

Effect of a Modified SAF on Aluminate Hydration of Cement

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Abstract. Sulfonated acetone formaldehyde (SAF) condensate type high range water reducer was modified by grafting with lignosulfonate for the sake of mitigation bleeding of concrete. Effect of the modified SAF (MSAF) on assemblage of aluminate hydrates in hardened cement paste was investigated by XRD and SEM. Experimental results indicated that the MSAF inhibits the hydration progress of C_3A , reduces the intercalation between superplasticizer molecules and aluminate hydrates and changes the dissolution-precipitation process of limestone filler blend cement. Reaction between C_3A and calcite is controlled by MSAF. Consequently, monosulfoaluminate was still observed in the paste containing limestone filler hydrated for 28 days, which was comparable with hydrates in control and polynaphthalene sulphonate (PNS) dispersed pastes. Different in aluminate hydrates explains why MSAF or MSAF-maleic type polycarboxylate admixture (MSAF-PCA) combined superplasticizer is more compatible with cements containing limestone filler than PNS.

1. Introduction

High range water reducers or superplasticizers are absolutely necessary for modern concrete mixture. High performance concrete, which has been widely applied in engineering, is a successful example of the combination of chemical admixtures and concrete technology [1-3]. Although the dosage of superplasticizer is usually less than 1 wt. % of cement, it does play an important role in improving homogenous characteristic, rheological property, strength and durability of cementitious materials [4, 5].

Polynaphthalene sulfonate (PNS) has been employed as high range water reducer in concrete for more than thirty years. Application of PNS will be blocked for environmental issues of the large consumption of industrial naphthalene which derives from coal tar, and for the incompatible problem with cement blended with limestone filler [6]. There were also some limitations about the use of polycarboxylate type admixtures (PCA) because of their high cost. Sulfonated acetone formaldehyde (SAF) condensate based high water-reducer, one of dominant superplasticizers in the market, has been widely developed in China for one decade. The advantages of SAF are high water reducing efficiency, better compatibility with cements, mineral admixtures and other chemical admixtures, lower application cost, and energy-saving production process (ie. no heat resource is needed). But, there is a flaw in deed. Concrete or mortar superplasticized with SAF is prone to bleeding, which results in red coloured surface. Although lots of researches have been done concerning upgrading the performance of SAF in both experimental and theoretical aspects, little references are available for industry production. Heat release of aldol reaction during synthesis of SAF at high pH (13-14) solution makes it more difficult to graft SAF with most commonly used chemicals. Lignosulfonate,

concentrated from black liquor, can be modified by oxidation and polymerization as high range water reducer at similar conditions for SAF production [7]. The present study synthesized lignosulfonate modified SAF (MSAF) by catalyzed condensation. Concrete added with MASF shows excellent stability and viscosity, and better slump retention.

As is known, mechanism of condensate type water reducer is always linked with electrostatic repulsion, and ettringite and AFm (monosulfoaluminate, monocarboaluminate, etc.) formation are involved [8-10]. It seems that limestone filler favors crystallization of monocarboaluminate hydrate rather than monosulfoaluminate. But the present research showed different assemblage of aluminate hydrates in MSAF dispersed hardened cement paste, which implies fundamental mechanism of cement-MSAF interaction should be explored, especially when limestone filler is used.

2. Experiment

2.1. Materials

Cement: A kind of Portland cement equivalent to Chinese P.II 52.5 containing 4 wt. % limestone filler was employed. Chemical composition of cement is shown in Table 1. The mineral content of C_3S , C_2S , C_3A and C_4AF are calculated by Bogue equation as 53.6%, 23.0%, 7.4% and 9.4% by mass respectively.

Table 1. Chemical composition of cement [wt. %].

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	LOI
64.5	22.0	4.8	3.1	0.9	1.9	1.0

Chemicals: $CaCO_3$, Al_2O_3 , acetone, sodium sulfite, lignosulfoaluminate, formaldehyde solution (wt. 37%), naphthalene (wt. 95%), oil of vitriol (wt. 98%), sodium hydrate solution (wt. 30%), lime (wt. 86.2%), catalyst, and maleic anhydride type PCA. All of the chemicals were obtained from Jiangsu Provincial general building materials research institute, China.

Water: Deionized water.

MSAF: The MSAF was synthesized following the progress: In a 1000 ml three-necked, round bottomed flask equipped with a reflux condenser and a thermometer, 150 g lignosulfonate solution with 30 wt. % concentration was added and modified by oxidation according to reference [7]. Temperature was cooled to 50 °C by cooling with cold water. 45 g sodium sulfite were dissolved in 197.1 ml DI water at 40 °C by vigorous stirring. Then 40.6 g acetone was added. The reaction flask was then kept at 40 °C for 1 h with constant stirring. After sulfonation, 123.3 g aqueous formaldehyde of 37 wt. % concentration was gradually fed into the reactor through a dropping funnel. When the temperature reached 60 °C ~65 °C, the fed of aqueous formaldehyde was pause and the temperature was maintained for 1 h. Then, formaldehyde addition was continued, and temperature was allowed to rise to 95 °C ±2 °C and the reaction continued for 3 h under catalysis. Finally, the solution was cooled to ambient temperature. An aqueous, brown MSAF solution and a solids content of 30 wt. % was obtained.

C_3A : Pure tricalcium aluminate (C_3A) was prepared via a sol-gel progress followed by calcination of a 3:1 molar ratio of $CaCO_3$ and Al_2O_3 for 6h at 1350 °C. The progress was repeated until the content of f-CaO was less than 0.5%.

2.2. Experimental method

XRD analyses: To begin with, hydration of C_3A in the presence of various superplasticizers was studied. For this purpose, C_3A was hydrated in deionized water. 1g C_3A and superplasticizer were added into 100ml deionized water. The suspension was stirred at 20 °C for 48h under argon, the centrifuged and the precipitated finally dried at 50 °C for 48h. XRD patterns were obtained with a

BD90 diffractometer operating at 30kV and 30mA, using Cu-K α radiation at 0.02°s^{-1} between 5° and 40° 2θ angles.

SEM analyses: Cement paste with initial w/c = 0.29 and 1.5 % aqueous superplasticizer (the combined superplasticizer comprises of 70 % MSAF and 30% PCA) on a mass basis was mixed at $20^\circ\text{C}\pm 2^\circ\text{C}$ in blender using the following protocol: 120 seconds of low speed mixing, a rest of 15 seconds while the sides of the mixing vessel were scraped down, and 120 seconds more of high speed mixing to prepare the final product. Cast wafers of the prepared pastes, 30 mm in diameter and 5 mm in thickness, were placed in small, capped copper vials. Then the vials were cured inside of a curing box maintained at $20^\circ\text{C}\pm 2^\circ\text{C}$ and RH >90%. At 3 and 28 days, wafers were removed from their vials and crushed into small pieces. Some of the small pieces (typically 2 to 3 mm in size) were retained for SEM. After the water remaining in the small pieces was replaced by ethanol, the pieces were dried in an oven at $60^\circ\text{C}\sim 65^\circ\text{C}$. The specimens were aurum sprayed before SEM analysis and were observed using Japanese JSM5610LV SEM analyzer.

3. Results and discussions

3.1. Hydration of C_3A in the presence of MSAF

With the fastest hydration rate among cement miners, C_3A has the biggest influence on the adaptability between the superplasticizer and cement. Figure 1, 2 and 3 shows the XRD spectrum of C_3A hydration products incorporating PNS, MSAF and MSAF-PCA, respectively. It was obvious that the main hydration product of C_3A were katoite and C_4AH_{13} while superplasticizer was added in. Compare with the hydration products of C_3A within PNS (Figure 1), C_3A diffraction peak were observed apparently in the XRD spectrum within MSAF (Figure 2) and PNS- MSAF (Figure 3), which indicated that residual C_3A were remained in hydration products. The result demonstrated that the hydration of C_3A would be restrained when the MSAF or MSAF-PCA was added in cement paste.

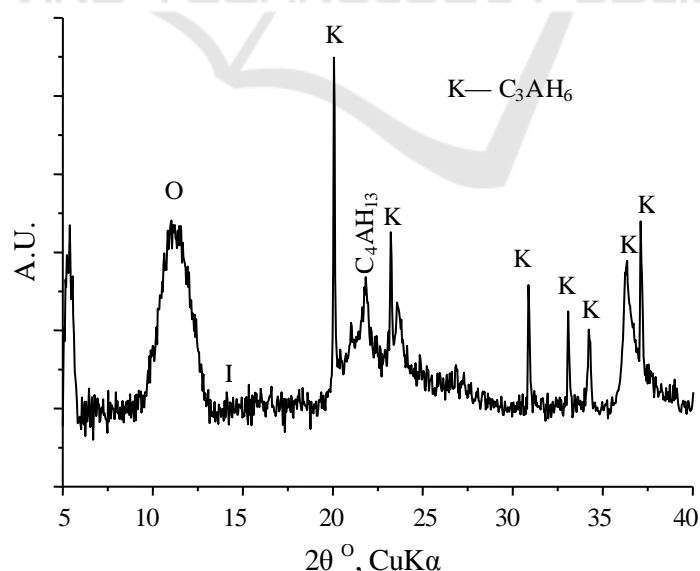


Figure 1. XRD pattern of the hydration products of C_3A incorporating PNS (K=katoite, I=Inorganic LDH, O=Organic LDH).

It was found that C_3A hydrating in aqueous superplasticizer solution may partially incorporate the anionic superplasticizer in between its $[Ca_2Al(OH)_6]^+$ main layers. The result is an organo-mineral phase with layered structure similar to those of C_2AH_8 and C_4AH_{13} , respectively. This could be proved by the diffraction peak of organic layered double hydroxide(LDH) found in Figure 1 which corresponded to the hydration products incorporating PNS, but the much weaker diffraction peak could only found in the C_3A hydration products incorporating MSAF(Figure 2), and barely exist in the C_3A hydration products incorporating MSAF-PCA(Figure 3). It shows that PNS molecules can insert in C_3A hydration products, and form Organic LDH phase, which on the contrary hardly exists in C_3A hydration products with MSAF or MSAF-PCA added in. Organic LDH phase existing in hydration productions means the intercalation of superplasticizer molecules in the internal surface of C_3A hydration productions, which would cause the reduction of superplasticizer molecules affective absorption on the surface of cement particles, consequently greatly weakened the beneficial effect of superplasticizer.

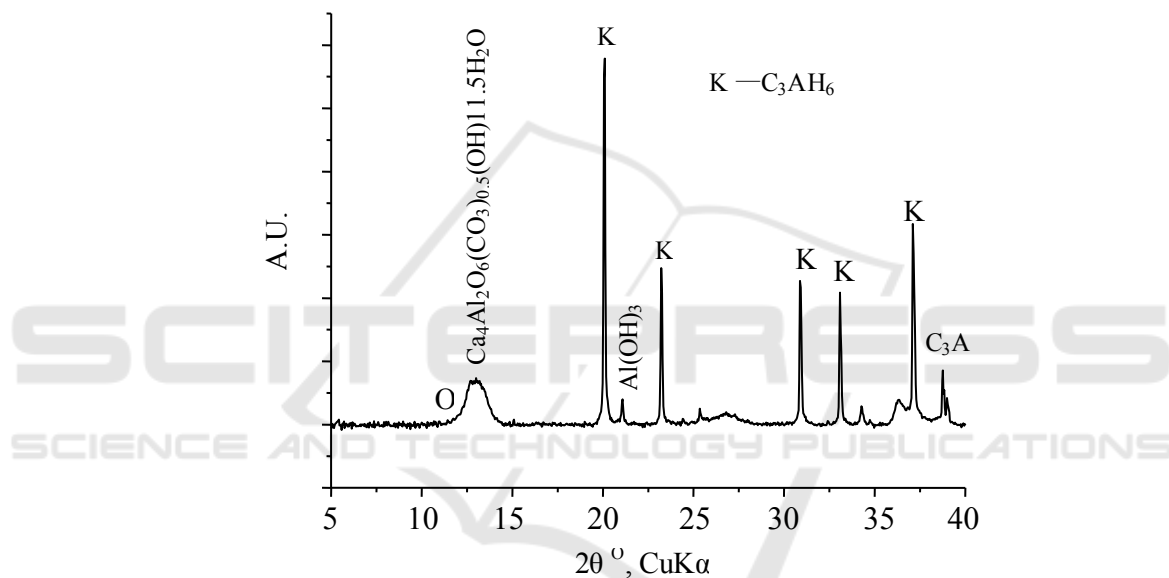


Figure 2. XRD pattern of the hydration products of C_3A incorporating MASF (K=katoite, I=Inorganic LDH, O=Organic LDH).

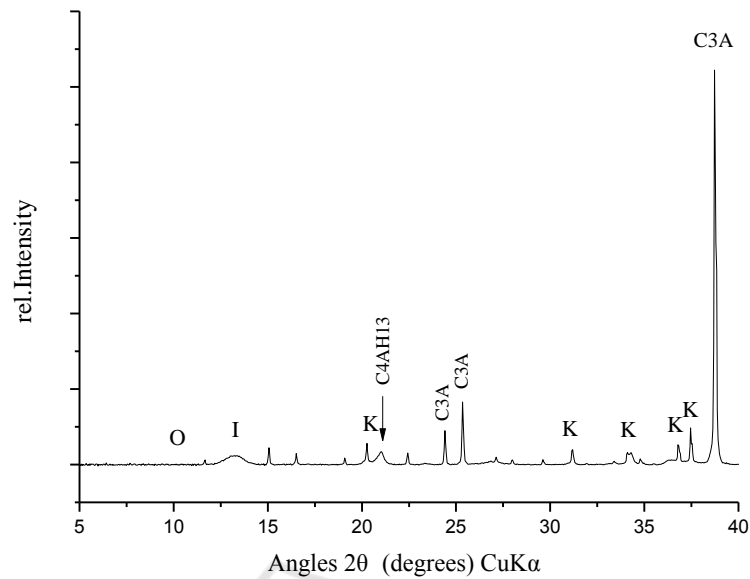
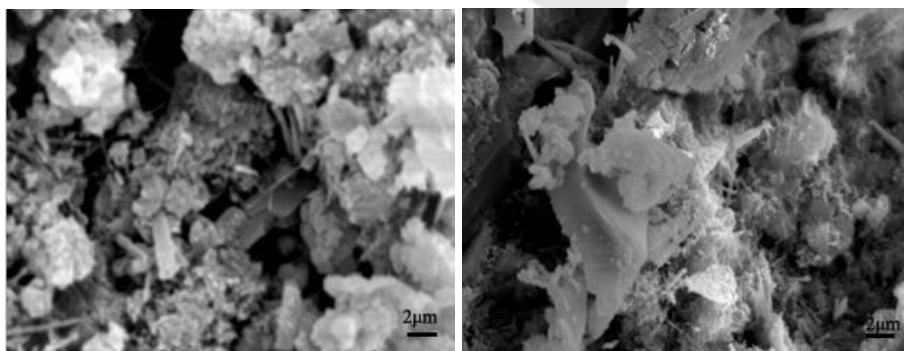


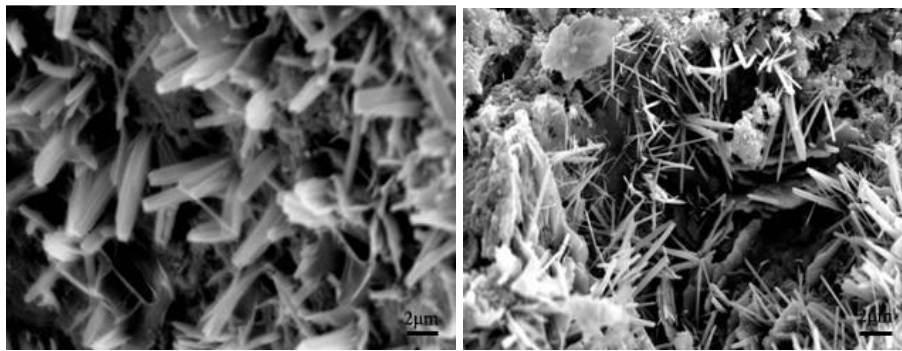
Figure 3. XRD pattern of the hydration products of C_3A incorporating MSAF-PC (K=katoite, I=Inorganic LDH, O=Organic LDH).

3.2. Morphology of aluminate hydrates

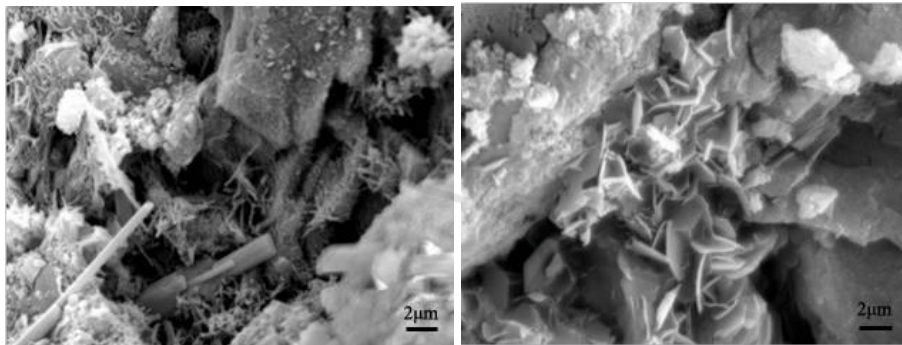
The morphology of hydrate assemblage of cement pastes with limestone was shown in Figure 4-a. Ill-crystallized and nearly amorphous character of C-S-H, thin needle-like ettringite crystals shape of flocculation-like and cubic calcite were observed in Figure 4-a(left). Because of the reaction between aluminate and the limestone, the hydration products of aluminate tend to be monocarbonate rather than monosulfate, which could be proved by the phases shaped as sheet-like crystals in Figure 4-a(right). As it reported, the calcite would act as a preferential substrate for the germination and growth of hydration products, thus accelerating the hydration progress, the C-S-H and needle-like ettringite crystals around calcite grains found in 28d SEM picture could support this idea.



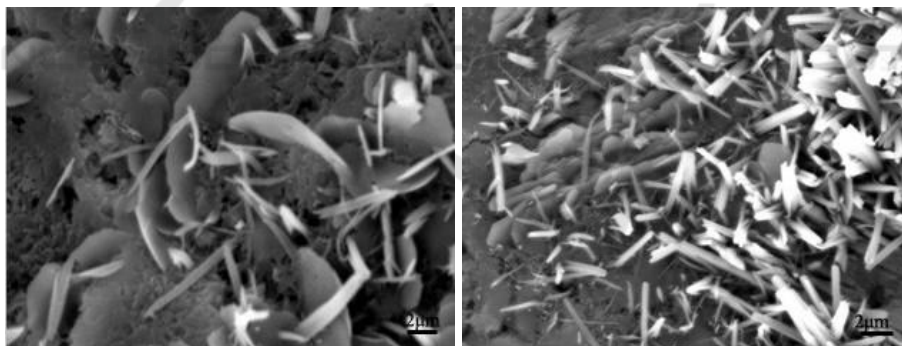
Blank: 3d (left), 28d (right)
(a)



PNS: 3d (left), 28d (right)
(b)



MSAF: 3d (left), 28d (right)
(c)



MSAF-PCA: 3d (left), 28d (right)
(d)

Figure 4. Microstructure of aluminate hydrates of cement pastes with and without superplasticizer.

Figure 4-b, Figure 4-c and Figure 4-d corresponded to the pastes incorporating PNS, MSAF and MSAF-PCA respectively. Ettringite that crystallized in the presence of superplasticizer, especially the MSAF and MSAF-PCA, were found to have a morphology quite different from the ones observed in the absence of superplasticizer. In the presence of superplasticizer, ettringite crystals lost its needle-like shape to form rather different crystals. Ettringite crystals keep its needle-like but thinner and longer in the presence of PNS. The typical morphology of ettringite crystals were hardly found at the early age of hydration in the cement paste incorporated MSAF and MSAF-PCA. Some block-like

and cluster-like AFt phases which shape contrasts with the long needle-like ones observed in the absence of superplasticizer were found in the cement paste incorporated MSAF. And the amounts of ettringite crystals were much fewer compared with ones observed in the absence of superplasticizer, in other words, could retard or even restrain the formation of ettringite crystals at the early time.

Compared with the cement paste without MSAF or MSAF-PCA, the sheet-like crystals of monocarboaluminate were hardly found the SEM picture. In the pastes incorporating MSAF, many needle-like crystals of ettringite and hexagonal crystals of monosulfoaluminate was still observed in the paste containing limestone filler hydrated for 28 days (Figure 4-d right), which was comparable with hydrates in control and polynaphthalene sulphonate (PNS) dispersed pastes. It was indicated that the reaction between C_3A and calcite is restricted. Ettringite and calcium monosulfoaluminate, other than ettringite and calcium monocarboaluminate or hemicarboaluminate, are coexisting in hardened cement paste blended with limestone filler and dispersed by MSAF or MSAF-PCA combined superplasticizer.

4. Conclusions

According to the analysis and discussion, conclusions are drawn as follows:

Sulfonated acetone formaldehyde condensate superplasticizer has been modified by catalyzed condensation with lignosulfonate. Drawbacks of SAF, promotion bleeding of and putting colour on cementitious materials, were overcome by the modification. Dissolution-precipitation process of C_3A at early age may be controlled by MSAF to some extent which results in little intercalation of superplasticizer into Ca-Al-LDH and more ettringite formation at initial stage and dormant period of cement hydration. Consequently, unhydrated C_3A reacts with ettringite to form calcium monosulfoaluminate via topochemical reaction at later age. As such, MSAF changes the assemblage of C_3A - $CaSO_4$ - $CaCO_3$ hydrates. Reaction between C_3A and calcite is restricted. Ettringite and calcium monosulfoaluminate, other than ettringite and calcium monocarboaluminate or hemicarboaluminate, are coexisting in hardened cement paste blended with limestone filler and dispersed by MSAF or MSAF-PCA combined superplasticizer. This explains how MSAF modifies the stability of fresh cementitious materials and why MSAF is more compatible with cements containing limestone filler than PNS.

Further investigation should be down to clarify action mechanism of MSAF for better understanding C_3A -MSAF interaction and reasonably use of MSAF.

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