Bauxite free iron rich calcium sulfoaluminate cement: Preparation, hydration and properties

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HIGHLIGHTS

- The clinker can be prepared at 1175–1225 °C for 10 min.
- More c-C₄A₃S forms with the rise of Fe₂O₃ content of the clinker.
- The setting time is prolonged and expansion rate lowers down.
- The cement exhibits low early strength and high late strength.

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ABSTRACT

For the preparation of calcium sulfoaluminate (CSA) cement without bauxite, the iron rich CSA cement was prepared by the partial substitution of Al for Fe in C₄A₃S. Besides, the hydration and properties of iron rich CSA cement were investigated. Raw meal proportioning shows that iron rich CSA cement clinker can be prepared without bauxite when the x value of C₄A₃ₓ₋₁FₓS exceeds 0.7. Results demonstrate that the iron rich CSA cement clinker can be prepared at 1175–1225 °C with the heat preservation time of 10 min. With the rise of Fe₂O₃ content in the raw meal, the C₄A₃S content of iron rich CSA cement clinker lowers down, more C₄AF and C₃S forms, more c-C₄A₃S forms at the expense of o-C₄A₃S, and the crystal size of C₄A₃S becomes smaller. For the iron rich CSA cement, the setting time is prolonged and the expansion rate lowers down with the rise of Fe₂O₃ content. For the compressive strengths, the iron rich CSA cements are lower than that of CSA cement at early hydration age. However, the compressive strength of iron rich CSA cement exceeds that of CSA cement at 90 d. Therefore, it is available to prepare bauxite-free iron rich CSA cement with high late age strength.

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1. Introduction

CSA cements mainly consist of ye’elimite (C₄A₃S), belite (C₃S), calcium sulfates and calcite, and the mineral composition varies with raw materials and applications [1,2]. CSA cement clinker are generally produced by the calcination of limestone, bauxite and gypsum at approximately 1250–1350 °C, which is 100–200 °C lower than the temperature for manufacturing Portland cement (PC) clinker [3,4]. Besides, due to its low lime saturation factor, compared with PC clinker, the CO₂ emission is relatively lower. Therefore, CSA cements are considered as an alternative cement to PC [5].

CSA cements gain many advantages over PC in the performances, such as rapid setting (followed by high early strengths), volume expansion and low alkalinity [6–8]. In the engineering construction, CSA cements are mainly used in high early strength concrete for pre-cast products, cold environments, self-leveling screed, self-leveling repair mortar, high performance glass fiber reinforced composites and 3D printing [9,10]. However, despite the increasing interests and performance advantages of CSA cements, the industrial scale production and large scale application are limited due to the scarcity of alumina bearing raw materials such as bauxite [11,12]. Therefore, it is expected to seek alternative alumina sources or reduce the demand for aluminum material in CSA cement clinker production. In recent years, some Al-rich industrial wastes have been successfully used for the laboratory production of CSA clinkers, such as fly ash and red mud [13–16]. However,
due to high content of SiO$_2$, the Al$_2$O$_3$ content still can not meet the demands for the proportioning of the raw meal. To achieve the goal of the production of CSA clinker without using bauxite, it is proposed whether Fe$_2$O$_3$ could be used to replace Al$_2$O$_3$ in C$_4$A$_3$S to reduce the demand for Al$_2$O$_3$ in cement raw meal and produce CSA cement clinker without using bauxite. If the assumption is feasible, the wastes with relatively lower Al$_2$O$_3$ content could completely substitute bauxite for CSA cement clinker production.

In the single phase system of ye'elimite (4CaO·3Al$_2$O$_3$·SiO$_2$·3H$_2$O), it was demonstrated that Al$_2$O$_3$ can be substituted by Fe$_2$O$_3$, obtaining C$_4$A$_3$S$_x$F$_y$$_3$ where $x$ is the molar number of Al$_2$O$_3$ substituted by Fe$_2$O$_3$. Although the Fe$_2$O$_3$ content in C$_4$A$_3$S$_x$F$_y$$_3$ solid solution has been investigated by several researchers, the results are inconsistent. Bullerjahn [17] synthesized C$_4$A$_3$$_{3-x}$F$_x$$_3$ with $x$ ranging from 0.0 to 0.8, found that the maximum substitution level of $x$ is equal to 0.32 and seems to depend on the F/A ratio of the raw mix. Chen [18] have determined that 22.31% ($x = 1.0$) is the maximum incorporation level for Fe$_2$O$_3$ in C$_4$A$_3$$_{3-x}$F$_x$$_3$ in the single phase system. In CSA cement clinker system, $F/(F + A)$ is the only parameter influencing the value of $x$. Halstead [19] and Bullerjahn [20] pointed out that the structure of C$_4$A$_3$S and $S/(F + A)$ was also a key factor affecting the maximum incorporation level.

For the industrially produced CSA cement clinker, due to the low Fe$_2$O$_3$ content in raw meal, the incorporation level of Fe$_2$O$_3$ in C$_4$A$_3$S is quite low. The Fe$_2$O$_3$ content has been measured and the weight fraction is between 0.6 and 1.6% ($x$ ranges between 0.02 and 0.06) [21,22]. To lower down the requirements of Al$_2$O$_3$ content of the materials for the proportioning of CSA cement raw meal, more Fe$_2$O$_3$ is expected to substitute the Al$_2$O$_3$ in C$_4$A$_3$S. Therefore, a high content of Fe$_2$O$_3$ in raw mixtures needs to be considered during the synthesis of CSA clinker. The CSA cement with high Fe$_2$O$_3$ can be named as iron rich CSA cement.

The majority of steel slag has a high content of Fe$_2$O$_3$ and CaO, and a low content of SiO$_2$, which is suitable to be used as a material to prepare iron rich CSA cement clinker. The Fe$_2$O$_3$ in steel slag can partially substitute the Al$_2$O$_3$ in C$_4$A$_3$S, which lowers down the requirements of alumina material and makes it available to produce iron rich CSA clinker without using bauxite. In this study, three types of iron CSA clinkers with varying $x$ (0.7, 1.0, 1.3) in C$_4$A$_3$$_{3-x}$F$_x$$_3$ were prepared without using bauxite. The effect of Fe$_2$O$_3$ on the formation and composition of iron rich CSA cement clinkers were studied. Besides, the hydration and properties of the produced iron rich CSA cement were also investigated.

2. Experimental
2.1. Materials

The chemical compositions of the raw materials, including limestone, bauxite, steel slag, kaolin, fly ash and gypsum, are listed in Table 1. All of the materials are produced in Chongqing, China. The steel slag does not go iron separation treatment and the Fe$_2$O$_3$ content is high. Bauxite was used to synthesize the CSA clinker with low Fe$_2$O$_3$ content. All the raw materials were dried in an oven at 40°C to constant weight, and then grinded in a planetary ball mill to pass through a 75 μm sieve.

2.2. Synthesis of iron rich CSA cement clinker

The aimed phase assemblage of the iron rich CSA cement clinker is 30% C$_4$A$_3$$_{3-x}$F$_x$$_3$, 55% C$_3$S, 10% CAF and 5% C$_2$. According to the aimed phase assemblage, the theoretical oxide composition of iron rich CSA cement clinker can be determined. To produce the targeted clinker without using bauxite, the Al$_2$O$_3$ in C$_4$A$_3$$_{3-x}$F$_x$$_3$ is partially substituted by Fe$_2$O$_3$. The samples were labeled as Fe$_x$ where $x = 0, 0.7, 1.0, 1.3$ standing for the molar of Al$_2$O$_3$ substituted by Fe$_2$O$_3$ in C$_4$A$_3$S$_x$F$_y$$_3$. Based on the oxide compositions of the materials and the theoretical oxide composition of iron rich CSA cement clinker, the proportions of the raw meal can be figured out and are shown in Table 2. When the $x$ reaches 0.7, bauxite can be completely substituted by steel slag and kaolin.

The raw meals were pre-homogenized by a mixer. Then, after mixing the raw meals with 8% water, the raw pastes were pressed into disks with the dimension of ø 50 mm × 8 mm and dried at 40°C for 24 h. The raw meal disks were sintered by an electric furnace to obtain the clinkers. To optimize the sintering process, the clinkers were sintered at 1100°C, 1125°C, 1175°C and 1225°C for 0 min, 10 min, 20 min and 30 min, separately. After the termination of the sintering program, the clinkers were cooled by forced air to stabilize the phase with relatively higher hydration activity. The clinkers prepared at 1225°C were grinded in a ball mill to pass through a 75 μm sieve. The cements were prepared by mixing the clinker and gypsum in a fixed proportion of clinker/gypsum = 90/10.

2.3. Testing methods

The setting time of the iron rich CSA cement was tested according to the Chinese standard of GB/T 1346-2001.

The compressive strengths were measured on cubic cement paste samples with the dimension of 20 mm × 20 mm × 20 mm. All the cement pastes were prepared with a water to cement ratio (w/c) of 0.3. After curing at a temperature of (20 ± 1)°C and a humidity of (95 ± 1)% for 4 h, the samples were demoulded and then cured in water at (20 ± 1)°C. The compressive strengths were tested at hydration ages of 6 h, 12 h, 1 d, 3 d, 7 d, 28 d and 90 d on six cubic samples.

The cement mortar with the cement, sand and water ratio of 1:3:0.5 was applied to prepare the samples by the moulds with the dimension of 25 mm × 25 mm × 280 mm. Then the moulds were placed in the standard curing chamber with a temperature of (20 ± 1)°C and a humidity of (95 ± 1)% at 24 h, the mortar samples were demoulded and the initial lengths were recorded. Then the CSA cement mortar samples were cured in water with a temperature of (20 ± 1)°C and the lengths were recorded at specified ages. The expansion rate can be calculated by Eq. (1).

$$\omega = \frac{L_t - L_0}{280}$$

where $L_t$ and $L_0$ denote the linear expansion rate, length at specified age and the initial length of the cement mortar samples, separately.

TG-DSC analysis was conducted on a Mettler Toledo TGA/DSC 1/1600 thermal analyzer The reactive gas and the protective gas are Air and N$_2$, and the gas flows are 30 ml min$^{-1}$ and 50 ml min$^{-1}$, separately. 50 mg raw cement sample was heated form 50°C to 1300°C with a heating-up rate of 10°C/min.

The hydration of the cement paste was terminated by dipping the samples in ethanol for 24 h. The dried cement paste was milled by an agate mortar to pass a 75 μm sieve. The powders were used for the mineralogical compositions analysis, which was performed on a PANalytical X-Pert Powder diffractometer using Cu Kα radiation at 40 kV and 40 mA with a step size of 0.02°. The scan speed for the qualitative analysis and quantitative analysis are 10°/min and 2°/min, separately. The qualitative analysis and quantitative analysis are conducted using Jade 6 software and TOPAS-Academic software, separately. Table 3 listed the crystallographic structures used for the quantitative analysis.

Fractured samples were applied for the scanning electron microscopy (SEM) analysis to characterize the morphological feature of iron rich CSA cement clinkers. The test was performed on a TESCAN VEGA 3 at a voltage of 25 kV, a current of 20 μA, and a working distance of 15 mm. After being embedded in the epoxy resin, the clinkers were carbon coated to satisfy the conductivity and polished to obtain a smooth surface. Then the clinkers were applied for the energy dispersive spectrom-

<table>
<thead>
<tr>
<th>Materials</th>
<th>CaO</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>SO$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>MgO</th>
<th>TiO$_2$</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>LOI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Limestone</td>
<td>52.90</td>
<td>2.66</td>
<td>0.20</td>
<td>0.43</td>
<td>0.45</td>
<td>0.27</td>
<td>0.40</td>
<td>0.12</td>
<td>0.02</td>
<td>42.09</td>
</tr>
<tr>
<td>Fly ash</td>
<td>9.79</td>
<td>36.57</td>
<td>31.32</td>
<td>5.80</td>
<td>11.69</td>
<td>0.85</td>
<td>0.24</td>
<td>0.23</td>
<td>0.16</td>
<td>3.02</td>
</tr>
<tr>
<td>Bauxite</td>
<td>0.76</td>
<td>16.10</td>
<td>51.25</td>
<td>0.45</td>
<td>13.65</td>
<td>2.01</td>
<td>0.37</td>
<td>0.12</td>
<td>0.05</td>
<td>14.27</td>
</tr>
<tr>
<td>Steel slag</td>
<td>29.48</td>
<td>12.22</td>
<td>2.91</td>
<td>0.53</td>
<td>40.06</td>
<td>1.33</td>
<td>1.26</td>
<td>0.23</td>
<td>0.08</td>
<td>9.32</td>
</tr>
<tr>
<td>Kaoline</td>
<td>1.14</td>
<td>58.76</td>
<td>25.80</td>
<td>0.38</td>
<td>0.51</td>
<td>0.59</td>
<td>0.87</td>
<td>0.12</td>
<td>0.02</td>
<td>8.63</td>
</tr>
<tr>
<td>Gypsum</td>
<td>31.06</td>
<td>3.16</td>
<td>0.37</td>
<td>44.14</td>
<td>0.42</td>
<td>0.02</td>
<td>0.01</td>
<td>–</td>
<td>0.01</td>
<td>20.16</td>
</tr>
</tbody>
</table>
etry (EDS) analysis with an accelerating voltage of 15–25 kV and a beam current of 1–2 nA. For the chemical composition of C\textsubscript{4}A\textsubscript{3}s, it is determined by the average value of five points.

The heat release of iron rich CSA cement hydration was investigated by an eight channel TAM AIR isothermal calorimetric calorimeter with internal mixing method. Experiments were performed using 2 g cement with 1 g water and the heat flow was recorded for 24 h at a constant temperature of 20°C. The resulting heat flow curves were integrated to obtain the cumulative heat.

3. Results and discussions

3.1. Preparation of the iron rich CSA cement clinker

The DSC-TG curves of the raw meals are shown in Fig. 1. The weight loss and heat absorption located at ~780 °C is referred to the decomposition of CaCO\textsubscript{3} [23]. With the rise of Fe\textsubscript{2}O\textsubscript{3} content in the raw mixture, the peak temperatures of DSC curves lower down from 796.5 °C to 767.5 °C and the turning point temperatures of TG curves lower down from 804.1 °C to 776.4 °C. Therefore, it is concluded that Fe\textsubscript{2}O\textsubscript{3} could promote the decomposition of CaCO\textsubscript{3} in the raw mixture at relatively lower sintering temperature, which contributes to the energy conservation of iron rich CSA cement clinker production. In the C\textsubscript{4}A\textsubscript{3}s single phase system, previous investigations also found that the Fe\textsubscript{2}O\textsubscript{3} could promote the decomposition of CaCO\textsubscript{3} [24].

When the sintering temperature exceeds 1225 °C, an obvious weight loss could be observed in the TG curves. It is caused by the decomposition of CaSO\textsubscript{4} into CaO and SO\textsubscript{3} [25]. With the rise of Fe\textsubscript{2}O\textsubscript{3} content in the clinker, the weight loss becomes more and more obvious, proving that Fe\textsubscript{2}O\textsubscript{3} could promote the decomposition of CaSO\textsubscript{4}. Touzo [26] also found that the presence of significant proportion of Fe\textsubscript{2}O\textsubscript{3} in the raw mixtures promoted the decomposition of CaSO\textsubscript{4}, which makes CaSO\textsubscript{4} in the raw mixture insufficient for the formation of C\textsubscript{4}A\textsubscript{3}s and change the phase composition of the clinker [25]. Therefore, the optimum sintering temperature of iron rich CSA cement clinker should be below 1225 °C.

Sintering temperature plays a key role in the formation of clinker phases. When the sintering temperature is too low, the clinker phases could not form sufficiently. It inevitably leads to a decrease of cement properties. Inversely, when the sintering temperature is too high, C\textsubscript{4}A\textsubscript{3}s and CaSO\textsubscript{4} in the clinker would decompose largely. It would also lead to a decrease of cement properties and exert a burden on the treatment of cement kiln exhaust. Therefore, the optimum sintering temperature is investigated.

Fig. 2 shows the XRD patterns of iron rich CSA clinkers prepared at different sintering temperatures with the preservation time of 30 min. For All the clinkers, with the rise of sintering temperature, there is a downward trend for the diffraction peak intensity of CaO and CaSO\textsubscript{4} and an upward trend for the diffraction peak intensity of C\textsubscript{4}A\textsubscript{3}s and C\textsubscript{2}S. For clinker F\textsubscript{0}, when the sintering temperature is 1225 °C, the diffraction peak of CaO vanishes and the clinker forms sufficiently. For clinker F\textsubscript{0.7}, F\textsubscript{1.0} and F\textsubscript{1.3}, when the sintering temperature is 1175 °C, the diffraction peak of CaO vanishes and the clinker forms sufficiently. Therefore, it is concluded that Fe\textsubscript{2}O\textsubscript{3} could promote the formation of the clinker at relatively lower temperature.

### Table 2
Proportions of the raw meal for 100 g clinker (g).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Limestone</th>
<th>Gypsum</th>
<th>Fly ash</th>
<th>Kaolinite</th>
<th>Bauxite</th>
<th>Steel slag</th>
</tr>
</thead>
<tbody>
<tr>
<td>F\textsubscript{0}</td>
<td>89.96</td>
<td>12.31</td>
<td>20.58</td>
<td>10.28</td>
<td>15.22</td>
<td>–</td>
</tr>
<tr>
<td>F\textsubscript{0.7}</td>
<td>78.16</td>
<td>9.46</td>
<td>38.43</td>
<td>0.73</td>
<td>–</td>
<td>16.56</td>
</tr>
<tr>
<td>F\textsubscript{1.0}</td>
<td>75.71</td>
<td>10.51</td>
<td>28.43</td>
<td>5.80</td>
<td>–</td>
<td>22.08</td>
</tr>
<tr>
<td>F\textsubscript{1.3}</td>
<td>73.13</td>
<td>11.18</td>
<td>19.04</td>
<td>10.46</td>
<td>–</td>
<td>27.84</td>
</tr>
</tbody>
</table>

### Table 3
Crystallographic structures used for Rietveld quantitative phase analysis.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>ICSD code</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{4}A\textsubscript{3}s-c</td>
<td>I4-3m</td>
<td>9560</td>
</tr>
<tr>
<td>C\textsubscript{4}A\textsubscript{3}s-o</td>
<td>Pmcm</td>
<td>80,361</td>
</tr>
<tr>
<td>β-C\textsubscript{2}S</td>
<td>P121/n1</td>
<td>81,096</td>
</tr>
<tr>
<td>C\textsubscript{2}AF</td>
<td>Pcmn</td>
<td>9197</td>
</tr>
<tr>
<td>C\textsubscript{2}A</td>
<td>P121/n1</td>
<td>1841</td>
</tr>
<tr>
<td>C\textsubscript{2}F</td>
<td>Pnma</td>
<td>47-1744</td>
</tr>
<tr>
<td>C\textsubscript{s}</td>
<td>Amma</td>
<td>15,876</td>
</tr>
</tbody>
</table>

### Table 4
Phase composition of iron rich CSA cement clinkers prepared at 1225 °C for 10 min/wt%.

<table>
<thead>
<tr>
<th>Clinker</th>
<th>Phase/wt%</th>
<th>R\textsubscript{wp}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C\textsubscript{4}A\textsubscript{3}s-c</td>
<td>C\textsubscript{4}A\textsubscript{3}s-o</td>
</tr>
<tr>
<td>F\textsubscript{0}</td>
<td>6.7</td>
<td>30.8</td>
</tr>
<tr>
<td>F\textsubscript{0.7}</td>
<td>10.2</td>
<td>19.8</td>
</tr>
<tr>
<td>F\textsubscript{1.0}</td>
<td>13.2</td>
<td>14.2</td>
</tr>
<tr>
<td>F\textsubscript{1.3}</td>
<td>15.8</td>
<td>9.2</td>
</tr>
</tbody>
</table>

c = cubic, o = orthorhombic.
sintering temperature. For the iron rich CSA cement clinker it can be sintered with the temperature range of 1175–1255°C.

With the rise of Fe2O3 content in the raw meals, the diffraction peaks of C4AF and C2F become more and more obvious. It is suggested that not all of the Fe2O3, the part which is intended to form C4A3-Fxs, participates the formation of C4A3-Fxs. Therefore, more and more Fe2O3 participate the formation of C4AF, which contributes to the diffusion of CaO and the formation of clinker minerals [27,28].

Heat preservation time also plays a key role in the formation of clinker phases. When the heat preservation time is too short, the clinker phases could not form sufficiently. Inversely, when the heat preservation time is too long, it not only causes energy dissipation, but also leads to a decrease of the hydration activity of the clinker phases. Therefore, the optimum heat preservation time of CSA cement clinker is investigated.

Fig. 3 shows the XRD patterns of the clinkers prepared at 1175 °C for different preservation times. When the heat preservation time is 0 min, obvious f-CaO diffraction peak can be observed. When the heat preservation time is 10 min, f-CaO diffraction peak vanishes and the peak intensities of C4A3s and C2S increase. With the prolonging of heat preservation time, the peak intensities of C4A3s and C2S do not increase anymore. It demonstrates that CSA clinker has formed sufficiently. Therefore, the optimum heat preservation time is 10 min.

3.2. Characterization of the iron rich CSA cement clinker

Table 3 shows the phase composition of CSA cement clinkers prepared at 1225 °C for 10 min. With the rise of Fe2O3 content, the total C4A3s content lowers down and the iron phase contents of C4AF and C2F increase. Previous studies also found that, in the single phase system of C4A3s, an increase of Fe2O3 could promote the formation of C2F [29]. For F0, the C4A3s content is higher than the designed content. Inversely, for F1.0 and F1.3, the C4A3s content is lower than the designed content. Therefore, it is concluded that not all of the Fe2O3 intended to substitute the Al2O3 in C4A3s participate the formation of C4A3s.

The polymorph of C4A3s in the CSA clinker was orthorhombic and cubic [30]. For F0, the orthorhombic C4A3s (o-C4A3s) content is higher than cubic C4A3s (c-C4A3s) content. Previous investigation also found the same law [1]. With the rise of Fe2O3 content, the c-C4A3s content increases and o-C4A3s content decreases. Previous investigation also found that Fe2O3 could stabilize c-C4A3s in the single phase system of C4A3s [31].

Fig. 4 shows the SEM photos of iron rich CSA cement clinker sintered at 1225 °C for 10 min. For clinker F0, the crystal size of C4A3s is 1–4 μm. With the rise of Fe2O3 content, the crystal size of C4A3s becomes smaller and smaller. For clinker F1.3, the crystal size of C4A3s is smaller than 1 μm. The formation of C4A3s crystal involves two steps of nucleation and crystal growth. Compared with crystal
growth, the Fe₂O₃ is more favorable in the nucleation. Therefore, the C₄A₃S crystal size of CSA cement clinker is smaller than that of iron rich CSA cement clinker.

Table 5 presents the average formula of C₄A₃₋ₓFₓS analyzed by EDS. For C₄A₃₋ₓFₓS in CSA cement clinker F₀, the practical value of x is higher than the theoretical value. It is due to that the part of Fe₂O₃ intended to form C₄AF participates the formation of C₄A₃S. Therefore, the practical C₄AF content is lower than the theoretical content and C₄A₃S is higher than the theoretical content (Table 4). Previous investigations also found the reverse correlation between the amount of C₄A₃S and C₄AF [32]. With the rise of Fe₂O₃ contents in the raw meals, the Fe₂O₃ contents of C₄A₃₋ₓFₓS in all the clinker presents a rising trend. However, the practical value of x is lower than the theoretical value.

3.3. Hydration and properties of iron rich CSA cement

The setting time of the cementitious materials is defined as the initial solidification and subsequent hardening [33], which has close tie with the workability and early hydration of C₄A₃S. Fig. 1 shows the water demand for normal consistency and setting time of iron rich CSA cement. The water demand for the normal consistency of CSA cement clinker F₀ is 0.29 and the Fe₂O₃ content does not affect the water demand for the normal consistency. With the rise of Fe₂O₃ content, both the initial and final setting time are prolonged, which allows a longer operation time for the application of iron rich CSA cement based materials. It also indicates that Fe₂O₃ lowers down the hydration activity of C₄A₃S.

Fig. 6 shows the compressive strength development of iron rich CSA cement. Within 28 d, with the rise of Fe₂O₃ content, the compressive strength lowers down gradually. It is mainly caused by the following reasons: i) With the rise of Fe₂O₃ content, C₄A₃S content of the iron rich CSA cement clinkers lower down. ii) With the rise of Fe₂O₃ content, more o-C₄A₃S is stabilized at the expense of c-C₄A₃S. In the presence of gypsum, the hydration reactivity of c-C₄A₃S is lower than that of c-C₄A₃S [31].

After 28 d, compared with F₀, the compressive strengths of F₇₀, F₆, and F₃ have a larger increase. At 90 d, the compressive strength of F₇₀ and F₆ exceeds that of F₀ and the compressive strength for F₇₀ is almost the same as that of F₀. It may be caused by the following reasons: i) The hydration of C₄F promotes the late age compressive strength development. Previous investigation has concluded that, in the single phase system of C₄F, the 96 d compressive strength increased substantially [34]. ii) The increased Fe₂O₃ content may lead to a higher incorporation level of Fe₂O₃ in belite, which could promote the hydration of belite at later hydration age.

The expansion of CSA cement is mainly caused by the formation of expansive ettringite [35]. It has been proved that if most of the ettringite forms before hardening, then non-expansive and rapid
hardening CSA cement can be achieved, but significant ettringite formation after hardening can cause expansion and cracking [36]. Therefore, C₄A₃ₛ content and the hydration activity of C₄A₃ₛ would affect the expansion of CSA cement [6]. Therefore, the expansion of iron rich CSA cement was investigated.

Fig. 7 shows the expansion rate of the iron rich CSA cement mortars cured in water. The increased Fe₂O₃ lowers down the hydration activity of C₄A₃ₛ, which could cause an increase of the expansion rate of CSA cement mortars. Inversely, the increased Fe₂O₃ lowers down the C₄A₃ₛ content, which could cause a decrease of the expansion rate of CSA cement mortars. From Fig. 7, it is observed that, with the rise of Fe₂O₃ content, the expansion rate of CSA cement mortar lowers down. Therefore, it is concluded that the C₄A₃ₛ content prevails over the hydration activity of C₄A₃ₛ in controlling the expansion rate of iron rich CSA cement.

Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical formula</th>
<th>Average formula</th>
<th>Practical x value</th>
</tr>
</thead>
<tbody>
<tr>
<td>F₀</td>
<td>C₄A₃ₛ</td>
<td>C₁.782±0.019A₂.703±0.013F₀.124±0.006F₀.053±0.009</td>
<td>0.13</td>
</tr>
<tr>
<td>F₀.₇</td>
<td>C₄₂F₀.₇</td>
<td>C₁.843±0.022A₂.382±0.025F₀.213±0.009F₀.082±0.008</td>
<td>0.30</td>
</tr>
<tr>
<td>F₁.₀</td>
<td>C₄₂F₁.₀</td>
<td>C₁.802±0.002A₂.244±0.011F₀.185±0.006F₀.044±0.007</td>
<td>0.45</td>
</tr>
<tr>
<td>F₁.₃</td>
<td>C₄₂F₁.₃</td>
<td>C₁.884±0.015A₂.124±0.017F₀.548±0.005F₀.086±0.009</td>
<td>0.62</td>
</tr>
</tbody>
</table>

Fig. 4. SEM photos of the iron rich CSA cement clinkers sintered at 1225 °C for 10 min.

Fig. 5. Water demand for normal consistency and setting time of iron rich CSA cement.

Fig. 6. Compressive strength development of iron rich CSA cement.

Fig. 7. Expansion rate of iron rich CSA cement mortars cured in water.
Fig. 8 shows the heat release of iron rich CSA cement within 24 h. For F₀ and F₀.7, the heat flow curves are characterized by three heat release peaks. The first heat release peak locates at ~0.05 h. It is mainly caused by wetting of the system, dissolution of the cement phase and the formation of the hydration products [37]. With the rise of Fe₂O₃ content, the intensity of first heat release peak lowers down gradually. Therefore, it is concluded that the increased Fe₂O₃ content inhibits the dissolution of the cement phase and the formation of the hydration products. Therefore, compared with the CSA cement, the setting time of iron rich CSA cement is prolonged (Fig. 5).

The second heat release peak locates at ~3 h. It is mainly caused by the rapid formation of ettringite [38]. With the rise of Fe₂O₃ content, the intensity of second heat release peak lowers down

![Fig. 8. Heat release of iron rich CSA cement within 24 h.](image)

![Fig. 9. XRD patterns of the hydration products of iron rich CSA cement at 6 h, 1 d and 28 d.](image)
content in iron rich CSA cement, the crystal size of the ettringite of become larger and larger. For F0, the ettringite is disorderly stacked. For F0.7, F1.0 and F1.3, some well organized ettringite clusters are formed. Therefore, it is concluded that Fe2O3 in C4A3,Fs participates the formation of ettringite with large crystal size and well organized ettringite clusters.

In the presence of gypsum, the hydration of C4A3,Fs may occur according to Eq. (2). For the Fe2O3 in C4A3,Fs, it either participates the formation of ettringite or forms Fe(OH)3.

\[
\text{C4A3,Fs} + 2\text{C} \rightarrow \text{H}_2 + 34\text{H} = \text{C}_6\text{A}_1.5\text{F} \rightarrow \text{H}_3 + (x-y)\text{F} \text{H}_3 + (2-x+y)\text{A} \text{H}_3
\]  

(2)

The chemical compositions of ettringite analysed by EDS on the polished section are shown in Table 5. The Maximum \( \frac{\text{Fe2O3}}{\text{Al2O3+Fe2O3}} \) is calculated based on the average Fe2O3 content in C4A3,Fs listed in Table 6, which is comprehended as that all of the Fe2O3 participate the formation of ettringite. The value of Maximum \( \frac{\text{Fe2O3}}{\text{Al2O3+Fe2O3}} \) is far below the value of Actual \( \frac{\text{Fe2O3}}{\text{Al2O3+Fe2O3}} \).

Therefore, it is concluded that only a minority of Fe2O3 in C4A3,Fs participates the formation of ettringite and the majority of Fe2O3 in C4A3,Fs forms Fe(OH)3. Besides, the hydration of C3F may also form a slight amount of Fe(OH)3. The formation of Fe(OH)3 endows iron CSA cement excellent compact resistance and sea water erosion resistance.

4. Conclusions

The iron rich CSA cement could be prepared without bauxite when the x value of C4A3,Fs exceeds 0.7. From investigation of the preparation of iron rich CSA cement clinker, the hydration and properties of iron rich CSA cement, the following conclusions can be drawn:

(1) The optimum calcining process for iron rich CSA cement clinker is at 1175–1225°C with the heat preservation time of 10 min.

(2) With the rise of Fe2O3 content in the raw meal, the C4A3,Fs content of iron rich CSA cement clinker lowers down, more C4AF and C3F forms, more c-C4A3,Fs forms at the expense of o-C4A3,Fs, and the crystal size of C4A3,Fs becomes smaller.

(3) With the rise of Fe2O3 content of CSA cement, both the initial setting and final setting are prolonged. For the compressive strength, the iron rich CSA cements are lower than CSA cement at early hydration age. However, the compressive strength of iron rich CSA cement has a larger increase at the 90 d.

(4) The Fe2O3 in C4A3,Fs promotes the formation of ettringite with large crystal size and well organized ettringite clusters. The majority of Fe2O3 in C4A3,Fs participates the formation of Fe(OH)3 and the remaining Fe2O3 forms of ettringite, which endows iron CSA cement excellent compact resistance and sea water erosion resistance.

### Table 5

<table>
<thead>
<tr>
<th>Sample</th>
<th>CaO/%</th>
<th>Al2O3/%</th>
<th>Fe2O3/%</th>
<th>SO3/%</th>
<th>Maximum ( \frac{\text{Fe2O3}}{\text{Al2O3+Fe2O3}} )</th>
<th>Actual ( \frac{\text{Fe2O3}}{\text{Al2O3+Fe2O3}} )</th>
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</thead>
<tbody>
<tr>
<td>F0</td>
<td>50.24</td>
<td>14.72</td>
<td>0.47</td>
<td>34.57</td>
<td>0.13</td>
<td>0.02</td>
</tr>
<tr>
<td>F0.7</td>
<td>49.90</td>
<td>14.23</td>
<td>1.17</td>
<td>34.70</td>
<td>0.30</td>
<td>0.05</td>
</tr>
<tr>
<td>F1.0</td>
<td>48.68</td>
<td>13.75</td>
<td>1.88</td>
<td>35.69</td>
<td>0.45</td>
<td>0.08</td>
</tr>
<tr>
<td>F1.3</td>
<td>47.89</td>
<td>13.10</td>
<td>2.80</td>
<td>36.20</td>
<td>0.62</td>
<td>0.12</td>
</tr>
</tbody>
</table>
Yongbo Huang: Conceptualization, Methodology, Software, Investigation. Yan Pei: Validation, Formal analysis, Visualization, Software, Writing - review & editing. Jueshi Qian: Validation, Formal analysis, Visualization. Xin Gao: Writing - review & editing. Jiao Liang: Writing - review & editing. Guangbin Duan: Writing - review & editing. QiQi Zhao: Writing - review & editing. Lingchao Lu: Writing - review & editing. Xin Cheng: Writing - review & editing.

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