Factors Affecting the Solidification and Stabilization Effect of Hazardous Waste

WANG Luyao1,2,3,4, YAO Sisi1,2,3,4
1 Institute of Land Engineering and Technology, Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi’an 710075, China.
2 Shaanxi Provincial Land Engineering Construction Group Co., Ltd., Xi’an 710075, China.
3Key Laboratory of Degraded and Unused Land Consolidation Engineering, the Ministry of Natural Resources of China, Xi’an 710075, China.
4Shaanxi Provincial Land Consolidation Engineering Technology Research Center, Xi’an 710075, China.

Abstract: Solidification and stabilization is one of the main methods for handling hazardous waste, which can quickly control pollutants, and has the advantages of simple process, low cost and reusable finished products. In this process, the use of curing agents, stabilizers, and other conditions can affect the curing of hazardous wastes and the mechanical properties of the resulting product. This paper summarizes the relevant literature in the past ten years, and describes the effects of waste/binder, water/binder, bulk density, contaminant characteristics, and initial solidification time and carbonization reaction on the stabilization effect of solidification, in order to concretely stabilize the solid waste for solidification. Studies have confirmed that Metal-containing waste may reduce the strength of the final solidified product. Provide theoretical support to meet environmental emission standards and meet corresponding mechanical requirements.

1. Introduction
Solidification and stabilization is a solid waste treatment process before landfilling. It has been applied to the treatment of different types of industrial waste, and is particularly suitable for wastes containing heavy metals [1]. The solidification and stabilization process is to form stable solid by chemical reaction of water, solid waste residue and some dangerous wastes containing water. The solidified / stabilized materials not only solidify the hazardous solid wastes by chemical methods, but also make the harmful components no longer dissolve, diffuse, transfer or otherwise interact with each other, and eventually become harmless or less harmful.

The effectiveness of solidification and stabilization is generally studied through physical and chemical characteristics and microstructure. Strength and leaching resistance are two commonly used indicators [2]. The strength can generally be used as an important parameter to distinguish whether it is stable or not. The shear strength of solid waste without solidification is generally not high, but if it is stabilized into a fast form of cement, its shear strength may be somewhat improved. Leaching resistance, also known as leaching toxicity, is a property that determines the migration and transformation of solidified and stabilized pollutants.

Cement is the most widely studied and most commonly used solidified and stabilized raw material, which is simple, convenient, and low cost. In general, the partial replacement of cement with other materials, such as sulfate-resistant Portland cement (SRPC), white cement, kiln ash, lime, fly ash, silicate, may affect setting time and hydration [3,4]. In addition, there are many factors influencing this process, such as the ratio of waste to binder, the ratio of water to binder, bulk density, characteristics of pollutants, and carbonization reaction.
2. Factors affecting the setting time and strength of cement

2.1 Waste / Binder and Water / Binder Ratio

In most solidified / stabilizing preparations, unconfined compressive strength (UCS) decreases with increasing water addition. After the chlor-alkali plant sludge was stabilized with a commercial curing agent, it was found through durability, unconfined compressive strength, and leaching toxicity tests that the smaller the ratio of sludge to binder, the more stable the physical and chemical properties of the solidified / stabilizing product. Some scholars have found that the increase in water addition leads to a decrease in UCS, which due to the increase in the pore size of the solidified body and the change in the pore structure. When OPC is mixed with fly ash, if the ratio of fly ash / OPC increases, the water demand of the mixture increases, then the intensity decreases [5]. Therefore, in order to ensure sufficient strength, usually, the ratio of waste / binder is 0.4~0.5, and the ratio of water / solid is 0.4~0.6. At the same time, fluidity can be improved by reducing the water / binder ratio or adding a super plasticizer (20 mL/kg cementitious material).

2.2 Bulk density

Increasing the binder content (OPC, OPC + sulfur, OPC + sulfur pitch) will increase the bulk density, because the binder can fill the voids of the solidified sample [7]. Some scholars compared the unit weight and bulk density of the newly prepared sample with the cured sample, and observed the volume change during curing stabilization. As a result, the unit weight of the sample after 28 days of curing was greater than the unit weight of the newly prepared sample. The unit weight of the solidified / stabilizing product increases with the increase of the curing time, which is caused by the hydrated calcium silicate formed by the hydration reaction of the active silica, activated alumina and calcium hydroxide in the adhesive, which continuously fills the voids [8].

3. Pollutant characteristics

The solidified / stabilizing product generally hardens within 2 to 5 days. Studies have found that when a small amount of industrial waste is added to OPC, such as electroplating waste, blast furnace slag, sludge, its strength will be severely lost. Some scholars have studied the effect of waste on strength by adding different amounts of waste to OPC. When a small amount of waste is added, a serious loss of strength is observed. When 1% by mass of Zn, Pb, and Cd-containing metal plating waste is added, the strength does not change much. But if 3% Zn, Pb, Cd metal plating waste is added, the 28-day unconfined compressive strength is reduced by 99% [9].

| Raw material type                      | proportion | Curing time | UCS (MPa) |
|----------------------------------------|------------|-------------|-----------|
| OPC+ W+ Water                          | 3: 4: 3    | 28          | 1.0       |
| OPC+ Fly ash+ W+ Water                 | 8.5: 1.5: 7: 8 | 28          | 2.9       |
| OPC+ blast furnace slag + W+ Water     | 9: 6: 25: 10 | 28          | 3.7       |
| OPC+ Sand+ Water                       | 5: 3: 2    | 28          | 15.2      |

Note: W is a mixed heavy metal waste generated by electroplating, galvanizing, metal fine processing, etc. As shown in Table 1 [10], tests have shown that when different raw materials are prepared in the proportions in the table, the unconfined compressive strength can be maximized in 28 days. Analyzing the type of raw materials, it can be found that when mixed heavy metal waste is added, the unconfined compressive strength decreases significantly, up to 93.4%. When only OPC and mixed heavy metal waste are used as raw materials, the unconfined compressive strength is the lowest, followed by the solidified / stabilizing product containing 6% fly ash, and finally the solidified body containing 12% blast furnace slag. The unconfined compressive strength is 3.7 MPa. This is not only related to the type of material, but also the amount of water added. The amount of water added by OPC+ W and OPC+ Fly Ash + W is 30% and 32%, respectively, while the water addition amount of OPC+ blast furnace slag + W and OPC+ sand is 20%.
4. Hydration reaction and initial setting time

The calcined products of cement are mainly composed of four mineral phases, which are tricalcite (C₃S), oblique wollastonite (C₂S), aluminate (C₃A) and ferrite (C₄AF). The other phases are free lime (CaO) and gypsum (CaSO₄·2H₂O). Among them, tricalcite (C₃S) and attapulgite (C₂S) can undergo a hydration reaction to form hydrated silicate and silicate [11]. Whenlime and gypsum are present, the aluminate hydrate is converted to calcium aluminate hydrate, and the hydrated silicate will decrease as the crystal phase increases.

The hydration of OPC is exothermic. Some scholars have studied it through the isothermal conduction heat method. The heat generation rate is related to the composition, hydration rate, temperature and other factors [12]. When the aluminate and water in OPC are mixed for less than 10 minutes, it can produce aluminum iron calcium hexaaluminate. In a short time, the formation of a gelatinous layer can also be observed. The formation of a gelatinous layer around cement particles is an important step in determining the reaction rate. However, after the waste is added, the process may hinder the penetration of the gelatinous layer due to the possible complexation and precipitation reactions of the components in the waste, and then affect the hydration reaction. For example, the complexation of anionic / cationic reagents with calcium ions on the surface of cement particles will limit the production of CH and C-S-H [13].

In general, the standard initial solidification time and final solidification time of OPC should be not less than 45 minutes and 10 hours, respectively. However, when 10% and 40% PbO were added to the cement slurry, the initial and final solidification times increased to 3~5 h 40 min and 7~27 h 15 min, respectively [14]. Some studies have also found that the addition of Cd²⁺ can significantly shorten the initial setting time, Pb²⁺ will lengthen the initial and final setting time, and reduce the strength of OPC mortar by 30%. Cr does not affect the solidification time.

5. Carbonation

The carbonation reaction that occurs when CO₂ is passed to the curing process can significantly reduce the hydration reaction, and then affect the solidification and strength of the solidified product. Compared with uncarbonated solidified products, carbonized cured stabilized products have higher strength [15]. The carbonation process affects the properties of waste components in cement in many ways.

6. Pore volume

Hardened cement is a porous material with a trimodal pore distribution. The smallest pore system is composed of all tiny pores and gel pores down to 0.01 μm; secondly, when the porous cement gel is filled with water, it is composed of capillary pores with an average diameter of about 0.1 μm. Proportionate; the last is a large pore system consisting of stomata. Darcy's permeability proves the continuity of all pore systems.

Metal elements in the waste can significantly change the pore physical structure. For example, lead in Portland cement will cause the disappearance of 1 μm holes and increase the number of 0.1 μm holes. Various pore sizes appear after the addition of chromium, and small pores with a diameter of 0.01 μm dominate, indicating that the metal participates in the formation of silicates. The addition of mercury has no effect on the pore volume. Micropores dominated after zinc was added, and the volume of mesopores was only 31% [16]. The addition of metal nitrates will reduce the cement hydration by more than 50%, and the total porosity will also decrease. The strength is related to the cement gel / porosity in the cement microstructure and also to the hydration degree. Higher hydration levels correspond to higher levels of cement gel and lower levels of residual porosity and therefore higher strength [17].

7. Conclusion

The addition of waste usually affects the hydration reaction during the solidification and stabilization process, but currently has little effect on the widespread use of this technology, especially when the wastes to be fixed and stabilized are fixed, corresponding quality acceptance standards can be used to make them "suitable" for disposal. However, fundamentally there is a lack of actual data related to the performance of curing stabilized products. Therefore, in the future design of curing stabilization, the following factors should be noted:

a. An in-depth analysis of all test process parameters and conditions is necessary to ensure that the effect of curing stabilization is achieved.

b. The design of curing stabilization equipment and infrastructure depends on the content of waste.

c. Important parameters for assessing curing are strength, setting time and degree of hydration. Mixing the waste material with the cement will have a positive or negative impact on the performance of the cement matrix. Other adhesives are often used to replace OPC. The final compressive strength of the solidified product depends on the quality of the pore structure of the cementitious matrix.
d. Metal-containing waste may reduce the strength of the final solidified product. In the solidified / stabilized matrix, different scrap metals have different effects alone or in combination with the binder (along with other typical metals).

e. The performance of the solidified product can be improved by the following methods: silicon powder, sulfur polymer, CaCl₂, Ca(OH)₂, Na₂SO₄ and K₂SO₄ and other additives.

Acknowledgement
This research is supported by Internal issues of Shaanxi Provincial Land Engineering Construction Group Co., Ltd (DJNY2019-24), and we thank research staffs for their contributions to this work.

References
[1] J.R. Conner, Chemical Fixation and Solidification of Hazardous Waste, Van Nostrand Reinhold, New York, 1990.
[2] C.D. Hills, S.J.T. Pollard, Influence of interferences effect on the mechanical, microstructural and fixation characteristics of cement- solidified hazardous waste forms, J. Hazard. Mater., 52 (1997), 171-191.
[3] F.P. Glasser, Chemistry of cement solidified waste forms, in: R.D. Spencer (Ed.), Chemistry and Microstructure of Solidified Waste Form, Lewis publishers, New York, 1993.
[4] A. Roy, H.C. Eaton, F.K. Cartledge, M.E. Tittlebaum, Solidification/stabilization of heavy metal sludge by a Portland cement/fly ash binding mixture hazard, Waste Hazard. Mater. 8 (1991), 33-39.
[5] F. Lombardi, T. Mangialardi, L. Piga, P. Sirini, Mechanical and leaching properties of cement solidified hospital solid waste incinerator fly ash, waste management, Waste Manage., 18 (1998), 99-106.
[6] A. Roy, E.C. Harvill, F.K. Cartledge, M.E. Tittlebaum, The effect of sodium sulphate on solidification/stabilization of synthetic electroplating sludge in cementious binders, J. Hazard. Mater., 30 (1992), 297-316.
[7] R. Malviya, R. Chaudhary, Study of treatment effectiveness of solidification/stabilization process for waste bearing heavy metals, J. Hazard. Mater. Cyc., 6 (2004), 147-153.
[8] K.L. Knoll, C.B. Andres, Fluidized bed-combustion ash for the solidification and stabilization of a metal hydroxide sludge, Air Waste Manage., 48 (1998), 35-43.
[9] A. Bobrowski, M. Gawlicki, J. Malolepszy, Analytical evaluation of immobilization of heavy metals in cement matrices, Environ. Sci. Technol., 31 (1997), 745-749.
[10] S.L. Lin, W.H. Cross, E.S.K. Chian, J.S. Lai, M. Giabbai, C.H. Hung, Stabilization and solidification of lead in contaminated soils, J. Hazard. Mater., 48 (1996), 95-110.
[11] J. Bensted, in: S.N. Ghosh (Ed.), Advances in Cement Technology, Pergamon Press, Oxford, 1983, 307.
[12] D.J. Lee, A. Fenton, in: T.M. Gillam, C.C. Wiles (Eds.), Stabilization and Solidification of Hazardous and Radioactive Wastes, ASTM STP 1123, ASTM, Philadelphia, 1992, 348.
[13] D.L. Cocke, The binding chemistry and leaching mechanism of hazardous substances in cementitious solidification/stabilization systems, J. Hazard. Mater., 24 (1990), 231-253.
[14] V. Zivica, Hardening and properties of cement-based materials incorporating heavy metals oxides, Bull. Mater. Sci., 20 (1997), 677-683.
[15] A. Roy, F.K. Cartledge, Long term behavior of a Portland cement—electroplating sludge waste form in presence of copper nitrate, J. Hazard. Mater., 52 (1997), 265-286.
[16] S. Goto, D. Roy, Diffusion of ions through hardened cement pastes, Cem. Concr. Res., 11 (1981), 757-775.
[17] C.D. Hills, The hydration of OPC during cement based solidification of toxic waste, Ph.D. thesis, University of London (1993).