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**Immobilization of Pb and Zn leached from mining residual materials in Kabwe, Zambia:
Performance of calcined dolomite in column experiments.**

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Abstract

Legacy Pb-Zn mine in Kabwe, Zambia, has left massive stockpiles of mining residual materials (MRM) that contain potentially toxic elements, such as lead (Pb) and zinc (Zn), which pollute the environment. In situ remediation of the contaminated area is an attractive technique for immobilizing hazardous metals. In this study, the efficacy of modified dolomite, i.e., calcinated dolomite (CD), was evaluated by mixing with MRM at 1, 5, and 10% ratios (CD₁, CD₅, and CD₁₀, respectively). The immobilization mechanisms of MRM were assessed through the leaching of hazardous metals, Pb and Zn, by four-column experiments. Measurements of mineralogical and chemical constituents of the MRM, sequential extraction, and thermodynamic modeling of the leachates were carried out to determine the attenuation mechanisms. Sequential extraction results indicated that the sources of Pb and Zn in the MRM were mainly from the exchangeable and carbonate fractions. Furthermore, the effluents from the MRM exceeded the Zambian effluent regulatory values throughout 30 weeks of the experimental period. The introduction of the CD into the MRM increased effluent pH and decreased the leaching concentrations of Pb and Zn. The CD₅ was enough to decrease the leaching concentrations of both hazardous metals below the Zambian effluent standard by prohibiting the release of Pb and Zn via the dissolution of carbonate minerals and retaining them in the carbonate fraction. The saturation indices of Pb and Zn suggest that the retention mechanisms by the CD accredit to precipitation, co-precipitation, and adsorption reactions. These results present an effective and inexpensive immobilization technology for hazardous wastes in abandoned mines.

Keywords: Mine wastes; column experiments; lead; zinc; immobilization; Zambia.

1. Introduction

Mining activities come with economic development and rapid industrialization; however, environmental degradation is inevitable after decommissioning. The negative aspect may include the anthropogenic influence of the by-products, i.e., the mine wastes. The mine wastes from abandoned mine sites have been identified as the most crucial source of pollution in many countries (Iavazzo et al., 2012; Guillevic et al., 2022; Khoeurn et al., 2018; Wang et al., 2019). Previous studies have shown that without proper management practices and remediation strategies, the risk of contaminating the surrounding environment with high contents of hazardous metals in soil (Lu et al., 2010), groundwater (Santos et al., 2002), and surface water (Bhuyan et al., 2017) is inevitable. For example, in Sardinia, Italy, the mine closure action plan and remediation control were not considered adequately (Cidu, 2011; Cidu et al., 2012); during the rainy season, concentrations of lead (Pb) and zinc (Zn) increased in the nearby stream waters due to high runoff from weathering of the exposed residue materials in the abandoned mine site.

Similarly, the abandoned mine in Kabwe, Zambia, was regarded as one of Africa's most significant Pb and Zn producers, supplying over 1.8 and 0.8 Mt of Pb and Zn, respectively (Kamona and Friedrich, 2007). It was discovered in 1902, started full-scale operation in 1906, and shut down in 1994. After the mine closure, massive stockpiles of mining residue materials (MRM) were left unattended. The lack of remediation action to control the impacts of mine wastes led to the town's widespread contamination of Pb and Zn (Kribek et al., 2019; Mufalo et al., 2021; Nakamura et al., 2021, 2022; Yabe et al., 2015). According to the studies of our research group, these materials still contain Pb and Zn to a great extent, and more than 40% of the elements can mobilize under ambient conditions (Silwamba et al., 2020; Tangviroon et al., 2020). Hazardous metals in the MRM can be transported through surface water, groundwater seepage, and wind

dispersion. Remediation of the contaminated site could help reduce the long-term transportation and redistribution of the toxic elements from the wastes to the surrounding environments (Kribek et al., 2019; Mufalo et al., 2021; Nakamura et al., 2021, 2022).

In situ remediation of mine wastes is a promising technic for reducing the risks associated with these toxic elements. The in situ method is more cost-effective than the ex situ, while the latter has a higher efficiency in remediation. Many ex situ remediation costs come from excavating and transporting contaminated materials from the polluted area. On the other hand, the in situ technique can be performed on-site. One of the most popular in situ remediation methods is chemical immobilization, where a chemical agent (immobilizer) is added to the contaminated area. This method is inexpensive, easily implemented, and quick in execution (Gray et al., 2006; Liu et al., 2018). The technique is based on reducing metal mobility, either by precipitation or increasing sorption and decreasing solubility (Gomes et al., 2022), thus reducing the deleterious environmental effects. Operational costs mainly depend on the price of the immobilizer, remediation efficiency, eco-friendliness, and availability (Xu et al., 2022). Chemical immobilizers such as phosphate are very efficient in stabilizing heavy metals (Andrunik et al., 2020, Seshadri et al., 2017); however, extensive use may lead to water eutrophication (Xu et al., 2022). Magnesium oxide (MgO) has excellent efficiency in removing heavy metals in water, but the high cost of MgO (Schiller, J.E. and Khalafalla, 1984, Shen et al., 2019) for the large-scale practice of this technology could probably be limited for application on the vast area of the MRM. Other naturally abundant adsorbents, like clay minerals (Zhang et al., 2021), are usually applied on a laboratory scale. Modified clay minerals by organic, acid, or nano zero-valent iron (nZVI) may improve their properties; at the same time, additional costs arise from modification, and new chemical agents might increase environmental threats (Xu et al., 2022).

The author's previous study investigated several potential chemical immobilizers, i.e., raw dolomite, calcinated dolomite (CD), and magnesium oxide, to remediate Pb and Zn leached from MRM (Tangviroon et al., 2020). Among all selected immobilizers, the CD proved efficient, cheap, locally available, and non-toxic (Khoshraftar et al., 2022) since it could effectively immobilize both Pb and Zn. The CD is a modified product of the abundant local material (dolomite; $\text{CaMg}(\text{CO}_3)_2$). Dolomite is formed when the limestone or carbonate mud is modified by replacing limestone's calcium ions (Ca^{2+}) with magnesium-rich ions (Pehlivan et al., 2009). Calcination (Calugaru et al., 2016) of dolomite produces a new immobilizer that contains magnesia (MgO) and calcite (CaCO_3). In addition, the thermal treatment by partial calcination enhances its adsorption properties (Calugaru et al., 2016; Khoshraftar et al., 2022). The mine wastes amended with the CD may form metal complexes such as cerussite (PbCO_3), hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$), smithsonite (ZnCO_3), and hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$), which could decrease Pb and Zn mobility (Goienaga et al., 2015, Redwan et al., 2021). In the previous study, the analyses were done based on the batch leaching experiments (Tangviroon et al., 2020), where the CD was added to the MRM in a predetermined volume of water and then shaken for a specific period, thus allowing us to assess the immobilization potential of the CD. In other words, the batch leaching experiments do not seem to be a reasonable prediction of the actual transport of contaminants due to several reasons, such as different solid-to-liquid ratios and flow paths of water from those in the field (Tabelin et al., 2010, 2014).

The CD immobilization efficacy has not been confirmed in column experiments. An in-depth understanding of the Pb and Zn immobilization from the MRM and CD mixtures is still needed under intermittent or unsaturated flow of water (Arima et al., 2021; Tabelin et al., 2017), because metal speciation and geochemical form may vary depending on environmental conditions

(Vrinceanu et al., 2019). The column test provides essential information on the leaching of toxic elements in the MRM and their transport (Tabelin et al., 2017; Tangviroon and Igarashi, 2017; Voegelin et al., 2003), consequently obtaining insight into the release and immobilization mechanisms of the elements under field conditions (Wang et al., 2019). Unfortunately, little information is known on the attenuation of Pb and Zn mimicking actual flow conditions in the environment using the CD. Therefore, this study aims to investigate the potency of the CD in decreasing Pb and Zn concentration from the MRM in the column experiments. Specific objectives are; (1) to investigate the leaching of Pb and Zn in MRM with CD; (2) to simulate the metal complex formation via saturation indices (*SIs*) of the CD and MRM mixtures for a period of 30 weeks; and (3) to evaluate the changes in the solid-phase partitioning of Pb and Zn of the residues after the experimental period. The current study will assist in developing chemical immobilization for remediating contaminated sites by Pb and Zn in Zambia.

2. Materials and Methods

2.1 Sample collection, preparation, and characterization

The sampling of the MRM and dolomite were conducted at the dumping site of Pb-Zn mine waste located in Kabwe, Zambia (Figure S1), and a dolomite quarry source nearby the MRM storage site. The MRM was randomly collected using shovels, brought to the laboratory, dried under ambient conditions, crushed, sieved through a 2 mm aperture screen, and kept in air-tight containers before usage. The dolomite was sieved through the same aperture screens. The CD was produced by burning the dolomite in a furnace at 700 °C for 2 h.

Pressed samples of finely crushed powder (< 50 µm in diameter) of the MRM and the CD were prepared for chemical and mineralogical analyses by an X-ray fluorescence spectrometer (XRF)

(SpectroXepos, Rigaku Corporation, Tokyo, Japan) and X-ray diffractometer (XRD) (MultiFlex, Rigaku Corporation, Tokyo, Japan). All the XRD patterns of the minerals were analyzed using Match!® software (Crystal Impact, Germany) and classified into strong, moderate, or weak depending on percentage abundance. The total organic carbon (TOC) content was obtained by subtracting the total carbon (TC) content from the inorganic carbon (IC) content of the solid samples < 2 mm; 100 mg and 50 mg of samples were burnt at 200 °C and 900 °C for IC and TC, respectively, in the combustion unit of the total carbon analyzer (TOC-VCSH-SSM-5000A, Shimadzu Corporation, Kyoto, Japan).

Sequential extraction was conducted to determine the solid-phase speciation of Pb-Zn in the MRM. The procedure used in this study was taken from Marumo et al. (2003). The improved method is based on two well-known techniques, Tessier et al. (1979) and Clevenger. (1990), which have been used extensively to characterize tailings, mineral processing wastes, and leaching residuals (Anju and Banerjee, 2010; Dang et al., 2002; Khoeurn et al., 2018). It fractionates toxic elements into five phases: exchangeable, carbonates, Fe-Mn oxides, sulfide/organic matter, and residual. Details of the sequential extraction procedure are illustrated in Table 1. The experiments were conducted on 1 g of samples < 2 mm in diameter. After each extraction step, the centrifugation of the suspension was done at 3,000 rpm for 30 min to retrieve the extractant. The residual was washed with 20 mL of deionized water, followed by centrifugation to separate the residual from the washing solution for each extraction step. The extractant and washing solution were combined and diluted to 50 mL for steps 1 to 4 and 100 mL for step 5, filtrated through 0.45-µm Millex® filters (Merck Millipore, Burlington, MA, USA), and kept in polypropylene bottles before analysis. Note that our previous studies have proved this extraction procedure to be reproducible with an average precision of 7% (Huyen et al., 2019; Vongphuthone et al., 2017).

Table 1 Sequential extraction for cationic element speciation

Step	Extractant	pH	Liquid to solid ratio (mL/g)	Temperature (°C)	Duration (h)	Mixing speed (rpm)	Extracted phase
1	1 M MgCl ₂	7	20/1	25	1	120	Exchangeable
2	1 M CH ₃ COONa 0.04 M NH ₂ OH·	5	20/1	25	5	120	Carbonates
3	HCl in 25% acetic acid 0.04 M NH ₂ OH·		20/1	50	5	120	Reducible
4	HCl in 25% acetic acid; 30% H ₂ O ₂ ; 0.02 M HNO ₃		36/1	85	5	120	Oxidizable
5	60% HNO ₃		20/1	60	1	-	Residual

2.2 Column Experiments

Figure 1 shows the schematic illustration of the columns. The column experiment is designed to mimic water flow through a porous bed of granular material (Tabelin et al., 2017). The input water for the column tests can be continuous or intermittent with a down-flow or up-flow direction. Each of the combinations is suitable for specific applications. Thus, we employed the intermittent with a down-flow type of column since the intermittent input represents rainfall and a downward direction, creating unsaturated water flow. Chemical immobilization is usually implemented on the top surface, where the contaminant tends to be mobilized by the water flowing within the vadose zone.

The columns were vertically mounted on a steel stand and covered with rainfall simulators. These covers were designed with small holes to simulate the raindrops and protect the sample inside the column from dust contamination. The experimental setup included pure MRM (CD₀) and MRM mixed with 1%, 5%, and 10% of the CD, denoted as CD₁, CD₅, and CD₁₀, respectively.

The sample packaging in the columns was homogenized to 245 g with a bulk density of 1.154 g/cm³ to a thickness of 10 cm for each column. The bulk density is designed to allow the water poured from the top part to percolate into the column. Irrigation (100 mL) was done every week using deionized water (18 MΩ cm) (Milli-Q® Integral water purification system, Merck Millipore, USA), which was introduced through the rainfall simulators and gravitationally percolated in the packed samples. At the bottom of each column, a filter paper was placed on top of the polytetrafluoroethylene net (PTFE) on a PVC plate with holes to prevent the leaking of the solid particles. Polypropylene bottles were used to collect the effluent at the lower end of each column, followed by pH, electrical conductivity (EC), and oxidation-reduction potential (ORP) measurements. Before chemical analysis, the effluents were filtered through 0.45-μm Millex® filters and stored in air-tight polypropylene bottles.

After the termination of the experiments, all columns were disassembled. The solid residuals were then air-dried and separately kept in polypropylene bottles before the sequential extraction experiments. Finally, sequential extraction experiments were performed to compare the variability of solid-phase (Pb and Zn) speciation for each column. The extraction procedure was the same as illustrated in section 2.1.

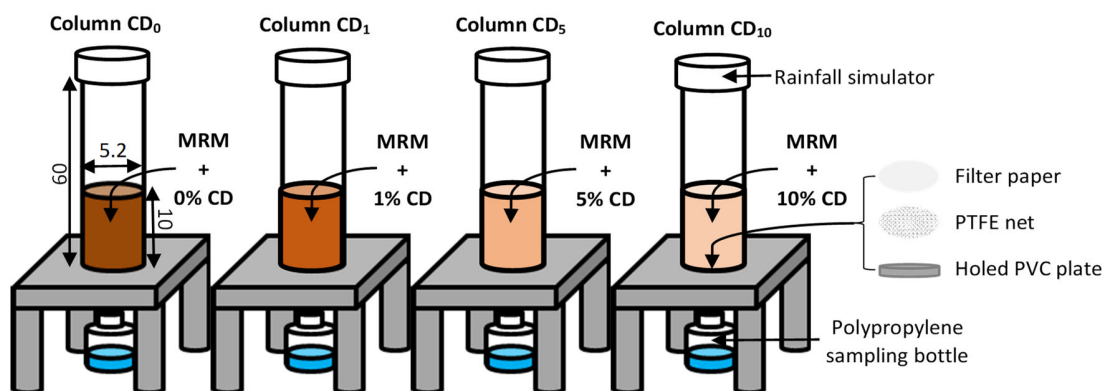


Figure 1 Schematic diagrams of the columns (all units are in cm)

2.3 Chemical analysis of liquid samples

Concentrations of Pb, Zn, Ca, Mg, (Na, K, Fe, Si, and SO_4^{2-} are in Table S2) were quantified by an inductively coupled plasma atomic emission spectrometer (ICP-AES) (ICPE-9000, Shimadzu Corporation, Kyoto, Japan). Determination limits were calculated three times for each analytical session of the blank solutions (Millipore Milli-Rx 12 α system, Merck Millipore, USA) with certified reference materials traceable to NIST SRM[®] (Merck KGaA, Darmstadt, Germany) (Table S1). Calibrations were conducted on concentrations ranging from 0.1 to 20 mg/L to obtain the mean and relative standard deviation for each element (margin of error = $\pm$ 2~3%, determination limit 0.01-0.001 mg/L). Prior to chemical analyses, pretreated samples were prepared by adding 1% by volume of 60% reagent-grade nitric acid (HNO_3) to the filtrated samples. The pretreatment was performed to ensure the complete dissolution of the target elements. The non-acidified samples were used for alkalinity determination, in which a known sample volume was titrated with 0.01 M reagent-grade sulfuric acid (H_2SO_4) until pH 4.8. All chemicals used were reagent grade (Wako Pure Chemical Industries Ltd., Osaka, Japan).

2.4 Geochemical Modeling

The aqueous geochemical conditions of the effluents were determined using PHREEQC (Version 3, U.S. Geological Survey, Sunrise Valley Drive Reston, VA, USA). The input data included temperature, pH, pe calculated from ORP and temperature, alkalinity as HCO_3^- , and concentrations of Pb, Zn, Ca, Mg, Na, K, Fe, Si, and SO_4^{2-} . Thermodynamic properties of all calculations were taken from the MINTEQ database. The thermodynamic properties of additional carbonate minerals, hydrocerussite ($\text{Pb}_3(\text{CO}_3)_2(\text{OH})_2$) (Mendoza-Flores et al., 2017) and hydrozincite ($\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$) (Mercy et al., 1998) were manually input into the database. Both

minerals have been reported to be one of the common minerals found in the high carbonate system (Parkhurst and Appelo, 1999).

3. Results and discussion

3.1 Properties of the MRM and CD

The chemical and mineralogical compositions for the MRM and immobilizer (CD) are illustrated in Tables 2 and 3, respectively. The MRM has slightly different contents from those reported in the author's previous study (Tangviroon et al., 2020). The MRM used in the current study was taken at another time, and the samples were randomly collected in the vast waste disposal area. The content of Fe_2O_3 (41.1%) was the highest among all chemical components detected. The Pb (7.1%) and Zn (2.3%) contents were lower than what was previously recorded (10.9% for Pb and 8.1% for Zn). Mineralogy of the MRM comprises anglesite (PbSO_4), zincosite (ZnSO_4), quartz (SiO_2), and minor amounts of goethite (FeOOH), hematite (Fe_2O_3), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Although sulfide minerals were not detected in the MRM, the non-sulfide mineral, anglesite, may be attributed to the weathering and alteration of galena (Fazli et al., 2018; Lara et al., 2011). The chemical and mineralogical compositions of the CD include CaO (62.4%) and MgO (33.3%) in the forms of dolomite ($\text{CaMg}(\text{CO}_3)_2$), calcite (CaCO_3), and magnesia (MgO). Many studies have reported that the three chemical components can immobilize heavy metals, including Pb and Zn (Trakal et al., 2011; Vrînceanu et al., 2019).

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Table 2 Chemical composition of solid samples (the unit is in wt%)

	MRM	CD
SiO ₂	21.4	0.37
TiO ₂	0.3	<0.01
Al ₂ O ₃	1.91	0.11
Fe ₂ O ₃	41.1	0.68
MnO	1.4	0.43
MgO	<0.01	33.3
CaO	6.7	62.4
Na ₂ O	<0.01	<0.01
K ₂ O	<0.01	0.16
P ₂ O ₅	<0.01	<0.01
SO ₃	16.2	0.2
Pb	7.1	<0.01
Zn	2.3	<0.01
TOC	<0.01	<0.01

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Table 3 Mineralogical composition of solid samples

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	MRM	CD
Quartz	++	-
Gypsum	+	-
Anglesite	+++	-
Zincosite	++	-
Hematite	+	-
Goethite	+	-
Dolomite	-	+++
Calcite	-	+
Magnesia	-	+

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+++ : strong、 ++ : moderate、 + : weak、 - : none

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3.2 Effect of CD on leachate pH and major coexisting ions

The changes in the effluent pH, Mg^{2+} , SO_4^{2-} , and Ca^{2+} in the columns CD_0 , CD_1 , CD_5 , and CD_{10} is illustrated in Figure 2. The pH (Figure 2a) gradually increased with the addition of the CD (0 to 10%). Initially, the pH was low for MRM (CD_0), then slightly increased after adding 1% (CD_1), stabilizing at around 7.25. The pH values in the columns with 5% (CD_5) and 10% (CD_{10}) fluctuated within a narrow range of about 7.75 and 8, respectively. The results manifest the improvement of alkaline effluent properties due to the CD liming effect. The alkalinity (Figure S2) was high (CD_5 and CD_{10}) in the first and second weeks of the experiment. After the 5th to 10th week, the alkalinity of CD_5 and CD_{10} moderately decreased. The addition of the CD to the MRM controls the pH by the equilibrium dissolution of dolomite (Equation 1), calcite (Equation 2), and magnesite (Equation 3) (Liu and Dreybrodt, 1997; Pokrovsky and Schott, 2001; Xing et al., 2018). The lower pH in CD_0 and CD_1 could mainly be attributed to not enough carbonate mineral dissolution to consume hydrogen ions (H^+) generated by the oxidation of sulfide minerals. Generally, under atmospheric conditions with pH ranging from slightly acidic to moderately alkaline, ferrous (Fe^{2+}) produced from sulfide minerals is oxidized to ferric (Fe^{3+}) and Fe^{3+} precipitates as Fe oxyhydroxide/oxide, which produces H^+ as a by-product (Chandra and Gerson. 2010; Lindsay et al., 2015). The inclusion of the CD yields divalent cations and generates carbonate species.



Figures 2b, c, and d indicate the leaching behavior of Mg^{2+} , SO_4^{2-} , and Ca^{2+} , respectively. The leaching concentrations of Mg^{2+} and SO_4^{2-} were high at first and dramatically decreased before

becoming steady. The behavior of these ions was observed in two distinct regions. The first one is characterized by high leaching and sharp reduction of Mg^{2+} and SO_4^{2-} concentrations, which lasted for 11 weeks. The trend reflects rapid releases of SO_4^{2-} and Mg^{2+} , indicating dissolutions of soluble secondary minerals, such as Fe and Mg sulfates (typical ubiquitous assemblages in acid mine drainage (AMD) affected systems) (Nordstrom and Alpers, 1999; Valente et al., 2016). The second one was a consistent trend from week 12 until the end of the experiments. Meanwhile, the leaching concentration of Ca^{2+} was disorderly, and no distinct trend could be observed in all the columns. The trend could be attributed to the inhibition of dolomite and calcite dissolution or the solubility of Ca-contained mineral(s).

Thermodynamic modeling (PHREEQC code) indicated that the *SIs* of all effluents were under equilibrium conditions to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) but were undersaturated with respect to $\text{Mg}(\text{OH})_2$ (Figure 3a-d). The solubility of gypsum restricted the leaching of Ca^{2+} , and thus, calcite and dolomite played an essential role in controlling effluent pH. Although the *SIs* of dolomite and calcite were less than the lower boundary of the standard error interval used to indicate saturation equilibrium (-0.2) in CD_1 , the dissolution of dolomite and calcite helped to increase leachate's pH in addition to the dissolution of magnesite. While the *SIs* of dolomite and calcite were higher than -0.2 throughout the experimental period in cases CD_5 and CD_{10} , only calcite behaved in the same way. Saturation indices of dolomite in CD_5 was over -0.2 at the beginning of the experiment and then fell into an unsaturated zone just after the end of the flushing-out period (week 13th). The *SIs* variations of both minerals in CD_5 and CD_{10} revealed that Ca^{2+} concentration was controlled by the solubility of gypsum and those of calcite and dolomite. Moreover, over-saturated and saturated conditions of calcite and dolomite imply that those minerals did not increase leachate pH. In other

words, when there was high enough MgO in the column (CD₅ and CD₁₀), MgO was hydrolyzed to Mg(OH)₂ and took control of rising pH of the effluents.

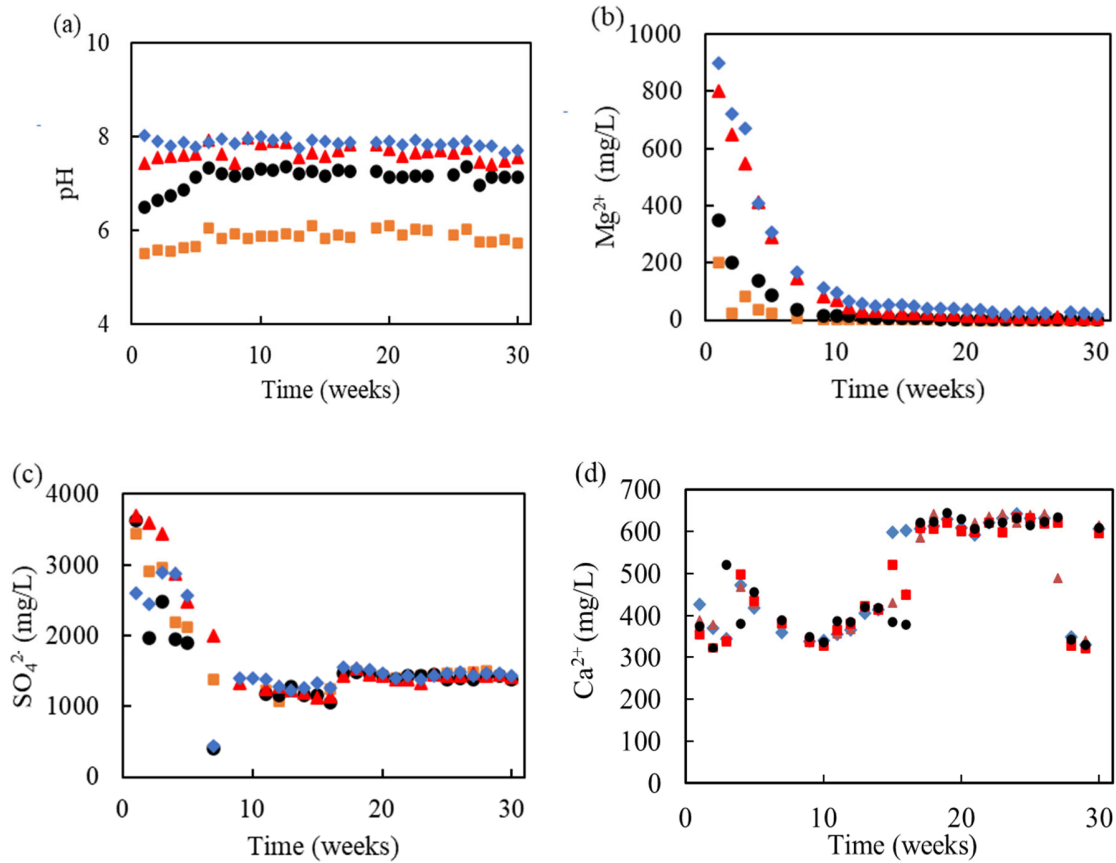


Figure 2 Changes in pH, Mg²⁺, SO₄²⁻, and Ca²⁺ concentrations with time: pH vs time (a), Mg²⁺ concentration vs time (b), SO₄²⁻ concentration vs time (c), and Ca²⁺ concentration vs time (d) (case CD₀ (■), case CD₁ (●), case CD₅ (▲), and case CD₁₀ (◆))

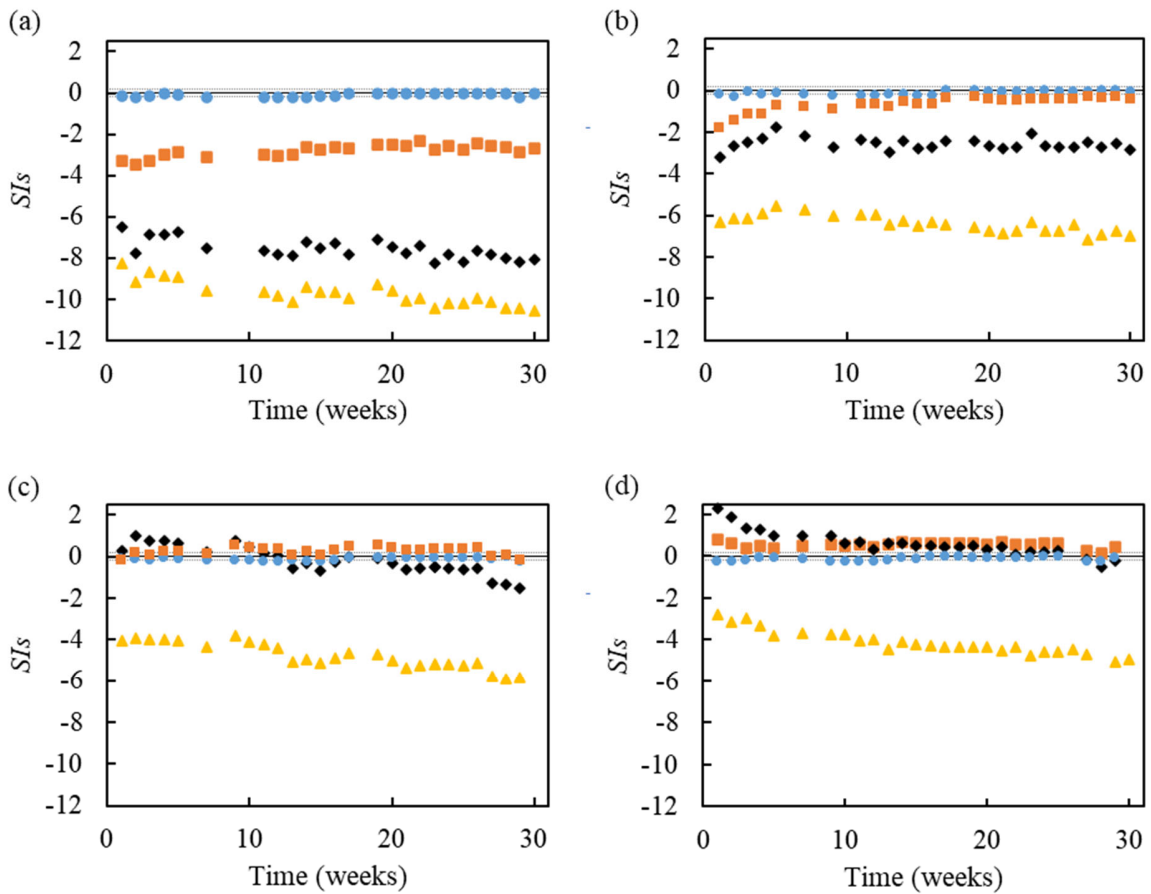


Figure 3 Saturation indices of calcite (■), dolomite (◆), $Mg(OH)_2$ (▲), and gypsum (●) in the effluents of cases CD₀ (a), CD₁ (b), CD₅ (c), and CD₁₀ (d)

3.3 Effects of CD on Pb and Zn release

The concentration of Pb and Zn in CD₀ exceeded Zambia's effluent and wastewater values for Pb (0.5 mg/L) and Zn (1 mg/L) (The Zambia Environmental Management Act, 2013) (Figure 4). The leaching concentration of Pb (Figure 4a) in CD₀ exhibited hill-shaped patterns during the first 11 weeks of the study before becoming relatively stable until the 30th week. The addition of the CD was more apparent to immobilize Pb since only CD₁ could reduce the leaching concentration after the first week. However, CD₅ was enough to suppress the leaching concentration of Pb lower than its regulatory limit (0.5 mg/L) at the beginning of the experiments. The leachability of Zn

(Figure 4b) in CD₀, CD₁ and CD₅ followed similar trends. It was initially high but rapidly decreased over time and stabilized after the 10th week in columns of CD₀, CD₁, and CD₅, respectively. After the 10th week, CD₅ was enough to bring the leaching concentration of Zn down below its regulatory value. The addition of CD₁₀ reduced Zn concentration in the effluent below the regulated value from the beginning toward the end of the experiment, and it only took three weeks to suppress the leaching concentration of Zn below the detection limit ICP-AES (0.01 mg/L). This indicates that the CD effectively decreased the Pb and Zn concentrations from the MRM in the experimental period.

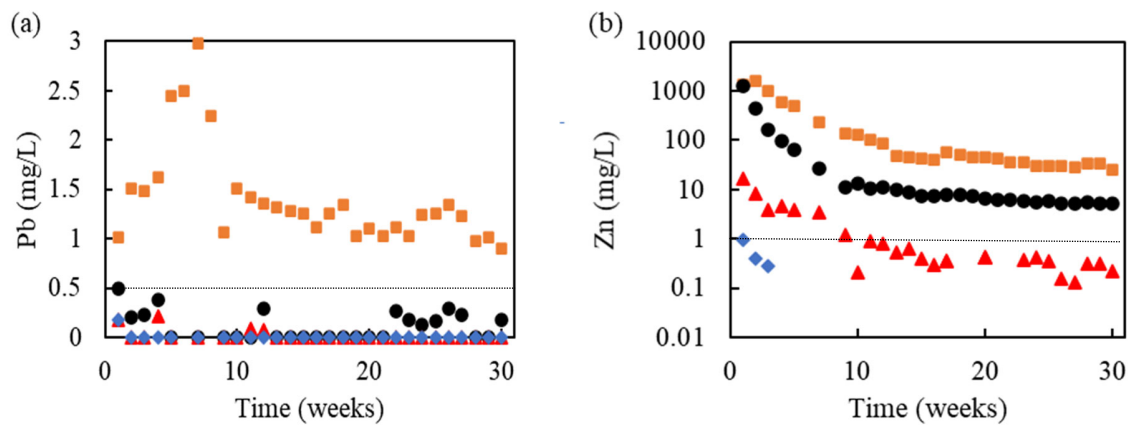


Figure 4 Changes in heavy metal concentrations: Pb (a) and Zn (b) (CD₀ (■), CD₁ (●), CD₅ (▲), and CD₁₀ (◆)) (dash lines represent the effluent standard in Zambia)

3.3 Solid-phase partitioning and the liming effect of CD

The contents Pb and Zn after sequential extraction of fresh MRM and the residues (CD₀, CD₁, CD₅, and CD₁₀) of each column are shown in Figure 5. When the average precision of 7% is considered, the oxidizable and residual phase contents remained unchanged. The identical residual contents emphasize that they were significantly stable and did not leach and deposit. However, Pb and Zn are expected to be released from the oxidizable minerals (e.g., oxidation of pyrite,

sphalerite, and galena). The assumption is due to the following reasons: sulfide minerals were expected to be available even though they could not be detected by XRD (discussed in section 3.1), the experiments were done under atmospheric conditions in which oxygen in the atmosphere was freely dissolved and reacted with sulfide minerals. Based on the mass balance calculations, Pb and Zn were leached at the maximum amounts of ca. 0.02% and 3.5%, which are less than the average precision of the currently employed sequential extraction technique (7%). According to the last reason, we should not have observed Pb and Zn content changes within the same fraction among all samples. However, noticeable differences in Pb and Zn contents were detected within the exchangeable, carbonate, and reducible fractions. The changes in Pb and Zn fractionations among the three fractions played an essential role in controlling their mobility, allowing us to identify the immobilization mechanisms by the CD.

The exchangeable contents of both metals were generally lower in the columns (CD₁, CD₅, and CD₁₀) than those in fresh MRM, indicating that this fraction is an essential source of Pb and Zn. The exchangeable Pb decreased following the trend MRM > CD₀ > CD₁ > CD₅ > CD₁₀. The reduction of exchangeable Pb content with the amount of the CD addition most likely occurred due to the formation of carbonates, meaning that the released Pb precipitates as carbonates (Cappuyns et al., 2014). This interpretation is supported by a significant negative correlation between the exchangeable Pb content and the average pH value of the leachate from each column ($r = 0.97$ at the 0.05 significance level (2-tailed)) (Figure 6). The exchangeable Zn content was reduced to almost zero in cases CD₀ and CD₁ and zero in the other columns (CD₅ and CD₁₀). With increasing MRM pH, specific sorption of Zn to metal oxides and carbonates becomes more relevant; consequently, formation of Zn precipitates such as zincite (ZnO), Zn hydroxide

(Zn(OH)₂), and Zn carbonates in alkaline condition decrease Zn solubility and causes Zn deficiency (Wisawapipat et al., 2017).

The carbonate contents of both metals in CD₀ were lower than those in the fresh MRM. This indicates that, without treatment, Pb and Zn also leached from the carbonate fraction due to the acid dissolution of carbonate minerals supported by the leachate's slightly acidic pH in CD₀ (Helser and Cappuyns, 2021). On the contrary, in the columns with CD addition, the carbonate contents of Pb and Zn were higher than those of the fresh MRM and increased with the amount of CD addition. The results reveal that the addition of the CD immobilized Pb and Zn as carbonate fractions due to the CD's abundance of calcite, dolomite, and magnesite. These minerals are known to have the ability to sequester Pb²⁺ and Zn²⁺ via adsorption and surface precipitation reactions (Gruszecka-Kosowska et al., 2017; Trakal et al., 2011); moreover, the precipitations of calcite and dolomite proved to be thermodynamically favorable (Figures 3c and d), co-precipitation of Pb and Zn with calcite and dolomite was also expected in CD₅ and CD₁₀ (Ahmad et al., 2012, Godelitsas et al., 2007).

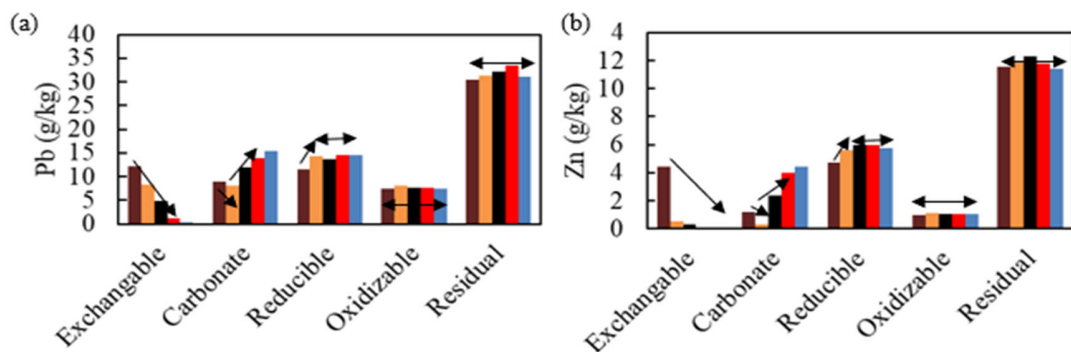


Figure 5 Changes in Pb (a) and Zn (b) contents of fresh MRM (brown) and the residuals of CD₀ (orange), case CD₁ (black), case CD₅ (red), and case CD₁₀ (blue)

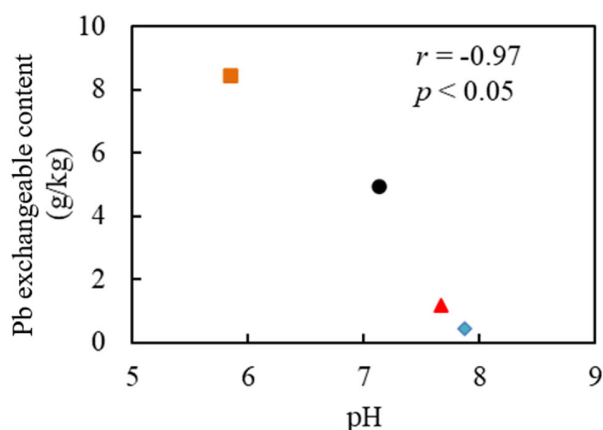


Figure 6 Exchangeable content of Pb in the residuals of columns CD₀ (■), CD₁ (●), CD₅ (▲), and CD₁₀ (◆)

The reducible contents of Pb and Zn were higher in all the residuals than those from the fresh MRM. Interestingly, regardless of the amount of the CD addition, the contents of both metals remained unchanged, indicating precipitations of Pb and Zn in the reducible fraction; however, the CD cannot play a role in such an event. Theoretically, as pH increases, freer divalent Pb (Pb (II)) and Zn (Zn (II)) should be precipitated as hydroxides and/or be adsorbed or co-precipitated with iron-(oxy)hydroxides. There are two possible explanations for this phenomenon: 1) competition between the solubility of the hydroxides and the other immobilization mechanisms of Pb and Zn and 2) change in aqueous speciation of Pb (II) and Zn (II). As mentioned earlier, the pH alteration by the CD led to more immobilization of Pb and Zn as carbonate forms. Likewise, Pb (II) and Zn (II) in the leachate decreased, hindering their hydroxide precipitation potential. The decrease of Pb (II) and Zn (II) fractions could also occur via the formation of carbonate and hydroxide complexes of Pb and Zn. Figures 7a-d illustrates the thermodynamic calculations on the *SIs* of Pb- and Zn- carbonate minerals; cerussite, smithsonite, hydrocerussite, and hydrozincite. Note that the *SIs* of the minerals of concern could not be obtained in the leachates having lower concentration(s) of Pb, Zn, or both than the detection limit of ICP-AES. In CD₀, those carbonate minerals were unable to

precipitate ($SI_s \ll -0.2$) even though Pb and Zn leached at the highest concentrations. Conversely, in CD₁, except for Pb-carbonates at the first four weeks of the experiment, at least one of the Pb- and Zn-carbonate minerals were saturated or supersaturated ($SI_s > -0.2$) in most effluents over the experimental period. The low SI_s values of the Pb-carbonates at the beginning of the experiment were probably due to the lower effluent pH. In cases CD₅ and CD₁₀, whenever the leaching concentration of Pb was over the detection limit of ICP-AES, the SI_s of Pb-carbonates were greater than -0.2. For Zn, the SI_s of only hydrozincite was thermodynamically favorable to precipitate first and then reduced to the unsaturated zone afterward. It should be noted that the unsaturated condition of hydrozincite was observed only when Zn concentration was very low (below the regulatory value of Zn). The undersaturation of hydrocerussite with respect to cerussite in the CD₀ entails that several factors affect the adsorption/precipitation of dissolved Pb in solution, e.g., $PbCO_{3(aq)}$ (Cidu et al., 2009), $PbHCO_3^+$ and $PbSO_{4(aq)}$. The speciation's in solution do not only hinder Pb- and Zn-hydroxide/carbonate precipitation potential but also inhibit the abilities of Pb and Zn to get absorbed and co-precipitated onto/with iron-(oxy) hydroxides since they tend to have a larger size with a lower charge compared to those of Pb (II) and Zn (II) (Badawy et al., 2002; Namie'snik and Rabajczyk, 2010; Powell et al., 2009). However, the equilibrium condition of cerussite might control the Pb content because it was relatively unchanged. In addition, the Zn content could also be governed by the equilibrium conditions of smithsonite and hydrozincite.

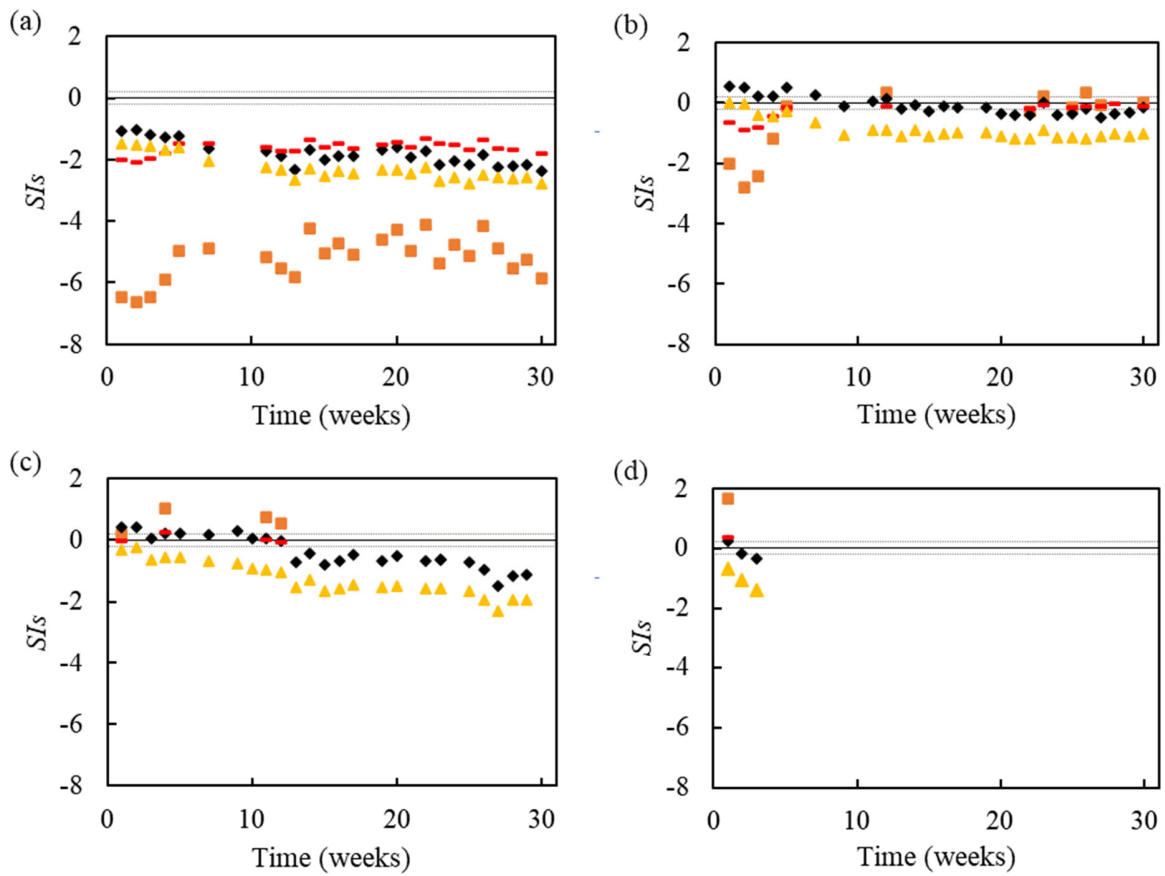


Figure 7 Saturation indices of cerussite (■), smithsonite (▲), hydrocerussite (■), and hydrozincite (◆) in the effluents of cases CD₀ (a), CD₁ (b), CD₅ (c), and CD₁₀ (d)

4. Conclusion

This paper discussed the performance of the CD in immobilizing Pb and Zn leached from MRM using laboratory column experiments. The significant findings of the present study are summarized as follows:

1. The release of Pb and Zn from the MRM exceeded the Zambian effluent standard throughout the experimental period. Addition of the CD to the MRM increased effluent pH and lowered Pb and Zn migration. Five percent addition (CD₅) was adequate to bring both

Pb and Zn's leaching concentrations below the effluent standard and had a lasting effect on the system throughout the 30 weeks.

2. Sequential extractions of pre- and post-experimental MRM revealed that Pb and Zn were mainly leached from exchangeable and carbonate phases, but portions of them were redeposited in reducible fractions.
3. The CD could not reduce the release of exchangeable Pb and Zn. However, exchangeable Pb and Zn were transformed to carbonate and reducible ones. The carbonate contents of both Pb and Zn were higher than those of the pre-experimental MRM and increased with the amount of CD added, suggesting that the addition of CD headed the attenuation of Pb and Zn as carbonate forms.
4. Immobilization of Pb and Zn by the CD addition might occur via adsorption and precipitation mechanisms; the Pb and Zn mobilities could be controlled by the equilibrium conditions of cerussite, smithsonite, and hydrozincite under the ambient conditions; however, considering long-term assessment, the change in solution speciation due to variations in environmental conditions might affect the mobility of the Pb and Zn.

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CRedit authorship contribution statement

Pawit Tangviroon, Walubita Mufalo; Conceptualization; Formal analysis; Investigation; Methodology; Writing - original draft; Writing - review & editing. **Takahiko Arima**; Formal analysis; Writing - review & editing. **Toshifumi Igarashi**; Conceptualization, Supervision; Methodology; Validations; Writing-review & editing. **Mayumi Ito, Tsutomu Sato, Imasiku Nyambe**; Resources; Writing-review & editing. **Kenta Noto, Takeshi Kawashima**; Sample collection; Writing-review & editing. **Hokuto Nakata, Shouta Nakayama, Mayumi Ishizuka**; Project administration; Funding acquisition; Writing-review & editing.

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