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Effect of $SnSO_4$ on physical and chemical properties of cement

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HIGHLIGHTS

- Two new formations were found in the stannous sulfate cement.
- Early hot temperture hardly affect stannous sulfate cement strength for 60 d.
- Hot temperature can decrease the reducing ability to Cr^{6+}.

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ABSTRACT

Tin sulfate ($SnSO_4$) can change the setting time and strength of cement due to the presence of sulfate (SO_4^{2-}), and can reduce the content of hexavalent chromium (Cr^{6+}) in cement owing to its strong reduction ability. This paper studies the influence of stannous sulfate on physical and chemical properties of cement under different temperature and humidity conditions. Adding $SnSO_4$ to the cement mixer resulted in formation of calcium hydroxo-tin, ($Sn_6O_4(OH)_4$) and $CaSn(OH)_4$. The setting time and strength of cement are obviously enhanced by the addition of stannous sulfate than that of gypsum ($CaSO_4{\cdot}2H_2O$) and stannous chloride ($SnCl_2$), which can be attributed to the coupling of sulfate and stannous ions; Compared with gypsum ($CaSO_4{\cdot}2H_2O$), $SnSO_4$ could hardly produce delayed ettringite (60 days) under hot temperature curing conditions; and water conservation may ensure the full use of stannous sulfate in cement. The total reducing capacity of the $SnSO_4$ on hexavalent chromium (Cr^{6+}) may decrease under hot temperature, but its reduction capacity is still higher than that of ferrous sulfate ($FeSO_4$) under the same conditions. Results from SEM showed that $SnSO_4$ was incorporated into the hydrated cement matrix.

1. Introduction

Tin (Sn) plays an important role in industry and daily life for its plentiful natural resources and physicochemical property. The corresponding tin salts and organic compounds (Sn(II) and Sn(VI)) show great potential in a variety of applications including fuel [1], spices [2], mirrors [3], electroplating [4], aluminum alloy surface oxidation coloring [5]. However, with the development of related industries, a large amount of wastes containing tin elements (Sn(II) and Sn(VI)) have become a new environmental problem [6]. Utilizing these sequestered elemental wastes once again can not only protect ecosystems but also reduce waste of resources and conserve natural resources.

Recently, severs studies have been carried out to illustrate the effect of Sn(II) and Sn(IV) on the performance of cement. Bhatty [7] suggested Sn could mix into the cement with the cement raw material. With the nature of non-volatile (boiling point, 2265 °C), Sn could exist in the process of cement clinker calcining. Kolovos [8] studied that waste ammunition materials (WAM) contain Sn and could increase significantly the burn ability of the cement raw mixture, however, the hydration rate of cement was not affected considerably. Nabajyoti et al. [9] discovered that the addition of Sn could limit the content of free calcium oxide in cement (<0.5%). Kolovos et al. [10] had examined the SnO_2 in the raw mix using a scanning electron microscope (SEM), the results indicated that very little Sn can consolidate with C_3S and none of the Sn combined with C_2S. Hill et al. [11] confirmed Sn(II) chloride could affect the hydration of the Portland cement, retarding form a compound of calcium hydroxo-tin, $CaSn(OH)_6$ [12]. Yue [13] detected that stannous sulfate ($SnSO_4$) added to Portland cement could eliminate the possibility of false set occurring in ground cement. Devesh K. Sharma et al. [14] compared the effect of $FeSO_4{\cdot}2H_2O$ and $SnCl_2{\cdot}H_2O$ on Cr^{6+} reduction in the cement by FTIR and UV–

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Visible Spectra, the effectiveness of reducing agent depends not only the excess molar ratio and the form of additives of $FeSO_4·2H_2O$ and $SnCl_2·H_2O$ could affect the reduction effect of Cr^{6+}. Vaity et al. [15,16] studied the effect of $SnSO_4$ on the compressive strength setting time and reducing ability of Cr^{6+} in cement. And $SnSO_4$ has an advantage in reducing Cr^{6+} and increasing cement strength and setting time than $MnSO_4$ and $NaBH_4$. In addition, $SnSO_4$ can hardly influence the surface of concrete due to its chemical property [17].

$SnSO_4$, combined with tin ions (Sn^{2+}) and sulfate ions (SO_4^{2-}), has the characteristics of sulfates and tin(II) salts, is a common stannous salt relatively. Sulfate (SO_4^{2-}) can hydrate with cement to form ettringite (Aft). The formation and stability of ettringite have close relations with the external temperature and humidity. Lawrence [18] considered that the maximum allowable curing temperature to prevent instability of ettringite was between 65 °C and 70 °C, and AFt could decompose over 70 °C. However, tin (Sn^{2+}) is prone to hydrolysis reaction and oxidation reaction under the condition of hydrogen ions and oxygen ions due to its strong reducing ability [19]. This study evaluates the influence of $SnSO_4$ on the physical and chemical properties of cement, under different temperature and humidity curing conditions. X-Ray Diffraction (XRD), scanning electron microscope (SEM) and energy dispersive spectrometry (EDS) were used to test the hydrate of $SnSO_4$ on cement pastes. The limit and determination of the water-soluble Cr(VI) content of cement with $SnSO_4$, $SnCl_2$ and $FeSO_4$ were also measured under different temperature in this paper.

2. Materials and methods

2.1. Materials

The basic materials used in this paper included Type-I ordinary Portland cement (P.O) 42.5, tin sulfate ($SnSO_4$) (>99.0%, Cl < 0.005%, Fe < 0.005%, insoluble substance < 0.005%), tin chloride ($SnCl_2$) (AR, ≥99.0%), gypsum ($CaSO_4·2H_2O$), iron sulfate heptahydrate ($FeSO_4$) (AR, ≥99.0%), quartz sand, water. The C_3S, C_2S, C_4AF and C_3A, concentrations in the cement were 61.5, 17.7, 9.3 and 8.9 wt%, respectively. The particle-size ranges of quartz sand were 0.625–1.25 mm, 0.315–0.625 mm, and 0.16–0.315 mm, with a grading of 1:4:2. Portland cement contains certain chromium elements (Cr, 18.0 mg/kg) used in water-soluble chromium (VI) content test, specially.

2.2. X-ray diffraction (XRD)

The mineral phases analysis of the hydration of cement with and without $SnSO_4$ (3 wt%) at 28 days and 60 days were estimated at the intensity by the X-ray diffraction analysis (XRD). The XRD was obtained using X-ray diffractometer with Cu-Ka radiation source of the range of 15–85°/2θ using step size of 0.02°/2θ and a scan rate of 1°/2θ per minute.

2.3. Physical properties test

Setting time of cement pastes with different mix amounts of $SnSO_4$, $SnCl_2$ and $CaSO_4·2H_2O$ (0.5%, 1.0%, 1.5%, 2.0%, 2.5%, 3.0%, 3.5%, 4.0%, 4.5% and 5.0 wt% respectively) were measured by referring to ISO 9597:2008 [20], with a manually operated Vicat apparatus, under temperature of 20 ± 2 °C. Cement paste without $SnSO_4$ was prepared and tested following procedures given by ASTM ISO 9597:2008. Because the $SnSO_4$ could be dissolved in water (water-soluble, 330 g/L), water requirement of normal consistency of the cement pastes was carried out following the ISO 9597:2008 before the setting time test.

Flexural strength and compressive strength of cement mortars with different additions of $SnSO_4$, $SnCl_2$ and $CaSO_4·2H_2O$ were measured by referring to ISO 679:2009 [21], by electrically driven flexure testing device and 40 mm × 40 mm Jig for cement compressive strength test machine, under temperature of 20 ± 2 °C. The test groups are provided with Table 1.

To study the effect of $SnSO_4$ on cement under different curing temperature conditions, this paper selected three curing temperatures as the focus, which are 25 °C, 65 °C and 90 °C. The curing method of various test specimen is as follows: after stirring and molding, test molds are covered with a film covering pre-curing at 25 °C for 3 h. For the hot temperature test group (65 °C and 90 °C), test molds are placed in an autoclave for hot temperature curing for 12 h, and heated at a rate of 30 °C/h. Then the test molds were cooled to room temperature for 1d and detached the mold. The specimens were immersed into the saturated lime water to the specified age at 25 °C.

The humidity of the environment can affect the formation and stability of ettringite, which in turn affects the effectiveness of stannous sulfate in cement. To study the effect of $SnSO_4$ on cement under different curing humidity conditions, three different curing methods were used to obtain different humidity environments: dry curing (RH ≈ 50%), seal maintenance (RH ≈ 90%) and soak curing (RH = 100%). Water-cement ratio is 1:2.5, and the forming and curing of the specimens are all completed at 25 °C.

2.4. Mercury intrusion porosimetry (MIP)

Pore volume fractal dimensions of cement with different mix amounts of $SnSO_4$ were established by mercury intrusion porosimetry (MIP). The water-binder ratio was 0.4, and the test temperature is 25 °C. Varying percentages (1.0%, 2.0%, 3.0%, 4.0% and 5.0 wt%) of $SnSO_4$ was added into the cement to make the test specimens. The 20 mm × 20 mm×20 mm specimens molded from the prepared blend were kept in molds for 24 h at room temperature, after that, those specimens were immersed in water at a temperature of 20 °C for 27 days. Then, specimens were knocked at 3–5 mm small particles, and those particles were put into alcohol hydration to stop the hydration. Before to test the pore volume fractal dimensions of specimen, the particles were put in the dryer for 6 h at 105 °C.

2.5. Water-soluble chromium (VI) content test

Hexavalent chromium (Cr(VI)) is water soluble and carcinogenic in nature, and it can mix in cement frequently [22]. $FeSO_4$ was usually employed to remove Cr(VI) [23,24] for its powerful chemical reduction ability. Recently, Rina etc. found that Sn (II) could reduce Cr(VI) in cement [25,26]. The safe disposal of the chromium [Cr (VI)] waste generated from cement-based solidification/stabilization (S/S) to protect human health and environment is an issue of concern [26].

In this study, 1,5-diphenylcarbohydrazide [$(C_6H_5NHNH)_2CO$] were used to test the limit and determination of the water-soluble chromium (Cr) content of cement with $SnSO_4$, $SnCl_2$ and $FeSO_4$ (0, 0.02, 0.04, 0.08, 0.1, 0.12, 0.14, 0.16, 0.18, 0.20 wt%, respectively). To study the effect of curing temperature on the reduction capability of the Cr^{6+} in cement about the $SnSO_4$, $SnCl_2$ and $FeSO_4$, four different temperatures were chosen in this paper, and that were 25 °C, 45 °C, 65 °C, 90 °C. Specifically, the Cr(VI)–Portland cement (Cr, 18.0 mg/kg) was used in this test. The fundamental principle of the test is that the Cr(VI) meets with the $(C_6H_5NHNH)_2CO$ could generate a stable purple complex, by UV–visible spectrophotometer (540 nm, pH = 2.1–2.5). The cement mortar of the test was prepared reference to the stipulation of GB 31893-2015 [27].

In addition, to determine stability of $SnSO_4$ in reducing Cr^{6+}, stability tests of different ages (3, 7, 14, 28, 30, 45, 60 days) were carried out with 0.2 wt% $SnSO_4$, and control experiments with $FnSO_4$ (0.2 wt%) and $SnCl_2$ (0.2 wt%) were performed. The process of stability test is as follows: $SnSO_4$, $FnSO_4$ and $SnCl_2$were mixed into the cement respectively, and stirred by cement mixers for 5 min. Then those mixtures were stored at normal room temperature laboratory. The limit and determination of the water-soluble chromium (Cr) content of cement with $SnSO_4$, $SnCl_2$ and $FeSO_4$ were test reference to the stipulation of GB 31893-2015.

2.6. SEM/EDS

Surface images of cement pastes with varying percentages of $SnSO_4$ at 28 days were conducted on scanning electron microscopes (SEM) under a current of 20 mA and a voltage of 20 kV. Energy dispersive spectrometry (EDS) was also applied in this study. When EDS was used to measure the constitution of hydration products, 20 μm spots were made to analyze the away from phases such as cement, $SnSO_4$ and gypsum to acquire chemical information about the hydration products.

3. Results and discussion

3.1. Phase composition

The XRD analysis of reaction to ordinary Portland cement samples (OPC) with and without $SnSO_4$ was conducted to analyze the different element of cement hydration generated. Correlate hydration reaction products of (A) the OPC and (B) the related cement hydration reaction products using water containing 3 wt% $SnSO_4$ through the XRD test are shown after 28 days in Fig. 1 and after 60 days in Fig. 2.

The XRD patterns of the neat OPC (Figs. 1A and 2A) showed the common products of cement hydration: calcium hydroxide (portlandite) (at d = 1.78, 1.91, 2.60, 3.12 and 4.91 Å), $CaSO_4·2H_2O$ (at d = 2.08, 2.29, 3.03 and 3.95 Å) and ettringite (at d = 2.20, 3.86,