

YONGHUI XI¹, HUAQI WANG¹, LINAN GUO¹, MIN ZHANG¹

UTILIZATION OF CEMENT AND OTHER ADDITIVES FOR SOLIDIFICATION/STABILIZATION OF SOIL CONTAMINATED SIMULTANEOUSLY WITH Cd²⁺ and Pb²⁺ IONS

Various additives, including cement, quicklime, fly ash, montmorillonite, sepiolite and their proportions were employed to stabilize/solidify artificially prepared soils contaminated simultaneously with two kinds of ions such as Cd²⁺ and Pb²⁺. The unconfined compressive strength of the stabilized soils was measured to estimate the possibility of recycling. The efficiency of Cd²⁺ and Pb²⁺ immobilization in contaminated soils was also evaluated using the US EPA TCLP toxicity test. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to elucidate the mechanisms responsible for the immobilization of heavy metals. The experimental results demonstrate that in terms of soils simultaneously polluted with Cd²⁺ and Pb²⁺ ions, the curing effect of fly ash is better than that of montmorillonite and sepiolite. When Cd²⁺ and Pb²⁺ coexist in soil specimens, the curing is more difficult than for Cd²⁺ or Pb²⁺ alone, which is antagonistic mechanism. Also, the leaching concentration of Cd²⁺ and Pb²⁺ gradually decreases upon increasing pH when pH < 8. For pH ≥ 8, the leaching concentration of Cd²⁺ and Pb²⁺ reached a minimum. Besides, the results of XRD and SEM are in agreement with those of the strength and leaching tests.

1. INTRODUCTION

With the development of industry, the emissions of heavy metal waste that has a lot of harmful effects to natural environment and human life have been increasing, causing increase of the proportion of heavy metal contaminated soil. These will be a serious threat to the safety of surface water and groundwater, and it will restrict the development of society, so the effective disposal of heavy metal contaminated soil has been a hot issue concerned by people. Stabilization has been widely used to dispose of low-level radioactive hazardous wastes, mixed wastes, and remediation of contaminated sites. Compared with other technologies, solidification/stabilization has many advantages,

¹Department of Structural Engineering, Tongji University, Shanghai 200092, China, corresponding author Y. Xi, e-mail address: yhcnyh@126.com

such as relatively low cost, good long-term stability, good mechanical and structural characteristics, high resistance to biodegradation [1].

In some European countries and America, solidification/stabilization technology has been widely used in restoration works of heavy metal industrial contaminated sites and solid waste landfills, in which the vast majority of projects are based on the use of cementitious binders. Wang et al. [2] stabilized/solidified ground soils of the Project SMiRT (Soil Mix Remediation Technology) site with twenty four binders, and found that MgO is very effective in immobilizing both heavy metals and organics while its mechanical performance is poor. Ahn and Song [3] developed a simple solidification/stabilization method using hydrated lime and water glass for the construction of hardpan on the tailings surface which should be easily applicable in the field, and a tailings cover system with hardpan installed in the field to assess its performance for a relatively long period. Voglar and Lestan [4] used three different cements in combination with five additives as binders, proposed and applied an empirical solidification/stabilization efficiency model to assess the performance of the tested cementitious formulations. The mechanical and pH-dependent leaching performance of a mixed contaminated soil treated with Portland cement, and a mixture of Portland cement (CEMI) and pulverized fuel ash (PFA) have been evaluated. Design charts were also produced from the results of CEMI-PFA study [5, 6]. Galiano and Pereira [7] stabilized/solidified residue containing heavy metals such as Pb, Cd, Cr and Zn from municipal solid waste incineration, using fly ash-based geopolymerization technology, and assessed solidification/stabilization process by means of the mechanical and leaching properties obtained.

With the emergence of environmental problems in recent years, more and more attention was paid to the environment in China. Chinese researchers also conducted a number of tests on solidification/stabilization of heavy metal contaminated soil and achieved certain results in recent years. Xu [8], Zha and Liu [9, 10] studied strength properties, wet and dry cycle characteristics, leaching characteristics and engineering properties of contaminated soil solidified with cement. They found that the strength and leaching characteristics have been significantly improved with cement content increasing. Du et al. [11] studied effects of carbonation on the contaminant leachability and unconfined compressive strength of contaminated soils stabilized with a composition of oxalic acid-activated phosphate rock, monopotassium phosphate and reactive magnesia, and found that carbonation has positive effects on leachability and strength of the soils. Zhang et al. [12] used twelve amendments to immobilize the Pb in soil and assess the stabilization efficiency by toxicity leaching tests, then got three amendments (KH_2PO_4 , KH_2PO_4 with oyster shell powder (1:1), and KH_2PO_4 with sintered magnesia (1:1) having higher remediation efficiencies. Zhang et al. [13] focused on the resistivity and strength of cement cured cadmium contaminated soil, and obtained the quantitative relationship between those parameters. Zhang et al. [14] found that the electrical resistivity method can be used as a non-destructive, economical and continuous way to evaluate the quality of

solidified heavy metal-contaminated soils, through studying the relationship between resistivity and unconfined compressive strength when Pb polluted soil was solidified/stabilized with cement. Wang et al. [15] studied the stress–strain properties of cement solidified copper-contaminated soil, and found that the soil unconfined compressive strength will be significantly reduced when the content of copper ion is greater than 0.3 percent.

In addition to cement-based binders, a lot of works in order to find more cost-effective binders have been made. Moon et al. [16] utilized a novel mixture of calcined oyster shells (COSs) and waste cow bones (WCBs) to immobilize Pb^{2+} and Cu^{2+} in army firing range soils, and a significant reduction of Pb^{2+} and Cu^{2+} leach ability was attained. Du et al. [17] presented a new binder, KMP, composed of oxalic acid-activated phosphate rock, monopotassium phosphate and reactive magnesia. The effectiveness of stabilization using this binder is investigated on soils spiked with Zn and Pb, individually and together.

However, among common studies, the antagonistic mechanism during concomitant contamination by different metals has not been well documented. Michalkova et al. [18] investigated the potential of three Fe- and Mn-nanooxides for stabilizing Cd, Cu and Pb in contaminated soils, using batch and column experiments, adsorption tests and tests of soil microbial activity. This study presents the results of the stabilization of soil simultaneously polluted with Cd^{2+} and Pb^{2+} based on the research of soils contaminated with one kind of ions – either cadmium or lead, aiming to find the optimum ratio of binders.

2. MATERIALS AND METHODS

Materials. Natural soil for the study was provided by a construction site in Shanghai. It was determined as silty clay through the particle size analysis by the densimeter method. The original pH of soil was 6.8. The content of organic matter was 4 wt. % and water – 35.1 wt. % of. The additives used for stabilization were Portland cement, quicklime, montmorillonite, sepiolite, and fly ash, due to their relatively low cost, suitability for the solidification/stabilization (S/S), and ready availability. The Portland cement was provided by Anhui Conch Cement Company (China), the quicklime by the Chinese Medicine Group Chemical Reagent Co., Ltd. (China), the montmorillonite by the Zhejiang Fenghong Clay Chemical Company (China), the sepiolite by the Hunan Liuyang Guangda sepiolite factory (China), the fly ash by the Shanghai Shidongkou Power Plant (China). The compositions of the soil and additives used are presented in Table 1.

$Pb(NO_3)_2$ was used with a purity of 98.0%, containing iron, copper, dilute hydrochloric acid, hydrogen sulfide, chloride. $CdCl_2 \cdot 2.5H_2O$ was used with a purity of 99.0%, containing only trace amounts of iron, lead, zinc, calcium, copper and sulfates.

Table 1

Composition of the materials used in the present study [%]

Oxide	Soil	Cement	Fly ash	Sepiolite	Montmorillonite
Na ₂ O	2.05	–	0.48	–	3.68
MgO	1.91	1.60	6.35	16.1	3.15
Al ₂ O ₃	10.0	6.19	17.2	2.31	13.9
SiO ₂	66.8	22.0	35.3	56.2	51.2
SO ₃	–	2.29	1.75	–	–
K ₂ O	2.09	0.86	0.41	0.21	6.77
CaO	3.92	60.6	33.7	2.87	2.32
TiO ₂	0.64	0.33	0.61	0.12	0.08
Cr ₂ O ₃	0.03	0.03	–	–	–
MnO	0.06	0.10	0.26	0.11	0.03
Fe ₂ O ₃	3.44	3.16	2.27	1.01	1.20
SrO	0.02	0.14	0.11	–	0.02
BaO	–	–	0.18	–	–

Methods. 40 kg soil sample was air-dried and sieved using a sieve with openings 2.5 mm in diameter. 10 dm³ of solution containing 80 g of CdCl₂·2.5H₂O and 717.3 g of Pb(NO₃)₂ was prepared and added to the sieved, air-dried soil to obtain soil contaminated simultaneously with two kinds of ions (DI soil) containing 1000 mg Cd²⁺/kg and 10000 mg Pb²⁺/kg). The content of additives was based on our previous study [22, 23].

Table 2

Composition of samplings with additives [wt. %]

Number	Symbol	Cement	Quicklime	Fly ash	Sepiolite	Montmorillonite
1	C0	–	–	–	–	–
2	C5	5	–	–	–	–
3	C10	10	–	–	–	–
4	C5S2.5	5	2.5	–	–	–
5	C5S3	5	3	–	–	–
6	C5S5	5	5	–	–	–
7	C5F2.5	5	–	2.5	–	–
8	C5F3	5	–	3	–	–
9	C5F5	5	–	5	–	–
10	C5S2.5F2.5	5	2.5	2.5	–	–
11	C5S2.5H2.5	5	2.5	–	2.5	–
12	C5S2.5M2.5	5	2.5	–	–	2.5

C – cement, S – quicklime, F – fly ash, H – sepiolite, M – montmorillonite.

The additives (cement, fly ash, montmorillonites, etc., cf. Table 2)) were added to the artificially prepared DI soil in a certain mass ratio (e.g., 5%, 10%), and water was

added to saturation (40 wt. %). Referring to the standard method [24], the product was transferred to cubic steel molds ($70.7 \times 70.7 \times 70.7$ mm [19, 24], and three samplings were prepared for every additive composition. They were then aged at a constant temperature (20 ± 2 °C) and humidity ($\geq 95\%$) for two days, and tested for unconfined compressive strength after 28 days of standard aging.

Samples taken from these specimens were tested for the heavy metal leachability with the US Environmental Protection Agency (EPA) TCLP (Toxicity Characteristic Leaching Procedure) program. Before the leaching test, the solid samples were first pulverized and sieved using a sieve with openings 9.5 mm in diameter. The powder samples were then mixed with leaching solution at the solution/soil ratio of 20. The leaching solution was prepared by mixing of 5.7 cm^3 of glacial acetic acid, $\text{CH}_3\text{CH}_2\text{OOH}$, with 64.3 cm^3 of 1 mol/dm^3 NaOH, and then diluting the solution to the volume of 1 dm^3 . The suspension was stirred for 18 h and the leachate was isolated by centrifugation. The metal concentration in leachate was determined by the atomic absorption spectroscopy.

3. RESULTS AND DISCUSSION

3.1. UNCONFINED COMPRESSIVE STRENGTH TEST

The unconfined compressive strength of examined samples is shown in Fig. 1. Among 11 specimens, the highest strength was 1.45 MPa for C5F5, the second-highest strength was 1.05 MPa for C10.

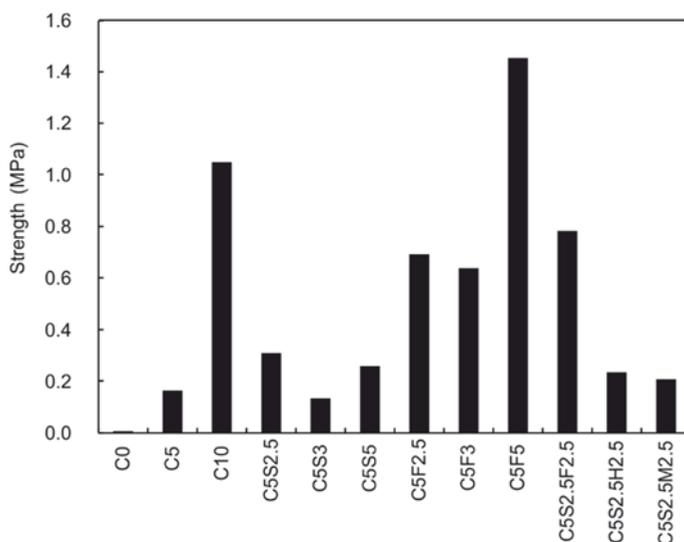


Fig. 1. The strength of cured DI contaminated soil with Cd^{2+} and Pb^{2+} ion mixture; the composition and meaning of symbols are given in Table 2

The strength of the solidified samples was continuously enhanced upon increasing the cement content (cf. samples C0, C5, C10). The comparison of the strengths of C5S2.5 and C5F2.5, C5S3 and C5F3, C5S5 and C5F5 indicate that fly ash has a better curing effect than quicklime when Cd^{2+} and Pb^{2+} coexist in soil. Through the comparison of the strengths of C5S2.5M2.5, C5S2.5H2.5, C5S5(wt.5% cement + 5 wt. % of quicklime), C5S2.5F2.5 and C5F5, it was found that the strengths of specimens cured by montmorillonite, sepiolite and quicklime slightly differ from each other but the strength of specimens cured by fly ash is the highest. It is probably that the active material in fly ash could be triggered by alkali materials. Hydrates forming cementitious pozzolanic products are similar to those formed during the hydration of Portland cement or lime [19].

3.2. LEACHING TEST

The TCLP leaching tests were carried out using soil samples contaminated simultaneously with Pb^{2+} and Cd^{2+} ions (DI samples), and for those contaminated with only one kind of ions (Pb^{2+} or Cd^{2+} , OI samples). The leaching concentrations when either of ions was present [23, 25] or both of them coexisted have been compared. The results are shown in Figs. 2 and 3.

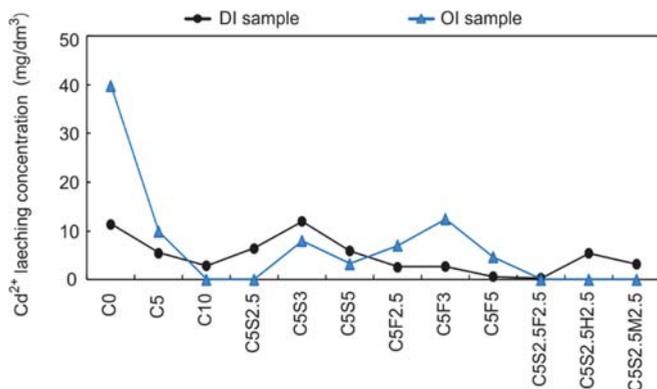


Fig. 2. Leaching concentrations of Cd^{2+} for OI and DI soil samples; the composition and meaning of symbols are given in Table 2

TCLP was used to determine the effect of curing experiments. The upper limit of cadmium ion leaching concentration provided by TCLP [26] and Chinese standards [27] was 1 mg/dm^3 . From Fig. 2 it can be seen that the leaching concentrations of Cd^{2+} in C5F5 and C5S2.5F2.5 specimens are lower than 1 mg/dm^3 for dual ionic contaminated soil, which indicates that fly ash and quicklime have a better curing effect. The leaching concentrations of Cd^{2+} in C5S2.5, C5S3 (5 wt. % of cement + 3 wt. % of quicklime), C5S5 are lower than

C5F2.5, C5F3, C5F5, respectively, indicating that fly ash has a better curing effect than quicklime.

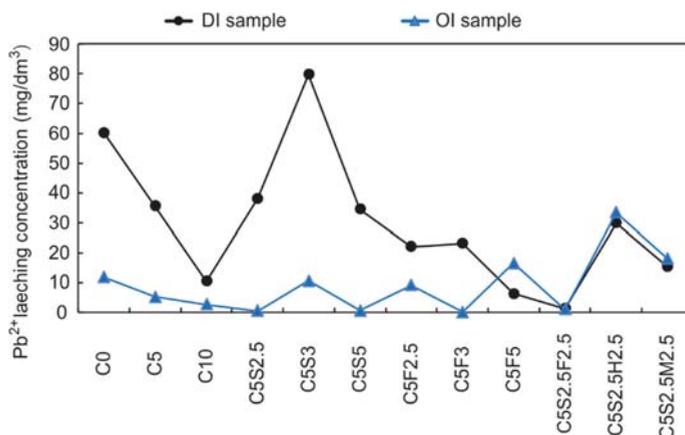


Fig. 2. Leaching concentrations of Pb^{2+} for OI and DI soil samples; the composition and meaning of symbols are given in Table 2

The leaching concentrations of Cd^{2+} in C5S2.5F2.5, C5S2.5M2.5, C5S2.5H2.5 was 0.26 mg/dm^3 , 3.17 mg/dm^3 , 5.44 mg/dm^3 , respectively, indicating that the curing effect of fly ash is better than that of montmorillonite and sepiolite. The leaching concentrations of Cd^{2+} in C0, C5, C10 were 11.41 mg/dm^3 , 5.48 mg/dm^3 , 2.88 mg/dm^3 , respectively, which means that the leaching concentrations of Cd^{2+} decreased upon increasing the cement contents. Through comparing the leaching concentration of SI and DI samples, it can be concluded that the number of groups of binders meeting the leaching upper limit of Cd^{2+} (1 mg/dm^3) reduced from 5 (C10, C5S2.5, C5S2.5F2.5, C5S2.5H2.5, C5S2.5M2.5) to 2 (C5F5, C5S2.5F2.5), suggesting that the presence of Pb^{2+} may increase the curing difficulty of Cd^{2+} .

The upper limit of Pb^{2+} leaching concentration provided by TCLP [26] and Chinese Standards [27] was 5 mg/dm^3 . The leaching concentration of Pb^{2+} in C5S2.5F2.5 specimen was lower than 5 mg/dm^3 for DI sample of soil (Fig. 3). The leaching concentrations of Pb^{2+} in C5S5, C5S2.5F2.5, C5S2.5H2.5, C5S2.5M2.5 were 34.50 , 1.27 , 29.92 , 15.28 mg/dm^3 , respectively, indicating that fly ash has a better curing effect than quicklime, montmorillonite and sepiolite.

Xi et al. [23] conducted a series of experiments to stabilize/solidify soil contaminated with Pb^{2+} using cement, quicklime, fly ash, montmorillonite, sepiolite and their various proportions as additives, and found that C5F2.5S2.5 and C10 had good curing effects. Through comparing the leaching concentration of SI and DI samples, it can be found that the groups of binders meeting the leaching upper limit of Pb^{2+} (5 mg/dm^3) reduced from 5 (C10, C5S2.5, C5S5, C5F3, C5S2.5F2.5) to 1 (C5S2.5F2.5), suggesting that the presence of Cd^{2+} will increase the curing difficulty of Pb^{2+} .

3.3. pH OF THE LEACHATE

Figures 4 and 5 show that when $\text{pH} < 8$ the leaching concentrations of Cd^{2+} and Pb^{2+} gradually decreased upon increasing pH. When $\text{pH} \geq 8$, the leaching concentrations of Cd^{2+} and Pb^{2+} reached a minimum.

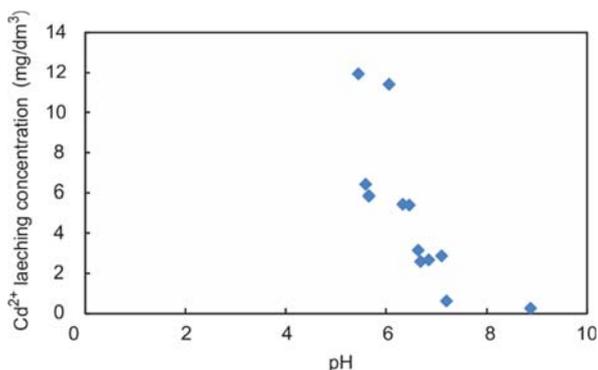


Fig. 4. Dependence of the leaching concentration of Cd^{2+} for DI soil on pH

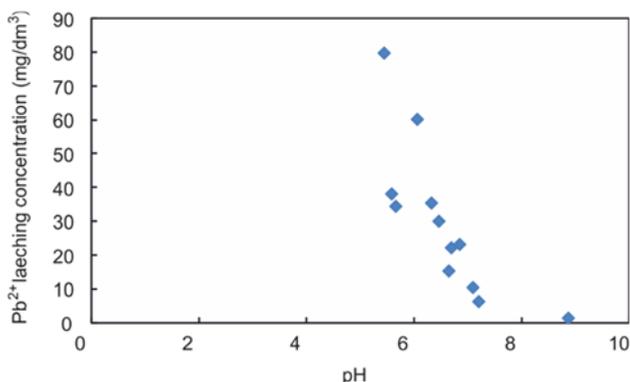


Fig. 5. Dependence of the leaching concentration of Pb^{2+} for DI soil on pH

Among 12 samples, the highest Cd^{2+} leaching concentration was nearly 10 times higher than the lowest one, and the highest Pb^{2+} leaching concentration was nearly 80 times higher than the lowest one. Within a certain range, at low pH, leaching of heavy metal ions increased, while at high pH the leaching of heavy metal ions was reduced. pH played an important role in leachability of Cd^{2+} and Pb^{2+} ions, when curing agent binder was based on cement, lime and fly ash. This conclusion agrees with the results of tests of Kogbara et al.[6] who claimed that the *contaminant leachability is mainly determined by the binder dosage applied and the pH of the leachate*. Different heavy metals have different responses to pH. Thus, in order to achieve a better curing effect, it is necessary to study the behavior of various heavy metals depending on pH.

Cheng et al. [21] studied the influence of adsorption on stabilizing/solidifying effect. They obtained the strong correlation for different heavy metal ions depending on pH. pH of the sorption edge was 5–6.5 for Pb^{2+} , and 6–8.5 for Cd^{2+} . Similarly as in the present paper, the results of this study show that the suitable pH for curing Pb^{2+} and Cd^{2+} was 7–9. These results do not differ markedly, it seems that simultaneous presence of Pb^{2+} and Cd^{2+} ions increased the difficulty of curing.

3.4. MICROANALYSES

The two best cured groups C5S2.5F2.5 and C5F5 were selected to take X-ray diffraction analysis (XRD). The results are shown in Figs 6 and 7.

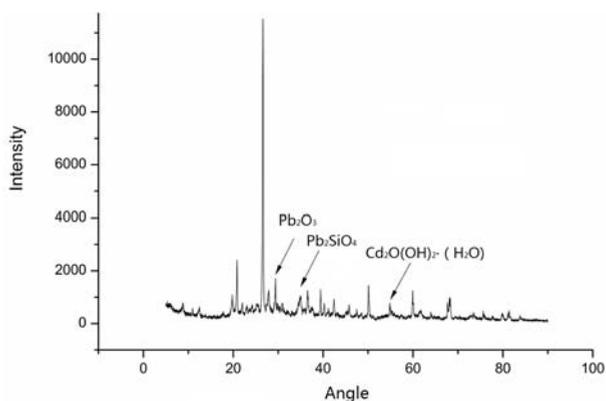


Fig. 6. Results of the XRD analysis of sample C5S2.5F2.5

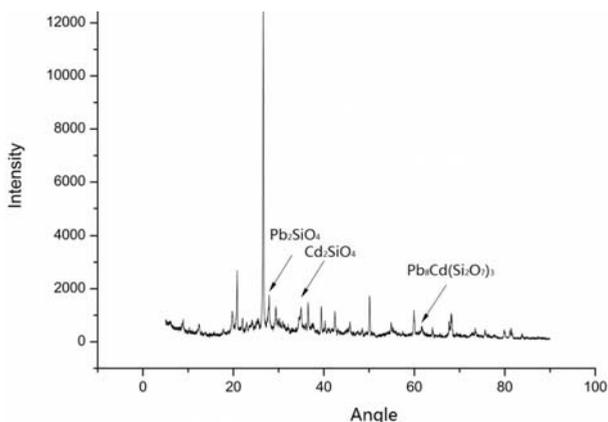


Fig. 7. Result of the XRD analysis of sample C5F5

After Jade 6.5 phase analysis, it can be seen that both specimens contain a lot of SiO_2 being the component of soil. Pb_2O_3 , Pb_2SiO_4 and $\text{Cd}_2\text{O}(\text{OH})_2 \cdot (\text{H}_2\text{O})$ were detected

in the sample C5S2.5F2.5, and Cd_2SiO_4 , Pb_2SiO_4 and $\text{Pb}_8\text{Cd}(\text{Si}_2\text{O}_7)_3$ were detected in the sample C5F5. As is seen, the binder reacted with heavy metal ions to form corresponding compounds in the soil, so as to achieve effective solidification/stabilization effect.

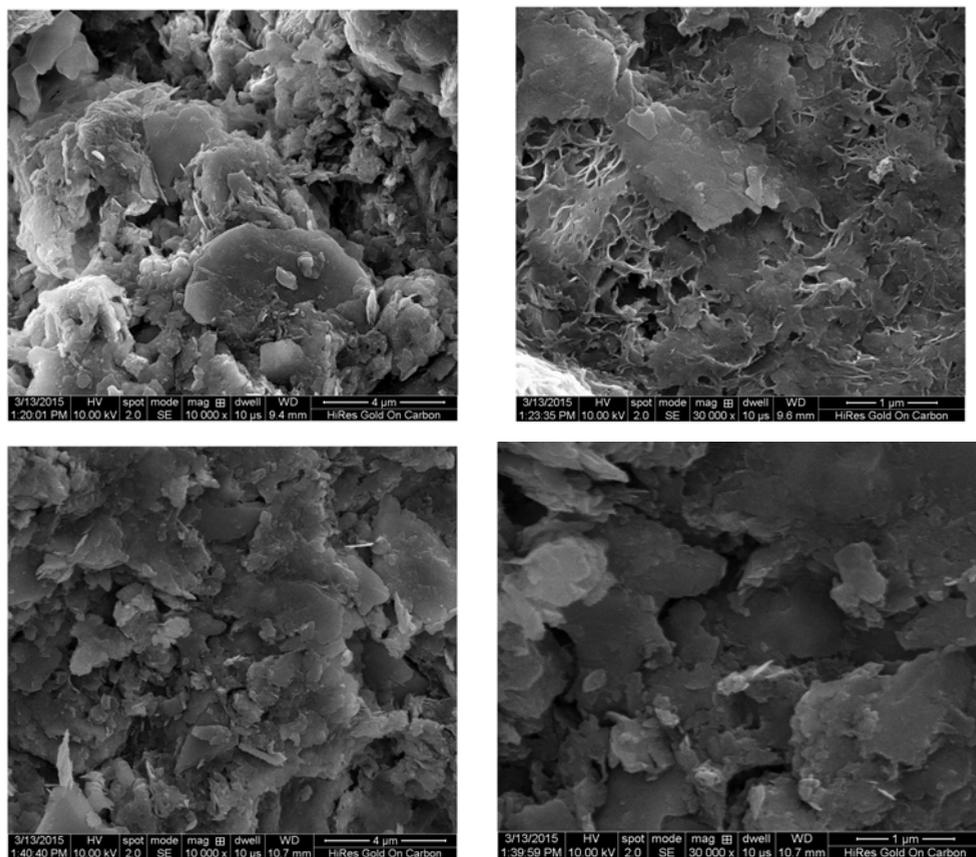


Fig. 8. SEM micrographs of: a), b) sample C5S2.5F2.5, and c), d) sample C5F5

Samples C5S2.5F2.5 and C5F5 were selected to take SEM analysis. The micrographs differing in magnification are shown in Fig 8. A large number of plate structures are present in the sample C5S2.5F2.5, and fine granular materials exist in the structural gaps. In addition, a large number of plate porous structures with a rough surface are observed in Fig. 8b, namely microscopic pores, which have a strong adsorption and parcel effect to the heavy metal ions. The sample C5F5 has a smaller plate structural units and denser structure than the sample C5S2.5F2.5. The structure units are of various shapes, some are regular, but the most are irregular having distinct edges and corners.

This is more conducive to the formation of cemented aggregate package, micro-encapsulated heavy metal ions, thus having a better curing effect, being in agreement with the leaching results. The strength of sample C5F5 is higher than that of sample C5S2.5F2.5. The results indicate that the microstructure and macroscopic mechanical characteristics of specimens C5S2.5F2.5 and C5F5 are uniform.

4. CONCLUSIONS

Compared to montmorillonite, sepiolite and quicklime, fly ash has a better effect to improve the strength of the cured product, probably due to the triggering of the active material in fly ash by alkali materials.

Among 12 soil specimens, only specimen C5S2.5F2.5 met the TCLP leaching threshold of two heavy metal ions, which indicated that in terms of soil contaminated with cadmium and lead, the curing effect of fly ash is superior to that of quicklime, sepiolite and montmorillonite.

Comparing the leaching effect for soil contaminated with one or two ions, it was found that when Cd^{2+} and Pb^{2+} coexisted in contaminated soil, the curing tougher than for Cd^{2+} or Pb^{2+} alone.

pH played an important role in leachability of Cd^{2+} and Pb^{2+} when the curing agent binder was based on cement, lime or fly ash. The leaching concentration of Cd^{2+} and Pb^{2+} gradually decreased upon increasing pH when $pH < 8$. For $pH \geq 8$, the leaching concentration of Cd^{2+} and Pb^{2+} reached a minimum.

The results of XRD and SEM analysis were in agreement with the results of strength and leaching test. Pb_2O_3 , Pb_2SiO_4 and $Cd_2O(OH)_2 \cdot (H_2O)$ were found in the C5S2.5F2.5 sample, and Cd_2SiO_4 , Pb_2SiO_4 and $Pb_8Cd(Si_2O_7)_3$ were detected at the sample C5F5. The results of SEM showed that a large number of plate structures and plate porous structures present in the sample C5S2.5F2.5 and sample C5F5 had a denser structure than C5S2.5F2.5.

ACKNOWLEDGMENTS

This work was financially supported by the Shanghai Science and Technology Support Program, China (13231202300).

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