Assessment of feasibility of using an innovative binder to solidify/stabilize site soils contaminated by mixed zinc and chloride

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ABSTRACT

This study presents an evaluation of feasibility of using a new phosphate-based binder, named KMP, to solidify/stabilize mixed zinc (Zn) and chloride (Cl) contaminated soil collected from an abandoned industrial electroplating company site. The solidified/stabilized soils cured at 1, 3, 7, and 28 days were subjected to various tests including unconfined compression, soil pH and leachability. The analyses of Zn speciation, X-ray diffraction, and SEM-Mapping were performed to investigate immobilization mechanisms of Zn and Cl in the solidified/stabilized soils. The test results showed that the unconfined compressive strength of the soils solidified/stabilized with 6% KMP was significantly improved, and the leached Zn and Cl concentrations were well below their corresponding remediation goals. The addition of the KMP binder to the contaminated soil transformed large amounts of extractable Zn to stable chemical species. The XRD and SEM-Mapping results indicated the formation of phosphate-bearing precipitates containing Zn and Cl were the predominant mechanisms of immobilizing Zn and Cl with KMP binder.

Keywords: solidification/stabilization, zinc, chloride, strength, leachability.

1 INTRODUCTION

Soil pollution by heavy metals has been both serious and widespread in some developing countries (Du et al., 2014a; Yang et al., 2014a; Xia et al., 2019a). The risky industrially abandoned sites nearly account for 70% of the contaminated sites in China. It is reported that, for instance, some heavy metals and chloride are accumulated in the shallow soil nearby the electroplating plant (Adhoum et al., 2004). The presence of those contaminants not only poses threats to human health and the surrounding environment but also leads to degradation of the mechanical properties of the soil (Yang et al., 2014b; Xia et al., 2019b). Accordingly, it is necessary to implement effective remediation measures to detoxify the contaminated soils and to improve the engineering properties of the contaminated soils.

Solidification/Stabilization technique is widely used to detoxify the heavy metal-contaminated soils (Du et al., 2014a). Along various binders, high-alkaline cementitious materials such as Portland cement (PC) and quicklime are extensively used in the solidification/stabilization projects (Sharma and Reddy, 2004; Du et al., 2014a). However, PC and quicklime production is associated with intensive consumption of energy and nonrenewable resources. For instance, PC production emits 5% to 8% of anthropogenic greenhouse gas into the atmosphere (Scrivener and Kirkpatrick, 2008). Furthermore, the presence of certain heavy metals in the soils such as zinc (Zn) and lead (Pb) has a significant retardation effect on cement-based binders hydration and consequently hinders strength development and heavy metals immobilization in the solidified/stabilized soils (Du et al., 2014a). In addition, it is reported that chloride-induced rebar corrosion may lead to a reduction in the strength, serviceability, and esthetics of underground structures (Shi et al., 2012). Therefore, it is necessary to develop alternative binders to remediate the contaminated soils with relatively high concentrations of Zn and Cl, especially when the remediated site (or soil) will be reused as a foundation (or foundation soil) to retain reinforced concrete structures.

Recently, some new materials have been developed and applied in solidification/stabilization of heavy metal contaminated soils (Du et al., 2014b; Xia et al., 2017; Xia et al., 2018). A novel phosphate-based binder known as KMP has been developed by the authors to stabilize spiked and real site soils with mixed Pb, Zn...
and Cd contaminants (Du et al., 2014b; Xia et al., 2017). The KMP binder consists of monopotassium phosphate (KH₂PO₄), reactive magnesia (MgO) and oxalic acid-activated phosphate rock power in 1:2:1 proportion by dry weight basis. Previous test results showed that the KMP solidified/stabilized soil has many advantages over PC solidified/stabilized soil, such as higher heavy metals immobilization efficiency, higher strength, relatively lower pH of solidified/stabilized soil, lower remediation cost, and superior freeze-thaw, sulfate-attack and carbonation resistance (Du et al., 2014b; Wei et al., 2015; Du et al., 2016). However, based on the literature review, the KMP application in treating soils with relatively high concentrations of mixed Zn and Cl has not been well addressed.

In the present study, the feasibility of applying the KMP binder to solidify/stabilize an industrial site soil contaminated with mixed Zn and Cl was evaluated. A series of tests containing soil strength, soil pH and contaminants leaching characteristics were conducted to investigate the performances of the KMP binder. Furthermore, the immobilization mechanisms of Zn and Cl were investigated based on modified European Communities Bureau of Reference three-step sequential extraction procedure (BCR SEP), X-ray diffraction (XRD), and SEM-Mapping analyses.

2 MATERIALS AND TEST METHODS

2.1 Materials

The contaminated soil used in this study was collected from an abandoned electroplating industrial site. A large amount of Zn and Cl has accumulated in the shallow ground. Approximately 50 kg of contaminated soil collected within the surface 0.50-m depth was transported to the laboratory for subsequent tests. The soil was then air-dried, passed through a 10-mesh sieve and stored in a polyethylene container for physicochemical properties tests and the results were shown in Table 1.

| Property                      | Valueb |
|-------------------------------|--------|
| Specific gravity, Gₛ         | 2.64   |
| Liquid limit, w₁ (%)         | 31.8   |
| Plastic limit, wₛ (%)        | 16.0   |
| Optimum water content, wₜ (%)| 19.2   |
| Maximum dry density, ρₛ (g/cm³)| 1.75 |
| Average soil pH              | 4.23   |
| Soil classification           | CL     |
| Grain size distribution (%)  |        |
| Clay (<0.002 mm)             | 21.3   |
| Silt (0.002-0.075 mm)        | 55.5   |
| Sand (0.075-20 mm)           | 23.2   |
| Contaminants Concentration (mg/kg) |       |
| Zinc, Zn                     | 8555   |
| Chloride, Cl                 | 2050   |

a Measured using a laser particle size analyzer Mastersizer 2000 (Malvern, USA).
b Number of replicates=3, and coefficient of variance (COV) < 5%.

The KMP binder is a mixture of KH₂PO₄, reactive MgO, and phosphate rock powder with a dry mass ratio of 1:2:1 and this ratio shows relatively low leachability and high strength for the solidified/stabilized soil (Du et al., 2014). The industrial-grade phosphate rock was crushed, ground and passed through a 0.075 mm opening sieve. To accelerate the release of phosphate from the phosphate rock and contaminants immobilization, the phosphate rock powder was acidized with oxalic acid according to the procedures presented by Du et al. (2014). The industrial-grade monopotassium phosphate (KH₂PO₄) and MgO powder were used. The physicochemical properties of phosphate rock and MgO are listed in Table 2. The binder was prepared by dry-mixing of the raw materials in designed proportions prior to use.

| Oxidea  | Value (%) |
|---------|-----------|
| Phosphate rock | MgO |
| CaO     | 45.93    | 0.23 |
| SiO₂    | 6.14     | 0.28 |
| Al₂O₃   | 1.23     | 0.28 |
| P₂O₅    | 25.10    | NAb |
| SO₃     | NAb      | 0.45 |
| Fe₂O₃   | NAb      | 88.0 |
| MgO     | NAb      | 0.01 |
| K₂O     | NAb      | 2.35 |

a Analyzed using ARL 9800 XP+XRF spectrometry.
b Not available.

2.2 Specimen preparation

Preliminary test results suggested that an appropriate water content of 23% and binder dosage of 6% (on dry weight of soil basis) yield relatively low contaminant leachability and high strength of the KMP solidified/stabilized soil. So a predetermined amount of distilled water was firstly added into the contaminated soil to achieve the target water content of 23%. Then, the binder with predetermined weight (6% wt, dry weight basis) was poured into the contaminated soil and mixed thoroughly using an electronic mixer for 15 min to achieve homogeneity. After that, approximately 260 g of the mixture was statically compacted into a stainless steel cylindrical mold with 50-mm-diameter and 100-mm-height to achieve a dry density of 1.31 g/cm³. This target dry density was selected to simulate the density that was achieved during a field pilot-scale test performed at the same site. The specimen was then extruded from the mold using a hydraulic jack, sealed in a polyethylene bag and cured under the standard condition (temperature of 20±2 °C and relative humidity of 95%). For comparison, the contaminated soil without binder addition was used to prepare the control check (CK) specimen. The preparation method and curing condition of the CK specimen were same as those of the KMP solidified/stabilized soil specimens.

After respective 1, 3, 7, and 28 d curing, the soil specimens were subjected to various tests including soil pH, unconfined compressive strength (qₜₚ) and TCLP.

| Test Method | Value (%) |
|-------------|-----------|
| Soil pH     | 4.23      |
| Unconfined compressive strength (qₜₚ) | 16.0 |
| TCLP        | 23.2      |

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approximately 20 g of broken samples collected from the unconfined compression test at 28 d curing were air-dried for BCR SEP test. Also, after curing of 28 days, approximately 1 cm³ of subsamples with fresh surface were collected from the broken specimens of unconfined compression test. The subsamples were frozen-dried and coated with gold for SEM-EDS analysis. The identical CK and solidified/stabilized soil specimens were prepared in triplicate for soil pH, $q_u$, and TCLP tests. The average values of these triplicate values are reported in this study. The error bars representing the standard deviations are also plotted in the corresponding figures. One CK specimen and one solidified/stabilized soil specimen were prepared and subjected to the BCR SEP test and SEM-EDS analysis.

To investigate the effects of coexisting Zn and Cl on the immobilization mechanisms, comparative tests were conducted to analyze Zn- or Cl- and mixed Zn and Cl-bearing products formed in the binder paste matrix with Zn or Cl alone and Zn and Cl mixed contaminants. A series of Zn and/or Cl-spiked paste samples were prepared for XRD analysis. The binder paste specimens with Zn or Cl alone and mixed Zn and Cl were prepared by spiking binder powders with $\text{Zn(NO}_3\text{)}_2\cdot5\text{H}_2\text{O}$ and/or NaCl solutions. Paste specimens were designated as binder+$\text{Zn}$, binder+$\text{Cl}$ and binder+$\text{Zn}+\text{Cl}$ to denote specimens with individual Zn or Cl and mixed Zn and Cl, respectively (Table 3). Firstly, the individual $\text{Zn(NO}_3\text{)}_2\cdot5\text{H}_2\text{O}$ or NaCl solution and solution containing mixed $\text{Zn(NO}_3\text{)}_2\cdot5\text{H}_2\text{O}$ and NaCl were prepared by dissolving $\text{Zn(NO}_3\text{)}_2\cdot5\text{H}_2\text{O}$ or NaCl powder and mixed $\text{Zn(NO}_3\text{)}_2\cdot5\text{H}_2\text{O}$ and NaCl powders in deionized water. Then, the KMP binder was poured into the solution and the mixture was stirred thoroughly for 10 minutes to achieve homogeneity. Later the admixed paste was poured into a polyethylene mold to cure. After 28 days under the standard curing condition, the paste specimens were carefully crushed using a rubber hammer. Then, approximately 1 cm³ of subsamples with fresh surface were immediately collected from each crushed paste specimen and frozen-dried for XRD analysis. One CK specimen and one solidified/stabilized soil specimen were prepared for the XRD analysis. The concentration of contaminants and binder-solution ratio are listed in Table 3.

### Table 3. Binder paste specimens for XRD analysis.

| Mix denotation | Contaminant | Concentration (%) | Binder:solution ratio |
|----------------|-------------|-------------------|-----------------------|
| KMP            | -           | -                 | 1:0.75                |
| KMP+$\text{Zn}$ | Zn          | 14                | 1:0.75                |
| KMP+$\text{Cl}$ | Cl          | 3.5               | 1:0.75                |
| KMP+$\text{Zn}+\text{Cl}$ | Cl and Zn | 3.5 and 14        | 1:0.75                |

- Prepared by dissolving zinc nitrate and/or sodium chloride in the distilled water.
- The percentage of the contaminant to binder on dry weight basis.
- The ratio of binder weight (mg) to solution volume (ml).

### 2.3 Test methods

The laboratory cured solidified/stabilized soil specimens were subjected to unconfined compression test with controlled strain rate of 1%/min as per ASTM D4219 (ASTM, 2008). The fragments from the broken specimens were collected and subjected to pH, TCLP and BCR SEP tests. The soil pH measurement was conducted using a HORIBA D-54 pH meter as per ASTM D4972 (ASTM, 2013). The Zn leachability was evaluated using TCLP as per USEPA Method 1311 (USEPA, 1996). The Cl leachability was determined based on China GB/T 50123 (China MOC, 1999). The BCR SEP was performed in accordance with the procedures provided by Davidson et al. (1998) to determine the exchangeable, reducible, oxidizable and residue fractions of the Zn in the soil sample. The XRD analysis for paste specimens were conducted using a Rigaku D/Max-2500 X-ray diffractometer with Cu-\(\text{K}\alpha\) radiation (\(\lambda=1.540538\) Å) in the 20 range of 5° to 55° with the step of 0.02° at room temperature.

### 3 RESULTS AND DISCUSSION

#### 3.1 Unconfined compression tests

Fig. 1 shows the results of unconfined compressive tests conducted on the solidified/stabilized soils with various curing time. The $q_u$ of the solidified/stabilized soil is approximately 30 to 70 kPa after 1 day of curing, which is remarkably greater than that of the original contaminated soil (20 kPa). Besides, the $q_u$ of the solidified/stabilized soil has a significant increase by approximately 5 times as compared to the original contaminated soil at 28 d. This agrees well with the work by Du et al. (2014) that the acid-base reaction products of KMP can both provide bonding strength of the soil particles and fill the soil pores, which consequently yields a dense soil structure and improved mechanical properties.

![Fig. 1. Variation of $q_u$ with curing time for the KMP solidified/stabilized soil specimens (Number of replicates=3, COV<3.5%).](image)

#### 3.2 Soil pH tests

Fig. 2 shows the pH value variation of the KMP solidified/stabilized soil with curing time. It is seen that the pH of the solidified/stabilized soil significantly increases by approximately 1.84 units after merely 1 day curing as compared to that of the original soil (i.e. 4.23). Then, the pH value of the solidified/stabilized soil increase to 7.22 at day 7. After that, a marginal decrease in the soil...
pH is observed from day 7 to day 28. The reasons for the soil pH variation are attributed to that (1) the production of hydroxide ion (OH\(^-\)) after dissolution of a certain quantity of alkaline substance (i.e. MgO); and (2) the formation of some Zn-bearing products in the KMP stabilized soil, i.e. Zn(OH)\(_2\) and CaZn\(_2\)(OH)\(_6\)·2H\(_2\)O, consumes some OH\(^-\).

3.4 Zn speciation analysis

Fig. 4 shows the chemical speciation of Zn for the original contaminated soil and KMP solidified/stabilized soils after 28 d of curing. It is seen that the acid soluble and the oxidisable fraction decrease, and the reducible and residual fractions increase with the KMP addition. For instance, the acid soluble fraction in the original contaminated soil notably decreases from 92% to 53% for KMP solidified/stabilized soil, while the oxidisable fraction remarkably increases from 2% to 33%. The results indicate that the addition of the KMP binder to the contaminated soil can result in significant amounts of more stable chemical species (i.e. residual fraction). The results are consistent with those obtained from the TCLP tests in which the addition of the KMP binder results in a noteworthy reduction in the leached concentration of Zn.

3.5 X-ray diffraction analysis

Fig. 5(b) presents the XRD diffractograms of KMP pastes spiked with Zn or Cl alone and mixed Zn and Cl. The farringtonite (Mg\(_5\)(PO\(_4\))\(_2\):8H\(_2\)O, 2\(\theta\) of 30.92\(^\circ\)), potassium struvite (MgKPO\(_4\):6H\(_2\)O, 2\(\theta\) of 20.86\(^\circ\)), collinsite (Ca\(_2\)Mg(PO\(_4\))\(_2\):2H\(_2\)O, 2\(\theta\) of 29.34\(^\circ\)), brucite (Mg(OH)\(_2\), 2\(\theta\) of 37.98\(^\circ\)), fluorapatite (Ca\(_5\)(PO\(_4\))\(_3\)F, 2\(\theta\) of 31.94\(^\circ\)) and fluorspar (CaF\(_2\), 2\(\theta\) of 47.00\(^\circ\)) are detected in all specimens. It is noticed that the products of hopeite (Zn\(_2\)(PO\(_4\))\(_2\):4H\(_2\)O, 2\(\theta\) of 31.30\(^\circ\)), zinc hydroxide (Zn(OH)\(_2\), 2\(\theta\) of 27.16\(^\circ\)), schocholite (CaZn\(_2\)(PO\(_4\))\(_2\):2H\(_2\)O, 2\(\theta\) of 10.32\(^\circ\)) and calcium zincate (CaZn\(_2\)(OH)\(_6\)·2H\(_2\)O, 2\(\theta\) of 28.58\(^\circ\)) containing Zn contaminant alone are detected in the KMP+Zn and KMP+Zn+Cl specimens. The products of korshunovskite (Mg\(_5\)(OH)\(_2\)Cl:4H\(_2\)O, 2\(\theta\) of 30.98\(^\circ\)), calcium chloride hydroxide (Ca(OH)Cl, 2\(\theta\) of 38.26\(^\circ\)) containing Cl alone, are identified in the KMP+Cl and KMP+Zn+Cl specimens. In addition, the presence of simonkolleite (Zn\(_3\)(OH)\(_8\)Cl:2H\(_2\)O), containing mixed Zn and Cl, is identified at 2\(\theta\) of 15.62\(^\circ\) in the KMP+Zn+Cl specimen, respectively. When compared with previous study results, it is found that the products of Zn\(_2\)(PO\(_4\))\(_2\):4H\(_2\)O, CaZn\(_2\)(PO\(_4\))\(_2\):2H\(_2\)O and Zn(OH)\(_2\) are also reported in the KMP stabilized soil spiked with Zn.
alone and mixed Zn and Pb (Du et al., 2014b) and in the phosphate rock immobilized mine waste soils with mixed Cd, Cu, Pb, and Zn (Mignardi et al., 2012). However, the products of $\text{Zn}_2\text{Mg}(\text{PO}_4)_2$, $\text{CaZn}_2(\text{OH})_6\cdot2\text{H}_2\text{O}$ and $\text{Zn}_3(\text{OH})_8\text{Cl}_2$ formed in the KMP paste spiked with Zn and Cl of this study are not identified by Mignardi et al. (2012) and Du et al. (2014).

**3.6 SEM-EDS analysis**

Fig. 6(a) shows SEM images for the KMP stabilized soil. Fig. 7((b)-(g)) shows the distribution maps of Zn, Cl, phosphorus (P), magnesium (Mg), calcium (Ca) and potassium (K), respectively. It is seen that the products of $\text{Zn}_3(\text{PO}_4)_2\cdot4\text{H}_2\text{O}$, $\text{Zn}(\text{OH})_2$, $\text{CaZn}_2(\text{PO}_4)_2\cdot2\text{H}_2\text{O}$ and $\text{CaZn}_2(\text{OH})_6\cdot2\text{H}_2\text{O}$, which are detected by XRD analysis in the KMP paste spiked with Zn (Fig. 5(b)), are identified in Fig. 6(a) when overlapping the distribution maps for the elements Zn, P, O and/or Ca. The $\text{Mg}_2(\text{OH})_3\text{Cl}\cdot4\text{H}_2\text{O}$ or $\text{Ca(OH)Cl}$ are identified, which is substantiated by the XRD analysis for the KMP paste spiked with Cl as shown in Fig. 5. The $\text{Zn}_3(\text{OH})_8\text{Cl}_2$ highlighted by overlapping the distribution maps of Zn, O and Cl is also observed in the KMP paste spiked with mixed Zn and Cl by XRD analysis (Fig. 5).

**Fig. 5.** X-ray diffractograms of the KMP paste spiked with Zn or Cl alone and mixed Zn and Cl after 28 d curing (Number of replicate=1).

**Fig. 6.** SEM-EDS image of the KMP stabilized soil and the element distribution maps: (a) SEM image; (b) distribution map of Zn; (c) distribution map of Cl; (d) distribution map of P; (e) distribution map of Mg; (f) distribution map of Ca; and (g) distribution map of K.

**4 CONCLUSIONS**

This study presented a series of test results to assess the feasibility of using KMP binder to solidify/stabilize a mixed zinc and chloride contaminated soil. Based on the results, the following conclusions can be drawn:

1. With KMP stabilization, the strength of the contaminated soil significantly increased by 5 times after 28 days of curing. KMP addition could increase the soil pH to 6.75 and 6.96 after 28 days of curing as compared to the original value of 4.23.
2. The leached Zn and Cl concentrations in the soils were significantly reduced with stabilization by using KMP. The 6% of KMP addition can well meet the remediation goals after 1 d of curing.
3. The addition of the KMP binder to the contaminated soil transformed significant amounts of Zn.
to more stable chemical species. The XRD and SEM-Mapping results revealed that the formation of precipitates in the KMP stabilized soil including Zn\(_5\)(PO\(_4\))\(_3\), Zn(OH)\(_2\), CaZn\(_2\)(PO\(_4\))\(_2\)-2H\(_2\)O, CaZn\(_2\)(OH)\(_2\)-2H\(_2\)O, Mg\(_2\)Cl( OH)\(_3\)-4H\(_2\)O, CaCl(OH), Ca\(_3\)(PO\(_4\))\(_3\)Cl and Zn\(_2\)(OH)\(_3\)Cl\(_2\) mainly contributed to Zn and Cl immobilization.

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**REFERENCES**

1. Adhoum, N., Monser, L., Bellakhal, N. and Belgaied, J.E. (2004) Treatment of electroplating wastewater containing Cu\(^{2+}\), Zn\(^{2+}\) and Cr(VI) by electrocoagulation, *Journal of Hazardous Materials*, 112(3), 207-213.

2. American Society for Testing and Materials (ASTM) (2008): ASTM standard D4219 Standard test method for unconfined compressive strength index of chemical grouted soils, West Conshohocken, PA.

3. American Society for Testing and Materials (ASTM) (2013) ASTM standard D4972 Standard test method for pH of soils, West Conshohocken, PA.

4. China Ministry of Construction (China MOC) (1999): GB/T 50123 Standard for soil test method. China Ministry of Construction, Beijing.

5. Davidson, C.M., Duncan, A.L., Littlejohn, D., Ure, A.M. and Garden, L.M. (1998): A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land, *Analytica Chimica Acta*, 363(1), 45-55.

6. Du, Y.J., Jiang, N.J., Liu, S.Y. Jin, F., Singh, D.N. and Puppala, A.J. (2014a): Engineering properties and microstructural characteristics of cement-stabilized zinc-contaminated kaolin, *Canadian Geotechnical Journal*, 51(3), 289-302.

7. Du, Y.J., Wei, M.L., Reddy, K.R., Jin, F., Wu, H.L. and Liu, Z.B. (2014b): New phosphate-based binder for stabilization of soils contaminated with heavy metals: Leaching, strength and microstructure characterization, *Journal of Environmental Management*, 146, 179-188.

8. Du, Y.J., Wei, M.L., Reddy, K.R. and Wu, H.L. (2016): Effect of carbonation on leachability, strength and microstructural characteristics of KMP binder stabilized Zn and Pb contaminated soils, *Chemosphere*, 144, 1033-1042.

9. Mignardi, S., Corami, A. and Ferrini, V. (2012): Evaluation of the effectiveness of phosphate treatment for the remediation of mine waste soils contaminated with Cd, Cu, Pb, and Zn, *Chemosphere*, 86, 354-360.

10. Scrivener, K.L. and Kirkpatrick, R.J. (2008): Innovation in use and research on cementitious material, *Cement and Concrete Research*, 38(2), 128-136.

11. Sharma, H.D. and Reddy, K.R. (2004): Geoenvironmental engineering: Site Remediation, Waste Containment, and Emerging Waste Management Technologies. Wiley, Hoboken, NJ.