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Evaluation of the Applicability of Concrete Sludge for the Removal of Cu, Pb, and Zn from Contaminated Aqueous Solutions

Jongchan Yoo, Heeyoung Shin * and Sangwoo Ji

Center for Carbon Mineralization, Climate Change Mitigation and Sustainability Division, Korea Institute of Geoscience and Mineral Resources (KIGAM), 124 Gwahak-ro, Yuseong-gu, Daejeon 34132, Korea; jcyoo@kigam.re.kr (J.Y.); swji@kigam.re.kr (S.J.)

* Correspondence: hyshin@kigam.re.kr; Tel.: +82-42-868-3574; Fax: +82-42-868-3429

Received: 9 July 2018; Accepted: 24 August 2018; Published: 25 August 2018

Abstract: In this study, the possibility of using concrete-sludge recycling as an immobilizer, including dried sludge (DS), precipitated calcium carbonate (PCC), and calcite-coated particles (CCP), was evaluated for the remediation of Cu-, Pb-, and Zn-contaminated aqueous solutions. Experimental variables characterizing immobilization, including reaction time, initial solution pH, and immobilizer dosage, were selected. After DS was applied, 98.3% of Cu, 99.9% of Pb, and 95.2% of Zn were removed via metal-hydroxide coprecipitation onto the surface of DS, which increased in pH within the shortened contact time. On the contrary, PCC and CCP removed metals (above 99.9% removal) via the formation of metal carbonates, which was highly dependent on both the pH and the carbonates released from the immobilizers. The acidic solution pH contributed to the dissolution of calcite (leading to an increase in carbonates in solution), thus enhancing the removal of metals. An increase in PCC and CCP dosage (liquid to solid ratio of 1000 to 100) was effective in removing Cu with an increasing final pH and number of carbonates in solution. Our results show that concrete sludge can be recycled to reduce environmental loads, including alkaline wastewater discharge, waste disposal, CO₂ emissions, and metal-contaminated aqueous solutions.

Keywords: heavy metals; concrete sludge; immobilization; carbon mineralization; environmental load; calcium carbonate

1. Introduction

The metallic contamination of groundwater by industrial developments and human activities (e.g., mining, smelting, and refining) have serious, harmful effects on human health and the ecosystem. Several remediation techniques, including immobilization (e.g., sorption, solidification, and stabilization), permeable reactive barriers, coprecipitation, coagulation, membrane filtering, and ion exchange, were developed in an effort to remediate metal(loid)-contaminated groundwater over the past few decades [1,2]. Among them, the immobilization method using Fe/Mn/Al oxides, clay minerals, or calcium (Ca)-bearing amendments is an attractive technique for the inhibition of the mobility and toxicity of metallic contaminants in a groundwater environment [3,4]. Ca-bearing materials/waste/minerals, such as gypsum (CaSO₄·2H₂O), quicklime (CaO), slaked lime (Ca(OH)₂), fly ashes, hydroxyapatites (Ca₅(PO₄)₃(OH)), and limestone (CaCO₃), are attractive alternative immobilizers that are easily accessible and cost-effective for reducing contamination [5–10].

In Korea, vast amounts of waste concrete are annually generated by reconstruction projects for deteriorated and aged buildings. Screening and crushing processes are essential for the recycling of waste concrete as aggregate materials, which are classified as dry- and wet-based processes. Although it is simpler, cheaper, and easier to maintain the system using dry-based processes,

the wet-based crushing process is commonly applied to remove impurities and to wash the concrete surface [11] and reduce air pollution. During this process, a significant amount of concrete sludge with a high moisture content (approximately 92.5 wt%), containing fine-grained particles from the mortar, is unfortunately generated. The liquid phase, which involves Ca-rich and severely alkaline wastewater, is separated from the sludge through a flocculation–precipitation process, before being recycled during the wet-based crushing process without any treatment, such as pH neutralization. The carbon mineralization process, which is a part of the carbon capture utilization and sequestration (CCUS) technology, is widely applied for reducing atmospheric carbon-dioxide (CO_2) concentrations. During this process, carbonate-based materials, including CaCO_3 , magnesite (MgCO_3), and dolomite ($\text{CaMg}(\text{CO}_3)_2$), are produced as commercially valuable materials [12,13]. In our previous study, a carbon mineralization process was performed in an effort to neutralize Ca-supersaturated alkaline wastewater from concrete sludge [14]. The process produced precipitated calcium carbonate (PCC; rhombic calcite, CaCO_3) with a purity of 99.2%, and sequestered CO_2 through a wastewater neutralization process. The solid phase (waste), which is emitted at a rate of 10 tons/day in waste concrete recycling plants, is useless in any industry; therefore, we should consider the concept of reuse with respect to waste recycling. Some studies investigated whether the application of concrete sludge as an (ab)sorbent could remove harmful elements/metalloids, including fluoride (F), boron (B), and arsenic (As) [15–17]. Concrete sludge contains a considerable number of Ca ions due to the dissolution of calcium hydroxide ($\text{Ca}(\text{OH})_2$), and is strongly alkaline. Therefore, these properties could be applied to the removal of divalent heavy metals in aqueous solutions [8,18,19].

In this study, the applicability of materials originating from concrete sludge as a metal-immobilizer was evaluated for the reduction of the mobility of metals, including copper (Cu), lead (Pb), and zinc (Zn), in aqueous solutions. Three materials from concrete sludge used in this study were prepared as follows: (1) dried sludge (DS; solid phase); (2) PCC produced via the carbon mineralization process using wastewater (liquid phase); and (3) calcite-coated particles (CCP) produced via the carbon mineralization process using dried sludge and wastewater (solid–liquid phase). The presented study focused on reducing environmental loads with respect to the neutralization of alkaline wastewater, CO_2 sequestration, the treatment of metal-contaminated aqueous solutions, and recycling of concrete sludge waste (Figure 1).

Figure 1. A schematic flow diagram of waste/wastewater recycling and the application of carbon mineralization processes using waste concrete sludge.

2. Materials and Methods

2.1. Preparation of Immobilizers

2.1.1. Dried Sludge (DS)

The concrete sludge sample used in this study was collected from a resource recycling plant of construction waste in Incheon, Korea. The concentration of the components in the sludge

solution (liquid phase) diluted and acidified by 5 vol% nitric acid (HNO_3) for dissolution of hydroxide-precipitates was analyzed using inductively coupled plasma optical emission spectroscopy (ICP-OES; 720-ES, Agilent, Santa Clara, CA, USA). The moisture content of the concrete sludge was determined based on oven-drying at 105 °C until there was no change in weight. The sludge was separated into liquid and solid phases via vacuum filtration using a membrane filter (Advantech, Tokyo, Japan) with a 0.45 μm pore size. The filtrate sample was completely sealed to prevent a decrease in pH and Ca concentration in solution via natural CaCO_3 precipitation between Ca and atmospheric CO_2 , and was kept in an amber bottle at room temperature. The particle size distribution of the sludge was determined via the wet-sieving method using 20-, 100-, 325-, and 500-mesh sieves. In order to achieve a DS sample (<25 μm), the slurry containing fine particles was sieved through a 25 μm sieve, and was filtered with a 0.45 μm pore-sized membrane filter. After oven-drying the residual solids at 105 °C for 24 h, they were used as a metal-immobilizer sample.

2.1.2. Precipitated Calcium Carbonate (PCC) and Calcite-Coated Particles (CCP)

Laboratory-scale carbon mineralization experiments, with a neutralization of the alkaline wastewater in concrete sludge, previously described in Reference [14], were carried out to produce the PCC and the CCP. The experiment was conducted according to the following procedure: 2.5 L of sludge solution, with solids removed, was carbonated in a reactor at ambient temperature and pressure, with a CO_2 gas flow rate of 8 mL CO_2 /min/L solution (99.9% CO_2 purity) until the solution pH dropped to 8.5 (reaction time of approximately 65 min). The CO_2 gas flow rate was chosen to achieve the optimal CO_2 sequestration (100.0%), removal of Ca in solution (99.2%), and purity of PCC (99.2%) when the solution pH was neutralized (target solution pH of 8.5). The process using 2.5 L of sludge solution produced approximately 2.7 g of PCC, which was highly dependent on the solution pH and Ca concentration.

In order to coat completely the surfaces of the mother particles (DS) with calcite, CCP was produced under the same conditions using a mixture of 2.5 L of sludge solution and 12.5 mg of DS (0.005 w/v). A fixed quantity of DS, which was dispersed with a little sludge solution in order to prevent its aggregation, was added into the sludge solution. After the solution pH reached 8.5 (reaction time of approximately 65 min), the slurry was immediately filtered with a membrane filter (0.45 μm pore size) before the solid residue (CCP) was oven-dried at 105 °C.

2.1.3. Characterization of Immobilizers

The pH of the immobilizers was determined using a mixture with a particles-to-deionized (DI) water ratio of 1:5 (w/v) according to the Korean Standard Test Method (KSTM-ES 07032) before the pH of the mixture was measured using a pH meter (ORION VSTAR-PH, Thermo Fisher Scientific Inc., Waltham, MA, USA). The surface morphology and elemental mapping, as well as the specific surface area of the immobilizers, were analyzed using scanning electron microscopy with energy-dispersive spectroscopy (SEM-EDS; 6380LA, JEOL Ltd., Tokyo, Japan), and an N_2 -based Brunauer–Emmett–Teller (BET) surface-area analyzer (BET analyzer; Tristar 3000, Micromeritics, Norcross, GA, USA), respectively. The mineralogy of the immobilizers was analyzed by X-ray diffraction (XRD; X'pert MPD, Philips, Amsterdam, The Netherlands) in combination with Reitveld quantification analysis. The XRD analysis was conducted with a $\theta/2\theta$ goniometer using a $\text{Cu-K}\alpha$ radiation. The patterns were obtained by step scanning from 3° to 65° with a step size of 0.01° 2 θ .

2.2. Immobilization Experiments

2.2.1. Reaction Time

Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$; Junsei Chemical Co. Ltd., Tokyo, Japan), lead nitrate ($\text{Pb}(\text{NO}_3)_2$; Junsei Chemical), and zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$; Junsei Chemical) were dissolved in deionized (DI) water to prepare the artificial metal-contaminated solutions. Specifically,

2.5 g of immobilizers (DS, PCC, and CCP) were added into 250 mL of metal solution at a concentration of 100 mg/L in an Erlenmeyer flask, before being mixed using a magnetic stirrer for 1440 min at room temperature. Ten milliliters of sample were collected periodically and filtered through a 0.45 µm syringe filter, before immediately measuring the pH of the filtrate. The concentration of elements in the filtrate was analyzed using ICP-OES. After 1440 minutes, the mixture was filtered via gravity filtration using a 0.45 µm pore-sized filter paper, and the residue was used for the identification of mineralogy using XRD, following oven-drying at 105 °C. In addition, some experiments using an increased concentration of 250 mL of metal solution (1000 mg/L) for 1440 min were conducted with 2.5 g of PCC, considering the detection limit of the XRD analysis. The chemical species, according to the pH and Eh in the aqueous phase, were simulated using the geochemical modeling program (Geochemist's Workbench; GWB, Ver. 12.0.2, Aqueous Solutions LLC, Andover, MA, USA) based on the Lawrence Livermore National Laboratory (LLNL) thermo database (thermo.com.V8.R6+.tdat).

2.2.2. Solution pH and Immobilizer Dosage

Batch experiments as a function of solution pH were carried out in order to evaluate the immobilization efficiency of metals. A mixture of 0.3 g of immobilizer (DS, PCC, and CCP) with 30 mL of metal solution with a concentration of 100 mg/L was adjusted to pH values of 1–5 with 1 M HNO₃ in a 50 mL centrifuge tube before being mixed using an end-over-end shaker at 30 rpm for 1440 min at room temperature. In addition, the immobilization efficiency of the metals in aqueous solution, according to immobilizer dosage, was evaluated at 1:200, 1:500, and 1:1000 (*w/v*) with metal solutions of 100 mg/L for 1440 min at room temperature. After mixing, the final mixture was filtered using a 0.45 µm syringe filter before the filtrate was used to analyze the metal concentration using ICP-OES. The filtrate pH was immediately measured using the pH meter to prevent pH changes due to atmospheric CO₂. The experimental conditions are summarized in Table 1.

Table 1. The conditions for the immobilization experiments.

Immobilizer	Time (min)	Conc. of Metals (mg/L)	L/S Ratio ¹	Temp. (°C)	Initial Metal Solution pH
Effect of reaction time					
DS PCC CCP	1440	100	100 (250 mL : 2.5 g)	25	Nonadjusted
Effect of initial solution pH					
DS PCC CCP	1440	100	100 (30 mL : 0.3 g)	25	1.0 2.0 3.0 4.0 5.0
Effect of immobilizer dosage					
DS PCC CCP	1440	100	100–1000 (30 mL : 0.03–0.3 g)	25	Nonadjusted

¹ Liquid-to-solid ratio. DS—dried sludge; PCC—precipitated calcium carbonate; CCP—calcite-coated particles.

3. Results and Discussion

3.1. Properties of Immobilizers

Table 2 shows the physico-chemical properties of the concrete sludge and the immobilizers used in this study. The pH values of the sludge solution, DS, PCC, and CCP were 12.4, 8.7, 11.0, and 10.5, respectively. Sludge solution pH varied between 12.2 and 12.7, which was highly dependent on the

supply of tap water during the wet-based crushing process. The pH of DS was quite a bit lower (pH of 8.7) because DS contains a considerable amount of quartz, muscovite, and feldspar, which does not affect the pH increase significantly, derived from cement/mortar in the wet sieving process of waste concrete. In addition, more than 53% of sludge particles were separated from the sludge with a 500-mesh sieve (<25 µm) using the wet-sieving procedure.

Table 2. Physico-chemical properties of the concrete sludge and the immobilizers used in this study.

Concrete Sludge		
	pH	12.4 ± 0.3
	Moisture content (%)	92.5 ± 2.5
	Ca ²⁺ (mg/L) (liquid phase)	375.0 ± 63.0
	Na ⁺ (mg/L) (liquid phase)	426.5 ± 1.9
	K ⁺ (mg/L) (liquid phase)	307.2 ± 1.3
Particle size distribution (wt%)	>850 µm	1.0 ± 0.1
	850–150 µm	4.2 ± 0.2
	150–45 µm	26.2 ± 1.0
	45–25 µm	15.2 ± 3.6
	<25 µm	53.4 ± 3.0
Immobilizer		
pH	DS (<25 µm)	8.7 ± 0.2
	PCC	11.0 ± 0.0
	CCP	10.5 ± 0.1
Brunauer–Emmett–Teller (BET) surface area (m ² /g)	DS (<25 µm)	23.1
	PCC	2.3
	CCP	4.7
Mineralogy	DS (<25 µm)	Quartz (19.3 wt%), Calcite (24.2 wt%), Muscovite (30.9 wt%), Albite (11.3 wt%), Vaterite (6.7 wt%), Orthoclase (5.5 wt%), Chlorite (2.0 wt%)
	PCC	Calcite (100 wt%)
	CCP	Calcite (100 wt%)

The concentration of Ca in the sludge was in the range of 310–430 mg/L following the dissolution of Ca(OH)₂ into the cement phases of concrete, which contributed to the changes in sludge pH according to the following Equation [14]:

The mineralogy and morphology of the immobilizers are shown in Figures 2a–c and 3, respectively. Quartz (SiO₂), muscovite (KAl₂(Si₃AlO₁₀)(OH)₂), and albite (NaAlSi₃O₈), derived from cement/mortar, were identified using XRD analysis to be the dominant minerals in DS. In addition, calcite (CaCO₃) was partially observed, formed via the natural carbonation of lime (CaO) with atmospheric CO₂ [20].

Figure 2. Qualitative mineralogical analysis results before (a–c) and after (d–f) immobilization experiments for 1000 mg/L of metal concentration; Q—quartz (SiO_2); C—calcite (CaCO_3); A—albite ($\text{NaAlSi}_3\text{O}_8$); M—muscovite ($(\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F,OH})_2$); V—vaterite (CaCO_3); M1—malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$); Cl—cerussite (PbCO_3); H—hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$); S—smithsonite (ZnCO_3); Z—hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$).

Figure 3. The results of scanning electron microscopy (SEM) elemental dot-mapping analysis of the initial immobilizers; (a) dried sludge (DS); (b) precipitated calcium carbonate (PCC); (c and d) calcite-coated particles (CCP).

For PCC and CCP, calcite was formed as the predominant mineral via the carbon mineralization process. Calcite in the supersaturated solution was formed through the stages of spontaneous nucleation and crystal growth [21]. The morphology of PCC exhibited a step-like growth of rhombic or rhombohedral calcite (Figure 3b). On the other hand, rhombohedral calcite was spherically agglomerated with spontaneous crystal growth on the rough surfaces of DS (Figure 3c), which led to the production of calcite-coated particles. Here, the rhombohedral calcite grown on the surfaces of the DS might provide sufficient reaction sites to accelerate the reactions with heavy metals in the aqueous solution during the immobilization processes. Unfortunately, an increase in pulp density of up to 0.2 (*w/v*) (Figure 3d) when producing CCP led to an inhibition of calcite-coating onto the surfaces of sludge particles, and to a decrease in calcite content (75.9%). The BET surface areas of the immobilizers, in increasing order, were DS (23.1) >> CCP (4.7) > PCC (2.3). These values might be increased due to the heterogenetic and rough fine-particles contained in the DS.

3.2. Metal Immobilization in Aqueous Solution

3.2.1. Effect of Reaction Time

The removal of metals from the solution and the change in solution pH with reaction time are shown in Figure 4, with the efficiencies (*R*) calculated according to the following equation:

$$R (\%) = \left(1 - \frac{C_t}{C_0} \right) \times 100, \quad (2)$$

where C_t and C_0 are the concentrations of the metals remaining in solution after a specified reaction time and before the reaction, respectively. The immobilizers increased the removal of Cu, Pb, and Zn from solution with increasing reaction time, with a removal efficiency of 98.3–100.0% for Cu, 99.9–100.0% for Pb, and 95.2–100.0% for Zn for DS; 19.6–99.9% for Cu, 99.9–100.0% for Pb, and 30.1–99.9% for Zn for PCC; and 9.2–100.0% for Cu, 99.9–100.0% for Pb, and 19.6–100.0% for Zn for CCP during 1440 min (Figure 4a-1,b-1,c-1).

Interestingly, the removal trends of the metals were significantly influenced by the changes in solution pH during the reaction, regardless of immobilizer type (Figure 4a-2,b-2,c-2). The behavior of the metals in aqueous solution in the presence of the immobilizers was highly influenced by the equilibrium pH, reaction time, and immobilizer dosage. In particular, divalent metals, including Cu, Pb, and Zn, formed various complexes via a combination with anionic ligands in aqueous solution, depending on the equilibrium pH [22]. The removal mechanisms of the metals by calcite-bearing immobilizers, including PCC and CCP, can be associated with the interactions between metals and the carbonates released from calcite, as well as the equilibrium pH. However, in the case of DS, the metals might be removed through the coprecipitation of metal hydroxides (Me–OH) onto the surface of DS under high-pH conditions, rather than through metal-carbonate precipitation, due to an insignificant amount of calcite contained in DS [5,23].

Figure 4. The removal efficiency of metals, and the changes in solution pH over time during the immobilization experiments for Cu (a), Pb (b), and Zn (c).

Calcite might affect the behavior of metals through the interactions occurring via ionic exchange, surface complexation, and precipitation [24]. In the case of precipitation, the stability of the chemical species of metals is heavily influenced by their solubility under certain pH and Eh conditions [4]. The concentration of Ca dissolved in solution during the reactions is shown in Figure 5. In the aqueous phase, calcite can be dissolved into Ca^{2+} , HCO_3^- , and CO_3^{2-} according to the following stoichiometric equations [25]:

Figure 5. The concentration of Ca released from immobilizers over time during the immobilization experiments for Cu (a), Pb (b), and Zn (c).

The dissolution of calcite is dependent on the solubility product (K_{sp} of calcite = $10^{-8.48}$) [24], which increases with an increasing number of protons (i.e., acidic pH). In addition, the solutions containing each metal, which show different solution pH, might affect the dissolution of calcite because of their different acid dissociation constant (pKa) values of metal complexes in the solution. Although bicarbonate (HCO_3^-) is the predominant ion in weakly alkaline pH ranges (approximately 8.0–9.0), based on the acid dissociation constant (pKa) for carbon species, metal-carbonate minerals are preferentially precipitated via complexation between Me^{2+} and CO_3^{2-} in the presence of metals in solution. Therefore, the CO_3^{2-} concentration ($[\text{CO}_3^{2-}]$) consumed by the precipitation of metal carbonates, regardless of atmospheric CO_2 dissolution, can be indirectly calculated from $[\text{Ca}^{2+}]$ in solution, based on the molar ratio between $[\text{Ca}^{2+}]$ and $[\text{CO}_3^{2-}]$ dissolved in solution (Equation 3). The carbonates might originate from calcite in the immobilizers, including PCC and CCP. The molar ratios between $[\text{CO}_3^{2-}]$, calculated from the stoichiometry equation, and $[\text{Me}^{2+}]$, removed from solution via metal-carbonate precipitation, were approximately 1.1–2.4 for Cu, 1.2–1.4 for Pb, and 1.1–1.7 for Zn (Figure 6). This indicates that sufficient carbonates were dissolved from calcite during the reactions. In addition, approximately 0.35%–2.26%, 0.57%–0.66%, and 0.33%–2.59% of the calcite contained in PCC and CCP were dissolved by Cu, Pb, and Zn during the reactions, respectively (the results were indirectly calculated from the concentration of Ca^{2+} and/or carbonates released into solution). In the case of DS, although the Ca released from DS was much higher than that from PCC and CCP, $[\text{CO}_3^{2-}]$ could not be calculated according to the equation because atmospheric CO_2 dissolution was potentially a substantial source of carbonates.

The mineralogical analysis using XRD did not detect Cu- and Zn-bearing minerals due to the lower initial concentration of the metals (100 mg/L); only hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) was detected as minor peaks (Figure S1; Supplementary material). A higher concentration of metals (1000 mg/L) were carbonate-bearing minerals, including malachite ($\text{Cu}_2(\text{OH})_2\text{CO}_3$), cerussite (PbCO_3), hydrocerussite, smithsonite (ZnCO_3), and hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), which were detected (Figure 2). The final solution pH values for Cu, Pb, and Zn after 1440 min were approximately 6.8, 7.6, and 6.9, respectively. Du et al. [26] reported that the application of razor clam shells (aragonite phase) and oyster shells (calcite phase) as sorbents removed Pb and Zn through the precipitation of cerussite and hydrozincite upon combining with the carbonate ions released from sorbents. Furthermore, Sarioglu et al. [27] reported that the removal mechanism of Cu in artificial drinking water involves the formation of complexes between Cu and carbonate, sulfate (SO_4^{2-}), and hydroxide ions in biosolids, such as waste sludge cake derived from wastewater treatment plants.

Figure 6. Summary of the relationship between the removal of Cu/Zn and final solution pH or carbonate levels in solution during the immobilization experiments according to reaction time.

The formation of these carbonate-bearing minerals corresponded exactly with the Pourbaix diagrams simulated using the geochemical modeling program (Figure 7a-1,b-1,c-1). It might be considered that the reactions in the immobilization processes were carried out at positive Eh (oxidation states). For the PCC and CCP immobilizers, in thermodynamic equilibrium, the predominant chemical species of metals in aqueous solution in the presence of (bi)carbonate ions were malachite, cerussite, hydrocerussite, hydrozincite, and smithsonite in their respective pH ranges [8,28–31]. In the results of XRD analysis (Figure 2), actually, metal-bearing precipitates contained in the immobilizer were identified after immobilization experiments for only a higher concentration of heavy metals (1000 mg/L). However, the predominant chemical species of metals in concentrations of 100 and 1000 mg/L might be the same because the final solution pHs are in their respective pH ranges for formation of the species. In detail, the removal efficiency of Cu in solution was approximately 46.6% for PCC and 30.8% for CCP after 120 min of reaction time at a solution pH of 6.4 (Figure 4d–f). Subsequently, the concentration of Cu gradually decreased until 540 min despite a negligible change in pH for both PCC and CCP. This indicates that the unstable malachite formed at the beginning of the reaction was aged for 1440 min of reaction time before being precipitated onto the surface of calcite as the reaction progressed. For Zn, the removal in solution was sharply increased by approximately 35.1% in PCC for 5 min and 67.9% in CCP for 10 min, through the formation of smithsonite in the pH range of 7.1–7.2. Subsequently, removal reached 99.9% after 1440 min following the increase in pH beyond 8.0 and aging with hydrozincite, producing a very stable Zn hydroxycarbonate phase (K_{sp} of hydrozincite = $10^{-14.9}$) [32,33]. In contrast, with Cu and Zn, significant Pb removal via the precipitations of cerussite and hydrocerussite was observed due to the presence of sufficient carbonates in solution, and the

maintenance of a high solution pH (above 8.3) until the end of the experiments. Actually, this study suggests only the removal mechanisms of metals by immobilizers derived from concrete sludge in model solutions, thus it should be conducted to evaluate the applicability of the processes to actual wastewater. When the processes are applied in a scaled-up version, a large amount of sludge wastes (by-products) containing heavy metals, which are inevitably generated, should be considered to treat through separation with sedimentation and/or filtration. For this, the environmental impacts of heavy metals in by-products should be evaluated via detailed characterizations of the metals including fractionation and mobility/bioaccessibility.

Figure 7. Pourbaix diagrams for Cu (a), Pb (b), and Zn (c) using the Lawrence Livermore National Laboratory (LLNL) thermodynamic database simulated with the Geochemist's Workbench (GWB) software (dashed lines; stability limits of water at 1 atm pressure). Input data: $a[\text{Cu}^{2+}] = 0.0016$, and $a[\text{HCO}_3^-] = 0.0021$ (a-1) and 0.0549 (a-2); $a[\text{Pb}^{2+}] = 0.00048$, and $a[\text{HCO}_3^-] = 0.00073$ (b-1) and 0.0492 (b-2); $a[\text{Zn}^{2+}] = 0.0015$, and $a[\text{HCO}_3^-] = 0.002$ (c-1) and 0.0511 (c-2). Minerals: Malachite, $\text{Cu}_2(\text{OH})_2\text{CO}_3$; Tenorite, CuO ; Cuprite, Cu_2O ; Cerussite, PbCO_3 ; Hydrocerussite, $\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$; Plattnerite, Pb_2O ; Hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$; Zincite, ZnO .

3.2.2. Effect of Initial Solution pH and Immobilizer Dosage

Initial solution pH is considered as an important variable in the immobilization process via the precipitation of metals. The removal of metals as a function of initial solution pH (1–5) is shown in Figure 8. In the application of DS, the removal efficiencies of Cu, Pb, and Zn in an initial pH of 1.0 were approximately 2.9%, 12.6%, and 0.0%, respectively. Clearly, the metal species exist in the ionic form of Me^{2+} in acidic conditions; thus, a much lower removal efficiency of metals was observed due to the inhibition of metal-hydroxide precipitation [31,34]. On the contrary, in the case of carbonate-bearing immobilizers, PCC and CCP, the removal of metals was significantly enhanced due to a sufficient amount of carbonates released from calcite under the weakly acidic conditions. Furthermore, the removal of metals might be enhanced with a longer reaction time of 1440 min, which would contribute to the aging of unstable precipitates. In addition, large amounts of carbonate resulted in the inhibition of a significant pH decrease through the formation of bicarbonate (HCO_3^-) as a buffer

to protons [35]. Hence, more than 95% of the metals were effectively removed in the initial pH range of 2–5.

Figure 8. Summary of metal removal, final solution pH, and carbonate level in solution after the immobilization experiments for Cu (a), Pb (b), and Zn (c) as a function of initial solution pH (experimental conditions: initial metal concentration, 100 mg/L; reaction time, 1440 min; liquid/solid ratio, 100).

Based on the experimental results, the mechanism of metal removal in aqueous solution involves precipitation onto the surface of immobilizers, which is strongly influenced by the concentration of carbonates and the equilibrium pH. Therefore, metal removal is heavily dependent on the immobilizer dosage. Figure 9 shows the removal of metals at various ratios of liquid to solid in the immobilization experiments. As expected, the removal of metals was highly dependent on immobilizer dosage due to changes in pH and the release of carbonates. It was clearly observed that the application of a smaller

immobilizer dosage did not enhance the removal of Cu and Zn, due to the low content of carbonates and the insignificant increase in solution pH.

Figure 9. Summary of metal removal, final solution pH, and carbonate level in solution after the immobilization experiments for Cu (a), Pb (b), and Zn (c) at various ratios of liquid to solid (experimental conditions: initial concentration of metals, 100 mg/L; reaction time, 1440 min).

In addition, the amount of carbonates released in solution increased with increasing immobilizer dosage. The removal of Pb was not directly affected by immobilizer dosage because higher final solution-pH ranges of 8.8–10.2 were maintained during the experiments. In the application of CCP, it was confirmed that the removal mechanism of metals from aqueous solution involved the precipitation of metals, according to pH and the amount of carbonate released from CCP, as opposed to calcite-coating onto the surface of sludge particles.

3.3. Estimation of Environmental Impact

In this study, we estimated the environmental impact of the application of metal-immobilization processes using materials derived (DS) and manufactured (PCC and CCP) from concrete sludge, based on the metal-immobilization experimental results (Table 3). For a volume of 3600 m³/day generated from the plant, approximately 345.6 tons/day of DS can be achieved through the wet-sieving procedure. As demonstrated, the direct use of DS as a metal-immobilizer was effective in utilizing vast amounts of waste and removing Cu, Pb, and Zn from contaminated aqueous solutions. In contrast, CCP (3.8 tons/day) produced through carbon mineralization could significantly reduce environmental loads, in terms of CO₂ sequestration (3.4 tons/day), wastewater/waste recycling, and the treatment of contaminated solutions. Therefore, concrete sludge can be utilized for the reduction of environmental loads. In addition, further studies are required to understand the effect of increasing the pulp density of sludge wastes on the production of CCP through carbon mineralization, to enhance the recycling rate for sludge waste.

Table 3. Estimation of environmental impact in the immobilization processes for metals in aqueous solution using concrete sludge, based on the experimental results.

Materials		Output (m ³ /d)	Production ² (tons/d)	CO ₂ sequestration ⁶ (tons/d)	Treatment ⁷ (m ³ /d)
Concrete sludge	Wastewater (Liquid phase)	3330.0 ¹	-	-	-
	Waste (Solid phase)	270.0 ¹	-	-	-
DS		-	345.6 ³	-	34,560.0
PCC		-	3.6 ⁴	3.4	359.6
CCP		-	3.8 ⁵	3.4	376.3

¹ Moisture content: 92.5% based on 3,600 m³/day from the field-resource recycling plant of construction waste selected in this study; ² waste recycling; ³ portion of <25 µm in waste: 53.4 wt%, and bulk density of concrete: 2400 kg/m³; ⁴ PCC production: 1.08 g PCC/L wastewater during carbon mineralization process; ⁵ CCP production: mixture with DS-to-wastewater ratio of 200 (v/w) in PCC-producing process; ⁶ conditions of carbon mineralization: 8 mL CO₂/min (99.9% CO₂ purity) for 65 min until the solution pH dropped to 8.5 (CO₂ sequestration: 100.0%); ⁷ treatment of Cu-, Pb-, and Zn-contaminated aqueous solution in a concentration of 100 mg/L: liquid/solid ratio of 100 (v/w) for 1440 min without pH adjustments (metal removal of 100.0%).

4. Conclusions

The main purpose of this study was to evaluate the applicability of immobilizers derived from concrete sludge for the removal of Cu, Pb, and Zn from aqueous solution. For immobilizers, dried sludge (DS) and calcite-predominant (precipitated calcium carbonate, PCC; calcite-coated particles, CCP) particles were produced via a wet-sieving method using a 25 µm sieve and a carbon mineralization process, respectively. It was confirmed that DS was able to remove metals in aqueous solution through the coprecipitation of metal hydroxides onto the surface, depending on pH. In the applications of PCC and CCP, the main mechanism of metal removal involved the formation of metal carbonates, which was heavily dependent on both increases in pH and the amount of carbonates released from the immobilizers. A longer reaction time could contribute to the stability of unstable metal-carbonate precipitations. In particular, Pb was completely removed via the formation of stable chemical species with an increase in pH within the shortened contact time, regardless of immobilizer type. In this study, the applicability of concrete sludge as an immobilizer for the removal of metals including Cu, Pb, and Zn in aqueous solution was demonstrated through the application of traditional techniques of pH control and coprecipitation. In addition, carbon mineralization process using abandoned concrete sludge for production of immobilizers is expected to solve environmental issues including wastewater/waste discharge, resource depletion, and CO₂ emission.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2075-4701/8/9/666/s1>, Figure S1: The results of XRD analysis for PCC and CCP after immobilization experiments in a metal concentration of 100 mg/L; C—calcite (CaCO_3); H—hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$).

Author Contributions: Conceptualization, H.S.; Methodology, H.S., J.Y., and S.J.; Validation, J.Y. and S.J.; Formal Analysis, J.Y.; Investigation, J.Y., H.S., and S.J.; Resources, H.S. and S.J.; Data Curation, J.Y.; Writing—Original Draft Preparation, J.Y.; Writing—Review & Editing, H.S. and S.J.; Visualization, J.Y.; Supervision, H.S.; Project Administration, H.S.; Funding Acquisition, H.S.

Funding: This research received no external funding.

Acknowledgments: This research was supported by the Basic Research Project (18-3422) of the Korea Institute of Geoscience and Mineral Resources (KIGAM).

Conflicts of Interest: The authors declare no conflict of interest.

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