Research on the solidification of silt with cement and zeolite as additives

Feng Cheng¹,²*, Wang Baotian¹,², Li Shoude¹,²

¹Key Laboratory of Ministry of Education for Geomechanics and Embankment Engineering, Hohai University, Nanjing 210098, China
²Geotechnical Research Institute of Hohai University, Nanjing 210098, China

Abstract: Silt solidification is an important method of silt disposal, and it’s proved to be quick effectiveness and time saving and large in capacity. In recent years, the industrial pollution has made the silt in the lake or the sea rich in harmful elements, such as heavy metal and organic matter, etc., which may strongly influence the solidification effect of silt and trigger secondary pollution. The author proposed a kind of choice, which could effectively decrease harmful elements leaching, based on engineering application. The performances of solidification with different ratio of cement and zeolite, such as unconfined compressive strength, compression coefficient, heavy metal fractions, heavy metal short-term stability and long-term stability are systematically studied. The article confirmed that the addition of the cement and the zeolite increase the strength of the soil and effectively enhance its deformation resistant capability. Furthermore, they significantly decrease the activity of harmful elements and greatly reduce the threat to the environment, which finds an effective solution to the environment problem.

Keywords: silt solidification; strength; heavy metal; organic matter; adsorption

Citation: Feng C, Wang BT, Li SD. Research on the solidification of silt with cement and zeolite as additives. Int J Geol 2016; 1(1): 35–43; http://dx.doi.org/10.18282/ijg.v1.i1.7.

Introduction

The silt is clay mineral sediment that slowly forms in the lake or the sea under the influence of the molecular force and the electrostatic forces between particles. The flood storage capacity of reservoirs decreased due to long-term neglect river training. To solve this, large-scale silt-dredging projects have been undertaken, and vast quantities of dredging silt were produced. The total dredgings of Yangtze River, Yellow River, Poyang and Dongting Lakes reached to 120 million cubic meters from 1998 to 2003. Let alone of the Jiangsu Province, Zhejiang Province and Shanghai.

Whether to abandon the mud to the land or the sea, these traditional treatments would cause tremendous influence on ecological environment, complete damage of natural resources, environmental pollution and etc. The best method of the dredged mud treatment and disposal is the integrated utilization as resource, which was categorized into three systems: the physical treatment, the heat treatment process, and the chemical treatment. One of the best silt treatments is the solidification technology that falls under chemical treatment due to fast process time, cheaper, and ready to be used. And the cement was mainly used as hardener to solidified mud owing to its hydration ability and gelling property.

However, the pollution made this uneconomic. The solidification was often ineffective when the cement was only
material used. With the development of the economy, industrial, and agricultural, wastewater that contained large amounts of heavy metal, organic matter, and other harmful elements that were discharged, cause extreme pollution to the river. However, these harmful materials combined with the mud in the lake. When the dredged silt was used for solidification technology, the harmful elements contained in the mud greatly hindered the hydration of cement, causing the setting time to be delayed, the formation of strength was lagged and the chemical contaminant was unstable, etc.

Domestic and overseas experts and scholars have made great efforts on the research of this issue. The contaminants variously affected the hydration process of cement and the ranking for final setting time values was \( \text{Zn(NO}_3\text{)}_2 > \text{K}_2\text{SO}_4 > \text{NaCl} > \text{mean response} > \text{Cr(NO}_3\text{)}_3 > \text{NaCl}+\text{Cr(NO}_3\text{)}_3, \text{Cd(NO}_3\text{)}_2+\text{Pb(NO}_3\text{)}_2 \) or \( \text{CuCl}_2+\text{Zn (NO}_3\text{)}_2 \) interaction, whereas the ranking for UCS values during hardening was \( \text{Zn(NO}_3\text{)}_2 > \text{CuCl}_2 > \text{NaCl}+\text{K}_2\text{SO}_4, \text{CuCl}_2+\text{Pb(NO}_3\text{)}_2 \) or \( \text{Cd(NO}_3\text{)}_2+\text{Zn(NO}_3\text{)}_2 \) interaction > mean response\(^1\). Zn and ZnO severely retarded the hydration of cement at short ages\(^{2,3}\), and it could probably the zinc which changed fundamental hydrates forming a thin layer of amorphous zinc hydroxide around anhydrous particles\(^4\). The organic matter has also seriously affected the hydration process of cement, and the organic acids producing a pH lower than 9 in the pore solution strongly affected the development of cementing products and almost no strength gain was noted\(^{5,6}\).

The negative effect of the heavy metal and organic matter to the solidification. Problems occurred when cement was used alone, such as delivering bad result and high cost in the point of immature and ineffective method. Therefore, based on the use of the cement, a new additive is required in order to change the condition. However, less study has been carried out to choose the right additive for solidification. If cement was used as the main curing agent, the zeolite was chosen as additive to adsorb the harmful matter in the solidification, ensuring less heavy metal leaching to meet stricter demand of environmental pollution control, while the strength and resistance to deformation were satisfied.

Natural zeolite (clinoptilolite), a crystalline hydrated aluminosilicates of alkali and alkaline earth element, could offer environmental protection through sorption and binding toxic elements since it has extraordinary ion exchange capacities. During the last few years, natural zeolites have been individually tested successfully for treatment of waste water and agriculture\(^{7,8}\). However, there were no studies done in the combination of cement and zeolite used together as additives for solidification in the field of civil engineering.

The aim of the present work is to investigate the use of natural zeolite and cement together as soil additives, and to improve the mechanical properties, deformation resistant capability and the stability of toxic elements.

### Materials and methods

The polluted soil samples were obtained from different locations in Wuxi, Jiangsu Province. The samples were then stored in plastic barrels and thoroughly mixed to ensure uniformity at room temperature for subsequent use in the experiments. The results of experiments conducted to characterize contaminated soil samples are given in Table 1. The heavy metals content of the polluted soil is also presented in Table 1.

| Table 1. Characterization of contaminated soil samples |
|------------------|------------------|------------------|------------------|
| \( w_i/\% \) | \( w_{soil}/\% \) | \( I_p \) | Content of organic matter/\% |
|------------------|------------------|------------------|------------------|
| 45.0 | 23.0 | 22.0 | 4.60 |

In the experiments, zeolite and cement were used as additives. The natural zeolite (clinoptilolite) was supplied from Qingdao, Shandong Province, and the cement with strength of grade #325 was used in the experiments. Twenty samples of cement and zeolite with different additive: soil ratio (Table 2) was mixed thoroughly until the mixture became paste. These samples were brought into polyvinyl chloride (PVC) cylindrical molds at room temperature (22 ±
1℃) in a container. The container was then kept at saturated humidity in a curing room for 7 and 28 days.

Table 2. The heavy metals content of polluted soil samples (mg/kg)

| Metal | As | Cd | Cu | Zn | Pb | Cr |
|-------|----|----|----|----|----|----|
|       | 40 | 10 | 80 | 60 | 38 | 60 |

To choose a sequential extraction procedure that can effectively assess the environmental risk with less effort and time, three most commonly used extraction procedures are compared as shown in Table 3: a five-step method, a four-step method\(^9\) and a short three-step method\(^{10}\). Through a contrastive analysis in Table 4, the short three-step sequential extraction method was used in this work.

Table 3. Additive: soil ratios of cement and zeolite in the samples

| Sample number | Cement (%) | Zeolite (%) |
|---------------|------------|-------------|
| 1             | 10         | 0           |
| 2             | 4          | 6           |
| 3             | 6          | 8           |
| 4             | 15         | 0           |
| 5             | 4          | 6           |
| 6             | 8          | 8           |
| 7             | 20         | 0           |
| 8             | 4          | 4           |
| 9             | 8          | 8           |
| 10            | 6          | 6           |
| 11            | 6          | 8           |
| 12            | 25         | 0           |
| 13            | 4          | 4           |
| 14            | 6          | 8           |
| 15            | 6          | 8           |
| 16            | 8          |             |

Table 4. The comparison between three sequential extraction procedures

| Methods                      | Heavy metal fraction | Extractant                                      | Time | Advantages and disadvantages                                    |
|------------------------------|----------------------|-------------------------------------------------|------|-----------------------------------------------------------------|
| Tessie Five-step method (1979) | exchangeable         | 1mol/L MgCl\(_2\), pH = 7                       | 15 h | Shortcoming: time consuming, laborious, not all the available forms are equally important from the point of view of the environmental risk |
|                              | bound to carbonates  | 1mol/L NaOAc/HOAc, pH = 5                       |      |                                                                  |
|                              | Bound to Fe ± Mn oxides | 0.04mol/L NH\(_2\)OH, 25% HOAc/HCl             |      |                                                                  |
|                              | bound to organic matter | 0.02mol/L HNO\(_3\), 30%H\(_2\)O\(_2\)           |      |                                                                  |
|                              | residual             | HNO\(_3\)-HCl-HF                                |      |                                                                  |
| Ure Four-step method (1993)  | exchangeable         | 0.01mol/L HOAc                                  | 50 h | Shortcoming: time consuming                                     |
|                              | reducible            | 0.1mol/L NH\(_2\)OH·HCl, pH = 2                 |      |                                                                  |
|                              | oxidizable           | 8.8mol/L H\(_2\)O\(_2\)                        |      |                                                                  |
|                              | residual             | HNO\(_3\)-HCl-HF                                |      |                                                                  |
| Maiz Three-step method (1997) | mobile               | 0.01mol/L CaCl\(_2\)                           | 8 h  | Advantages: time saving, labor saving, can assess the environmental risk |
|                              | mobilisable          | 0.005mol/L DTPA, 0.01 mol/L CaCl\(_2\) and 0.1mol/L TEA solution |      |                                                                  |
|                              | residual             | HNO\(_3\)-HCl-HF                                |      |                                                                  |
Research on the solidification of silt with cement and zeolite as additives

The method yielded two aqueous solutions: A1 (mobile fraction) and A2 (mobilisable fraction). The rest of the heavy metals, that in this paper would be considered as residual were removed by a mixture of HNO₃-HCl-HF. The first one was obtained by suspending under agitation, for 2 h at room temperature, the ground soil in a 0.01 mol/L CaCl₂ solution (1:10, soil: solution ratio). The suspension was centrifuged and the supernatant (solution A1) was removed for analysis. The residue raised, the washing solution discharged, and the residue was then ready for the second step. The solution A2 (mobilisable fraction was obtained by suspending under agitation the residue), for 4 h at room temperature, in a 0.005 mol/L DTPA, 0.01 mol/L CaCl₂ and 0.1 mol/L triethanolamine (TEA) solution at pH 7.3 (1:2, soil: solution ratio). The short-term leaching procedure was as follows: A 25 g sample of solidified soil was leached with 100 cm³ of deionized water for 48 h with continuous agitation on a shaker platform as described in ASTM 1311 (TCLP).

The following long-term leaching procedure was taken from NEN 7343 (Determination of leaching of inorganic components from granular materials with the column test). Glass columns of 20 cm length with internal diameter of 5 cm were filled with solidified soil to a height of four times the internal diameter and leached with acidified deionized (acidified to pH 4) with concentrated nitric acid (HNO₃), analytical reagent grade, having a conductivity of 1 μS/cm. The soil was leached upwards from the base of the column with a continuous flow of water (1 cm³ min⁻¹) maintained by a peristaltic pump. Each column was fitted with an acrylic jacket, which allowed leaching to be maintained at a constant temperature. All columns were fitted with pre-filters (pore size 1.5 μm) and membrane filters were also fitted at the top of each column (pore size 0.45 μm). Polyethylene tubing material was used throughout the process. Elute samples were collected over a three-week period.

The heavy metals (Cu, Pb, Zn and Cr) were analyzed by inductively coupled plasma mass spectrometry ICP-MS. The chemical oxygen demand (COD) was analyzed by ultraviolet and visible spectrophotometer (UVS). The pH of solution was also recorded by using pH meter.

Result and discussion

The unconfined compression test

Unconfined compressive strength for different cured batches was tested at the end of 7 days and 28 days during the curing time. Figure 1 showed the value of unconfined compressive strength with the sample number. The maximum compressive strength was for the sample that contains 25% cement and 8% zeolite with a value of 178 N/mm². The results showed that the strength and the dry density of solidified soil were increasing with the addition of cement and zeolite ratio, respectively. It is observed that the ratio of cement was the predominant factor to the strength that increased with time. The increased in curing time for all samples would lead to a better compression resistance. This was due to the slow formation of hydrated calcium silicates. This showed that the more cement used, the higher increasing rate of the strength.

![Figure 1. The value of unconfined compressive strength with the sample number](image-url)
The value of dry density with sample number was also presented in Figure 2. As cement and zeolite ratio increased, the dry density increased. But the increasing rate of dry density was not high as compared to the strength. The reaction of cement hydrolysis and hydration was one of the reasons whereas another reason was the zeolite itself, particularly because of its large specific surface area and low porosity, in which, the pores are filled up by the soil that turns the structure into compact solidification; thus, contributing to the strength development.

![Figure 2](image2.png)

**Figure 2.** The value of dry density with the sample number

### One-dimensional compression test

From the Figure 3, it was observed that the initial void ratio and the compressibility factor decreased as the cement ratio increased. The cement played a remarkable role in improving the compactness and increasing the resistance to deformation of solidification.

![Figure 3](image3.png)

**Figure 3.** The compressibility factor with the sample number

When the cement ratio reached 20%, the compression coefficient decreased rapidly and has reached medium compressibility, which could meet the demand of general engineering filling. This shows that the resistance to deformation may be fully met until the cement ratio reached certain content.

On the other hand, the zeolite admixture has significantly improved the compactness that attribute to the fact that the zeolite, because of its low porosity, effectively filled the pores of the solidified silt.

The study on heavy metal stability of solidified soil with constant 20% cement concentration with various zeolite concentrations (0%, 4%, 6%, and 8%) would be carried out. Cu, Pb, Zn, Cr, COD, and pH value in extracts of the heavy metal will be recorded.

### Heavy metal fraction experiment

Four heavy metal fractions of Cu, Pb, Zn, and Cr are shown in Figure 4 to Figure 7 with different ratio of cement and
zeolite, respectively. It was observed that with the absence of zeolite, the mobile fraction of Cu, Pb, Zn, and Cr accounted for 4.6%, 12.7%, 16.8% and 4.9% of the total amount. This fraction was very important from the point of view of the environmental risk and the mobilisable fraction, which could give an idea of the potentially risky form accounted for 39.9%, 13.4%, 13.7% and 7.2%, much larger than the previous study. However, when the zeolite was added, the environmental risk and the potential risk were significantly reduced, while the mobile fraction of Cu, Pb, Zn, and Cr reduced to 4.3%, 2.9%, 0.0%, and 0.8%, and the mobilisable fraction decreased to 16.6%, 5.6%, 4.7%, and 3.6%, respectively. When compared, the residual fraction of heavy metal increased. The result indicated that the heavy metal activity of Cu, Pb, Zn, and Cr could be greatly reduced with the increased ratio of zeolite. It could also be seen that the availability order of Cu, Pb, Zn, and Cr in the soil follows as below: Cr > Cu > Pb > Zn.

Figure 4. The fraction of Cu with the sample number

Figure 5. The fraction of Pb with the sample number

Figure 6. The fraction of Zn with the sample number

Figure 7. The fraction of Cr with the sample number

Heavy metal short-term leaching experiment

The value of pH and COD with different ratio of zeolite is shown in Figure 8. It can be seen that the value of pH increased from 9.2 to 10.2, while the value of COD reduced to 0. It seemed that the addition of zeolite enhanced the value of pH, and effectively adsorbed the organic matter. The reason that organic matter unable to dissolve in alkaline environment was that, the cement contained high rate of Ca²⁺ which bound with the organic matter.
The percentage of Cu, Pb, Zn, and Cr leached are presented in Figure 8 to Figure 12. As ratio of zeolite increased, the percentage of Cu, Pb, Zn, and Cr leached has reduced from 12.2%, 21.0%, 18.3%, and 6.3% to 2.5%, 3.9%, 0.0%, and 1.6%, respectively. The result indicated that, no matter what the ratio of zeolite is, the percentage of Cu, Pb, Zn, and Cr leached is between the mobile fraction and the mobilisable fraction. Hence, we should understand that not only mobile fraction would endanger the environment; even the mobilisable fraction could cause the same danger. The incorporation of zeolite and cement effectively reduced the heavy metal and organic matter leaching, improved the short-term stability of heavy metal, and greatly reduced the threat to the environment.

Heavy metal long-term leaching experiment

In the heavy metal long-term leaching experiment, the study on heavy metal long-term stability of solidified soil of 20% cement concentration with various concentration of zeolite (0% and 8%) were carried out.

Figure 13 shows the COD of different zeolite addition leachate with time in the long-term leaching experiment.
The result showed during the period from day 0 to day 1, the value of COD has uniform increased and reached its maximum by day 1. But the concentration tends to drop off over time until one steady count at last. The result indicated that the peak and the steady count decreased significantly when 8% zeolite was added; it seemed that the addition of zeolite greatly reduced the COD availability.

![Figure 13. The COD with time](image)

The percentage of heavy metal Cu, Pb, Zn, and Cr leached are shown in Figure 14 to Figure 17. Part of heavy metal leached when one day is over, then the leaching rate slowed down, and finally the leaching came to balance. It seemed that the percentage of Cu, Pb, Zn, and Cr leached were slightly less than the mobilisable fraction. Hence, it has once again proved the Maiz’s conclusion.

By comparing with the short-term leaching experiment, it is found that the percentage of Cu, Pb, Zn, and Cr leached were larger than that of short-term leaching experiment. This could be attributed to the use of acidified deionized (acidified to pH 4) with concentrated nitric acid (HNO₃), which weaken the immobilization of heavy metal by cement.
Conclusion

The addition of cement and zeolite increase the strength of the soil and effectively enhanced its deformation resistant capability. The ratio of cement is the most important factor for the soil’s strength, which proportionally increase with time. On the other hand, the zeolite admixture has also significantly improved the compactness. When the cement ratio reached 20%, the compression coefficient decreased rapidly and has reached medium compressibility that meets the demand of general engineering filling. The heavy metal activity of Cu, Pb, Zn, and Cr could be greatly reduced with the increased ratio of zeolite. It could be observed that the availability order of Cu, Pb, Zn, and Cr in the soil is as follows: Cr > Cu > Pb > Zn. The incorporation of zeolite and cement effectively reduced the heavy metal and organic matter leaching, improved the short-term stability of heavy metal, and greatly reduced the threat to the environment. The result of long-term leaching experiment indicated that the peak and the steady count decreased significantly when 8% zeolite was added. This showed that the addition of zeolite has high effect in reducing the COD availability. Furthermore, the percentage of Cu, Pb, Zn, and Cr leached were slightly lesser than the mobilisable fraction. Hence, it has once again proved the Maiz’s conclusion.

Conflict of interest

The authors declare no potential conflict of interest with respect to the research, authorship, and/or publication of this article.

Reference

1. Tashiro C, Oba J, Akama K. The effects of several heavy metal oxides on the formation of ettringite and microstructure of hardened ettringite. Cem Concr Res 1979; 9(3): 303–308.
2. Hamilton IW, Sammes NM. Encapsulation of steel foundry bag house dusts in cement mortar. Cem Concr Res 1999; 29(1): 55–61.
3. Fernandez OI, Chacon E, Irabien A. Influence of lead, zinc, iron (III) and chromium (III) oxides on the setting time and strength development of Portland cement. Cem Concr Res 2001; 31(8): 1213–1219. doi: 10.1016/S0008-8846(01)00545-2.
4. Arligue G, Grandet J. Etude de l’hydratation du ciment en presence de zinc influence de la teneur en gypse (French) [A study of cement hydration in the presence of zinc: The influence of gypsum content]. Cem Concr Res 1990; 20(3): 346–354. doi: 10.1016/0008-8846(90)90023-Q.
5. Helene T. Influence of the nature of organic compounds on fine soil stabilization with cement. Can Geotech J 2002; 39(2): 535–546.
6. Feng C, Wang BT, Li SD. An experimental study on solidification / stabilization of organic silt. Geotech Eng Tech 2010; 109(3): 142–146.
7. Misaelides P, Godelitsas A. Removal of heavy metals from aqueous solutions using pretreated natural zeolite material: The case of mercury(II). Toxicol Environ Chem 1995; 51: 21–30. doi: 10.1080/02772249509358223.
8. Reyes O, Sanchez E, PelloÂ A, Borja R, Colmenarejo MF, et al. A comparative study of sand and natural zeolite as filtering media in tertiary treatment of waste water from tourist areas. J Environ Sci Health 1997; 32(9–10): 2483–2496. doi: 10.1080/10934529709376697.
9. Ure AM, Quevauviller PH, Munteau H, Griepink B. Speciation of heavy metals in soils and sediments. An account of the improvement and harmonization of extraction techniques undertaken under the auspices of the BCR of the commission of the European Communities. Int J Environ Anal Chem 1993; 51(1–4): 135–151. doi: 10.1080/03067319308027619.
10. Maiz I, Arambarr I, Garcia R, Millán. Evaluation of heavy metal availability in polluted soils by two sequential extraction procedure using factor analysis. Environ Pollut 2000; 110: 3–9. doi: 10.1016/S0269-7491(99)00287-0.