Study on properties of steel slag-blast furnace slag-zeolite binder for solidification/stabilization of heavy metals

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Abstract. Steel slag-blast furnace slag-zeolite (SBZ) binder is a low-clinker cement, which can be used for solidification/stabilization of heavy metals. The solidification efficiency of SBZ binder for heavy metal is proved higher than that of OPC cement in most cases but the cost is lower. The solidification/stabilization mechanism of SBZ binder was discussed. Hydrated calcium silicate, hydrated calcium aluminate, ettringite, and zeolite in the system have important contributions to solidification/stabilization of heavy metals.

1. Introduction
With the rapid development of industry, the quantity of hazardous industrial wastes increase significantly [1]. The solid wastes not only occupy land, but also pose a substantial threat to the environment and human health[2-4]. Solidification/stabilization is one of the most important methods to deal with heavy metal contained waste. Because cement-based materials can transform toxic and hazardous contaminants into low-solubility, low-toxicity and low-permeability substances[5], cement solidification has become the most widely used in developed countries in recent decades. Research on solidification/stabilization of heavy metals with ordinary Portland cement is quite mature at present. However, the solidification effect of cement is not so satisfied and the cost is higher [6]. Therefore, it is imperative to develop a cost-effective cementing material to replace cement.

As the main waste residue of metallurgical industry [7], steel slag can be used to prepare cementing materials by combining blast-furnace slag (BFS) and zeolite. In this study, SBZ binder was used to completely replace cement for the purpose of solidifying lead (Pb\(^{2+}\)) and chromium( Cr\(^{6+}\)). The binder pastes containing different concentrations of lead and chromium ion were used to investigate the solidifying effect.

| Ingredient | SiO\(_2\) | CaO | MgO | Fe\(_2\)O\(_3\) | Al\(_2\)O\(_3\) | MnO | f-CaO | SO\(_3\) | Others |
|------------|----------|-----|-----|-----------------|----------------|-----|-------|---------|--------|
| Steel slag | 19.95    | 34.49 | 5.91 | 18.83           | 8.49           | 5.51 | 4.86  | —       | 1.96   |
| BFS        | 39.05    | 30.98 | 8.47 | 13.65           | 2.53           | 1.15 | —     | —       | 4.17   |
| Zeolite    | 57.24    | 8.56 | 2.15 | 11.48           | 15.50          | —   | —     | 0.21    | 4.86   |
2. Experimental materials
Anhydrous sodium sulphate, zeolite and 42.5# ordinary Portland cement are commercially available; desulfurization gypsum is an industrial by-product produced from wet desulfurization of coal-fired power plants; steel slag and BFS slag are provided by Zunhua Zhonghuan Solid Waste Utilization Co.; The chemical composition of the main raw materials is shown in Table 1.

3. Experimental methods

3.1. Raw material pre-treatment
Steel slag and blast furnace slag were ground using a SM-500 test ball mill to a specific surface area of 405 m²/kg and 307 m²/kg, respectively. Modified desulfurization gypsum was prepared by calcining desulfurization gypsum at 800 °C for 1 hour. SBZ binder was obtained by mixing various materials with the proportioning: steel slag 35.38%, slag 35.38%, zeolite 10%, modified desulfurization gypsum 10%, Na₂SO₄ 0.25%, cement clinker 9%.

3.2. Standard curve
Prepare lead nitrate solution and potassium dichromate solution with a certain concentration gradient, and measure it with a UV spectrophotometer. Draw a standard curve with the concentration (C) as the abscissa and the absorption value (A) as the ordinate [8-9].

3.3. Leaching tests
Leaching tests of heavy metals were performed according to HJ557-2010. The absorbance of heavy metal in the leaching solution was determined by ultraviolet spectro-photometry. The concentration of the leaching solution was calculated by the equation fitted by the lead and chromium standard curve determined by the previous experiment. The solidification effect was expressed by solidification rate, which is calculated by the following eq.

\[
\text{Solidification rate} = \frac{H_{\text{in}} - H_{\text{out}}}{H_{\text{in}}} \times 100\%
\]  

Where \(H_{\text{in}}\) is the addition of heavy metals in cementing paste, and \(H_{\text{out}}\) is the detection amount of heavy metals in leaching solution.

4. Results and discussion

4.1. Solidification properties of SBZ binder for lead
The results of the experiment are shown in Figures 1-3.

![Figure 1. Pb²⁺ solidification effect of SBZ binder and cement (24h steaming curing).](image)
As can be seen from Figure 1 that SBZ binder shows higher solidification effect for Pb\(^{2+}\) than cement at lower concentration under the condition of steam curing for 24h. When Pb\(^{2+}\) concentration is 1mg/L, the solidification performance of SBZ binder is much better than cement. The Pb\(^{2+}\) solidification rate of SBZ binder is equivalent to cement when the concentration of Pb\(^{2+}\) is 2 mg/L.

![Graph showing Pb\(^{2+}\) solidification effect of SBZ binder and cement (3d standard curing).](image1)

**Figure 2.** Pb\(^{2+}\) solidification effect of SBZ binder and cement (3d standard curing).

Figure 2 shows the Pb\(^{2+}\) solidification effect of SBZ binder and cement under the standard curing conditions (3d). At low concentration, the solidification rate of SBZ binder is a little lower. When Pb\(^{2+}\) concentration increases to 1.5 mg/L, the solidification performance of SBZ binder is higher than cement.

![Graph showing Pb\(^{2+}\) solidification effect of SBZ binder and cement (28d standard curing).](image2)

**Figure 3.** Pb\(^{2+}\) solidification effect of SBZ binder and cement (28d standard curing).

Figure 3 shows that under the standard curing condition of 28d, Pb\(^{2+}\) solidification effect of SBZ binder is roughly superior to or no lower then cement at wider concentration range.
In brief, the basic rules of curing lead in two kinds of cementing materials under three curing conditions are basically the same, and the solidification effect of SBZ binder is better than ordinary Portland cement.

4.2. Curing properties of SBZ binder for chromium

In view of the fact that the solidification rules of lead with SBZ binder are almost the same under three different curing conditions, solidification experiment of chromium with SBZ binder was conducted under the condition of steam curing for 24h. The chromium contents in were also determined with ultraviolet spectrophotometer. The results are shown in Figure 4.

![Figure 4. Chromium solidification effect of SBZ and cement (24h steaming curing).](image)

As can be seen from Figure 4, when the concentration of chromium is less than 0.2mg/L, the solidification rate of SBZ binder is higher than that of cement. With chromium concentration increased to 0.4 mg/L, the solidification rate of SBZ binder is a little lower than cement. It is proved that the solidification effect of SBZ binder is equivalent to cement.

5. Analysis and discussion of heavy metal solidification mechanism

The solidification effect of SBZ cement is closely related to its hydration products (calcium silicate hydrate, calcium aluminate hydrated, ettringite and zeolite) and material structure.

The basic structure of steel slag, blast furnace slag and zeolite is a three-dimensional network cage structure composed of silicon oxytetrahedron and aluminoxy tetrahedron. This special structure can effectively solidify heavy metals in the form of chemical bonds and/or by physical adsorption [10]. The mechanism of steel slag in hydration reaction is different from that of pozzolanic material. The main products of hydration are C-S-H gel and C-A-H. In addition, Ca(OH)2 is also formed in the system to increase the alkalinity of the slurry, which is conducive to promoting the later hydration reaction. Under alkaline conditions, steel slag and the active ingredients in zeolite react with water and calcium hydroxide to form a calcium silicate and a calcium aluminate hydrates. As the hydration goes, a dense network structure is formed inside the SBZ system. The dense structured may encapsulate heavy metals. In addition, lead and hexavalent chromium ions can be adsorbed by Ca(OH)2, C-S-H etc. to form a hydroxide precipitate, and the cementing material formed by the hydration reaction of the SBZ binder can prevent its dissolution [11].

The solidification process involves a mineral called ettringite \(\{Ca_{6}Al_{2}(SO_{4})_{3}(OH)_{12}\cdot12H_{2}O\}\), which is formed by gypsum and hydration products CAH. Ettringite is a crystal with a columnar structure [12]. The inter-column and intra-slot structure can solidify most heavy metal ions by chemical reaction.
Lead ions and hexavalent chromium ions can enter the ettringite crystal lattice to realize solidification and stabilization.

6. Conclusions

(1) When SBZ binder is used for solidification of different concentrations of lead, the overall performance is better than ordinary Portland cement. As the curing age increases, the ability to solidify lead is enhanced.

(2) When the concentration of hexavalent chromium is less than 0.2 mg/L, the solidification rate of SBZ binder is higher than that of cement. While the concentration of chromium is above 0.2 mg/L, the solidification/stabilization effect of SBZ binder is equivalent to that of OPC cement.

(3) The solidification/stabilization effect of SBZ binder attributes to hydrated calcium silicate, hydrated calcium aluminate, ettringite and zeolite structure material formed in hydration process, resulting in solidification/stabilization effect for heavy metals by chemical bonds and/or physical adsorption.

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