Rheological Behavior of Portland Clinker-Calcium Sulphoaluminate Clinker-Anhydrite Ternary Blend

Tingjie Huang, Ph.D student
School of Civil Engineering, National Engineering Laboratory for High Speed Railway Construction, Central South University, Changsha 410075, China
Email: huangtj@csu.edu.cn, Tel: +86 15608461125

Baiyuan Li, Master student
School of Civil Engineering, National Engineering Laboratory for High Speed Railway Construction, Central South University, Changsha 410075, China
Email: Libaiyun@csu.edu.cn

*Qiang Yuan, Ph.D, Professor, Corresponding author
School of Civil Engineering, National Engineering Laboratory for High Speed Railway Construction, Central South University, Changsha 410075, China
Email: Yuanqiang@csu.edu.cn, Tel: +86 13548955591

Zhenguo Shi, Ph. D,
Laboratory for Concrete & Construction Chemistry, Swiss Federal Laboratories for Materials Science and Technology (Empa), 8600 Dübendorf, Switzerland
Email: zhenguo.shi@empa.ch

Youjun Xie, Ph.D, Professor
School of Civil Engineering, National Engineering Laboratory for High Speed Railway Construction, Central South University, Changsha 410075, China
Email: xieyj@csu.edu.cn

Caijun Shi, Ph.D. Professor
Key Laboratory for Green & Advanced Civil Engineering Materials and Application Technology of Hunan Province, College of Civil Engineering, Hunan University, Changsha, 410082, China
Email: cshi@hnu.edu.cn

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Abstract

In this paper, the rheological behavior of blended cements consisting of calcium sulfoaluminate clinker (CSA), ordinary Portland clinker (OPC) and anhydrite (C₅) were investigated. The shear stress-shear rate curves of OPC-CSA-C₅ blends with different OPC/CSA/C₅ ratios were analyzed. Several rheological models were used to fit the rheological curves of cement pastes. The evolution of static yield stress was also monitored to evaluate the structural build-up rate of the blends. Besides, zeta potential measurement, calorimetric test, XRD and TGA analysis were carried out to reveal the physico-chemical kinetics of the rheological evolution of fresh blends. It was found that not only CSH gel but crystals of AFt and gypsum formed at the early age make contributions to the rheological parameters, i.e. plastic viscosity, yield stress and structural build-up.

Keywords:
Ordinary Portland cement, Calcium sulfoaluminate cement, Anhydrite, Physico-chemical kinetics, Rheology

1. Introduction

Blends of ordinary Portland cement (OPC) and calcium sulfoaluminate (CSA) cement are expected to combine advantages of these two cements and control specific properties of each, such as shrinkage of OPC-based material, expansion of CSA-based material and their setting time [1-9].

Binary systems of OPC-CSA or ternary systems mixed with various calcium sulfates (dihydrate, hemihydrate and anhydrite) have been well investigated, including the mechanical properties, the
microstructure [10, 11] and hydration process [12-14]. The ratio between the cements and the amount
of calcium sulfate available in the system determines to a great extent the properties of composite
systems. The setting time of OPC can be shortened by adding CSA, and the higher addition of CSA
is, the shorter setting time is [15, 16]. Moreover, the composition of the OPC and the type of sulphates
can considerably vary it [14, 15]. Higher CSA cement content increased crystallization stress, which
lead to more expansion-induced cracks, larger porosity, weaker tensile strength and smaller dynamic
modulus [1]. The increase of CSA increased the compressive strength of blends at high OPC/CSA
mass ratio, but decreased the strength at low OPC/CSA [10~12].

A lot of researches indicated that the mixing of these two cements promoted early silicate and
aluminate hydration [12, 13, 18]. They reacted very fast and AFt was formed within the first 5 min by
the reaction between Ye'elimite (i.e., C₄A₃S, the main component of the CSA clinker) and the calcium
sulphates. Subsequently C₂ASH₈ and CSH were formed due to the reaction of C₃S at early period [13].
In case of OPC, the addition level of calcium sulphate should be optimized considering the content
and reactivity of C₃A, which leads to the formation of AFt at early age [17, 19]. However, calcium
sulfate ion pairs are expected to adsorb onto tricalcium aluminate and reduce the overall reaction rate
of OPC [20, 21]. In case of CSA cement, calcium sulphate content controls the formation rate and the
amount of AFt, affects the AFt/AFm ratio and the water demand to achieve complete hydration [22,
23]. For ternary blend, high calcium sulphate content increases AFt contents at early age, although it
does not strongly influence the hydrate assemblage of the ternary binders at late period [13].

In addition to the properties of hardened cement-based materials, the favorable rheological property at
fresh stage is also of significance, it affects the construction quality of casting and forming process and also the properties of hardened concrete [24]. Particularly, in some advanced construction technologies, such as concrete 3D printing, smart casting and formless construction [25~27], the rheology of cement-based materials should make a balance between flowability before deposition and rate of structural build-up at rest [28]. CSA was applied to improve the shape holding capacity and enhance early strength of 3D printing OPC paste [29] and OPC-based self-levelling screed [30].

The chemical composition and physical characteristics of cement greatly influence its rheological properties. Mork et al. [31] noted that the yield stress and plastic viscosity of OPC paste increased with SO$_3$ content. Dils et al. [32] pointed out that the OPC paste with high C$_3$A content, and lower SO$_3$ content performed the worst rheological properties. García-Maté et al. [33] believed that the SO$_3$ content did not present an important effect on the plastic viscosity of fresh CSA cement paste.

Recently, more and more attention has been focused on a time-dependent rheological parameter (i.e., the structural build-up rate) of cement-based material, which is due to the physical interactions between particles and the hydration of cement at early age [34, 35]. The structural build-up is responsible for the increase of static yield stress and storage modulus of cement-based materials over time [36, 37]. A high build-up rate leads to a sufficient strength to sustain the weight of subsequent casting layers, as well as ensure strong bond between cast layers [38~40]. Furthermore, fast structural build-up rate can lead to high resistance of segregation and bleeding that can improve the quality of interface between aggregate and cement paste [41,42]. This directly affects the permeability, bond to steel and mechanical properties [43]. The structural build-up rate of ordinary Portland cement-based materials
can be optimized by incorporating mineral admixtures [44-47], clays [48-52] and chemical additives [53].

Hydration kinetics plays an important role on structural build-up of cement-based material [34]. With the hydration of Portland cement particles going on, the precipitation of CSH gel on the surface of particles bridges the particles. It was considered as the main origin of structural build-up [35]. Therefore, the requirement of rheological properties of cement-based material leads to the new challenges of controlling the hydration at very early age. Hydration kinetics must be delayed to avoid setting during conveying and casting, but accelerated substantially after placing in the position in order to obtain the quick structuration [27, 28].

Although there are some studies on the rheological properties of Portland cement with CSA cement, the rheological properties of binary binder are affected by many factors, such as the type and content of calcium sulfate, the compositions of Portland cement and CSA cement. These are not well addressed in literature. By using three pure minerals, i.e. clinker of Portland cement, clinker of CSA and calcium sulfate, the rheological properties of binary binder of CSA and Portland can be studied in more details.

The objective of the present study is to characterize the rheological behaviors of ternary blends composed of OPC clinker, CSA clinker and anhydrite. The influence of anhydrite dosage and of the OPC/CSA mass ratio on the instantaneous and time-dependent rheological parameters were studied. In order to provide more insightful evidence of rheology, zeta potential test was used to measure the electro-kinetic parameters, calorimetric test was conducted to evaluate the hydration reaction of cement paste, and X-ray diffraction and thermogravimetric analysis were employed to characterize the
hydrates formed during rheological test period. Hopefully, this study can provide useful information for designing a new binder with adopted rheological and setting behaviors.

2. Experimental

2.1 Materials and sample preparation

The raw materials used in this study to prepare the composite cements were ordinary Portland cement clinker and calcium sulfoaluminate clinker and anhydrite (C₅S). In the following, OPC refers to ordinary Portland cement clinker and CSA refers to calcium sulfoaluminate clinker. All the raw materials were supplied by China Building Materials Academy®. The chemical compositions and physical properties of the OPC, CSA and C₅S are presented in Table 1. Their particle size distributions are shown in Fig. 1.

![Graph: Particle size distributions of powder materials](image)

Fig. 1. Particle size distributions of powder materials

The mix proportions of the studied OPC-CSA-C₅S systems are given in Table 2. The influence of the OPC/CSA mass ratio was investigated at certain C₅S content. Two C₅S contents (5% and 10%) were employed to check the influence of the calcium sulphate content on the hydration mechanism and
rheological behaviors of the composite cements. The water-to-powder (w/p) ratio of 0.5 was used to prepare the paste samples. Water was first added into the Hobart N50 mixer, followed by adding the powders. The mixture was first mixed at 60 rpm for 60 s, and then stopped and the paste sample was manually homogenized for 30 s, followed by mixing at 120 rpm for 90 s, and then at 60 rpm for 30 s.

Table 1 Chemical compositions and physical properties of cementitious materials

<table>
<thead>
<tr>
<th></th>
<th>OPC</th>
<th>CSA</th>
<th>CS$^5$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$ (%)</td>
<td>20.76</td>
<td>11.72</td>
<td>3.03</td>
</tr>
<tr>
<td>Al$_2$O$_3$ (%)</td>
<td>4.58</td>
<td>22.83</td>
<td>0.59</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (%)</td>
<td>3.27</td>
<td>1.50</td>
<td>0.29</td>
</tr>
<tr>
<td>CaO (%)</td>
<td>62.13</td>
<td>46.79</td>
<td>39.53</td>
</tr>
<tr>
<td>MgO (%)</td>
<td>3.13</td>
<td>1.72</td>
<td>0.68</td>
</tr>
<tr>
<td>SO$_3$ (%)</td>
<td>12.21</td>
<td>1.20</td>
<td>0.69</td>
</tr>
<tr>
<td>Other minor oxides</td>
<td>2.12</td>
<td>1.33</td>
<td>0.57</td>
</tr>
<tr>
<td>Loss on ignition (%)</td>
<td>3.14</td>
<td>2.81</td>
<td>2.97</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>2845</td>
<td>3770</td>
<td>3840</td>
</tr>
</tbody>
</table>

Table 2 Mix proportions of the OPC-CSA-C$^5$ systems under investigation

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass fraction (wt.%)</th>
<th>OPC/CS A mass ratio</th>
<th>Solid volume fraction (%)</th>
<th>Sample</th>
<th>Mass fraction (wt.%)</th>
<th>OPC/CS A mass ratio</th>
<th>Solid volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-10/0</td>
<td>95 0 5 10/0*</td>
<td>38.98</td>
<td></td>
<td>10-10/0</td>
<td>90 0 10 10/0*</td>
<td>39.05</td>
<td></td>
</tr>
<tr>
<td>5-9/1</td>
<td>85.5  9.5  5 9/1</td>
<td>39.24</td>
<td></td>
<td>10-9/1</td>
<td>81 9 10 9/1</td>
<td>39.30</td>
<td></td>
</tr>
<tr>
<td>5-8/8</td>
<td>76  19  5 8/2</td>
<td>39.50</td>
<td></td>
<td>10-8/8</td>
<td>72 18 10 8/2</td>
<td>39.54</td>
<td></td>
</tr>
<tr>
<td>5-7/3</td>
<td>66.5  28.5  5 7/3</td>
<td>39.76</td>
<td></td>
<td>10-7/3</td>
<td>63 27 10 7/3</td>
<td>39.79</td>
<td></td>
</tr>
<tr>
<td>5-6/4</td>
<td>57  38  5 6/4</td>
<td>40.02</td>
<td></td>
<td>10-6/4</td>
<td>54 36 10 6/4</td>
<td>40.03</td>
<td></td>
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<td>40.27</td>
<td></td>
<td>10-5/5</td>
<td>45 45 10 5/5</td>
<td>40.27</td>
<td></td>
</tr>
<tr>
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<td>38  57  5 4/6</td>
<td>40.53</td>
<td></td>
<td>10-4/6</td>
<td>36 54 10 4/6</td>
<td>40.51</td>
<td></td>
</tr>
<tr>
<td>5-3/7</td>
<td>28.5  66.5  5 3/7</td>
<td>40.78</td>
<td></td>
<td>10-3/7</td>
<td>27 63 10 3/7</td>
<td>40.75</td>
<td></td>
</tr>
<tr>
<td>5-2/8</td>
<td>19  76  5 2/8</td>
<td>41.02</td>
<td></td>
<td>10-2/8</td>
<td>18 72 10 2/8</td>
<td>40.98</td>
<td></td>
</tr>
<tr>
<td>5-1/9</td>
<td>9.5  85.5  5 1/9</td>
<td>41.27</td>
<td></td>
<td>10-1/9</td>
<td>9 81 10 1/9</td>
<td>41.22</td>
<td></td>
</tr>
<tr>
<td>5-0/10</td>
<td>0  95  5 0/10*</td>
<td>41.51</td>
<td></td>
<td>10-0/10</td>
<td>0 90 10 0/10*</td>
<td>41.45</td>
<td></td>
</tr>
</tbody>
</table>

Note: *: Binary blend, OPC+ C$^5$ blend or CSA+C$^5$ blend, 5-9/1 denotes 5% C$^5$ in the powder with 90% OPC and 10%.
2.2 Rheological test

Anton paar Rheolab QC rheometer was used for rheological test. The type of rotator was CC39 with a diameter of 4.000 cm, and the inner diameter of the cylinder was 4.194 cm. In order to minimize the slip, the surfaces of the container and rotator which are in contact with cement paste were sandblasted. After mixing, the paste was immediately poured into the cylinder. Two batches of mixtures were prepared for both dynamic test and static test.

2.2.1 Dynamic test

Dynamic yield stress test was started at 5 min after the contact of cement and water, and the test was conducted as follows: pre-shear the paste at 100 s⁻¹ for 60 s, then stop for 15 s, followed by linearly increasing shear rate from 0 to 100 s⁻¹ within 60 s.

In order to choose the best model to characterize the dynamic rheological behavior of the different blends, four common models (Eq. 1~4) were used to fit descending curve of shear rate from 20 s⁻¹ to 100 s⁻¹ respectively and calculate rheological parameters.

Bingham (B) model:

\[ \tau = \tau_0 + \mu \gamma \]  

(1)

Modified Bingham (MB) model:

\[ \tau = \tau_0 + \mu \dot{\gamma} + c \dot{\gamma}^2 \]  

(2)

Herschel-Bulkley (H-B) model:

\[ \tau = \tau_0 + K \dot{\gamma}^n \]  

(3)

Casson (C) model:
\[ \tau = \tau_0 + \eta_\infty \dot{\gamma} + 2(\tau_0 \eta_\infty)^{1/2} \gamma^{1/2} \]  

(4)

where \( \tau_0 \) is dynamic yield stress, \( \mu \) is apparent viscosity, \( c \) is the second order parameter in Pa·s², \( K \) is consistency index, \( n \) is non-Newton index and \( \eta_\infty \) is infinite viscosity.

### 2.2.2 Static test

For static test, a thin layer of oil was dropped on the surface of the sample to prevent the evaporation of water after pouring the sample into cylinder. The paste was at rest until specific testing time (10~45 min), static yield stress test was performed by constant shearing paste at 0.005 s⁻¹ for 60 s to reach steady state [37]. The peak value of shear stress measured during this period was recorded as the static yield stress. For each resting time a new sample was employed. Since the capacity of shearing force of the equipment was 450 Pa, some samples reached the limit before 45 min, and the test was stopped. During the entire test, the temperature of the sample was maintained at 25 °C by water bath.

In this study, the model (see in Eq. 5) proposed by Perrot et al. [54] was employed to fit the data of static yield stress \( \tau_c \). The parameter \( A_{\text{thix}} \) was introduced to characterize the structural build-up rate of plain and composite cement paste. The higher \( A_{\text{thix}} \) reflects faster structural build-up of cement paste [76].

\[ \tau_0(t) = \tau_{0,0} + A_{\text{thix}} t_c \left( e^{t_{\text{rest}} / t_c} - 1 \right) \]  

(5)

where \( t_c \) is a characteristic time, the value of which is adjusted to obtain the best fit with experimental values.

### 2.3 Zeta potential measurement
The zeta potential was measured using the “ZetaProbe” equipment based on the electroacoustic technique. A diluted blend was made for zeta potential measurement. The w/p ratio was 5. The mix proportion of samples were the same to those in rheological test, as shown in Table 2. OPC, CSA, CS and distilled water were mixed in a mixer for 2 min at 300 rpm. About 300 ml of the paste was poured in the sample cell of ZetaProbe. During the test, the samples were kept stirring at a speed of 300 rpm so that a uniform cement suspension passes through the electrodes of the cell. The zeta potential, pH value and the conductivity of the cement solution were measured every 20s and Debye length was calculated automatically by the apparatus [55].

2.4 Calorimetric test

2.4.1 Test procedure

TAM Air thermal activity micro-calorimeter was used to measure the hydration heat of the blended cements. The twin-chamber testing channel is the typical characteristics of this apparatus, and one contains the distilled water and the other contains the predetermined amount of paste. The mixing program was the same as rheological test. After mixing, the paste was immediately transferred into the apparatus. During the test, the ambient temperature around the samples were maintained at 25 °C. The test started at 6 min after mixing the blended cements with water. The data were recorded every 10 s.

2.4.2 Calculation of hydration kinetic parameters

The boundary nucleation and growth (BNG) model [56] has shown some advantages to describe the hydration kinetics of Portland cement [57] and calcium sulphaaluminate cement [58]. In this model, the rates of nucleation and growth are assumed to be constant throughout the whole hydration process,
and the nucleation of hydrates occurs randomly on the surface of cement particles.

According to BNG model, the volume fraction of hydrates \(X(t)\) at a given time was used to estimate the degree of hydration \(\alpha(t)\), which can be expressed as Eq. 6 [57–62].

\[
\alpha(t) = X(t) = 1 - \exp \left\{ - S \int_0^t \left[ 1 - \exp \left( - \frac{\pi N}{2} G^2 t^3 \left( 1 - \frac{3y^2}{G^2 t^2} + \frac{2y^3}{G^3 t^3} \right) \right) \right] \, dy \right\}
\]

\[
S = \frac{\text{Blaine specific surface area of particles}}{\text{density of particles}}
\]

where \(S\) is the value of surface area for the solid particles per unit volume (μm\(^{-1}\)) and calculated by Eq. 7, \(G\) is the growth rate of nuclei (μm/h), \(N\) is the formation rate of nuclei (μm\(^{-2}\)h\(^{-1}\)) and \(y\) is a dummy variable. The degree of hydration \(\alpha(t)\) is estimated by calorimetric test using Eq. 8.

\[
\alpha(t) = \frac{Q(t)}{Q_{max}}
\]

\(Q_{max}\) is the total heat released from the hydration of cementitious materials as measured by calorimetric test.

The formation rate of nuclei \((N)\) and its growth rate \((G)\) are both dominant parameters controlling the early hydration. Because the nuclei growth is anisotropic, the rate of tangent direction was defined as \(gG\). Additionally, a parameter \(p\) was proposed to describe the proportion of growth rate inside and outside grain [56]. By further defining \(\mu = y/(Gt)\), Eq. 6 can be written as Eq. 9:

\[
X(t) = 1 - \exp \left\{ - 2pSGt \int_0^\mu \left[ 1 - \exp \left( - \frac{\pi N}{3} G^2 t^3 (1 - \mu)^2 (1 + 2\mu) \right) \right] \, d\mu \right\}, \mu < 1
\]

Two independent rate constants \(k_N\) and \(k_G\) were proposed to describe the kinetics of a boundary-nucleated process (Eq. 10 and 11).
\[ k_N = \pi g G^2 N/3 \quad (10) \]
\[ k_G = p S G \quad (11) \]

According to refs. [56, 57], 1/kG was defined as the time for hydration products reaching the radius of “reaction vessel”. 1/(K_N)\(^{1/3}\) was the time needed for part of hydration products along the boundary of cement particles to become unity. Thus, the X(t) can be expressed as follows (Eq. 12).

\[
X(t) = 1 - \exp\left( -2 k_G t \int_0^t \left[ 1 - \exp \left( - k_N t^3 (1 - \mu)^2 (1 + 2 \mu) \right) \right] d\mu \right), \mu < 1 \quad (12)
\]

According to the literature [57], the BNG model fits well the calorimetric data, and the heat flow can be defined as A(dx/dt), where A is the scaling parameter. The measured heat flow data, in particular the data between the minimum in the induction period and the second peak, were used to determine K_N and K_G values.

2.5 Solid phase Analysis

2.5.2 X-ray diffraction analysis

After mixing of the blended materials, the fresh paste was placed on a glass microscope slide and set at X-ray diffractometer at 25°C. The XRD measurements started at 15 min and 30 min after the contact of cement and water. X-ray diffraction analyses was carried out at 25 °C with a Bruker D8 Advance diffractometer (Cu Kα radiation, 45mA, 35kV) with a Super speed detector, in the 2θ range 5~35°, with a scanning step size of 6° 2θ/min (total measurement time of 5 min). The crystalline phases were analyzed using the EVA software.
2.5.3 Thermogravimetric analysis

The hydration of the blend was stopped before thermogravimetric analysis (TGA). 5 grams of the sample after hydration of 10, 20, 30 and 45 min was ground with 100 ml of acetone to fine powder in an agate mortar prior to stopping hydration. The ground samples were filtrated with a Whatman filter (90 mm diameter with a pore size of 2.5 μm) and a Teflon support. The samples were washed twice with acetone and finally washed with diethyl ether [63]. The resulting samples were stored in a desiccator to avoid further hydration and any possible carbonation.

TGA was carried out with a TGA 2(SF)-Mettler Toledo. Approximately 50 mg of the prepared powdered samples were tested from 35 °C to 950 °C at a heating rate of 10 °C/min under a N₂ atmosphere.

3 Results

3.1 Dynamic rheology

3.1.1 Rheological models of OPC-CSA-C₅ blend

The typical shear stress vs. shear rate flow curves of OPC-CSA-C₅ blends are plotted in Fig. 2. The paste shows shear thinning behavior in the measured shear rate region regardless of OPC/CSA mass ratio and C₅ content. In order to evaluate whether the mathematic equations are suitable for the measured data, standard deviation (SD) calculated by Eq. 12 was adopted to compare the compliance of various rheological models and shear stress–shear rate data. In Eq. 12, \( y_{\text{mea}} \) is measured shear stress, \( y_{\text{pre}} \) is the predicted value by the rheological models. The results are shown in Table 3.

\[
SD = \sqrt{\frac{\sum_{i=1}^{n} (y_{\text{mea}} - y_{\text{pre}})^2}{n - 1}} \quad (12)
\]
As seen in Table 3, the Herschel-Bulkley (H-B) and modified Bingham (MB) models have lower SD values than Bingham (B) and Casson (C) models, particularly in case of lower OPC/CSA ratio and higher C\textsubscript{S} content. However, the H-B model has higher SD values for ternary blends with higher OPC/CSA ratio and binary CSA-C\textsubscript{S} blends than that of MB model. This means that the modified Bingham model has the best fitting for shear stress-shear rare data of OPC-CSA-C\textsubscript{S} blends.

![Typical rheological curves of blends](image)

**Fig. 2** Typical rheological curves of blends

<table>
<thead>
<tr>
<th>OPC/CSA ratio</th>
<th>5% C\textsubscript{S}</th>
<th>10% C\textsubscript{S}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B</td>
<td>MB</td>
</tr>
<tr>
<td>10/0</td>
<td>0.1098</td>
<td>0.1375</td>
</tr>
<tr>
<td>9/1</td>
<td>0.1807</td>
<td>0.0408</td>
</tr>
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<td>8/2</td>
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<tr>
<td>0/10</td>
<td>0.5230</td>
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</tr>
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</table>
3.1.2 Yield stress and plastic viscosity

Yield stress and plastic viscosity are two parameters, which should be fitted to quantitatively assess the rheological behavior of the blends. Fig. 3 presents the yield stress obtained by four models. The H-B model predicts the lowest yield stress, which is one order of magnitude lower than the yield stress predicted by other rheological models. Nevertheless, the results calculated by different models shows a similar trend. It reveals that the dynamic yield stress of blend depends not only on OPC/CSA ratio, but also relates to C\text{Si}. Independent of the types of models used, for a given C\text{Si} content, the dynamic yield stress ($\tau_0$) of ternary composite cement paste is higher than binary OPC+C\text{Si} paste. The models predict that the $\tau_0$ value of ternary blends is even higher than that of CSA+C\text{Si} paste. Additionally, the $\tau_0$ value is smaller at higher OPC/CSA ratio, while the dynamic yield stresses of those with 10% C\text{Si} are lower than those with 5% C\text{Si} at the same OPC/CSA ratio.

![Fig. 3. The dynamic yield stress of pastes obtained by various models.](image)

Fig. 4 shows the plastic viscosity and consistency index predicted by Bingham model and MB model. The result obtained from Bingham model is similar to that obtained from MB model at high OPC/CSA
ratio, however, the Bingham model shows higher values at lower OPC/CSA ratio. For ternary blends, the influence of OPC/CSA/C$_S$ mass ratio on the plastic viscosity/consistency index calculated by these two models are similar. The plastic viscosity/consistency index increases both with CSA content and C$_S$ content. Most of the plastic viscosities of ternary blends are larger than that of binary OPC+C$_S$ and CSA + C$_S$ pastes.

Fig. 4. The apparent viscosity of samples obtained by Bingham and Modified-Bingham

3.1.3 Shear-thinning intensity

In order to evaluate the shear-thinning intensity of the blends, the non-Newton index n was calculated based on the H-B model as summarized in Table 4. It can be observed that all of the n values of blends are less than 1, which means that all of them exhibit shear-thinning behavior [64]. The lower n value indicates a higher intensity of shear-thinning when n<1[64]. The results show that with the addition of C$_S$ the shear-thinning intensity is increased for the OPC paste, but decreased for the CSA paste. The result also shows that the shear-thinning intensity of ternary OPC-CSA-C$_S$ blend is enhanced with increasing the C$_S$ content. However, the highest shear-thinning intensity is obtained for the blends when the OPC content is close to CSA content (in this study, the highest shearing-thinning intensity is observed at OPC/CSA=6/4 or 5/5, when the content of C$_S$ is 5% or 10%).
In summary, the initial rheological parameter of cement pastes with ternary OPC-CSA-\( \text{CS} \) system depends not only on OPC/CSA ratio, but also on the content of \( \text{CS} \). The decrease of the OPC/CSA ratio leads to a higher yield stress and a higher plastic viscosity. However, increasing the percentage of \( \text{CS} \) in ternary system results in a lower dynamic yield stress but a higher plastic viscosity and a higher shear-thinning intensity.

<table>
<thead>
<tr>
<th>OPC/CSA ratio</th>
<th>5% ( \text{CS} )</th>
<th>10% ( \text{CS} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10/0</td>
<td>0.420</td>
<td>0.450</td>
</tr>
<tr>
<td>9/1</td>
<td>0.440</td>
<td>0.449</td>
</tr>
<tr>
<td>8/2</td>
<td>0.420</td>
<td>0.445</td>
</tr>
<tr>
<td>7/3</td>
<td>0.411</td>
<td>0.429</td>
</tr>
<tr>
<td>6/4</td>
<td>0.389</td>
<td>0.435</td>
</tr>
<tr>
<td>5/5</td>
<td>0.389</td>
<td>0.410</td>
</tr>
<tr>
<td>4/6</td>
<td>0.387</td>
<td>0.442</td>
</tr>
<tr>
<td>3/7</td>
<td>0.390</td>
<td>0.420</td>
</tr>
<tr>
<td>2/8</td>
<td>0.402</td>
<td>0.505</td>
</tr>
<tr>
<td>1/9</td>
<td>0.440</td>
<td>0.601</td>
</tr>
<tr>
<td>0/10</td>
<td>0.736</td>
<td>0.427</td>
</tr>
</tbody>
</table>

### 3.2 Electro-kinetic characteristics

Table 5 shows the average values of electro-kinetic parameters (zeta potential, Debye length, conductivity and pH value) of \( \text{CS} \) solution, OPC solution, CSA solution, OPC + \( \text{CS} \) diluted blends and CSA + \( \text{CS} \) diluted blends over 20 min. The change in zeta potential depends on either a change in surface charge or adsorption of ions to the surfaces. Debye length reflects the scope where repulsive electrostatic effect persists. Debye length relates on the ionic strength of the bulk electrolyte. The conductivity of cement solution reflects the ionic concentration and ionic conductivity. [65]
It can be seen that the zeta potentials (ζ) of the suspensions of C₅, OPC, CSA are all positive, the value of OPC solution is the largest while that of CSA solution is the smallest and close to zero. Although 5% C₅ content shortens the Debye length of OPC solution and CSA solution while 10% C₅ content enlarges the value of Debye length, the influence of C₅ in zeta potential values of OPC solution and CSA solution differs. In case of OPC+C₅ binary blend, the increase in C₅ content decreases the zeta potential. Conversely, in case of CSA+C₅ blend, larger proportion of C₅ leads to higher ζ value.

The average electro-kinetic parameters of OPC-CSA-C₅ blends are also listed in Table 6. The result notes that except for sample 5-3/7, the zeta potentials of ternary blends are positive, the increase of CSA content reduces ζ value of blends. For blends with 5% C₅, increasing CSA content decreases the conductivity and pH value. The lower conductivity and pH value reflect the less dissolved ions stemming from blend. It may contribute to lower value of ionic strength. Thus, Debye length increases. For blends with 10% C₅, the conductivity and pH value decrease with the CSA content when OPC/CSA is larger than 4/6, but it turns to increase with CSA content at the lowers. The Debye length of blends with 10% C₅ thus shows an opposite trend. Furthermore, the increase of C₅ content results in the increase of Debye length and leads to the increases of zeta potential.

Therefore, larger CSA content in ternary system results in longer Debye length but lower zeta potential, while higher proportion of C₅ contributes to larger value of Debye length and higher and zeta potential.

<table>
<thead>
<tr>
<th>Samples</th>
<th>ζ (mV)</th>
<th>Debye length (nm)</th>
<th>Conductivity (mS/cm)</th>
<th>pH value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only C₅</td>
<td>2.31</td>
<td>1.61</td>
<td>5.33</td>
<td>6.89</td>
</tr>
</tbody>
</table>

Table 5 Electro-kinetic parameters of diluted C₅, OPC, CSA paste and their binary blends
Table 6 Electro-kinetic parameters of diluted OPC-CSA-C₅ pastes

<table>
<thead>
<tr>
<th>OPC/CS</th>
<th>5% C₅</th>
<th>10% C₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>A mass ratio</td>
<td>ζ (mV)</td>
<td>Debye length (nm)</td>
</tr>
<tr>
<td>9/1</td>
<td>2.14</td>
<td>1.19</td>
</tr>
<tr>
<td>8/2</td>
<td>2.46</td>
<td>1.19</td>
</tr>
<tr>
<td>7/3</td>
<td>1.62</td>
<td>1.33</td>
</tr>
<tr>
<td>6/4</td>
<td>1.63</td>
<td>1.35</td>
</tr>
<tr>
<td>5/5</td>
<td>1.12</td>
<td>1.44</td>
</tr>
<tr>
<td>4/6</td>
<td>0.45</td>
<td>1.64</td>
</tr>
<tr>
<td>3/7</td>
<td>-0.23</td>
<td>1.89</td>
</tr>
<tr>
<td>2/8</td>
<td>0.39</td>
<td>1.95</td>
</tr>
<tr>
<td>1/9</td>
<td>0.47</td>
<td>2.03</td>
</tr>
</tbody>
</table>

3.3 Evolution of static yield stress with resting time

The static yield stress vs. resting time curves of OPC pastes and CSA cement paste with different contents of C₅ were given in Fig. 5. Perrot’s model was employed to fit these data and the result is given in Table 7. The result shows that the C₅ influences the static yield stress of the OPC paste and CSA cement paste differently. For the OPC pastes, 5% of C₅ reduces the initial yield stress τ₀,₀, while the τ₀,₀ is higher when the dosage of C₅ is 10%. After longer resting time, the increase of yield stress at 10% C₅ is indicating a significant increase of setting time. On the contrary, the incorporation of C₅ significantly increases not only the τ₀,₀ value but also the structural build-up rate Aₜₙₜ of CSA cement paste comparing to the sample without C₅. However, no difference in Aₜₙₜ value of CSA cement paste is observed between samples with 5% and 10% C₅.
Fig. 5 The influence of CSSF on the evolution of static yield stress of OPC and CSA paste with resting time

Table 7 Effect of CSSF content on the structural build-up parameters of OPC paste and CSA paste obtained from Perrot model

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\tau_{0,0}$ (Pa)</th>
<th>$A_{thix}$ (Pa/min)</th>
<th>$t_c$ (min)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only OPC</td>
<td>9.65</td>
<td>3.118</td>
<td>66.488</td>
<td>0.9966</td>
</tr>
<tr>
<td>5-10/0</td>
<td>7.73</td>
<td>1.860</td>
<td>24.237</td>
<td>0.9663</td>
</tr>
<tr>
<td>10-10/0</td>
<td>14.01</td>
<td>0.209</td>
<td>1249.089</td>
<td>0.9293</td>
</tr>
<tr>
<td>Only CSA</td>
<td>6.142</td>
<td>9.306</td>
<td>12.072</td>
<td>0.9925</td>
</tr>
<tr>
<td>5-0/10</td>
<td>9.202</td>
<td>15.450</td>
<td>14.915</td>
<td>0.9875</td>
</tr>
<tr>
<td>10-0/10</td>
<td>11.256</td>
<td>14.709</td>
<td>9.182</td>
<td>0.9821</td>
</tr>
</tbody>
</table>

Fig. 6 plots the evolution curves of static yield stress of ternary OPC-CSA-CSSF blends. The structural build-up rate was calculated by Perrot’s model as well. The results are listed in Table 8. It shows a well fit between Perrot’s model and experimental data of ternary blends. As can be seen in Table 8, the proportions of OPC, CSA and CSSF affects the structural build-up of blends greatly. The initial yield stress $\tau_{0,0}$ of blends is increased with the CSA content and CSSF content. The higher CSA proportion is of benefit for structuration of blends. However, at the same OPC/CSA ratio, $A_{thix}$ value of those with 10% CSSF is always higher than that of those with 5% CSSF. Particularly, when OPC/CSA ratio is lower...
than 6/4, the structural build-up rates of blends containing 10% C$S$ have quadrupled in that of blends with 5% C$S$. It reveals that the higher percentage of C$S$ conduces to structural build-up of ternary blends, which is contrary to the result for CSA cement paste and OPC paste. It should be noted that when the OPC/CSA ratio drops to 1/9, the $A_{thix}$ of ternary composite cement paste with 5% C$S$ is over that of binary CSA+ C$S$ paste; and for 10% of C$S$ content, the build-up rate of the blend with only 7/3 of OPC/CSA ratio is already quicker than that of CSA+C$S$ paste.

Therefore, the increase of CSA content accelerates the structural build-up of ternary blends at rest. The incorporation of C$S$ is in favor of the re-structuration of ternary blends, and it becomes more significantly when CSA dominates.

![Fig. 6 Effect of OPC/CSA mass ratio on structural build-up of blends](image-url)
3.4 Hydration kinetics and phase changes

3.4.1 Hydration heat

Calorimetric testing results of OPC-CSA-C\(\bar{S}\) blends are given in Fig. 7. As can be seen in the figure, the hydration of OPC+ C\(\bar{S}\) paste is still in the induction period when it is subjected to the rheology test. The higher percentage of C\(\bar{S}\) slightly retards the induction period and reduces the heat releasing rate in that period. In contrast, there is no obvious induction period for the CSA+ C\(\bar{S}\) paste, whereas the rheology test period is within the accelerating period of hydration. During the rheology test period, the heat flow value of CSA+ 10% C\(\bar{S}\) is significantly higher than CSA+ 5% C\(\bar{S}\) paste. The main peak of heat flow of CSA+ 10% C\(\bar{S}\) blend occurs earlier than that of the blend with 5% C\(\bar{S}\). It is agreed with Refs. [13, 14] that the existence of C\(\bar{S}\) accelerates the hydration of CSA, but it delays the hydration of OPC.

For the ternary OPC-CSA-C\(\bar{S}\) systems, the hydration heat is influenced by OPC/CSA ratio as well as

<table>
<thead>
<tr>
<th>OPC/CSA mass ratio</th>
<th>5% C(\bar{S})</th>
<th>10% C(\bar{S})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\tau_{0,0}) (Pa)</td>
<td>(\Lambda_{\text{thix}}) (Pa/min)</td>
<td>(t_{c}) (min)</td>
</tr>
<tr>
<td>9/1</td>
<td>9.273</td>
<td>3.506</td>
</tr>
<tr>
<td>8/2</td>
<td>8.911</td>
<td>9.499</td>
</tr>
<tr>
<td>7/3</td>
<td>9.014</td>
<td>11.703</td>
</tr>
<tr>
<td>6/4</td>
<td>9.421</td>
<td>11.649</td>
</tr>
<tr>
<td>5/5</td>
<td>9.252</td>
<td>13.329</td>
</tr>
<tr>
<td>4/6</td>
<td>9.433</td>
<td>14.217</td>
</tr>
<tr>
<td>3/7</td>
<td>9.625</td>
<td>16.360</td>
</tr>
<tr>
<td>2/8</td>
<td>10.752</td>
<td>16.392</td>
</tr>
<tr>
<td>1/9</td>
<td>12.564</td>
<td>50.503</td>
</tr>
</tbody>
</table>
C\textsuperscript{S} content. When OPC is blended with CSA, it becomes more difficult to distinguish the induction period and the accelerating period, particularly at higher OPC/CSA ratio. The decrease of OPC/CSA ratio makes the main peak (i.e. silicate reaction [13]) occur earlier and causes a higher heat releasing rate during rheology test. When C\textsuperscript{S} content is 5% and OPC/CSA ratio drops to 6/4 or lower, the heat flow value including peak value of ternary pastes outnumbers the CSA+C\textsuperscript{S}, and accelerating period is also shortened. However, the larger C\textsuperscript{S} proportion performs an opposite effect. It reduces the heat flow values and delays the peak occurrence.

According to calorimetric data, it can be concluded that the higher CSA content is, the more rapid reaction rate is. Moreover, C\textsuperscript{S} retards the hydration of ternary system. The difference of hydration heat releasing rate reveals the difference of hydrates kinetics in cement pastes.

Based on the assumption that the rates of nucleation and growth are constant throughout the whole hydration process [57, 58, 60], the hydration kinetics of cement paste during structural build-up period can be investigated. Hydration kinetic parameters obtained by BNG model are listed in Table 9. According to Ref. [34], nucleation constant $K_N$ describes the rate of covering the surface of cement particles with hydration products in unit volume of paste and growth constant $K_G$ indicates the rate of filling the pore space between particles in unit volume of paste. Table 9 suggests that high CSA content results in considerable enhancements in the nucleation and growth rates. The $K_G$ value of ternary blends is significantly higher than that of the OPC+ C\textsuperscript{S} paste. Overall, an increasing trend on $K_G$ of ternary paste is observed with reducing the OPC/CSA ratio. The $K_G$ value of the ternary blends is higher compared to the value of CSA+C\textsuperscript{S} paste when OPC/CSA ratio is decreased to 2/8.
Moreover, the $K_N$ value of ternary blends is also higher than that of OPC+CS paste. The $K_N$ value is improved by more than an order of magnitude at higher CSA content. When the proportion of CSA is more than 60% of composite cement, the $K_N$ value is even larger than that of CSA+CS paste.

As shown in Table 9, the $K_G$ value of OPC+CS blend remains nearly unchanged with the increase of CS content, however, the $K_N$ value decreases. In contrast, the $K_N$ and $K_G$ values of CSA cement system are both increased at higher CS content. However, the effect of CS content on the hydration kinetics of ternary OPC+CSA+CS system depends on the OPC/CSA ratio. When OPC/CSA ratio is greater than 8/2, the $K_G$ values of those with 5% CS are higher than that of those with 10% CS. Opposite result is observed when the OPC/CSA value is lower than 8/2. When the content of OPC is larger than the content of CSA, the $K_N$ values of blends with 5% CS is greater than that of those with 5% CS. However, the former is smaller than the later when CSA dominates.

The results of hydration heat flow and hydration kinetics suggest that the presence of CSA accelerates the hydration evolution of ternary system, and increases the nucleation and growth kinetics of hydrates at structural build-up period. The addition of CS retards the hydration of ternary system while it further improves the hydration kinetics of nucleation and growth kinetics of hydrates at higher CSA content.
Table 9 Estimated surface area of cement particles per unit volume of paste and hydration kinetic parameters obtained from BNG model

<table>
<thead>
<tr>
<th>OPC/CSA mass ratio</th>
<th>5% CS</th>
<th>10% CS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>S (μm⁻¹)</td>
<td>K_G (h⁻¹)</td>
</tr>
<tr>
<td>10/0</td>
<td>0.9170</td>
<td>0.0239</td>
</tr>
<tr>
<td>9/1</td>
<td>0.9875</td>
<td>0.1338</td>
</tr>
<tr>
<td>8/2</td>
<td>1.0596</td>
<td>0.1780</td>
</tr>
<tr>
<td>7/3</td>
<td>1.1333</td>
<td>0.2238</td>
</tr>
<tr>
<td>6/4</td>
<td>1.2087</td>
<td>0.2260</td>
</tr>
<tr>
<td>5/5</td>
<td>1.2859</td>
<td>0.2362</td>
</tr>
<tr>
<td>4/6</td>
<td>1.3649</td>
<td>0.2211</td>
</tr>
<tr>
<td>3/7</td>
<td>1.4457</td>
<td>0.2125</td>
</tr>
<tr>
<td>2/8</td>
<td>1.5285</td>
<td>0.2568</td>
</tr>
<tr>
<td>1/9</td>
<td>1.6134</td>
<td>0.3001</td>
</tr>
<tr>
<td>0/10</td>
<td>1.7003</td>
<td>0.2417</td>
</tr>
</tbody>
</table>

3.4.2 XRD analysis and DTG results

In order to reveal the hydrates formed during the rheological test period, the XRD analysis and DTA analysis were carried out to characterize the solid phase in ternary blends during 10–30 min. Fig. 8
plots the XRD results of blends with different OPC/CSA ratios and C\textsuperscript{S} contents at 15 min and 30 min. It can be seen a very weak diffraction peak of calcium silicate hydrate occurs at 15 min in both two XRD patterns of OPC+C\textsuperscript{S} pastes in addition to the strong C\textsuperscript{S} peak. No significant changes in the XRD patterns are observed for OPC+ C\textsuperscript{S} pastes from 15 min to 30 min. Ettringite and gypsum are the main hydrates formed in both CSA+ 5\%C\textsuperscript{S} and CSA+10\% C\textsuperscript{S} pastes according to XRD data. It can be clearly observed that the AFt peaks become stronger with time. However, the gypsum peaks become weaker from 15 min to 30 min. It can also be seen that both calcium silicate hydrate and ettringite are formed in ternary OPC+ CSA+C\textsuperscript{S} pastes. The peak intensity of AFt increases with time, while the intensity of the peak relates to gypsum is reduced. The influences of OPC/CSA ratio on the peak intensity of ettringite and CSH are opposite. The peaks of OPC and CSA hydrates in ternary composite pastes are sharper than those in OPC+ C\textsuperscript{S} and CSA+C\textsuperscript{S} pastes. The lower OPC/CSA ratio results in much stronger ettringite peaks while corresponding weaker CSH peaks in ternary cement pastes. Furthermore, the increasing content of C\textsuperscript{S} leads to sharper peaks of ettringite and CSH. This positive effect of C\textsuperscript{S} becomes more significant with time.
Fig. 8 The XRD patterns of OPC-CSA-C S pastes with different compositions at 15 min (below curve) and 30 min (upper curve). E: Ettringite (PDF# 41-1451), Y: Ye’elimite (PDF# 33-0256), G: Gypsum (PDF# 33-0311), C: calcium silicate hydrate (Ca$_2$SiO$_4$·0.35H$_2$O [PDF# 15-0641], Ca$_2$SiO$_4$·H$_2$O [PDF# 03-0594], Ca$_{1.5}$SiO$_{3.5}$·xH$_2$O [PDF# 33-0306]), An: Anhydrite (PDF# 37-1496), A: Alite (PDF# 49-0442), B: β-Blite (PDF# 35-0642)

The TGA analyses shown in Fig. 9 and Fig. 10 confirm the observations from XRD. Fig. 9 shows the DTG curves of the samples after 30 min of hydration. Two major peaks are observed for the OPC+C S blends. The weight loss between 85–95 °C is attributed to the decomposition of CSH and/or ettringite. The second peak between 100–130 °C is due to decomposition of gypsum. Similar results
are also obtained for the CSA+ C₅ blends, where the peak around 100 °C is mainly due to the presence of ettringite according to XRD analysis. For the OPC+CSA+C₅ blends, it can be observed that two peaks present in the curves of those with high OPC/CSA ratio and lower content of C₅, while three peaks occur in the curves of those with low OPC/CSA ratio or high content of C₅. In addition to gypsum, ettringite and CSH, observed for all samples, the peak between 230~250 °C is associated with the decomposition of amorphous or micro-crystalline aluminum hydroxide (AH₃) according to the published studies [13, 66].

Moreover, it can be seen that the peak intensity for CSH/AFt and gypsum is increasing with the decrease of OPC/CSA ratio. This is attributed to the larger extent of CSH/ettringite and gypsum formation when the proportion of CSA is higher. In case of blends with 10% C₅, the intensity of AH₃ peak also becomes stronger with the increasing amount of CSA.

The DTG results of the samples over time are also shown in Fig. 10. It shows that the peak intensity of CSH, AFt and AH₃ increases with time for all cement blends. The peak intensity of gypsum shows an increasing trend over time for samples with 10% C₅, however for the samples with 5% C₅, no changes seem to be observed during 10~30 min. The results suggest the continuous increase on the amount of AH₃, AFt and CSH during the rheological test period. Besides, gypsum was formed before 10 min and the amount is not increased during that period if the C₅ was low. It can also be observed from Fig 10 that the ternary system with 10% C₅ exhibits the greater peak in the range of 80~110 °C compared to system with same OPC/CSA ratio but 5% C₅. It confirms the XRD result that the incorporation of C₅ favors the formation of AFt and CSH.
In summary, the XRD and DTA results indicated that compounding OPC and CSA not only accelerates the silicate reaction but also the aluminate reactions at very early hydration stage, which is in agreement with the conclusion of Ref. [13]. The gypsum, CSH and AFt are formed in a ternary system during the structural build-up period and the formation extent of those hydrates changes the whole time. The higher amounts of CSA and anhydrate tends to form CSH and AFt, as well as gypsum.
4 Discussion

The initial and time-dependent rheological parameters of Portland clinker-calcium sulfoaluminate clinker-anhydrite blends are closely related to their relative contents. According to the present study, it has been proved that the proportion of these three components affects the electro-kinetics of blend, which determines colloidal electrostatic interaction of particles in a ternary system. Besides, the relative amounts of three components also influences the assemblage and formation rate of hydrates in the ternary system, which is mainly responsible for the structure and the rigidity of fresh cement paste. This section compares the correlation between electro-kinetics, hydration kinetics and the evolution of rheological parameters of ternary blends. It aims to discuss how the rheology of OPC-CSA-C₅ blend is controlled by the physical action and hydration.

4.1 Relationship between the initial rheological feature, electro-kinetics and hydration kinetics of OPC-CSA-C₅ ternary blend

The dynamic yield stress of cementitious materials originates from the colloidal interaction and direct
contact between particles [67]. It is important in quantifying flowability and is related to the slump and
slump flow test in field [68–70]. It was noted that the higher dynamic yield stress is, the poorer the
flowability is.

According to above-mentioned results, the increase of CSA content slightly increases the dynamic
yield stress of fresh ternary OPC-CSA-CS\(\text{S}\) blends and significantly increases their viscosity. It means
that enlarging CSA content causes the loss of flowability.

Initial rheological feature of fresh paste relates strongly to the solid volume fraction. As shown in
Table 2, the increase of CSA content increases the solid volume fraction of ternary blend at constant
mass ratio, which is one of the reasons for increasing dynamic yield stress [71, 72]. Additionally, it
can be seen in Table 9, in case of ternary blends, the estimated surface area of particles per volume (S)
is enlarged significantly with the increase of CSA content. It also has positive effect on increasing
yield stress and viscosity [24, 75]. Besides, surface interactions and hydration occurring in blend also
should be responsible.

The surface interactions consist in a fresh blend of two opposing forces, the attractive van der Waals
and the repulsive electrical double layer force. The electrical double layer force is a function of the
square value of zeta potential \((\zeta^2)\). Namely, the larger \(\zeta^2\) is, the larger the electrical double layer force
is [65]. According to results shown in section 3.2, the increase of CSA content reduces the \(\zeta\) \((\zeta^2)\) of
blend, which means that the higher proportion of CSA weakens the repulsive electrical force between
particles in blend. It makes the attraction between charged particles become easier and the attractive
force become stronger [65]. When the blend is subjected to a shear force, it is more difficult to overcome the interforce between particles and make them move. Thus, the dynamic yield stress increases with CSA content.

As seen from Table 2 and Table 9, increasing CSA content leads to little changes in the solid volume fraction and the estimated surface area of particles per volume (S) of ternary blends. However, the increase of CSA compensates the flowability by significantly reducing the dynamic yield stress. The variation of zeta potential due to the increase of CSA can also explain it. According to the results, the zeta potential of ternary blends with 10% CSA is greater than the values of those with 5%. Moreover, Debye length of the former is nearly twice as that of the latter, which is also favorable for the improvement of electrostatic effect between particles [65]. It means that the larger content of CSA increases the repulsive electrical force between particles and reduces the possibility of aggregation. It is easier to break the electrostatic interaction between particles in ternary blends. Thus, CSA lowers the resistance of the blend to flow, which is responsible for the lower dynamic yield stress.

Kapur[73], Scales[74] and Johnson[75] believed that dynamic yield stress is negatively related to the ζ² value of a suspension. Fig. 11 plots the relationship between the ζ² value and dynamic yield stress of ternary blends obtained by MB model and HB model. It can be observed that the dynamic yield stress of the fresh blend decreases with the increase of the ζ² value. In particular, the dynamic yield stress data obtained by MB model presents better correlation with ζ².
The hydration of blends can affect the surface characteristic and solid volume fraction of blends. The coarseness of surface and volume fraction can significantly influence the initial rheological feature of the blend [24].

As shown in Table 9, blend with higher CSA content has the much higher nucleation and growth kinetics of hydrate. The quick formation of needle-like AFt crystal or denser hydrates aggregate makes the surface of cement grain become coarser, which enhances the friction between neighboring particles when paste is subjected to shear force. The quicker growth of hydrate covered on the surface of particles makes it more possible to increase the solid volume fraction of blend at very early stage. The higher solid volume fraction is, the larger yield stress is.

Likewise, the negative effect of C$S$ on dynamic yield stress is also attributed to the retarding effect of C$S$ on hydration and its negative effect on nucleation of hydrates (see Fig. 7 and Table 9). The adverse effect of C$S$ on hydration results in less amount of hydrates covered on the grains at very early age,
therefore particles could easily slip and pass through under shearing. Furthermore, the increase of apparent viscosity caused by the incorporation of $C_S$ is due to the higher viscosity of $C_S$ paste than that of OPC paste and CSA cement paste [77, 78].

Shear-thinning and shear-thickening are shear-induced responses, and their intensities are related to the nature of paste at the same testing program [79-81]. It relates to the interparticle force and dispersed efficiency of the system. Under the variation of shear-rate between 0~100 s$^{-1}$, the ternary OPC-CSA-$$C_S$$ blend behaves shear thinning, and the intensity increases with the content of $C_S$ and with the CSA content at higher OPC/CSA ratios. It reveals that the blends applied with a higher shear rate has a smaller size of aggregation and a lower level of flocculation. And the increase of CSA and $C_S$ makes this phenomenon more significant. The high shear rate may break the rigid “AFt linkage” between particles, untangled the interlock of hydrates and even polished the surface of cement grains. Because of the higher amount of “AFt linkage” in pastes with high CSA content, the sensitivity of the blends with high CSA content on shear rate is stronger. However, when the OPC/CSA ratio is lower, the faster growth of AFt makes the interaction of particle much stronger, which is difficult to break the aggregations. Therefore, the shear thinning intensity in this case becomes weaker.

4.2 Origin of the structural build-up of OPC-CSA-$$C_S$$ ternary blend

The structural build-up rate of the microstructure of fresh cement paste after casting is of importance to the multi-layer casting operations and the design of formwork [28, 41]. The structural build-up of cement suspensions is a complex phenomenon associated with the combined effect of both physical structuration due to inter-particles colloidal interactions and chemical rigidification resulting from
cement hydration [34, 76]. As soon as cement particles is mixed with water, the contact solution is enriched with multivalent ions including cations (Ca$^{2+}$, K$^{+}$, Na$^{+}$, Al$^{3+}$) and anions (SO$_{4}^{2-}$, OH$^{-}$). Once the bulk solution becomes saturated and causes the formation of ettringite-like compounds and the precipitation of CSH on the cement surface [19]. The surface of cements and their hydration products become charged either by dissociation of surface groups or adsorption of ions from the electrolyte solution [82, 83]. Roussel [35] observed that this physical process takes only a few seconds. During this period, the strength of the particle network is determined by the colloidal surface interactions. Although these products may not yet form rigid bonds between cement particles, they do fill pore space that was previously occupied by water. At a certain moment known as a percolation threshold, enough particles are connected to form a continuous solid path within the fluid medium, and gradually develops to a stronger skeleton. Roussel [35] attributed the rigid links between particles in OPC paste in this process to metastable CSH, and named it CSH bridge. The process can take up to 100s. The particle structure is further strengthened as the number and size of the hydrate bridges increase.

Differing with OPC paste, not only the ionic composition of liquid but also the hydrates and their contents are significantly altered when OPC is blended with CSA. Correspondingly, both colloidal surface interactions and rigid links between cement particles are changed.

In the case of ternary blend, AFt, CSH, gypsum and amorphous AH$_3$ are formed during the rheology test period, as discussed in section 3.4.2. Thus, the structure of fresh paste is developed by the formation and growth of these hydrates.
Fig. 12 demonstrates the networks of interacting cement particles in the structure of ternary blends. Excluding the “CSH bridge”, there are two main linkage in the structure of paste. One is contributed by AFt crystal and another is due to the gypsum network. The morphology of AFt is generally described by prisms or needles with a high specific surface area. The formation of AFt on the surface of cement grain results in a strong friction force between interparticle. The AFt crystal outside the grains interlace with each other to establish an interspace reticulate structure in fresh paste. The gypsum is yielded in the space among cement particles. The morphology of gypsum is rod-like and the size of gypsum is an order of magnitude bigger than needle-like AFt [19]. The network formed by gypsum provided a rigid tie for cement grain, which makes the structure of blend stronger.

Therefore, the structural build-up of OPC-CSA-C$\overline{S}$ ternary blends originated from the rigid links of CSH and AFt and the gypsum network, as well as colloidal surface interaction.

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By comparing phase analysis results (section 3.4.2), hydration evolution and kinetics (section 3.4.1)
and the structural build-up rate (section 3.3), it suggests that the role of CSA and C\textsubscript{S} on accelerating structural build-up is due to their positive effect on the hydration kinetics of main hydrates. The nucleation and growth kinetics of hydrates calculated from calorimetry data, shown in Table 9, is used to describe the relationship between hydration and structural build-up rate and it is a good evidence to explain the impact of the C\textsubscript{S} and CSA. 

Fig. 13 plots the structural build-up rate of blends A\textsubscript{thix} value with the growth kinetics of hydrates K\textsubscript{G} value. As the plot shows, the A\textsubscript{thix} value increases with K\textsubscript{G} value, and the curve agrees with the exponential relation. It means that the rate of filling the pore space between particles in unit volume of paste plays an important role on the structural build-up rate. And, the increase of CSA and C\textsubscript{S} accelerate the filling rate of hydrate in the pore of initial structure, thus they speed up the structural build-up rate of blends.

![Graph showing the relationship between growth kinetics of hydrates and structural build-up rate.](image)

**Fig. 13.** The relationship between the growth kinetics of hydrates K\textsubscript{G} and the structural build-up rate A\textsubscript{thix} of ternary blends

5 Conclusions

Based on the aforementioned results and discussion, the following conclusions can be drawn:

1. The OPC-CSA-C\textsubscript{S} blended pastes are non-Newtonian flow, and exhibit a shear thinning behavior.
Herschel-Bulkley model and modified Bingham model is suitable for calculating the rheological parameters of fresh ternary blends.

2. The rheological parameters of OPC-CSA-C₃S blends depend on OPC/CSA ratio and the content of C₃S. The high content of CSA causes a higher dynamic yield stress and apparent viscosity. The increase of C₃S favors the flowability of blends by reducing the dynamic yield stress, although it leads to a higher apparent viscosity. C₃S in a ternary system improves the extent of shear thinning. Besides, the higher amount of CSA and the high proportion of C₃S in system collectively accelerates the structural build-up of blends. Thus, the appropriate increase of C₃S not only benefits flowability under casting, but also helps re-structuration at rest.

3. CSA and C₃S have different effects on initial rheology, while they both make positive effects on the structural build-up of blends. This may stem from the difference between their effects on electro-kinetics and hydration kinetics.

4. The initial rheology of ternary blends depends on the electro-kinetics. The dynamic yield stress of the blend relates closely with zeta potential. The increase of CSA reduces the zeta potential of blends. It results in a weak repulsive electrostatic force and a correspondingly stronger attraction between particles, which improves the dynamic yield stress. Conversely, the increase of C₃S enlarges the zeta potential and thus decreases the dynamic yield stress.

5. The structural build-up of blend attributes to the formation of main hydrates, including CSH, AFt
and gypsum, and their nucleation and growth kinetics. The network established by crystal with various scales and rigid bridges between particles makes a stronger structure of ternary blends. The higher growth kinetics of those hydrates is, the faster structuration rate is. The CSA and anhydrate enlarge the $K_G$ value of hydrates, which accelerates the filling rate of hydrates in the spaces of the structure. It is responsible for their positive effect on structural build-up. Besides, the delaying action of $\text{CS}^-\text{S}$ on hydration process explains its desirable influence on initial flowability.

Acknowledgments

Financial supports by National Key R&D Program of China (contract No. 2017YFB0310100) and National Natural Science Foundation of China (contract No. 51778629) are greatly appreciated.

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