

Reducing Cement-Superplasticizer Incompatibilities by Adding Alkalis

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ABSTRACT

Superplasticizers are widely used in concrete technology. However, the interactions between superplasticizer and cement are not well studied, and understanding incompatibilities between superplasticizers and cements will allow the performance of superplasticizers to be substantially improved. This study used dynamic rheology to explore the flow behaviors of various cement-admixture combinations. Dispersing effects of polycarboxylate-based (CAE) and naphthalene-based (SNF) superplasticizers were investigated. Major incompatibilities were observed with SNF: affected mixtures showed gelation rather than dispersion. Minor incompatibilities were observed with CAE: affected mixtures showed only slight gelation at intermediate dosages. Results showed that the incompatibilities were reduced by addition of alkali to the mixing solution, either alkali hydroxide or alkali sulfate in the case of SNF and only alkali hydroxide in the case of CAE. Ettringite formation was affected by both SNF and added alkalis. It appears that the SNF incompatibility is associated with ettringite formation.

1. INTRODUCTION

With the widespread use of superplasticizers in modern concrete technology, incompatibility problem began to draw investigators' attention in the past decades. The incompatibility occurs when the high workability of superplasticized concrete is retained for only a short time and is followed by a rapid slump loss [1]. The incompatibility relates to the compositions of cements and superplasticizers. It is suggested that superplasticizers should be selected properly for cements with different compositions and the optimum dosage should be determined for each specific cement [2].

Alkalis are known to play an important role in the dispersing behaviors of cement pastes with SNF, and adequate alkalis are necessary to prevent the incompatibilities [1]. The alkali level in particular influences the adsorption behavior. It has been shown that SNF adsorbs much more strongly on C_3A and C_4AF than on C_3S and C_2S , but that this adsorption is inhibited by the addition of alkali sulfate [3-5]. Nawa et al. [6] argued that an optimum alkali sulfate level in clinker was required to ensure the fluidity

of cement paste, and suggested that an higher alkali sulfate increases the SNF adsorption on C_3S and C_2S as well as retards their hydration. They also suggested that excess alkali sulfate increases paste viscosity by compressing the electrical double layer and showed no clear correlation between the soluble alkali content during the early hydration and the total alkali content of the cement. Some studies similarly showed that addition of sodium sulfate or sodium hydroxide effectively reduced the viscosity or slump loss of the pastes using mini slump measurement [1, 5, 7, 8]. With CAE, the adsorption on calcium carbonate has also been shown to decrease with addition of K_2SO_4 [9, 10], and the decreased adsorption was attributed to ionic strength [9].

In this study, dynamic rheology was used to explore the compatibility between two cements and two superplasticizers with added alkalis. X-ray diffraction and microscopic observations were used to explain incompatibilities.

2. MATERIALS AND METHODS

Two commercial cements were used in this study, Cements A and B, the same as Cements C1 and C4 in the authors' previous work [11]. The chemical compositions and the calculated mineral compositions of those cements are summarized in Table 1. Both cements have similar C_3A levels, but Cement A has a higher alkali content than Cement B.

The two chemical admixtures used for this study were calcium salt of sulfonated naphthalene formaldehyde condensate (SNF) and sodium salt of carboxylated acrylic ester (CAE). Both admixtures were provided in liquid forms with solid contents of 28.2% and 40%, respectively.

The paste specimens used in this study had a water-cement ratio of 0.35. The dosage of admixture, expressed as the mass of solid admixture divided by the mass of cement, was varied to assess the dosage response. The desired amount of admixture was first dissolved in 3.5 g of de-ionized water and then mixed with 10.0 g of cement, and the resulting paste was mixed by hand for 2 min. In some cases, in order to explore the effects of additional alkalis, certain amounts of alkali sulfates or alkali hydroxides were added into the mixing solutions prior to making the pastes.

The flow behaviors of the cement pastes were assessed using dynamic rheology. Approximately 2 mL of paste were transferred to the rheometer (CS-10, Bohlin Rheologi Inc.). A cup and bob geometry was used. The bob has a smooth surface and a diameter of 14 mm and the gap between the cup and the bob is 0.7 mm. Temperature of the cup was maintained by circulating water at 25 °C. Most of the specimens were presheared at 200

Table 1. Chemical compositions of cements.

Cements	Cement A	Cement B
Chemical composition		
SiO ₂	19.83	20.00
Al ₂ O ₃	5.30	4.96
Fe ₂ O ₃	2.09	2.61
CaO	62.30	64.61
MgO	1.65	2.28
SO ₃	4.08	2.49
K ₂ O	1.20	0.58
Na ₂ O	0.09	0.17
Free lime	0.24	1.47
Gypsum	1.50	2.70
Plaster	0.20	0.40
Water soluble K ₂ O	0.88	0.36
Water soluble Na ₂ O	0.06	0.06

[†] Cement compositions were provided by Lafarge Inc.

Pa for 45 sec, allowed to rest for 300 s, and then tested using a stress sweep. In the stress sweep, a sequence of small oscillatory stress levels was applied, here ranging from 0.3 Pa to 300 Pa and all at 1 Hz, and the strain response was measured. Both elastic modulus and loss modulus were calculated. As discussed in Section 3, the extent of dispersion in the paste specimens was evaluated using the stress-sweep results. The stress-sweep was completed within 30 min of hydration time.

To assess their compositions, pore solutions of plain pastes were collected using a centrifuge at 2200 r/min for 5 min. The liquid phase was immediately passed through a 0.45- μ m filter, then stored in vials until analyzed. Metals were determined by atomic emission spectrometry and sulfate was determined by ion chromatograph.

Adsorption behaviors of the admixtures were assessed by measuring the amount of admixture adsorbed by the cement particles at a hydration time of 20 min, close to the ending time of rheological measurement. The pore solutions of the cement pastes with SNF or CAE were collected as described in previous paragraph. However, collected solutions usually remained turbid, so they were centrifuged a second time at 6000 r/min for 5 min. The liquid phase was then filtered as described previously. The filtered solution was then diluted with distilled water at 1:1000 by volume. During the dilution, hydrochloric acid was added so as to provide approximately 0.5 mM in the diluted solution to avoid possible precipitation. Residual content of SNF in the liquid phase was determined by UV spectrophotometry and residual content of CAE was determined by total organic carbon analysis (TOC).

X-ray diffraction (XRD) was used to identify the phases in the hydrated pastes. The 10-g samples were ground in acetone using a mortar and pestle for 5 min. The grinding was followed by filtration using a 2.5- μ m

filter. The samples were washed by acetone during the filtration to ensure that all water was removed quickly. Samples were then air-dried, usually within about 5 min. All XRD patterns were generated by the use of Cu-K α radiation over a 2θ range from 5° to 70° with a step size of 0.02° . The working voltage and current were 40 kV and 40 mA, respectively. After the patterns were collected, the phases were identified by matching with patterns in Powder Diffraction File (PDF). In addition, quantitative XRD analysis was conducted using commercial software TOPAS that performed quantitative Rietveld analysis by refining user-defined crystal structures. Initial crystal structure information was acquired from both the Inorganic Crystal Structure Database (ICSD) and the TOPAS structure database. The crystal size and the lattice parameters (i.e. a , b , c) of each phase were the only refined structure parameters.

Scanning electron microscopy (SEM) using secondary electron imaging was used to observe the morphologies of the cement particles. Chemical elements in selected SEM image areas were determined using energy dispersive X-ray analyses (EDS). Specimens prepared for XRD were used for these analyses because the hydration had been stopped by removing the water. Specimens were gold-coated and maintained in a vacuum chamber before the analyses. The specimen area was chosen with the objective of observing connected particles and newly formed crystals. In this study, the intensity counts of aluminum at 1.487 eV, sulfur at 2.308 eV, and iron at 6.404 eV were related to the intensity counts of silicon at 1.74 eV. The ettringite was assumed to exist when both Al/Si and S/Si were higher than in the neighboring area.

3. RESULTS AND DISCUSSION

The oscillatory stress-sweep technique was used to evaluate the extent of dispersion in the paste specimens. The results are plotted as dynamic elastic modulus (G') versus shear stress (τ). Pastes without admixture are expected to be flocculated, with a high G' at low stress levels and a low G' at high stress levels because the microstructure is broken down. The stress level at which this transition in G' occurs is how yield stress was determined in this study. Pastes with admixture are expected to be partially or fully dispersed, with a low G' at all τ levels. In compatible cement-admixture combinations, the moduli are progressively decreased with the increase of the admixture dosages (Fig. 1(a)), behavior described as *classical*. In incompatible cement-admixture combinations, the cement is flocculated instead of dispersed and its elastic modulus and yield stress are higher than in paste with no admixture, behavior described as gelled. Some incompatible cement-admixture combinations were gelled with increasing admixture dosage (Fig. 1(b)) and some were gelled at low dosages but showed classical dispersion at high dosages. It should be

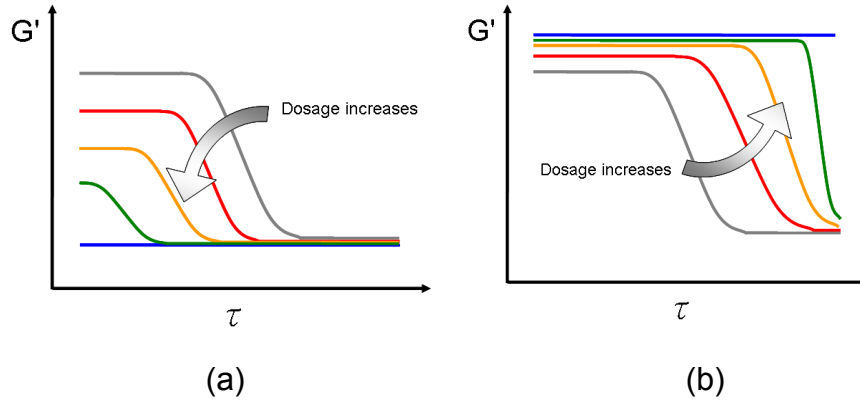


Fig. 1. Stress-sweep responses of (a) compatible and (b) incompatible cement-admixture combinations.

noted that a compatible combination is preferred in the use of the dispersing admixtures.

The dispersing behaviors of Cements A and B with CAE or SNF were presented in authors' previous work [11]. They had quite different dosage responses to the admixtures. Cement A was classically dispersed by both CAE (Fig. 2(a)) and SNF (Fig. 3(a)). On the other hand, Cement B with CAE required a minimum admixture dosage to induce dispersion (Fig. 2(b)), and Cement B was gelled by SNF (Fig. 3(b)). Cement B had strong incompatibilities with CAE at intermediate dosages and with SNF.

The compositions of the pore solutions extracted from the two cements were analyzed in order to understand how ion species and their concentrations influenced the dispersing behaviors of superplasticized cement pastes. The pore solution analyses are shown in Table 2. The Cement A pore solution had the higher concentration of alkalis, especially potassium, consistent with the composition in Table 1. Cement A pore solution analysis also had the higher concentration of sulfate. This result did not agree with the composition in Table 1, which showed that the Cement B contained the higher amounts of gypsum and plaster. This difference in pore solution composition suggests that either alkalis or the sulfates could be a factor influencing the compatibility.

Experiments were then conducted to observe how the dispersing behaviors were affected when the concentration of alkalis was increased in the mixing solutions. Potassium hydroxide (KOH) and potassium sulfate (K_2SO_4) were used in amounts selected to bring the composition of Cement B, incompatible with the admixtures, to the same level as Cement A, compatible with the admixtures.

Results of the pastes with CAE are shown in Fig. 4. A dosage of 0.1% CAE was used because Cement B showed incompatibility at this dosage. With Cement A, the dispersing behaviors were not influenced by KOH but

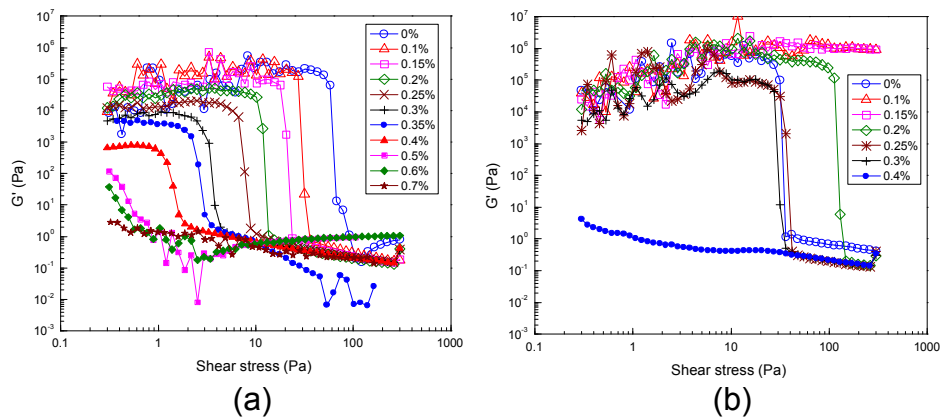


Fig. 2. Stress-sweep responses for pastes with CAE and (a) Cement A or (b) Cement B¹ [11].

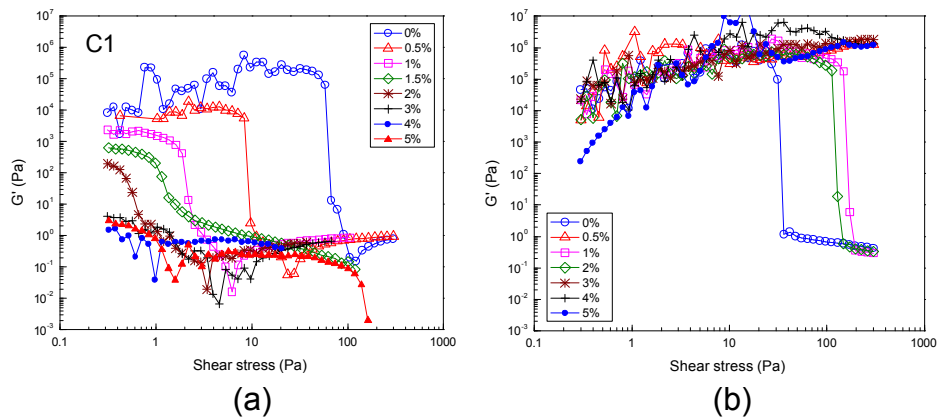


Fig. 3. Stress-sweep responses for pastes with SNF and (a) Cement A or (b) Cement B¹ [11].

the yield stress was increased slightly by K_2SO_4 (Fig. 4(a)). With Cement B, the effect of KOH was huge, fully dispersing the paste, but the K_2SO_4 did not affect the gelation (Fig. 4(b)).

Results of the pastes with SNF are shown in Fig. 5. All of the pastes were dispersed by adding 256 mM KOH or 64 mM K_2SO_4 . With Cement B, the dispersing effect was tremendous; the pastes were all fully dispersed by

Table 2. Chemical compositions of pore solutions extracted from plain pastes

Cements	Ion concentration (mM)			
	Calcium	Potassium	Sodium	Sulfate
A	21.5	410.3	42.5	166.7
B	25.4	197.4	29.2	80.2

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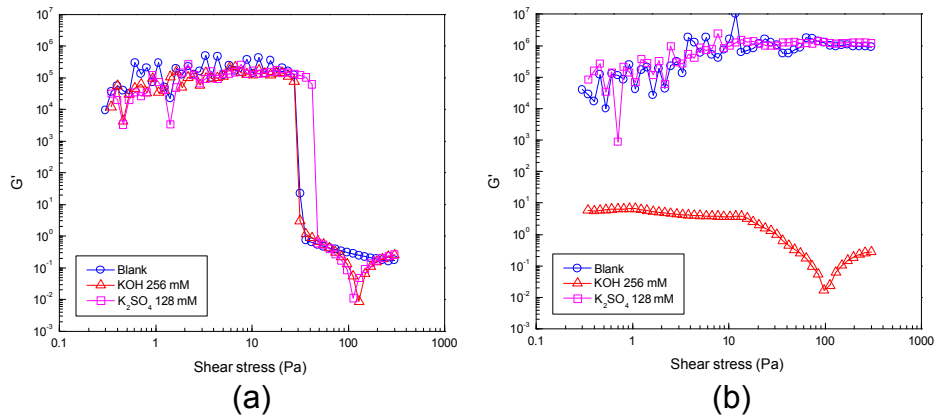


Fig. 4. Influence of the potassium addition on the rheology of the pastes with 0.1% CAE and (a) Cement A or (b) Cement B.

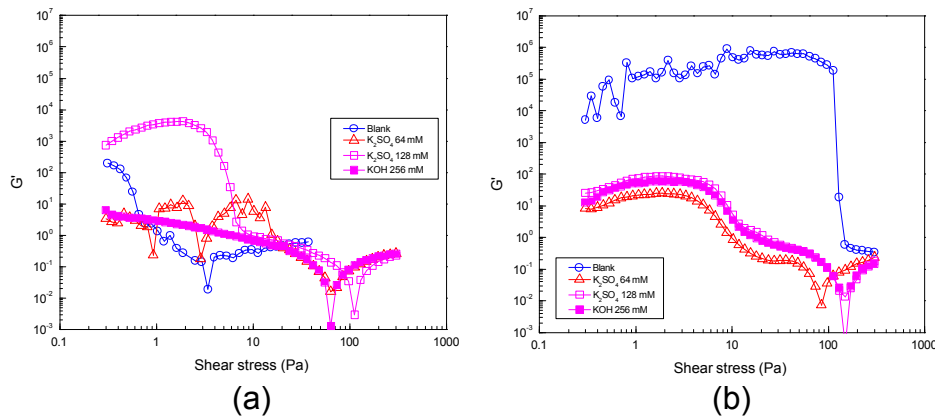


Fig. 5. Influence of the potassium addition on the rheology of the pastes with 2% SNF and (a) Cement A or (b) Cement B.

either addition (Fig. 5(b)). The dispersing behaviors were changed abruptly, not progressively, except with 128 mM K_2SO_4 and Cement A (Fig. 5(a)), whose elastic modulus and yield stress were only slightly increased.

In general, the role of the added anion was important in the dispersion of pastes with CAE. Pastes with K_2SO_4 addition had a stronger gelation than the ones with KOH addition. On the other hand, the dispersion of pastes with SNF was very sensitive to alkali addition and not to the anion. Most additions caused great reduction in both elastic modulus and yield stress, and whether the anion was sulfate ion or hydroxyl ion did not make much difference in dispersion.

The effect of these added alkalis on adsorption of the chemical admixtures was investigated. With CAE, addition of KOH and K_2SO_4 reduced the adsorption (Fig. 6(a)). The adsorption was reduced more by K_2SO_4 than

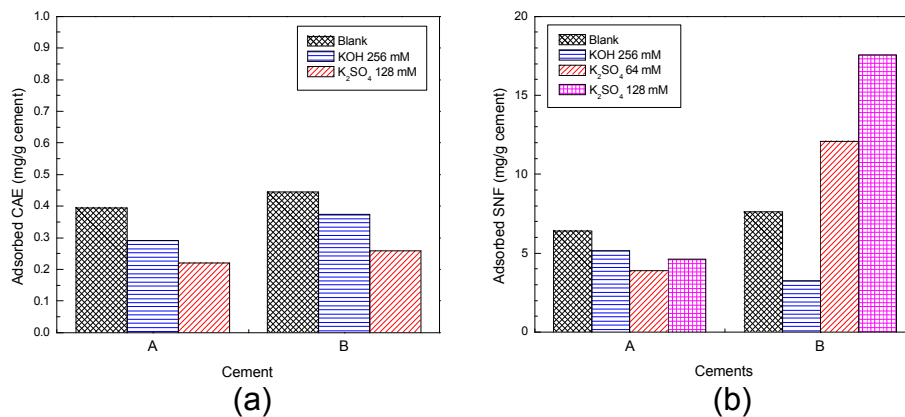


Fig. 6. Amounts of (a) CAE or (b) SNF adsorption influenced by the addition of KOH or K₂SO₄ at 0.1% CAE or 2% SNF.

by KOH, even though the added potassium concentrations were the same. On the other hand, with SNF the addition of KOH and K₂SO₄ generally reduced the adsorption, but Cement B with addition of K₂SO₄ was exceptional (Fig. 6(b)), adsorption was reduced by addition of KOH but increased by addition of K₂SO₄, and addition of higher concentrations of K₂SO₄ increased the adsorption more.

The hydrated cement pastes were investigated using X-ray diffraction to determine whether hydration reactions were altered by the admixtures, thereby causing the incompatibilities. The formation of ettringite was carefully examined because its formation has been found to be influenced by the addition of superplasticizer [12]. How admixture dosages influenced the ettringite formation of the pastes in this study is presented in Fig. 7 and Fig. 8. With CAE, higher CAE dosages generally reduced the ettringite (Fig. 7(a)), but with SNF, addition of SNF increased the ettringite, especially for mixtures of Cement B that showed strong incompatibility using dynamic rheology. The increase was not proportional to the applied dosage, and higher SNF dosages did not necessarily increase the ettringite more (Fig. 7(b)).

Since additional alkalis or alkali sulfates in the mixing solutions modified the dispersing behaviors of the cement pastes, how hydration was affected by additions of alkali hydroxide and alkali sulfate was of particular interest. With CAE, addition of alkali hydroxide or alkali sulfate increased the ettringite in the pastes with Cement A (Fig. 8(a)). With SNF, addition of alkalis or alkali sulfates generally reduced the ettringite, especially in pastes with Cement B (Fig. 8(b)). The addition of alkalis or alkali sulfates had impacts on the cement hydration.

The incompatibilities of Cement B with SNF appear to relate to the amount of ettringite. The rheological measurements showed that the gelation

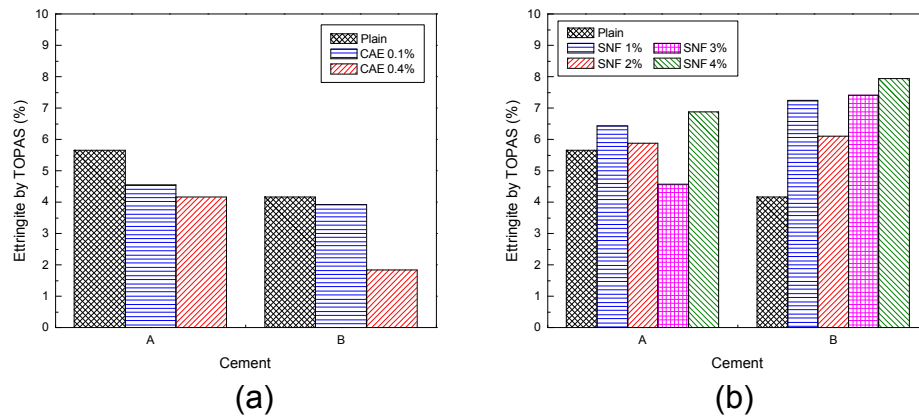


Fig. 7. Amounts of ettringite formation influenced by the addition of (a) CAE or (b) SNF.

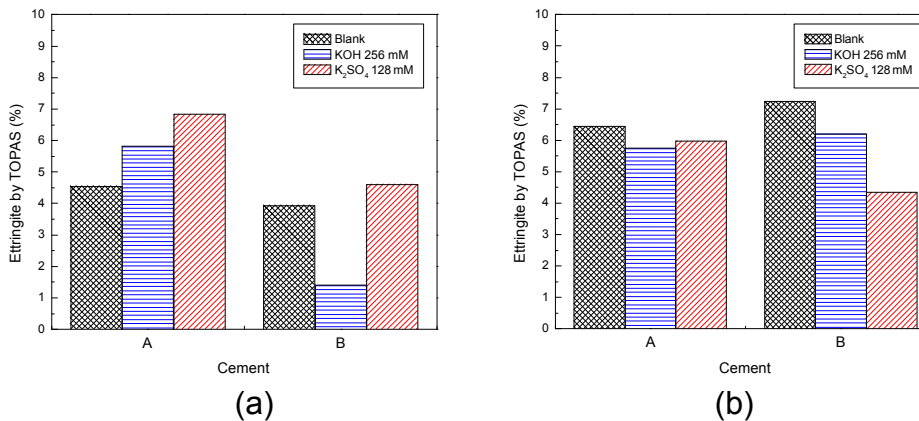
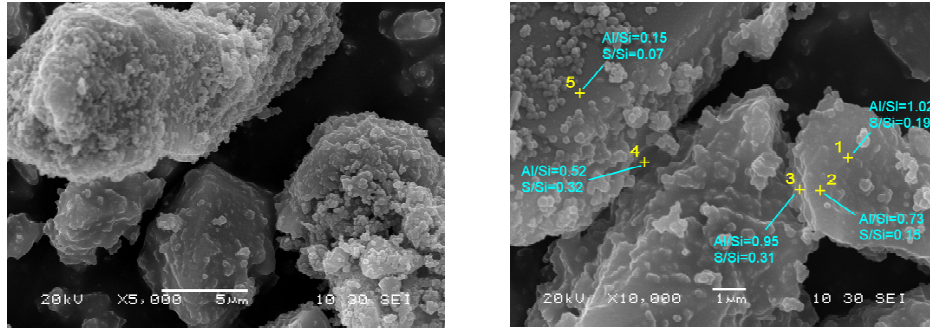


Fig. 8. Amounts of ettringite formation in (a) cements with 0.1% CAE or (b) cements with 2% SNF influenced by the addition of alkalis.

occurred within the first 20 minutes of hydration, and the ettringite is typically the most abundant crystalline hydrated phase formed during this very early hydration time. Quantitative XRD analyses showed that much more ettringite formed in the gelled pastes with SNF than in either the plain pastes or the dispersed pastes with SNF. In general, pastes with higher SNF dosages had higher amounts of ettringite.

Microscopic observations further supported the role of ettringite. The SEM images showed that pastes with Cement B and SNF had granular hydration products on the surface of the cement particles (Fig. 9) and the qualitative EDS showed that those crystals contained higher intensity ratios of sulfur and aluminum to silicon than the surrounding area, suggesting the presence of ettringite. The qualitative EDS further showed that the connections between cement particles also contained high ratios of sulfur and aluminum to silicon. Therefore, not only was the amount of ettringite increased by the addition of SNF, but also the ettringite was observed to bridge the cement particles.



(a) (b)
 Fig. 9. SEM images of Cement B with SNF at hydration time of 40 min.
 ((a): 5000X; (b) 10000X with EDS)

In addition, the amount of ettringite was reduced by the addition of alkalis. Higher concentrations of alkalis in pastes with Cement B and SNF generally led to greater reduction in the amounts of ettringite.

On the contrary, with CAE and Cement B, the ettringite appeared not to be responsible for the incompatibilities.

With SNF, the addition of alkalis inhibited the formation of ettringite so that the bridging effect was no longer strong and the dispersing effect by SNF dominated. Most combinations were fully dispersed even with a small amount of alkali addition. Possibly a small amount of alkali was sufficient to increase the surface adsorption, which was quite enough for full dispersion. However, adsorption measurements in this study showed that the total adsorption in some combinations was reduced by the addition of alkali, but those changes may just reflect the statistical variations in the surface adsorption.

Two mechanisms, competitive adsorption between the sulfates and SNF and reduced surface charge on C_3A , have been proposed in literature to explain the improvement in dispersing behavior of cement paste with SNF due to addition of alkalis. Nakajima et al. [13] suggested that the sulfates in the pore solutions affect the performance of SNF by competitive adsorption with SNF. Nawa et al. [5, 6] proposed that alkali sulfates inhibited the adsorption of SNF on C_3A and C_4AF , increasing the adsorption on C_3S and thus dispersing the pastes. Kim et al. [7] further found that not only alkali sulfates but also alkali hydroxide increased the concentration of sulfate ions by increasing the solubility of calcium sulfates in cements. They suggested that the amount of adsorption on C_3A was reduced because the surface potential was reduced at high pH. The increased fluidity by the addition of alkalis can be attributed to both mechanisms [7, 8]. However, we found that the total amount of adsorption was not necessarily reduced by adding alkalis. In contrast, results in this study suggest that the mitigation of the incompatibilities by the addition of

alkalis was a result of reduction in ettringite formation. A link between alkali level and ettringite has also been proposed in previous work. Ghorab and Kishar [14] showed that ettringite decomposed to monosulfate in high alkaline solutions. Their later studies suggested that alkali depressed the formation of ettringite and accelerated the formation of calcium hydroxide [15]. Clark and Brown [16] found that the amount of ettringite was reduced by the increase of sodium hydroxide concentration and suggested that the ettringite formation competed with the formation of calcium hydroxide and the sodium-substituted monosulfate. Taylor et al. [17] reviewed the papers on delayed ettringite formation (DEF) and suggested that high pH favors the presence of monosulfate rather than ettringite. Therefore, assuming that the bridging effect by ettringite was responsible for gelation found in this study, the mitigation of incompatibilities by addition of alkali could be attributed to the reduction in the amount of ettringite.

4. CONCLUSION

Incompatible cement-admixture combinations exhibited high elastic moduli and yield stresses in dynamic rheology. Low-alkali cement had strong incompatibilities with SNF. Those incompatibilities were related to ettringite formation. Addition of alkali hydroxide or alkali sulfate mitigated the incompatibilities by inhibiting the ettringite formation. More subtle incompatibilities were noted with CAE that were mitigated by alkali hydroxide but not by alkali sulfate addition.

5. ACKNOWLEDGEMENT

This work was funded by the Center for Advanced Cement-Based Materials (ACBM). The microscopic observations were carried out in the Center for Microanalysis of Materials, University of Illinois, which is partially supported by the U.S. Department of Energy under grant DEFG02-91-ER45439. The authors thank the staff in Waste Management and Research Center at University of Illinois for analyzing the compositions of the pore solutions and performing total organic carbon analysis. They are also grateful to Professor Zukoski for the use of his experimental facilities.

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