THE EFFECT OF CALCIUM FORMATE ON THE PERFORMANCE OF SUPERSULFATED CEMENT

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Lower early strength has been one of the bottlenecks of low-carbon supersulfated cement (SSC), consisting of slag (~85 wt. %), gypsum (~10 wt. %), and a small amount of an alkali activator (Portland cement (PC), ~5 wt. %). The work aims at improving the early strength of SSC with the addition of calcium formate (CF). Different dosages (1 wt. %, 2 wt. %, 3 wt. %) of CF were added to the SSC. Then, compressive strength, heat flow, hydration product assemblage, and hydration degree of slag were obtained to reveal the role of CF. The results show that CF would significantly increase the compressive strength of the SSC, and the higher the dosage of CF, the more pronounced the effect is. 3 wt. % of CF would increase the 3-day and 28-day compressive strength of the SSC by 126 % and 172 %, respectively. CF would accelerate the hydration of slag, increase the hydration degree of slag and production of C-(A)-S-H gels; however, it would inhibit the rapid production of AFt during the first 3 days, and have little influence on the final production of AFt. In addition, the lower the crystal-gel ratio (the ratio between AFt and C-(A)-S-H gel by mass) is, the higher the compressive strength. The enhancement effect of CF was attributed to a more appropriate hydration environment (higher Ca\(^{2+}\) concentration and lower pH value), which could promote the precipitation of C-(A)-S-H gels, inhibit the rapid formation of Af, and reduce the crystal-gel ratio of the system.

INTRODUCTION

The global production of Portland cement (PC) has reached 4.6 billion tonnes recently [1], and the quantity is expected to go up to 6 billion tonnes by 2050 [2]. However, the production of PC would consume huge amounts of resources and energy and emit a great deal of CO\(_2\) [3, 4]. To reduce the carbon footprint of the cement industry, low-carbon cement has been a focus of researchers. Supersulfated cement (SSC) is a typical low-carbon cement, consisting of less than 5 wt. % of an alkaline activator (such as cement clinker), more than 80 wt. % industrial solid waste (such as slag, steel slag) and around 10-25 wt. % of gypsum [5, 6], and has received much attention recently. However, the strength development of SSC is quite slow due to the lower alkaline activator content (a higher alkaline activator would reduce the long-term strength of the SSC [7]), which is one of its main shortcomings.

Many scholars are devoted to methods of improving the mechanical properties of SSCs from the properties of the raw materials of SSCs. Wang et al. [8] found that increasing the fineness of slag would promote the strength development. Masoudi et al. [9] found slag at a 13 % Al\(_2\)O\(_3\) content displayed a higher hydration degree that of a 7 % Al\(_2\)O\(_3\) content in the SSC. Dutta et al. [10] further demonstrated the Al\(_2\)O\(_3\) content of slag must be more than 13 % with a Ca/Si ratio greater than 1. Gao et al. [11] found phosphogypsum must be calcined to prepare an SSC with excellent properties. The mechanical properties of the SSC can be improved by processing the raw materials; however, it does not change the slow hydration characteristics of the early performance development.

Other scholars have attempted to enhance the mechanical properties of the SSC using chemical admixtures. Gruskovnjak et al. [12] observed that the addition of Al\(_2\)(SO\(_4\))\(_3\)·16H\(_2\)O could not promote the
hydration degree of the slag with a low \(\text{Al}_2\text{O}_3\) content. Masoudi et al. [13] found 1-3% lactic acid salts (Na and K-lactate) could improve the compressive strength of the SSC with a low alumina content (<11%). However, Zhou et al. [14] found both a 2% sodium lactate solution (60% water) and 2.4% potassium lactate solution (50% water) would deteriorate the early strength, although they could improve the later mechanical properties and carbonation resistance of the SSC with a high alumina slag (14.347%). Xing et al. [15] also found 1% sodium lactate would decrease the mechanical performance of the SSC, though it could enhance the frost resistance of the SSC. Therefore, the addition of lactic acid and lactate salts are promising methods of enhancing the mechanical properties of SSCs, however, the relevant mechanism has not been resolved completely, and even no consensus has been reached on the effectiveness of these chemical reagents. A new admixture is urgently needed to promote the early strength without having any negative effect on the later strength of the SSC.

Calcium formate (CF) is a commonly used early-strength agent of PC and can improve the early strength of cement mortars and concrete [16, 17], although it has a little beneficial effect on the long-term strength. However, CF has a beneficial effect on both the early and long-term strength of high-volume slag cementsitious systems [18]. CF could promote the precipitation of AFt in the slag-fly ash cementsitious system, accelerating the hydration of silicate in SCMs [19]. In addition, CF could improve the dissolution of the slag of a CaO-activated slag system, by increasing the calcium ions and aluminate ions, producing more hydration products such as C-S-H and C\(_2\)AH\(_8\) [20]. Dalconi [21] also found that formate ions could react with calcium aluminate to produce formate-based hydration products similar to calcium aluminate hydrates. In fact, SSC is also a typical high-volume slag system, and CF could have the potential to efficiently improve the performance of the SSC.

In this study, different dosages of CF (1 wt. %, 2 wt. %, 3 wt. %) were added to the SSC. The compressive strength, hydration heat flow, hydration products, and hydration degree of the slag were obtained to find the role of the CF on the mechanical performance and hydration mechanism of the SSC.

### EXPERIMENTAL

#### Materials

The main components of the SSC are slag, PC, and gypsum. The chemical compositions of the PC (Chinese P-I 42.5) and slag are presented in Table 1. The used gypsum and CF were of an analytical grade. The particle size distributions of the slag, PC and gypsum are shown in Figure 1.

<table>
<thead>
<tr>
<th>No.</th>
<th>Portland cement</th>
<th>Slag</th>
<th>Gypsum</th>
<th>Calcium formate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ctrl</td>
<td>5</td>
<td>85</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>CF1</td>
<td>5</td>
<td>85</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td>CF2</td>
<td>5</td>
<td>85</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>CF3</td>
<td>5</td>
<td>85</td>
<td>10</td>
<td>3</td>
</tr>
</tbody>
</table>

The CF solution was first dissolved into the mix water, then the solution was mixed with the PC, slag, and gypsum in a mixer as specified in the Chinese standard GB 175-2023 [22]. Mortars with a size of 4 cm × 4 cm × 16 cm were cast with a water binder (PC + Slag + Gypsum) ratio (w/b) of 0.5 and sand binder ratio of 3.0. The w/b of pastes was 0.4. One part of the mixed pastes was used for the hydration heat tests, another part was poured into several 10 mL centrifuge tubes for the liquid composition tests, and the other parts were poured into several 200 mL disposable plastic cups for the phase assemblage test. Both the pastes and mortars were cured at 20 ± 3 °C and relative humidity (RH) ≥ 95%.
Methods

Compressive strength of the SSC
The compressive strength of all the samples were measured at 3, 7 and 28 days (curing at 20 °C and 95 % RH) by an electronic universal testing machine (CMT5504) loading at a rate of 2400 ± 200 N∙s⁻¹.

Isothermal calorimetry
An 8-channel isothermal calorimetry apparatus (TAM Air) was used to measure the early hydration heat of the SSC. The paste with a w/b of 0.4 was stirred for 2 min and tested at 20 °C.

Phase assemblage of the SSC
The X-ray diffraction (XRD) patterns were acquired by a D8 Advance diffractometer with Cu Kα-1 radiation at 40 kV and 40 mA, with a scanning range of 2θ is from 5° to 80°, a step size of 0.02° and a scanning speed of 10°∙min⁻¹. Meanwhile, the hardened samples were mixed with 20 wt. % corundum for the XRD quantitative analysis using TOPAS 4.2.

TG analysis
The thermogravimetric (TG) data were obtained by a TGA55 thermogravimetric analyser from 40 °C to 750 °C with a heating rate of 10 °C∙min⁻¹ under a nitrogen atmosphere. The chemically bound water content was obtained by integrating the Derivative Thermogravimetry (DTG) curve over the range 50 °C to 530 °C.

Hydration degree of slag
The degree of the slag hydration of the samples was determined by the selective dissolution method (Ethylenediaminetetraacetic acid - EDTA) [23]. The hydration degree of the slag was calculated by Equation 1.

\[
\alpha_s = 1 - \frac{W_{Wn}W_{C,E}}{W_{S,0}W_{C,0}} \tag{1}
\]

where: \(\alpha_s\) : the hydration degree of the slag (%); \(W_E\) : the weight mass ratio of the insoluble substance of the samples in the EDTA solution (wt. %); \(W_{Wn}\) : the weight mass ratio of the chemically bonded water (wt. %); \(W_{C,0}\) : the weight mass ratio of the PC in the mixture proportion (wt. %); \(W_{C,E}\) : the weight mass ratio of the insoluble substance of the PC in the EDTA solution (wt. %); \(W_{S,0}\) : the weight mass ratio of the slag in the mixture proportion (wt. %); \(W_{S,E}\) : the weight mass ratio of the insoluble substance of the slag in the EDTA solution (wt. %).

The content of C-(A)-S-H gel
Based on the results of the XRD, TG and the hydration degree of the slag, the content of C-(A)-S-H gel can be calculated as shown in Equation 2.

\[
C_\text{C-(A)-S-H} = \frac{C_{Amor} - W_{S,0}}{W_{Wn}} \tag{2}
\]

where: \(C_\text{C-(A)-S-H}\) : the C-(A)-S-H gel content (%); \(C_{Amor}\) : the amorphous substance content (%); \(\alpha_s\) : the hydration degree of the slag (%); \(W_{S,0}\) : the weight mass ratio of the slag in the mixture proportion (wt. %); \(W_{Wn}\) : the weight mass ratio of the chemically bonded water (wt. %); \(W_E\) : the weight mass ratio of the chemically bonded water in gypsum (wt. %).

pH and Ca²⁺ concentration
The pore solutions were obtained by centrifugation (10000 rpm, 3 min) of the paste samples and passed through a 0.45 μm filter. The pH value of the pore solutions after 1, 3, 5, 9 and 18 hours of hydration was measured by a pH meter (PHSJ-3F) at 25 °C. The Ca²⁺ concentration was measured by inductively coupled plasma-optical emission spectroscopy (ICP-OES, Optima 3000).

RESULTS
Compressive strength of the different SSC mortars
Figure 2 presents the compressive strength of the SSC mortars with 0 wt. %, 1 wt. %, 2 wt. % and 3 wt. % CF. It can be seen that the compressive strength of the SSC hardly developed after 3 days, thus its compressive strength was very low, probably due to the higher alkaline activator content [7, 24]. However, with the addition
of the CF, both the early and late compressive strength of the SSC were clearly increased, and the higher CF dosage, the more pronounced the effect. The compressive strength of the SSC with 3 wt. % CF reached ~33 MPa at 28 days and continued to increase.

Figure 3 shows the compressive strength growth rate for the SSC with the different CF dosages. The 3-day compressive strength of mortars increased by 36 %, 95 % and 126 % with the addition of 1 wt. %, 2 wt. %, and 3 wt. % CF, respectively, compared to the control sample. The 28-day compressive strength increased by 37 %, 133 % and 172 %, respectively.

Hydration heat of the different SSC pastes

Figure 4 presents the hydration heat release rate and cumulative heat of all the samples. From the inset in Figure 4a, there could be two main peaks of heat flow difference between CFX (X = 1, 2, 3) and the control sample. One was at around 10 hours, which was from the hydration of the PC, whereas the other was at around 20 hours, which was from the hydration of the slag [25]. These two peaks represent the enhancement of the CF to PC and the slag hydration, respectively. The intensity of the hydration peak of the PC was much higher than that of the slag, so part of the hydration peak of the slag was covered by the PC in Figure 4. Therefore, the heat flow of the slag hydration phase was always reduced, and the pre-induction period, induction period, acceleration period and deceleration period could not be distinguished. The addition of CF would significantly increase the intensity of the hydration peak, but hardly change the time of the hydration peak. This could mean that CF would not change the mode of the hydration of the SSC or any specific reaction step during the SSC hydration process, and it would accelerate the hydration rate of every reaction step. From Figure 4b, the cumulative heat of the SSC was increased by 13 %, 30 % and 35 % at 72 hours with the addition of 1 wt. %, 2 wt. %, and 3 wt.% CF, respectively.

Phase evolution of the SSC

The impact of the CF on the gypsum content is shown in Figure 5. It can be clearly observed that the gypsum consumption in the SSC mainly occurred during the first 3 days (the initial gypsum content was 10 g/100 dry SSC), and gypsum was basically not consumed afterward. During the first several days, due to the quick hydration of the PC, the high alkaline pore solution was more favourable to the precipitation of AFt [26], which would consume a large amount of $\text{SO}_4^{2-}$ from the gypsum. Meanwhile, since some $\text{SO}_4^{2-}$ could be absorbed in the structure of the C-(A)-S-H gel [27], the precipitation of C-(A)-S-H gels could also promote the consumption of gypsum. From Figure 5, the addition of CF would promote the consumption of gypsum, meaning that the CF would accelerate the formation of AFt or C-(A)-S-H gel.
Since slag is the main component of SSC, its hydration degree determines the mechanical properties of the SSC [28]. To explain the reason for the enhancement effect of the CF on the performance of the SSC, the hydration degree of the slag was calculated as shown in Figure 6. The accelerating effect of CF decreased with time. Compared to the control sample, the hydration degree of CF2 was improved by 57 % at 3 days, however, the improvement rate dropped to 55 % at 7 days and only 44 % at 28 days. This may be related to the hydration environment of the SSC.

Figure 7 shows the relationship between the compressive strength and the hydration degree of slag. The compressive strength of all the samples improved with the increase in the slag hydration degree, which is consistent with the literature [28]. For the Ctrl, the compressive strength first increased with the hydration degree of the slag, however, the compressive strength hardly changed with it after 7 days. A similar phenomenon occurred with the CF1 sample, instead of the CF2 and CF3 samples. CF could improve the contribution of the unit hydration degree of the slag to the compressive strength, probably due to the modification of the hydration products. Therefore, the content of AFt and C-(A)-S-H gel of the hardened SSC pastes was investigated.

The content of AFt and C-(A)-S-H gel is displayed in Figure 8. For the control sample, a large amount of AFt was generated in 3 days. However, the AFt content gradually decreased with time, consistent with the evolution of gypsum, as shown in Figure 5, due to fact that the hydration of slag had almost stopped as shown in Figure 7. Interestingly, all the samples with CF had less AFt content than the control sample at 3 days and had more AFt content afterward. Why did the AFt content hardly change with the hydration time or the hydration of the slag? Figure 8b presents the evolution of the C-(A)-S-H gel as a function of time. The C-(A)-S-H gel increased with time for all the samples. The addition of CF would greatly increase the C-(A)-S-H gel content, consistent with the developmental pattern of the compressive strength growth rate in Figure 3. Since the C-(A)-S-H gel could combine aluminium in its structure [29], the higher the C-(A)-S-H gel content could be the reason why the AFt content hardly changed with time.

The AFt content plays a crucial role in the early strength of the SSC [6, 30], whereas in this study, the 3-day compressive strength of the SSC with CF was still 36 % - 126 % higher than that of Ctrl, although...
they had a similar AFt content. This may be related to the content of crystal-gel ratio [31, 32] (mass ratio of AFt to C-(A)-S-H) as shown in Figure 9a. At 3 days, the crystal-gel ratio of the Ctrl was more than 1.5, which is much higher than that of the groups doped with CF (< 1.0). The lower the crystal-to-gel ratio, the higher the compressive strength in the SSC [30] as shown in Figure 9b. Although the crystal-gel ratio of all the samples decreased with time, the samples doped with CF were always lower than the Ctrl, and the more the CF was doped, the lower the crystal-gel ratio. In addition, the effect of the crystal-gel ratio on the compressive strength was greater in Figure 9b, and this pattern was also more pronounced with the increase in the CF. This explains why the incorporation of CF in Figure 7 affected the relationship between the hydration degree slag and the compressive strength, mainly because the CF reduced the crystal-gel ratio of the SSC.

From Figure 9b, we can find that the crystal-gel ratio of the system was an important factor that affected the hydration degree of the slag in the SSC, as well as the compressive strength. Numerous studies have pointed out that CF can significantly increase the Ca^{2+} concentration, reducing the pH value, and promote the rapid and massive formation of the PC and C-S-H gel, respectively. Consequently, the early performances of the PC system are enhanced. Our results found that CF could also significantly enhance the rapid formation of C-(A)-S-H gel in the SSC and inhibit the over-rapid formation of AFt. It has been shown that the rapid formation of AFt may form a dense reaction product layer around the slag, which, in turn, hinders the further sustained hydration of the slag. However, with the addition of CF, the rapid formation of AFt was suppressed (as can be seen from Figure 8a, at 3 days, the AFt content of the CF addition groups were all lower than that of the Ctrl), and the
C-(A)-S-H gel was formed rapidly in large quantities, which prevented the formation of a dense reaction product layer around the slag, and ensured the long-term sustained hydration of the SSC. Chen [30] found that the addition of nano-silica to the SSC could also significantly decrease the crystal-gel ratio of the system and enhance its mechanical properties, which is consistent with this study. This suggests that the formation of the C-(A)-S-H gel in the SSC could be promoted by increasing the \( \text{Ca}^{2+} \) concentration or providing C-(A)-S-H gel nuclei, which inhibited the over-rapid formation of AFt and enhanced the hydration degree of the slag and increased the mechanical properties of the SSC.

The CF influence on the evolution of the liquid phase during the hydration reaction is investigated by the pH value and \( \text{Ca}^{2+} \) concentration at 1, 3, 5, 9 and 18 hours as shown in Figure 11. As can be seen, the pH value increased during induction period and then gradually decreased during the acceleration period both in the Ctrl and CF2 (Figure 11a). The pH value eventually decreased with time due to the precipitation of AFt and the C-(A)-S-H gel. The addition of CF could reduce the pH value, because the \( \text{Ca}^{2+} \) and OH\(^-\) concentration were negatively correlated, where an increase in \( \text{Ca}^{2+} \) concentration (Figure 11b) in the solution and a decrease in OH\(^-\) concentration would result in a decrease in the pH value [23, 33, 34]. Singh [35] also reported that the addition of CF would decrease the pH value during C3S hydration because of its weak alkalinity. Although the decrease in the pH value was not favourable for the dissolution of the slag [15, 36], the hydration degree of the slag was improved by adding CF as shown in Figure 6. This indicates that CF has a unique role in the hydration of slag. On the one hand, CF provided \( \text{Ca}^{2+} \) to promote the precipitation of hydration products to reduce the ionic concentration in the pore solution, to achieve a new ionic equilibrium, thus accelerating the dissolution and release of ions from the slag. On the other hand, HCOO\(^-\) can react with OH\(^-\) and thus bind silicate groups in the pore solution to promote the precipitation of C-(A)-S-H gels [18], which is also why the effect of CF on the C-(A)-S-H content is greater than that of AFt (Figure 8b).

CONCLUSIONS

To improve the early strength of SSC, different dosages (1 wt. %, 2 wt. %, 3 wt. %) of CF were added to the system. Based on the results, the following conclusion can be made:
(1) CF significantly increases the 3-day and 28-day compressive strength of the SSC. Moreover, the higher the dosage of the CF is, the more pronounced the effect is.
(2) The heat flow difference between samples with CF (CF1 CF2 CF3) and control sample can be divided into two distinct peaks (hydration peak of the PC and slag). CF would significantly increase both peaks without changing their peak time, indicating CF would increase the hydration of both the PC and slag.

(3) CF promotes the dissolution of the slag and gypsum and increases the hydration degree of the slag and the production of C-(A)-S-H gels. However, CF has little influence on the amount of AFt, probably because most aluminate from the dissolution of the slag was combined by the C-(A)-S-H gels.

(4) The crystal-gel ratio (the ratio between AFt and C-(A)-S-H gel by mass) plays a critical role in the compressive strength of SSC. At the same hydration degree, the lower the crystal-gel ratio is, the higher the compressive strength of the SSC is.

(5) The enhancement effect of CF is attributed to a more appropriate hydration environment (higher Ca²⁺ concentration and lower pH value), which promotes the precipitation of C-(A)-S-H gels and inhibits the over-rapid formation of AFt and reduces the crystal-gel ratio of the system.

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