

# PROPERTIES AND ENVIRONMENT IMPACT OF CEMENTITIOUS MATERIALS PREPARED WITH FLUORGYP SUM AND STEEL SLAG

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*The industrial by-products of fluorgypsum (FG) and steel slag (SS) were recycled for the preparation of gypsum-based cementitious materials (GBCMs).  $\text{Na}_2\text{SO}_4$  and  $\text{KAl}(\text{SO}_4)_2$  were applied to activate the hydration of FG and SS, respectively. The properties of the GBCM were investigated. The residual  $\text{H}_2\text{SO}_4$  and soluble F in the FG poses a great threat to the environment. Hence, the environmental impacts of the GBCM were also studied. The results demonstrate that, with an increase in the SS content of the GBCM, the water requirement for normal consistency increases, the setting times are obviously prolonged, while the mechanical strength and the linear expansion rate are lower. Due to the hydration of SS and the formation of ettringite at a late hydration age, both the compressive strength and flexural strength for FG : SS = 9 : 1 and FG : SS = 8 : 2 are close to that of FG : SS = 10 : 0 at 90 d. The water resistance of the GBCM paste is also improved by adding SS into the FG. Hence, considering the mechanical strength and water resistance, the SS content of the GBCM should not exceed 20 %. The  $\text{H}_2\text{SO}_4$  in the GBCM can be neutralised by SS. Furthermore a novel quick and effective method, through the precipitation of  $\text{AlF}_3$ , for the immobilisation of soluble F was proposed. Therefore, FG and SS can be recycled for the production of GBCM without bringing about an adverse environmental impact.*

## INTRODUCTION

Fluorgypsum (FG) is a by-product of manufacturing hydrofluoric acid resulting from sulfuric acid and fluorite reactions. [1-2]. It mainly consists of II-anhydrite [1, 3-4]. Moreover, it also contains a slight amount of  $\text{H}_2\text{SO}_4$ , soluble F and  $\text{CaF}_2$ . For 1 tonne of hydrofluoric acid, ~4 tonnes of FG are produced [5-6]. In China, more than  $1 \times 10^6$  tonnes of FG are discharged annually. However, merely 25 % of this is recycled due to the low hydration activity of II-anhydrite and the soluble F as well as the residual  $\text{H}_2\text{SO}_4$  [1, 7]. The majority of FG piles up in the open air, which occupies a considerable amount farmland. Furthermore, the residual  $\text{H}_2\text{SO}_4$  and soluble F could also bring about serious pollution to the air and underground water [8]. Therefore, it is urgent to find methods for the effective recycling of FG.

The acceleration of the hydration of II-anhydrite is a key issue in the recycling of FG for the production of cementitious materials, which endows the FG paste with mechanical strength. At present, sulfates and chlorine salts have been utilised to activate the hydration activity of II-anhydrite [8-11]. Compared with the pastes prepared with hemihydrate gypsum, the paste prepared with activated FG shows a relatively lower hydration rate

and a lower compressive strength at the early hydration age. However, the long-term compressive strength is somewhat higher [10-12]. Therefore, FG is a suitable alternate for the preparation of gypsum-based materials with a higher long-term compressive strength.

The poor water resistance of gypsum-based cementitious material is the second factor limiting FG recycling. To improve the water resistance of the gypsum paste prepared with FG, cementitious materials, such as Portland cement (PC), fly ash (FA), granulated blast furnace slag (GBFS), silica fume (SF) and metakaolin (MK), are frequently used. The gypsum-based cementitious materials of FG-FA-PC clinker-slag-lime [13], FG-GBFS-MK [14], FG-PC-GBFS [15] and FG-PC-FA [3, 16-18] have been prepared. However, adding PC, lime, and MK increases the cost and consumes less solid waste. Therefore, to lower the cost and recycle more industrial waste, industrial waste with hydraulic activity must be added to the FG to prepare gypsum-based cementitious materials with good water resistance.

Steel slag (SS) is a by-product generated in steel-making [19]. Diverse mineral phases have been reported for SS due to the variation in the chemical compositions. The mineral phases include olivine, merwinite ( $\text{C}_3\text{MS}_2$ ), tricalcium silicate ( $\text{C}_3\text{S}$ ), dicalcium silicate ( $\beta\text{-C}_2\text{S}$  and

$\gamma$ -C<sub>2</sub>S), tetracalcium aluminoferrite (C<sub>4</sub>AF), calcium ferrite (C<sub>2</sub>F), RO phase (CaO–FeO–MnO–MgO solid solution), lime, periclase, fluorite (CaF<sub>2</sub>) and an amorphous phase [19–20]. Although C<sub>3</sub>S,  $\beta$ -C<sub>2</sub>S,  $\gamma$ -C<sub>2</sub>S and C<sub>4</sub>AF are considered to have high hydration activity in Portland cement, the minerals in the SS are considered as slightly active due to the high calcining temperature during steelmaking. However, the hydration activity of SS could be activated by chemicals. A previous study investigated NaOH, K<sub>2</sub>SO<sub>4</sub>, Na<sub>2</sub>SO<sub>4</sub>, KAl(SO<sub>4</sub>)<sub>2</sub>, CaCl<sub>2</sub>, AlCl<sub>3</sub> and NaAlO<sub>2</sub> on the hydration activity of SS, which caused the SS to possess good long-term cementitious properties [21–22]. The results demonstrate that KAl(SO<sub>4</sub>)<sub>2</sub> is the best activator for SS [22]. Therefore, when a certain amount of SS is added into FG to prepare gypsum-based cementitious materials, the water resistance of the gypsum-based cementitious material may be improved by adding KAl(SO<sub>4</sub>)<sub>2</sub>.

Another factor limiting the recycling of FG is the slight amount of residual H<sub>2</sub>SO<sub>4</sub> and the soluble F [1]. Both H<sub>2</sub>SO<sub>4</sub> and the soluble F could seep into underground water and can pollute it. Therefore, the pH value of the hydration products and the immobilisation of the soluble F should be considered when FG and SS are used to prepare GBCMs.

In this study, five GBCMs with an FG to SS ratio (by weight) of 10:0, 9:1, 8:2, 7:3 and 6:4 were prepared. Na<sub>2</sub>SO<sub>4</sub> and KAl(SO<sub>4</sub>)<sub>2</sub> were used to activate the hydration activity of FG and SS, respectively. The water requirement for normal consistency and the setting time,

strength development and hydration of the GBCM were studied. In addition, the water absorption, softening coefficient and pore structure of the hardened GBCM pastes were tested. Moreover, the neutralisation of the residual H<sub>2</sub>SO<sub>4</sub> and the immobilisation of soluble F in GBCM were also investigated.

## EXPERIMENTAL

### Materials

Fresh FG (Dongyue Group Ltd., Shandong, China) and SS (Shandong Iron and Steel Group Co., Ltd, Shandong, China) were utilised to prepare the GBCM. The SS was outdoor weathered for three months to promote the complete hydration of the free CaO, which was intended to ensure a volume stability GBCM paste. The phase compositions of FG and weathered SS are shown in Figure 1. The FG is mainly composed of anhydrite and calcium fluoride. For the SS, the crystalline phases are mainly composed of calcite, quartz, an RO phase, calcium silicate (C<sub>2</sub>S), merwinite and pyroxene. No Ca(OH)<sub>2</sub> was detected in the weathered SS, which is due to that Ca(OH)<sub>2</sub> can easily be carbonated to form CaCO<sub>3</sub>. The chemical compositions of the SS and FG, expressed in oxides, are shown in Table 1.

The FG was dried and milled by a disc mill to pass through a 200-mesh sieve with a residue of 10.3 %. The SS was ground by a ball mill to pass through a 200-mesh sieve with residue of 3.5 %. The particle size distribution of the ground SS and FG are presented in Figure 2.

Table 1. Chemical compositions, expressed in oxides, of the FG and SS (wt. %).

Oxide	CaO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	MnO	K <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	Na <sub>2</sub> O	F	Others	LOI
FG	38.62	1.99	0.32	0.21	0.48	54.84	–	-0.14	–	–	0.11	1.09	1.36	0.83
SS	37.06	21.49	8.69	6.23	3.04	0.69	0.95	0.67	0.59	0.29	0.25	–	0.32	19.73

The soluble F content of the FG is 0.37 %, the pH value of the FG is 1.12

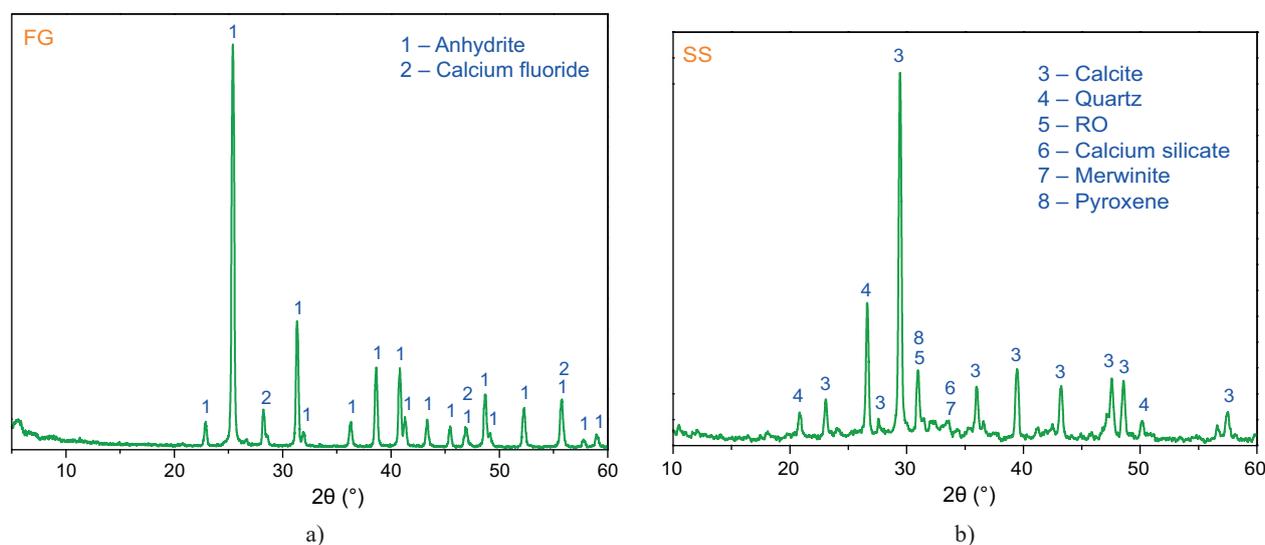


Figure 1. XRD patterns of the FG and weathered SS. (RO is defined as a CaO–FeO–MnO–MgO solid solution).

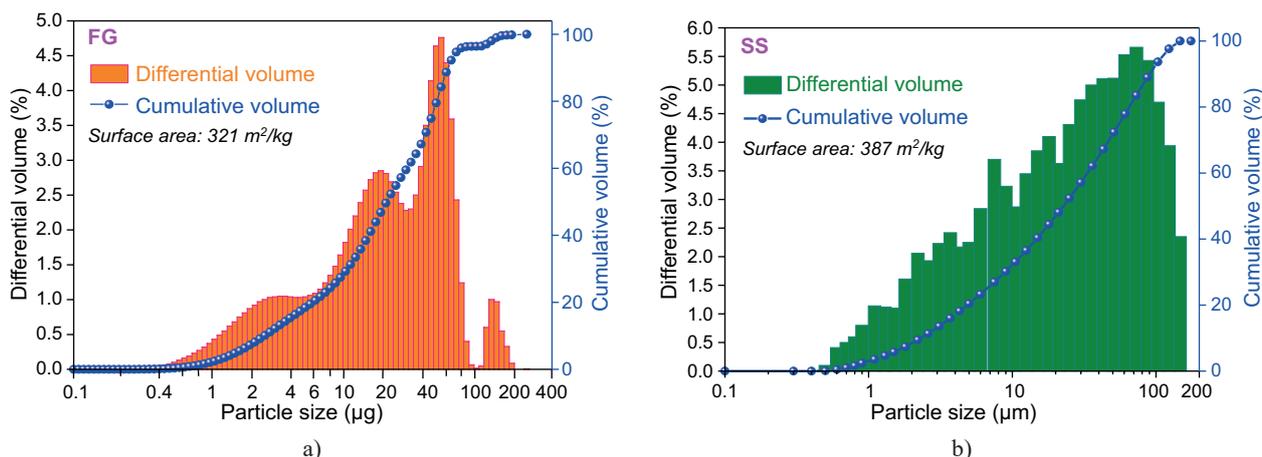


Figure 2. Particle size distributions of the FG and SS powders.

The FG and SS were mixed in the following proportions (by weight): 10:0, 9:1, 8:2, 7:3 and 6:4 for the preparation of the GBCM. 2.0 %  $\text{Na}_2\text{SO}_4$  and 3.5 %  $\text{KAl}(\text{SO}_4)_2$  (industrial grade) were used as the accelerators to promote the hydration of the FG in the GBCM.

### Methods

#### *Water requirement for normal consistency and the setting time*

The water requirement for normal consistency and the setting time of the GBCM were tested according to the Chinese standard GB/T 9776-2008.

#### *Mechanical strength and linear expansion rate*

The samples with dimensions of  $40 \times 40 \times 160$  mm and  $25 \times 25 \times 280$  mm were applied for testing the mechanical strength and linear expansion rate, respectively. All the samples were prepared with the paste with a water to binder ratio (w/b) of 0.35. The samples in the moulds were firstly cured in a standard chamber at a temperature of  $(20 \pm 1)$  °C and a humidity of  $(95 \pm 1)$  % for 24 h. After demoulding, the samples were then cured at  $(20 \pm 1)$  °C in air. The mechanical strength was measured at the hydration age of 1, 3, 7, 28, and 90 days. Each value of the compressive strength and flexural strength was determined by an average value of six samples and three samples, respectively. The linear expansion rate of the hardened GBCM pates was calculated by Equation 1.

$$\omega = \frac{L_T - L_0}{280} \quad (1)$$

where  $\omega$ ,  $L_T$ ,  $L_0$  and 280 denote the linear expansion rate, length at the specified age, length of the samples at 24 h and the initial length of the sample, respectively.

#### *Water absorption rate and softening coefficient*

The water absorption of the samples was determined by the mass increments for the samples cured in water at

$(25 \pm 1)$  °C for 2 h and 24 h, respectively. The softening coefficient was characterised by the retention ratio of the compressive strength after 24 h soakage in water.

#### *X-ray fluorescence analysis and particle size distribution*

The chemical compositions of the FG and SS were determined by X-ray fluorescence analysis (XRF, S8 TIGER) at 40 kV and 70 mA. The particle size distributions of the FG and SS were measured by a laser particle size analyser (LS13320).

#### *X-ray diffraction analysis*

After the termination of the hydration by absolute ethyl alcohol for 12 h, the hydration products of the GBCM pastes were dried at 40 °C in a vacuum oven for 24 h. Then the dried samples were ground to pass through a 76 µm sieve for the X-ray diffraction analysis (XRD, D8 Advance). The measurement was performed with Cu K $\alpha$  radiation at 40 kV and 40 mA within a  $2\theta$  range of  $(5-65)^\circ$  with a scan speed of 0.2 s for  $0.02^\circ$ .

#### *Heat release*

The heat flow for the hydration of the GBCM was recorded by an eight channel TAM AIR isothermal calorimetric calorimeter using 2 g of GBCM with 1 g of water for 72 h at a constant temperature of 20 °C. The resulting heat flow curves were integrated to obtain the cumulative heat during hydration.

#### *Pore structure analysis*

After vacuum drying for 24 h, the pore structure of the hardened GBCM paste was tested by a Mercury intrusion porosimeter (MIP, Quanta, Poremaster-60) within a pressure range of  $0-6 \times 10^4$  psia.

#### *pH value and the leaching behaviour of F for the hydration product*

The suspensions with a w/b of 1:1 (by weight) were stirred by a magnetic stirring apparatus for 1 min, 2 min,

5 min, 10 min, 30 min and 60 min. After filtering by a suction filter, the leachates were applied for testing the pH value by an FE28 pH-meter (Mettler Toledo). The F<sup>-</sup> concentrations of the leachates were tested by the chemical method, which is provided by the Chinese standard of GB/T 5484-2000. The Al<sup>3+</sup> concentrations of the leachates were tested by an ICP-AES (Baird, PS-6, USA).

*Chemically combined water content*

After the termination of the hydration, the hydration products of the GBCM were dried in a vacuum drying oven to remove the free water. Then the samples were calcined at 950 °C for 30 min. Finally, the samples were cooled down to room temperature to a constant weight. The chemically combined water content can be calculated by Equation 2.

$$W = [(m_a - m_b) / m_b - L] \times 100 \% \quad (2)$$

where *W*, *m<sub>a</sub>*, *m<sub>b</sub>*, and *L* denote the chemically combined water content, weight before calcination, weight after calcination and the weight loss of ignition, respectively.

RESULTS AND DISCUSSIONS

Environmental impact

Generally, the pH value of the FG is within the range of 1.1-2.1 [6], which is attributed to the residual H<sub>2</sub>SO<sub>4</sub> and considered highly corrosive. If the residual H<sub>2</sub>SO<sub>4</sub> in the FG seeps into the underground water, it can change the pH value of the underground water and pose a great threat to the environmental safety. The pH value of the FG used in this study is 1.12. To avoid any environmental pollution caused by the residual H<sub>2</sub>SO<sub>4</sub>, it must be neutralised.

The variations of the pH value of the leachates for the hydration products of the GBCM are shown in Figure 3. For FG:SS = 10:0, the pH value of the leachate keeps

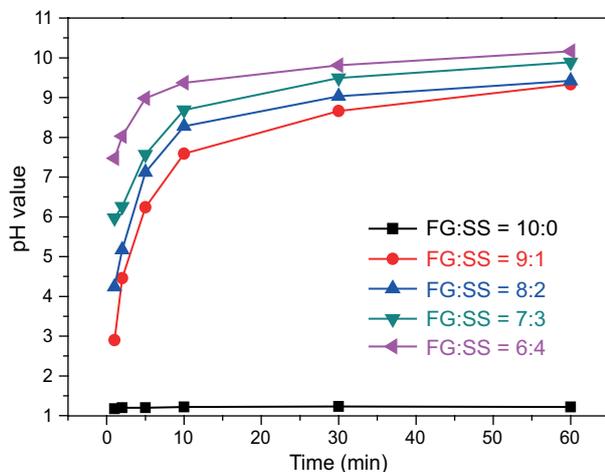


Figure 3. Variations in the pH value of the leachates for the hydration products of the GBCM paste.

at a constant value of ~1.10. For the hydration products of the other composite cementing materials, the pH value of the leachate increases dramatically within 0-60 min. Within 10 min, all the pH values for the leachates of the hydration products of the GBCM exceed 7. The weathered SS contains a great deal of CaCO<sub>3</sub> (Figure 1), which is considered an alkaline material. Therefore, the residual H<sub>2</sub>SO<sub>4</sub> in the GBCM can be easily neutralised.

For human beings, an excessive F intake over a long period of time could lead to fluorosis, which is characterised by dental mottling and skeletal manifestations, such as crippling deformities, osteoporosis and osteosclerosis [31]. For plants, the excessive F in the water could also inhibit the seed germination. Moreover, F could destroy the enzymes in plants, which thereby adversely affects the plant growth [32]. Therefore, the immobilisation of the soluble F is a precondition for the recycling of FG for the production of GBCMs.

The variations in the Al<sup>3+</sup> and F<sup>-</sup> concentrations of the leachates for the hydration products of the GBCM are shown in Figure 4. When prolonging the hydration time, the F<sup>-</sup> concentrations in the leachates of the

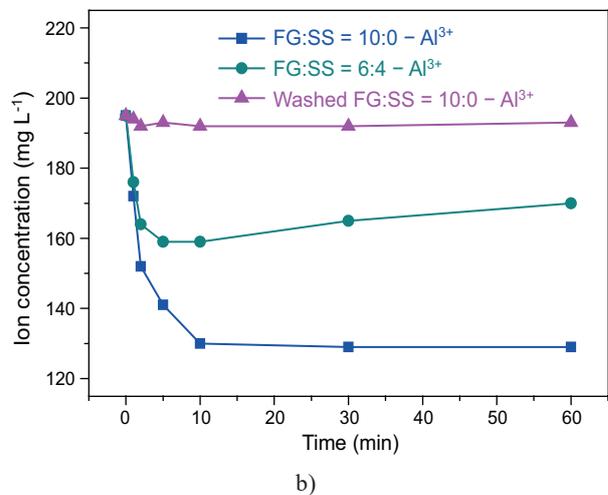
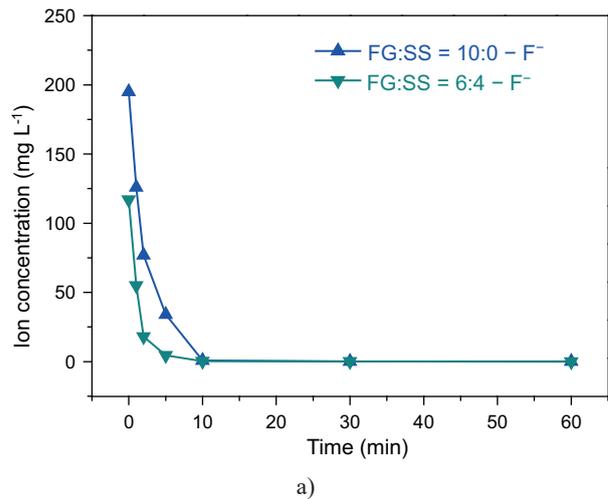


Figure 4. Variation in the Al<sup>3+</sup> and F<sup>-</sup> concentrations of the leachates of the GBCM paste.

FG:SS = 10:0 paste and FG:SS = 10:0:SS = 6:4 paste decrease sharply. At 10 min, almost all the F<sup>-</sup> is well immobilised. Meanwhile, the Al<sup>3+</sup> concentrations of the leachates of the FG:SS = 10:0 paste and FG:SS = 6:4 paste decrease sharply within 0-10 min. In the following hydration period, the Al<sup>3+</sup> concentrations of the leachates keep at a constant value. For the washed FG, all the soluble F has been removed. The Al<sup>3+</sup> concentration keeps at a constant value. Therefore, it is concluded that the following reaction (Equation 3) takes place and the water insoluble AlF<sub>3</sub> forms.



At 10 min, the F<sup>-</sup> concentrations of the leachates of the FG:SS = 10:0 paste and FG:SS = 6:4 paste are 0.82 mg·L<sup>-1</sup> and 0.34 mg·L<sup>-1</sup>, respectively. It is far below the safe level of 1 mg·L<sup>-1</sup> which is required in the Chinese standard for drinking water [33]. Therefore, it is concluded that FG could be utilised for the production of GBCM without bringing about F pollution.

### Properties

#### Water requirement for normal consistency and setting time

The water requirement for normal consistency and the setting time of the GBCM are shown in Table 2. With the increase in the SS content of the GBCM, the water requirement for normal consistency increases. It is due to the fact that the surface area of the SS is relatively higher than the FG (Figure 1), which increases the contact area between the GBCM and the water and makes it absorb more water.

The setting time of the cementitious materials is defined as the initial solidification and subsequent hardening [23], which is closely related to the workability and early hydration of the minerals. For FG:SS = 10:0, the initial setting time and final setting time are 103 min and 185 min, respectively, which is much longer than the setting time of hemihydrate gypsum [24] due to the fact that the hydration activity of the activated II-anhydrite is lower than hemihydrate gypsum. [24]. For the GBCM paste, the initial solidification and subsequent hardening is caused by the hydration of II-anhydrite to form gypsum. With the increase in the SS content of the

Table 2. Water requirement for the normal consistency and setting time of the GBCM.

FG:SS	Water requirement for normal consistency (%)	Setting time (min)	
		Initial	Final
10:0	34.4	103	185
9:1	34.8	145	226
8:2	35.0	168	258
7:3	35.2	183	277
6:4	35.3	206	295

GBCM, the FG is diluted and less gypsum forms at the early age. Therefore, both the initial setting time and final setting time are obviously prolonged.

### Strength development

Figure 5 shows the compressive strength and flexural strength development of the GBCM paste. The compressive and flexural strength increase remarkably within the hydration age of 28 d. After 28 d, for FG:SS = 10:0, the compressive strength and flexural strength keep at a constant value, while the compressive strength and flexural strength for FG:SS = 9:1, FG:SS = 8:2, FG:SS = 7:3 and FG:SS = 6:4 increase. So it is that the hydration of anhydrite dominates the early age strength development to form gypsum. At the late hydration age, KAl(SO<sub>4</sub>)<sub>2</sub> activates the hydration activity of the SS [22], promoting strength development at the late hydration age.

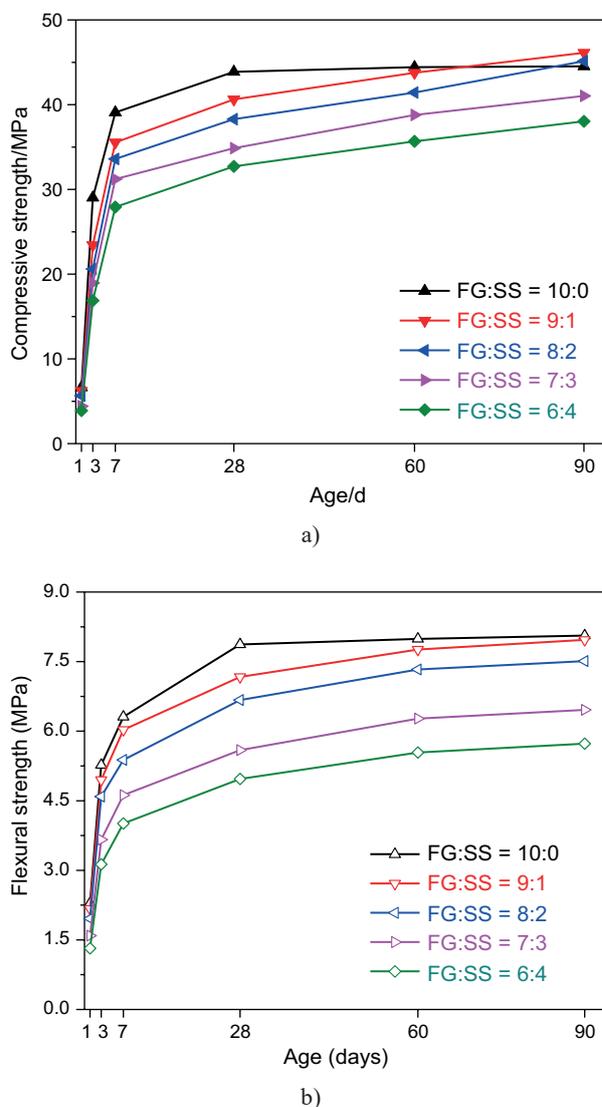


Figure 5. Compressive and flexural strength development of the GBCM paste.

At the hydration age of 90 days, both the compressive strength and flexural strength of FG:SS = 9:1 and FG:SS = 8:2 are close to that of FG:SS = 10:0, while the compressive strength and flexural strength of FG:SS = 7:3 and FG:SS = 6:4 are much lower than that of FG:SS = 10:0. Therefore, from the perspective of the mechanical strength, the SS content of the GBCM should not exceed 20 %.

#### Water absorption and softening coefficient

Poor water resistance is the main drawback of gypsum-based cementitious materials [13] and the water resistance is closely tied with the service life of gypsum-based cementitious materials. For gypsum-based cementitious materials with poor water resistance, they are easy to deform and corrupt [25]. Therefore, it is of great importance to improve the water resistance. Usually, a softening coefficient is used to characterise the water resistance of gypsum-based cementitious materials [26].

Figure 6 shows the water absorption and softening coefficient of the hardened GBCM pastes at 90 days. With the increase in the SS content in the GBCM, the water absorption of the hardened GBCM paste decreased from 7.0 % to 5.0 %, the softening coefficient increased from 0.38 to 0.64. This indicates that  $KAl(SO_4)_2$  could activate the hydration activity of the SS, which improves the water resistance of the GBCM.

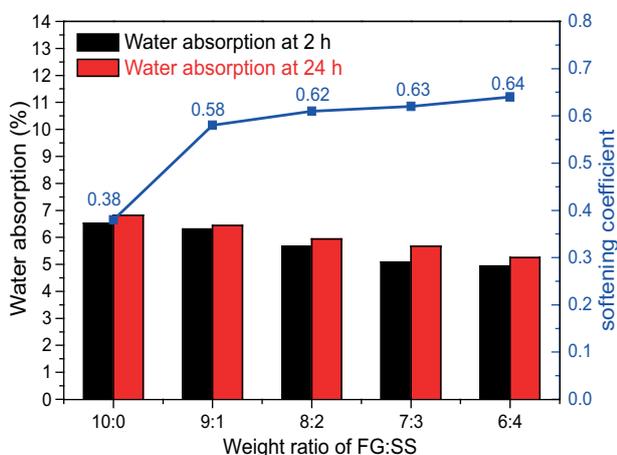


Figure 6. Water absorption and softening coefficient of the GBCM pastes at the hydration age of 90 days.

When the SS contents of the GBCM are 10 % and 20 %, the softening coefficients increase from 0.38 to 0.56 and 0.62, respectively. For the GBCM containing 30 % and 40 % SS, there is merely a slight increase of the softening coefficients. Therefore, taking the water resistance and mechanical strength into consideration, the SS content of the GBCM should not exceed 20 %.

#### Dimensional stability

Figure 7 presents the dimensional changes to the GBCM. The hardened GBCM pastes present a linear ex-

panation. A previous investigation found the same law in the composite cementitious materials of FG-PC-GBFS [27], FG-GBFS-SF [28] and FG-PC-FA [17] with sulfate as the activators of II-anhydrite. With the increase in the SS content, the linear expansion rate of the GBCM paste presents a downward trend. Within 28 days, the linear expansion rate increases sharply, which is mainly caused by the hydration of anhydrite to form gypsum. After 28 days, the expansion rate of the GBCM paste keeps at a constant value.

Throughout the hydration period, no cracks were observed on the paste. It is attributed to that, after three months of weathering, all the free CaO in the SS has been hydrated and carbonated to form  $CaCO_3$ , which avoids the volume expansion caused by the hydration of the free CaO [29].

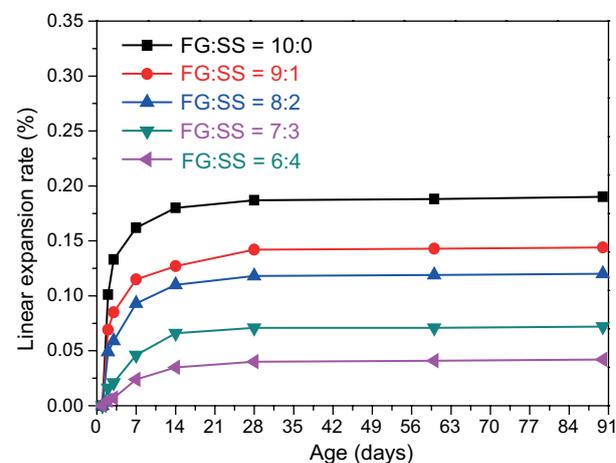


Figure 7. Linear expansion rate for the hardened GBCM paste.

#### Hydration

To investigate the hydration of GBCM, the heat flow and cumulative heat were tested. Figure 8 shows the hydration heat of GBCM with a w/b of 0.50. The heat flow curve is characterised by one exothermic peak. The obvious endothermic peak observed within 0-0.15 h is caused by the rapid dissolution of  $Na_2SO_4$ ,  $Al_2(SO_4)_3$  and  $KAl(SO_4)_2 \cdot 12H_2O$ . The exothermic peak within the hydration period of 0.15-72 h is mainly caused by the hydration of FG. With the increase in the SS content in the GBCM, the FG in the GBCM is diluted and less anhydrite hydrates, which thereby results in an obviously decreasing trend of the heat flow. At 72 h, the cumulative hydration heat for FG:SS = 10:0, FG:SS = 8:2 and FG:SS = 6:4 are  $91.27 J \cdot g^{-1}$ ,  $75.02 J \cdot g^{-1}$  and  $47.33 J \cdot g^{-1}$ , respectively. The results are in accordance with the compressive strength and flexural strength at 3 days.

To investigate the variation in the phase composition of the hydration product, the hydration products of the GBCM of FG:SS = 8:2 at the hydration age of 1, 3, 7, 28, and 90 days were used for the XRD analysis

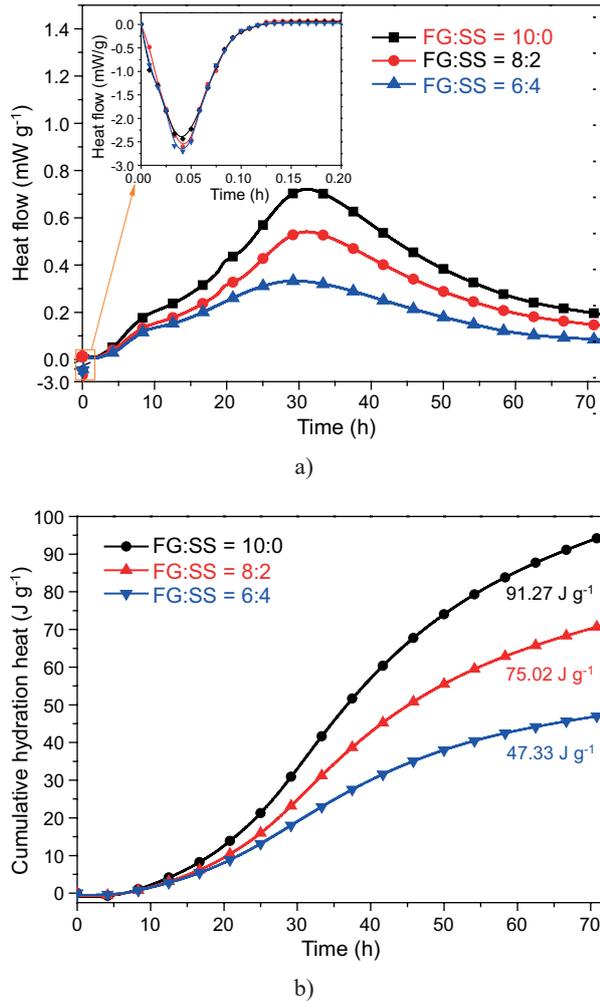


Figure 8. Hydration heat of the GBCM with a water to binder ratio of 0.50.

and the XRD patterns are shown in Figure 9. From 1 to 7 days, the diffraction peak intensity of anhydrite decreases sharply and the diffraction peak intensity of gypsum increases dramatically. At the hydration age of 28 days, the diffraction peak of anhydrite vanishes, which demonstrates that all the FG has hydrated. At the same time, the diffraction peak of AFt is observed, demonstrating that the Ca and Al in the SS react with the gypsum to form AFt in the later hydration period. In the early stage of hydration, the rapid hydration of f-CaO generates  $\text{Ca}(\text{OH})_2$ , which provides polar  $\text{OH}^-$  ions for the hydration reaction of SS (Equation 2), which breaks the Si-O-Si, Si-O-Al and Al-O-Al bonds on the surface of SS, prompting it to disperse and dissolve. The  $\text{Ca}^{2+}$  and  $[\text{AlO}_2]^-$  dissolved by the SS react rapidly with the  $[\text{SO}_4]^{2-}$  and  $\text{Ca}^{2+}$  provided by gypsum to form ettringite (Ettringite or AFt), and the  $[\text{SiO}_4]^{4-}$  and  $\text{Ca}^{2+}$  dissolved by the SS with  $\text{H}_2\text{O}$  to form calcium silicate hydrate (C-S-H). Therefore, the mechanical strength of FG:SS = 9:1, FG:SS = 8:2, FG:SS = 7:3, FG:SS = 6:6 increases and the water resistance is improved at the later hydration period.

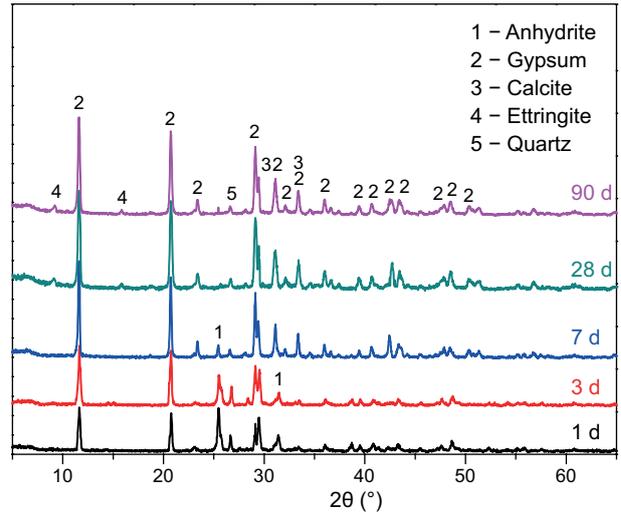


Figure 9. XRD patterns of the hydration products of the GBCM of FG:SS = 8:2 at the hydration age of 1, 3, 7, 28, and 90 days.

To investigate the hydration of SS activated by  $\text{KAl}(\text{SO}_4)_2$  at the late hydration age, the chemically combined water content of the hydration product of the GBCM at 1, 3, 7, 28, and 90 days were tested and the results are shown in Figure 10. For FG:SS=10:0, within the hydration age of 28 days, the chemical combined water content increases when prolonging the hydration age. After 28 days, the chemically combined water content keeps at a constant value. It demonstrates that the hydration of anhydrite mainly occurs within the hydration age of 28 days. For FG:SS = 9:1, FG:SS = 8:2, FG:SS = 7:3 and FG:SS = 6:4, the chemically combined water content increases within the hydration age of 28-90 d. It is concluded that  $\text{KAl}(\text{SO}_4)_2$  could promote the hydration of SS after 28 days. Therefore, the compressive strength, flexural strength and the softening coefficient present an increasing trend.

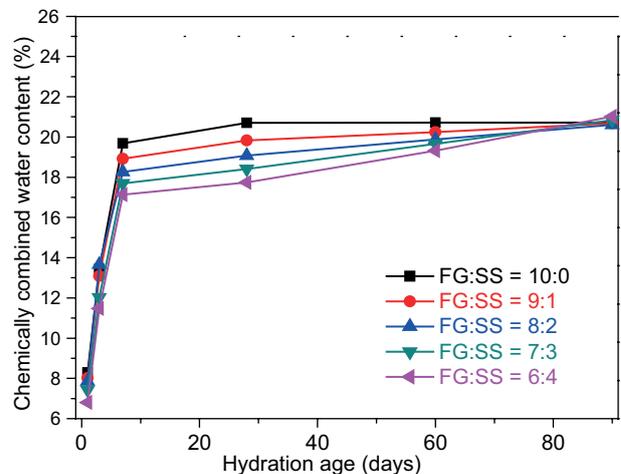


Figure 10. Chemically combined water content of the hydration product of GBCM at 1, 3, 7, 28, and 90 days.

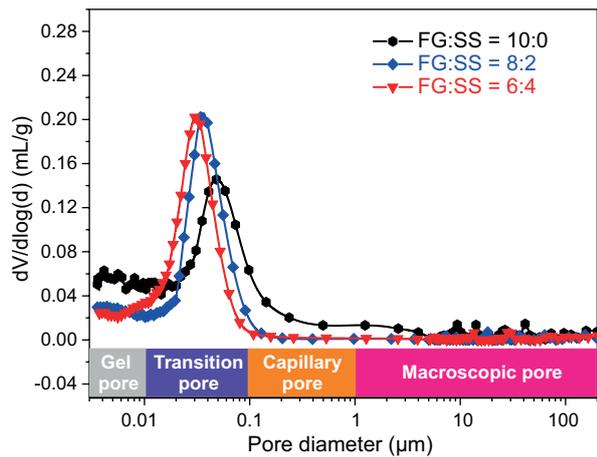
Pore structure

MIP was applied to reveal the relationship between the pore structure and water absorption of the hardened GBCM pastes. The pore structures of the hardened GBCM pastes of FG:SS = 10:0, FG:SS = 8:2 and FG:SS = 6:4 at the hydration age of 90 days are shown in Figure 11. Based on the pore size, the pores of the cementitious materials can be classified into the four types [30]: gel pore (diameter < 0.01 μm), transition pore (diameter, 0.01-0.1 μm), capillary pore (diameter, 0.1-1 μm) and macroscopic pore (diameter > 1 μm). With the increase in the SS content in the GBCM, the capillary pores and macropores decrease, whereas the transition pores increase. It is mainly attributed to the following reasons: i) the hydration products of SS and the ettringite could fill the pores. ii) compared with FG, the particle size of SS is smaller and the fine SS could fill the macropores.

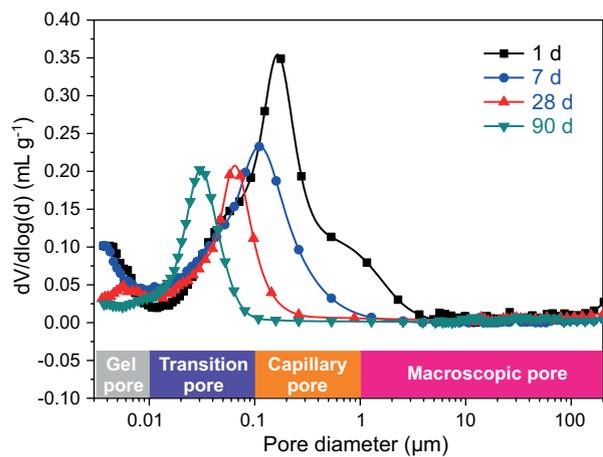
At the hydration age of 90 days, the porosity of the hardened GBCM of FG:SS = 10:0, FG:SS = 8:2 and FG:SS = 6:4 are 24.01 %, 25.90 % and 27.51 %, re-

spectively. Although the porosity increases, the amount of capillary pores and macropores decrease. The water could enter the capillary pores and macropores, whereas it is hard to enter the transition pores. Therefore, compared with FG:SS = 10:0, the water absorption decreases for FG:SS = 9:1, FG:SS = 8:2, FG:SS = 7:3 and FG:SS = 6:4 (Figure 6).

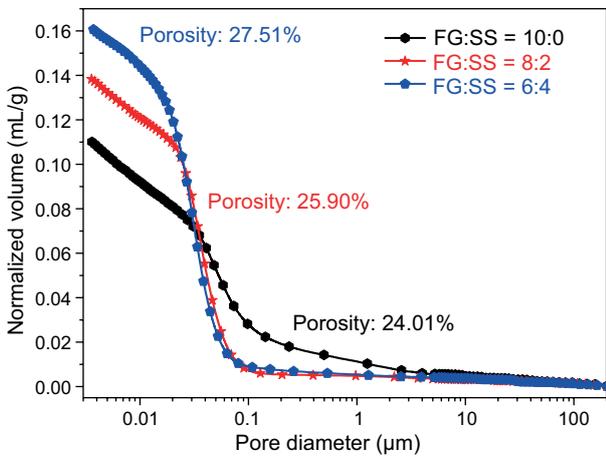
The pore structure development of the hardened GBCM pastes of FG:SS = 8:2 at the hydration age of 1, 3, 7, 28, and 90 days is shown in Figure 12. When prolonging the hydration age, the pore diameters shift toward a smaller size and the total pore volume decreases gradually. From 1 to 90 days, the porosities of the hardened GBCM pastes lowered from 41.03 % to 24.51 %, contributing to the strength development of the GBCM. Within the hydration age of 28 days, the refinement of the pores is mainly caused by the hydration of FG to form gypsum. After the hydration age of 28 days, almost all the FG has hydrated (Figure 9). Therefore, it is concluded that the refinement of the pore



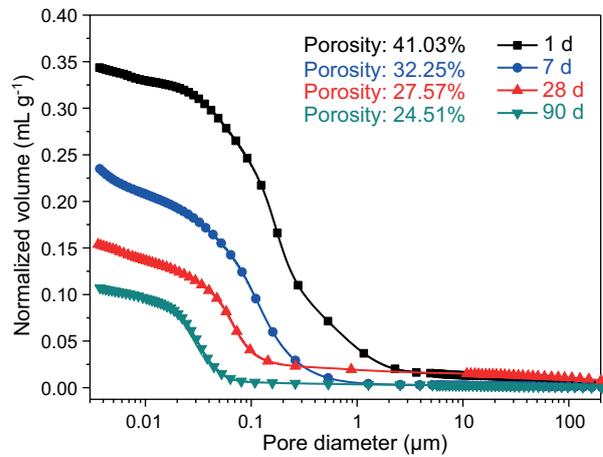
a)



a)



b)



b)

Figure 11. Pore structure of the hardened GBCM pastes of FG:SS = 10:0, FG:SS = 8:2 and FG:SS = 6:4 at the hydration age of 90 days.

Figure 12. Pore structure development of the hardened GBCM pastes of FG:SS = 8:2 at the hydration age of 1, 3, 7, 28, and 90 days.

structure is mainly caused by the following reasons: i) the ettringite formed after 28 days fills the pores (Figure 9). ii)  $KAl(SO_4)_2$  activates the hydration activity of SS at the late hydration age and the hydration products fill the pores.

## CONCLUSIONS

In this paper, FG and SS were used to prepare gypsum-based cementitious materials (GBCMs). The properties and environmental impacts of the GBCM were studied. The following conclusions can be drawn from the study:

- With the increase in the SS content of the GBCM, the water requirement for normal consistency increases, the initial and final setting time are obviously prolonged, the linear expansion rate decreases.
- With the increase in the SS content of the GBCM, the mechanical strength decreases. Due to the hydration of SS and the formation of ettringite at the late hydration age, both the compressive strength and flexural strength of FG:SS = 9:1 and FG:SS = 8:2 are close to that of FG:SS = 10:0 at 90 days.
- $KAl(SO_4)_2$  could activate the hydration of SS at the late hydration age. The hydration of SS and the formation of ettringite contribute to the improvement in the water resistance. Taking the mechanical strength and water resistance into consideration, the SS content of GBCM should not exceed 20 %.
- The  $H_2SO_4$  of the GBCM can be neutralised by SS and the soluble F can be immobilised through the precipitation of  $AlF_3$ . Therefore, it is concluded that FG and SS can be recycled for the preparation of GBCMs without bringing about any adverse environmental impacts.

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