

Article

Mutual Activation Mechanism of Cement–GGBS–Steel Slag Ternary System Excited by Sodium Sulfate

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Abstract: To promote the large-scale recycling of solid waste, the hydration characteristics of blended cement with different amounts of GGBS (ground granulated blast-furnace slag) and SS (steel slag) were investigated. The optimum blending amounts of GGBS and SS in cement were 40% and 10% by mass, and the optimum dosage of Na₂SO₄ in the C50-S40-SS10 (50 wt.% cement–40 wt.% slag–10 wt.% steel slag) system was 2 wt.%. The flexural and compressive strengths of the C50-S40-SS10 system after adding 2 wt.% Na₂SO₄ are 57.95% and 9.28% higher than that of pure cement at 28 d. XRD, FT-IR and Ca(OH)₂ content analysis were chosen to investigate the hydration products of pure cement and blended cement. The results show that GGBS enhanced the hydration of both cement and SS. And GGBS contributed to the generation of calcium silicoaluminate hydrate (C–A–S–H) in the blended cement system. The addition of Na₂SO₄ promoted the hydration reaction and contributed to the generation of ettringite (AFt) in the ternary system. The hydration heat evolution results showed that GGBS and SS can reduce the hydration heat of cement. Na₂SO₄ had similar effects and delayed the time of AFt conversion to monosulfide calcium sulfoaluminate (AFm). A mutual activation mechanism of cement–GGBS–SS ternary system mixed with Na₂SO₄ was proposed in this study.

Keywords: cement; ground granulated blast-furnace slag; steel slag; sodium sulfate; hydration; activator; mutual activation mechanism



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1. Introduction

Ground granulated blast-furnace slag (GGBS), which is one kind of by-product of steel manufacturing, has been used as a kind of supplementary cementitious material (SCMs) for more than one hundred years [1]. On the one hand, replacing part of the cement with GGBS can reduce the carbon emission in the cement production process. On the other hand, the activated SiO₂ and Al₂O₃ in GGBS will decompose under alkaline conditions and then react with Ca(OH)₂ to form cementitious material. The pozzolanic reactions of GGBS can promote the hydration of cement and generate additional calcium silicate hydrate (C–S–H) and aluminum substituted calcium silicate hydrate, i.e., calcium silicoaluminate hydrate (C–A–S–H) gel, leading to an improvement in gelation and the structural density of cement [2–7]. Previous studies have achieved better excitation by combining GGBS with other materials or activators [4,8–12]. Recently, it has been studied that the synergistic effect of alumina-enriched mineral admixtures (such as GGBS) and limestone has been shown to maximize the contribution of admixtures to cement gelling properties [13].

As a kind of by-product of the steel industry, most of the SS is used as building materials or subgrade materials [14–16]. Similar to cement, SS contains calcium silicate (i.e., dicalcium silicate (C₂S) and tricalcium silicate (C₃S)), tetracalcium aluminoferrite (C₄AF) and other active mineral components [17]. Compared with cement, the reactive activity of SS is relatively lower because of its slow cooling process and high content of

inert components [18]. In addition, it is important that the chemical composition of SS varies greatly with the changes in raw materials and processes, which is unfavorable for the actual promotion and application of SS [17,19,20]. This also adds difficulty to the study of GGBS–SS composite cementitious materials.

At present, some researchers have explored the use of mechanical grinding and the chemical excitation method to improve the slag activity in order to achieve a more efficient use of SS [18,19,21,22]. As shown in Figure 1, the current study is limited to the exploration of the composite effect of GGBS–SS [22–24], cement–GGBS [5–7,9–11] or cement–SS [14–16,19,20,25]. The pozzolanic reactions of active silicon aluminum oxide in GGBS can promote the hydration of C_3A , C_3S , C_2S and C_4AF in cement and SS, so that SS and GGBS can interact with each other to enhance the hydration rate and increase the amount of C–S–H precipitation. Ultra-fine SS can improve the density of cement and has little influence on its mechanical properties when the replaced content is low [18]. In this way, GGBS and SS can be used as cement admixtures for large-scale recycling. Studies have shown that GGBS can make up for the deficiency of SS and a suitable GGBS/SS ratio is conducive to the development of concrete strength and helpful to control the hydration heat release to a lower range [23,24]. However, the reaction mechanism of the synergistic effect of SS and GGBS is still unclear, and the excitation mechanism of the chemical activator also needs further exploration when GGBS and SS are used in concrete.

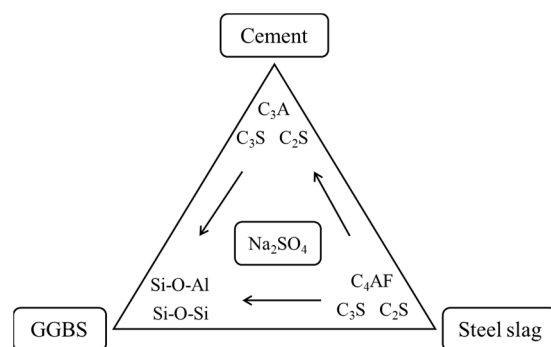


Figure 1. The scope of the previous studies.

Typically, activators are important influencing factors on the performance of alkali-activated composite materials [26,27]. Traditional activators, such as NaOH [28] and Na_2SiO_3 [29], have been widely used for slag-containing blended cement. However, due to the high hidden energy and carbon content brought by the production of NaOH and Na_2SiO_3 [30], and the high cost and high corrosiveness [31], their widespread application is limited. As a naturally occurring industrial by-product with an uncomplicated production process, Na_2SO_4 is safe, cheap and highly sustainable. Therefore, understanding the activation effect and mechanism of Na_2SO_4 is crucial for promoting its research and application progress. In this research, GGBS and a kind of hot stew SS are selected to explore the mutual activation mechanism of the components in the cement–GGBS–SS ternary system. Na_2SO_4 is used as an activator in the system to explore its excitation effect and mechanism.

2. Experimental Details

2.1. Materials

According to the provisions of GB8076-2008 [32] and ASTM C150-2012 standards [33], ordinary Portland cement (OPC), which had a specific surface area of $330.5 \text{ m}^2/\text{kg}$, was used in this study. The GGBS used in this work was supplied by Dunshi new building materials Co., Ltd. (Tangshan, China). and had a specific surface area of $537.5 \text{ m}^2/\text{kg}$. The SS supplied by Shanghai Metallurgical Environmental Engineering Co., Ltd. (Shanghai, China). was a type of hot stew SS, which had a specific surface area of $675.3 \text{ m}^2/\text{kg}$. To obtain the chemical compositions of cement, GGBS and SS, an X-ray fluorescence

spectroscopy (XRF, S4-Explorer, Bruker, Saarbrücken, Germany) was employed. The results are summarized in Table 1.

According to Table 1, the main components of GGBS are SiO_2 , Al_2O_3 and calcium magnesium oxide, and the basicity index of GGBS can be calculated:

$$M = (\text{CaO} + \text{MgO})/(\text{SiO}_2 + \text{Al}_2\text{O}_3) = 0.83 < 1.0 \quad (1)$$

where M is the basicity index. The basicity index represents the activity of the GGBS [34]. Equation (1) demonstrates that the GGBS used in this work is acidic slag. In addition, the chemical composition in Table 1 shows that SS contains much higher Fe_2O_3 and much lower CaO than cement.

X-ray diffractograms (XRD) and SEM images of cement, slag and SS are summarized in Figure 2. Figure 2 shows that the GGBS composition is relatively simple, mainly containing SiO_2 , Al_2O_3 and other oxides, which is consistent with the conclusion of XRF, and the particles have an irregular shape, a dense structure and a smooth surface. The main mineral components of cement are C_3S , C_2S , C_3A , C_4AF and CaSO_4 , and cement has a surface topography similar to GGBS. In contrast, SS particles have a slightly loose structure and a rough surface, and the mineral composition of SS is more complex. The most abundant active mineral composition in SS is C_2S , along with a small amount of C_3S and C_4AF . In addition, a large number of inert components, such as the solid solution of the RO phase (continuous solid solution formed by MgO , FeO and MnO), is present in SS, which is an inert component and the main reason for restricting the large-scale application of SS. In this experiment, some inert or negligible trace components were excluded, and the experimental focus was placed on these active mineral components that account for a large proportion and are involved in the mutual activation process in the ternary system. Add the Na_2SO_4 activator to the system to study the mutual activation mechanism between the activator and components.

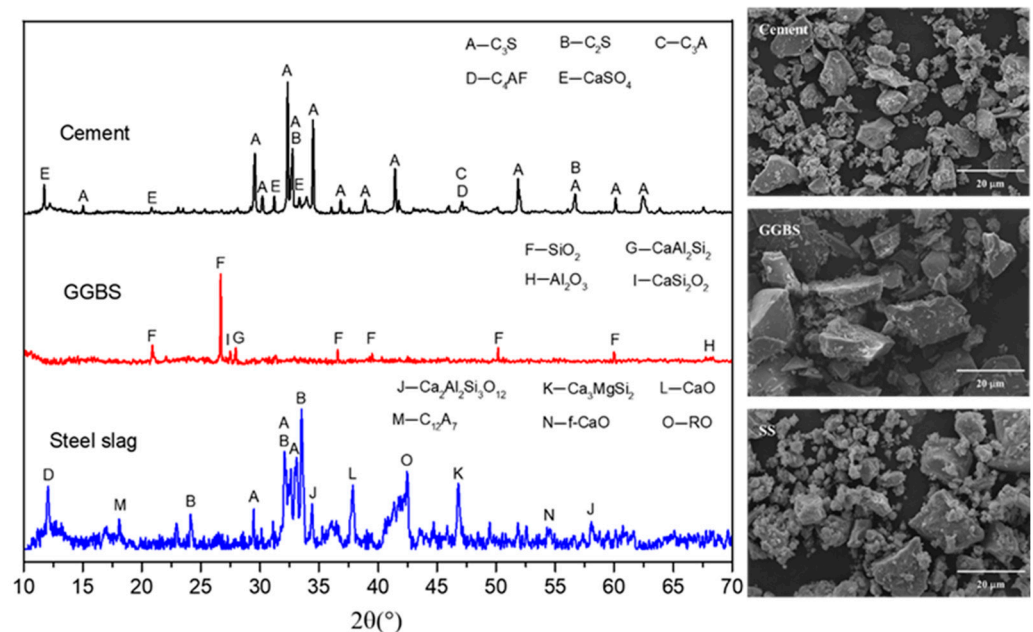


Figure 2. X-ray diffractograms and SEM images of cement, GGBS and steel slag.

Table 1. Chemical composition of materials.

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	MnO	P_2O_5	TiO_2	SO_3
OPC	18.7	4.22	3.33	66.33	1.97	0.854	—	0.11	0.27	2.77
GGBS	35.8	14.4	0.69	34.9	6.57	1.01	0.24	—	0.66	1.86
Steel slag	10.78	2.32	30.22	43.6	6.55	0.024	2.01	1.76	0.5	0.25

2.2. Cement Pastes

In order to obtain the best proportion of GGBS and SS in cement, the blended cement pastes with different levels of replacement by weight are shown in Table 2. Eleven mixtures were prepared by varying the GGBS and SS contents with the water–solid ratio (w/b) maintained at 0.4. The preparation of the composite cement paste was based on the DBJ/T13-196-2014 standard [35]. The mechanical properties of the samples are tested after curing to different ages under the standard condition.

Table 2. Blended cement pastes with different content of GGBS and steel slag.

	Cement (%)	Slag (%)	Steel Slag (%)
C100	100	0	0
C50-S50	50	50	0
C50-S45-SS5	50	45	5
C50-S40-SS10	50	40	10
C50-S35-SS15	50	35	15
C50-S30-SS20	50	30	20
C50-S25-SS25	50	25	25
C50-S20-SS30	50	20	30
C50-S15-SS35	50	15	35
C50-S10-SS40	50	10	40
C50-S5-SS45	50	5	45
C50-SS50	50	0	50

2.3. Test Methods

The mineral components of the hydration product were explored by X-ray diffraction (XRD, D8 Advance, Bruker) with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$). The XRD uses a D max/RB diffractometer. The scanning range varied between 10° and 70° with a scanning rate of $0.1^\circ/\text{s}$.

A Nicolet 6700 Fourier Transform Infrared (FT-IR) Spectrometer was employed to analyze the chemical bond changes in the hydration products in different systems. The scanning range was from 400 to 4000 cm^{-1} by 32 times per measurement.

A Quanta TM 250 FEG Environmental Scanning Electron microscope (ESEM) and Energy Dispersive Spectrometer (EDS) were used to observe the changes in the surface morphology and mineral composition of hydration products.

The isothermal calorimetry of different systems was conducted on 5.0 g of paste prepared with a 0.4 w/b ratio. The heat of the hydration reaction was measured continuously for 72 h at 25°C by an isothermal calorimeter (TAM Air 8-channel, TA Instruments, Newcastle, WA, USA).

The mechanical properties of hardened cement paste were in accordance with GB/T 17671-1999 (ISO method) [36].

The hydration degree of cement with different admixtures was tested by the TG/DTA6300 thermogravimetric analyzer (TG STA 409PC, NETZSCH-Gerätebau GmbH, Selb, Germany). The $30\text{--}1000^\circ\text{C}$ temperature range was used for this test and the heating rate was set at $10^\circ\text{C}/\text{min}$.

3. Results and Discussion

3.1. Mechanical Properties of Composite Cement

Figures 3 and 4 show the mechanical properties of composite cement. The flexural strength shown in Figure 3 has different degrees of decline after mixing with different contents of GGBS or SS in cement. However, when the substituted amount of GGBS and SS are $40 \text{ wt.}\%$ and $10 \text{ wt.}\%$, respectively, the flexural strength of the composite cement reaches the maximum at any hydration age. The compressive strength shown in Figure 4 also has different degrees of decrease after mixing with different contents of GGBS or SS in cement at an early hydration age (3d and 7d). However, in the later stage of hydration, the

compressive strength shows a slight increase when the GGBS content is 40 wt.% and the SS content is 10 wt.%. It can be indicated that the optimum content of GGBS and SS in cement are 40 wt.% and 10 wt.% in this study.

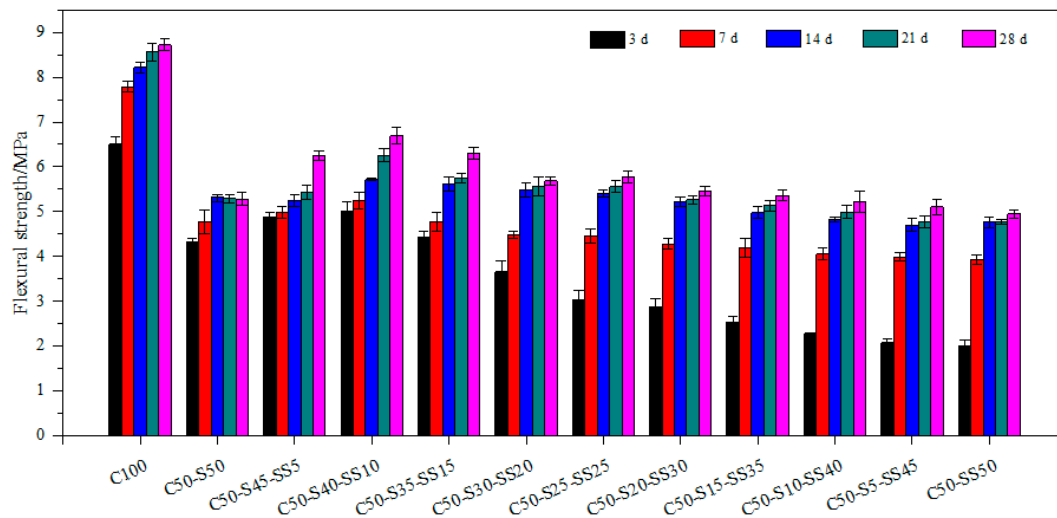


Figure 3. Flexural strength of pure cement and cement with different contents of GGBS and steel slag.

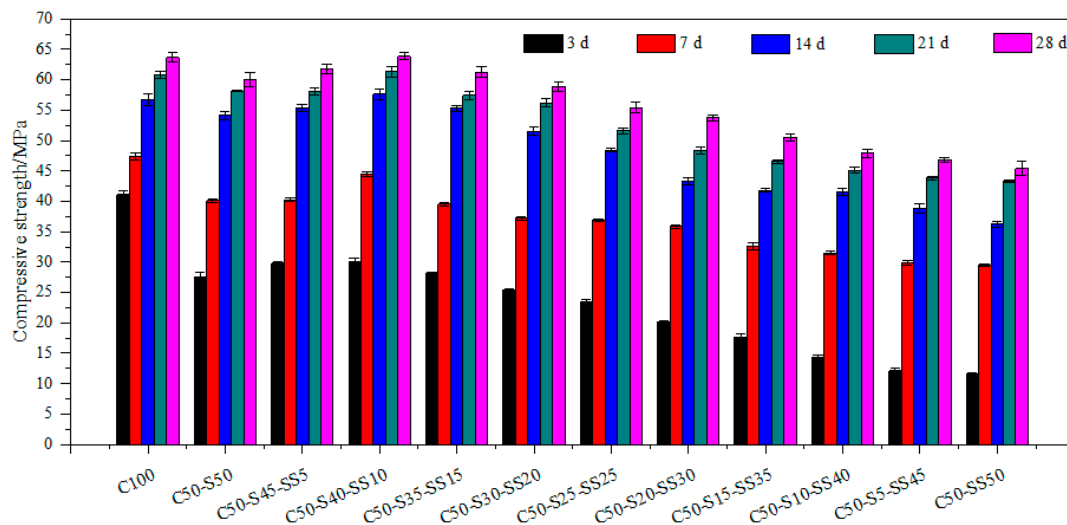
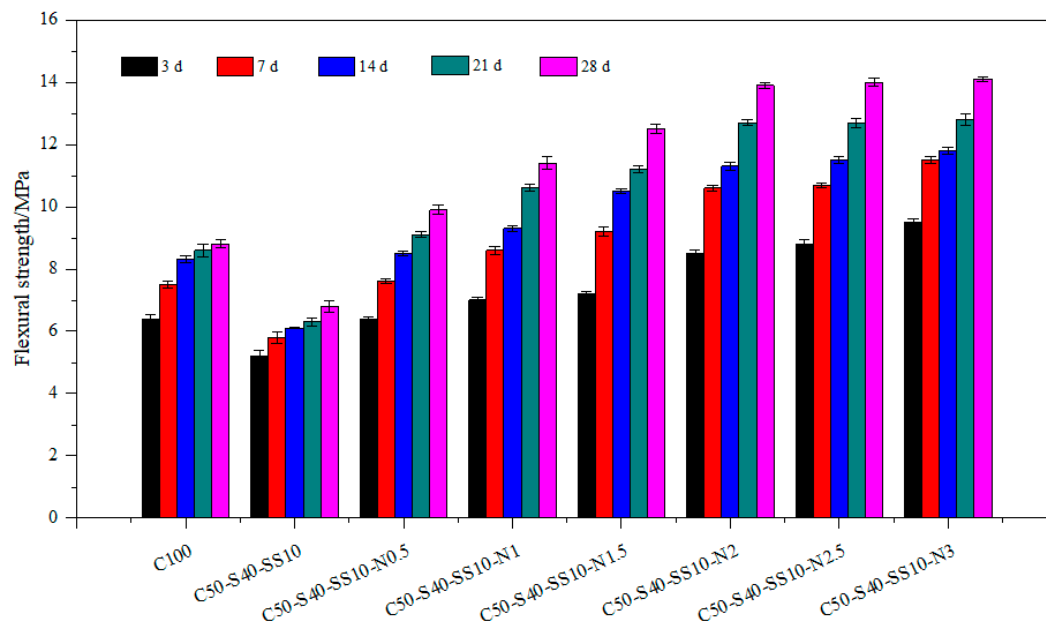
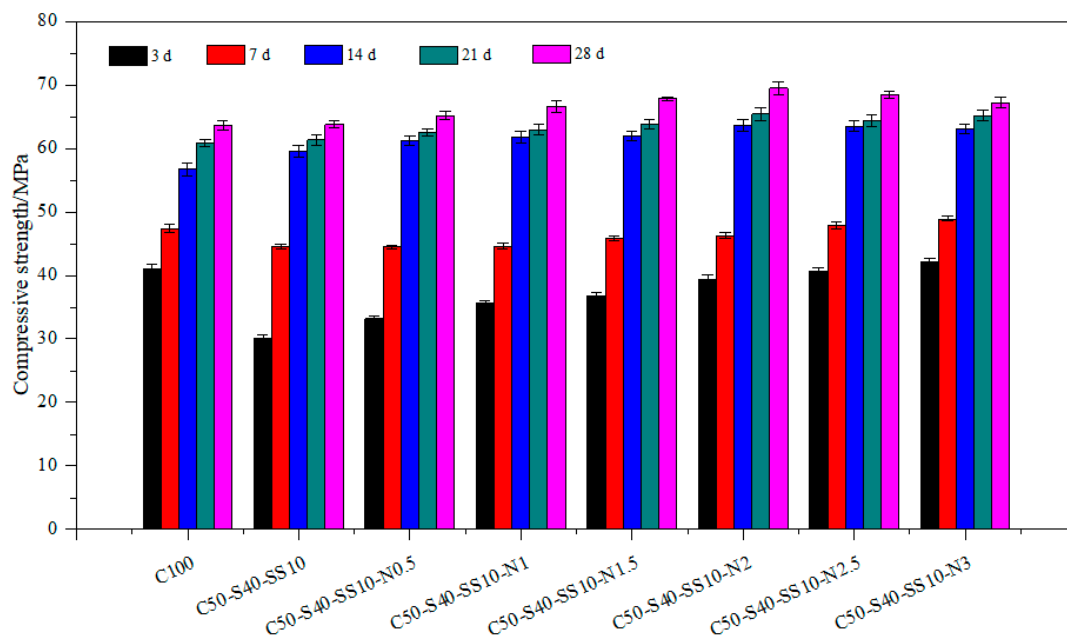


Figure 4. Compressive strength of pure cement and cement with different contents of GGBS and steel slag.

With the aim of obtaining the optimum amount of Na_2SO_4 in the C50-S40-SS10 system, different amounts of Na_2SO_4 were added to this system (as shown in Table 3), and the mechanical properties were tested after curing to a certain age under standard conditions (Figures 5 and 6). Figure 5 shows that the flexural strength of the C50-S40-SS10 system is obviously improved after the addition of Na_2SO_4 . The flexural strength of the blank group is 8.8 MPa, and when the dosage of Na_2SO_4 is 2%, it increases by 57.95% to 13.9 MPa. In addition, when the dosage is higher than 2%, the growth rate of the flexural strength becomes slower. Figure 6 shows that with the increase in the amount of Na_2SO_4 , the compressive strength of the C50-S40-SS10 system showed a rising trend at the early age. When the Na_2SO_4 content is 2%, the compressive strength of the system reaches its highest at 28 d (69.5 MPa), which is 9.28% higher than that of pure cement. Thus, 2% is chosen to be the optimum amount of Na_2SO_4 in the C50-S40-SS10 system.

Table 3. Pure cement and C50-S40-SS10 system with different contents of Na_2SO_4 .

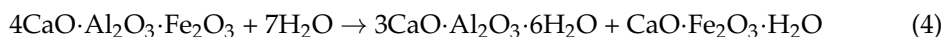
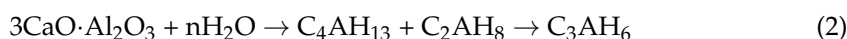
	Cement (%)	GGBS (%)	Steel Slag (%)	Na_2SO_4 (%)
C100	100	0	0	0
C50-S40-SS10	50	40	10	0
C50-S40-SS10-N0.5	50	40	10	0.5
C50-S40-SS10-N1	50	40	10	1
C50-S40-SS10-N1.5	50	40	10	1.5
C50-S40-SS10-N2	50	40	10	2
C50-S40-SS10-N2.5	50	40	10	2.5
C50-S40-SS10-N3	50	40	10	3

**Figure 5.** Flexural strength of pure cement and C50-S40-SS10 paste with different contents of Na_2SO_4 .**Figure 6.** Compressive strength of pure cement and C50-S40-SS10 paste with different contents of Na_2SO_4 .

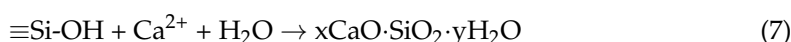
The strength of pure cement, composite cement and composite cement with different contents of Na_2SO_4 was analyzed synthetically. In order to clarify the mutual activation mechanism of each component in the C50-S40-SS10-N2 system with the best mechanical performance in the ternary system and explore the excitation effect and mechanism of Na_2SO_4 , a comparative analysis of microscopic experiments was conducted. The following five groups of samples were selected: pure cement, C50-S50, C50-SS50, C50-S40-SS10 and C50-S40-SS10-N2.

3.2. XRD Results of Hydration Products

The order of the hydration reaction rates of the four main mineral components in cement is $\text{C}_3\text{A} > \text{C}_3\text{S} > \text{C}_4\text{AF} > \text{C}_2\text{S}$. Therefore, after the mixing of cement and water, the hydration reactions of the four mineral components are shown in Equations (2)–(5) [37]. Figure 7 shows the XRD patterns of different system hydration products curing for 3 d and 28 days in the range of $6\text{--}14^\circ$, which shows the impact of the different contents of GFBS and SS on the evolution of AFt and AFm phases. Figure 7a shows that AFt is contained in the hydrated product of pure cement at 3 d, which is due to the presence of about 5 wt.% CaSO_4 in pure cement. As shown in Equation (6), the C_3AH_6 produced by Equation (2) will react with CaSO_4 to produce ettringite (AFt) [38].

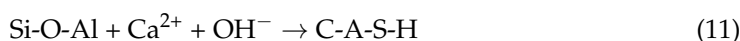


Equation (1) indicates that the GGBS used in the experiment is a kind of acidic slag, and its activity is more likely to be excited under alkaline conditions. Studies have shown that, under the effect of OH^- , Si–O and Al–O bonds can break down, then react with Ca^{2+} to produce C–S–H gel and C–A–S–H gel [9,39]. The corrosion of active SiO_2 by $\text{Ca}(\text{OH})_2$ is shown in Equations (7) and (8) [12]. Equation (7) is the neutralization reaction of silicon hydroxyl groups of GGBS to produce C–S–H, and Equation (8) indicates that the internal Si–O bond is gradually destroyed and the $[\text{SiO}_4]^{4-}$ structure is disintegrated.



$\text{Ca}(\text{OH})_2$ generated by Equations (3) and (5) in the system continuously dissolves Ca^{2+} and OH^- . OH^- is retained in the pore fluid to maintain a higher pH, and Ca^{2+} reacts with $\equiv\text{Si}-\text{OH}$ to generate C–S–H, so that the reaction is carried out continuously.

The aluminum oxide contained in the GGBS can react with Ca^{2+} in the solution to produce C_3AH_6 under alkaline conditions (as shown in Equations (9) and (10)) [14]. In addition, the silicon aluminum oxide in GGBS can dissolve in the alkaline environment in cement to generate the C–A–S–H gel (as shown in Equation (11)).



When cement is replaced by 50 wt.% of the GGBS, the content of CaSO_4 in the system is reduced and the amount of C_3AH_6 is relatively increased. As shown in Equation (12), the AFt will react with the C_3AH_6 produced by reaction (2), (4) and (9) to generate AFm [38].

The XRD patterns of 3 d and 28 d paste samples clearly showed reflection peaks for AFm at about 10.7° (as shown in Figure 7).

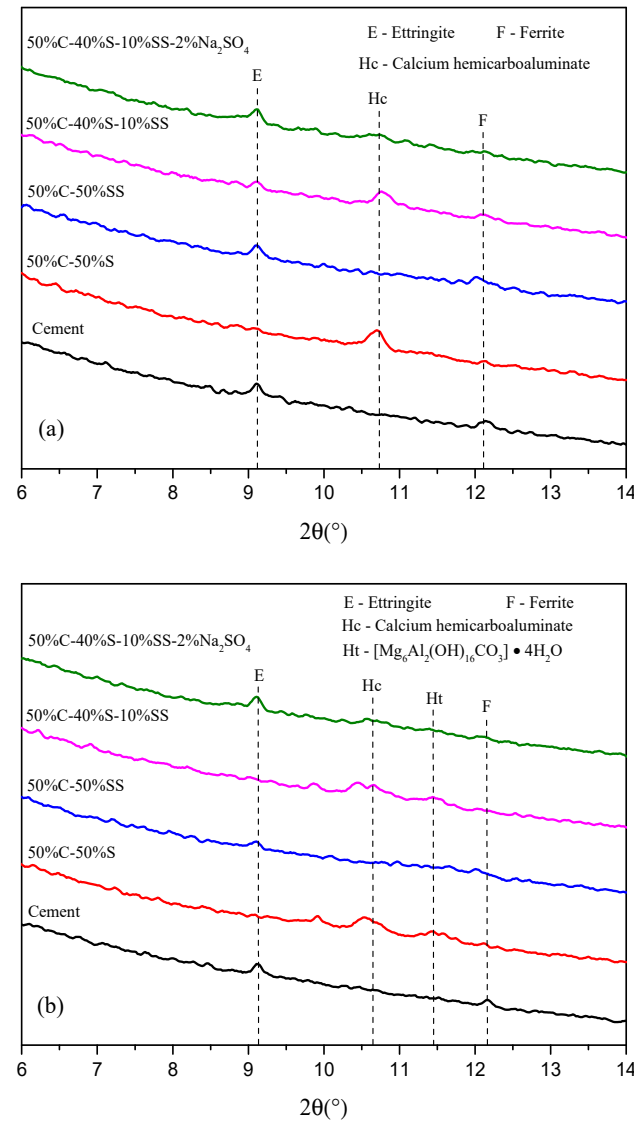
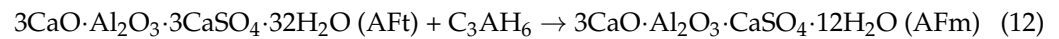


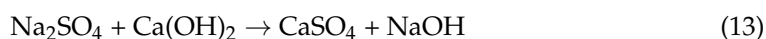
Figure 7. XRD patterns of samples: (a) hydration for 3 d; (b) hydration for 28 d.

Wang et al. found that SS showed a higher reaction rate in the later stage of hydration, which can effectively accelerate the later hydration reaction in the blended cement system [23]. The hydration of SS is similar to pure cement (as shown in Equations (3)–(5)). Therefore, CaSO_4 content decreased when the cement is replaced by 50 wt.% SS, and due to the low hydration rate of SS, the reaction of C50-SS50 is mainly based on the hydration of cement at the early stage. Figure 7 shows that more AFt in the hydration products was found in the C50-SS50 system at 3 d, while the amount of AFt was slightly decreased at 28 d. This may be due to the fact that the system does not have enough CaSO_4 , which leads to the conversion of AFt to AFm in the late stage of hydration.

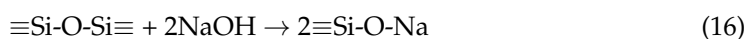
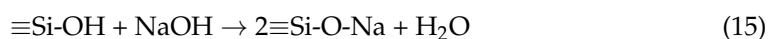
Compared with C50-S50, the dosage of GGBS is slightly lower in the ternary system. In addition, Figure 7a shows that the hydration product of the ternary system (without Na_2SO_4) at 3 d has a weak reflection peak standing for AFt at 9.1° and a strong reflection peak of AFm at 10.7° , which proves that there was still a certain amount of AFt that was

not converted to AFm at 3 d. When the hydration age reached 28 d, the AFt reflection peak disappeared, indicating that all AFt had transformed into AFm (Figure 7b).

Na₂SO₄ will precipitate with Ca(OH)₂ to generate CaSO₄ and NaOH (Equation (13)) after it was added in the ternary system, which improves the alkalinity of the system and contributes to the depolymerization of the [SiO₄]^{4−} and the [AlO₄]^{4−} [40].



The CaSO₄ produced by the reaction of Equation (13) has better dispersibility than the original CaSO₄ in cement, and is easier to react with C₃AH₆ to generate AFt. When Na₂SO₄ is added into the ternary system, at the early stage of hydration, the SO₄^{2−} and Ca²⁺ in the composite cement pore solution can react with the aluminum oxide to form AFt [14]. And this chemical reaction is shown as Equation (14), which also contributes to the increase in the amount of AFt in the ternary system (Figure 7b).



The erosion of [SiO₄]^{4−} by NaOH is shown in Equations (15) and (16) [41]. In the ternary system, the Ca(OH)₂ generated by Equations (3) and (5) is continuously eluted Ca²⁺ and OH[−]. ≡Si-O-Na is soluble in the void solution, so Na⁺ can be replaced by Ca²⁺ to generate the C–S–H precipitate, while OH[−] is retained in the pore fluid to maintain a higher pH, so that the above reaction is carried out continuously.

As the hydration reaction of SS is slow, the GGBS in the ternary system will still consume the Ca(OH)₂, which was produced by SS hydration, to promote the hydration of the ternary system. Because of the existence of cement, for the generated C–S–H, a good gelation can be presented. In addition, the C–A–S–H generated by the pozzolanic reactions of GGBS and the constant formation of AFt due to the presence of Na₂SO₄ can effectively fill the gap between the gel and the unhydrated particles [42]. At the later stage of hydration, this is also the main cause to enhance the mechanical properties of the ternary system.

3.3. FT-IR Analysis of Hydration Products

The FT-IR spectra of different samples curing for 3 d and 28 d are presented in Figure 8. The broad peak at about 3430 cm^{−1} as well as the narrow peak at about 1634 cm^{−1} for all samples are related to the tensile vibrations of the O–H bonds in chemical-bound H₂O and the H–O–H bending vibrations in the interlayer H₂O [38,43]. It can be seen from Figure 8 that all the samples exhibit an obvious and wide peak at 973 cm^{−1}, which stands for the asymmetric stretching vibrations of Si–O bonds or Al–O bonds in C–(A)–S–H [8,44]. Compared with the pure cement and binary system samples, the vibration band at 973 cm^{−1} for the ternary system samples was slightly lower at 3 d, and then increased to a higher wavenumber at 28 d of curing. This indicates that the ternary system, especially after the addition of Na₂SO₄, increases the dosage of Al in C–(A)–S–H and reduces the Ca/Si ratio during the 3 days of hydration. During the hydration period from 3 d to 28 d, the polymerization of C–(A)–S–H was improved, and the tetrahedral material was condensed as a result of the improved aluminum content in the gel [45,46]. This indicates that Na₂SO₄ has a significant effect on the decomposition of activated alumina in GGBS and the generation of C–(A)–S–H gel. The weak vibration band at 465 cm^{−1} and 789 cm^{−1} of C50-S50 and the ternary system samples also show the presence of Al elements in the network of cemented materials [47]. The sharp peaks at about 3637 cm^{−1} for the cement and C50-SS50 system pastes at 3 d and 28 d are related to the stretching vibration of the O–H bond in Ca(OH)₂ [48]. In contrast, the reflection peaks at 3637 cm^{−1} for the three systems mixed with GGBS are relatively weak, indicating that the GGBS has significant consumption on the Ca(OH)₂ in system (Figure 8a). The peak at 613 cm^{−1} for the C50-

S40-SS10-N2 system is due to the bending vibration of the S–O bonds in SO_4^{2-} , and it disappeared at the hydration time of 28 d, indicating that the activation of Na_2SO_4 on the system is mainly concentrated in the early stages of hydration. The shoulder-like vibrating band at about 1487 cm^{-1} (asymmetric stretching of the C–O bond) and the small vibrating band at 870 cm^{-1} (the out-of-plane bending of the C–O bond) indicate the presence of carbonate in the system (Figure 8a) [4].

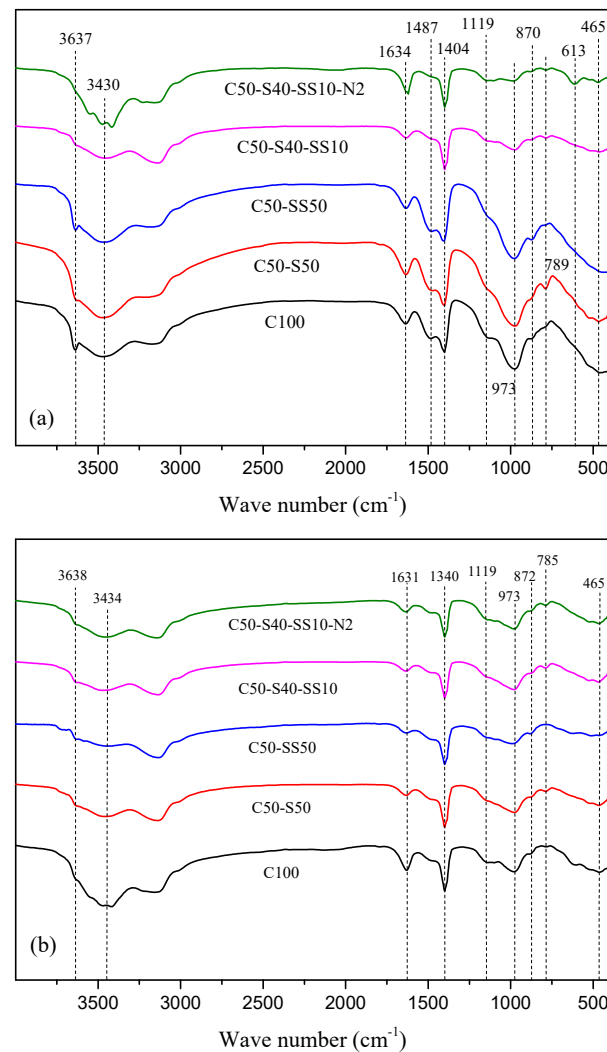


Figure 8. FT-IR spectra of samples: (a) hydration for 3 d; (b) hydration for 28 d.

3.4. Hydration Heat Evolution

The early hydration heat release characteristics of pure cement and blended cement with or without Na_2SO_4 over the first 72 h of hydration reaction at $25\text{ }^{\circ}\text{C}$ are shown in Figure 9. As reported, the hydration process of pure cement is roughly divided into five stages: (1) hydration induction period; (2) dormant period; (3) hydration acceleration period; (4) hydration deceleration period; (5) hydration stabilization period [18]. A few minutes after the mixture of blended cement and water, the first exothermic peak appeared due to the initial hydration of C_3A and C_3S as well as the formation of AFt [23]. Then the hydration of blended cement enters the dormant period. The silicate mineral in the cement hydrate reacts to generate C–S–H. A saturation state of $\text{Ca}(\text{OH})_2$ concentration can be reached gradually. The concentration of active silica–alumina in the slurry decreases and the rate of hydration and heat release is slow [23]. It can be seen from Figure 9a, compared with pure cement, that the influence of adding 50 wt.% GGBS in cement on the dormant period is limited. The reason for this can be attributed to that the GGBS used in this work

is acidic slag (Equation (1)). When the Ca^{2+} in the system reaches a certain concentration, the GGBS will quickly carry out a volcanic ash reaction, which makes the dormancy period shorter. However, the dormant period of C50-SS50 and the ternary system are significantly longer. It was reported that mixing SS in cement increases the setting time due to the fact that SS extends the dormant period [16,20]. The cause of this phenomenon can be attributed to the low activity of SS [25]. The ternary system with or without Na_2SO_4 has a longer dormancy period due to the early formation of AFt, which covers the surface of the cementitious material particles and delays the hydration reaction. And a longer setting time facilitates the transportation and pouring of concrete in many cases.

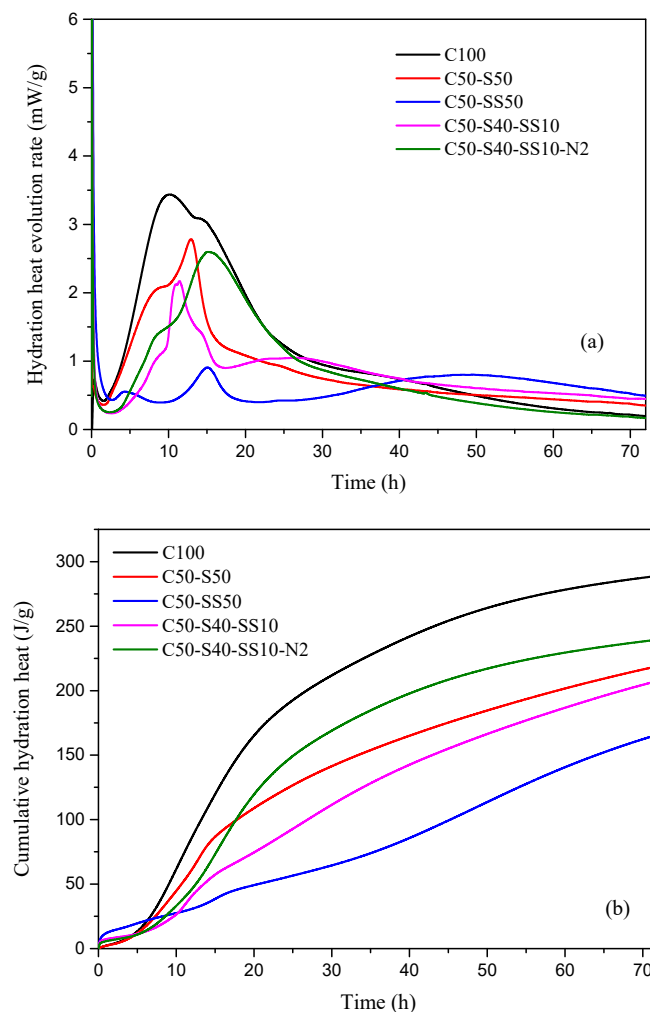


Figure 9. Hydration heat evolution of pure cement and blend cement: (a) hydration heat evolution rate; (b) cumulative hydration heat.

Figure 9a shows that the second exothermic peak of all composite cement material samples is much lower than pure cement. Although the second exothermic peak of SS appeared at the earliest time (at about 4.5 h), the exothermic peak was the lowest (about 0.6 mW/g). The second exothermic peak of the ternary system increased after the addition of Na_2SO_4 , which proved that the accelerator could increase the hydration rate of C_2S and C_3S in the system. However, the second exothermic peak of the ternary system is lower than that of the C50-S50 system, indicating that the formation of AFt in the hydration induction period has an important influence on decreasing the hydration heat release rate of the binder. The third exothermic peak shown in Figure 9a represents the transformation of AFt to AFm phases in the system [5]. This is clearly shown in Figure 9a, as the transformation of AFt to AFm phases occurred earlier in C50-S50 and C50-S40-SS10 than that of C50-S40-

SS10-N2. This proves that Na_2SO_4 contributes to the formation of AFt in the system and delays its transformation to AFm, which is consistent with the phenomenon obtained in Section 3.2.

Compared with pure cement, Figure 9b shows a reduction in the cumulative hydration heat for all blend cement material samples. The cumulative hydration heat of pure cement in 72 h is 289 J/g. The C50-SS50 system has the lowest cumulative hydration heat, which is about half that of pure cement [16]. This phenomenon is mainly due to the lower hydration activity of SS. In addition, the cumulative hydration heat of the ternary system mixed with Na_2SO_4 in 72 h is 239 J/g, which is significantly lower than pure cement. It is proved that adding mineral admixture in the cement, even if the chemical activator is added, will help to decrease the hydration heat of the cement, which can reduce the temperature shrinkage of the concrete structure, thereby preventing its cracking [23,49]. The excellent property of decreasing the hydration heat of GGBS and SS will contribute to its widespread use in concrete [49,50].

3.5. SEM and TG Analysis of Hydration Products

Figure 10 shows SEM images of the hydration products of different samples after 28 days of curing. It can be seen that the flaky $\text{Ca}(\text{OH})_2$, the needle-shaped AFt and dense C–S–H gel are cross-linked to each other. It is obvious that pure cement contains more closely packed flake $\text{Ca}(\text{OH})_2$. And compared with the sample containing GGBS, Figure 10c shows that the hardened paste of C50-SS50 has a looser structure. In addition, compared to Figure 10d, Figure 10e shows that the hardened paste is more compact and uniform after the addition of Na_2SO_4 . In fact, the SEM results can only be used to generally determine the composition and structure of the hardened paste. Therefore, the TG experiment will compare the hydration degree of each group by quantifying the content of $\text{Ca}(\text{OH})_2$ in the hardened paste.

As shown in Figure 11, during the various periods of hydration, the $\text{Ca}(\text{OH})_2$ content in pure cement was the highest in five groups, followed by the C50-SS50 system. And the development of the $\text{Ca}(\text{OH})_2$ content in these two groups increases with the growth of the hydration age; however, the rate of increase is gradually flattened. When 50 wt.% GGBS is added in cement, the $\text{Ca}(\text{OH})_2$ dosage decreases with the growth of the age and reaches the lowest content among the five groups after 21 days of hydration. This proves that the pozzolanic reactions of GGBS can consume $\text{Ca}(\text{OH})_2$ with a higher rate than the $\text{Ca}(\text{OH})_2$ formation by cement hydration.

Figure 11 shows that the content of $\text{Ca}(\text{OH})_2$ in the C50-S40-SS10 system showed a tendency to decrease first and then increase with the growth of the hydration age, which proves that the $\text{Ca}(\text{OH})_2$ consumption rate is higher than its formation rate in the early age of the ternary system. At a later stage of hydration, the pozzolanic reactions of GGBS slowed down and the hydration reaction of SS accelerated, which improved the $\text{Ca}(\text{OH})_2$ dosage in the ternary system. After adding Na_2SO_4 in the ternary system, the $\text{Ca}(\text{OH})_2$ dosage also showed a trend of decreasing first and then increasing with the growth of the hydration age. However, the content of $\text{Ca}(\text{OH})_2$ is lower than that of the ternary system without Na_2SO_4 in all hydration ages. It is proved that Na_2SO_4 promotes the hydration reaction of GGBS in the ternary system at all hydration ages.

For pure cement and the C50-SS50 system, the fitting curve of the $\text{Ca}(\text{OH})_2$ content changing with the hydration age is presented in Figure 12. It can be found that, for pure cement and the C50-SS50 system, the $\text{Ca}(\text{OH})_2$ dosages have a good power function relationship with the hydration age. The relationship between $\text{Ca}(\text{OH})_2$ content and the hydration age in pure cement is:

$$Y = 13.22296X^{0.08132} \quad (R^2 = 0.98746) \quad (17)$$

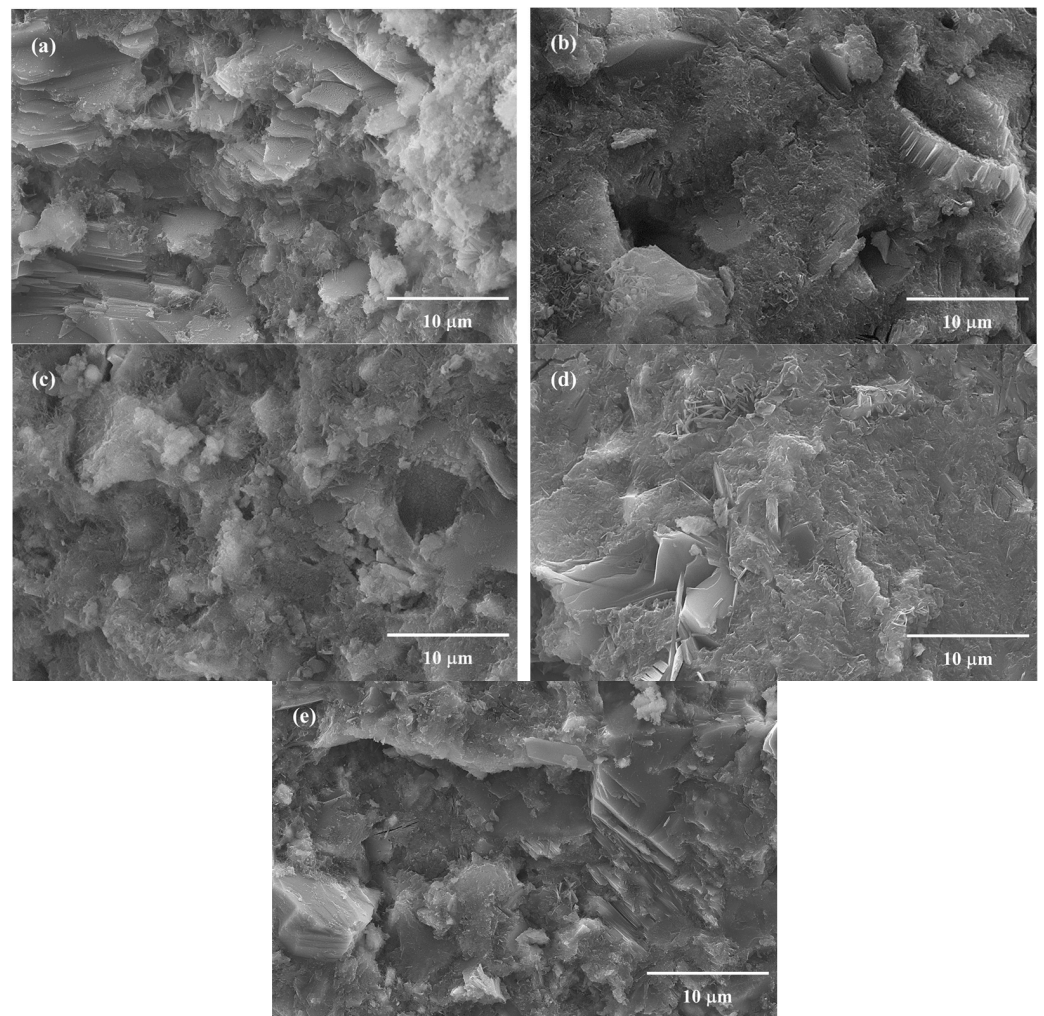


Figure 10. SEM of hydration products of different samples after 28 days of curing: (a) pure cement, (b) C50-S50, (c) C50-SS50, (d) C50-S40-SS10, (e) C50-S40-SS10-N2.

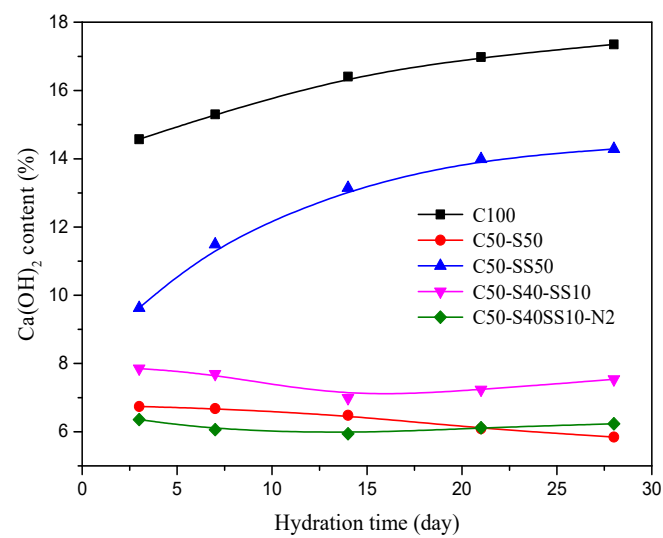


Figure 11. Changes in Ca(OH)_2 content with hydration age.

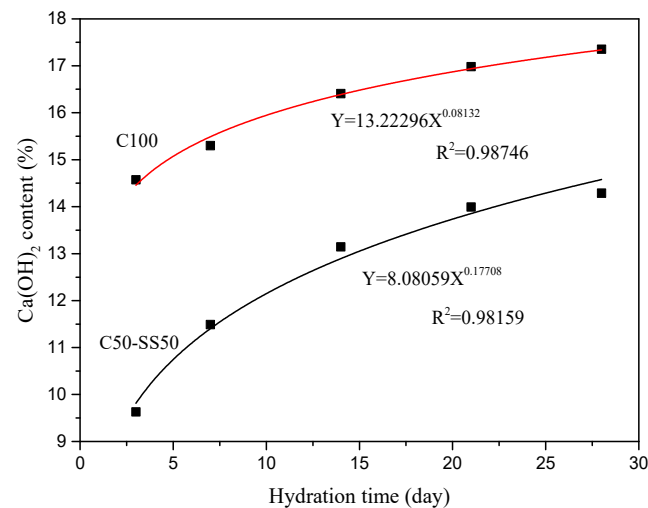


Figure 12. Fitting curve of Ca(OH)_2 content in pure cement and C50-SS50 system.

And the relationship between Ca(OH)_2 content and the hydration age in C50-SS50 system paste is:

$$Y = 8.08059X^{0.17708} \quad (R^2 = 0.98159) \quad (18)$$

Derived on both sides of Functions (17) and (18), it can be seen that the growth velocity of Ca(OH)_2 dosage in pure cement is $dy/dx = 1.08x^{-0.91868}$. In addition, the Ca(OH)_2 growth rate in the C50-SS50 system paste is $dy/dx = 1.43x^{-0.82292}$. It can be proved that the Ca(OH)_2 growth rate in pure cement is higher than that of the C50-SS50 system at the early stage of hydration, but the growth rate of the Ca(OH)_2 content of C50-SS50 exceeds that of pure cement after a certain time. This also proves that SS has a catalytic influence on the hydration of the ternary system at the late stage.

3.6. Hydration Mechanism

The mutual activation mechanism of the cement–GGBS–SS ternary system mixed with Na_2SO_4 is summarized in Figure 13. Figure 13 shows that C–S–H gel and C–F–H can be generated by the hydration reactions of C_3S and C_2S in cement and SS. At the same time, Ca(OH)_2 can be provided for pozzolanic reactions of GGBS. In turn, the continuous consumption of Ca(OH)_2 can promote the cement hydration reaction, especially SS hydration in the later stages. In addition, the decomposition and recombination reactions of the active silica–alumina oxide in GGBS provide additional C–S–H and C–(A)–S–H gel, making the structure of the ternary system more compact. The C_3A in cement is rapidly hydrated to produce C–A–H after mixing with water, which then reacts with calcium sulfate to produce AFt. The C–A–H produced by the reaction of Al_2O_3 in the GGBS with Ca(OH)_2 also reacts with calcium sulfate to produce AFt; however, the time of the reaction is relatively late. Moreover, AFt will be converted into AFm in the later stages of hydration if the content of calcium sulfate in the ternary system is not enough. The addition of Na_2SO_4 provides Na^+ and SO_4^{2-} with high dispersibility into the ternary system. The presence of Na^+ also increases the pH of the system, and the SO_4^{2-} can react with the Ca^{2+} in the system to produce CaSO_4 , which is more dispersible, making it easier to react with C–A–H to generate AFt.

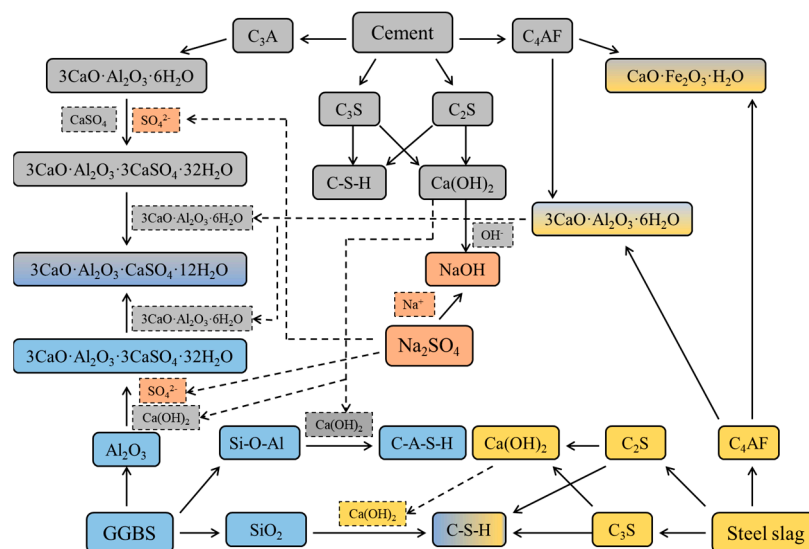


Figure 13. Hydration reaction mechanism of cement-slag-steel slag system activated by Na_2SO_4 .

4. Conclusions

The mutual activation mechanism of the cement–GGBS–SS ternary system mixed with Na_2SO_4 was experimentally studied and summarized in this research. The main conclusions can be summarized as follows:

The optimum blending amount of GGBS and SS in cement is 40 wt.% and 10 wt.%, respectively. The compressive strength of the composite cement is slightly higher than pure cement. The optimum blending amount of Na_2SO_4 in the C50–S40–SS10 system is 2%. The flexural strength of the C50–S40–SS10 system increases by 57.95% to 13.9 MPa, and the compressive strength is 9.28% higher than that of pure cement at 28 d.

Based on the analysis of AFt, AFm and C–A–S–H gel in products of the hydration reactions by XRD and FT-IR, the hydration process of C_3A in cement, the pozzolanic reactions of activated alumina in GGBS and the promoting effect of Na_2SO_4 on the formation of AFt in the ternary system were confirmed.

The comparative analysis of the hydration heat evolution and $\text{Ca}(\text{OH})_2$ dosage of pure cement and blended cement confirms the effect of GGBS on $\text{Ca}(\text{OH})_2$ consumption and the improvement of the hydration reaction of cement and SS. The enhancement effect of Na_2SO_4 on pozzolanic reactions and its influence on the hydration heat evolution rate of the ternary system were also confirmed.

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Conflicts of Interest: Authors Lingzhi Cui and Chaohui Zhang were employed by the company Shenzhen Metro Group Co., Ltd. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

References

1. Gong, K.; White, C.E. Impact of chemical variability of ground granulated blast-furnace slag on the phase formation in alkali-activated slag pastes. *Cem. Concr. Res.* **2016**, *89*, 310–319. [CrossRef]

2. Lothenbach, B.; Scrivener, K.; Hooton, R.D. Supplementary cementitious materials. *Cem. Concr. Res.* **2011**, *41*, 1244–1256. [[CrossRef](#)]
3. McLellan, B.C.; Williams, R.P.; Lay, J.; van Riessen, A.; Corder, G.D. Costs and carbon emissions for geopolymer pastes in comparison to ordinary portland cement. *J. Clean. Prod.* **2011**, *19*, 1080–1090. [[CrossRef](#)]
4. Kovtun, M.; Kearsley, E.P.; Shekhovtsova, J. Chemical acceleration of a neutral granulated blast-furnace slag activated by sodium carbonate. *Cem. Concr. Res.* **2015**, *72*, 1–9. [[CrossRef](#)]
5. Ogrigbo, O.R.; Black, L. Influence of slag composition and temperature on the hydration and microstructure of slag blended cements. *Constr. Build. Mater.* **2016**, *126*, 496–507. [[CrossRef](#)]
6. Çetin, C.; Erdoğan, S.T.; Tokyay, M. Effect of particle size and slag content on the early hydration of interground blended cements. *Cem. Concr. Compos.* **2016**, *67*, 39–49. [[CrossRef](#)]
7. Liu, J.; Yu, Q.; Zuo, Z.; Yang, F.; Duan, W.; Qin, Q. Blast furnace slag obtained from dry granulation method as a component in slag cement. *Constr. Build. Mater.* **2017**, *131*, 381–387. [[CrossRef](#)]
8. Bernal, S.A.; Provis, J.L.; Rose, V.; Mejía de Gutierrez, R. Evolution of binder structure in sodium silicate-activated slag-metakaolin blends. *Cem. Concr. Compos.* **2011**, *33*, 46–54. [[CrossRef](#)]
9. Day, R.L.; Shi, C. Early strength development and hydration of alkali-activated blast furnace slag/fly ash blends. *Adv. Cem. Res.* **1999**, *11*, 189–196.
10. Gesoğlu, M.; Güneyisi, E.; Özbay, E. Properties of self-compacting concretes made with binary, ternary, and quaternary cementitious blends of fly ash, blast furnace slag, and silica fume. *Constr. Build. Mater.* **2009**, *23*, 1847–1854. [[CrossRef](#)]
11. Deboucha, W.; Leklou, N.; Khelidj, A.; Oudjit, M.N. Hydration development of mineral additives blended cement using thermogravimetric analysis (TGA): Methodology of calculating the degree of hydration. *Constr. Build. Mater.* **2017**, *146*, 687–701. [[CrossRef](#)]
12. Schöler, A.; Lothenbach, B.; Winnefeld, F.; Zajac, M. Hydration of quaternary Portland cement blends containing blast-furnace slag, siliceous fly ash and limestone powder. *Cem. Concr. Compos.* **2015**, *55*, 374–382. [[CrossRef](#)]
13. Adu-Amankwah, S.; Zajac, M.; Stabler, C.; Lothenbach, B.; Black, L. Influence of limestone on the hydration of ternary slag cements. *Cem. Concr. Res.* **2017**, *100*, 96–109. [[CrossRef](#)]
14. Shen, W.; Zhou, M.; Ma, W.; Hu, J.; Cai, Z. Investigation on the application of steel slag-fly ash-phosphogypsum solidified material as road base material. *J. Hazard. Mater.* **2009**, *164*, 99–104. [[CrossRef](#)] [[PubMed](#)]
15. Zhang, T.; Yu, Q.; Wei, J.; Li, J.; Zhang, P. Preparation of high performance blended cements and reclamation of iron concentrate from basic oxygen furnace steel slag. *Resour. Conserv. Recycl.* **2011**, *56*, 48–55. [[CrossRef](#)]
16. Kourounis, S.; Tsivilis, S.; Tsakiridis, P.E.; Papadimitriou, G.D.; Tsibouki, Z. Properties and hydration of blended cements with steelmaking slag. *Cem. Concr. Res.* **2007**, *37*, 815–822. [[CrossRef](#)]
17. Li, J.; Yu, Q.; Wei, J.; Zhang, T. Structural characteristics and hydration kinetics of modified steel slag. *Cem. Concr. Res.* **2011**, *41*, 324–329. [[CrossRef](#)]
18. Qiang, W.; Mengxiao, S.; Jun, Y. Influence of classified steel slag with particle sizes smaller than 20µm on the properties of cement and concrete. *Constr. Build. Mater.* **2016**, *123*, 601–610. [[CrossRef](#)]
19. Rosales, J.; Cabrera, M.; Agrela, F. Effect of stainless steel slag waste as a replacement for cement in mortars. Mechanical and statistical study. *Constr. Build. Mater.* **2017**, *142*, 444–458. [[CrossRef](#)]
20. Yilmaz, I.A.A.I.s. Study on steel furnace slags with high MgO as additive in Portland cement. *Cem. Concr. Res.* **2002**, *32*, 1247–1249.
21. Liu, Q.; Liu, J.; Qi, L. Effects of temperature and carbonation curing on the mechanical properties of steel slag-cement binding materials. *Constr. Build. Mater.* **2016**, *124*, 999–1006. [[CrossRef](#)]
22. Liu, S.; Wang, Z.; Li, X. Long-term properties of concrete containing ground granulated blast furnace slag and steel slag. *Mag. Concr. Res.* **2014**, *66*, 1095–1103. [[CrossRef](#)]
23. Wang, Q.; Yan, P.; Mi, G. Effect of blended steel slag-GBFS mineral admixture on hydration and strength of cement. *Constr. Build. Mater.* **2012**, *35*, 8–14. [[CrossRef](#)]
24. Wang, Q.; Yan, P.; Yang, J. Comparison of hydration properties between cement-GGBS-fly ash blended binder and cement-GGBS-steel slag blended binder. *J. Wuhan Univ. Technol.-Mater. Sci. Ed.* **2014**, *29*, 273–277. [[CrossRef](#)]
25. Han, F.; Zhang, Z.; Wang, D.; Yan, P. Hydration heat evolution and kinetics of blended cement containing steel slag at different temperatures. *Thermochim. Acta* **2015**, *605*, 43–51. [[CrossRef](#)]
26. Shi, C.J.; Day, R.L. Some factors affecting early hydration of alkali-slag cements. *Cem. Concr. Res.* **1996**, *26*, 439–447. [[CrossRef](#)]
27. Kozhukhova, N.I.; Alfimova, N.I.; Kozhukhova, M.I.; Nikulin, I.S.; Glazkov, R.A.; Kolomytceva, A.I.J.R. The Effect of Recycled Citrogypsum as a Supplementary Mineral Additive on the Physical and Mechanical Performance of Granulated Blast Furnace Slag-Based Alkali-Activated Binders. *Recycling* **2023**, *8*, 22. [[CrossRef](#)]
28. Collins, F.; Sanjayan, J.G. Early age strength and workability of slag pastes activated by NaOH and Na₂CO₃. *Cem. Concr. Res.* **1998**, *28*, 655–664. [[CrossRef](#)]
29. Kozhukhova, N.; Shurakov, I.; Alfimova, N.; Zhernovskaya, I.; Kozhukhova, M. Using of Citrogypsum in Alkali Activated Systems. In *International Scientific Conference on Innovations and Technologies in Construction*; Springer: Cham, Switzerland, 2023; pp. 17–22.

30. Adesina, A.; Kaze, C.R. Physico-mechanical and microstructural properties of sodium sulfate activated materials: A review. *Constr. Build. Mater.* **2021**, *295*, 123668. [\[CrossRef\]](#)
31. Provis, J.L.; Palomo, A.; Shi, C.J. Advances in understanding alkali-activated materials. *Cem. Concr. Res.* **2015**, *78*, 110–125. [\[CrossRef\]](#)
32. GB 8076-2008; Concrete Admixtures. General Administration of Quality Supervision, Inspection and Quarantine of the People's Republic of China. Standardization Administration of the People's Republic of China: Beijing, China, 2008.
33. ASTM C150-12; Standard Specification for Portland Cement. American Society for Testing Materials: Philadelphia, PA, USA, 2012.
34. Scrivener, K.; Capmas, A. *Lea's Chemistry of Cement and Concrete*, 4th ed.; Elsevier Butterworth-Heinemann: Oxford, UK, 2004.
35. DBJ/T 13-196-2014; Specification for Mix Proportion Design and Test of Cement Paste. Fujian Provincial Institute of Building Research, Cscec Straits Construction Development Co., Ltd.: Fuzhou, China, 2014.
36. GB/T 17671-1999; Method of Testing Cements—Determination of Strength. National Cement Standardization Technical Committee, China Building Materials Federation. China Building Materials Academy Co., Ltd.: Beijing, China, 1999.
37. Bullard, J.W.; Jennings, H.M.; Livingston, R.A.; Nonat, A.; Scherer, G.W.; Schweitzer, J.S.; Scrivener, K.L.; Thomas, J.J. Mechanisms of cement hydration. *Cem. Concr. Res.* **2011**, *41*, 1208–1223. [\[CrossRef\]](#)
38. Mollah, M.Y.A.; Yu, W.; Schennach, R.; Cocke, D.L. A Fourier transform infrared spectroscopic investigation of the early hydration of Portland cement and the influence of sodium lignosulfonate. *Cem. Concr. Res.* **2000**, *30*, 267–273. [\[CrossRef\]](#)
39. Douglas, E.; Brandstetr, J. A preliminary study on the alkali activation of ground granulated blast-furnace slag. *Cem. Concr. Res.* **1990**, *20*, 746–756. [\[CrossRef\]](#)
40. Fraay, A.; Bijen, J.M.; Vogelaar, P. Cement-stabilized fly ash base courses. *Cem. Concr. Compos.* **1990**, *12*, 279–291. [\[CrossRef\]](#)
41. Douglas, E.; Bilodeau, A.; Brandstetr, J.; Malhotra, V.M. Alkali activated ground granulated blast-furnace slag concrete: Preliminary investigation. *Cem. Concr. Res.* **1991**, *21*, 101–108. [\[CrossRef\]](#)
42. Wilson, W.; Rivera-Torres, J.M.; Sorelli, L.; Durán-Herrera, A.; Tagnit-Hamou, A. The micromechanical signature of high-volume natural pozzolan concrete by combined statistical nanoindentation and SEM-EDS analyses. *Cem. Concr. Res.* **2017**, *91*, 1–12. [\[CrossRef\]](#)
43. Ylmén, R.; Jäglid, U.; Steenari, B.-M.; Panas, I. Early hydration and setting of Portland cement monitored by IR, SEM and Vicat techniques. *Cem. Concr. Res.* **2009**, *39*, 433–439. [\[CrossRef\]](#)
44. García-Lodeiro, I.; Fernández-Jiménez, A.; Blanco, M.T.; Palomo, A. FTIR study of the sol–gel synthesis of cementitious gels: C–S–H and N–A–S–H. *J. Sol-Gel Sci. Technol.* **2007**, *45*, 63–72. [\[CrossRef\]](#)
45. Bernal, S.A.; de Gutierrez, R.M.; Provis, J.L.; Rose, V. Effect of silicate modulus and metakaolin incorporation on the carbonation of alkali silicate-activated slags. *Cem. Concr. Res.* **2010**, *40*, 898–907. [\[CrossRef\]](#)
46. Ismail, I.; Bernal, S.A.; Provis, J.L.; San Nicolas, R.; Hamdan, S.; van Deventer, J.S.J. Modification of phase evolution in alkali-activated blast furnace slag by the incorporation of fly ash. *Cem. Concr. Compos.* **2014**, *45*, 125–135. [\[CrossRef\]](#)
47. Walkley, B.; San Nicolas, R.; Sani, M.-A.; Rees, G.J.; Hanna, J.V.; van Deventer, J.S.J.; Provis, J.L. Phase evolution of C-(N)-A-S-H/N-A-S-H gel blends investigated via alkali-activation of synthetic calcium aluminosilicate precursors. *Cem. Concr. Res.* **2016**, *89*, 120–135. [\[CrossRef\]](#)
48. Nasrazadani, S.; Springfield, T. Application of Fourier transform infrared spectroscopy in cement Alkali quantification. *Mater. Struct.* **2013**, *47*, 1607–1615. [\[CrossRef\]](#)
49. Wang, X.-Y.; Lee, H.-S. Modeling the hydration of concrete incorporating fly ash or slag. *Cem. Concr. Res.* **2010**, *40*, 984–996. [\[CrossRef\]](#)
50. Langan, B.W.; Weng, K.; Ward, M.A. Effect of silica fume and fly ash on heat of hydration of Portland cement. *Cem. Concr. Res.* **2002**, *32*, 1045–1051. [\[CrossRef\]](#)

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