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Study on corrosion resistance of Portland cement-calcium sulphoaluminate cement binary system in a sodium chloride environment

Shilin Song[a], Tao Xing[a], Yu Zhang[a,b]*, Jianzheng Wang[a], Xiaodong Shen[a,b]*, Ying Ma[a]
a. College of Materials Science and Engineering, Nanjing Tech University,
Nanjing 211816, P. R. China.
b. State Key Laboratory of Materials-Oriented Chemical Engineering, Nanjing Tech University,
Nanjing 211816, P. R. China
Corresponding authors: zhangyuzeus@njtech.edu.cn (Yu Zhang); xdshen@njtech.edu.cn (Xiaodong Shen).

ABSTRACT

Under marine condition, chloride migration is the main cause of the failure of concrete structures. In our previous study, Portland cement (PC) mixed with $C_4A_3\$$ showed good performance in compressive strength, linear expansion and volume stability. In this work, Portland cement- calcium sulphoaluminate (CSA) cement binary system was detailed analysed, while 10%, 20% and 30% of Portland cement was replaced by calcium sulphoaluminate cement. Testing methods of isothermal calorimetry, X-ray diffractometry (XRD), X-ray fluorescence (XRF) were also performed. Results show that binary system of 80% PC and 20% CSA cement showed a good performance in compressive strength, the compressive strength can be up to 50 MPa and was higher than the other blended samples at 28 days in NaCl solution. Moreover, blended sample with 20% CSA cement shows good performance in chloride ions corrosion resistance.

1. INTRODUCTION

Portland cement (PC) is widely used in concrete for construction due to its versatility, durability and economic value. However, the amount of carbon dioxide emitted by PC production accounts for about 5% of the worldwide total carbon emissions [1, 2]. The corrosion resistance of PC-based materials is weak, and is easy to be corroded by seawater in marine environment. With the rapid development of cement industry, energy conservation, emissions reduction and full utilization of natural resources have become a trend during cement production [3, 4]. More attention has been paid on finding environmental friendly cementitious materials to substitute PC. In 1970s, calcium sulphoaluminate (CSA) cement was invented by Chinese researchers to enhance the resistance against shrinkage cracking of PC [5-7]. With the extensive research on CSA cement, some researchers found that CSA cement has lower carbon emission than that of PC and has good performances in high early strength, low setting alkalinity and good seawater corrosion resistance [8, 9].

In order to control the hydration rate and improve the corrosion resistance, compressive and flexural strength of PC, CSA cement was added to replace PC with various proportions and formed the PC-CSA binary blended cement system [10-12]. The reaction mechanisms of the blended systems have been detailed introduced in many articles. The hydration process of PC-CSA cement system appeared mutual promotion and hydration superposition effect, and the hydration and hardening rate of blended cement was accelerated [13]. Wolf et al [14] investigated the process of PC-CSA cement binary system by heat flow calorimetry, XRD and TG. The result showed that the initial hydration was rapid, leading to very high amount of ettringite in the first few hours. Julphunthong P. et al [15] found that when PC was replaced between 20 wt.% and 40 wt.% by CSA cement, the rapid setting and high early strength can be achieved. Laure Pelletier-Chaignat et al[16] introduced that high proportions of ettringite can be formed in PC-CSA binary system, and the ettringite reaction was delayed compared to CSA cement paste. There are two different pathways for the initial stages of ettringite formation. The mechanism of ettringite formation is the hydration of the C_3A phase in PC and ye'elimite phase in CSA in the presence of calcium sulfate [17, 18].

Equation 1 $C_3A + 3CS + 32H = C_3A\cdot 3CS\cdot 32H$

Equation 2 $C_4A_3\$ + 2C\$ + 38H = C_3A\cdot 3C\$\cdot 32H + 2AH_3$

High proportion of ettringite acts as fillers and densifies the microstructure of hydrated paste, which can improve the compressive and flexural strength, as well as the corrosion resistance. In recent years, researches about PC-CSA binary system concentrated on strength properties and hydration produces. However, the property of corrosion resistance has not been well studied, as well as the corrosion resistance of reinforced concrete under marine condition.

In this study, PC-CSA binary system was investigated on the hydration of mortar and the corrosion resistance. 10%, 20% and 30% of Portland cement was replaced by calcium sulphoaluminate cement. The mixture proportion used in this study is shown in Table 1. Meanwhile, the blended samples were cured in 3.5% NaCl solution.

2. EXPERIMENTAL PROCEDURES

2.1 Materials

The cements used in this study are commercial CSA cement and OPC cement, while table 2 summarizes the chemical compositions of the two kind of cements. Fig. 1 presents the XRD patterns of the two cements.

2.2 Specimens preparation

In PC-CSA binary system, PC cement was replaced by CSA cement partially. The effect of different CSA cement dosages on the cement hydration and microstructure development and corrosion resistance was explored. The addition of CSA cement in the study was 10%, 20% and 30% by weight, with water/binder ratio of 0.5. The mortar of samples was made into rectangular with the size of 40×40×160 mm. All specimens were cured in standard condition with temperature of 20±1 ℃ and humidity of 95±1%. After curing 28 days, the specimens were soaked in 3.5% NaCl solutions for 7 days, 14 days, 28 days, and the compressive strength and flexural strength would be tested.

2.3 Testing methods

2.3.1 Isothermal calorimetry

An 8-channel isothermal calorimeter was used to record the hydration heat evolution of blended cement paste of PC-CSA binary system. 4g of binder and 2g of water were mixed in the standard plastic bottle and the bottle was placed in the isothermal calorimeter immediately. Hydration heat flow curves of paste were recorded for 3 days at a constant temperature of 20℃.

2.3.2 X-Ray diffraction analysis

A Rigaku SmartLab 3000A diffractometer with CuKa radiation source (wavelength = 0.154 nm) was used to characterize the X-ray patterns, and the changes in the phase composition during cement hydration would be recorded. The accelerating voltage and accelerating current of the tests were 40 kV and 35 m A, respectively. The data were collected over a range of 5–65° at a speed of 5°/min with the step of 0.01°

2.3.3 Compressive strength measurement

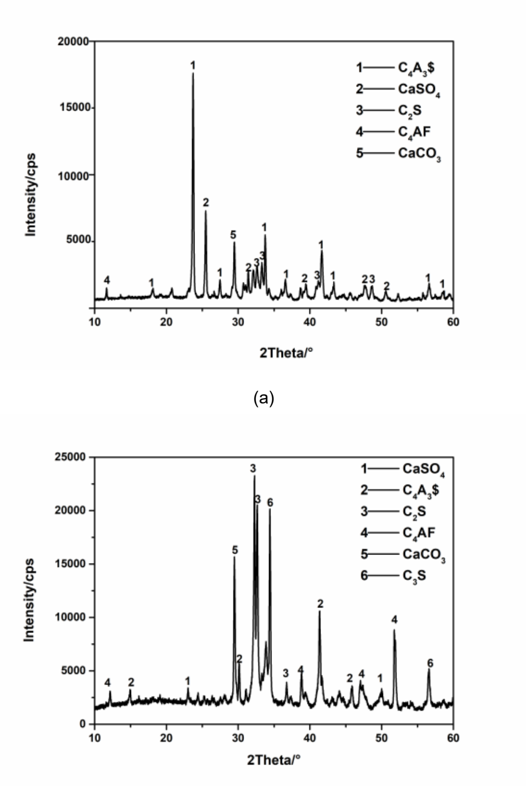
According to EN-196-1-2005, compressive strength of specimens were tested with an AEC-201-type automatic cement strength testing machine after curing for 1, 3, 7, 28, 56 and 90 days. In order to guarantee the accuracy of the collected data, 6 specimen were tested for each batch and the average value was regarded as the final result.

Table 1 Mixture proportion used in this study. (%)

Sample name	PC	CSA
Blank	100	0
CSA-10%	90	10
CSA-20%	80	20
CSA-30%	70	30

Table 2 Chemical composition of raw materials. (wt%)

	OPC cement	CSA cement
SiO_2	21.75	10.94
Al_2O_3	5.21	19.43
Fe_2O_3	2.91	2.75
TiO_2	0.25	1.07
CaO	62.13	43.2
MgO	2.09	2.46
SO_3	1.97	12.82
K_2O	0.63	0.52
Na_2O	0.13	0.11
P_2O_5	0.16	0.11
MnO	0.053	0.016
LOI	1.8	5.98



(a)

(b)

Fig.1. XRD pattern of CSA cement (a) and OPC cement (b)

3. RESULTS AND DISCUSSION

3.1 Heat evolution

The isothermal calorimetry data of PC cement and PC-CSA binary system are shown in Fig. 2. Four dosages of CSA cement, 0%, 10%, 20% and 30%, were considered. As shown in Fig. 2, the dominate periods of all samples ended before 24 h. With the increase of CSA cement, the main exothermic peak was shifted to left (earlier), which means the main hydration of blended samples was advanced by the introduction of CSA. The initial stage is induction period, which is related to the nucleation of C-S-H gel. During the induction period, the dissolution of anhydrite and precipitation of ettringite still proceeds very slowly. Every curve has two exothermic peaks. The first peak is attributed to the formation of ettringite, partial dissolution of aluminate and rapid dissolution of sulfates and ye'elimite. Wolf et al. [8] assumed that this phenomenon is attributed to the consumption of AH_3 for further ettringite precipitation via the coupled PC-CSA reaction pathway. During the first 2h, the hydration heat rate was increase with the increase of CSA cement. That is due to the higher content of sulfates and ye'elimite induced by the incorporation of CSA cement. The second peak is attributed to the hydration of C_3S and dissolution of gypsum.

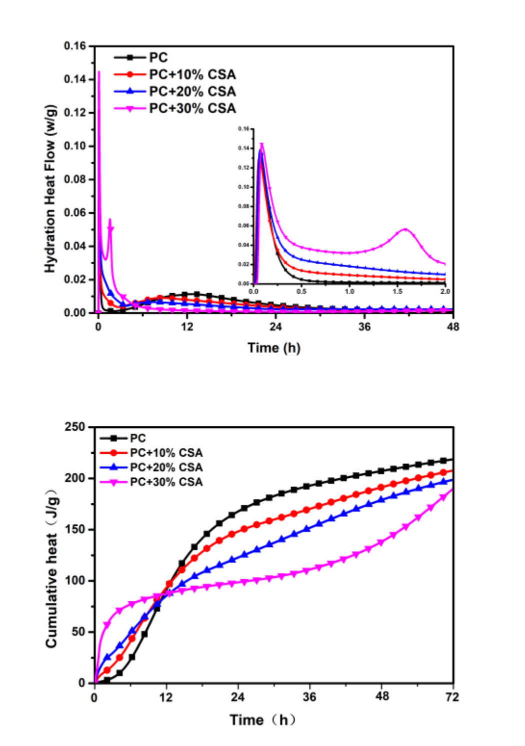


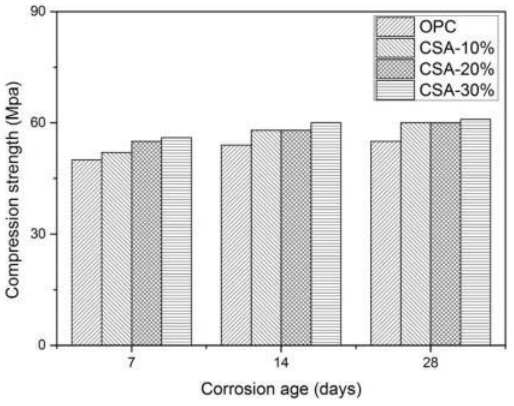
Fig. 2. Isothermal calorimetry data for PC-CSA binary system.

3.2 The compressive strength of PC-CSA binary system

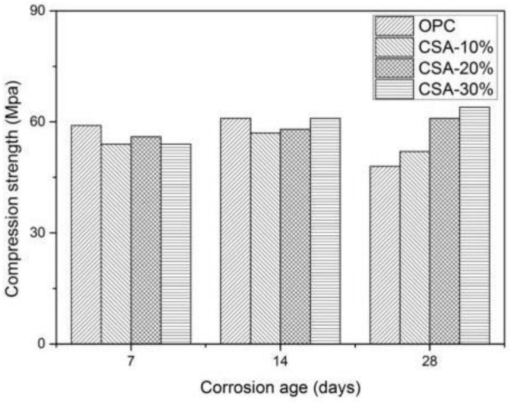
Fig. 3 shows the variation of compressive strength of PC blended with CSA cement under corrosion condition at different curing ages. Blended cement mortar was standard cured for 28 d, and then immersed in 3.5% NaCl solutions. It is clear that PC mortar showed good strength development in fresh water, while the compressive strength can be reached up to 54 MPa at 28d. However, the compressive strength of PC reduced sharply in corrosion solution. When curing in pure water, the compressive strength of PC-CSA blended sample was higher than that of PC. This can be attributed to rapid formation of ettringite (AFt) crystals at early ages. These crystals deposit on the surface of solid particles and occupy the C-S-H gel formation site. For each PC-CSA sample, the compressive strength was increased which immersed in sodium chloride solution. That can be attributed to the formation of $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}31H_2O$ (Frieded's salt) as equation 3. Furthermore, abundant ettringite and Friedel's salt could fill the pore of cement mortar and prevent corrosive ions from entering the internal structure of cement mortar.

Equation 3 $3CaO{\cdot}Al_2O_3{\cdot}6H_2O + CaCl_2 + 25H_2O = 3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}31H_2O$

However, the excessive formation of AFt and Frieded's salt will produce large expansion and cause internal cracks, which will generate a harmful effect on late age strength of cement mortars.



(a)



(b)

Fig.3. Compressive strength of cements: (a) Curing in freshwater, (b) Curing in NaCl solution.

3.3 Corrosion resistance coefficient

The compressive corrosion resistance coefficient (K_c) is the ratio of the strength of the specimens at the same age in the corrosive solution and the standard curing in water and calculated with formula 3.1. Fig.4 presents the K_c of PC and PC-CSA binary system after different curing age. The K_c of PC was much lower than that of PC-CSA binary system in the initial stage, but it increased sharply with the development of corrosion ages. However, the K_c of every PC-CSA binary system increased slightly with the development of corrosion age. This phenomenon can be attributed to the porosity of PC higher than PC-CSA binary system. A large amount of chloride ions migrated into cement pastes to form Frieded’s salt and improved the density of PC. For long-term erosion specimens, lots of Frieded’s salt will accumulate in cement mortar and cause expansion stress. It can be seen that chlorine resistance of PC was improved in the presence of CSA cement, which is attributed to the reason that CSA cement promotes the early hydration of PC cement and improves the early strength and compactness.

$$K_c = \frac{R_S}{R_W} \qquad (3.1)$$

K_c : Corrosion resistance coefficient;

R_s : Compressive strength of specimen in corrosive solution;

R_w :Compressive strength of standard curing specimen.

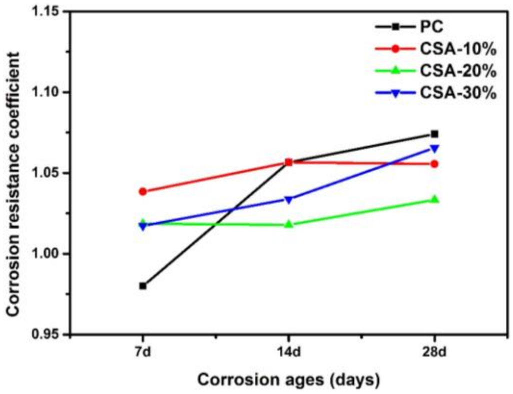
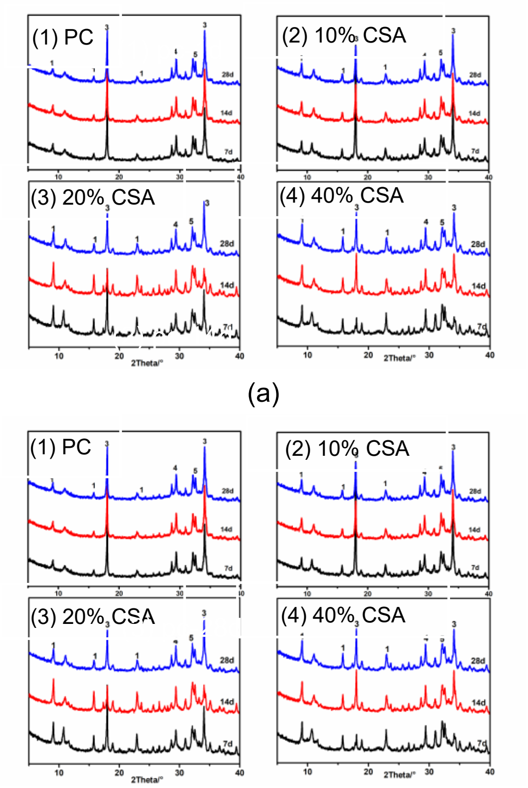


Fig.4 Compressive corrosion resistance coefficient of samples in 3.5% NaCl solution.

3.4 Hydration products of PC-CSA binary system

Fig.5 shows the XRD patterns of hydrated cement pastes with different dosages of CSA cement at different solutions and different curing ages. All specimens were cured in standard condition for 28 days, and soaked in different kinds of corrosion solutions for 7 days, 14 days, 28 days. As shown in Fig.5a, ettringite was found in the hydrated cement paste and increased with the rise of CSA cement in blended samples. In Fig.5b, ettringite and Friedel's salt were found in the hydrated cement paste. When chloride ions penetrated into the mortar, it’s easy to react with calcium hydroxide and produce Friedel's salt. The formation of Friedel's salt reduced the concentration of chloride ions and decreased the porosity, furthermore, the compressive strength increased. Comparing to PC, the blended binary system shows good performance in adsorbing chloride ions and corrosion resistance.



(a)

(b)

Fig.5. XRD patterns of hydrated cement pastes at different curing environments (a) curing in water, (b) curing in sodium chloride solution. (1-ettringite, 2-Friedel's salt, 3-Portlandite, 4-$CaCO_3$, 5-larnite)

3.5 Scanning electron microscope

The microstructure of PC system and PC-CSA binary system was observed with SEM at different ages. SEM images of PC system are shown in Fig.4a. In hydrated cement paste of PC, C-S-H gel can be found in the surface of AFt. Comparing to PC system, much more AFt and AFm was formed in PC-CSA binary system than that of PC system(Fig.4b). Ettringite was formed in the pore of cement pasted and reduced the porosity, which was positive to develop strength.

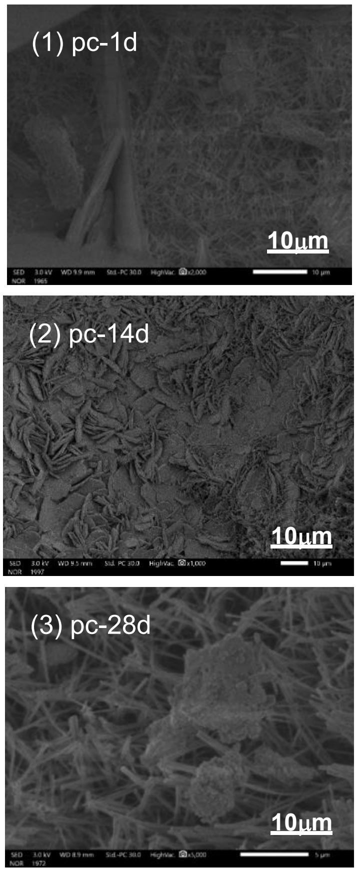


Fig.4a. SEM images of PC system at different ages.

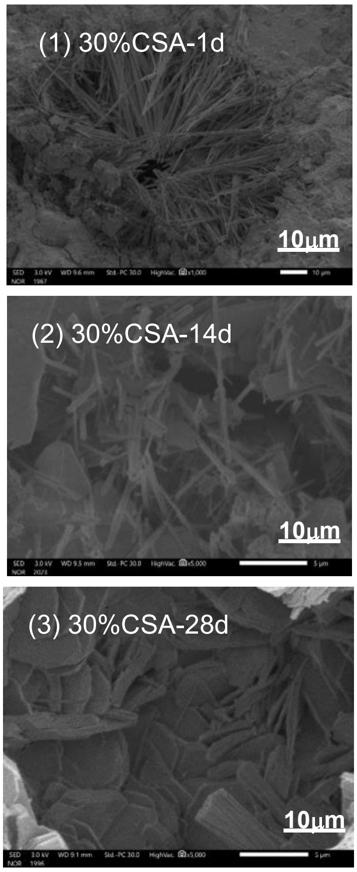


Fig.4b. SEM images of PC-CSA system at different ages.

4. CONCLUSIONS

This paper investigated the effect of CSA cement on the corrosion resistance of Portland cement. Hydration heat evolution, hydration products, compressive strength and corrosion resistance coefficient were discussed. The results can be drawn as follows.

The addition of CSA cement increases the main exothermic peak and facilitates early hydration of PC. However, the second hydration peak of blended cement shifts forward with the increase of CSA cement, which is accused to the formation of AFt during the hydration of $C_4A_3\$$ of CSA cement. The PC-CSA binary system have higher compressive strength and compactness than that of PC cement in fresh water, and the trend tends to be more obvious with the increase of CSA cement. Comparing to PC, the PC-CSA binary blended system shows good performance in compressive strength and chlorine resistance. As a result, the addition of CSA cement can significantly improve the corrosion resistance coefficient of PC.

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