Hydration Characteristics and Mechanic Properties of Basic Magnesium Sulfate Cement Containing Steel Slag

Zhengyi Huang\textsuperscript{1}, Lei Huang\textsuperscript{2*} and Xuan He\textsuperscript{3}

Abstract

The hydration characteristics and mechanical properties of basic magnesium sulfate (BMS) cement containing steel slag (SS) are studied in the work. The heat release of the composite binders during hydration process was monitored, the phase compositions of hydration products were analyzed, the microstructures of hardened pastes were investigated, moreover, the compressive strength was tested. The results show that the hydration exothermic rate of BMS is slowed and the cumulative heat of BMS is suppressed by SS addition. The incorporation of SS leads to the formation of C-S-H, CaSO\textsubscript{4}·2H\textsubscript{2}O and Mg(OH)\textsubscript{2}, and suppresses the formation of 5-1-7 phase. Compared to plain BMS, the pore structure of the composite paste with SS addition is much coarser, the crystallization and growth of Mg(OH)\textsubscript{2} lead to the occurrence of microcrack and large pores of the paste. The mechanical property of BMS is decreased by SS addition, especially when the content of SS addition reaches 20%, the compressive strength is significantly weakened in all tested ages.

1. Introduction

Basic magnesium sulfate (BMS) cement is a kind of modified magnesium oxysulfate cement, which is made of active magnesium oxide, magnesium sulfate, water and admixture (Walling et al. 2016). It is concerned by researchers and engineers for its excellent mechanical properties (Runčevski et al. 2013), such as high compression resistance, high tensile strength and high toughness (Zeng et al. 2017; Zhang et al. 2019). In addition to mechanical properties, BMS is also a new construction material of potential use for its characters of light weight, low thermal expansion, high fire resistance etc.

However, there are also some unfavorable characters which limit the application of BMS, including the water resistance and the high cost of the raw material. Chemical additives are the first choice to modify the properties of BMS. Up to now, kinds of chemical additives have been proven to be effective for the modification of the properties of BMS, such as sodium citrate, citric acid, sodium silicate, tartaric acid, phosphates, phosphoric acid etc. (Wang et al. 2018; Wu et al. 2014, 2015). The mechanism of the chemical additives effect has been thoroughly revealed (Wu et al. 2017), when the active MgO is immersed into MgSO\textsubscript{4} solution, OH\textsuperscript{-} is released into the liquid solution, a hydration shell around MgO grain with positive charge formed in early stage. In the absence of chemical additives, this hydration shell could react with the dissolved OH\textsuperscript{-} soon and therefore lead to the formation of Mg(OH)\textsubscript{2}. In the presence of chemical additives, the negative charged ions dissolved from the additives are absorbed on the shell, which can reduce the interface energy of the shell and suppress the reaction of the shell and the OH\textsuperscript{-} in solution, the formation of Mg(OH)\textsubscript{2} is restrained. The ions dissolved into solution is continuously accumulated until the solution is over saturated with respect to $5\text{MgSO}_{4}\cdot\text{Mg(OH)}_{2}\cdot7\text{H}_{2}\text{O}$ (5-1-7 phase), the main hydration products phase of BMS.

Many researchers focus on the modification of BMS properties and the reduction of its raw material cost through the incorporation of supplementary cementitious material (SCM). As a kind of excellent SCM used in Portland cement, fly ash has been incorporated into BMS to replace part of the light-burned magnesia (LBM), the general source of active magnesium oxide. It has been reported that a high dosage incorporation of fly ash could lead to a prominent decrease in compressive of BMS (Wu et al. 2014), some other researchers found that the effect of fly ash on the properties of BMS was determined by the calcium content of fly ash (Zhang et al. 2019, 2020), the incorporation of low-calcium fly ash can optimize the pore structure and improve the water resistance of BMS, whereas, due to the formation of CaSO\textsubscript{4}·2H\textsubscript{2}O, the addition of high-calcium fly ash can lead to a compressive strength loss and a weaker water resistance.

The hydration process and properties of BMS with some other SCM also have been studied. It has been found the incorporation of raw rice husk has little influence on the hydration products of BMS (Qin et al. 2018), the interfacial transition zone between the rice

\textsuperscript{1}Postgraduate student, School of Civil Engineering, Qinghai University, Xining 810016, China.
\textsuperscript{2}Associate Professor, School of Civil Engineering, Qinghai University and Qinghai Provincial Key Laboratory of Energy-saving Building Materials and Engineering Safety, Xining 810016, China.
\textsuperscript{*}Corresponding author, E-mail: leihyx@foxmail.com
\textsuperscript{3}Postgraduate student, School of Civil Engineering, Qinghai University, Xining 810016, China.
husk and matrix was improved. The incorporations of pulverized fuel ash and incinerated were found to change the needle-like morphology of 5-1-7 into a lath-like structure (He et al. 2020), the change resulted in the improvement of its water resistance. Circulating fluidized bed combustion ash addition was found to be beneficial to compressive strength of BMS at low dosage (Xu et al. 2020), the dosage of 20% was the optimal dosage for the mechanical property. The incorporation of silicon fume can extend the induction and acceleration period of BMS and therefore delay its setting (Tan et al. 2021), due to the filling effect, the incorporation of silicon fume could also increase the compressive strength of BMS, especially when the dosage was 10%; the compressive strength reached the highest level, moreover, magnesium silicate hydrate (M-S-H) gel was found to form in the system. The formation of M-S-H gel was also confirmed by other researcher (Li et al. 2020), it was proposed that the pozzolanic reaction led by SCM added to BMS resulted in the formation of M-S-H, which could be further accelerated by CO2 curing, the coupling utilization of CO2 curing and pozzolanic materials could enhance the water resistance of BMS.

Similar to SCM mentioned above, steel slag (SS) is a by-product of steelmaking, statistics show that annual discharge of steel slag in the world is more than 200 million tons (Zhuang et al. 2021), the utilization rate of SS is less than 20%. Many studies have focused on the utilization for SS as SCM in Ordinary Portland Cement (OPC), its effects on hydration progress (Wang et al. 2011; Han et al. 2015), setting behavior (Zhuang et al. 2021), mechanical property (Sun et al. 2020) and the mechanisms behind have been well revealed. Considering the mineral composition of SS (mainly calcium silicates), the incorporation of SS into BMS is desirable to low its cost and achieve energy savings.

In this work, SS was incorporated into BMS to form a composite cementitious material, the mechanical properties of the composite cementitious material were tested, the hydration process was monitored, the phase compositions and the microstructures of the hydration products were investigated to explore the mechanism behind.

2. Materials and methods

2.1 Raw materials

The chemical composition of LBM and SS used in the study were analyzed by X-ray fluorescence and shown in Table 1, the active content of LBM is 66.24%, tested according to the standard hydration method (Chau et al. 2008). Accurately weigh 2.0 g of LBM sample and place it into a 25 × 40 mm glass weighing bottle, the sample was added with 20 ml distilled water and hydrated for 24 hours in the bottle under the conditions of 20 ± 2°C and 70 ± 5% relative humidity. Then the bottle was placed into an oven and the temperature was kept at 100°C. After 24 h, the sample was dried to constant weight at 150°C. Afterwards, the sample was cooled to room temperature in a dryer and weighed, the active MgO content in the sample could be calculated according to Eq. (1).

\[
W = \frac{W_2 - W_1}{0.45W_1} \times 100\%
\]

where \(W\) is the content of active MgO in LBM (%); \(W_1\) is the mass of LBM sample (g); \(W_2\) is the mass of the hydrated LBM sample (g); 0.45 is the molecular weight ratio of H2O to MgO.

The XRD patterns of LBM and SS are shown in Fig. 1. The particle size distribution of the LBM and the SS were analyzed by a laser particle sizer and are shown in Fig. 2. Analytic grade MgSO4·7H2O and critic acid were used in the study.
2.2 Sample preparation

The molar ratio of MgO, MgSO$_4$, and H$_2$O was fixed at 7:1:20, the replacement levels of the LBM were 5%, 10% and 20% respectively, the dosage of citric acid added was 0.5% by weight of the light-burned MgO. The exact mix proportions are shown in Table 2.

MgSO$_4$$\cdot$7H$_2$O was dissolved in deionized water firstly to obtain MgSO$_4$ solution, the molar ratio of H$_2$O/MgSO$_4$ was 20:1, then citric acid was added into the solution, after that, pre-weighted powder was mixed together with the prepared solution to form BMS cement, the obtained paste was casted into steel mold with the size of 20 $\times$ 20 $\times$ 20 mm$^3$, cured at 20 ± 2°C and 95% relative humidity for 1 day. After demolding, the specimens were cured in the same condition till the scheduled ages (t = 1, 3, 7 and 28 days).

2.3 Test methods

An isothermal calorimeter (Calmetrix-4000HPC) was used to monitor the hydration heat evolution rate and the cumulative hydration of the composite pastes, the recordation was conducted for 120 hours continuously. Before testing, the calorimeter was equilibrated at 20°C for 6 hours.

When curing time came to the scheduled ages the prepared pastes were crushed and dried by a vacuum drying oven at 105°C for 6 h, then the dried pastes were ground for the testing of XRD analysis and TG analysis. XRD patterns of the samples were collected by an X-ray diffractometer (D/max-2500PC, Rigaku Corporation, Tokyo, Japan) with an acceleration voltage of 30 kV, the 2θ was in the range of 5 to 65° and the scanning speed was kept as 6°/min. A thermal gravimetric analyzer (HCT-1, HENVE, Beijing, China) was used to determine the thermal properties of the samples, the heating rate was 5°C/min and the samples were heated from 30°C to 1050°C. The pore distribution of the samples was measured through MIP method with an automatic mercury porosimeter (AutoPore IV 9500, Micromeritics, Norcross, Georgia, USA). SEM-EDS. (JSM-6610LV, JEOL Ltd., Tokyo, Japan). The microstructures of the samples were observed and analyzed by SEM-EDS. (JSM-6610LV, JEOL Ltd., Tokyo, Japan). The compressive strength of the samples were tested at 1, 3, 7 and 28 days, respectively.

3. Results and discussion

3.1 Hydration process

It has been proposed that the hydration of BMS could be divided into five stages (Wu et al. 2017; Miao et al. 2020), including pre-induction, induction, acceleration, deceleration and stable period, two heat evolution peaks present in exothermic rate curves. The first heat evolution peak results from the hydrolysis reaction of MgO, the second one could be attributed to the reaction between the ions in solution, including Mg$^{2+}$, SO$_4^{2-}$, OH$^-$ etc. to form 5-1-7 phase. Figure 3(a) shows the exothermic rate of the composite binders, it can be seen that there are five stages and two heat evolution peaks in the curves, in line with the findings of other researchers. The lengths of the induction periods and the heights of the two heat evolution peaks are obviously altered by SS addition. Compared to BMS, the heights of the first heat evolution peaks are increased 1.18 mw/g, 4.01
5-1-7 phase crystallizes and grows at the solid-liquid interface during induction period (Wu et al. 2017), because the nucleation of 5-1-7 phase at the begging of this stage is limited, which cannot provide enough space for the growth of 5-1-7 phase, the hydration rate of BMS keeps at a low level in the induction period. When a sufficient number of 5-1-7 nucleus are accumulated, which can support a rapid growth of the hydrates, the induction period finishes and the hydration process goes into the acceleration period. The prolonged induction periods of the composite binders led by SS addition, shown in Fig. 3(a), result from the suppression on the crystallization of 5-1-7 phase. The content of active MgO in the samples with SS addition is lower than that of BMS, which could lead to a lower concentration of ions (including Mg$^{2+}$ and OH$^{-}$) resulting in a lower supersaturation with respect to 5-1-7 phase, and therefore the formation of 5-1-7 phase is restrained. Besides, the nucleation of 5-1-7 phase tends to occur on the solid-liquid surface and prior to forming on the surface of MgO grain compared to that of SS, the SS addition leads to a decrease in the interface favoring the nucleation of 5-1-7 phase, which also suppresses formation of 5-1-7 crystal nucleus, thus, the induction period of the composite binders is prolonged by SS addition. When the hydration process goes into acceleration period, the growth rate of the 5-1-7 phase is mainly determined by the dissolution rate of MgO, the higher active MgO content could account for the higher second heat evolution peaks.

Due to the decrease in heat release rate in early age, the cumulative hydration heat of the composite binders is suppressed by SS addition. As shown in Fig. 3(b), the cumulative hydration heat of the composite binders decreases from 196.11 to 135.85 J/g when the dosage of SS increases from 0 to 20% at the age of 48 hours. With the prolong of curing age, the gap of the cumulative hydration between the samples reduces, which decreases from 60.26 at 48 hours to 36.44 J/g at 120 hours, meaning that the restrained effect led by SS addition on hydration is weakened. Compared to OPC, the reactivity of SS is much slower, which often exerts an inhibition effect on the early age hydration of cement (Zhuang et al. 2021). The decrease in cumulative hydration heat led by SS addition obviously due to the low reactivity of SS. With the increase in curing age, the hydration of SS progress gradually, compensating the gap of the cumulative hydration heat between BMS and the composite binders with SS addition.

### 3.2 Hydration products analysis

5-1-7 phase in the hydration products of BMS is the main carrier of its mechanical properties, while the formation of Mg(OH)$_2$ is thought to be harmful to the mechanical properties of BMS, because its formation is magnesium-consumed and restrain the formation of 5-1-7 phase. As shown in Fig. 4, the diffraction peaks of 5-1-7 phase are present in the patterns of BMS cement in 3 days, another prominent diffraction peaks in the patterns of BMS is MgO, even when the curing age comes to 28 days, the diffraction peaks of MgO still exist, meaning that part of MgO in BMS have not been depleted. As introduced in Section 2.1, the active content of LBM used in the study is 66.24%, the remainder 33.76% MgO in LBM is inactive. Thus, the diffraction peaks of MgO in the patterns are mainly due to the diffraction of the inactive MgO, besides, it could also be due to the diffraction of the residual active MgO in BMS. Moreover, the diffraction peaks of MgCO$_3$ are shown in the patterns.

The diffraction peak intensity of 5-1-7 phase is weakened by SS addition in the patterns of the samples both in 3 and 28 days, resulting from the decrease in active MgO content, whereas the diffraction peak intensity of MgCO$_3$ is enhanced by the SS addition both in 3 and 28 days, which might result from the increase in carbonate led by SS addition. Moreover, the SS addition leads to the formation of other hydrates, the diffraction peak of C-S-H is shown in the patterns, indicating that the SS added into BMS is hydrated in 3 days. Another hydration product should be noted is CaSO$_4$·2H$_2$O, it can be seen both in Figs. 4(a) and 4(b) that the diffraction peaks intensity of CaSO$_4$·2H$_2$O are enhanced by SS addition.

The mineral phases of SS include C$_3$S, C$_2$S, Portlandite etc., and C$_3$S is the most reactive phase among them (Sun et al. 2020). With the progress of hydration, the dissolution of C$_3$S leads to the release of Ca$^{2+}$ and SiO$_3^{2-}$ into pore solution. The solution of BMS is rich in SO$_4^{2-}$ and Mg$^{2+}$ (Wu et al. 2020), when Ca$^{2+}$ concentration reaches to a certain point, Ca$^{2+}$ and SO$_4^{2-}$ would be consumed to form CaSO$_4$·2H$_2$O. Thus, the molar ratio of magnesium to sulfur of the solution is increased, which is disadvantageous to the formation of 5-1-7 phase and results in the formation of Mg(OH)$_2$, as shown in Figs. 4(a) and 4(b).

In addition to the formation of CaSO$_4$·2H$_2$O, Ca$^{2+}$ was also consumed by the formation of C-S-H when the content of Ca$^{2+}$ and SiO$_3^{2-}$ dissolved in solution reach to the certain supersaturation with respect to C-S-H. It has been found that C-S-H would be eroded by magnesium, when C-S-H exposes to a solution rich in Mg$^{2+}$, Ca$^{2+}$ in C-S-H could be substituted by Mg$^{2+}$ (Huang et al. 2021), leading to the transformation of C-S-H to M-S-H, a non-cohesive magnesium silicate hydrate. Thus, it can be speculated that the formation of C-S-H in the com-
posite system is temporality, with the progress of hydration, the formed C-S-H would decalify which might cause the degradation of mechanical property for the samples with SS addition in long ages.

The mass loss curves of BMS cement paste with different SS content with respect to the change of temperature are shown in Fig. 5. Five peaks are present in the DTG curves, P1 which occurs below 100°C has little indication on the composition of hydration products, because in addition to the dehydration of 5-1-7 phase (lose 3H₂O), the loss of free water and the dehydration of CaSO₄·2H₂O (lose 1.5H₂O) also contribute to the mass loss in this temperature interval. The reactions resulting the occurrences of P2, P3, P4, P5 and P6 are shown in Eqs. (2), (3), (4), (5) and (6), respectively.

\[
5\text{Mg(OH)₂} \cdot \text{MgSO}_4 \cdot 4\text{H}_2\text{O(s)} \rightleftharpoons 5\text{Mg(OH)₂} \cdot \text{MgSO}_4 + 4\text{H}_2\text{O}
\]  

(a) Aged 3 days

(b) Aged 28 days

Fig. 4 XRD patterns of BMS and the composite pastes containing SS.

Fig. 5 TG and DTG curves of BMS and the composite pastes containing SS.
CaSO₄·0.5H₂O(s) $\xrightarrow{360^\circ C}$ CaSO₄ + 0.5H₂O \ (3)

5Mg(OH)₂·MgSO₄(s) $\xrightarrow{350^\circ C}$ +5MgO(s) + 5H₂O + MgSO₄(s) \ (4)

MgCO₃(s) $\xrightarrow{550^\circ C}$ MgO(s) + CO₂ \ (5)

MgSO₄(s) $\xrightarrow{950^\circ C}$ MgO(s) + SO₃ \ (6)

As shown in Fig. 5, the intensity of P2 and P4 both in 3 and 28 days decrease with the increase in SS content, which means less bounder water loss for the samples containing SS compared to BMS, confirming that the incorporation of SS lead to a decrease in 5-1-7 formation, in line with the results of XRD analysis. It should be noted that P3 does not occur in DTG curves of BMS, indicating there is no CaSO₄·2H₂O formed in the hydration products of BMS. Similar to the variation trend of P2 and P4, the intensity of P6 both in 3 and 28 days are weakened by SS addition, because MgSO₄, the desulfurization of which accounts for P6, originates from the thermal decomposition of 5-1-7 phase, the variation trend of P6 furtherly confirm that there is less 5-1-7 phase formed in SS containing samples.

### 3.3 Pore structure

The results of MIP analysis are shown in Figs. 6 and 7.

It can be seen in Fig. 6(a) that the samples with different SS content have little difference in the cumulative pore volume in 3 days, which are between 0.31 and 0.325 ml/g. Whereas the characteristics of pore size distribution are quite different, as shown in Fig. 6(b), the most probable pore size of SS20 is the largest, greater than 100 nm, the other three samples have the similar size of the most probable pore which are around 100 nm. Based on the size of pore diameter, the pores existing in cement paste could be divided into three types (Wu et al. 2021): gel pores (<20 nm), small intergranular pores (20 to 100 nm) and large intergranular pores (>100 nm). The majority of the pores formed in SS20 paste belong to large intergranular pores, compared to SS20, the large intergranular pores formed in SS10 paste are a small part, the pores formed in SS5 and BMS pastes are mainly small intergranular pores. Then it can be obtained that the SS addition promote the formation of large intergranular pores. The intergranular pores are formed by the interlock and crisscross of the reactants and hydration products (Wu et al. 2021), the larger hydration products lead to the formation of larger intergranular pores. It has been found in Fig. 3(a) that the SS addition promote the formation of CaSO₄·2H₂O, MgCO₃ and Mg(OH)₂, all of which have larger crystal size compared to 5-1-7 phase, so the pore structure of the pastes with high SS addition is coarser than that of...
BMS pastes.

With the prolong of curing age, the gaps between the cumulative pore volume of the samples are enlarged. As shown in Fig. 7(a), the cumulative pore volume of BMS is 0.26 ml/g in 28 days, whereas the cumulative pore volume of SS20 is higher than 0.3 ml/g, indicating the refining of the pore structures of the BMS paste is suppressed by SS addition. The most probable pore size of BMS, SS5 and SS10 paste has no obvious change, shown in Fig. 7(b), whereas the pores around 100 nm increase. It might be due to the continuous consumption of MgO for hydrating, the spaces initially occupied by MgO cannot be fully fill by the new formed hydrates. The small pores, including some small intergranular pores and gel pores, formed in 3 days disappear when the age comes to 28 days. The needle-like 5-1-7 phase accounts for this filling effect. Besides, the C-S-H formed in the pastes with high content of SS addition might also contribute to this filling effect.

The most probable pore size of SS20 is getting larger when the age comes to 28 days. For OPC, the pore size is getting smaller and the pore structure tends to become denser with the continuous hydration of cement (Han et al. 2018; Zhang et al. 2016), because the large pores formed in early age are partly filled by the new hydration products. The morphology of BMS in 3 and 28 days are shown in Fig. 9. It can be seen that the matrix of BMS in 3 days is very compact, the amount of the large pores in the matrix in 28 days is more than that of the matrix in 3 days, consistent with the results of MIP analysis, the new formed 5-1-7 phase can’t fully fill the large pores formed in early age [Fig. 9(c)]. The matrix of SS20 in 28 days is porous compared to the matrix of SS20 in 3 days. As shown in Fig. 10(c), tabular crystals (regions 1 and 2) are formed in the intervals between the hydration products of SS20, which has been verified as Mg(OH)₂ based on EDS analysis shown in Table 3. Besides, large cracks related to the formation of Mg(OH)₂ are also observed in the hydration products of SS20.

### 3.4 Morphology of the hydration products

The morphology of the hydration products of BMS and the sample with 20% SS additions in 3 days are shown in Fig. 8. For BMS, the typical needle-like 5-1-7 phase is formed, it can be seen that the 5-1-7 phase formed is compact and homogeneous. Compared to BMS, the 5-1-7 phase formed in SS20 is sparse. Besides, some other flocculent aggregates and big crystal products are formed [region 1 in Fig. 8(b)]. Taking into the morphology characters and the results of XRD analysis, the flocculent aggregates could be C-S-H. Based on the EDS analysis, shown in Table 3, the crystal products could be identified as Mg(OH)₂.

The morphology of BMS in 3 and 28 days are shown in Fig. 9, it can be seen that the matrix of BMS in 3 days is very compact, the amount of the large pores in the matrix in 28 days is more than that of the matrix in 3 days, consistent with the results of MIP analysis, the new formed 5-1-7 phase can’t fully fill the large pores formed in early age [Fig. 9(c)]. The matrix of SS20 in 28 days is porous compared to the matrix of SS20 in 3 days. As shown in Fig. 10(c), tabular crystals (regions 1 and 2) are formed in the intervals between the hydration products of SS20, which has been verified as Mg(OH)₂ based on EDS analysis shown in Table 3. Besides, large cracks related to the formation of Mg(OH)₂ are also observed in the hydration products of SS20.

### 3.5 Mechanical properties

The compressive strengths of BMS containing SS pastes in different ages are shown in Fig. 11. In 1 day, the compressive strength of BMS is higher than 16 MPa, 5% SS addition has not significantly changed the compressive strength of the pastes, when 10% and 20% SS are added into the pastes, compared to BMS, the compressive strengths decrease 28.9% and 63.1% respectively. The addition of SS exerts the similar effect on the strength development in different ages. In 28 days, the compressive strength of BMS paste reaches to 75 MPa, 5%, 10% and 20% SS addition decrease the compressive strength.

| Region | Weight percentage (%) | Atomic percentage (%) |
|--------|-----------------------|-----------------------|
|        | Mg | O | Mg | O |
| 1      | 39.7 | 60.4 | 30.2 | 69.8 |
| 2      | 39.9 | 60.1 | 30.4 | 69.6 |
| 3      | 37.2 | 62.8 | 28.1 | 71.9 |

Table 3 Results of EDS analysis.
sive strength 11.8%, 19.6% and 44.2% respectively.
The MIP analysis has verified that SS addition leads
to the formation of a coarser pore structure which is
more fragile and vulnerable to damage, so the mechani-
cal properties of the BMS pastes is significantly de-
creased by SS addition. In addition to the pore structure,
the type, content and crystallinity the of hydration
products also affect the mechanical properties of BMS

Fig. 9 The matrix of BMS in different ages.

Fig. 10 The matrix of SS20 in different ages.
(Wu et al. 2021), in other words, the content and crystallinity of 5-1-7 phase have a significant effect on the mechanical properties of BMS. As shown in Fig. 8, the crystallinity of 5-1-7 phase has not been modified by SS addition obviously, however, with the increase in SS addition the content of 5-1-7 phase formed in pastes decrease, which could also lead to the decrease in compressive strength. Then it is understandable that though the pore structure of SS20 is getting coarser in 28 days compared to that of in 3 days, the compressive strength of SS20 still increases, it is attributed to the continuous formation of 5-1-7 phase.

4. Conclusions

Based on the results of isothermal calorimetry, XRD, TG, MIT, SEM-EDS analysis and the mechanical testing. The following conclusions can be drawn:

(1) The hydration exothermic rate of BMS is slowed down and the cumulative heat of BMS is suppressed by SS addition, 5-1-7 phase formed in paste is decreased by SS addition.

(2) The incorporation of SS which is mainly composed of portlandite and C₃S introduces a generous amount of calcium to BMS, and therefore change the composition of hydration products significantly. The introduction of calcium leads to the formation of C-S-H and CaSO₄·2H₂O directly and the formation of Mg(OH)₂ indirectly.

(3) Compared to plain BMS, the pore structure of the paste with SS addition is much coarser, the crystallization and growth of Mg(OH)₂ led to the occurrence of microcrack and large pores of the paste.

(4) The mechanical property of BMS is decreased by the SS addition, especially when the content of SS addition reaches 20%, the compressive strength is significantly weakened in all tested ages.

Based on the above work, the mechanical performance of BMS with a moderate dosage (5%, and 10% in the study) of SS addition is acceptable, a high temperature curing might be helpful to improve its mechanical property taking into account the low reactivity of SS, which need be further studied. Meanwhile, more properties should be concerned, including water resistance and volume stability to achieve a rational utilization of SS in BMS.

Acknowledgments

The authors would like to acknowledge the financial support of the Natural Science Foundation of China (Grant No.52002202) and the Youth Science Research Fund Project of Qinghai University (Grant No. 2020-QGY-7).

References

Cao, F. Z., Miao, M. and Yan, P. Y., (2018). “Hydration characteristics and expansive mechanism of MgO expansive agents.” Construction and Building Materials, 183, 234-242.

Cao, F. Z., Liu, Y. and Yan, P. Y., (2021). “Properties and mechanism of the compound MgO expansive agent (CMEA) produced by calcining the mixture of dolomite and serpentine tailings.” Construction and Building Materials, 277, 122331.

Chau, K. and Li, Z. J., (2008). “Accelerated reactivity assessment of light burnt magnesium oxide.” Journal of the American Ceramic Society, 91(5), 1640-1645.

Han, F. H. and Zhang, Z. Q., (2018). “Properties of 5-year-old concrete containing steel slag powder.” Powder Technology, 334, 27-35.

Han, F. H., Zhang, Z. Q., Wang, D. M. and Yan, P. Y., (2015). “Hydration heat evolution and kinetics of blended cement containing steel slag at different temperatures.” Thermochimica Acta, 605,43-51.

He, P. P., Poon, C. S., Richardson, I. G. and Tsang, D. C. W., (2020). “The mechanism of supplementary cementitious materials enhancing the water resistance of magnesium oxychloride cement (MOC): A comparison between pulverized fuel ash and incinerated sewage sludge ash.” Cement and Concrete Composites, 109, 103562.

Huang, Q., Zhu, X. H., Xiong, G. Q., Zhang, M. T., Deng, J. X., Zhao, M. and Zhao, L., (2021). “Will the magnesium sulfate attack of cement mortars always be inhibited by incorporating nanosilica?” Construction and Building Materials, 305, 124695.

Li, Q. Y., Zhang, L. C., Gao, X. J. and Zhang, J. Y., (2020). “Effect of pulverized fuel ash, ground granulated blast-furnace slag and CO₂ curing on performance of magnesium oxy sulfate cement.” Construction and Building Materials, 230, 116990.

Miao, M., Wu, C. Y., Tan, Y. S. and Yu, H. F., (2020). “Mechanistic study of the effects of magnesia reactivity on setting and hardening of basic magnesium sulfate cement.” Journal of Advanced Concrete Technology, 18(11), 678-688.

Qin, L., Gao, X. J. and Chen, T. F., (2018). “Recycling of raw rice husk to manufacture magnesium oxy sulfate cement based lightweight building materials.”
Journal of Cleaner Production, 191, 220-232.
Ručevski, T., Wu, C. Y., Yu, H. F., Yang, B. and Dinnebier, R. E., (2013). “Structural characterization of a new magnesium oxysulfate hydrate cement phase and its surface reactions with atmospheric carbon dioxide.” Journal of American Ceramic Society, 96, 3609-3616.
Sun, J. W., Zhang, Z. Q., Zhuang, S. Y. and He, W., (2020). “Hydration properties and microstructure characteristics of alkali-activated steel slag.” Construction and Building Materials, 241, 118141.
Tan, Y. S., Yu, H. F., Sun, S. K., Wu, C. Y. and Ding, H., (2021). “Properties and microstructure of basic magnesium sulfate cement: Influence of silica fume.” Construction and Building Materials, 266, 121076.
Walling, S. A. and Provis, J. L., (2016). “Magnesium-based cements: A journey of 150 years, and cements for the future?” Chemical Reviews, 116(7), 4170-4204.
Wang, N., Yu, H. F., Bi, W., Tan Y. S., Zhang, N., Wu, C. Y., Ma, H. Y. and Hua, S., (2018). “Effects of sodium citrate and citric acid on the properties of magnesium oxysulfate cement.” Construction and Building Materials, 169, 697-704.
Wang, Q., Yan, P. Y. and Feng, J. W., (2011). “A discussion on improving hydration activity of steel slag by altering its mineral composition.” Journal of Hazardous Materials, 186, 1070-1075.
Wu, C. Y., Chen, W. H., Zhang, H. F., Yu, H. F., Zhang, W. Y., Jiang, N. S. and Liu, L. X., (2017). “The hydration mechanism and performance of modified magnesium oxysulfate cement by tartaric acid.” Construction and Building Materials, 144, 516-524.
Wang, Q. Y., Miao, M. and Yu, H. F., (2021). “Effect of MgO activity and ratio on the strength of basic magnesium sulfate cement and its mechanism.” Journal of Building Materials [online]. Available from: <https://web02.cnki.net/kmobile/Journal/detail/DKCI/JZCX20210305004>. (in Chinese)