Solidification/Stabilization (S/S) of High Concentration Zinc-Contaminated Soils Using Soda Residue

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Abstract. Solidification/stabilization (S/S) has been considered as one of the most effective techniques for remediation of the heavy metal-contaminated sites. Among various binders adopted in S/S, soda residue is extensively accepted and investigated due to its strong adsorptive capacity for heavy metal ions. In this paper, the engineering properties of the high concentration zinc-contaminated soil solidified/stabilized by soda residue blended with cement have been investigated. Test results showed that the unconfined compressive strength (UCS) of the treated specimen increased with the increase of the soda residue content and the curing time. A higher UCS can be obtained for specimens with lower zinc concentration. In toxicity characteristic leaching procedure (TCLP) test, the concentration of the leached heavy metal ions decreased with the increase of the curing time. Results of UCS and TCLP illustrated that cement-soda residue stabilized zinc-contaminated soil satisfied the standard of strength and leachability when the mass ratio of cement to soda residue was 2 to 8. X-ray diffraction (XRD) analysis obviously showed the formation of the hydrated products such as CSH, CAH and Aft. Zinc ions can be immobilized by precipitating as $Zn(OH)_2$ or incorporating with hydrates to form $CaZn_2(OH)_6H_2O$.

Keywords: Stabilization/solidification · Zinc-contaminated soil
Soda residue · Unconfined compressive strength · Leachability

1 Introduction

Stabilization/solidification (S/S) is an effective method for remediation of the heavy metal contaminated site for its convenience and cost-effective [1]. In the S/S process, cement-based materials are the commonly used binders that can increase the soil strength and reduce the mobility of heavy metal ions according to the complex interactions between the binders and the contaminants [2]. However, during the cement production, greenhouse gas will be generated and discharged into the atmosphere due to the calcination of limestone and consumption of fossil fuel [3, 4]. Therefore, more effective additives need to be investigated and assessed in treatment of the contaminated site alone or mixing with the cement on the basis of the economic benefits, resource and environment conservations and immobilization effectiveness [5, 6].

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Among the alternative binders, soda residue, which is the by-product generated from the manufacturing soda industry, generally consists of extremely fine particles with size ranged from 0.01 mm to 0.074 mm. In recent years, several researches reported that soda residue can not only effectively adsorb the heavy metal contaminants but also improve the engineering properties of soils [7–9]. Therefore, it is very necessary to evaluate the effectiveness of soda residue on the remediation of heavy metal contaminated soils.

In the present work, the soda residue mixing with the cement, was introduced for remediation of the zinc-contaminated soils. Unconfined compressive strength test and toxicity characteristic leaching procedure, as well as the XRD techniques, were adopted to assess the effectiveness of the S/S technique and determine the optimum proportion of mixture.

2 Experimental Materials and Procedures

2.1 Experimental Materials

Zinc-Contaminated Soil. The tested soil was excavated from a construction site with depth of 3–5 m in Hefei City, which is in the eastern part of China. The basic physical properties and chemical compositions of the soils are listed in Table 1. The maximum dry density and the optimal moisture content are 1.72 g/cm^3 and 22.14% respectively obtained by the compaction test.

Table 1. Physical and chemical properties of the tested soil and additives

Items		Soil	Cement	Soda residue
Chemical compositions (%)	SiO_2	54.63	27.21	10.20
	Al_2O_3	21.56	9.90	9.00
	CaO	0.48	43.80	62.81
	Fe_2O_3	17.19	2.88	1.31
	MgO	1.77	1.57	12.5
	Na_2O	0.65	0.44	0.23
Physical properties	Water content (%)	25.19	–	–
	Density (g/cm^3)	2.10	–	–
	Specific gravity	2.8	–	–
	Void ratio	0.62	–	–
	Liquid limit (%)	51.49	–	–
	Plastic limit (%)	25.84	–	–

The soil was oven-dried at 105 °C for 24 h, then pulverized and passed through the 2 mm sieve. $Zn(NO_3)_2$ solution was prepared by solving a target quantity of Zn $(NO_3)_2 \cdot 6H_2O$ in the distilled water. After that, $Zn(NO_3)_2$ solution was sprayed into the sieved soil and mixed thoroughly. The mass ratio of the Zn^{2+} to the dry soil was controlled as 1000, 5000 and 10000 mg/kg (denoted as Zn0.1, Zn0.5 and Zn1.0), respectively. Finally, the prepared zinc-contaminated soil was sealed in the plastic bags and cured for 28 days under the standard curing condition (temperature 22 ± 2 °C, humidity 95 ± 2%).

Cementitious Additives. The Portland blast furnace slag cement (denoted as C) and soda residue (denoted as SR) were selected as the cementitious additives in the present work. Cement was the commercial cement and the soda residue was the by-products of the alkali plant located in Weifang City, Shandong Province of China. The main chemical compositions of the two additives are also listed in Table 1.

Specimen Preparation. The pre-prepared zinc-contaminated soil and cementitious materials were oven-dried at 105 °C for 24 h, pulverized and sieved with 2 mm and 0.5 mm sieves, respectively. After that, the cement and soda residue were added into the zinc-contaminated soil. The mass ratio of the binders to the dry soil was 20% and 30% (the mass ration of C to SR were designed as 1:4, 3:7, 2:3 and 1:1). After thorough mixing, distilled water was mixed with the powders at the optimum water content. Then the mixture was cast into a test ring and statically compacted to obtain a cylinder specimen with a diameter of 5 cm and a height of 5 cm. The dry density of the prepared specimen was controlled at 95% of the maximum dry density. Finally, the specimens were demoulded from the test ring with hydraulic jack and cured for 7, 14, 28, 56 and 90 days under standard curing condition (temperature of 22 ± 2 °C and humidity of 95 ± 2%).

2.2 Experimental Procedures

Unconfined Compressive Strength Test (UCS). According to the Methods of Soils for Highway Engineering (2007), the UCS test was conducted at a shearing speed of 1 mm/min after the designed curing period by using a strain controlled unconfined pressure apparatus. The stress and strain were recorded at intervals of 15 s. After shearing, samples were selected to perform the TCLP and XRD tests.

Toxicity Characteristic Leaching Procedure (TCLP). After UCS test, the specimen was pulverized and sieved through a 2-mm sieve. Then the pulverized specimen was mixed with the extracted solutions at a solid/liquid mass ratio of 1:20. The extraction solution was the 0.1 M acetic acid solution with pH of 2.88 according to the U.S. EPA protocol (1992). The prepared mixtures were sealed in polypropylene bottles and horizontally vibrated with an oscillation apparatus at 80 rpm for 18 h. The suspending liquids were filtered by using a 0.45-μm filter membrane. Finally, the pH values and Zn^{2+} concentrations were measured using a pH-meter and an atomic adsorption spectrometer, respectively.

X-Ray Diffraction (XRD) Analysis. The mineral compositions of the stabilized contaminated specimens were tested by X-ray diffraction (XRD) technique. The XRD was performed with Cu-Kα radiation on a Rigaku D/Max-2005V. Before measurement, the specimens need to be freeze-dried, pulverized and passed through 0.075 mm sieve.

3 Test Results and Discussions

3.1 Unconfined Compressive Strength

Effect of the Curing Time. The evolutions of the unconfined compressive strength of the stabilized zinc-contaminated soils with the curing time are shown in Fig. 1. It is evident that, the UCS of the specimen increase with the curing time increasing due to the formation of cementitious products during hydration process. In Fig. 1(b), the strength increasing rate of the Zn0.5-specimens stabilized with 20% dosage of additives decreases after 28 days-curing. As the Zn^{2+} concentration increases to 10000 mg/kg, UCS of the specimens treated with cement-soda residue increase slightly after 28-day curing (Fig. 1(c)). Therefore, it can be concluded that higher Zn^{2+} concentration has little influence on the development of the initial strength of the stabilized specimens but will hinder the long-term development of the strength.

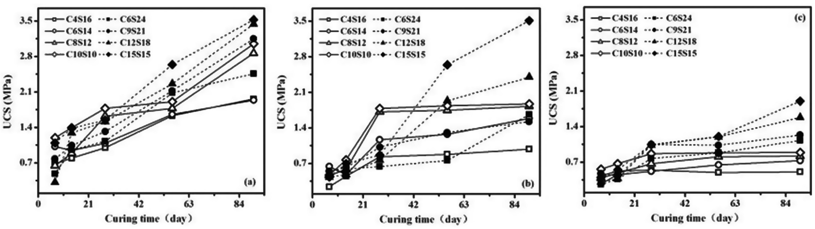

Fig. 1. Relationships between the UCS and the curing time: (a) Zn 1000 mg/kg; (b) Zn 5000 mg/kg and (c) Zn 10000 mg/kg.

Effect of the Binder Proportions. The effects of the binder proportions on the UCS are shown in Fig. 2. The stabilized specimens cured for more than 28 days all satisfy the required strength for S/S treated waste. In details, after 28 days-curing, the strength of specimen treated with 20% dosage of additives is slightly lower than that of specimen treated with 30%. As the curing time increases to 90 days, the UCS of the specimens stabilized by 30% binders are significantly higher than that of stabilized by 20% additives. This is because that, the increased cement content results in more hydrated products and the increasing content of soda residue may create the alkaline environment, which will activate the long-term hydration process. Additionally, a large amount of $CaCO_3$ contained in the soda residue can also enhance the soil strength [10]. As shown in Fig. 2(b), comparison between the C6SR14 specimen and C6SR24 specimen indicates that, the increase of the soda residue content will lead to an obvious increase in the UCS. It is evident that soda residue exhibits a strong capacity of adsorption for heavy metal ions. Then the Zn^{2+} or $Zn(OH)_2$ precipitate will be absorbed on the surface of the soda residue particles, which can prevent the hydration process from disturbing.

Besides, as shown in Fig. 2, increasing Zn^{2+} concentration from 1000 mg/kg to 10000 mg/kg lead to an obviously decrease in the UCS for all specimens. This may be

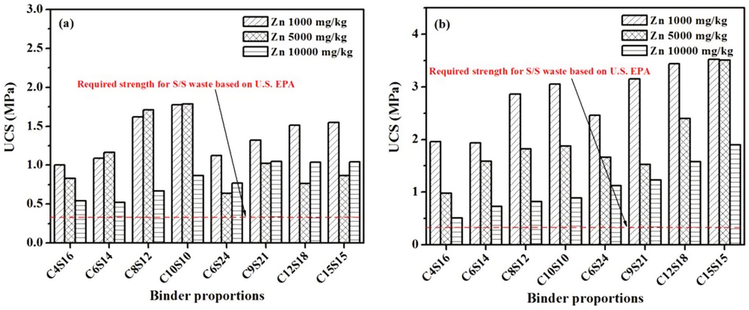

Fig. 2. Effects of the additive proportions on the UCS: (a) curing for 28 days and (b) curing for 90 days

attributed to the formation of $Zn(OH)_2$, which will encapsulate the components of the cement/soda residue and finally hinder the cement hydration process [11].

3.2 Toxicity Characteristic Leaching Procedure

Effect of the Curing Time. Relationships between the leached Zn^{2+} concentration and the curing time for different Zn^{2+} concentrations are shown in Fig. 3. It can be observed that, the leached Zn^{2+} concentration decreases significantly during the initial stage (less than 28 days) and the decreasing rate reduces in the following curing time. For specimens contaminated with 1000 mg/kg Zn^{2+}, the leached Zn^{2+} concentrations are relatively low at 28 curing days, even cannot be detected after 90 days curing. That is the reason for the absence of the data recorded at 90 days of curing (Fig. 3(a)). As the Zn^{2+} concentrations increase to 5000 mg/kg and 10000 mg/kg, the leached Zn^{2+} concentrations increase as shown in Fig. 3(b) and (c). However, the leached Zn^{2+} concentrations are still lower than the regulatory limit of 100 mg/L except for the specimens treated by 20% additives and cured less than 7 days. For explanation of such excellent treatment efficiency, Li *et al.* [12] had reported that, Zn^{2+} can be immobilized in the specimen by forming the hydroxide precipitation during cement hydration. Additionally, the high alkaline environment created by cement and soda residue will result in the low solubility of Zn^{2+}. With the curing time increasing, more hydrated products form and incorporate the Zn^{2+} into the crystalline network of the hydrated compound, which will significantly decrease the Zn^{2+} mobility [13].

Effect of the Binder Proportions. The leached Zn^{2+} concentrations of the specimens stabilized with different binders are shown in Fig. 4. The addition of the designed binders can effectively reduce the leached Zn^{2+} concentrations to less than the regulatory limit of 100 mg/L. Therefore, a common conclusion can be reached that the cement/soda residue mixture is an effective additive to solidified/stabilized contaminated soils with high concentration Zn^{2+} (even with concentration of 10000 mg/kg).

As shown in Fig. 4, increasing the soda residue content in the mixture effectively decreases the quantity of Zn^{2+} released out, which implies the important role soda residue played in decreasing the Zn^{2+} mobility. Hale *et al.* [14] suggested that Zinc

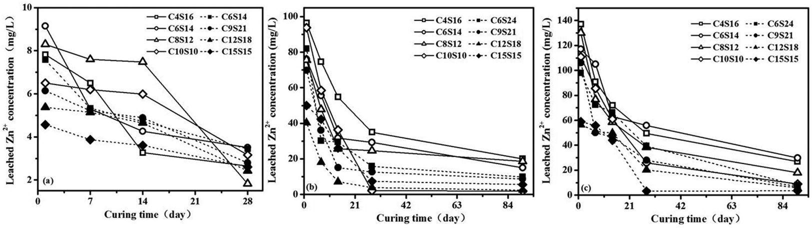

Fig. 3. Relationships between the leached Zn^{2+} concentrations and the curing time: (a) Zn 1000 mg/kg; (b) Zn 5000 mg/kg and (c) Zn 10000 mg/kg.

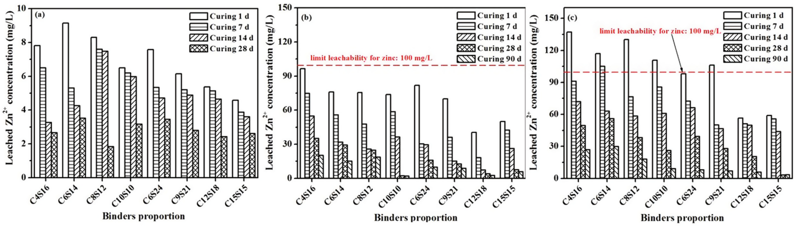

Fig. 4. Effects of additive proportions on the leached Zn^{2+} concentrations: (a) Zn 1000 mg/kg; (b) Zn 5000 mg/kg and (c) Zn 10000 mg/kg.

exhibited the lowest solubility when pH value varied from 8 to 12. As a result, Zn^{2+} can be effectively immobilized due to the high alkaline environment created by the cement and soda residue. Moreover, adsorption is also a predominant mechanism to stabilize the Zn^{2+} due to the extremely high specific surface area possessed by soda residue. As a conclusion, partial substitution of cement with soda residue is a cost-effective way to treat zinc-contaminated soils.

3.3 XRD Analysis

XRD results of the stabilized specimens with different additive proportions and curing time are given in Fig. 5. It is clear that, CSH, AFt, CAH and CH are the main products of cement hydration that can be identified in the diffractograms. A little monosulfate can be observed in the specimens (corresponding to 2θ of about 19.84°) for the presence of sulfate in both cement and soda residue. Due to these complicated hydration products, the strength of the specimens will be enhanced obviously and Zn^{2+} can be effectively encapsulated or adsorbed. Owning to the high alkaline environment created by cement and soda residue, Zn^{2+} can be precipitated as $Zn(OH)_2$ with the peak appeared at 2θ of 27.9°. With curing time increasing, $CaZn_2(OH)_6H_2O$ will be formed as the peaks appeared at 2θ of 27.45° and 36.55°. These results confirm that Zn^{2+} can be immobilized not only by precipitation but also incorporation with the hydrated products. After curing for 90 days, peak stood for $CaCO_3$ at 37.8° disappears, which suggests that $CaCO_3$ may react with the cement phases or the hydrates during the curing period and the formed calcium carbonate complex may improve the soil strength as well.

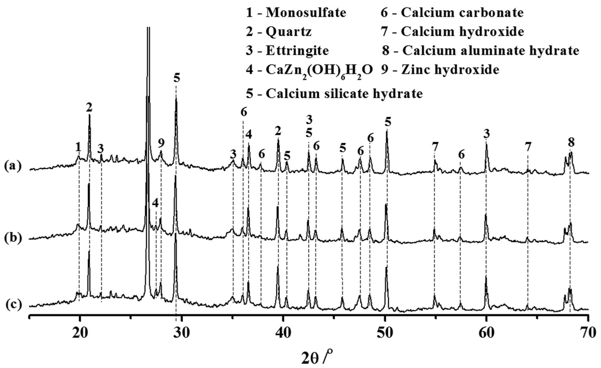

Fig. 5. Diffractograms for stabilized Zn1.0 specimens: (a) C6S14, curing for 7 days; (b) C6S14, curing for 90 days and (c) C6S24, curing for 90 days

4 Conclusions

In the present work, the engineering properties of the high concentration zinc-contaminated soils solidified/stabilized by cement/soda residue mixtures were investigated. Some major conclusions were summarized as follows.

(1) Unconfined compressive strength increased with the increase of soda residue content and curing time, and decreased with the increase of zinc concentration.
(2) The leached Zn^{2+} concentration decreased with increasing of curing time. Partial substitution of the cement with soda residue can immobilize Zn^{2+} effectively.
(3) For specimens with lower zinc concentrations, stabilization with the additive proportion of C4S16 will satisfy the requirements of both engineering and environmental standards. While for specimens with higher zinc concentrations, the curing time of 14 days needed to be guaranteed.
(4) In analysis of the microstructural characteristics, CSH, CAH, AFt and calcite can be easily observed, and Zn^{2+} can be immobilized by precipitating as $Zn(OH)_2$ or incorporating with hydrates to form $CaZn_2(OH)_6H_2O$.

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