Removal of Cd\(^{2+}\) and Pb\(^{2+}\) from Wastewater through Sequent Addition of KR-Slag, Ca(OH)\(_2\) Derived from Eggshells and CO\(_2\) Gas

Lulit H. Ekubatsion, Thenepalli Thriveni, and Ji W. Ahn*

**ABSTRACT:** The effect of heavy metals in aqueous solutions has been addressed by several methods. Precipitation using lime, slaked or quick, is one of the commonly used techniques. In this work, KR-slag was used in addition to Ca(OH)\(_2\) that served as a seeding material. Furthermore, CO\(_2\) has been injected into the suspensions for pH stabilization, which further increases the removal efficiency. Accordingly, results have shown a great performance regarding both removal efficiency and reduced sludge production. More than 99% of Cd\(^{2+}\) and Pb\(^{2+}\) was removed with 1 g/L of KR-slag, 0.5 g/L of Ca(OH)\(_2\), and CO\(_2\) injection at a rate of 1 L/min. The effect of carbonation has been evaluated by examining the removal efficiency before and after carbonation. Following the injection of CO\(_2\), removal efficiency has increased from 58.7 to 99.8 and 71.2 to 99.3% for Cd\(^{2+}\) and Pb\(^{2+}\), respectively. Moreover, sludge volume from this treatment method was obtained as 103 mL/L, which is much less than the sludge volume obtained from the carbonation of only Ca(OH)\(_2\), that is, 361 mL/L. Leaching of residues was also conducted to evaluate the environmental performance of the removal process. After carbonation, there was a lower concentration of metals when leached out in a wide range of pH solutions. Contrarily, it was observed that a relatively higher concentration of metals was released in acidic solutions due to the substitution of metal ions (Cd\(^{2+}\) and Pb\(^{2+}\)) with H\(^+\) ions. Residues were then characterized by X-ray diffraction and differential thermal analysis/thermogravimetric analysis for phase identification. Both characterizations detected the presence of CaCO\(_3\), which was an indication of the transformation of Ca(OH)\(_2\) to CaCO\(_3\).

1. **INTRODUCTION**

Heavy metals, for example, cadmium (Cd\(^{2+}\)) and lead (Pb\(^{2+}\)), are a threat to water bodies because of their harmfulness by creating intense and persistent harm to human and oceanic life.\(^1\) They are ineluctable because of their wide production and applications in different industries. Currently, treatment of aqueous solutions containing toxic heavy metals has been conducted through various techniques such as Fenton-chemical precipitation,\(^2\) chemical precipitation,\(^3\) electrocoagulation,\(^4\) ion flotation,\(^5\) adsorption,\(^6\) ion exchange,\(^7\) layered double hydroxide precipitation,\(^8\) and reverse osmosis.\(^9\) However, these techniques have some limitations. For instance, adsorption is less effective for aqueous solutions containing higher concentrations of heavy metals. Membrane filtrations such as reverse osmosis have high operation costs and high energy consumption and need skilled manpower, which limit the use of this method. Ion exchange has a high cost for ion exchange materials, and some resins are not available for specific metal ions. Chemical precipitation is ordinarily applied because of its better performance and simplicity of use. It is the conversion of dissolved heavy metal ions to insoluble solid precipitates. However, chemical precipitations such as hydroxide precipitation leave alkaline solutions after treatment, redissolve back of formed metal hydroxides at lower pH, suitability problem for chelated wastewaters and difficulty of filtration because of the gelatinous behavior of metal hydroxides.

Industrial residues such as fly ash, bottom ash, steel slags, cement waste, kiln dust, and so forth are produced as byproducts in the industries. They are composed of different metal oxides and complex minerals that can be used for further application such as for backfilling or construction. They also contain toxic heavy metals that should not be disposed of to the environment without treatment.\(^10\) Industrial residues have abundant alkaline earth metals that can be used as an adsorbent for CO\(_2\).\(^11\) They can also be used for the adsorption of pollutants from aqueous solutions\(^12\) and also the solidification of heavy metals.\(^13\) Kambara reactor slag (KR-slag) is an industrial byproduct generated from the desulfurization of molten iron in a steel factory. Lime is used as a desulfurizer from the KR mechanical stirring process that reacts with sulfur resulting in CaS. For the improvement of the desulfurization processes, it is crucial to understand and study the effect of heavy metals in aqueous solutions.
process, excess lime is added, resulting in unreacted CaO. The products CaS and unreacted CaO have a low specific gravity rising to the surface of the molten iron and then slag is formed. The main constituents of KR-Slag are calcium oxide, iron oxide, and silicon oxide, in which calcium oxide is more than 45% depending on the amount of the desulfurizer (lime) used in the KR mechanical stirring process. Due to the high content of calcium oxide, it has versatile applications such as a cement-free binder in concrete, in acid mine drainage treatment, as an alkali activator of an alkali-activated system, and backfill material. In contrast, solid wastes such as eggshells have valuable applications in versatile fields. Eggshells have been generated abundantly causing serious environmental problems. An approximate annual generation of 5.92 Mt of eggshells has been estimated. Although the waste eggshell is composed of a valuable constituent [mainly calcium carbonate (CaCO₃)], which has numerous applications, most of the waste is being disposed of to the environment.

In this paper, KR-slag was used for heavy metal removal by accelerated carbonation of Ca(OH)₂. This method overcomes most limitations of the current removal techniques mentioned above. It leaves the treated water at neutral pH due to the dissolution of CO₂ gas that also reduces the solubility of heavy metals. It is also an effective, less time-consuming, eco-friendly, and sustainable approach because it utilizes waste materials. Furthermore, it can be considered as a CO₂ emission mitigation approach along with heavy metal treatment. In this work, Cd²⁺ and Pb²⁺ removal efficiencies with carbonation of only Ca(OH)₂, only KR-slag, and both Ca(OH)₂ and KR-slag were compared. The effect of carbonation has been studied by evaluating the removal efficiency before and after the addition of CO₂ gas. The performance of residues was evaluated by conducting a leaching test on the precipitates. Moreover, precipitates were analyzed further to study their removal mechanism.

![Removal efficiency (a) with only KR-slag, (b) with only Ca(OH)₂, and (c) with Ca(OH)₂ and KR-slag.](https://doi.org/10.1021/acsomega.1c00946)
2. RESULTS AND DISCUSSION

2.1. Heavy Metal Removals. Figure 1a gives the removal efficiency of heavy metals by KR-slag carbonation without the addition of Ca(OH)\(_2\). The dosage of KR-slag used was in the range of 0.25 to 3 g/L. In all the dosages, Cd\(^{2+}\) has shown a lower removal efficiency than Pb\(^{2+}\). It was observed that the removal efficiency of Cd\(^{2+}\) increased from 15.4 to 74.4% when KR-slag dosage was increased from 0.25 to 3 g/L. Contrarily, the removal efficiency of Pb\(^{2+}\) increased from 79.0 to 96.1% when KR-slag dosage was increased from 0.25 to 3 g/L. Cd\(^{2+}\) and Pb\(^{2+}\) were removed (74.4 and 96%, respectively) at a dosage of 3 g/L.

Figure 1b shows the removal efficiency of heavy metals by Ca(OH)\(_2\) carbonation without the addition of KR-slag. Conditions of the experiment were Ca(OH)\(_2\) dosage of 1–3 g/L, 100 mg/L initial metal concentration, and 1 L/min of CO\(_2\) flow rate. The removal efficiency obtained at 3 g/L of Ca(OH)\(_2\) was higher for both metals (nearly 99%). The detailed results were given in a previous work. 33

Although the removal efficiency with only Ca(OH)\(_2\), or KR-slag as discussed above is nearly 99% at 3 g/L, the sludge produced is significant, leading to environmental pollution. The production of sludge needs to be reduced by using less dosage of precipitants taking environmental protection into account. Therefore, KR-slag was used as a seeding material in the Ca(OH)\(_2\) carbonation process. Figure 1c shows the removal efficiency of heavy metals by Ca(OH)\(_2\) carbonation with the addition of KR-slag. Dosage of Ca(OH)\(_2\) was used in the range of 0–0.9 g/L, whereas 1 g/L of KR-slag was used in addition to Ca(OH)\(_2\) for coagulation and flocculation. At 0 g/L of Ca(OH)\(_2\) (only 1 g/L of KR-slag), 46 and 92% of Cd\(^{2+}\) and Pb\(^{2+}\) were removed, respectively. However, as the dosage of Ca(OH)\(_2\) increased, the removal efficiency has also increased. At 0.5 g/L of Ca(OH)\(_2\), 99% of both metals was removed. Therefore, desired removal efficiency and reduced sludge production were achieved at a KR-slag dosage of 1 g/L and Ca(OH)\(_2\) dosage of 0.5 g/L.

The kinetics of Cd\(^{2+}\) and Pb\(^{2+}\) removal was conducted with an initial metal concentration of 100 mg/L using 1 g/L of KR-slag and 0.5 g/L of Ca(OH)\(_2\) synthesized from eggshells. The precipitation process was completed within 10 min. Initially, both metals showed lower removal efficiencies, which increased with time and were nearly 99% at 10 min, as shown in Figure 2. Moreover, initial rapid precipitation was observed up to 6 min, followed by slower precipitation.

Suspension pH is one of the indispensable parameters in heavy metal removals. The change in pH during removal of Cd\(^{2+}\) and Pb\(^{2+}\) is shown in Figure 3. It shows the pH change both before and after the injection of CO\(_2\). The initial pH of the synthetic aqueous solution was ∼6.0–6.2 before the addition of KR-slag and of Ca(OH)\(_2\). It increased rapidly, as both precipitants were introduced to the solution and stabilized after few minutes. The increase in pH had shown an insignificant difference in rate: Cd\(^{2+}\) has a slower rate than Pb\(^{2+}\). This difference rate might be significant if higher concentrations of heavy metals were considered. Then, CO\(_2\) gas was then injected at 10 min, followed by a rapid decrease in solution pH and stabilized ∼pH 7.

To evaluate the effect of carbonation, CO\(_2\) with a purity of 99.9% was injected into heavy metal-containing (concentration of 100 mg/L) suspensions with 1 g/L of KR-slag and 0.5 g/L of Ca(OH)\(_2\). Initially (without the addition of KR-slag and Ca(OH)\(_2\)), the pH of all suspensions was in the range of 5.6–6.1. However, the pH immediately increased to 12 after the addition of KR-slag and Ca(OH)\(_2\). Then, it finally reduced to pH 7 after coming in contact with CO\(_2\). Figure 4 shows that the injection of CO\(_2\) gas has increased heavy metal removal significantly. Before carbonation, both metals have shown lower removal efficiencies. This result has also been obtained in a previous study in which Cr\(^{3+}\), Zn\(^{2+}\), Pb\(^{2+}\), and Cu\(^{2+}\) were removed by carbonation of fly ash and lime.\(^{34}\) For cadmium (see Figure 4a), the removal efficiency before carbonation at 0.5 g/L of Ca(OH)\(_2\) was 58.7%. However, the removal efficiency increased to 99.8% after carbonation. However, for lead (see Figure 4b), the removal efficiency before and after carbonation at 0.5 g/L of Ca(OH)\(_2\) was 71.2 and 99.3%, respectively. It can also be seen that the removal efficiency decreased from 71.2 to 60.3%, as the dosage increased from 0.5 to 0.9 g/L. It can be because of the thermodynamic stability of the lead–H\(_2\)O system. Pb\(^{2+}\) ions will be released, as pH of the solution is low (<6). Additionally, Pb(OH)\(_2\) will redissolve to form [Pb(OH)\(_4\)]\(^{2−}\) (eq 1), as pH of the solution is high (>12). This elaborates on the cause of the reduction in removal efficiency at higher dosages.\(^{33}\)

\[
Pb(OH)_2 + 2OH^- = [Pb(OH)_4]^{2−}
\]

2.2. Residue Characterization. 2.2.1. Sludge Amount. The main advantage of this work is the reduction of sludge production. The sludge characteristics were given in Table 1. The sludge volume was obtained as 361 mL/L for carbonation of only Ca(OH)\(_2\), whereas 103 mL/L for carbonation of both KR-slag and Ca(OH)\(_2\), indicating that more than one-third of sludge production has been reduced. Moreover, the weight of the solid after dewatering was recorded as 3.22 g/L for carbonation of only Ca(OH)\(_2\), while it was 1.52 g/L for carbonation of both KR-slag and Ca(OH)\(_2\).

2.2.2. Leaching. Leaching of residues obtained from the removal process was conducted in the pH range of 1 to 13. The results showed that the release of heavy metals from residues after carbonation was slower than that from the residues before carbonation, as shown in Figure 5. Generally, Cd\(^{2+}\) exhibits lower metal concentration than Pb\(^{2+}\) at all pH ranges. However, both metals have shown a higher concentration of metals at lower pH due to the presence of
more H⁺ ions than the metal ions.³⁵ The leaching test shows the stabilization of heavy metals in the residue in a wide range of pH.

2.2.3. Phase Identification. The crystalline phase identified in KR-slag is given in Figure 6a. The main constituent of the raw material was portlandite with minor constituents of calcite, graphite, magnetite, ettringite, and free iron. Moreover, the X-ray diffraction (XRD) of Ca(OH)₂ synthesized from eggshells was given in a previous work,³⁶ which was mainly composed of portlandite. Figure 6b shows the crystalline phase identified in the residue after precipitation with carbonation of KR-slag and Ca(OH)₂. CaCO₃ was the only identified compound in the solid residue. This might be due to the difference in concentrations used of Cd²⁺, Pb²⁺, and Ca²⁺ ions. The main peak was substituted by calcite, where portlandite was no more dominant in the precipitate. This result confirmed the total transformation of the phase during the carbonation process.

The differential thermal analysis/thermogravimetric analysis (DTA/TGA) curve of KR-slag before carbonation and the precipitate is illustrated in Figure 6. Cd²⁺ and Pb²⁺ precipitated from the carbonation of both KR-slag and Ca(OH)₂ were analogous to carbonation of only Ca(OH)₂. The KR-slag showed weight losses of 12.90, 4.74, and 1.66%, corresponding to vaporization, decomposition of Ca(OH)₂ to CaO, and decomposition of CaCO₃ to CaO, respectively (see Figure 7a).³⁷ Moreover, the DTA/TGA curve of Ca(OH)₂ was given in a previous work.³⁶ On the other hand, the precipitate showed a total weight loss of 44.64% at 768.51 °C (see Figure 7b). This loss is mainly due to the release of CO₂ from CaCO₃.
decomposition. This result also shows a complete transformation of Ca(OH)$_2$ to CaCO$_3$. However, the decomposition temperature of the precipitate with Cd$^{2+}$ and Pb$^{2+}$ was found to be lower than that of the precipitate without heavy metals CaCO$_3$. A similar result has been obtained from another study.  

2.3. Removal Mechanism. Heavy metal removal with the addition of KR-slag and Ca(OH)$_2$ and carbonation depends on hydration and metal speciation. First, hydroxyl ions are released into the solution by hydration of KR-slag and Ca(OH)$_2$. The hydration of Ca(OH)$_2$ is given in eq 2.

\[
\text{Ca(OH)}_2 + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{OH}^-
\]  

(2)

The hydration of solid phases in KR-slag such as CaO, MgO, Ca$_2$SiO$_4$, Ca$_3$SiO$_4$, and CaO·7Al$_2$O$_3$ may occur as given in eqs 3–7.  

\[
\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{OH}^-
\]  

(3)

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + 2\text{OH}^-
\]  

(4)

\[
2\text{Ca}_2\text{SiO}_4 + 4\text{H}_2\text{O} \rightarrow 2\text{Ca}^{2+} + 4\text{OH}^{-} + 3\text{H}_2\text{O} + 3\text{Ca}^{2+} + 6\text{OH}^-
\]  

(5)

\[
2\text{Ca}_3\text{SiO}_4 + 6\text{H}_2\text{O} \rightarrow 3\text{Ca}^{2+} + 3\text{H}_2\text{O} + 3\text{Ca}^{2+} + 6\text{OH}^-
\]  

(6)

\[
\text{CaO} \cdot 7\text{Al}_2\text{O}_3 + 12\text{H}_2\text{O} \rightarrow 6\text{Al}^{3+} + \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} + 2\text{OH}^-
\]  

(7)

The abovementioned reactions resulted in the release of hydroxyl ions from the hydration of KR-slag and Ca(OH)$_2$ (before carbonation) that may result in heavy metal hydroxide precipitation. Moreover, sorption may also occur on the surface of solid phases of the KR-slag. The mechanism for treatment in the presence of Ca(OH)$_2$ is dependent on the pH of solution and metal concentrations. Therefore, it is important to observe cadmium and lead water systems. Cd$^{2+}$ decomposes in acidic and very alkaline solutions. In acidic and very alkaline solutions, Cd$^{2+}$ and HCD$_2$O$_2$ are released into the solution, respectively. Meanwhile, for solution pH in between, the stability of Cd(OH)$_2$ may prevent the mobility of Cd$^{2+}$. On the other hand, Pb$^{2+}$ tends to be stable thermodynamically when solutions are neutral or alkaline. In acidic and very high alkaline solutions, lead generally tends to decompose. Pb$^{2+}$ and HPbO$_2$ or PbO$_3^-$ (depending on the oxidation) are released to the acidic and high alkaline solutions, respectively. In the meantime, PbO or PbO$_2$ (depending on the oxidation) inhibits Pb$^{2+}$ mobility for solution pH in between acidic and alkaline solution.

Carbonic acid, bicarbonates, and carbonates obtained from the hydration of CO$_2$ gas in the presence of CO$_2$. Then, Cd(OH)$_2$ and Pb(OH)$_2$ will release metal ions to the solution due to low pH caused by the dissociation of CO$_2$ (aq) [eqs 9 and 10].  

\[
\text{CO}_2(g) \rightarrow \text{CO}_2(aq) + \text{H}_2\text{O}(aq) \rightarrow \text{H}_2\text{CO}_3(aq) \\
\rightarrow \text{H}^+(aq) + \text{HCO}_3^-(aq) \rightarrow \text{H}^+(aq) + \text{CO}_3^{2-}(aq) 
\]  

(8)

\[
\text{Cd(OH)}_2 \rightarrow \text{Cd}^{2+} + 2\text{OH}^- 
\]  

(9)

\[
\text{Pb(OH)}_2 \rightarrow \text{Pb}^{2+} + 2\text{OH}^- 
\]  

(10)

Lead carbonate and cadmium carbonate are the predominant species at neutral pH as predicted from the equilibrium of the Pb$^{2+}$(Cd$^{2+}$)–H$_2$O–CO$_2$ system. Figure 8 gives the stability of CdCO$_3$ and PbCO$_3$ thermodynamically in the presence of CO$_2$ at a neutral pH and temperature of 25 °C. The thermodynamics calculations were carried out using Matlab R2010a software with thermodynamics parameters of all possible reactions. The concentrations of Cd$^{2+}$, Pb$^{2+}$, and CO$_2$ were considered the same as the experimental condition, that is, 0.89 mM, 0.48 mM, and 0.1 M, respectively. Cd$^{2+}$ and Pb$^{2+}$ ion speciation was significantly affected by pH of the solution. At acidic and alkaline solutions, ions are released to the solution either in the form of free ions (Cd$^{2+}$ and Pb$^{2+}$) or complex ions [(Cd(OH)$_3^-$ and Pb(OH)$_2^-$]. At neutral pH, however, CdCO$_3$ and PbCO$_3$ precipitates are produced for Cd$^{2+}$ and Pb$^{2+}$, respectively.

Therefore, the possible reaction present in the treatment process is given in eqs 11–13. The crystal nucleation is followed by the crystal growth of CaCO$_3$, CdCO$_3$, and PbCO$_3$ by fast supersaturation of the abovementioned processes.

Figure 8. The stability of CdCO$_3$ and PbCO$_3$ thermodynamically in the presence of CO$_2$ at a neutral pH and temperature of 25 °C.
Figure 6. X-ray diffraction pattern of (a) KR-slag and (b) solid residue.

Figure 7. DTA/TGA of (a) KR-slag and (b) solid residue.
Ca\(^{2+}\) + CO\(_3^{2-}\) → CaCO\(_3\) (nuclei) → CaCO\(_3\)

\[
11
\]

Pb\(^{2+}\) + CO\(_3^{2-}\) → PbCO\(_3\) (nuclei) → PbCO\(_3\)

\[
12
\]

Cd\(^{2+}\) + CO\(_3^{2-}\) → CdCO\(_3\) (nuclei) → CdCO\(_3\)

\[
13
\]

3. CONCLUSIONS

KR-slag and Ca(OH)\(_2\) with carbonation have been applied for the removal of Cd\(^{2+}\) and Pb\(^{2+}\). High removal efficiency and reduced sludge production were obtained by the carbonation process with both Ca(OH)\(_2\) and KR-slag. The Ca(OH)\(_2\)–KR-slag–CO\(_2\) treatment of Cd\(^{2+}\) and Pb\(^{2+}\) achieved removal efficiencies of more than 99% with 1 g/L of KR-slag and 0.5 g/L of Ca(OH)\(_2\) for both metals. Furthermore, the sludge volume was obtained as 361 mL/L for carbonation of only Ca(OH)\(_2\) and 103 mL/L for carbonation of both KR-slag and Ca(OH)\(_2\). The weight of the solid after dewatering was obtained as 3.22 g/L for carbonation of only Ca(OH)\(_2\) and 1.52 g/L for carbonation of both KR-slag and Ca(OH)\(_2\). This revealed that the reduction in sludge production was significant that can minimize the environmental impact. The impact of carbonation was also significant, where removal efficiency has increased from 88.7 to 99.8 and 71.2 to 99.3% for Cd\(^{2+}\) and Pb\(^{2+}\), respectively, after the injection of CO\(_2\) gas. Leaching tests on residues were also conducted to evaluate the environmental performance of the removal method. The final metal concentration after carbonation had shown a decrease in the release of heavy metals to the environment. Moreover, Ca(OH)\(_2\) was completely transformed to CaCO\(_3\), indicating the complete carbonation of the precipitants. Therefore, the inclusion of KR-slag as a seeding material in the Ca(OH)\(_2\) carbonation process resulted not only in effective removal efficiency but also in a significant reduction in sludge production. Therefore, this technique of heavy metal treatment has several advantages such as CO\(_2\) sequestration, heavy metal removal, and KR-slag treatment (stabilization/solidification) prior to landfiling.

4. MATERIALS AND METHODS

4.1. Materials. Stock solutions with 1000 mg/L concentration of Cd\(^{2+}\) and Pb\(^{2+}\) were prepared by dissolving Pb(NO\(_3\))\(_2\) and Cd(NO\(_3\))\(_2\)·4H\(_2\)O in deionized water. Synthetic wastewater with 100 mg/L metal concentration was prepared by diluting the stock solution. Sodium hydroxide (NaOH), hydrochloric acid (HCl), and nitric acid (HNO\(_3\)) were used for pH adjustment. Carbon dioxide gas with 99.9% purity was provided by Jeil Gas Company, Seoul, South Korea. All chemicals were provided by Junsei Chemicals Ltd., Seoul, South Korea.

The sol–gel method has been used to synthesize Ca(OH)\(_2\) from waste eggshells. Powdered eggshells were first dissolved in 1 M of HCl (eq 11) to produce a homogeneous mixture of calcium chloride (CaCl\(_2\)), followed by the dropwise addition of
1 M of NaOH to CaCl2 solution (eq 12). The Ca(OH)2 gel was then formed, filtered, washed several times with distilled water, and dried in an oven at 60 °C for 24 h.

$$\text{CaCO}_3(s) + 2\text{HCl(aq)} \rightarrow \text{CaCl}_2(aq) + \text{H}_2\text{O(l)} + \text{CO}_2(g)$$ (11)

$$\text{CaCl}_2(aq) + 2\text{NaOH(aq)} \rightarrow \text{Ca(OH)}_2(s) + 2\text{NaCl(aq)}$$ (12)

KR-slag was obtained from a company in South Korea. It is a heterogeneous material consisting largely of calcium oxide. The KR-slag was prepared for use by sieving with 100 μm sieve size and oven drying at 105 °C for 5 h.

The chemical composition of waste eggshells and sieved KR-slag is given in Table 2. Moreover, heavy metal contents in KR-slag were also analyzed, as given in Table 3, because the slag can be exposed to various heavy metals.

| chemical composition | waste eggshells, % | KR-slag, % |
|----------------------|-------------------|-----------|
| SiO2                 | <0.01             | 11.2      |
| Al2O3                | <0.01             | 2.7       |
| Fe2O3                | <0.01             | 16.8      |
| CaO                  | 52.75             | 51        |
| MgO                  | 0.52              | 2.7       |
| K2O                  | 0.04              | 0.09      |
| Na2O                 | 0.05              | 0.07      |
| TiO2                 | <0.01             |           |
| MnO                  | <0.01             | 1.8       |
| SO3                  | 4.3               |           |
| P2O5                 | 0.22              |           |
| Ig. loss             | 46.62             | 7.2       |

Table 3. Heavy Metal Contents in KR-Slag

| chemical composition | KR-slag, % |
|----------------------|-----------|
| As                   | <0.01     |
| Pb                   | N.D       |
| Cu                   | N.D       |
| Cr                   | N.D       |
| Cd                   | N.D       |
| Ni                   | N.D       |
| Zn                   | N.D       |

Table 3. Heavy Metal Contents in KR-Slag (N.D = not detected.)

4.2. Methods. 4.2.1. Precipitation. KR-slag was used as a seeding material to enhance precipitation. Ca(OH)2 was also used together with the KR-slag to elevate the pH as required. The slag was added at a rate of 0.25 g to 1 L of the heavy metal solution, and then, Ca(OH)2 was added at a desired amount. To initiate coagulation and agglomeration, suspensions were rapidly stirred at 300 rpm for 3 min using a stirrer, followed by gentle stirring at 80 rpm for 7 min. Carbonation of suspensions was conducted simultaneously, with CO2 of 99.9% purity maintained at atmospheric pressure. Figure 9 gives the schematic representation of the carbonation process. Supernatants were then allowed to settle for 30 min and then filtered by a Whatman filter (0.45 μm) before analyzing by inductively coupled plasma optical emission spectroscopy (ICP-OES) (Optima 8300) (ICP-OES). Triplicate measurements of metal concentrations were performed, and their average values were obtained. For further analysis, sludges were dried at 105 °C for 12 h. The pH of suspensions was constantly monitored by using a pH meter.

4.2.2. Sludge Amount. The sludge amount was estimated both before and after dewatering. The volumetric method has been used to determine sludge volume before dewatering that was measured by Imhoff cones after settling the treated solution for 30 min. Moreover, the solution was filtered and dried at 105 °C for 24 h to measure the weight of the solids.

4.2.3. Leaching. The environmental performance of sludge in a landfill was evaluated by a leaching test. It was conducted on a shaker rotated at 150 rpm with a liquid to solid ratio of 10 for 24 h at room temperature. The leaching effect was conducted in the range of pH 1−13. The supernatant liquids were then filtered through a 0.45 μm Whatman filter and analyzed by ICP-OES.

4.3. Characterizations. TGA/DTA and XRD were used for the characterization of solids. Decomposition temperatures of raw materials and precipitates were analyzed by thermogravimetric analysis (TGA) (Shimadzu DTG-60H) in a platinum crucible at a heating rate of 10 °C/min from ambient temperature to 1000 °C. Phase identification and structural analysis of solids were conducted by powder XRD with 2θ ranging from 10 to 90° (BD2745N, Rigaku, Tokyo, Japan). An Orion Versa Star Pro (Thermo Scientific, USA) pH meter with a glass electrode was used to constantly monitor the pH of suspensions. Pb2+ and Cd2+ concentrations were analyzed by ICP-OES.

AUTHOR INFORMATION

Corresponding Author

Ji W. Ahn — Center for Carbon Mineralization, Mineral Resources Research Division, Korea Institute of Geosciences and Mineral Resources (KIGAM), Daejeon 34132, Republic of Korea; orcid.org/0000-0002-8621-7483; Email: ahnjw@kigam.re.kr

Authors

Lulit H. Ekubatsion — Resources Recycling Department, University of Science and Technology (UST), Daejeon 34113, Republic of Korea; School of Civil and Environmental Engineering Department, Addis Ababa Institute of Technology (AAiT), Addis Ababa University, Addis Ababa 1000, Ethiopia; Center for Carbon Mineralization, Mineral Resources Research Division, Korea Institute of Geosciences and Mineral Resources (KIGAM), Daejeon 34132, Republic of Korea; orcid.org/0000-0002-0249-9111
Thenepalli Thriveni — Department of Chemistry, Indian Institute of Technology Tirupati (IIT Tirupati), Tirupati, Andhra Pradesh 517506, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00946

Author Contributions
L.H.E.: Conceptualization, data curation, methodology, and writing—original draft. T.T.: Supervision. J.W.A.: Project administration, supervision, and writing—review and editing.

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS
This research was supported by the National Strategic Project-Carbon Mineralization Flagship Center of the National Research Foundation of Korea (NRF) funded by the Ministry of Science and ICT (MSIT), the Ministry of Environment (ME), and the Ministry of Trade, Industry, and Energy (MOTIE) (2017M3D8A2084752).

REFERENCES
(1) Malar, S.; Shivendra Vikram, S.; JC Favis, P.; Perumal, V. Lead Heavy Metal Toxicity Induced Changes on Growth and Antioxidative Enzymes Level in Water Hyacinths [Eichhornia Crassipes (Mart.)]. Bot. Stud. 2016, 55, 1–11.
(2) Fu, P.; Xie, L.; Tang, B.; Wang, Q.; Jiang, S. Application of a Novel Strategy-Advanced Fenton-Chemical Precipitation to the Treatment of Strong Stability Chelated Heavy Metal Containing Wastewater. Chem. Eng. J. 2012, 189–190, 283–287.
(3) Zhang, Y.; Duan, X. Chemical Precipitation of Heavy Metals from Wastewater by Using the Synthetic Magnesium Hydroxy Carbonate. Water Sci. Technol. 2020, 81, 1130–1136.
(4) Pohl, A. Removal of Heavy Metal Ions from Water and Wastewaters by Sulfur-Containing Precipitation Agents. Water, Air, Soil Pollut. 2020, 231, 503.
(5) Fakorede, O.; Adewumi, R. Effectiveness of electro-coagulation treatment method on the physio-chemical parameters and heavy metals in rubber latex wastewater. J. Eng. Mater. Technol. 2020, 14, 1–9.
(6) Taseidifar, M.; Makavipour, F.; Pashley, R. M.; Rahman, A. F. M. M. Removal of Heavy Metal Ions from Water Using Ion Floation. Environ. Technol. Innovation 2017, 8, 182–190.
(7) Ali, R. M.; Hamad, H. A.; Hussein, M. M.; Malash, G. F. Potential of Using Green Absorbent of Heavy Metal Removal from Aqueous Solutions: Adsorption Kinetics, Isotherm, Thermodynamic, Mechanism and Economic Analysis. Ecol. Eng. 2016, 91, 317–332.
(8) Argun, M. E.; Dursun, S.; Ozdemir, C.; Karatas, M. Heavy Metal Adsorption by Modified Oak Sawdust: Thermodynamics and Kinetics. J. Hazard. Mater. 2007, 141, 77–85.
(9) Demirbas, A. Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review. J. Hazard. Mater. 2008, 157, 220–229.
(10) Ihsanullah; Abbas, A.; Al-Amer, A. M.; Loaui, T.; Al-Marri, M. J.; Nesser, M. S.; Khraisheh, M.; Atieh, M. A. Heavy Metal Removal from Aqueous Solution by Advanced Carbon Nanotubes: Critical Review of Adsorption Applications. Sep. Purif. Technol. 2016, 157, 141–161.
(11) Inyang, M. I.; Gao, B.; Yao, Y.; Xue, Y.; Zimmermann, A.; Mosa, A.; Pullmannappallil, P.; Ok, Y. S.; Cao, X. A Review of Biochar as a Low-Cost Adsorbent for Aqueous Heavy Metal Removal. Crit. Rev. Environ. Sci. Technol. 2016, 46, 406–433.
(12) Koby, M.; Demirbas, E.; Senturk, E.; Ince, M. Adsorption of Heavy Metal Ions from Aqueous Solutions by Activated Carbon Prepared from Apricot Stone. Bioresources. Technol. 2005, 96, 1518–1521.
(13) Park, J.-H.; Ok, Y. S.; Kim, S.-H.; Cho, J.-S.; Heo, J.-S.; Delaune, R. D.; Seo, D.-C. Competitive Adsorption of Heavy Metals onto Sesame Straw Biochar in Aqueous Solutions. Chemosphere 2016, 142, 77–83.
(14) Uddin, M. K. A Review on the Adsorption of Heavy Metals by Clay Minerals, with Special Focus on the Past Decade. Chem. Eng. J. 2017, 308, 438–462.
(15) Zewail, T. M.; Youssef, N. S. Kinetic Study of Heavy Metal Ions Removal by Ion Exchange in Batch Conical Air Spouted Bed. Alexandria Eng. J. 2015, 54, 83–90.
(16) Ma, L.; Wang, Q.; Islam, S. M.; Liu, Y.; Ma, S.; Kanatzidis, M. G. Highly Selective and Efficient Removal of Heavy Metals by Layered Double Hydroxide Intercalated with the MoS42-. J. Am. Chem. Soc. 2016, 138, 2858–2866.
(17) Li, Y.; Xu, Z.; Liu, S.; Zhang, J.; Yang, X. Molecular Simulation of Reverse Osmosis for Heavy Metal Ions Using Functionalized Nanoporous Graphenes. Comput. Mater. Sci. 2017, 139, 65–74.
(18) Malviya, R.; Chaudhary, R. Factors Affecting Hazardous Waste Solidification/Stabilization: A Review. J. Hazard. Mater. 2006, 137, 267–276.
(19) Pan, S.-Y.; Chang, E. E.; Chiang, P.-C. CO2 Capture by Accelerated Carbonation of Alkaline Wastes: A Review on Its Principles and Applications. Aerosol Air Qual. Res. 2012, 12, 770–791.
(20) Gao, Y.; Jiang, J.; Tian, S.; Li, K.; Yan, F.; Liu, N.; Yang, M.; Chen, X. BOF Steel Slag as a Low-Cost Sorbent for Vanadium (V) Removal from Soil Washing Effluent. Sci. Rep. 2017, 7, 1–10.
(21) Li, Y.-C.; Min, X.-B.; Chai, L.-Y.; Shi, M.-Q.; Tang, C.-J.; Wang, Q.-W.; Liang, Y.-J.; Lei, J.; Liyang, W.-J. Co-Treatment of Gypsum Sludge and Pb/Zn Smelting Slag for the Solidification of Sludge Containing Arsenic and Heavy Metals. J. Environ. Manage. 2016, 181, 756–761.
(22) Sheng, G.; Huang, P.; Wang, S.; Chen, G. Potential Reuse of Slag from the Kambara Reactor Desulfurization Process of Iron in an Acidic Mine Drainage Treatment. J. Environ. Eng. 2014, 140, 04014023.
(23) Cho, B.; Choi, H. Physical and Chemical Properties of Concrete Using GGBFS-KR Slag-Gypsum Binder. Constr. Build. Mater. 2016, 123, 436–443.
(24) Tong, Z.; Ma, G.; Cai, X.; Xue, Z.; Wang, W.; Zhang, X. Characterization and Valorization of Kenbara Reactor Desulfurization Waste Slag of Hot Metal Pretreatment. Waste Biomass Valorization 2016, 7, 1–8.
(25) Cho, B. Hydration Characteristics of Cement-Free Binder Using Kambara Reactor Slag. Mag. Concr. Res. 2016, 68, 1143–1154.
(26) Kuo, W.-T.; Hou, T.-C. Engineering Properties of Alkali-Activated Binders by Use of Desulfurization Slag and GGBFS. Constr. Build. Mater. 2014, 66, 229–234.
(27) Akınwumi, I. Soil Modification by the Application of Steel Slag. Period. Polytech., Civ. Eng. 2014, 58, 371–377.
(28) Cho, B.-S.; Koo, K.-M.; Choi, S.-J. Compressive Strength and Microstructure Properties of Alkali-Activated Systems with Blast Furnace Slag, Desulfurization Slag, and Gypsum. Adv. Civ. Eng. 2018, 2018, 1–9.
(29) Laca, A.; Laca, A.; Diaz, M. Eggshell Waste as Catalyst: A Review. J. Environ. Manage. 2017, 197, 351–359.
(30) Cree, D.; Rutter, A. Sustainable Bio-Inspired Limestone Eggshell Powder for Potential Industrialized Applications. ACS Sustainable Chem. Eng. 2015, 3, 941.
(31) Shiferaw, N.; Habte, L.; Thenepalli, T.; Ahn, J. W. Effect of Eggshell Powder on the Hydration of Cement Paste. Materials 2019, 12, 2483.
(32) Hamideh, F.; Akbar, A. Application of Eggshell Wastes as Valuable and Utilizable Products: A Review. Res. Agric. Eng. 2018, 64, 104–114.
(33) Habte, L.; Shiferaw, N.; Thriveni, T.; Mula, D.; Lee, M.-h.; Jung, S.-h.; Ahn, J. W. Removal of Cd(II) and Pb(II) from Wastewater via Carbonation of Aqueous Ca(OH)2 Derived from Eggshell. Process Saf. Environ. Prot. 2020, 141, 278–287.
(34) Chen, Q.; Luo, Z.; Hills, C.; Xue, G.; Tyrer, M. Precipitation of Heavy Metals from Wastewater Using Simulated Flue Gas: Sequent Additions of Fly Ash, Lime and Carbon Dioxide. *Water Res.* 2009, 43, 2605−2614.

(35) Miretzky, P.; Muñoz, C.; Carrillo-Chávez, A. Experimental Binding of Lead to a Low Cost on Biosorbent: Nopal (Opuntia Streptacantha). *Bioresour. Technol.* 2008, 99, 1211−1217.

(36) Habte, L.; Shiferaw, N.; Mulatu, D.; Thenepalli, T.; Chilakala, R.; Ahn, J. Synthesis of Nano-Calcium Oxide from Waste Eggshell by Sol-Gel Method. *Sustain* 2019, 11, 3196.

(37) Mirghiasi, Z.; Bakhtiari, F.; Darezereshki, E.; Esmaeilzadeh, E. Preparation and Characterization of CaO Nanoparticles from Ca(OH)2 by Direct Thermal Decomposition Method. *J. Ind. Eng. Chem.* 2014, 20, 113−117.

(38) Beh, C. L.; Chuah, T. G.; Nourouzi, M. N.; Choong, T. Removal of Heavy Metals from Steel Making Waste Water by Using Electric Arc Furnace Slag. *J. Chem.* 2012, 9, 2557−2564.

(39) Montes-Hernandez, G.; Renard, F.; Geoffroy, N.; Charlet, L.; Pironon, J. Calcite Precipitation from CO2-H2O-Ca(OH)2 Slurry under High Pressure of CO2. *J. Cryst. Growth* 2007, 308, 228−236.