Technical report

Study on the Mechanical Properties and Leaching Mechanism of Cr\textsuperscript{3+} and Cu\textsuperscript{2+} Cured by Basic Magnesium Sulfate Cement

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Abstract

Cr\textsuperscript{3+} and Cu\textsuperscript{2+} can be cured using basic magnesium sulfate cement (BMSC). The influence of compressive strength, water resistance, and leaching characteristics of BMSC-solidified bodies was studied to evaluate the applicability of BMSC cement in industrial solid waste treatment. XRD, SEM, MIP, TG and FTIR were used to analyze the hydration products and microstructures of the solidified BMSC. The results show that when the content of Cr\textsuperscript{3+} or Cu\textsuperscript{2+} accounts for 0.2% to 2% of the molar mass of MgO, the addition of Cr\textsuperscript{3+} and Cu\textsuperscript{2+} inhibits the hydration reaction of BMSC, which causes the compressive strength to decrease, but the lowest strength is still have 27.6 MPa. The Cr\textsuperscript{3+} or Cu\textsuperscript{2+} BMSC-solidified body has good water resistance. The highest leaching concentrations in the solidified product are just 0.221 mg/L and 0.508 mg/L. XRD and microscopic analyses show that four new phases \([4\text{Cr(OH)}_3\cdot\text{Cr}_2\text{H}_2(\text{SO}_4)_4\cdot2\text{H}_2\text{O}, \text{Cr(OH)}_3\cdot3\text{H}_2\text{O}, \text{Cu(OH)}_2\cdot2\text{H}_2\text{O}\) and 3\text{Cu(OH)}_2\cdot\text{CuSO}_4\cdot2\text{H}_2\text{O}\) are formed after adding Cr\textsuperscript{3+} and Cu\textsuperscript{2+}, which shows that BMSC cement can cure heavy metals through chemical reactions. During the solidification process, the interplanar spacing of the 5\cdot1\cdot7 phases changed with varying amounts of copper and chromium ions. It was confirmed that copper and chromium ions entered the 5\cdot1\cdot7 phase crystal structure by atom substitution.

1. Introduction

With the rapidly developing economy, the nuclear industry, smelting, electroplating, mining and other industries produce a large amount of solid waste containing heavy metal ions every year, causing serious pollution to the natural environment. Heavy metal pollutants can exist in the environment for a long time and be transformed from inorganic to more toxic organic states, which can then accumulate along the food chain, posing greater threats to the surrounding environment and human health (Li et al. 2019; Roy and Stegemann 2017; Wang et al. 2015). For the treatment of solid wastes containing heavy metal ions, one of the more mature methods is stabilization/solidification technology (S/S). Curing refers to the process of adding a curing agent to the waste to make it non-flowable or form a solid; stabilization refers to the conversion of harmful pollutants into substances with low solubility, toxicity, and mobility to reduce harmful substances (Edwin 1990; Cho et al. 2016).

Over the past 20 years, cement-based systems are the most widely used and most important cementing materials in developed countries such as the United States, Germany, France, and Belgium. The US Environmental Protection Agency (USEPA) refers to the curing of cement-based materials as the best technology for treating toxic and hazardous substances (Song et al. 2013). Heavy metal ions can enter the cement system through various methods such as adsorption, chemisorption, precipitation, atom replacement, lattice replacement, passivation, surface complexation, and chemical infiltration (Glasser 1997). At present, research on the solid waste of Portland cement systems has become mature.

Tashiro et al. (1979) studied the effects of various heavy metal elements such as Cr, Cu, Zn, Hg, and Pb on the properties of cement. It was found that heavy metals can affect the hydration of cement and inhibit hardening and strength development. Stepanova (1981) reported that copper, cobalt, nickel, manganese, and zinc will react with silicate and aluminate in Portland cement, which has a certain negative effect on compressive strength. Park and Batchelor (1999) showed that the adsorption process has a positive effect on curing Cr\textsuperscript{6+}, Cd\textsuperscript{2+}, Pb\textsuperscript{2+}, and other metals. Chen and Bishop (2009) believe that C-S-H in cement-solidified bodies has the

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same adsorption effect on heavy metals as the amorphous silicone colloid, but this effect is greatly affected by the pH value. When pH > 9, the degree of heavy metal adsorption decreases. The fixation of C-S-H colloids to cations and anions is related to the ratio of calcium to silicon (C/S). The surface of calcium-rich C-S-H colloids has a positive charge and preferentially adsorbs cations. The silicon-rich C-S-H colloids preferentially adsorb anions. Study by Komarneni (1988) and other studies have found that Cu2+ can replace Ca2+ in C-S-H or exist or bind into AFt/AFm in the form of hydroxy carbonate. Similarly, studies by Yousuf et al. (1992) and others have found that Zn2+ can replace Ca in C-S-H to form an oxide or hydroxide containing Ca and Zn. Ivey et al. (1990) believe that Cr3+ can be incorporated into C-S-H by replacing Si2+ in C-S-H. According to these reports, during the curing process of Portland cement, Cu2+ and Cr3+ will enter the hydration products of the cement with atom substitution and lattice replacement, thereby changing the crystal structure of the hydration products (Kakali et al. 1998).

Magnesium gelling material is an effective way to solidify heavy metal ion-containing waste. Saad et al. (2006) reported that magnesium oxychloride cement is a good adsorbent for removing hexavalent chromium from wastewater. The adsorption capacity per gram of adsorbent was 21.4 mg Cr( VI). The best removal conditions were a pH of 5.5, contact time of 15 minutes and temperature of 25°C. Wu et al. (2017a, 2017b) and others used magnesium oxychloride cement to solidify Cr3+ and Ni2+ in industrial wastewater. The results show that the leaching toxicity of the solidified magnesium oxychloride is only 0.110 mg/L and 0.311 mg/L, and the compressive strength of the solidified body reaches 67 MPa, so the mechanical properties are good. Wang et al. (2014) used magnesium phosphate cement to solidify Pb2+, Zn2+, and Cu2+ heavy metal nitrates. It was found that the curing effect of magnesium phosphate cement on heavy metals is Pb2+ > Cu2+ > Zn2+, and the leaching toxicity value is far lower than the national standard. Pb2+ was found to promote the formation of hydration products, and Cu2+ and Zn2+ inhibited hydration.

According to the reports in the above literature, in the process of curing heavy metal ions with magnesium oxychloride cement and magnesium phosphate cement, both Cu2+ and Cr3+ will affect the production of cement hydration products, and the toxic leaching level can be controlled at a lower level. However, these two traditional magnesium cements still have disadvantages. For example, Magnesium phosphate cement is composed of dead-burned magnesium oxide powder, soluble phosphate and additives. According to the current status of the world’s phosphorus resources, the world is currently facing the danger of a shortage of phosphorus resources, and 75% to 85% of the phosphate rock is mined for the production of phosphate fertilizers for agricultural use. The expensive phosphorus resources have caused the cost of magnesium phosphate cement to be too high. Magnesium sulfate cement is composed of magnesium oxide and magnesium sulfate solution. China has abundant magnesium sulfate resources. The reserves of magnesium sulfate resources in salt lake brine alone are about 1.673 billion tons; in seawater, the amount of magnesium sulfate reaches 3570 trillion tons. The brine after bromine extraction and potassium extraction can obtain magnesium sulfate through natural crystallization. Therefore, in terms of cost, BMSC is more economical than magnesium phosphate cement. In addition, magnesium oxychloride cement also has disadvantages such as poor water resistance.

Basic magnesium sulfate cement is a new material developed after magnesium phosphate cement, magnesium oxychloride cement, and magnesium oxysulfate cement (Walland and Provins 2016; Deng 2005). Wu et al. (2017a, 2017b) proposed that after adding suitable additives, such as organic acids and phosphoric acid, to magnesium sulfate cement, the strength and water resistance of the magnesium sulfate cement were improved, a new hydration phase was formed and determined to be Mg(OH)2·MgSO4·7H2O (5·1·7 phase) and named as basic magnesium sulfate cement (BMSC). BMSC has characteristics of rapid hardening, no need for moisture curing, high strength, water resistance, salt resistance, fire resistance, and aging resistance (Wu et al. 2015, 2017a, 2017b). At the same time, BMSC (pH 9 to 10) has lower alkalinity than Portland cement (pH 12 to 13), which avoids the formation of insoluble heavy metal salts. The main hydration product 5·1·7 phase belongs to the monoclinic system, and Mg2+ has the potential to replace heavy metal ions in the structure, while the MgO6 octahedral box cage structure of the 5·1·7 phase has extremely high stability for solidified heavy metal ions (Wu et al. 2014).

Therefore, in this study, BMSC was used to solidify Cu2+ and Cr3+, and the applicability of BMSC as a heavy metal solid waste treatment material was systematically evaluated through mechanical properties, leaching toxicity, softening coefficient, pore structure and other test methods. In addition, by studying the crystal structure of the main hydration phase of BMSC, in order to reveal a certain solidification mechanism, it has evaluated its application potential in industrial waste solidification.

2. Experimental

2.1 Materials
The following are the materials that were used in this study to prepare the test specimens.

1) Light-burned magnesite, LBM: Magnesite was mined in Dashiqiao, Liaoning Province, China, prepared and calcined at 750°C. Its chemical composition is shown in Table 1. The content of active magnesium oxide (a-MgO) is 59.42% by hydration analysis (Dong et al. 2010).

2) Magnesium sulfate heptahydrate: Industrial-grade magnesium sulfate heptahydrate produced by
Yongxing Chemical Plant in Jinnan District, Tianjin City, with 98.5% MgSO₄·7H₂O content is 98.5%. Its chemical composition is shown in Table 2.

3) Copper nitrate dihydrate [Cu(NO₃)₂·2H₂O]: An analytically pure product (AR) of Tianjin Komi Europe Chemical Co., Ltd.

4) Chromium nitrate nonahydrate [Cr(NO₃)₃·9H₂O]: An analytically pure product (AR) of Tianjin Komi Europe Chemical Co., Ltd.

5) Citric acid, CA: An analytically pure product (AR) of Tianjin Komi Europe Chemical Co., Ltd.

2.2 Specimen preparation

In this experiment, the molar ratio of the basic magnesium sulfate cement curing system was α-MgO/MgSO₄=7, and the water-cement ratio of the whole cement slurry was controlled to 0.61. The calculation method of the water-cement ratio is shown in Eq. (1), where the amounts of LBM, anhydrous magnesium sulfate in magnesium sulfate solution and water in magnesium sulfate solution are expressed as \(m_{LBM}\), \(m_{MS}\) and \(m_w\), respectively. The amount of CA (C₆H₆O₆·H₂O) is 0.5% of the mass of LBM, and the amounts of Cu⁺² (or Cr⁺³) are 0.2%, 0.5%, 1%, and 2% of the mass of LBM. First, the MgSO₄·7H₂O was dissolved in deionized water to generate a 25% magnesium sulfate solution (H₂O/MgSO₄=7), and then the weighed LBM, CA and copper nitrate/chromium nitrate were added to the prepared magnesium sulfate solution and stirred mechanically to form the BMS cement slurry. Finally, the mixed MOS cement slurry was poured into a 20×20×20 mm stainless steel mold. Before being separated from the mold, it was sealed and cured with plastic wrap at 20±2°C and 50±5% relative humidity. After being cured for 24 hours, it was released from the mold and cured naturally in air. For ease of description, the various samples were labeled as Cr⁺ⁿ and Cu⁺ⁿ, where n represents the percentages of Cu⁺² or Cr⁺³. For example, the BMSC sample represented by Cr0.2 has a Cr⁺³ addition amount of 0.2%. The soaked samples were labeled as Cr⁺ⁿw” and “Cu⁺ⁿw”. For example, Cr₁w indicates the test group after the Cr1 is cured for 28 days and the sample is soaked in water for 30 days. See Table 3 for the detailed mix ratios used in this experiment.

\[
W = \frac{m_w}{m_{LBM} + m_{MS}}
\]  

2.3 Sample analysis

2.3.1 Compressive strength.

Compressive strength was determined according to Chinese standard GB 175-2007 for ordinary Portland cement. The compressive strengths of the BMSC samples after curing for 1 d, 3 d, 7 d, and 28 d were determined on a press at a constant loading rate of 2.4 kN/s.

2.3.2 XRD and SEM analyses.

The crystalline phase of the BMSC hydration product was tested by x-ray diffraction (XRD) analysis (Rigaku D/MAX 2500PC) under Cu2α radiation (\(\lambda=0.15419\) nm) and 30 kV accelerating voltage, and the sample powder (D₉₀<45μm) was analyzed under conditions of 2θ in the range of 5 to 70°. The detector uses a scintillation counter. The sample holder type is non-reflective plexiglass, the current is 200 mA, the gap width is 1 mm, and the scanning speed of the 0-2θ link continuous scanning mode is 2°/min. The crystal type was determined by comparing the sample pattern to the standard diffraction peak in the “Highscore” software. “Topas5.0” software was used to calculate the phase composition of the 5:1:7 phase.

A scanning electron microscope (SEM, JSM-5610LV)
was used to characterize the microstructure of the BMSC samples cured in air on the fractured surface after gold plating. The thickness of the gold spray was 20 nm, and the test voltage of the SEM was 15 kV.

2.3.3 Leaching toxicity test
Leaching toxicity analysis of 3 d, 7 d, and 28 d samples cured by BMSC curing system was completed in accordance with the Chinese standard (HJ557 2010). In this experiment, the sample powder was sieved. The extracted sample is powder that can pass through a 3 mm sieve but not a 0.5 mm sieve, and then a 20 g dry sample was reweighed and placed in a 2 L extraction bottle. The volume of deionized water was calculated according to a liquid-solid ratio of 10:1 and fixed on a horizontal shaker (CHA-S) to adjust the oscillation frequency to 110±10 cycles/min with an amplitude of 20 mm. After shaking at room temperature for 8 hours, the extraction bottle was removed, and the sample was centrifuged after standing for 16 hours, and finally filtered to obtain an extract.

The leaching of heavy metal ions was measured with an inductively coupled plasma spectrometer (ICAP6300).

2.3.4 Softening coefficient
According to the Chinese standard for magnesite cementing material (WB/T 1023 2005), the softening coefficient formula of the BMSC-solidified body is as follows:

\[ K = \frac{f}{F} \]  

In the formula, \( K \) is the softening coefficient, \( f \) is the strength of the test piece after being soaked for 30 days and \( F \) is the reference sample strength of the test piece being cured for 28 days.

2.3.5 FTIR
After the specimens were cured for 28 days, the samples were crushed, ground into powder, and mixed with KBr. Fourier transform infrared (FTIR) tests were performed on the samples using a Fourier Infrared Spectrometer (Nicolet 6700), ranging from 400 to 4000 cm\(^{-1}\). Scanning on the samples using a Fourier Infrared Spectrometer (FTIR) tests were performed were crushed, ground into powder, and mixed with KBr.

2.3.6 TG-DSC
After 28 days of curing, the sample was crushed and ground into a powder, and the sample was heated from 30°C to 1000°C at a rate of 10°C/min using a STA449 F3 synchronous thermal analyzer, and the thermogravimetry was recorded according to differential scanning calorimetry (TG) curve.

2.3.7 MIP
The porosity and pore distribution of the BMSC cured in air for 28 days were measured by the mercury intrusion method (MIP) using an automatic mercury intrusion meter (Auto Pore IV 9500). The pressure control range of the instrument is 1.36 kPa to 227 MPa, in which the contact angle of mercury with the sample is 135°, and the measurable pore size range is 5 nm to 1100 μm. For the cylindrical hole model, the size and pressure of the holes that mercury can enter are consistent with the Washburn equation. By controlling different pressures, the volume of mercury pressed into the pores can be measured, so that a cumulative distribution curve or a differential curve corresponding to the pore diameters with different pressures can be obtained.

For drying the MIP test samples, acetone was first used to terminate the hydration of the samples, which were then taken out and dried in vacuum drying oven at 50°C for 3 hours.

3. Results and discussion

3.1 Compressive strength of the BMSC curing system
The compressive strength of a cured body is an important index in evaluating the stability of the cured body. This article refers to the Chinese standard (GB 14569.1 2011) applicable to cement-based heavy metal solidified bodies that are used as materials for the final treatment of heavy metal waste. This standard stipulates that for cement solidified body used to solidify heavy metal wastes, the compressive strength of the cement solidified body sample should not be less than 7 MPa after curing and fully hardened in a greenhouse and airtight conditions.

Figure 1(a) shows the changes in the compressive strength of the BMSC curing system under the influence of different amounts of Cr\(^{3+}\). It can be found that the compressive strength of BMSC decreases with increasing concentrations of Cr\(^{3+}\). Its early strength decreased the most. By comparing the strength after 1 d, Cr1 (0.9 MPa) was reduced by 94.5% compared to the control (16.3 MPa), while the 1 d strength of Cr2 was lower than the minimum value detected by the press. For the samples cured for 28 days, the lowest strength Cr2 (42.2 MPa) was reduced by 30.8% compared to the control (61 MPa).

The early strength of the sample after Cu\(^{2+}\) addition was significantly reduced. When the amount was increased to 0.5%, it did maintain strength after 1 d. When Cu\(^{2+}\) was increased to 2%, the strength could not be measured after three days of curing. For samples cured by adding Cu\(^{2+}\) for 28 days, using Cu2 (27.6 MPa) as an example, its strength was 62.7% lower than the control (74 MPa).

Although the addition of copper or chromium ions reduces the mechanical properties of the cured body, the compressive strength (Cr2 and Cu2) of the 28 d BMSC curing system far exceeds the 7 MPa required by the Chinese standards for cement cured bodies.

3.2 Crystal composition of BMSC curing system
Figure 2 shows the x-ray diffraction results of BMSC cured for 28 days with the addition of Cu\(^{2+}\) and Cr\(^{3+}\).
Figure 2(a) shows that the main hydration products of BMSC are the 5·1·7 phase, SiO$_2$, Mg(OH)$_2$, MgCO$_3$, MgO, among which SiO$_2$, MgCO$_3$ and MgO are all from LBM (Wu et al. 2019). In addition, the residual Cr(NO$_3$)$_3$·9H$_2$O was found in Cr1 and Cr2 at high concentrations. The addition of Cr$_3^+$ produced two new crystalline phases, Cr(OH)$_3$·3H$_2$O (main diffraction peaks are 18.202°, 19.365° and 26.668°) and 4Cr(OH)$_3$·Cr$_2$H$_2$(SO$_4$)$_4$·2H$_2$O (main diffraction peaks are 17.634°, 28.943° and 29.333°).

By observing the main diffraction peak of the 5·1·7 phase around 18° in Fig. 2(b), it can be found that the diffraction peak of the 5·1·7 phase shifts to the left as the amount of Cr$_3^+$ added increases. This indicates that Cr$_3^+$...
has a lattice replacement effect in BMSC, which may replace Mg$^{2+}$ in the 5·1·7 phase, and achieve potential equilibrium with other ions. Ion replacement requires similar ions. The ionic radius of Cr$^{3+}$ (0.0615 nm) is similar to that of Mg$^{2+}$ (0.072 nm), so replacement can occur.

Figure 2(c) shows the BMSC crystal phase composition under the influence of Cu$^{2+}$. Similarly, the addition of Cu$^{2+}$ also caused BMSC to generate two new crystalline phases, Cu(OH)$_2$·2H$_2$O (main diffraction peaks are 13.263°, 26.956° and 35.774°) and langite, 3Cu(OH)$_2$·CuSO$_4$·2H$_2$O (Frost et al. 2010; Zittlau et al. 2013), with the main diffraction peaks being at 11.263°, 24.993° and 36.041°. Under the same ion content, the copper ion-containing cured body has the raw material Cu(NO$_3$)$_2$·2H$_2$O residue earlier than the chromium ion-containing cured body, which indicates that the ability of BMSC to replace copper ions is less than that of chromium ions. With the addition of Cu$^{2+}$, the intensities of the diffraction peaks of the 5·1·7 phase and Mg(OH)$_2$ became weaker, and the diffraction peaks of MgO increased. The main diffraction peak of the 5·1·7 phase was observed at 18°. At Cu0.2, a new small diffraction peak of the 5·1·7 phase appears. As the doping amount continues to increase, the small peak becomes larger and the original main peak disappears at Cu0.5, and the intensity of the new diffraction peak begins to decrease at Cu1 and greatly decreases at Cu2, indicating that Cu$^{2+}$ also showed a lattice substitution phenomenon. The ionic radius of Cu$^{2+}$ (0.073 nm) is very similar to that of Mg$^{2+}$ (0.072 nm), which provides a basis for Cu$^{2+}$ to undergo atomic substitution.

Table 4 shows the quantitative results of the phases after Topas5.0 fitting analysis. The addition of Cr$^{3+}$ or Cu$^{2+}$ makes the concentration of Mg(OH)$_2$ decrease first and then increase. When the content of Cr$^{3+}$ or Cu$^{2+}$ was increased to 0.2%, Cr0.5 (6.35%) and Cu0.5 (4.49%) were decreased by 2.59% and 4.45%, respectively compared with the control group (8.94%). With the further increases, the content of Mg(OH)$_2$ increased significantly, where Cr2 (15.65%), Cu2 (22.53%) increased by 6.71% and 13.59%, respectively, compared with the control group. The MgO content in the solidified body can also reflect the degree of hydration of BMSC. According to the results in Table 4, with increases of Cr$^{3+}$ or Cu$^{2+}$, the MgO content also further increased. Cr2 (23.56%) and Cu2 (58.09%) increased by 8.27% and 43.61%, respectively, compared with the control group (15.29%). This indicates that the solidified Cu$^{2+}$ BMSC sample had lower hydration at 28 days. The content of 5·1·7 phase in all samples showed a decreasing trend. Cr2 decreased by 14.51% compared with the control group, and Cu2 decreased by 51.77% compared with the control group. This is also one of the reasons for the decrease in the mechanical properties of the cured body.

### Table 4 Phase composition of the BMSC at 30 days with Topas5.0.

| Samples | 5·1·7 phase Mass fraction (%) | SiO$_2$ | Mg(OH)$_2$ | MgO | MgCO$_3$ |
|---------|-------------------------------|--------|------------|-----|----------|
| Control | 68.93                         | 0.92   | 8.94       | 15.29 | 5.92    |
| Cr0.2   | 66.66                         | 1.08   | 6.35       | 18.13 | 7.78    |
| Cr0.5   | 62.71                         | 1.32   | 7.49       | 17.81 | 10.68   |
| Cr1     | 57.51                         | 1.16   | 12.23      | 19.46 | 9.64    |
| Cr2     | 54.42                         | 1.18   | 15.65      | 23.56 | 5.19    |
| Cu0.2   | 65.60                         | 0.84   | 4.49       | 25.47 | 3.60    |
| Cu0.5   | 63.83                         | 1.05   | 7.02       | 21.71 | 6.39    |
| Cu1     | 50.82                         | 0.74   | 17.47      | 25.84 | 5.14    |
| Cu2     | 17.16                         | 0.45   | 22.53      | 58.09 | 1.76    |

3.3 Microstructure of the BMSC curing system

Figure 3 shows the fracture surface morphology of the control sample and BMSC doped with Cu$^{2+}$ and Cr$^{3+}$. The main structure of the control sample shows many 5·1·7 phase crystals with a needle-like structure (Wang et al. 2018a, 2018b). By observing Fig. 3(b), it can be found that the structure of the hydrated product after adding Cr$^{3+}$ is still 5·1·7 phase needle-like crystals, but the whiskers of the 5·1·7 phase are significantly shorter and the crystals are shorter. There are many incompletely hydrated burr clusters on the surfaces of the whiskers. Observing Fig. 3(c), it was found that the sample had more burr floe and the content of 5·1·7 phase whiskers was significantly reduced. Since cement hydration occurs from inside to outside, by contrasting the SEM image of a solidified 28 d sample at 500 times magnification, it can be clearly found that the degree of hydration of the cement shows a relationship: Control-Cr2-Cu2. This is consistent with the quantitative results of Topas5.0 in Table 4.

The mechanical strength of BMSC depends on the type of hydration product, the porosity, and pore size distribution. Figure 4(a) shows the cumulative porosity of BMSC doped with Cr$^{3+}$. In combination with Table 5, it can be seen that when 0 to 0.5% Cr$^{3+}$ is added to BMSC, the average pore size is 41.16 nm, which is 12.27 nm lower than that of the control group, and the proportion of 10 nm to 100 nm pores remains above 80%. When the content of Cr$^{3+}$ continues to increase to 1% and 2%, the average pore diameters increase to 82.38 nm and 65.59 nm, respectively. Observing Fig. 4(c), we can find that the peak of the most probable pore diameter of the BMSC shifts to the left, and the most likely pore diameter gradually decreases. With the addition of chromium ions, the peak diameter of the most desirable pore diameter decreases. The pore structure of BMSC was
originally many intercrystalline pores (10 nm to 100 nm) of the 5·1·7 phase (Wang et al. 2018a, 2018b), and the inhibition of the 5·1·7 phase generation caused the increase in the number of gel pores. This indicates that the crystallization process of BMSC cement is decreasing. The sample produced two most probable pore peaks starting from Cr1. Combined with the quantitative analysis results in Table 4, the most probable pore peaks around 400 nm are the pores between Mg(OH)2 and MgO particles that have significantly increased.

Figure 4(b) shows the cumulative porosity of BMSC doped with Cu2+. The pore size distribution is shown in Table 5. With the addition of Cu2+, the average pore size of BMSC gradually increases. For example, the average pore size of Cu2 is 173.59 nm, which is 120.16 nm larger than that of the control group. The ratio of pores larger than 100 nm in BMSC increased, and the ratio of pores between 10 nm and 100 nm decreased. Taking Cu2 as an example, the ratio of pores larger than 100 nm (65.4%) in Cu2 increased by 47.6% compared with the control group (17.8%). The ratio of pores between 10 nm and 100 nm (34.5%) decreased by 47.1% compared with the control group (81.6%). The cumulative porosity of the control group (from 310 nm to 5.5 nm) was about 28.5%, while the cumulative porosity of Cu2 decreased to 23.9%. At the same time, it can also be found in Fig. 4(d) that the addition of copper ions makes the most probable pores of BMSC continuously decrease, and the height of the most

| Samples | Average pore diameter (nm) | ≤10 nm (%) | 10 to 100 nm (%) | >100 nm (%) |
|---------|---------------------------|------------|-----------------|------------|
| Control | 53.43                     | 0.6        | 81.6            | 17.8       |
| Cr0.2   | 40.07                     | 1.1        | 91.2            | 7.7        |
| Cr0.5   | 41.16                     | 0.5        | 82.2            | 17.3       |
| Cr1     | 82.38                     | 0.5        | 48.2            | 51.3       |
| Cr2     | 65.59                     | 0.4        | 64.3            | 35.3       |
| Cu0.2   | 56.55                     | 0.3        | 79.5            | 20.2       |
| Cu0.5   | 50.26                     | 1.2        | 73.9            | 24.9       |
| Cu1     | 95.34                     | 0.1        | 47.9            | 52         |
| Cu2     | 173.59                    | 0.1        | 34.5            | 65.4       |

Fig. 3 Fracture surface morphology of the BMSC curing system at 28 days; (a): control, (b): Cr2 (c): Cu2.
probable pore peak decreases. Starting from Cu1, the two most probable pore peaks appear. This is due to the increasing number of Mg(OH)₂ and MgO particles, and more pore peaks between the two. Also, the degree of hydration of BMSC is lower, leaving a large number of pores in the water molecules after they disappear. Therefore, the highest possible peak height between 10 and 100 nm originally belonging to the 5·1·7 phase is reduced.

3.4 TG-DSC and FTIR of BMSC curing system
Figure 5 shows the TG-DSC image results of Cu2 and Cr2. The DSC results of BMSC are consistent with the results reported by Wu (2014) and others. The temperatures of 93°C and 146°C are the endothermic peaks of 5·1·7 phase crystal water decomposition. At 93°C, the 5·1·7 phase loses two crystal waters and decomposes into 5·1·5 phases. Then, at 146°C, two waters are decomposed into 5·1·3 phases, and then at 146°C to 250°C, it decomposes into anhydrous magnesium sulfate phase,
The BMSC sample spiked with Cu\(^{2+}\) in the amount of the 5·1·7 phase was reduced. 93°C, 146°C, and 375°C all decreased, which proved that decomposition peaks of the 5·1·7 phases represented by desulfurization peak of MgSO\(_4\). Cr\(^3+\), the hydration products are consistent. Observing that of the control sample. This shows that after adding Cu\(^{2+}\) was added, the endothermic peak of the 5·1·7 phase in the Cu\(^{2+}\)-added sample was basically the same as that of the control sample. This shows that after adding Cr\(^3+\), the hydration products are consistent. Observing DSC images, it was found that the endothermic decomposition peaks of the 5·1·7 phases represented by 93°C, 146°C, and 375°C all decreased, which proved that the amount of the 5·1·7 phase was reduced.

The overall weight loss of Cr2 (weight loss 42.8%) in the BMSC sample spiked with Cr\(^{3+}\) in Fig. 5(a) was increased by 1.7% compared with the control group (weight loss 40.1%). The weight loss rate of the 5·1·7 phase in the Cr\(^{3+}\)-added sample was basically the same as that of the control sample. This shows that after adding Cr\(^{3+}\), the hydration products are consistent. Observing DSC images, it was found that the endothermic decomposition peaks of the 5·1·7 phases represented by 93°C, 146°C, and 375°C all decreased, which proved that the amount of the 5·1·7 phase was reduced.

The overall weight loss of Cu2 (weight loss 36.4%) in the BMSC sample spiked with Cu\(^{2+}\) in Fig. 5(b) was reduced by 3.7% compared with the control group (weight loss 40.1%). It was shown that the weight loss rate of the 5·1·7 phase in the Cu\(^{2+}\)-added sample was lower than that of the control sample. In the DSC results, after Cu\(^{2+}\) was added, the endothermic peak of the 5·1·7 phase decreased, and the endothermic peak at about 410°C increased. This proves that the addition of Cu\(^{2+}\) will delay cement hydration, inhibit the formation of the 5·1·7 phase, and generate more Mg(OH)\(_2\).

Figure 6 shows the infrared spectrum of BMSC curing 28 d. The addition of heavy metals changes the vibration frequency of the following bonds: the absorption bands at 538 cm\(^{-1}\) and 1100 cm\(^{-1}\) correspond to the tensile and deformation vibrations of SO\(_3\)-O, respectively. 1438 cm\(^{-1}\) corresponds to the antisymmetric tensile vibration band of carbonate ions; the absorption bands of 647.3 cm\(^{-1}\) and 3417 cm\(^{-1}\) correspond to the deformation and tensile vibrations of HO-H in crystalline water; and 3701 cm\(^{-1}\) corresponds to the tensile vibration absorption band of the MgO-H bond. FTIR results show that the addition of heavy metals does not cause a change in the chemical structure of BMSC, but it affects the environment around the chemical bonds and changes its vibration frequency. Therefore, it can be inferred that Cu\(^{2+}\) and Cr\(^{3+}\) entered the BMSC by chemical bonding.

### 3.5 Water resistance

Cement solids containing heavy metals must maintain good mechanical properties in humid environments. The US Environmental Protection Agency (USEPA) recommends that the minimum compressive strength of the cured product after immersion in water for 28 days should not be less than 0.35 MPa (USEPA 1992).

Figure 7 shows the changes in the compressive strength and softening coefficient of the BMSC-solidified body after 28 days of curing after water immersion for 7 days and 30 days. Observing Fig. 7(a), it can be found that when the content of Cr\(^{3+}\) is 0 to 0.2%, the compressive strength after immersion in water for 30 days slightly decreases. Using Cu0.15, which has the largest decrease, as an example, the softening coefficient is 0.897. When the content of Cr\(^{3+}\) is increased to between 0.5% and 2%, the solidified BMSC still has good compressive strength. Focusing on Cr1 with the best water resistance as an example, the softening coefficient after immersion for 30 days reached 1.034, which is an increase of 13.9% compared with the control group (K=0.908).

Cu\(^{2+}\)-added BMSC-solidified bodies showed similar patterns. In Fig. 7(b), when the Cu\(^{2+}\) content was increased from 0 to 0.5%, its softening coefficient did not change significantly compared with the control group. When the Cu\(^{2+}\) content continued to increase, the softening coefficient of the cured body was significantly increased. The softening coefficient (K=1.064) of Cu1 for 30 days was increased by 18.6% compared with the control group (K=0.897).

Figure 8 shows the XRD image of the solidified BMSC after soaking in water for 30 days. Combined with the quantitative analysis in Table 6, it was found that the content of phase 5·1·7 in the control group increased by 3.45% after soaking in water, its MgO content decreased by 13.58%, and the magnesium hydroxide content increased by 7.58%. When Cu\(^{2+}\) or Cr\(^{3+}\) was added, the content of MgO decreased, the
content of 5·1·7 phase increased, and the content of Mg(OH)$_2$ decreased compared with that before the soaking. As shown in Fig. 9(a), the SEM image of the solidified body did not change significantly, and the 5·1·7 phase remained stable in water. Figure 9(b) shows less flocs than those that had not been fully hydrated at 28 d. It was verified that the BMSC sample added with Cr$^{3+}$ continued to hydrate in water to generate the 5·1·7 phase. This is the reason for the increased strength. Figure 9(c) shows a completely different morphology.

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Fig. 7 Compressive strength and softening coefficient of BMSC with different mixtures after soaking in water; (a): Cr$^{3+}$, (b): Cu$^{2+}$.

Fig. 8 XRD patterns of BMSC with different mixtures after soaking in water for 30 days; (a): Cr$^{3+}$, (b): Cu$^{2+}$.
After immersion in the solidified Cu\textsuperscript{2+} BMSC sample, the 5·1·7 phase changed from the original needle-like crystal to a gel-like crystal, and the needle-like 5·1·7 phase solubility is greater than the colloidal phase (Liu et al. 2010), so the colloidal 5·1·7 phase improves the water resistance of the cured body.

### Table 6 Phase composition of the BMSC at 30 days with Topas5.0.

| Samples | 5·1·7 phase (%) | SiO\textsubscript{2} (%) | Mg(OH)\textsubscript{2} (%) | MgO (%) | MgCO\textsubscript{3} (%) |
|---------|-----------------|--------------------------|-----------------------------|---------|--------------------------|
| Control | 68.93           | 0.92                     | 8.94                        | 15.29   | 5.92                     |
| Control(s) | 72.38         | 1.16                     | 16.52                       | 4.71    | 5.23                     |
| Cr2     | 54.42           | 1.18                     | 15.65                       | 23.56   | 5.19                     |
| Cr2w    | 72.13           | 1.21                     | 15.19                       | 5.13    | 6.34                     |
| Cu2     | 17.16           | 0.45                     | 22.53                       | 58.09   | 1.76                     |
| Cu2w    | 54.79           | 0.89                     | 18.9                        | 20.16   | 5.26                     |

Fig. 9 SEM images of BMSC with different mixtures after soaking in water for 30 days; (a): Control, (b): Cr2 and (c) Cu2.

### 3.6 Leaching toxicity of the BMSC curing system

A good solidification system should enable leaching toxicities of heavy metal ions to be low enough so that the solidified body can be safely buried in the ground without polluting the groundwater. Figure 10 shows the
leaching toxicity of the BMSC curing system after various curing durations. The results show that as Cu$^{2+}$ and Cr$^{3+}$ content increased in the solidified body, the leaching toxicity of the solidified body correspondingly increased. The total chromium and total copper in Fig. 10 are lower than the minimum leaching standard stipulated in the relevant Chinese standards (total chromium is less than 15 mg/L, and total copper is less than 100 mg/L).

At the same amount of ion addition, the sample with Cu$^{2+}$ added has higher leaching toxicity than the sample with Cr$^{3+}$ added. This is because Cu$^{2+}$ has a lower limiting atom substitution ability, and excess Cu$^{2+}$ adsorbed on the surface of the 5·1·7 phase is more easily leached. With the extension of the solidification period, the 5·1·7 phase grows and encapsulates Cu$^{2+}$ and Cr$^{3+}$, so the dissolution rate of the 5·1·7 phase at 28 d determines the leaching amount of copper and chromium. Therefore, the leaching toxicity of copper and chromium solidified in BMSC is low enough to be safely buried in the ground.

The most stable method for curing heavy metal ions is to let the heavy metal ions enter the crystal lattice of the 5·1·7 phase of the cement hydration product. To determine the shifting amount of the diffraction peak position in the XRD image, the index of the crystal plane spacing of the three strong diffraction peaks of the 5·1·7 phase is shown in Fig. 11. After the addition of heavy metal ions, the spacing of the 5·1·7 phase crystal planes increases with increasing amounts of heavy metal ions. This indicates that due to the difference in charge, hydrated ion radius, and other aspects of chromium, copper ions and magnesium ions, when chromium or copper ions enter the 5·1·7 phase lattice, lattice
rearrangement occurs. The 5·1·7 phase is a MgO octahedral box cage structure, which has high stability to the solidification of heavy metal ions.

In the study, the addition of Cu$^{2+}$ and Cr$^{3+}$ causes BMSC strength to decrease. This is because the addition of Cu$^{2+}$ and Cr$^{3+}$ seriously inhibits the early hydration reaction of BMSC. The reaction process of BMSC is shown in the following equation (Wu 2014):

$$\text{(solid)}_2 + 2 \text{(surface)}_2 \rightarrow \text{[CA Mg(OH)(H}_2\text{O)}_x\text{]}^{-\text{OH}^-}$$

(7)

$$\rightarrow \text{[CA Cu(OH)(H}_2\text{O)}_x\text{]}^{-\text{OH}^-} + \text{SO}_4^{2-}$$

(8)

$$\rightarrow \text{[CA Cr(OH)(H}_2\text{O)}_x\text{]}^{-\text{OH}^-} + \text{SO}_4^{2-}$$

(9)

When Cu$^{2+}$ and Cr$^{3+}$ are added to the BMSC, heavy metal ions will complex [OH$^-$] in the solution to form insoluble Cu(OH)$n$ and Cr(OH)$n$. The equilibrium constant of the complex reaction is expressed by the stability constant of the complex, also known as the formation constant of the complex. In Table 7, $lg\beta_n$ represents the complex stability constant of the metal-inorganic ligand complex, and $\beta_n$ represents the cumulative stability constant. For the same type of complex with the same number of ligands, the larger the stability constant value, the greater the tendency to form complex ions, and the more stable the complex is. These heavy metal ions are easier to complex the [OH$^-$] in the solution. Therefore, the time when the concentration of [OH$^-$] reaches its critical value is delayed, which leads to retardation of BMSC.

At a certain temperature, there is a balance of precipitation dissolution and generation between the insoluble electrolyte crystals and the ions dissolved in the solution, which is called the precipitation dissolution balance($K_{sp}$). The solubility product of the hydroxide produced by the reaction of metal ions can reflect the equilibrium dissolution of the insoluble matter in the solution or on particle surface (Wang et al. 2018a, 2018b). Taking magnesium ion as an example, the calculation process of its solubility product can be written as:

$$\text{Mg(OH)}_2(s) \leftrightarrow \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$$

(14)

$$K_{sp}(\text{Mg(OH)}_2) = c(\text{Mg}^{2+}) \cdot c(\text{OH}^-)^2$$

(15)

The precipitation equilibrium constants of the hydroxides of the three ions of magnesium, copper and chromium are listed in Table 8. It can be found that the hydroxides of heavy metal ions are more likely to precipitate on particle surface rather than in the solution (Chen et al. 2009). These precipitates adhere to the surface of magnesium oxide to prevent the active MgO from further reacting to form the 5·1·7 phase (5·1·7 phase as the main strength of BMSC), which directly leads to a decrease in the mechanical properties of the curing system.

### Table 7 Complex stability constants of metal-inorganic ligand complexes.

| Ligand | Metal ion | Number of ligands | $lg\beta_n$ |
|--------|-----------|-------------------|------------|
| OH$^-_1$ | Mg$^{2+}$ | 1                 | 2.58       |
| OH$^-_1$ | Cu$^{2+}$ | 1,2,3,4           | 7.0,13,68,17,00,18.5 |
| OH$^-_1$ | Cr$^{3+}$ | 2                 | 10.1,17,8,29.9 |

### Table 8 $lgK_{sp}$ of hydroxides of metal ions in solution and on the particle surface.

| Metal ions | In solution | On particle surface |
|------------|-------------|---------------------|
| Mg$^{2+}$  | -11.15      | -12.75              |
| Cu$^{2+}$  | -19.32      | -20.91              |
| Cr$^{3+}$  | -29.80      | -32.19              |

When Cu$^{2+}$ and Cr$^{3+}$ are added to the BMSC, heavy metal ions will complex [OH$^-$] in the solution to form insoluble Cu(OH)$_n$ and Cr(OH)$_n$. The equilibrium constant of the complex reaction is expressed by the stability constant of the complex, also known as the formation constant of the complex. In Table 7, $lg\beta_n$ represents the complex stability constant of the metal-inorganic ligand complex, and $\beta_n$ represents the cumulative stability constant. For the same type of complex with the same number of ligands, the larger the stability constant value, the greater the tendency to form complex ions, and the more stable the complex is. These heavy metal ions are easier to complex the [OH$^-$] in the solution. Therefore, the time when the concentration of [OH$^-$] reaches its critical value is delayed, which leads to retardation of BMSC.

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$$\text{Mg(OH)}_2(s) \leftrightarrow \text{Mg}^{2+}(aq) + 2\text{OH}^-(aq)$$

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The precipitation equilibrium constants of the hydroxides of the three ions of magnesium, copper and chromium are listed in Table 8. It can be found that the hydroxides of heavy metal ions are more likely to precipitate on particle surface rather than in the solution (Chen et al. 2009). These precipitates adhere to the surface of magnesium oxide to prevent the active MgO from further reacting to form the 5·1·7 phase (5·1·7 phase as the main strength of BMSC), which directly leads to a decrease in the mechanical properties of the curing system.
Conclusions

1) With increasing Cr\(^{3+}\) or Cu\(^{2+}\) content, the hydration process of cement will be inhibited and reduce the mechanical properties of the cured body, but the 28 d compressive strength of the solidified body at 27.6 MPa is still much higher than the compressive strength of hazardous waste landfill.

2) The addition of Cr\(^{3+}\) or Cu\(^{2+}\) will result in a new crystalline phase diffraction peak in the XRD diffraction pattern. The addition of chromium or copper ions leads to a reduction in the amount of 5·1·7 phase formation to varying degrees. The pore structure of BMSC samples solidified with Cr\(^{3+}\) or Cu\(^{2+}\) will change. With increasing amounts of Cr\(^{3+}\) or Cu\(^{2+}\), the average pore size increases and the proportion of pores larger than 100 nm increases.

3) The maximum leaching toxicity of total chromium and total copper in the cured body is only 0.221 mg/L and 0.508 mg/L, indicating that BMSC has a good curing effect on Cr\(^{3+}\) and Cu\(^{2+}\).

4) The addition of Cr\(^{3+}\) or Cu\(^{2+}\) improves the water resistance of BMSC. The compressive strength of Cr\(^{3+}\) (42.8 MPa) or Cu\(^{2+}\) (27.7 MPa) after the BMSC-cured body is immersed in water for 30 days is much higher than the relevant standard (28 d is 0.35 MPa).

5) The curing methods of copper or chromium ions in BMSC cement are as follows: It enters the 5·1·7 phase in the form of atomic substitution, which is the most important way for BMSC to solidify heavy metal ions. This is reflected in the corresponding changes in the interplanar spacing. In addition, heavy metal ions have high stability in the MgO\(_6\) octahedral structure of the 5·1·7 phase.

6) Four new hydration products are formed through chemical combination to solidify copper and chromium ions. They are, basic chromium sulfate \([4\text{Cr(OH)}_2\cdot\text{Cr}_2\text{H}_7\text{SO}_4\cdot2\text{H}_2\text{O}]\), hydrated basic copper sulfate \(3\text{Cu(OH)}_2\cdot\text{CuSO}_4\cdot2\text{H}_2\text{O}\), chromium hydroxide hydrate \([\text{Cr(OH)}_3\cdot\text{H}_2\text{O}]\) and copper hydroxide hydrate \([\text{Cu(OH)}_2\cdot2\text{H}_2\text{O}]\).

7) The hydration products of BMSC adsorb heavy metal ions.

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