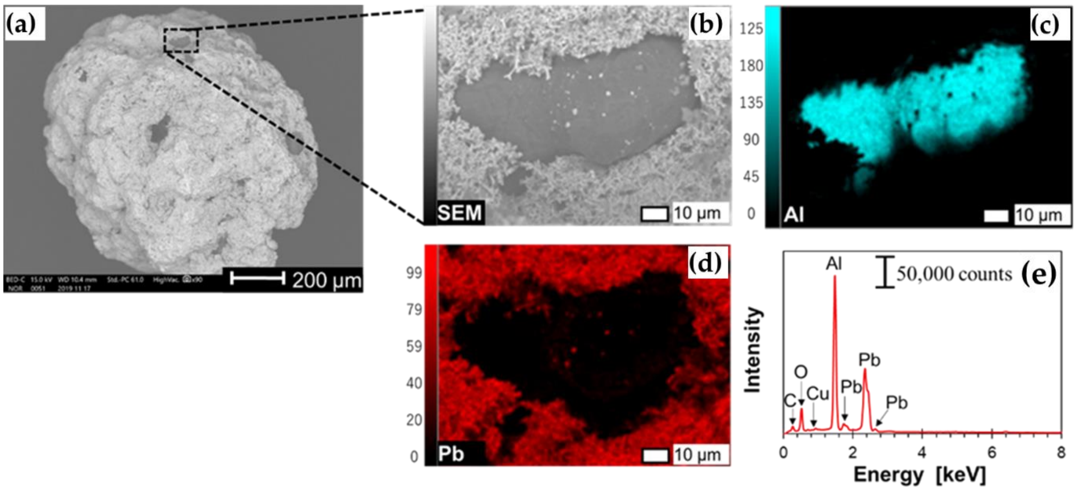

Figure 5. SEM-EDX of ZVAl "coated" with Pb from the +150 µm particles obtained after sieving the leaching pulp when ZVAl was added during leaching of ZPLRs: (**a**) SEM image of +150 µm particles, (**b**) zoomed SEM image, EDX elemental mapping of (**c**) Al and (**d**) Pb, as well as (**e**) EDX spectra.

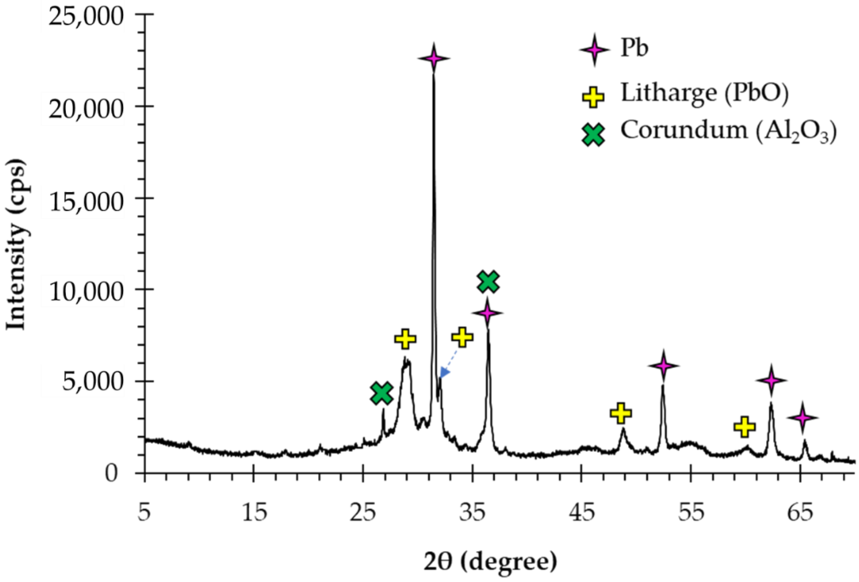

Figure 6. XRD pattern of the +150 µm fraction obtained after sieving the leaching residue in the experiments with ZVAl.

The explanation to why Zn could not be cemented by ZVAl in the leaching solution could be (a) the dissolution of cemented Zn by the proton (H^+) (Equation (11)) and (b) the reduction of H^+ to H_2 on ZVAl, which competes with the reduction of Zn^{2+} to Zn^0 (Equation (12)).

$$6\,H^+ + 3Zn \rightarrow 3H_2 + 3Zn^{2+} \tag{11}$$

$$6\,H^+ + 2Al \rightarrow 3H_2 + 2Al^{3+} \tag{12}$$

In an acidic region, the redox potential of H^+/H_2 redox pair is higher than that of Zn^{2+}/Zn redox pair, indicating that the reaction in Equation (11) ($\Delta G^0 = -6121.203$ kJ/mol) occurs, and Zn once cemented on the ZVAl surface would be dissolved [32]. Similarly, since the redox potential of H^+/H_2 redox pair is higher than that of Al^{3+}/Al redox pair, the reaction as shown in Equation (12) ($\Delta G^0 = -8168.614$ kJ/mol) also takes place. This reaction consumes the electron supplied from ZVAl and competes with Zn^{2+} reduction to Zn (Equation (10)). As a result, these reactions suppress the Zn cementation on ZVAl. The rates and equilibrium of these reactions (Equations (11) and (12)) depend on the H^+ concentration, hence, suppression of Zn cementation on ZVAl would decrease at higher pH.

To investigate the effects of H^+ concentration on cementation of Zn^{2+} from the solution using ZVAl, simulated (model) acidic and alkaline solutions containing both 8 mM Pb^{2+} and 10 mM Zn^{2+}, and to mimic the composition similar to what would be obtained by leaching ZPLRs, were prepared by dissolving $ZnCl_2$ and $PbCl_2$ (Wako Pure Chemical Industries, Ltd., Japan) in an acidified chloride solution (3 M NaCl and 0.05 M HCl, initial pH = 0.82) and alkaline solution (3 M NaOH, initial pH = 14.5), respectively. To cement both Pb and Zn, 0.15 g of ZVAl was added after N_2 purging.

Figure 7a shows the percentage of cemented Pb and Zn from the simulated acidified chloride solution. Only Pb (around 99.7% after 30 min) was cemented out leaving Zn in the solution, which is in line with the results obtained when ZVAl was added during ZPLRs leaching. However, in the alkaline solution around 99.8% of both Pb and Zn were cemented out of the solution (Figure 7b). The SEM-EDX analysis and mapping results showed that both Pb and Zn were deposited on the ZVAl surface (Figure 8). The results confirm the suppression of Zn cementation, which depends on pH. In the acidic region, Zn cementation is strongly suppressed by the reactions shown in Equations (11) and (12), while in the alkaline region the suppressive effects become negligible because of low H^+ concentrations.

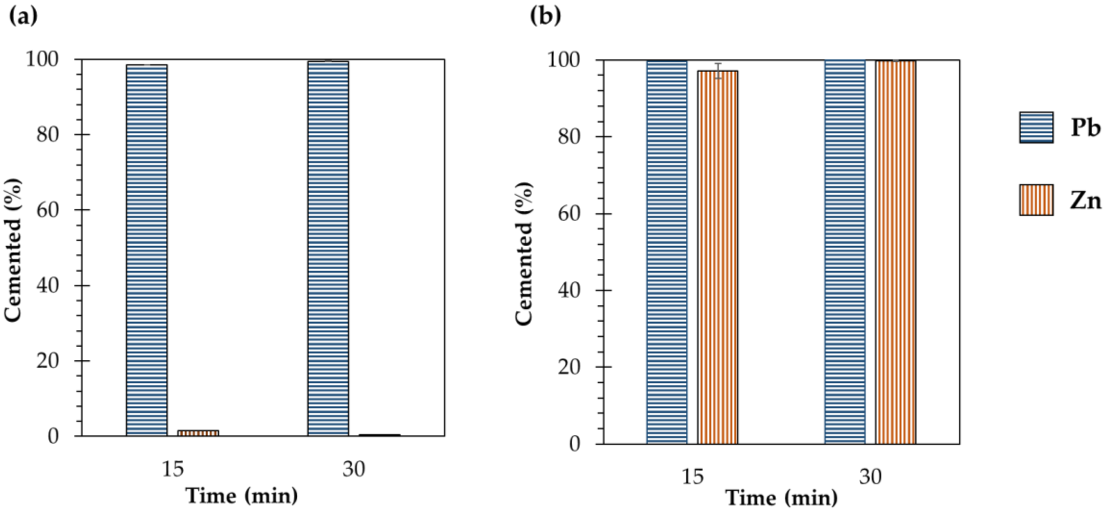

Figure 7. Amount of Pb and Zn cemented out using ZVAl in model experiments under (**a**) the simulated acidic chloride and (**b**) simulated alkaline solutions.

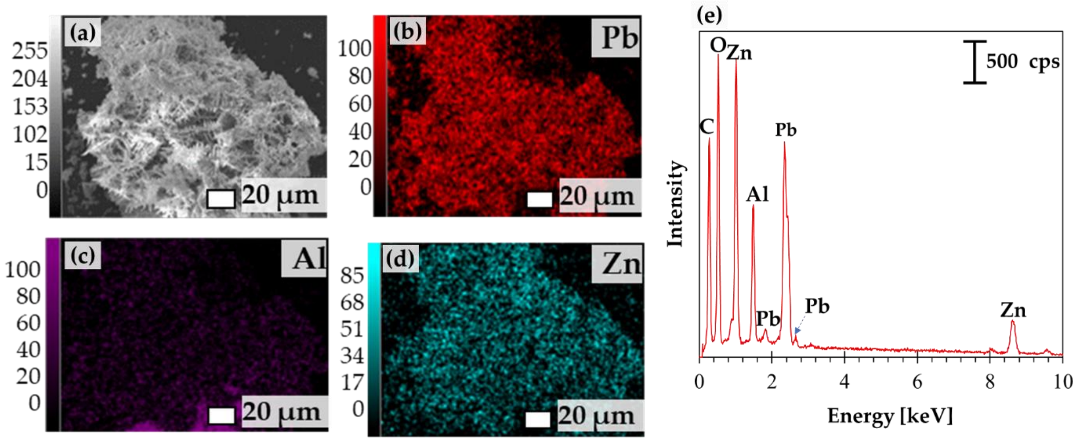

Figure 8. SEM-EDX of cementation product of Pb and Zn by ZVAl from the alkaline simulated solution: (**a**) SEM image, EDX elemental mapping of (**b**) Pb, (**c**) Al, (**d**) Zn, and (**e**) EDX spectra.

3.2. Effects of Solution Composition on Pb and Zn Removal from Zinc Plant Leach Residues

Lead and Zn removal from ZPLRs was evaluated for different solution compositions and compared with the removal efficiencies when ZPLRs was leached with and without ZVAl addition. When ZVAl was added during ZPLRs leaching, Pb was extracted into a leaching solution and concurrently cemented and agglomerated. The Pb distribution among the solution (i.e., extracted but uncemented Pb), +150 μm particles (i.e., cementation and agglomerated product), and −150 μm particles (unextracted Pb in residues). Since the amount of Pb that remained in the solution was negligible (in most cases below 0.1 mg/L), Pb removal in a case when ZVAl was added during ZPLRs leaching is referred to as Pb that was extracted, cemented, and separated as +150 μm particles. However, in the case when ZPLRs were leached without the addition of ZVAl, Pb removal is referred to as the Pb that was extracted into a leaching solution. The same definition was also applied to Zn removal with and without ZVAl addition since it was not cemented from the leaching solution, as discussed previously.

Lead removal when ZPLRs were leached without the addition of ZVAl increased with increasing both HCl and NaCl concentrations, as shown in Figure 9. Pb removal steadily increased from around 0% to 28%, 0.5% to 58%, and 0.5% to 72% for 0.01, 0.05, and 0.1 M HCl, respectively, when NaCl increased from 0 to 3 M, respectively. Lead dissolution from anglesite ($PbSO_4$) depends on (1) Cl^- concentration, (2) SO_4^{2-} concentration, and (3) solution pH (Figure 10). For example, for a 1:1 ratio of Pb concentration to SO_4^{2-} concentration (i.e., assuming the source of SO_4^{2-} in the leaching system is from $PbSO_4$) Pb dissolution depends on the Cl^- concentration only to form Pb-Cl complexes and not on pH (Equation (3)) (Figure 10a,b). However, even in this case, some Pb from $PbSO_4$ would remain in solid form as $PbCl_2(s)$ depending on the Cl^- concentration. The sample used in our study contains $CaSO_4{\cdot}2H_2O$ and $ZnSO_4$ and these minerals contribute SO_4^{2-} in the system. At high SO_4^{2-} concentration, Pb dissolution from $PbSO_4$ depends on pH (Figure 10c). As the pH increases (i.e., H^+ concentration decreases) HSO_4^- speciates to form SO_4^{2-}, which then reacts with dissolved lead in the leaching system to form $PbSO_4$ (Figure 10c,d). Meaning at high SO_4^{2-} concentration, the $PbSO_4$ dissolution is limited at high pH. Meanwhile, the release of Pb from other Pb-minerals such as cerussite ($PbCO_3$) in ZPLRs requires an H^+ attack in addition to the Cl^- concentration, as previously described in Equation (4) (Supplementary Information, Figure S1). This is the possible reason why Pb removal increased when NaCl and HCl concentrations were increased. The semi-quantitative analysis of the residues obtained after treating ZPLRs in a 3 M NaCl and 0.05 M HCl solution with the addition of ZVAl by XRD show the disappearance/decrease of peaks of anglesite, cerussite, gypsum, and other minerals (Supplementary Figure S2).

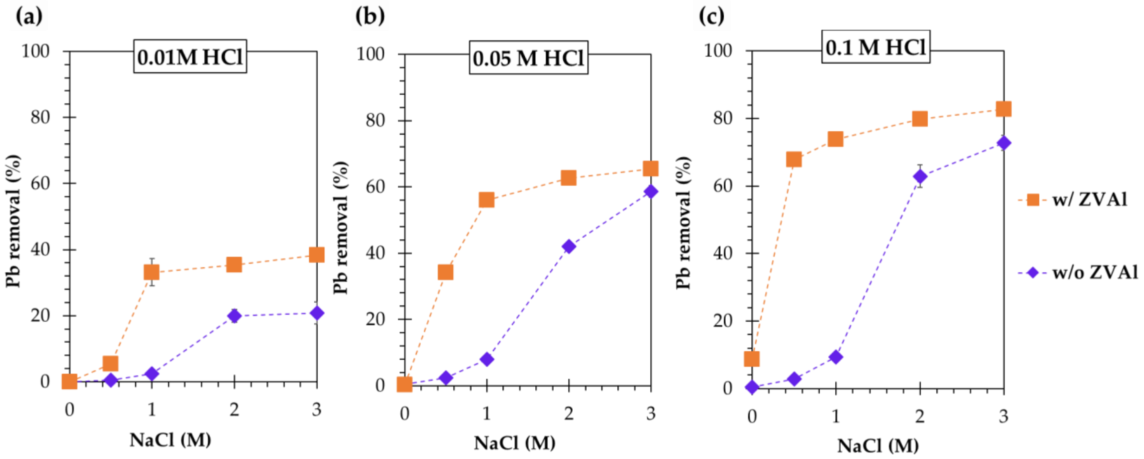

Figure 9. Effects of solution compositions on Pb removal from ZPLRs with and without ZVAl addition: (**a**) 0.01 M HCl and 0–3 M NaCl, (**b**) 0.05 M HCl and 0–3 M NaCl, and (**c**) 0.1 M HCl and 0–3 M NaCl.

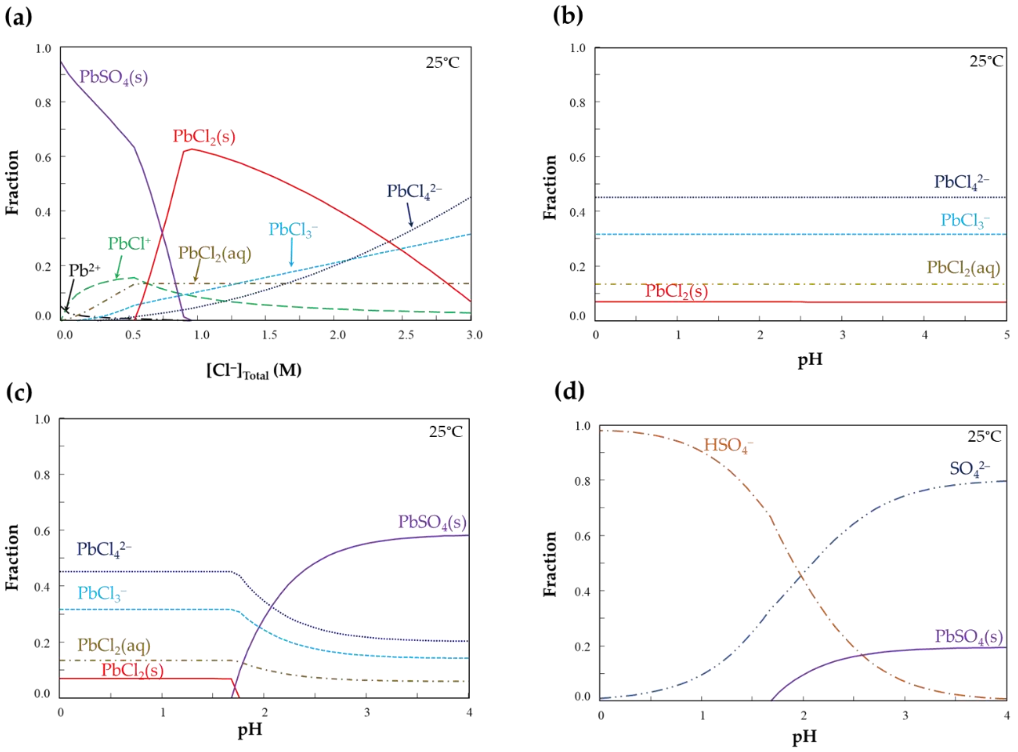

Figure 10. Thermodynamic calculation of dissolution of $PbSO_4$, speciation of Pb-Cl complexes, and SO_4^{2-} at (**a**) Pb^{2+} = 8 mM, SO_4^{2-} = 8 mM, pH = 1, (**b**) Pb^{2+} = 8 mM, SO_4^{2-} = 8 mM, Cl^- = 3 M, (**c**) Pb^{2+} = 8 mM, SO_4^{2-} = 24 mM, Cl^- = 3 M, and (**d**) Pb^{2+} = 8 mM, SO_4^{2-} = 12 mM, Cl^- = 3 M (created using the MEDUSA Ver. 1 software [33]).

The addition of ZVAl during leaching of ZPLRs significantly increased the Pb removal even at low NaCl concentration especially when HCl was increased from 0.01 to 0.05 and 0.1 M (Figure 9). For example, while maintaining HCl at 0.05 M, the addition of ZVAl during ZPLRs leaching increased the Pb removal from 2.5% to 35.5% and 8% to 57% for 0.5 and 1 M NaCl concentration, respectively. Meanwhile, for 0.1 M HCl, the addition of ZVAl during ZPLRs leaching increased the Pb removal from 3% to 69% and 9% to 72% for 0.5 and 1 M NaCl concentration, respectively. The dramatic increase of Pb removal at low NaCl concentration is attributed to the leaching solution not attaining saturated with dissolved Pb^{2+} and Pb-Cl complexes. In other words, when ZVAl was added during ZPLRs leaching, dissolved soluble Pb^{2+} and Pb-Cl complexes were simultaneously sequestered from the solution by cementation, hence, more Pb could dissolve from the host minerals (e.g., $PbSO_4$), as well as the conversion of intermediate sparingly soluble solid, $PbCl_2$, to more Pb-Cl complexes (Figure 11a,b).

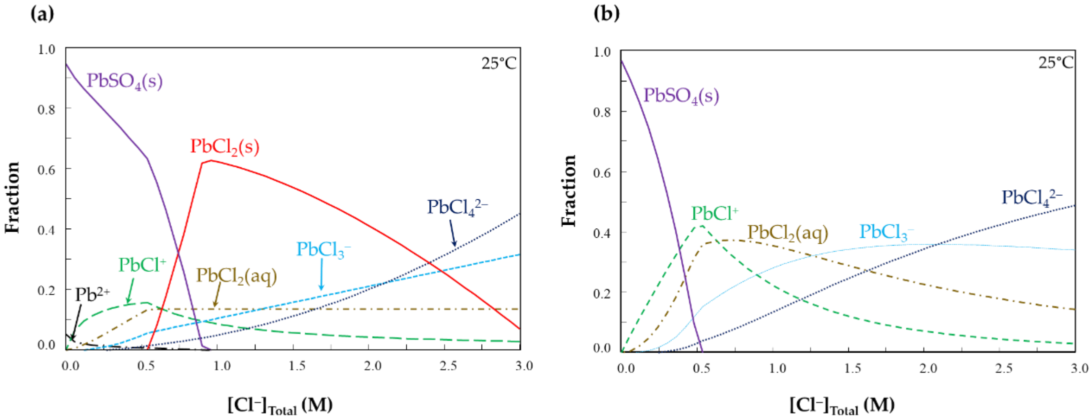

Figure 11. Effects of Pb^{2+} concentration on solubility and speciation of Pb^{2+} and Pb-Cl complexes in the lead-chloride-sulfate-water system under the condition (**a**) Pb^{2+} = 8 mM, SO_4^{2-} = 8 mM, pH = 1, and (**b**) Pb^{2+} = 1 mM, SO_4^{2-} = 8 mM, pH = 1.

Zinc removal was, however, independent of the increase of NaCl concentration, as well as the addition of ZVAl but it increased when the HCl concentration increased, as shown in Figure 12. When HCl increased from 0.01 to 0.05 and 0.1 M, Zn removal increased from around 27% to 60% and 70%, respectively. Increasing HCl concentration increased the H^+ concentration, which in turn increased Zn solubilization from minerals in ZPLRs by an H^+ attack mechanism (e.g., dissolution of Zn associated with amorphous iron oxyhydroxide phase fraction as determined elsewhere [34]). Zinc removal was not affected by the NaCl concentration. Unlike Pb that forms an intermediate solid ($PbCl_2$) at low chloride concentration and dissolves as the chloride concentration increases, Zn does form solid Zn-Cl species, and it does not complex strongly with chloride. Additionally, Zn removal was not affected by the addition of ZVAl because it was not sequestered (remained in solution) from the solution, as previously discussed. Since Zn was not be recovered by cementation using ZVAl from the leaching pulp, methods such as precipitation as ZnS [35] or electrowinning [36] can be employed to recover Zn from the solution. Unfortunately, these methods are beyond the scope of this study.

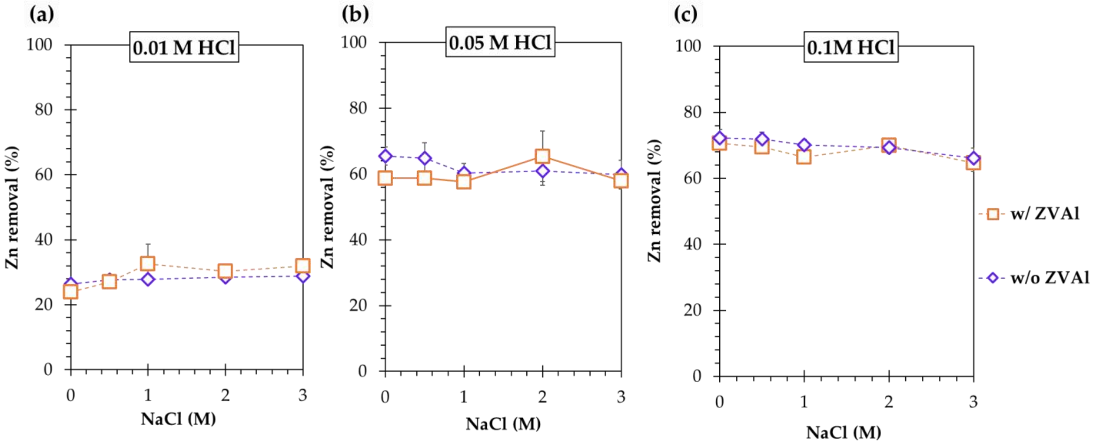

Figure 12. Effects of solution compositions on Zn removal from ZPLRs with and without ZVAl addition: (**a**) 0.01 M HCl and 0–3 M NaCl, (**b**) 0.05 M HCl and 0–3 M NaCl, and (**c**) 0.1 M HCl and 0–3 M NaCl.

3.3. Leachability of Lead and Zinc after Concurrent Dissolution-Cementation

To evaluate if the solid residues generated after treatment by concurrent dissolution-cementation meet environmental standards, the leachability of Pb and Zn using TCLP was examined out. The amounts of Pb and Zn leached before (untreated ZPLRs) and after treatment (treated by combined dissolution-cementation technique under the conditions 0.1 M HCl, 2 M NaCl, and 0.1 g ZVAl) were compared with the regulatory thresholds. As illustrated in Table 2, the levels of Pb and Zn that leached from untreated ZPLRs were substantially high: Pb was higher than environmental standards. In contrast, the amounts of Pb and Zn that leached from the residues after treatment by the concurrent dissolution-cementation method were dramatically lower. Leachable Pb (which was about 0.12 mg/L) was lower than the regulatory threshold, which entails the detoxification of ZPLRs.

Table 2. Toxicity characteristic leaching procedure (TCLP) leachability tests of untreated ZPLRs and treated residues after concurrent dissolution and cementation treatment.

Element	Untreated ZPLRs	Treated Residues	Threshold (USEPA)
Pb	12.95 mg/L	0.12 mg/L	5 mg/L
Zn	473.5 mg/L	21.5 mg/L	–*

* No Zn TCLP regulatory threshold.

3.4. Conceptual Flowsheet

Based on the results obtained in this study, the conceptual flowsheet for ZPLRs treatment by a concurrent dissolution-cementation technique to remove/recover Pb and Zn by using the HCl–NaCl solution with ZVAl is proposed (Figure 13). The flowsheet involves the removal of Pb—more toxic heavy metal to human beings than Zn—by cementation using ZVAl before solid-liquid separation. The Zn that remains in a solution can be recovered by precipitation or electrowinning. High removal of Pb and Zn can be achieved using a less concentrated NaCl (even as low as 1 M) solution acidified with 0.1 M HCl by the addition of ZVAl. The generated solid residues may not necessarily need to be washed because the most toxic metal that remains in the solution as a result of the inherent incomplete solid-liquid separation is negligible. In addition, this approach shortens and simplifies the treatment of ZPLRs compared to the conventional approach (i.e., leach, solid-liquid separation, and finally recovery of dissolved metals).

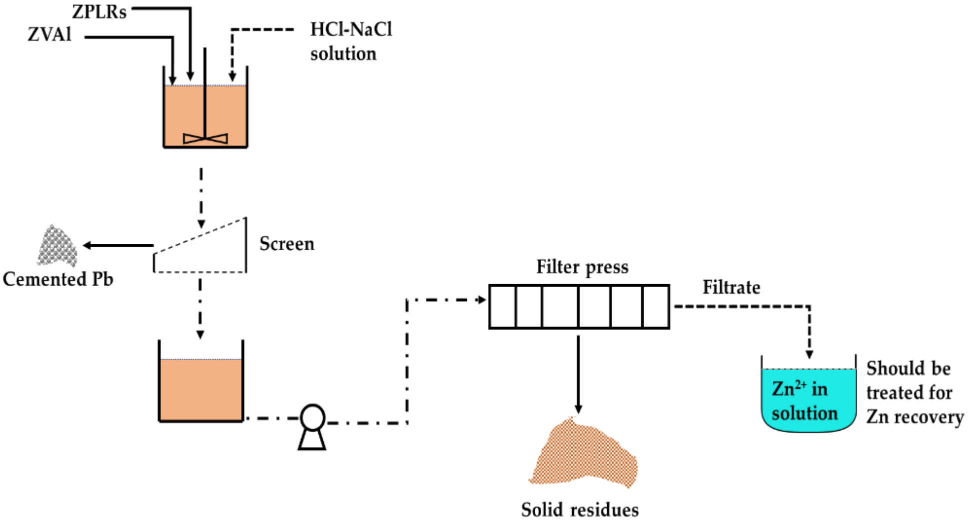

Figure 13. A conceptual flowsheet of the treatment of ZPLRs using the concurrent dissolution-cementation technique.

4. Conclusions

This study investigated Pb and Zn removal from ZPLRs using a concurrent dissolution-cementation technique in acidified chloride solution. The following is a summary of the findings:

1. Zinc removal from ZPLRs increased with increasing the HCl concentration (i.e., increased from 27% to 60% and 70% when the HCl concentration increased from 0.01 to 0.05 and 0.1 M, respectively) but it was neither affected by the increase of NaCl concentration nor the addition of ZVAl during leaching;
2. Zinc was not to be sequestered from the acidified chloride leaching pulp by cementation using ZVAl and was attributed to the dissolution of cemented Zn or preferential reduction of H^+ to H_2 by ZVAl over Zn^{2+} to Zn;
3. Lead removal from ZPLRs without the addition of ZVAl increased with increasing NaCl and HCl concentrations. Pb removal steadily increased from around 0% to 28%, 0.5% to 58%, and 0.5% to 72% for 0.01, 0.05, and 0.1 M HCl, respectively, when NaCl increased from 0 to 3 M, respectively. The increase of Pb removal with HCl concentration was attributed to an H^+ attack to dissolve Pb from carbonates, as well as fixing free $SO_4{}^{2-}$ as $HSO_4{}^-$, thereby, limiting the precipitation/formation of solid $PbSO_4$. Meanwhile, Pb removal increased at higher NaCl concentrations because of the formation of more soluble Pb-Cl complexes;
4. The addition of ZVAl during ZPLRs leaching (concurrent dissolution-cementation technique) dramatically increased the Pb removal even at low chloride concentration. Pb removal at 0.05 M HCl increased from 2.5% to 35.5% and 8% to 57% for 0.5 and 1 M NaCl concentration, respectively. Meanwhile, for 0.1 M HCl, the addition of ZVAl during ZPLRs leaching increased the Pb removal from 3% to 69% and 9% to 72% for 0.5 and 1 M NaCl concentration, respectively. The increase was attributed to shifting the equilibrium as the result of sequestration of dissolved Pb, thereby, enhancing dissolution of lead host minerals and dissolution of intermediate sparling soluble solid, $PbCl_2$; and
5. The most toxic metal, Pb, from ZPLRs was recovered and separated before solid-liquid separation, which simplifies the treatment flowsheet, as well as eliminates the need for extensive washing of the solid residues generated.

Supplementary Materials: The following are available online at http://www.mdpi.com/2075-4701/10/4/531/s1, Figure S1: log–log activity of Pb^{2+} and Cl^- at 25 °C, 1.013 bars, and $CO_3{}^{2-} = 10^{-5}$ M for (a) pH 4, (b) pH 2, and (c) pH 1 for 0.01, 0.05, and 0.1 M HCl (created using the Geochemist's Workbench® with the MINTEQ database). Figure S2: XRD pattern of (a) ZPLRs before being treated and (b) the residues obtained after treating ZPLRs by the concurrent dissolution-cementation technique in the solution composed of 3 M NaCl and 0.05 M HCl.

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