Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 1535–1540

Effect of sodium salt of naphthalene-formaldehyde polycondensate on ettringite formation

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Received 4 December 1998; accepted 20 April 1999

Abstract

The suspension hydration of C_3A with gypsum (in the molar ratio of 1:3) was investigated at room temperature and water/solid ratio of 4. The hydration was carried out in presence of 0, 1, and 3% sodium salt of naphthalene-formaldehyde polycondensate and the mixes were designated as I, II, and III, respectively. The only hydration product formed in the presence and absence of the superplasticizer was ettringite. The rate of ettringite formation was retarded by the presence of the superplasticizer. This effect was more pronounced at high dosage of the superplasticizer only during the first 24 h. The presence of sodium salt of naphthalene-formaldehyde polycondensate caused a decrease in the size of the formed ettringite crystals, and as the percentage of the admixture increased, the crystal size decreased. In addition, there was an interaction between the used superplasticizer and the formed ettringite as indicated from infrared analysis.

Keywords: Microstructure; X-ray diffraction; Ettringite; High-range water reducers

1. Introduction

Retardation of fresh Portland cements, sulfate attack on hardened Portland cement concrete, high early strength of supersulfated cement, and development of prestress in restrained concretes made with expansive cements are phenomena associated with ettringite formation. Therefore, ettringite formation is an important reaction in cement hydration. Superplasticizers or high-range water reducers are widely used as admixtures for Portland cement concrete and mortars to produce a more flowable concrete or very high strength and more durable concrete. Therefore, it is important to investigate the effect of superplasticizer on the rate of formation of ettringite as well as its microstructure. There are many factors, such as starting materials, water to cement ratio, temperature, and additives, that affect the rate of formation of ettringite as well as its microstructure and stability [1–7].

Sakai and coworkers [8] studied the influence of Na-benzene sulfonate, Na-p-dodecyl benzene sulfonate, and Na salt of β-naphthalene sulfonate formaldehyde on the hydration of C_3A and C_3A + gypsum. They concluded that all admixtures retarded the hydration of C_3A, with maximum retardation occurring with 4% naphthalene sulfonate. The formation of ettringite and its subsequent conversion to monosulfate was explained in terms of strong adsorption, formation of complexes, and orientation of the adsorbed species. Slanicka [9] used the X-ray diffraction and thermogranuimetric analysis (TGA) techniques to follow the hydration behaviors of C_3A + gypsum and C_3S containing sulfonated melamine formaldehyde. In both cases, hydration was retarded, but some acceleration occurred subsequently. Odler and Becker [10] compared the effect of three admixtures, Na salt of melamine formaldehyde, Na salt of naphthalene formaldehyde, and Ca salt of sulfonated lignin on the hydration of C_3S and two cements. The admixtures accelerated the formation of ettringite in the early high-strength cement but retarded it in normal cement.

Collepardi et al. [5] stated that with 0.6% sulfonated naphthalene formaldehyde, the hydration of C_3A and gypsum in the presence of $Ca(OH)_2$ remained the same as that of the sample without admixture. Ramachandran [11] in his study concluded that the addition of sulfonated melamine or naphthalene formaldehyde retards the hydration of C_3A and the rate of conversion of hexagonal to cubic aluminate hydrate, whereas the reaction between tricalcium aluminate and gypsum to form ettringite is accelerated in the presence of superplasticizer. Vovk and Ushenov-Marshak [12] investigated the effects of superplasticizer using various modes

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PII: S0008-8846(99)00110-6

of addition on the hydration of Portland clinker minerals C_3S and C_3A. Addition of superplasticizer significantly decreased the rate of heat evolution of both the C_3S and C_3A. The degree of hydration for C_3A was also notably lower in the early stages. Simard and Aitcin [13] noted that naphthalene sulfonate retarded the hydration of cement independent of the type of salt, calcium or sodium, or molecular weight. However, the rates of hydration differed with type of the salt, and the influence of the sodium salt was strongly dependent on the C_3A content of the cement.

Afridi et al. [14] reported the effects of polymers on the formation of AFt crystals in polymer-modified mortars (PMMs). They characterized the morphology of the AFt crystals in the unmodified mortars as lean, elongated, rodlike structures, whereas the crystal in the PMMs were referred to as more stout. Specific changes in the aspect ratio of the AFt crystals formed depended on the type of polymer. It was proposed that the polymer modifiers altered the rate of hydration of the C_3A during the first few minutes in solution, and also affected the supply of sulfate in solution and the formation of AFt.

2. Experimental

Ettringite was prepared in the laboratory from high purity C_3A and Gypsum (analytical grade) by stoichiometric proportions in absence and presence of superplasticizer. The hydration was carried out at room temperature (25°C) and by using a water/solid ratio of 4 for different time intervals (0.5 h to 7 days). The superplasticizer used was the sodium salt of naphthalene-formaldehyde polycondensate (commercial grade) with the ratios of 0, 1, and 3% by weight of the solid and the samples were designated as I, II, and III respectively. Each mix was mechanically stirred using a magnetic stirrer during the first few hours (3 h) until the mixture became a sticky homogeneous slurry; shaking from time to time then followed to prevent segregation. After each time interval a part of the sample mixture was withdrawn and filtered off. Hydration was halted by stirring in a mixture of acetone and methanol (1:1 volume ratio) for 1 h. The sample was then filtered off and washed by the same mixture several times, and thereafter washed by ether. The solid was dried at 50°C for 3 h. The following examinations were carried out on the dried samples:

1. Hydration kinetics were studied by determining the percentage of the degree of hydration based on the nonevaporable water content.
2. Phase composition of the formed hydrates was investigated by means of X-ray diffraction analysis.
3. Microstructure of the formed ettringite was examined by means of scanning electron microscopy (SEM).
4. The interaction of the superplasticizer with the formed ettringite was examined by using infrared (IR) analysis.

3. Results and discussion

3.1. Hydration kinetics

The rate of ettringite formation, through the suspension hydration of tricalcium aluminate and gypsum (in the molar ratio gypsum/C_3A = 3) in the presence of 0, 1, and 3% superplasticizer by weight of solid, was followed by determining the degree of hydration at various time intervals. The degree of hydration was calculated based on two successive measurements, which were found to be reproducible to within ±1% accuracy. The results of the degree of hydration are shown in Fig. 1. The degree of hydration increases with time up to 7 days for all mixes. Mix I shows an increase in the degree of hydration, from 0 to 45.90% after the first 30 min of hydration; this can be considered as the “predormant” period that represents a spontaneous reaction between the reactants. Then, the degree of hydration shows a slight and gradual increase up to 3 h. The low rate of hydration in the period of 30 min to 3 h can be attributed to the formation of ettringite layers around the C_3A grains, as indicated by various investigators. This stage is known as the “dormant” period. These coating layers retard the hydration during this period. Later, due to the development and growth of ettringite crystals during the dormant period, cracks also form. Then, the reaction rate increases markedly and much ettringite forms in the period of 3 to 8 h. This is the “acceleration” period. In this period the diffusion of water through the crystalline ettringite coating is unhindered, leading to the formation of larger amounts of ettringite located deeper on the C_3A grains. The formation of inner ettringite coatings blocks the cracks, and therefore a second “dormant” period occurs after 8 h hydration, up to 7 days. From the results in Fig. 1, the samples containing superplasticizer (mixes II and III) show a retardation effect during the first 30 min of hydration compared to mix I (without superplasticizer) and the degree of retardation increases with the increasing ratio of superplasticizer. At 3 h, the degree of hydration in the case of mixes II and III is higher than that of mix I at the same age. This can be attributed to the formation of incomplete coating layers of ettringite in the presence of superplasticizer (after the first 30 min), which cannot hinder the diffusion of water through these layers. After 3 h of hydration, well-coating layers form around C_3A grains; this can hinder the diffusion of water through such layers and thus retardation takes place. This retardation effect extends up to later ages of hydration (7 days).

In general, the presence of superplasticizer causes a retardation effect for the formation of ettringite, and the degree of retardation increases when increasing the percentage of the admixture, especially at the early hydration ages (during the first 24 h); however, there is no considerable effect when increasing the percentage of superplasticizer after the first day of hydration.

3.2. Phase composition

The formation of ettringite as a result of the hydration reaction of C_3A and gypsum in the presence and absence of

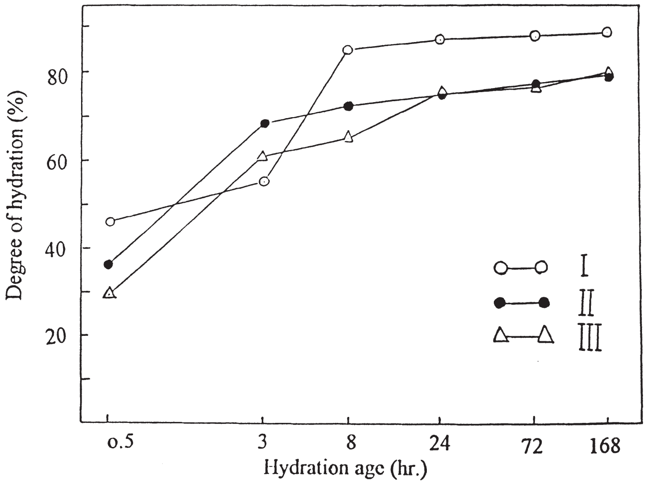


Fig. 1. Degree of hydration vs. time.

sodium salt of naphthalene-formaldehyde polycondensate was also followed by means of X-ray diffraction analysis. The results are shown in Figs. 2, 3, and 4 for the different mixes hydrated at 0.5, 8, and 168 h, respectively. The main hydration product in the different samples was ettringite, as was expected. Fig. 2 shows the results of X-ray analysis for mixes I, II, and III after 30 min of hydration. The characteristic peaks of ettringite appear after this period of hydration in the different mixes but with different intensities. The intensity of ettringite peaks in case of mixes containing super-

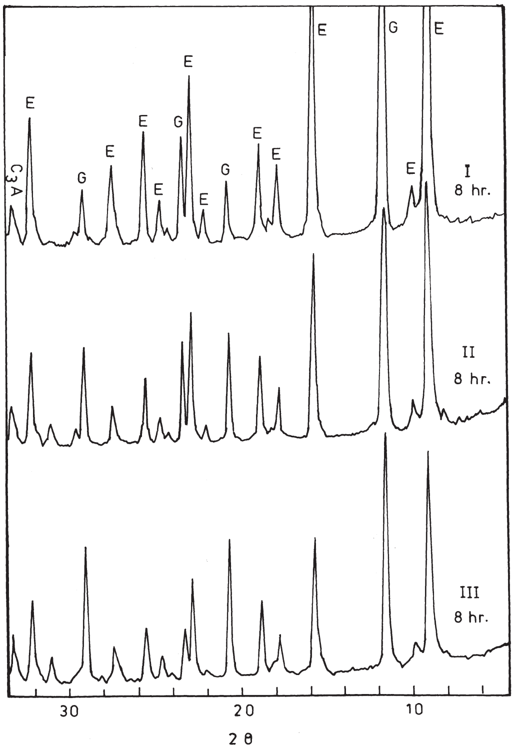


Fig. 3. XRD patterns after 8 h of hydration.

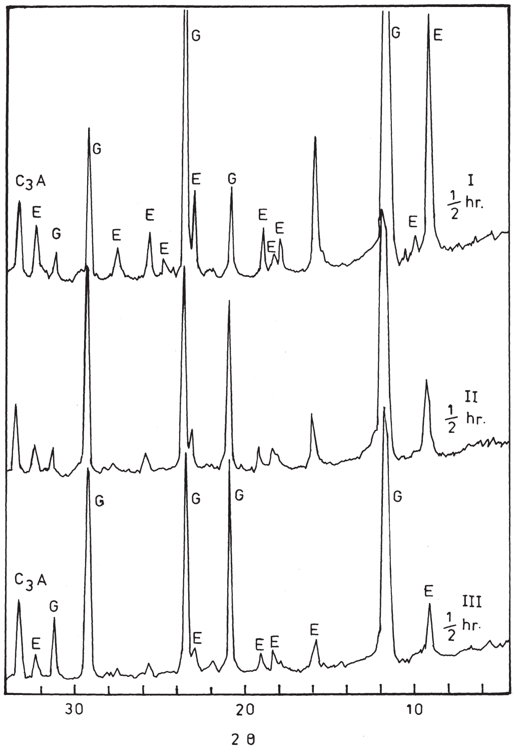


Fig. 2. XRD patterns after 30 min of hydration.

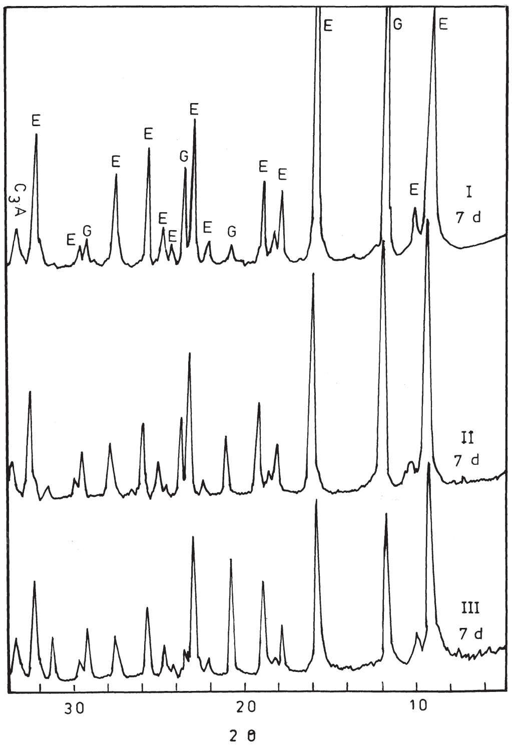


Fig. 4. XRD patterns after 7 days of hydration.

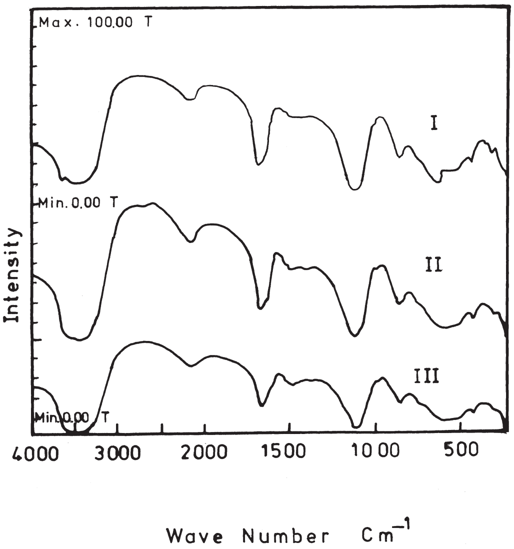
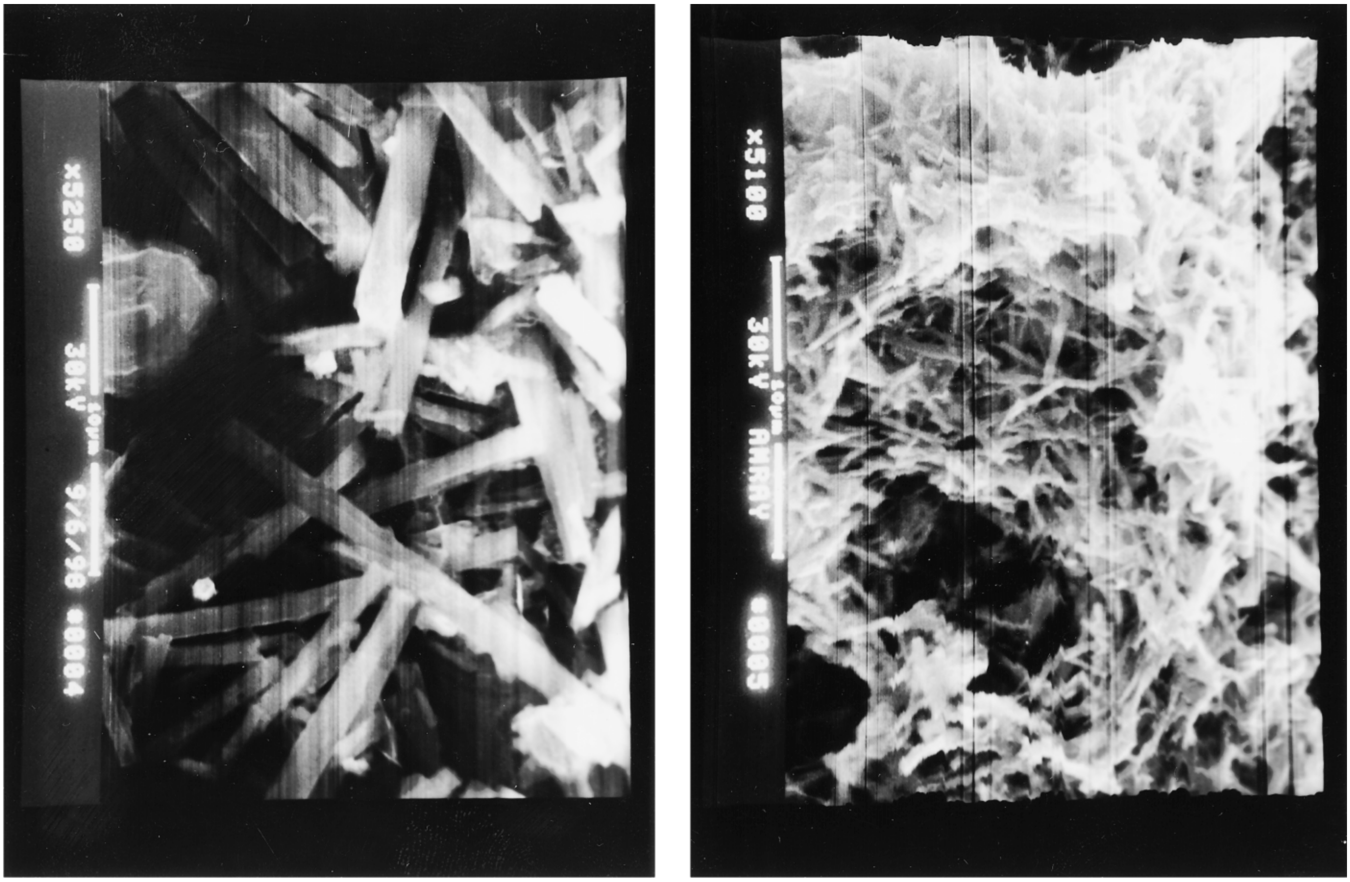


Fig. 5. IR spectra after 3 days of hydration.

plasticizer (II and III) is relatively lower compared to those in mix I (without admixture), and as the percentage of admixture increases the intensity of ettringite peaks decreases. This reveals that the presence of superplasticizer retards the formation of ettringite. As the hydration progresses, the intensity of the different peaks of reacting materials (C_3A and gypsum) continues to decrease and that of ettringite continues to increase (see Figs. 3 and 4). Obviously, the characteristic peaks of ettringite at all ages of hydration investigated for the samples containing superplasticizer (II and III) have lower intensities compared to those of the sample without admixture (mix I). The intensity of ettringite peaks decreases as the percentage of the superplasticizer increases in the mix.

3.3. IR analysis

The interaction of the superplasticizer used with the formed ettringite was investigated by using IR analysis for mixes I, II, and III that were hydrated for various time intervals. The results obtained show that there is a slight shift to-



Sample I

Sample III

Fig. 6. SEM micrographs after 8 h of hydration.

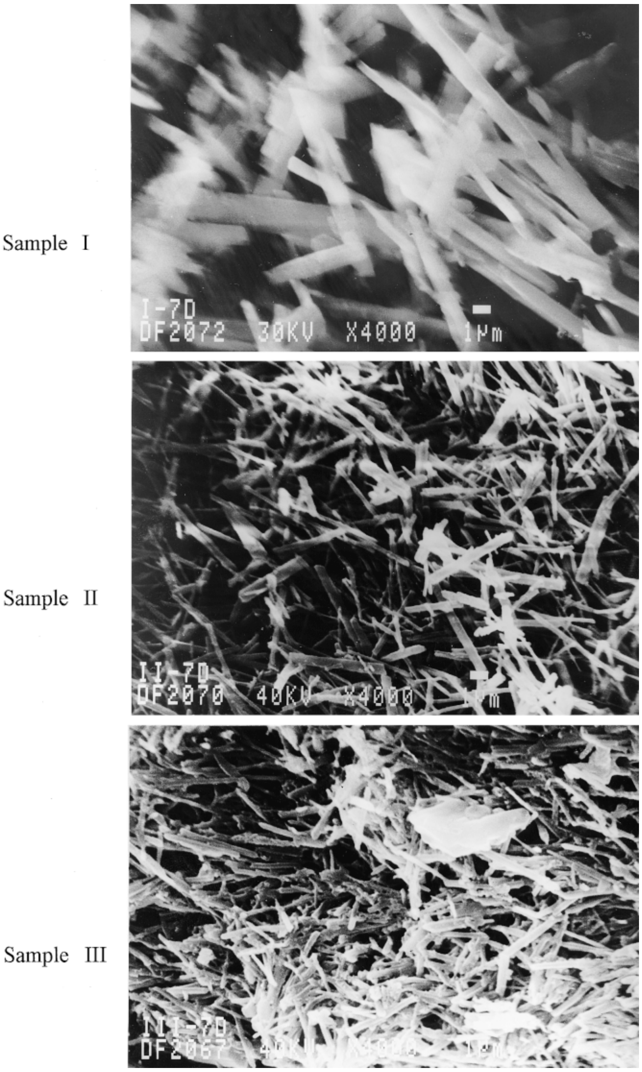


Fig. 7. SEM micrographs after 7 days of hydration.

wards higher wave number (ν) in the bands characteristic for H_2O and Al-OH of ettringite in the case of samples II and III, which contain superplasticizer, compared to those in sample I (without admixture) at all times of hydration from 3411 to 3430 and from 847 to 857 cm^{-1}, respectively. This shift indicates that there is an interaction between sulphonated naphthalene formaldehyde and the formed ettringite. Fig. 5 shows the IR spectra of samples I, II, and III hydrated for 3 days. These spectra are considered representative of those of the same samples hydrated at the various time intervals.

3.4. Microstructure

The microstructure of ettringite formed by the suspension hydration of C_3A and gypsum in the presence and absence of sodium salt of naphthalene-formaldehyde polycondensate was examined by SEM. Fig. 6 shows the microstructure of the ettringite formed after 8 h of hydration for mix I (without admixture, left) and mix III (3% admixture, right). It is evident that the ettringite formed in the absence of superplasticizer is in the form of large rod crystals, while that formed in presence of the admixture is in the form of fibers and fine rod crystals.

After 7 days of hydration, the main hydration products obtained in all the investigated mixes are rodlike ettringite crystals. It is worth noting that the ettringite rods formed in the absence of superplasticizer are larger in size than those obtained in presence of the admixture, and as the percentage of admixture increases the crystal size of the formed ettringite decreases (see Fig. 7).

4. Conclusions

The main conclusions derived from this study can be summarized as follows:

1. The presence of sodium salt of naphthalene-formaldehyde polycondensate causes a retardation for the formation of ettringite.
2. As the percentage of the added superplasticizer increases, the retardation effect increases, but only during the first 24 h of hydration.
3. The size of the formed ettringite crystals decreases as the percentage of superplasticizer increases in the sample.
4. There is an interaction between sodium salt of naphthalene-formaldehyde polycondensate and the formed ettringite.

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