Technical report

Investigation on the Unusual Hydration and Hardening Process of a Portland Cement with Low Alkali Sulfate Content

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Abstract

The infrequent setting behavior and hydration process of a Portland cement with very low alkali content were concerned. Gypsum and K₂SO₄ with different quantities and ratios were added into cement to adjust its sulfate and alkali content. The setting time and compressive strength of cements were tested, the hydration process and hydrates of cements were investigated by isothermal calorimetry, non-evaporable water content and XRD. The results show that gypsum addition is incapable of delaying the quick initial setting of the cement clinker. A moderate substitution of gypsum by K₂SO₄ in same reasonable sulfate content can promote the dissolution of gypsum, suppress the formation of h-AFm, and therefore prolong the initial setting time of the cement. Moreover, the Portland cement clinker shows a very hysteretic hydration exothermic process, accompanying with a hysteretic finial setting and a weak mechanical property in early age. An appropriate dosage of gypsum can promote the hydration of the cement and result in a reasonable final setting behavior and satisfactory strength development. The modification of gypsum on the properties of cement is influenced by its alkali content. The measures which could accelerate the sulfate-supply in cement is necessary to acquire a favorable hardening property when the cement with low alkali content is used in projects.

1. Introduction

As a minor component in cement clinker, alkali has a marked impact on the properties of cement, including the compatibility between cement and plasticizer, its setting behavior, hydration process, mechanical property and volume stability (Jiang et al. 1999; Li et al. 2016; Huang et al. 2019). Alkali in cement clinker mainly comes from clay minerals in raw materials, and its content and existing status are determined by the chemical composition of raw materials. When there is sulfur in the system, alkali would react with sulfur preferentially to form alkali sulfate in the process of clinker firing (Zhang et al. 2019), such as potassium sulfate (K₂SO₄), sodium sulfate (Na₂SO₄), potassium sodium sulfate (Na₂SO₄·3K₂SO₄) and calcium potassium sulfate (2CaSO₄·K₂SO₄). In addition, the excess K and Na will be incorporated into silicates and aluminates to form NaCa₈(AlO₃)₃, KCa₂₃(SiO₄)₁₂, NaCa₂₃(SiO₄)₁₂ and KCa₁₃(SiO₄)₁₂. It has been found that the incorporating of alkali changes the crystal form of C₃S from triclinic to monoclinic, the crystal form of C₃A is also modified by alkali introduction, from its normal cubic to orthorhombic (Jawed et al. 1977). Thus, the reactivity of silicates and aluminates is modified.

It is an important segment to get cement clinker be sulfated properly in cement production. When cement hydrates in the condition of insufficient sulfation, C₃A dissolves quickly and forms the platelets of calcium aluminates hydrates (h-AFm) (Jawed et al. 1977; Nedunuri et al. 2021), such as C₆A₈H₁₃ and C₂AH₈ that as in Eq. (1) according Quennoz et al. (2013). It is supposed that a colloidal percolate network (CPN) forms in cement paste after mixing, due to the interactions between particles and the bridging action of hydrate crystals in the very early age (Jiang et al. 1996; Nonat et al. 1994), shown as the loss of plasticity and a quick initial setting of pastes. The formed h-AFm can exert bridging effect on the particles in the paste and therefore leads to a quick initial stiffening of cement paste (Jawed et al. 1977). For the cement which has been properly sulfated, C₃A reacts with sulfate ion in solution to form ettringite [Eq. (2)] (Quennoz et al. 2013). The dissolution of C₃A is restrained and the setting of cement paste is delayed.

\[
2\text{C}_3\text{A} + 21\text{H} \rightarrow \text{C}_6\text{A}_8\text{H}_{13} + \text{C}_2\text{AH}_8 \quad (1)
\]

\[
\text{C}_3\text{A} + 3\text{CSH}_2 + 26\text{H} \rightarrow \text{C}_6\text{ASH}_{32} \quad (2)
\]

where S is the abbreviation of sulfur, C refers to calcium, A refers to aluminum and H refers to HOH.

The mechanical performance of cement is also affected by the sulfate content. As the hydration of C₃S, the main
mechanical property contributor, is negatively affected in Al-contain solutions (Sun et al. 2020; Begarin et al. 2011), the occurrence time of sulfate depletion is critical to the mechanical development of cement. Generally, the sulfate depletion occurring after the main C3S hydration peak is positive for the mechanical performance of cement (Neto et al. 2021). Lerch pointed that there is an optimum sulfate content (Lerch et al. 1946). Many factors influence this content, including physical-chemical and mineralogic properties of clinker, such as the fitness of cement, the C3A content, the C3S content and alkali content. The increases in all these variables factors lead to the advance of the time of the sulfate depletion, so the optimum sulfate content increases. Moreover, the optimum sulfate content is also affected by the physics, chemical, and mineralogic properties of sulphate source. The higher the sulphate solubility, the higher the optimum sulfate content (Barbosa et al. 2018).

Gypsum (CaSO4·2H2O) or natural anhydrite (CaSO4·H2O) are usually added and ground together with clinker in cement plant (Neto et al. 2021). In the grinding process, the increase in milling temperature results in the dehydration of gypsum, and therefore the formation of hemi-hydrate or anhydrite (Yamada 2011). The solubility of hemi-hydrate and anhydrite is different from that of gypsum. It has been verified that the fluidity and initial setting time of cement are affected by milling temperature due to the difference in reactivity of the calcium sulfates.

In addition to calcium sulfate, the alkali sulfate existing in cement clinker is a fast-sulfate-supplied source. The alkali sulfate in clinker dissolves into the liquid phase rapidly after contacting with water (Huang et al. 2019), changing the ionic composition of liquid phase, and then affects the dissolution of clinker minerals and the nucleation of hydrates. Plenty of researching results show that alkali sulfate can accelerate the hydration of cement in early age and suppress the hydration of cement in late age (Kumar et al. 2012; Mota et al. 2018; Ma et al. 2018; Huang et al. 2019). A high alkali content in cement often leads to a quick stiffening of cement paste, excessive alkali sulfate leads to the flash or false setting of cement (Jawed et al. 1978; Older et al. 1983; Sun et al. 2017). Besides, it has been found that the compatibility between cement and plasticizer is degraded by the high alkali content (Palacios et al. 2009; Golaszewski et al. 2012). The workability of cement paste with high alkali content cannot be effectively improved by plasticizer (Kashani et al. 2014).

The difference of calcium sulfate and alkali sulfate in the effect on the adjusting the hardening behavior is noteworthy. As the sulfate content in the liquid phase of cement is mainly from the dissolution of alkali sulfate which comes from the raw materials and its content is difficult to adjust, the alkali sulfate content in cement is critical and concerned by many researchers. Jiang et al. (1999) found that the fluidity of a cement with the alkali content of 0.31% Na2Oeq cannot be improved by both the gypsum and hemihydrate addition. He proposed that there is an optimum alkali content (0.4%-0.5% Na2Oeq) for the compatibility between cement and plasticizer. When the alkali content in cement is in this range, the paste with plasticizer has the largest fluidity and the smallest loss of fluidity. Some early researchers also pointed that a moderate alkali content is helpful to modify the hardening property and workability of cement (Jawed et al. 1978). Yang et al. (2017) reported an infrequent setting behavior of a cement clinker containing 0.19% Na2Oeq. The addition of gypsum, which usually plays as the role of setting regulator, is ineffective to delay the setting of cement, on the contrary, when gypsum with 0.5% SO3 was added into cement, its initial setting was significantly advanced.

Owing to the worry about harmful alkali-silica reaction or to acquire a favorable workability, a low alkali sulfate content is pursuing widely in modern cement production (Figueira et al. 2019; Afshin et al. 2020). However, an excessive low alkali content in cement might result in the insufficient supply of sulphate ions and induce other problems. In the work, the hardening and hydration process of a commercial cement clinker with very low alkali sulfate content were investigated. Based on the analysis on the impacting factors behind the unusual properties of the cement prepared with the clinker, a reminder of the utilization of such low alkali content cement clinker was proposed.

2. Experiment

2.1 Raw materials

A commercial Portland cement clinker (CC1) with low alkali content, manufactured by a dry-made rotary kiln, was found unusual in setting behavior and poor workability, and therefore was investigated. The other two commercial cement clinkers (CC2 and CC3), with similar compositions but higher alkali content, were chosen for comparative study. The chemical compositions of the clinkers were determined by X-ray fluorescence spectrometry and their mineral compositions were calculated by Bogue formula, which are shown in Tables 1 and 2, respectively. The XRD patterns of the clinkers are shown in Fig. 1.
The clinkers were grounded using a ball mill, and the particle size distribution of the clinkers, tested by a laser particle sizer, are presented in Fig. 2.

Analytical pure gypsum and K\textsubscript{2}SO\textsubscript{4} were used for the adjustment of the sulfate and alkali content in cement, the mix proportion of cement is shown in Table 3.

### 2.2 Test methods

The setting time of cement was tested by Vicat apparatus. The water requirement for the cement paste to obtain its normal consistency was identified firstly according to the Chinese standard GB/T 1346, then the initial setting time of paste was determined as the time when the penetration depth of the initial setting Vicat needle is 36 ± 1 mm, and the finial setting time was determined as the time when the penetration of the final setting Vicat needle is 0.5 mm.

The mortar samples were prepared according to Chinese standard GB/T 17671, with a water/binder ratio of 0.5 and sand/binder ratio of 3:1. ISO standard sand was used. The prepared mortar samples were cured at 20 ± 2°C and 95 ± 5% relative humidity. The demolding was conducted at the age of 3 d and then the mortar samples were cured in water at 20 ± 2°C. The compressive strength of mortars was tested at 3, 7 and 28 days.

The cement pastes with a water/binder ratio of 0.4 were prepared. After mixing by a paste blender, the pastes were cast into sealed containers and cured at 20°C. When it comes to the scheduled age, the pastes were immersed into ethanol for 12 h to stop the hydration. For non-evaporable water content testing, a 24 h of drying in an oven

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### Table 2 Mineral composition of the clinkers (%).

<table>
<thead>
<tr>
<th>Cement clinker</th>
<th>C\textsubscript{3}S</th>
<th>C\textsubscript{2}S</th>
<th>C\textsubscript{3}A</th>
<th>C\textsubscript{4}AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC1</td>
<td>58.08</td>
<td>18.57</td>
<td>6.86</td>
<td>11.73</td>
</tr>
<tr>
<td>CC2</td>
<td>63.33</td>
<td>12.35</td>
<td>5.05</td>
<td>12.31</td>
</tr>
<tr>
<td>CC3</td>
<td>61.62</td>
<td>13.84</td>
<td>5.88</td>
<td>11.98</td>
</tr>
</tbody>
</table>

### Table 3 Mix proportion.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CC1 %</th>
<th>CC2 %</th>
<th>CC3 %</th>
<th>Gypsum</th>
<th>K\textsubscript{2}SO\textsubscript{4}</th>
<th>SO\textsubscript{3} %</th>
<th>Na\textsubscript{2}O\textsubscript{eq} %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CC1</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0(G)</td>
<td>98.34</td>
<td>1.66</td>
<td>0.77</td>
<td>0.23</td>
<td>0.21</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.0(G)</td>
<td>96.17</td>
<td>3.83</td>
<td>1.77</td>
<td>2.0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5(G)</td>
<td>95.09</td>
<td>4.91</td>
<td>2.27</td>
<td>2.5</td>
<td>2.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0(G)</td>
<td>94.01</td>
<td>5.99</td>
<td>2.77</td>
<td>3.0</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0(G)</td>
<td>91.85</td>
<td>8.15</td>
<td>3.77</td>
<td>4.0</td>
<td>4.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5(G+0.5KS)</td>
<td>95.08</td>
<td>3.51</td>
<td>1.77</td>
<td>1.41</td>
<td>0.5</td>
<td>2.5</td>
<td>0.71</td>
</tr>
<tr>
<td>2.5(G+1.0KS)</td>
<td>95.07</td>
<td>2.11</td>
<td>1.27</td>
<td>2.82</td>
<td>1.0</td>
<td>2.5</td>
<td>1.21</td>
</tr>
<tr>
<td>CC2</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC2-1.0(G)</td>
<td>99.48</td>
<td>0.52</td>
<td>0.24</td>
<td>0.76</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC2-2.0(G)</td>
<td>97.33</td>
<td>2.67</td>
<td>1.24</td>
<td>1.0</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC2-2.5(G)</td>
<td>96.26</td>
<td>3.74</td>
<td>1.74</td>
<td>2.0</td>
<td>0.71</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC3</td>
<td>100.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC3-1.0(G)</td>
<td>99.66</td>
<td>0.34</td>
<td>0.16</td>
<td>1.0</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC3-2.0(G)</td>
<td>97.51</td>
<td>2.49</td>
<td>1.16</td>
<td>2.0</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CC3-2.5(G)</td>
<td>96.43</td>
<td>3.57</td>
<td>1.66</td>
<td>2.5</td>
<td>0.80</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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![Fig. 1 XRD patterns.](image-url)

![Fig. 2 Particle size distributions.](image-url)
at 60°C was conducted firstly to remove the free water in the pastes, then the pastes were heated in a muffle furnace at 1050°C for 2 h. The non-evaporable water content of pastes was calculated as the weight loss of the pastes between 60°C and 1050°C with the consideration of the loss on ignition of the cement. For the XRD analysis, a 0.5 h of drying in an oven at 105°C was conducted, then the dried cement pastes were powdered. The measurement was done using a X-ray diffractometer (Shimadzu, Japan), the 2θ-range went from 5° to 60° and the scanning speed kept as 6° per minute.

Isothermal calorimetry was adopted to monitor the hydration heat evolution of cements by an isothermal calorimeter (Tam Air). The water/binder ratio of paste was kept at 0.4. Before test, the isothermal calorimeter was equilibrated at 25°C for 12 h.

3 Results and discussion

3.1 Properties of the cement clinker with gypsum addition

3.1.1 Setting behaviors and compressive strength

To acquire a favorable hardening and hydrating property, the sulfate content in cement needs be strictly prescribed. The SO3 content in ordinary Portland cement (OPC) should be less than 3.5% according to Chinese standard GB 175. The addition of gypsum is the most common way to adjust the setting time of cement. Figure 3 shows the setting time of cement paste with different gypsum addition. It can be seen that the initial setting of CC1 paste occurs at 55 min, the gypsum addition has not effectively delayed the initial setting of cement. On the contrary, when the dosage of gypsum is more than 2.0% SO3, the initial setting time of cement is shortened. The initial setting of the cement with 3.0% SO3 addition occurs at 33 min, which is shorter than the allowable minimum initial setting time of cement stipulated in Chinese standard GB/T 175. Surprisingly, the final setting of CC1 paste is significantly lagging. As shown in Fig. 3, the final setting of CC1 and 1.0(G) paste has not occurred at 390 min, which is the allowable maximum final setting time of cement stipulated in Chinese standard GB/T 175. The gypsum addition effectively shortens the final setting time of cement paste. The final setting time of cement paste is shortened less than 390 min when the dosage of gypsum is more than 2.0% SO3.

The compressive strength evolution of cement mortars with different gypsum additions is shown in Fig. 4. CC1 and 1.0(G) mortars do not harden enough to demold at the age of 3 d, the strength cannot be measured, which is consistent with the final setting behavior. The sample with more gypsum addition shows a good compressive strength in 3 d. The shorter the final setting time of cement, the higher the 3 d strength of mortar. The 7 d compressive strength of CC1 and 1.0(G) is higher than the sample with 2.5% SO3 gypsum addition. In 28 d, CC1 shows the highest compressive strength.

3.1.2 Hydration and exothermic performance

The main exothermic peak of Portland cement is mainly attributed to the hydration of C3S (Sun et al. 2011). It is widely accepted that the induction period finishes when the hydration rate reaches a certain point, a sufficient number of C-S-H nucleus is accumulated to sustain enough sites for the growth of C-S-H (Zhang et al. 2017; Bullard et al. 2011). Figure 5 presents the exothermic performance of cement pastes with different gypsum additions. It is quite infrequent that the main exothermic peak of CC1 paste appears later than 72 h [Fig. 5(a)], which indicates that the accumulating time of the enough C-S-H nucleus is far more than other OPC. Because the nucleation of C-S-H is determined by its supersaturation in solution, two factors which might lead to the infrequent lag of acceleration period should be concerned: the consuming of dependent ions by other precipitation and the dissolution of C3S.

The induction period of cements is strongly modified by the gypsum addition. As shown in Fig. 5(a), gypsum addition with both 2.5% and 4.0% SO3 lead to a significant shortening of induction period. The main exothermic
peak appears at 14.45 h and 15.64 h, respectively. However, the appearance of the main exothermic peak is still much later than other OPC. Based on dissolution theory (Juilland et al. 2010; Scrivener et al. 2015), the formation and development of etch pit on the surface of crystal is the crucial factor to determine its dissolving behavior. The different crystal faces behave differently during etch pit formation and development. It can be inferred that the delayed hydration of cement which have been properly sulfated might be due to the different crystal characteristics of C₃S.

3.1.3 Non-evaporable water content
Some of free water in the paste is combined to form hydrates during the hydration of cement, namely non-evaporable water. The non-evaporable water content in the paste can characterize the content of the hydrates in cement paste and reflect the hydration degree of cement. Figure 6 shows the evolution of the non-evaporable water content of cement pastes with different gypsum additions. The non-evaporable water content of CC1 and 1.0(G) pastes is extremely low in 1 d, only 3.01% and 2.14% respectively. The non-evaporable water content of the two pastes is even less than 10% in 3 d, indicating that the formed hydrates are quite little, and that there are not enough hydrates to strength interactions between the separated particles. CPN is still weak, so the mortar samples cannot be demolded.

The non-evaporable water content of the pastes 2.5(G) and 4.0(G) is higher than 10% in 1 d, which is far more than CC1 and 1.0(G), conforming that the appropriate gypsum addition promotes the hydration of the pastes in early age and results in a satisfactory strength. However, the promoting effect of gypsum decreases with the prolongation of hydrating age and the cements with low gypsum addition hydrates quickly. As shown in Fig. 6, the greatest gap of the non-evaporable water content of cements with different gypsum additions is 8.25% in 1 d. It drops to 3.82% in 3 d and is almost same in 28 d.

3.1.4 XRD analysis
Figure 7(a) shows the XRD patterns of cement pastes hydrating for 2 h. It can be seen the diffraction peaks of h-AFm in the CC1 paste, which can exert bridging effect among particles and therefore accounts for rapid setting of cement. The gypsum addition leads to the increase of sulfate ion concentration in solution of 2.5(G) and 4.0(G) paste and therefore the formation of ettringite. However, the diffraction peaks of h-AFm also appear in the pastes 2.5(G) and 4.0(G). It can be inferred that the increase of sulfate ion in solution led by gypsum addition is limited, the aluminate in solution cannot be completely consumed by the formation of AFt. Compared to 2.5(G) and 4.0(G), the aluminate in the liquid phase of CC1 is more excessive.

The remaining content of C₃S in the pastes is quite different in 3 d. As shown in Fig. 7(b), the diffraction pattern of CC1 shows much higher diffraction peaks of C₃S than that of 2.5(G) and 4.0(G), accordingly the diffraction peaks of portlandite in pattern of CC1 is much lower than that of 2.5(G) and 4.0(G), indicating the hydration of C₃S in CC1 is very limited in 3 d, there is not enough C-S-H formed in CC1 to adhere the particles, so the mortar does not harden enough to demold. The gypsum addition effectively accelerated the reaction of C₃S in 2.5(G) and 4.0(G). Their mortars show much better mechanical performance than CC1 (Fig. 4). The gap of C₃S content among samples has narrowed in 7 d, a high diffraction peak of portlandite is shown in pattern of CC1. A major
hydration of C\(_3\)S in CC1 occurs between 3 d and 7 d, resulting in a significant increase of compressive strength (Fig. 4) and the non-evaporable water content (Fig. 6) of cement CC1.

### 3.2 Discussion

#### 3.2.1 Setting and hardening properties

Due to the dehydration of gypsum in grinding process, there are several kinds of calcium sulfate in cement, including CaSO\(_4\)·2H\(_2\)O, CaSO\(_4\)·0.5H\(_2\)O and CaSO\(_4\). In the study, gypsum (CaSO\(_4\)·2H\(_2\)O) was added to adjust the hydration and hardening properties of cement in consideration of the cement production practice. Because the dissolution rate of calcium sulfate is affected by its crystalline form, it can be inferred that the incapability of gypsum in adjusting the initial time of CC1 is related to its crystalline form. However, the comparative experiments show that the gypsum is capable in delaying the setting of CC2 and CC3, shown in Fig. 8. Therefore, the incapacity of gypsum in adjusting the initial time of CC1 is related to its crystalline form.

![XRD patterns of cement pastes with different gypsum additions at different hydration ages.](image)

Fig. 7 XRD patterns of cement pastes with different gypsum additions at different hydration ages. [AFt: Ettringite, CH: Portlandite, C$: Gypsum, h-AFm: Calcium aluminum hydrate (Ca\(_4\)Al\(_2\)O\(_7\)·nH\(_2\)O)].

![Setting time of CC2 and CC3 with gypsum addition.](image)

Fig. 8 Setting time of CC2 and CC3 with gypsum addition.
bility of gypsum in adjusting the initial time of CC1 cannot simply be attributed to the crystalline form of calcium sulfate.

For cement prepared with CC1 in this work, the specific surface area, C3A content and the water content in paste are fixed. The only factor affecting the interaction between C3A and sulfate ion is the content of sulfate ions in liquid phase. Previous study has confirmed that the dissolution of gypsum is affected by alkali content in cement (Huang et al. 2020). Gypsum dissolves fast in the solution with a high pH value. Some researchers also found that the alkali in cement has a promoting effect on the reaction of gypsum and aluminate (Yang et al. 2017; Ma et al. 2018). It should be noted that the alkali content in CC1 is quite low, which leads to the formation of the liquid phase with a low pH value, it takes a relative long period of time for the completed dissolution of gypsum due to its low dissolution rate. The gypsum addition cannot lead to an immediate and significant increase of sulfate ion concentration in liquid. The increase of sulfate ion concentration in solution of pastes 2.5(G) and 4.0(G) is limited, there are still many active sites on the surface of C3A without absorption of sulfate ion. The dissolution of C3A has not been effectively restrained in 2 h, resulting in the formation of h-AFm [shown in Fig. 6(a)] in 2.5(G) and 4.0(G) which leads to the quick initial setting. Thus, the incapable of gypsum addition on the retardation of the initial setting of CC1 is attributed to its low alkali content. Based on the above analysis, it can be inferred that an addition of alkali sulfate is helpful to modify the initial setting behavior of the clinker.

As expected, the K2SO4 addition effectively modifies the initial setting behavior of cement. The initial setting time of cement increases from 45 min to 93 min [Fig. 9(a)] when 0.5% Na2Oeq of K2SO4 is added to substitute gypsum in same sulfate content in cement 2.5(G). There is an optimal ratio of alkali and sulfate to obtain an ideal initial setting time of cement. But the initial setting time of cement shortens with the further increase of alkali content. The promoting effect of alkali on the reaction of gypsum and aluminate is predominant when the dosage of alkali is higher than ideal quantity. The final setting time of cement with the alkali content no more than 1.0% Na2Oeq does not alter obviously, but it shortens sharply when 1.5% Na2Oeq of K2SO4 is added into cement.

The XRD patterns of cement pastes with different K2SO4 additions hydrating for 2 h was shown in Fig. 10. It can be seen the formation of h-AFm is significantly suppressed by K2SO4 addition, resulting in the prolongation of initial setting time of cement (Fig. 7). When 1.5% Na2Oeq of K2SO4 is added, gorgyeite [K2Ca5(SO4)6·H2O] is formed in paste. It is similar to syngenite (K2Ca(SO4)2·2H2O), a kind of calcium sulfate hydrate, may lead to a fake setting of paste (Huang et al. 2020). The rapid setting of the paste 2.5(G+1.5KS) is attributed to the formation of ettringite. It should be noted also that the formation of ettringite is suppressed in such a high dosage of alkali.

The peak of gypsum in XRD patterns in 2 h is noteworthy, especially of the paste 2.5(G+0.5KS). The diffraction peak intensity of gypsum is quite weak. It cannot be simply attributed to the decrease of gypsum addition. When the paste with alkali sulphate addition is mixing with water, the quickly dissolving sulfate ion from alkali sulfate is rapidly consumed by the reactions of aluminate, leading to the release of hydroxyl ion, thus the alkali sulphate in paste can increase the pH value indirectly and promote the dissolution of gypsum. The prolonged initial setting of paste 2.5(G+0.5KS) cannot be attributed only to the increased sulfate ion dissolved from K2SO4, but also to the promoting effect of the increased alkali content on the dissolution of gypsum.

3.2.2 Hydration characteristics

It is well known that the content of silicate ion in the solution of Portland cement paste is very low in early age, playing as the key factor for the supersaturation of the solution with respect to C-S-H. It has been reported that silicen in C-S-H could be substituted by aluminum to form C-A-S-H (Pardal et al. 2009; Garrault et al. 2011). The Al/Si ratio of C-A-S-H is constant with a given solution composition. C-A-S-H is equalized within its interstitial solution. Thus, it can be speculated that C-A-S-H is formed in the paste of CC1, the nucleation of C-S-H is restrained. Though C-A-S-H could be similar with C-S-
H as the substitution of silicon by aluminate, the impact of these two hydrates on the hydration process of C-S is quite different. Garrault et al synthesized C-S-H and C-A-S-H for seeding (Garrault et al. 2011). It has been found that seeding C-S suspension with synthesized C-S-H strongly accelerates its hydration, which is also confirmed in Tomas’s experiments (Thomas et al. 2009). Whereas the seeding with the same quantity of synthesized C-A-S-H did not show any visible effect. The C-A-S-H nucleus is not as good as C-S-H nuclei to provide regions available for the growth of C-S-H. The aluminates ions in solution could poison C-S-H and delay the onset of accelerating period. The accelerating period of hydration begins only when the concentration of aluminate ion decreases to a certain limit no more to poison C-S-H and sufficient C-S-H nucleus is accumulated.

The gypsum addition leads to an increase in sulfate ion in solution which could react with aluminate ion primarily. The aluminate ion in solution is removed by the precipitation (e. g. formation of ettringite) and its content decreases to the certain limit as low as that it could not poison the C-S-H nucleus anymore. More C-S-H nucleus is accumulated and the accelerated period of hydration begins in an earlier age. Contrary to the cement 2.5(G) and 4.0(G), cement 1.0(G) shows the longest induction period more than 80 h. It might be due to the continuing poisoning of C-S-H by aluminate ion. There is still limited sulfate content in solution of paste 1.0(G), the aluminate ion in solution cannot be significantly removed. The adsorbing behavior of sulfate ion on C-S-H, which has been verified by Quennoz et al. (2013), also modifies the nucleation and growth of C-S-H, resulting in a delayed hydration of cement.

It can be drawn that the incapability of gypsum addition in retardation of initial setting, the hysteretic final setting and hydration, a low strength in early age for cement CC1 are resulted from its low alkali content. Due to the low dissolution rate of gypsum in the solution with a low pH value, the gypsum addition cannot lead to an immediate and significant increase of sulfate ions and therefore cannot restrain the quick reaction of C3A. With the increase in hydrating age, the gypsum dissolves gradually, sulfate ions accumulated in solution react with aluminate ions and favor the formation of C-S-H nucleus, so the gypsum addition significantly promote the hydration of C-S. Therefore, the addition of alkali sulphate is supposed to modify the setting behavior and to improve the mechanical properties of cement. In addition, the adjustment of the calcium sulphate to a more reactive kind is also hopeful to modify the properties of cement clinker with low alkali sulphate content.

4. Conclusions

(1) Gypsum addition is incapable of delaying the quick initial setting of the cement clinker with low alkali content, h-AFm forms in the paste of the clinker whether added with gypsum or not. A moderate substitution of gypsum by K2SO4 in same reasonable sulfate content can promote the dissolution of gypsum, suppress the formation of h-AFm, and therefore prolong the initial setting time of cement.

(2) The hydration of the cement clinker with low alkali content is severely lagged, accompanying with a hysteretic finial setting and a weak mechanical property in early age. An appropriate dosage of gypsum can promote the hydration and result in a reasonable final setting behavior and satisfactory strength development.

(3) The modification of gypsum on the properties of cement is influenced by its alkali content. The measures which could accelerate the sulfate-supply in cement is necessary to acquire a favorable hardening property when the cement with low alkali content is used in projects.

The work has revealed the law of the influence qualitatively, still, a quantitative instruction is needed in engineering application, more work is required to accomplish it.

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