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Comparison of Reactive Magnesia, Quick Lime, and Ordinary Portland Cement for Stabilization/Solidification of Heavy Metal-Contaminated Soils

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Abstract: This study systematically compares the solidification/stabilization of soils contaminated by six individual heavy metals (Pb, Cu, Zn, Ni, Cd, and Mn) using reactive magnesia (MgO), quick lime (CaO), and ordinary Portland cement (OPC). Laboratory tests were conducted to examine the mineralogical, thermal, leaching, and strength performance of treated soils. The results indicate that the addition of binders can transform soluble heavy metal salts to insoluble hydroxides and their complexes, and hence the leachability of heavy metals decreases after the treatment. However, the level, to which the leachability can be reduced, is significantly dependent on the pH of the treated soils. Contaminated soils treated with MgO have pH values of 9–10.5, at which the leachability of Pb, Cu, and Zn is lower than that of OPC- and CaO-treated soils with pH values of 10.5–13. Nevertheless, the leachability of Cd and Mn in treated soils with OPC is lower compared to MgO and CaO due to the CSH formation and the high pH value. OPC and CaO are more effective than MgO in decreasing the Ni leachability for soils contaminated with a high concentration of Ni, but less effective for soils with a low concentration of Ni. For most contaminated soils, the OPC treatment provides a higher strength in comparison with the CaO and MgO treatment, and MgO generally provides a similar strength level compared with CaO.

Keywords: Stabilization/solidification; Soil; Heavy metal; Binder; Leachability

- Comparison of MgO, CaO, and cement for treating heavy metal-contaminated soils
- pH of treated heavy metal-contaminated soils: $\text{MgO} < \text{cement} < \text{CaO}$
- Leachability of treated Pb- and Zn-contaminated soils: $\text{MgO} < \text{cement} < \text{CaO}$
- Leachability of treated Cd- and Mn-contaminated soils: $\text{cement} < \text{CaO} < \text{MgO}$
- Strength of treated Pb-, Cu- Cd-, and Mn-contaminated soils: $\text{MgO}, \text{CaO} < \text{cement}$

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1. Introduction

Soils contaminated by heavy metals becomes one of the serious environmental issues all over the world due to the emissions from industry and the use of gasoline, paints, fertilizers, pesticides, and so on (Cao et al., 2009; Khan et al., 2008; Zhang et al., 2010). Lead (Pb), copper (Cu), zinc (Zn), cadmium (Cd), manganese (Mn), and nickel (Ni) are frequently identified in contaminated soils among heavy metals (USEPA, 1996; Wuana and Okieimen, 2011). These heavy metals are very poisonous and pose significant threats to the human and the environment (Du et al., 2013; Wuana and Okieimen, 2011).

Stabilization/solidification (S/S) is commonly applied to treat heavy metal-contaminated soils (Harbottle et al., 2007; Wuana and Okieimen, 2011). This method involves the use of binders to immobilize heavy metal elements contained in contaminated soils and stabilize the chemical constituents of soils through a combination of absorption, chemical reactions, and encapsulation. The most commonly used binders to implement the S/S process are lime (CaO or $\text{Ca}(\text{OH})_2$) and ordinary Portland cement (OPC) (Brown et al., 2005; Castaldi et al., 2005; Chen et al., 2000; Geebelen et al., 2003; Guo et al., 2006; Kogbara et al., 2011; 2012; 2013; Kumpiene et al., 2008; Rodríguez et al., 2012; Roy et al., 1991; Wang et al., 2018). These binders can react with heavy metal salts, and hence form precipitation (i.e. insoluble complex compounds or hydroxides) due to their alkaline nature (Spence and Shi, 2004). Furthermore, the reaction products, e.g. calcium silicate hydrate (CSH) and calcium aluminate hydrate (CAH) formed due to hydration reactions, can also encapsulate and absorb heavy metals (Bishop, 1988). However, the production of lime and OPC is associated with high energy consumptions and high carbon dioxide (CO_2) emissions (EuLA, 2014; WBCSD, 2002). Additionally, the high alkaline conditions ($\text{pH} > 11$) that OPC and CaO produce, enable the formation of soluble hydroxide complexes for some heavy metals, e.g. Pb, Zn, and Cu,

negatively affecting the immobilization of these heavy metals (Garcia et al., 2004; Hartley et al., 2004; Heasman et al., 1997; Kumpiene et al., 2008; Teringo III, 1987).

Reactive magnesia (MgO) has attracted attentions due to the relatively low production temperature, the capability of consuming CO₂ (Al-Tabbaa, 2013; Liska and Al-Tabbaa, 2008; 2009; Liska et al., 2008; Unluer and Al-Tabbaa, 2013; Vandeperre and Al-Tabbaa, 2007; Yi et al., 2013a; 2015) and a pH around 10, around which the solubility of hydroxides for some heavy metals (e.g. Pb, Cu, and Zn) are minimal (Chimenos et al., 2000; Garcia et al., 2004; Jin and Al-Tabbaa, 2014; Shen et al., 2018; Suzuki et al., 2013; Wang et al., 2015). However, most of previous studies used a combination of MgO, OPC, and other industrial by-products (fly ash or slag) to treat contaminated soils (Hwang et al., 2014; 2015; Iyengar, 2008; Jin and Al-Tabbaa, 2014; Phan et al., 2017; Wang et al., 2015). It is difficult to separate the S/S efficacy of MgO from other combined materials on the immobilization of heavy metals. This is because apart from MgO, other combined materials yield the formation of calcium silicate hydrate (CSH)-like compounds (Jin et al., 2016; Shi et al., 2006; Wang et al., 2015; Yi et al., 2016), which also contribute to the immobilization of heavy metals.

Limited investigations (Garcia et al., 2004; Jin et al., 2016; Shen et al., 2018) were done to assess the effect of MgO alone on the immobilization of heavy metals contained in soils, which show that MgO is an effective immobilization binder for heavy metals. However, in these studies, the soils were contaminated by a mixture of multiple heavy metals, so the effectiveness of MgO on the immobilization of individual heavy metal was not clear. Therefore, this study investigates the S/S of soils contaminated by six individual heavy metal (Pb, Cu, Zn, Ni, Cd, and Mn) using MgO alone. This study is to understand the influence of reactive MgO on the leaching and strength properties of these contaminated soils compared with the use of CaO and OPC, as well as to explain the associated S/S mechanisms.

74

75 2. Materials and methods

76 2.1 Materials

77 In this study, the soil consists of 90% fine sand and 10% kaolin by mass. The particle size
 78 distribution of the soil is given in Fig. 1. The sand was obtained from Buildmate Pte Ltd,
 79 Singapore, and the kaolin was obtained from International Scientific (Pte) Ltd, Singapore.
 80 The chemical composition of kaolin is obtained from X-ray fluorescence (XRF) testing as
 81 provided in Table 1. The water content of the soil, defined as the ratio between water and dry
 82 soil by mass, was selected as 7.5% following the study of Yi et al. (2013b) to facilitate the
 83 soil compaction. Three binders (MgO, CaO, and OPC) were used in this study to treat Pb-,
 84 Cu-, Zn-, Ni-, Cd-, and Mn-contaminated soils. The MgO was purchased from Meishen
 85 Chemical Co. Ltd, Xingtai, China and its reactivity of 46 seconds was obtained using a
 86 method proposed by Shand (2006). The CaO, powder and puriss grade, was obtained from
 87 Sigma-Aldrich Pte Ltd, Singapore. The OPC, CEM I 52.5 R, was purchased from Buildmate
 88 Pte Ltd, Singapore. Table 1 also lists the chemical compositions of all binders.

89

90 **Fig. 1.** Soil particle size distribution.

Table 1

Chemical composition of materials (% by mass).

Composition	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O	SO ₃	Others	Loss on ignition
Kaolin	0.06	64.70	30.17	ND	0.80	3.57	0.05	0.65	0
MgO	0.50	ND	ND	0.03	89.50	ND	0.60	1.72	7.65
CaO	96.00	ND	ND	ND	0.25	ND	0.25	0	3.50
OPC	61.26	21.33	6.83	2.31	2.93	0.44	3.15	1.75	0

ND: not detected.

Each heavy metal-contaminated soil was made of the soil and one type of heavy metal salt solution, including lead nitrate ($\text{Pb}(\text{NO}_3)_2$), copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), zinc chloride (ZnCl_2), nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), cadmium chloride hydrate ($\text{CdCl}_2 \cdot \text{H}_2\text{O}$), and manganese sulphate hydrate ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$). These chemicals, supplied by Fisher Scientific, Singapore, were used to prepare contaminated soils with different heavy metal concentrations (1,000 to 16,000 mg/kg by the mass of the soil for Pb, Cu, Cd, and Mn, 1,500 to 24,000 mg/kg for Ni, and 2,000 to 32,000 mg/kg for Zn). These concentrations were determined to cover the maximum (Pb, Cu, Zn, Ni, Cd, or Mn) concentrations existed in natural and/or contaminated soils. The reported maximum concentrations for Pb, Cu, Zn, Ni, Cd, and Mn are 13,000, 3,700, 49,000, 26,000, 1,500, and 9,300 mg/kg, respectively (Kabata-Pendias, 2010). Subsequently, each concentration of heavy metal was dissolved in distilled water (7.5% of the soil by mass) to produce solutions, and then mixed with the dry soil and the binder.

2.2 Specimen preparation

In this study, a binder content of 5% (of dry soil by mass) was used. MgO, CaO, or OPC was firstly mixed with the dry sandy soil for 5 minutes using a laboratory mixer to achieve homogeneity, and then the heavy metal solution was added and mixed for another 10 minutes. After mixing, the contaminated soil was immediately transferred into a cylindrical mould (50

mm diameter and 100 mm height) and then compacted using a mini-compactor similar to that reported in Sridharan and Sivapullaiah (2005). Each specimen was compacted in three layers with five compaction blows per layer to achieve a uniform compaction; the compaction energy per unit volume was 582.51 kJ/m^3 , close to that required by the ASTM standard Proctor compaction test (ASTM, 2012). After the compaction, the moulded specimens were sealed with plastic bags and cured at the ambient temperature of 25°C for 28 days.

2.3 Experiments

The unconfined compressive strength (UCS) was performed in triplicate on the 28-day cured specimens. The crushed specimens after UCS tests were further crushed until all particles passed a 4 mm sieve. Subsequently, one stage batch leaching test was conducted using the crushed particles according to BSI (2002). In the leaching test, 90 g of dry particles and 900 ml distilled water were mixed in a 2-L polypropylene plastic bottle. The solid/water mixture was then rotated for 24 (± 0.5) hours at a speed of 7 rpm. This was followed by measuring the pH of the solid/water mixture. A 0.45 mm membrane syringe filter was employed to obtain the filtrate from the mixture, and the filtrate was analysed to determine the concentration of heavy metals using PerkinElmer Optima 8300 ICP-OES and PerkinElmer Elan DRC-e ICP-MS. The remaining crushed specimen was kept in ethanol to retard the hydration reactions between binders and water, and then dried using a freezing-vacuum drier. The dried specimen was further ground to produce powder samples with grain size less than 0.075 mm. These powder samples were then characterized using X-ray diffraction (XRD) and thermogravimetric analysis (TGA). XRD was carried out on the Bruker D8 X-ray diffractometer with a $\text{Cu K}\alpha$ source, running at 40 kV and 40 mA; and all data were collected at 2.4 degrees 2-theta per minute. The TGA test was conducted using the PerkinElmer TGA 4000 equipment from 30 to 900 degrees with a heating rate (nitrogen) of 10 degrees/min.

3. Results and discussions

3.1. XRD

Fig. 2 provides the XRD patterns of MgO-, CaO-, and OPC-treated soils with the highest concentration of heavy metals (i.e. 16,000 mg/kg for Pb, Cu, Cd, and Mn; 24,000 mg/kg for Ni and 32,000 mg/kg for Zn). Quartz, kaolinite, and mica are detected as the primary minerals of the original soil. Brucite ($\text{Mg}(\text{OH})_2$) produced from the MgO hydration and portlandite ($\text{Ca}(\text{OH})_2$) produced from the CaO hydration are identified in the MgO- and CaO-treated soils, respectively, regardless of the heavy metal type. This indicates that 5% MgO or CaO is enough to react with the highest concentration of each heavy metal. Similarly, CSH formed from the OPC hydration is detectable in all OPC-contaminated soils.

When MgO, CaO, and OPC are applied to the contaminated soils, the soluble heavy metal salts, i.e. $\text{Pb}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, ZnCl_2 , NiSO_4 , CdCl_2 , and MnSO_4 are absent in their respective contaminated soils. Instead, the hydroxides of heavy metals (i.e. lead hydroxide ($\text{Pb}(\text{OH})_2$), copper hydroxide ($\text{Cu}(\text{OH})_2$), zinc hydroxide ($\text{Zn}(\text{OH})_2$), nickel hydroxide ($\text{Ni}(\text{OH})_2$), cadmium hydroxide ($\text{Cd}(\text{OH})_2$), and manganese hydroxide ($\text{Mn}(\text{OH})_2$)) are generally present in MgO-, CaO- and OPC-treated contaminated soils, indicating that the addition of binders precipitates the heavy metals into hydroxides. It is notable that $\text{Pb}(\text{OH})_2$ is not identified in the XRD pattern of CaO-treated Pb-contaminated soil, suggesting that this mineral is insignificantly formed in the soil.

Various complexes of heavy metal hydroxides can be found in the XRD patterns of the treated contaminated soils. For instance, any treatment using MgO, CaO, or OPC facilitates the formation of copper hydroxyl nitrate ($\text{Cu}_2\text{NO}_3(\text{OH})_3$) for Cu-contaminated soils. Similarly, cadmium chloride hydroxide (CdOHCl) is produced from MgO-, CaO-, and OPC-treated Cd-contaminated soils, and manganese hydroxide sulfate ($7\text{Mn}(\text{OH})_2 \cdot 2\text{MnSO}_4 \cdot \text{H}_2\text{O}$) is found from three treated Mn-contaminated soils. As per Pb-contaminated soils,

hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) is clearly present after MgO and OPC treatment, but is not surely identified after the CaO treatment, as its XRD peak at 2 theta of 34° could overlap with that of $\text{Ca}(\text{OH})_2$. Similarly, zinc chloride hydroxide (ZnOHCl) can be detected for MgO- and OPC-treated Zn-contaminated soils, but is not detectable in the CaO-treated soil. Another complex called calcium zincate ($\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$) is observed in CaO-treated Zn-contaminated soils, which is expected to form from the reaction between $\text{Ca}(\text{OH})_2$ and $\text{Zn}(\text{OH})_2$. However, the presence of the complex of $\text{Ni}(\text{OH})_2$ (i.e. nickel sulfate hydroxide ($\text{Ni}(\text{SO}_4)_{0.3}(\text{OH})_{1.4}$)) in Ni-contaminated soils (Fig. 2(d)) cannot be reliably identified due to the overlap between the peaks of $\text{Ni}(\text{OH})_2$, magnesium sulfate (MgSO_4), and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

For Pb- and Cu-contaminated soils, as Pb and Cu nitrates are used to prepare contaminated soils, calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) and ($\text{Mg}(\text{NO}_3)_2$) are detectable after treated by OPC, CaO, and MgO, respectively. Calcium chloride (CaCl_2) and magnesium chloride (MgCl_2) are present in OPC-, CaO-, and MgO- treated ZnCl_2 - and CdCl_2 -contaminated soils, respectively. Similarly, due to the use of Ni and Mn sulfates in contaminated soils, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and MgSO_4 are formed after OPC, CaO, and MgO treatment. Additionally, ettringite is found in the OPC- and CaO-treated Ni- and Mn-contaminated soils.

B-Brucite ($\text{Mg}(\text{OH})_2$); C-Calcite (CaCO_3); CCl-Calcium chloride (CaCl_2); CdClH-Cadmium chloride hydroxide (CdOHCl); CdH-Cadmium hydroxide ($\text{Cd}(\text{OH})_2$); CN-Calcium nitrate ($\text{Ca}(\text{NO}_3)_2$); CuH-Copper hydroxide ($\text{Cu}(\text{OH})_2$); CuHN-Copper hydroxyl nitrate ($\text{Cu}_2\text{NO}_3(\text{OH})_3$); CSH-Calcium silicate hydrate; CZ-Calcium zincate ($\text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$); E-Ettringite; G-Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$); H-Hydrocerussite ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$); K-Kaolinite; LH-Lead hydroxide ($\text{Pb}(\text{OH})_2$); M-Mica; MCl-Magnesium chloride (MgCl_2); MN-Magnesium nitrate ($\text{Mg}(\text{NO}_3)_2$); MnH-Manganese hydroxide ($\text{Mn}(\text{OH})_2$); MnHS-Manganese hydroxide sulfate ($7\text{Mn}(\text{OH})_2 \cdot 2\text{MnSO}_4 \cdot \text{H}_2\text{O}$); MS-Magnesium sulfate (MgSO_4); NH-Nickel hydroxide ($\text{Ni}(\text{OH})_2$); NSH-Nickel sulfate hydroxide ($\text{Ni}(\text{SO}_4)_{0.3}(\text{OH})_{1.4}$); P-Portlandite ($\text{Ca}(\text{OH})_2$); Q-Quartz; ZH-Zinc hydroxide ($\text{Zn}(\text{OH})_2$); ZClH-Zinc chloride hydroxide (ZnOHCl).

Fig. 2. XRD patterns for six contaminated soils treated by MgO, CaO, and OPC.

3.2. TGA

Fig. 3 presents the TGA curves for six contaminated soils treated by MgO, CaO, and OPC also at the highest concentrations of heavy metals. For all contaminated soils, Mg(OH)_2 at $\sim 350^\circ\text{C}$ and Ca(OH)_2 within the temperature range of $400\text{--}500^\circ\text{C}$ can be identified in MgO- and CaO-treated soils, respectively, which is consistent with the XRD results. The presence of CSH at $600\text{--}650^\circ\text{C}$ is confirmed in OPC-treated Zn-, Ni-, and Mn-contaminated soils as the weight loss in this temperature range is thought to be induced by the CSH dehydroxylation (Gabrovšek et al., 2006). However, for OPC-treated Pb-, Cu-, and Cd-contaminated soils, the weight loss of CSH at $600\text{--}650^\circ\text{C}$ overlaps with those of $\text{Ca(NO}_3)_2$ for Pb- and Cu-contaminated soils (Chen and Zhao, 2017) and cadmium oxide (CdO) for Cd-contaminated soil (Fahim and Kolta, 1970).

Through differential analysis, Pb, Cu, Zn, and Mn hydroxides cannot be clearly distinguished at the temperature lower than 200°C in the derivative thermogravimetry (DTG) curves for MgO, CaO and OPC treatments as the weight loss within this temperature range could be induced from the decomposition of CSH (for OPC treatment) and the dehydration of other minerals. For Cd- and Ni-contaminated soils, when MgO is used, Cd and Ni hydroxides cannot be confirmed as the weight loss could overlap with that for Mg(OH)_2 , which occurs in the range of $300\text{--}400^\circ\text{C}$ (Kumari et al., 2009). However, the weight loss for Cd and Ni hydroxides can be identified for both CaO- and OPC-treated soils, in which both hydroxides decompose to oxides and water at $\sim 300^\circ\text{C}$ (Sato et al., 1975; Shanmugam et al., 2014).

Apart from the hydroxides, the complexes of Pb and Cu hydroxides can be identified in the DTG curves. For instance, the occurrence of $2\text{PbCO}_3\cdot\text{Pb(OH)}_2$ mainly contributes to the weight loss at 253°C (Ciomartan et al., 1996) for MgO-, CaO-, and OPC-treated Pb-contaminated soils, which is consistent with the XRD results. Regarding Cu-contaminated soils, with the MgO, CaO, or OPC treatment, the presence of $\text{Cu}_2\text{NO}_3(\text{OH})_3$ can be confirmed by the weight loss at a temperature of $\sim 240^\circ\text{C}$ (Kong et al., 2008; Schildermans et al., 1993).

207 However, the TGA method is unable to separate the complexes of Zn, Ni, Cd, and Mn
208 hydroxides from other minerals (below 200°C) as the decomposition of CSH and the
209 dehydration of other minerals may contribute to the weight loss within this temperature range.
210 Other products, such as CaCl_2 and MgCl_2 , can be identified at the temperature of 800-850°C
211 and ~400°C, respectively, for Zn- and Cd-contaminated soils after the treatment. For Ni- and
212 Mn-contaminated soils, MgSO_4 is formed through the MgO treatment and its weight loss on
213 the DTG curves can be found at ~900°C. Nevertheless, ettringite and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ may be
214 formed after the CaO and OPC treatment, but cannot be confidently confirmed by TGA as
215 their weight losses overlap with that for CSH at the temperature below 200°C. For Pb-
216 contaminated soils, $\text{Mg}(\text{NO}_3)_2$ is present and it decomposes at ~400°C when MgO is used;
217 whereas when CaO and OPC are used, $\text{Ca}(\text{NO}_3)_2$ cannot be surely identified since its
218 decomposition temperature (600-650°C) is similar to that of CSH. Likewise, $\text{Ca}(\text{NO}_3)_2$ cannot
219 be identified in CaO and OPC-treated Cu-contaminated soils, either. In addition, no weight
220 loss for $\text{Mg}(\text{NO}_3)_2$ is found at ~400°C for MgO-treated Cu-contaminated soil, so the presence
221 for $\text{Mg}(\text{NO}_3)_2$ cannot be confirmed.

Fig. 3. TGA and DTG curves for six contaminated soils treated by MgO, CaO, and OPC (abbreviations are the same as those in Fig. 2).

3.3. Leachability

Fig. 4 shows the leachate pH values of Pb-, Cu-, Zn-, Ni-, Cd-, and Mn-contaminated soils treated with MgO, CaO and OPC. Most contaminated soils treated with MgO have lower leachate pH values ranging from 9 to 10.5 than the corresponding values for OPC- and CaO-treated soils (10.5 to 12.5 for OPC and 12 to 13 for CaO). This is mainly attributed to the higher pH of hydration products of OPC and CaO (e.g. CSH and $\text{Ca}(\text{OH})_2$) than that of MgO

hydration products (e.g. $\text{Mg}(\text{OH})_2$). The only exception is the OPC-treated contaminated soil with the original Zn concentration of 32,000 mg/kg, which yields the lowest pH of 7.3. Regardless of the treatment methods, the leachate pH presents a decreasing trend with the increasing concentrations of heavy metals for contaminated soils. This is due to the acidic nature of heavy metal salts, which can help to neutralize the alkaline conditions induced by the addition of binders. Nevertheless, the pH at a Zn concentration of 32,000 mg/kg (Fig. 4(c)) drops sharply for OPC-treated soils. The likely reason is that the OH^- produced from the OPC hydration is insufficient to bind H^+ produced by the ZnCl_2 (Li and Yi, 2019).

Fig. 4. Leachate pH values of six contaminated soils treated by MgO, CaO, and OPC.

Fig. 5 shows the heavy-metal leachability for Pb-, Cu-, Zn-, Ni-, Cd-, and Mn-contaminated soils treated with MgO, CaO, and OPC, along with two limit states defined in the European standard (EN, 2003). It can be observed that the leached concentration of any heavy metal after the treatment is significantly lower than the corresponding original concentration. This illustrates that the addition of binders facilitates the decrease of leachability for heavy metals contained in contaminated soils, which is mainly attributed to the occurrence of their insoluble hydroxides and/or complexes as indicated in the XRD and TGA results.

For Pb-, Cu-, and Zn-contaminated soils (Fig. 5(a), (b) and (c)), when they are treated by MgO, the leached concentrations of Pb, Cu, and Zn are on the lowest level among the three binders. It is known that the leaching of metal hydroxides is dependent on the leachate pH, and the optimum pH for minimizing the leaching concentration of Pb, Cu, and Zn hydroxides is around 9.5 (Boardman, 1999; Wilk, 1997), which is close to the pH range of MgO-treated soils. With the OPC treatment, the leached Pb, Cu, and Zn concentrations increase, and the highest leachability of these heavy metals occurs when CaO is used. This illustrates that MgO is the most effective binder in reducing the leachability of Pb-, Cu-, and Zn-contaminated soils among the three binders. Moreover, with the MgO treatment, the Pb-contaminated soil has the leached Pb concentration that is significantly lower than the limit (10 mg/kg) for non-

hazardous waste specified by the European standard (EN, 2003) but exceeds the limit for inert waste (0.5 mg/kg). For Cu- and Zn-contaminated soils, the leached Cu and Zn concentrations can reduce to a level that is lower than the limit (2 and 4 mg/kg for Cu and Zn, respectively) for inert waste specified by the European standard (EN, 2003). Although OPC and CaO are not as effective as MgO in decreasing the leachability of Pb, Cu, and Zn, the leached Cu and Zn concentrations comply with the limit for non-hazardous waste except the one with original Zn concentration of 32,000 mg/kg treated by OPC. The exception is because that the addition of 5% OPC is insufficient to treat the 32,000 mg/kg Zn in the soil, resulting in a low pH of 7.3 (Fig. 5(c)), and hence the leached Zn concentration increases significantly (Li and Yi, 2019). Additionally, for Cu- and Zn-contaminated soils treated by OPC and CaO, the leached Cu and Zn concentrations generally stay stable with the increasing original concentrations of Cu and Zn. However, for OPC- and CaO-treated Pb-contaminated soils, the leached Pb concentration gradually increases with the increase of original Pb concentration. Furthermore, regardless of the amount of Pb originally in the soil, when OPC and CaO are used, the leached Pb concentrations always exceed the limit (10 mg/kg) for non-hazardous waste specified by the European standard (EN, 2003). This indicates that OPC and CaO are not suitable for treating Pb-contaminated soils in practice.

For Ni-contaminated soils (Fig. 5(d)), MgO, CaO, and OPC are all able to reduce the leached Ni to a level that is lower than the limit of 0.4 mg/kg for inert waste, except the MgO-treated soil containing an original Zn concentration of 24,000 mg/kg. This result reveals that the three binders are all very effective in decreasing the leachability of Ni. However, OPC and CaO are more effective than MgO when treating the soil contaminated with high concentration of Ni (i.e. more than 6,000 mg/kg). This is also related to the leachate pH. The pH for minimizing the leaching Ni concentration is approximately 10 (Boardman, 1999; Wilk, 1997), which is close to the pH (9.8–10.1) produced by MgO-treated soils with an original Ni

concentration of 1,500 to 6,000 mg/kg. However, at pH range below 10, i.e. the pH of the MgO-treated soils, the pH-leachability curve is much sharper than that at pH range above 10, i.e. produced by OPC and CaO. The Ni leachability of the MgO-treated soils increases much more significantly than that of OPC- and CaO-treated soils when pH changes significantly with increasing original Ni concentration. Consequently, at high original Ni concentration (12,000 and 24,000 mg/kg), the pH values of 9.6 and 9.37 are obtained for the soil treated by MgO, resulting in higher leached Ni concentrations than the soil treated by OPC and CaO.

For Cd- and Mn-contaminated soils (Fig. 5(e) and (f)), OPC has the best S/S efficacy among the three binders, which can decrease the leached Cd and Mn concentrations to the lowest level. The MgO-treated Cd- and Mn-contaminated soils produce the highest leachability of Cd and Mn. Particularly, the Cd leachability of MgO-treated soils is even more than the limit for non-hazardous waste (1 mg/kg) when a high original concentration of Cd (i.e. more than 4,000 mg/kg) is contained in the soils. However, CaO reduces the leached Cd concentration to be less than the limit for non-hazardous waste and OPC even reduces it to be below the limit of 0.04 mg/kg for inert waste. This is mainly because the optimum pH for minimizing the leaching concentration of Cd and Mn is in the pH range of 11–12 (Boardman, 1999; Wilk, 1997), which could be produced by CaO and OPC. It is noted that the limit values for Mn are not defined in the European standard (EN, 2003).

(c)

(d)

(e)

(f)

Fig. 5 Leached concentrations of heavy metals for six contaminated soils treated with MgO, CaO, and OPC.

The relationship between leachate pH and leached concentration of heavy metals for treated contaminated soils is plotted in Fig. 6. When binders are used to treat contaminated soils, it is well anticipated that the heavy metal ions will bind OH^- released from the binders to form precipitation of Pb, Cu, Zn, Ni, Cd, and Mn hydroxides. Consequently, the theoretical solubility curves (solid line) of hydroxides are plotted in Fig. 6, which are obtained from Wilk (1997) and Lewis (2010), representing the trend of solubility with pH for the hydroxides of heavy metals.

It can be observed that the leachability of heavy metals generally follows the solubility curves and is pH dependant. However, the leachability for each heavy metal is generally lower than the corresponding solubility, mainly attributed to three reasons. The first one is the amount of hydroxides formed in contaminated soils is insufficient to reach their solubilities for the required amount of water in the leaching test. The second one is that the released heavy metals are absorbed and encapsulated by kaolinite, CSH, and magnesium and calcium compounds. The third reason is from the insoluble complexation between heavy metals and minerals contained in contaminated soils, which may inhibit the leachability of heavy metals (Dou et al., 2017). However, a few treated contaminated soils present the leachability above the solubility curves (e.g., CaO- and MgO-treated Cu-contaminated soils in Fig. 6(b), MgO-treated Ni-contaminated soils in Fig. 6(d), and MgO-treated Cd-contaminated soils in Fig. 6(e)). For Cu-contaminated soils treated by CaO and MgO, the higher Cu leachability above the solubility curve perhaps results from the more soluble copper complex formation (i.e. $\text{Cu}_2\text{NO}_3(\text{OH})_3$) or the organic carbon contained in sand and kaolinite, which facilitates the Cu release in the leachate (Arickx et al., 2010). These factors also exist in the OPC treatment, but the CSH formed during the OPC treatment could offset the effect of above-mentioned factors and reduce the leached Cu concentration to be less than the solubility of $\text{Cu}(\text{OH})_2$. For CaO and OPC-treated Ni-contaminated soils, the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} \cdot 26\text{H}_2\text{O}$), and CSH contributes to the decrease of leached Ni concentration to a level that is lower than the solubility curve of $\text{Ni}(\text{OH})_2$ for Ni-contaminated soils treated by OPC and CaO. In contrast, these minerals are not formed in MgO-treated Ni-contaminated soils, so that the leached Ni is very close to the theoretical solubility curve, while part of leached Ni concentrations are slightly above the solubility curve. Regarding MgO-treated Cd-contaminated soils, the factor leading to a high Cd leachability above the solubility curve is that the chloride (Cl) from the formed MgCl_2

increases the leachability of Cd (Wei et al., 1998). Nevertheless, calcium chloride (CaCl_2) formed in OPC- and CaO -treated Cd-contaminated soils is expected to decrease the leached Cd (Wei et al., 1998).

Fig. 6 Relationship between leachate pH and leached concentrations: (a) Pb, (b) Cu, (c) Zn, (d) Ni, (e) Cd, and (f) Mn.

3.4. UCS

Fig. 7 shows the UCS results of the six contaminated soils treated with MgO, CaO, and OPC. For most contaminated soils, the OPC treatment provides higher strength in comparison with the CaO or MgO treatment except for Zn-contaminated soils. Three types of UCS trends can be observed for OPC-treated contaminated soils with different heavy metals. One is that the UCS increases with the increasing concentration of heavy metals until the maximum UCS is achieved, after which the UCS decreases significantly. For this type, Pb- and Mn-contaminated soils show the maximum UCS of 2,023 kPa at 2,000 mg/kg and 2,669 kPa at 1,000 mg/kg, respectively. The trend of UCS for OPC-treated Pb-contaminated soils is consistent with the existing findings (Boardman, 1999; Olmo et al., 2001; Yin et al., 2006). Boardman (1999) attributed the increase of UCS for OPC-treated soils at low amount of Pb to the soluble aluminium released from the soil, which enhanced the pozzolanic solidification reactions and the formation of CAH. A further increase of Pb amount could retard the OPC hydration, causing the decrease of UCS for OPC-treated soils. No related research has been, however, reported on the influence of Mn on the UCS of OPC-treated contaminated soils.

Cu, Cd, and Ni-contaminated soils treated by OPC can be classified as another type that the UCS continuously decreases with the increasing original concentration of heavy metals. OPC-treated Zn contaminated soils belong to the third type, of which Zn has a significant negative effect on the UCS of OPC-treated soils, such that the UCS decreases considerably from ~1,800 kPa to ~100 kPa even when a relatively small concentration of Zn (1,000 mg/kg) is present in the soil. Beyond a Zn concentration of 1,000 mg/kg, the UCS of OPC-treated soils becomes stable. The significant negative effect of Zn is likely due to the release of OH⁻

from $\text{Ca}(\text{OH})_2$ in OPC, which can react with heavy metal ions to form hydroxides (Roy et al., 1991). The Zn hydroxide has the lowest solubility than other heavy metals hydroxides, so that the release of OH^- in OPC-treated Zn-contaminated soils becomes slower (Li and Yi, 2019). Hence, the OPC hydration and the formation of C-S-H are significantly retarded in Zn-contaminated soils due to the loss of OH^- (Minocha et al., 2003).

The CaO treatment generally produces a low UCS level (less than 500 kPa) for each contaminated soil and the UCS keeps stable with the increasing original concentration of heavy metals. MgO generally provides a similar UCS level for treated contaminated soils compared with CaO, and the UCS also keeps stable with the original concentration of heavy metals except for Ni- and Mn-contaminated soils. As shown in Fig. 7(d), increasing Ni concentrations facilitates the strength development for MgO-treated soils (i.e. from 161.4 kPa at 0 mg/kg to 699.7 kPa at 24,000 mg/kg), and the UCS for MgO-treated soils becomes much higher than that for lime-treated soils at Ni concentrations of 3,000 to 24,000 mg/kg. Similarly, increasing Mn concentrations from 0 to 4,000 mg/kg increases the UCS of MgO-treated soils, but the UCS decreases slightly after the maximum value of 375.7 kPa at 4,000 mg/kg is reached (as shown in Fig. 7(f)). Mn-contaminated soils treated by MgO also present higher UCS values than those treated by CaO.

(a)

(b)

(c)

(d)

(e)

(f)

Fig. 7. UCS of six contaminated soils treated with MgO, CaO and OPC.

4. Conclusions

The results of XRD and TGA show that the addition of binders can transform soluble heavy metal salts to hydroxides and their complexes. Due to the low solubility of hydroxides and complexes, the leachability of heavy metals decreases after the contaminated soils are treated by binders. However, the level, to which the leachability can be reduced, is significantly dependent on the pH of the treated soils. Contaminated soils treated with MgO have pH values of 9–10.5, at which the leachability of Pb, Cu, and Zn becomes lower than that obtained at pH of 10.5–13 produced by OPC and CaO. OPC-treated contaminated soils

present lower leachability of Pb, Cu, and Zn than CaO-treated contaminated soils, being attributed to the formation of CSH, which could absorb and encapsulate heavy metals. Nevertheless, the leachability of Cd and Mn in soils treated by OPC is the lowest among the three binders due to the CSH formation and the high pH of OPC. A lower leachability of Cd and Mn is obtained for CaO-treated contaminated soils compared to MgO-treated contaminated soils due to the high pH of CaO. OPC and CaO are more effective than MgO in decreasing the Ni leachability for soils contaminated with high original concentration of Ni, but less effective for low original concentration of Ni. The Ni leachability is also related to the leachate pH.

For most contaminated soils, the OPC treatment provides higher strength in comparison with the CaO and MgO treatment except for Zn-contaminated soils, of which the strength provided by OPC is similar to that by CaO or MgO. Additionally, MgO generally provides a similar UCS level compared with CaO for all contaminated soils.

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