Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 71–78

Importance of adequate soluble alkali content to ensure cement/superplasticizer compatibility

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Manuscript received 25 March 1998; accepted manuscript 1 October 1998

Abstract

The effect of soluble alkalis on cement/superplasticizer compatibility has not yet been thoroughly understood. This paper establishes the impact that soluble alkalis have on the compatibility of cement and polynaphthalene sulfonate superplasticizer during the first few minutes of hydration. The amount of soluble alkalis that go into solution during the first few minutes is a key parameter in controlling fluidity and fluidity loss of a cement paste made with superplasticizer. The optimum soluble alkali content for increasing initial fluidity and decreasing fluidity loss with time was found to be on the order of 0.4%–0.5% Na_2O equivalent in the six cements under study. Furthermore, this optimum alkali content is independent of the superplasticizer dosage and cement type. In cement with an optimum amount of soluble alkalis, the C_3A content has practically no effect on fluidity loss.

Keywords: Alkalis; High-range water reducers; Rheology

In high-performance concrete, which necessarily means superplasticized concrete with a low water-to-cement (w/c) ratio, the high initial workability is sometimes short-lived and followed by a rapid slump loss. In such cases, the cement and superplasticizer are said to be rheologically incompatible.

A literature survey [1] reveals that the rheology of superplasticized high-performance concrete can be affected by many parameters related to the cement, the superplasticizer, or their interaction, namely:

- Chemical and phase compositions of cement, especially C_3A and alkali contents,
- Cement fineness,
- Amount and type of calcium sulfate in the cement,
- Chemical nature and average molecular weight of the superplasticizer,
- Superplasticizer degree of sulfonation and nature of the counter-ion, and
- Superplasticizer dosage and addition method.

The crucial role of sulfates has been underlined in the literature. Several studies on cement and superplasticizer compatibility have looked at calcium sulfate and superplasticizer interactions [2–7]. This phenomenon is usually attributed to changes in the solubility rate of SO_4^{2-} ions. Until now, the literature has focused on the effect of the calcium sulfate (form and content) on cement/superplasticizer compatibility. The effect of alkali sulfate on the rheological behavior of cement paste containing a superplasticizer has received very little attention [8].

When not used with superplasticizers, cements with a high alkali content usually exhibit poorer rheological behavior than their low-alkali counterparts [9]. But when used with polynaphthalene sulfonate (PNS) superplasticizer, it has been advocated that the rheological properties of low-alkali cement pastes can be improved if some alkali sulfate (Na_2SO_4) is added to the mix [8]. On the other hand, it also has been reported that lowering alkali content enhances fluidity of superplasticized mixtures [5,10,11]. Finally, the effect of alkali sulfate on initial fluidity of cement pastes was studied [8], but not on fluidity loss (slump loss) with time.

The objective of this investigation is to highlight the role of soluble alkalis in ensuring compatibility between Portland cement and PNS superplasticizer.

1. Experimental

1.1. Materials

1.1.1. Portland cements

Six commercial cements were used for the investigation. The chemical and phase composition of these cements as

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0008-8846/99/$–see front matter
PII: S0008-8846(98)00179-3

Table 1
Chemical and mineralogical composition of the cements

Chemical composition (%)	C1	C2	C3	C4	C5	C6
SiO_2	21.39	21.53	20.39	21.0	19.93	21.14
Al_2O_3	3.74	3.52	5.02	4.2	4.76	5.23
Fe_2O_3	3.96	4.11	2.20	3.1	3.23	2.04
CaO	65.43	63.69	62.30	61.5	64.95	64.60
MgO	1.40	2.18	2.49	2.6	1.37	2.75
SO_3	1.95	2.85	2.90	3.4	2.67	2.95
K_2O	0.33	0.56	1.05	0.80	0.25	0.21
Na_2O	0.06	0.10	0.22	0.21	0.18	0.18
Na_2O eq.	0.31	0.52	0.92	0.74	0.35	0.31
CaO free	1.82	0.81		0.50		
C_3S	73	66	53	51	69	56
C_2S	6	12	18	20	5	17
C_3A	3	2	10	6	7	11
C_4AF	12	13	7	9	10	6
Blaine (m^2/kg)	420	480	370	410	380	380

well as their fineness are presented in Table 1. Cements C1 and C2 are characterized by low C_3A content and correspond roughly to ASTM type V cement. Cements C3 to C6 correspond to type I cement. The selected cements display a wide composition range: their C_3A contents vary from as low as 2.4% for cement C2 up to 11% for cement C6, according to Bogue composition. Their total Na_2O equivalent contents range from 0.31% for cements C1 and C6 to 0.92% for cement C3.

1.1.2. Superplasticizer

A sodium salt of PNS superplasticizer was used in this investigation. It is an aqueous solution having 41% solids. Its pH (10% solution) is 7.85; its sulfate content is 1.08%; its viscosity is 65 cps (22°C); and its specific gravity is 1.21.

1.2. Measurement and methods

As things stand, there is no way of predicting the rheological behavior of a specific cement and superplasticizer at low w/c ratios simply by looking at their specification sheets. Some initial rheological work with grouts and pastes is necessary. The rheological behavior of cement pastes as a function of time and superplasticizer dosage provides relevant information on key properties, such as slump and slump loss, which can be transferred to fresh concrete. The compatibility of a specific cement and superplasticizer pair in terms of slump loss therefore can be initially studied by measuring the fluidity of the cement paste or grout with a kind of slump test (Kantro mini-slump test) or the Marsh cone flow test [12]. The results obtained with the cement paste have to be validated afterwards on concrete.

1.3. Mixing procedure of cement paste

The cement pastes were prepared at a w/c ratio of 0.35. Superplasticizer was added to the mixing water, which was then mixed with the cement. The paste was initially mixed manually for 1.5 min, then with a high-speed hand-held mixer for 2.5 min to obtain a well-dispersed grout. Mixing was carried out at a controlled temperature of 25 ± 1°C. The superplasticizer concentration in the mix is expressed on a dry mass basis (mass of solids of the superplasticizer relative to the mass of cement).

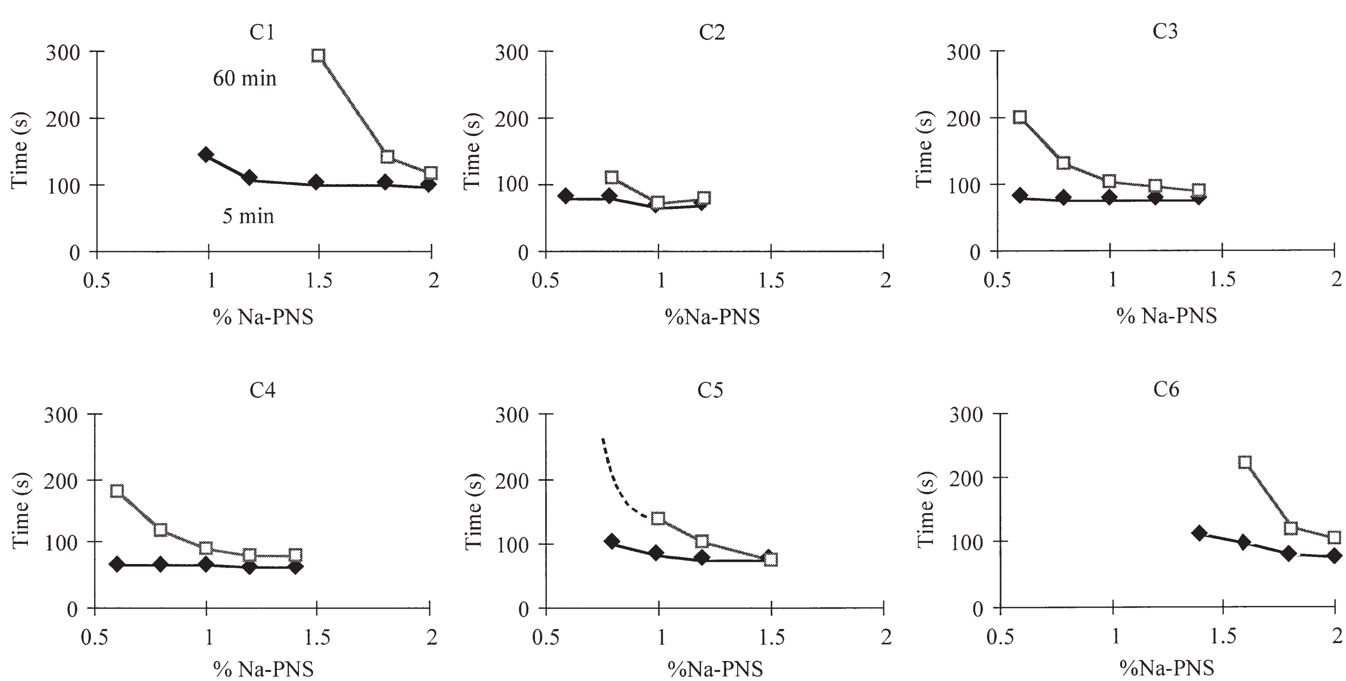

Fig. 1. Marsh cone flow time as a function of superplasticizer dosage for the different cements.

Table 2
Comparison of fluidity of the different cements with the Marsh cone test

Cement	C_3A (%)	Blaine (m^2/kg)	SO_3 %	Na_2O equiv (%)	SP dosage at 1.0% t_5 (s)	SP dosage at 1.0% t_{60} (s)	Saturation point 5 min (SP%)	Saturation point 60 min (SP%)
C1	3.2	420	1.95	0.31	141	n.m.	1.2	1.8–2.0
C2	2.4	480	2.85	0.52	66	74	0.6	0.8–1.0
C3	9.6	370	2.90	0.92	75	105	0.6	1.0
C4	6	410	3.40	0.74	65	90	0.6	0.8–1.0
C5	7	380	2.46	0.35	85	140	0.8	1.2–1.5
C6	11	380	2.40	0.31	n.m.	n.m.	1.4	1.8–2.0

Na_2O equivalent: $Na_2O + 0.658\ K_2O$; n.m., not measurable; SP, superplasticizer.

1.4. Mini-slump test

As indicated by its name, this method consists of carrying out a slump test on a small amount of cement paste. The cement paste is poured into a Plexiglas cone with the same geometry as Abram's cone for regular slump tests, but with reduced dimension (height of 60 mm). The minicone is removed and the diameter of the spread of the cement paste is measured.

1.5. Marsh cone test

The test consists of measuring the time required for 1.0 L of paste to flow through a Marsh cone with a diameter of 5 mm and containing 1.2 L of paste. The flow times at 5 and 60 min after mixing were measured. Between the measurements, the paste was kept in a closed vessel and gently stirred. A more detailed experimental procedure is described elsewhere [12].

1.6. Tests on concrete

The concrete was prepared with a w/c ratio of 0.30. The slump was measured at 10, 30, 60, and 90 min according to ASTM C143-90a. The compressive strength test was carried out on 100 × 200-mm concrete cylinders according to ASTM C39-94. The values given are the averages of the results obtained for three specimens.

2. Results and discussion

2.1. Identification of incompatibility between cements and superplasticizer

The results of Marsh cone measurements for the pastes made with different cement/superplasticizer combinations are shown in Fig. 1. These curves yield a number of parameters that are used to characterize the rheological properties of each cement/superplasticizer combination, namely:

- "Saturation point": the minimum superplasticizer dosage required to achieve constant fluidity at 5 or 60 min;
- Flow time at 5 and 60 min with a superplasticizer dosage of 1.0% and with superplasticizer dosage at the saturation point.

The data presented in Table 2 show that cements C1 and C6 have a double superplasticizer dosage at their saturation point as compared to cements C2, C3, and C4. Cements C1 and C6 recorded much higher flow times than cements C2, C3, and C4 at the same dosage of superplasticizer (1%). The fluidity loss in C1 and C6 was so rapid that the flow time could not be measured at 60 min. Cement C5 presents an intermediate behavior. The comparison of these results clearly indicates that cements C1 and C6 are incompatible with the superplasticizer, that cements C2, C3, and C4 are compatible, and that cement C5 is partially compatible.

The same conclusion also can be drawn from the mini-slump test. As illustrated in Fig. 2, cement C1 showed a greater flow loss when the superplasticizer dosage was lower than 1.0%, whereas cement C2 had a smaller flow loss when the superplasticizer dosage was higher than 0.6%.

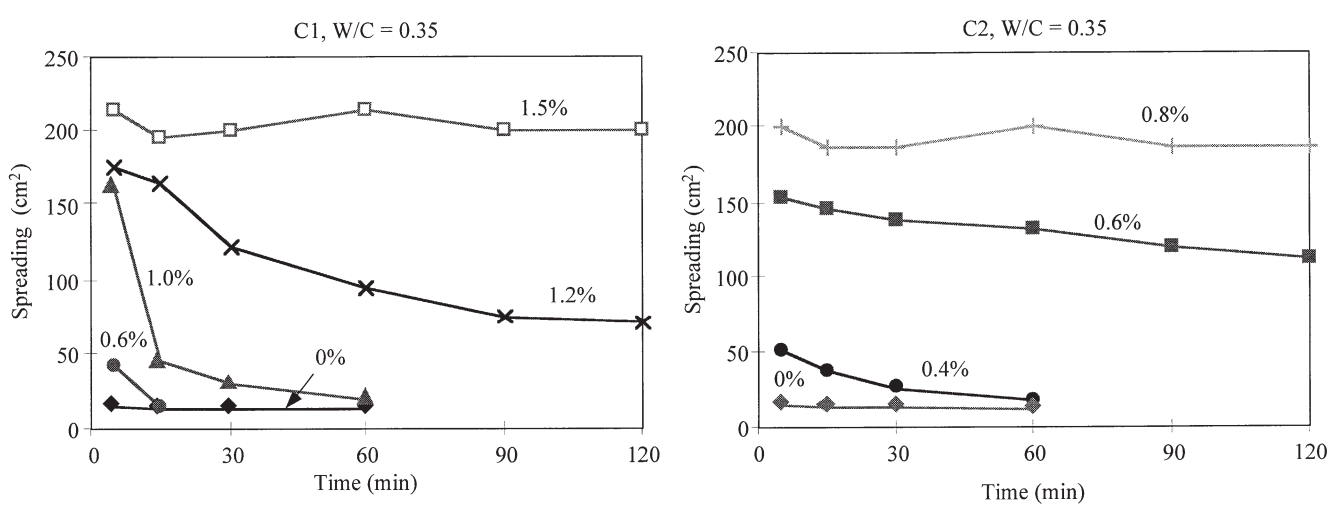

Fig. 2. Mini-slump vs. hydration time at the different superplasticizer dosages.

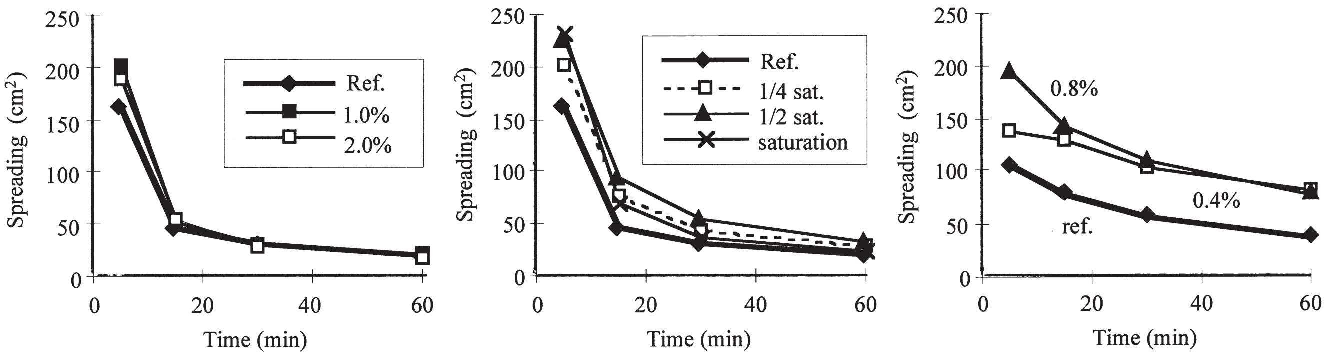

Fig. 3. Effect of calcium sulfate addition on the mini-slump of cement pastes with w/c = 0.35 and 1.0% PNS superplasticizer. Cement C1, addition of gypsum (left panel); cement C1, addition of calcium sulfate solution (middle panel); cement C6, addition of hemihydrate (right panel).

A high dosage (as high as 1.5%) of superplasticizer was needed to overcome the flow loss in cement C1, with the resulting side effects of bleeding and strong retardation.

2.2. Effect of calcium sulfate addition

As suggested by Tagnit-Hamou et al. [13], cement/superplasticizer incompatibility could result from inadequate calcium sulfate in the cement in low w/c ratio pastes with superplasticizer. Indeed, in cements C1 and C6, the SO_3 contents are quite low: 1.95% and 2.40%, respectively. To verify if cements C1 and C6 were actually undersulfated, various amounts of hemihydrate ($CaSO_4 \cdot 1/2H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) of analysis grade were added to the mixture, although the w/c ratio and the superplasticizer dosage remained the same.

Fig. 3 left panel shows the mini-slump results for cement C1 vs. hydration time with 0, 1.0%, and 2.0% gypsum added. With 2.0% gypsum added, the SO_3 content in cement C1 is 2.88%, about the same as cement C2 (2.85%). However, the slump loss of cement C1 was not improved by the addition of gypsum. Considering the low solubility rate of gypsum and in an attempt to increase the initial concentration of sulfate ions, gypsum was dissolved in the mixing water to yield a saturated gypsum solution at 25°C. Although the use of gypsum-saturated mixing water (Fig. 3 middle panel) or the addition of hemihydrate (Fig. 3 right panel), which has higher solubility than gypsum, can increase initial fluidity somewhat, it cannot prevent fluidity loss.

2.3. Effect of alkali sulfate addition

The chemical analysis of the cements also revealed that the alkali contents of cements C1, C5, and C6 (incompatible) were much lower than that of cements C2, C3, and C4 (compatible). Therefore, cement alkali content might be an important parameter affecting the compatibility of the cement with a given superplasticizer.

Depending on the clinker SO_3 content, alkalis in cement can be present as alkali sulfates (Na_2SO_4 or K_2SO_4), and/or double sulfate forms, or trapped in C_3A and C_2S. The ratio of sulfur to total alkali determines the quantity of alkali sulfates in a clinker. When a clinker contains relatively large amounts of SO_3, a substantial fraction of alkalis goes into solution within a few minutes. In low SO_3 clinker, Na_2O

Table 3
Soluble alkali content in the cements as determined by the inductivity coupled plasma method

Cement	C1	C2	C3	C4	C5	C6
Na_2O (%)						
2 min	0.03	0.08	0.13	0.22	0.01	0.01
5 min	0.03	0.08	0.12	0.22	0.01	0.02
15 min	0.03	0.08	0.13	0.23	0.01	0.02
30 min	0.03	0.08	0.12	0.23	0.01	0.02
K_2O (%)						
2 min	0.23	0.49	0.66	0.66	0.07	0.06
5 min	0.24	0.49	0.58	0.71	0.08	0.07
15 min	0.25	0.50	0.68	0.75	0.09	0.07
30 min	0.25	0.50	0.68	0.75	0.09	0.07
Na_2O eq. (%)						
2 min	0.17	0.40	0.56	0.66	0.05	0.05
5 min	0.19	0.40	0.50	0.68	0.06	0.06
15 min	0.19	0.41	0.58	0.72	0.07	0.06
30 min	0.19	0.41	0.57	0.72	0.07	0.06

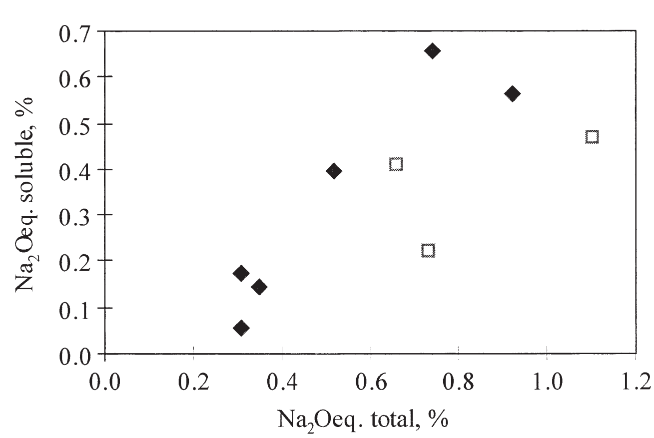

Fig. 4. Relation between the soluble alkali content determined in the first few minutes of hydration and the total alkali content in the cement composition (closed diamond, this study; open square, from ref. 8).

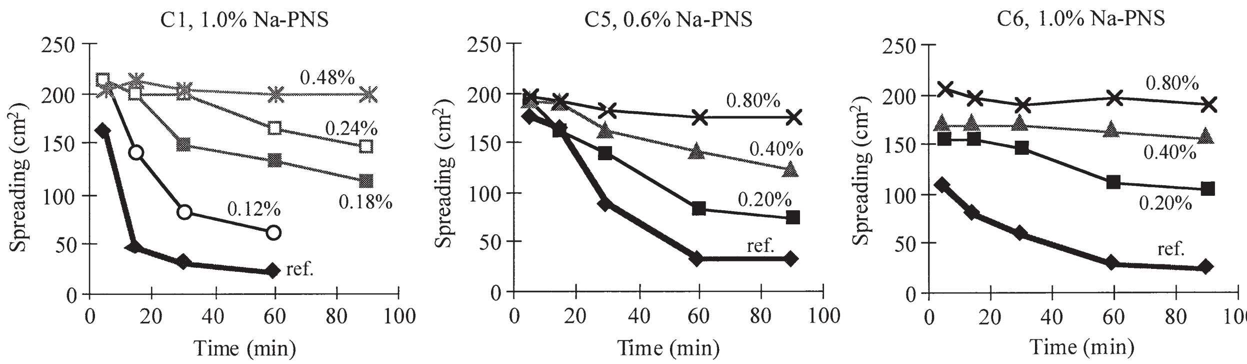

Fig. 5. Effect of sodium sulfate addition on the mini-slump of cement paste with w/c = 0.35 in low-alkali cements (C1, C5, and C6).

and K_2O are incorporated preferentially into the C_3A phase, but also into the C_2S phase of Portland clinker [14]. Therefore, although the cements may have similar SO_3 and total alkali contents, the amount of alkalis that are readily soluble in them can vary widely.

The soluble alkali contents of the tested cements were measured using the inductivity coupled plasma method. The measurements were carried out on the pore solution of cement pastes (w/c = 0.35) with no superplasticizer at 2, 5, 15, and 30 min after mixing. The pore solution was extracted with a pressure filtration device through a 0.45-μm membrane filter at a nitrogen pressure of about 60 psi (0.4 MPa). The filtrate was immediately acidified and diluted to 1:150 with 5% HCl. The results presented in the Table 3 clearly illustrate the rapid solubilization rate of the alkalis in the cements, because almost the maximum alkali concentration was obtained only 2 min after mixing. The results also show that the compatible cements (C2, C3, and C4) contained a much higher amount of soluble alkalis compared to the incompatible ones (C1, C5, and C6). Of course, the amount of alkalis that are readily soluble during the first few minutes cannot be determined from the total alkali content found when analyzing the cement composition. Figure 4 clearly shows that no correlation can be drawn between the soluble alkali content in the first few minutes of hydration and the total alkali content as given by the chemical analysis of the cement.

To determine the role played by the soluble alkalis in controlling the fluidity loss, a sodium sulfate of analysis grade was added to the mixing water so that different soluble alkali contents could be obtained.

Fig. 5 presents the mini-slump vs. hydration time in pastes made with low-alkali cements (C1, C5, and C6, respectively), in which different amounts of sodium sulfate were added. The results indicate that the slump loss at different times continually decreased as the Na_2SO_4 addition increased. When the Na_2SO_4 addition was increased to 0.48% for cement C1 and to 0.80% for cements C5 and C6, the mini-slump spreading area remained at 200 cm^2 for more than 60 min, so slump loss was completely inhibited.

With high-alkali cements (C2, C3, and C4), the addition of Na_2SO_4 decreased initial fluidity and increased the slump loss, as shown in Fig. 6. This inverse effect is particularly noticeable with the Na_2SO_4 addition at 1.0% for C2 and 0.4% for C3 and C4.

Even in low-alkali cements (C1, C5, and C6), an excessive Na_2SO_4 addition increases the slump loss at 60 min, as shown in Fig. 7. Therefore, the curves in Fig. 7 clearly indicate that there is an optimum level of soluble alkali sulfates with respect to initial fluidity and fluidity loss.

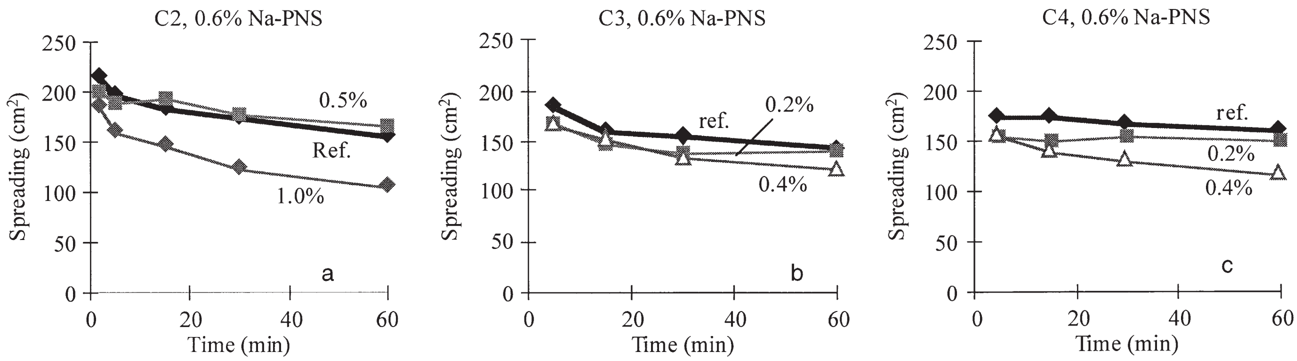

Fig. 6. Effect of Na_2SO_4 addition on mini-slump of cement pastes with w/c = 0.35 in high-alkali cements (C2, C3, and C4).

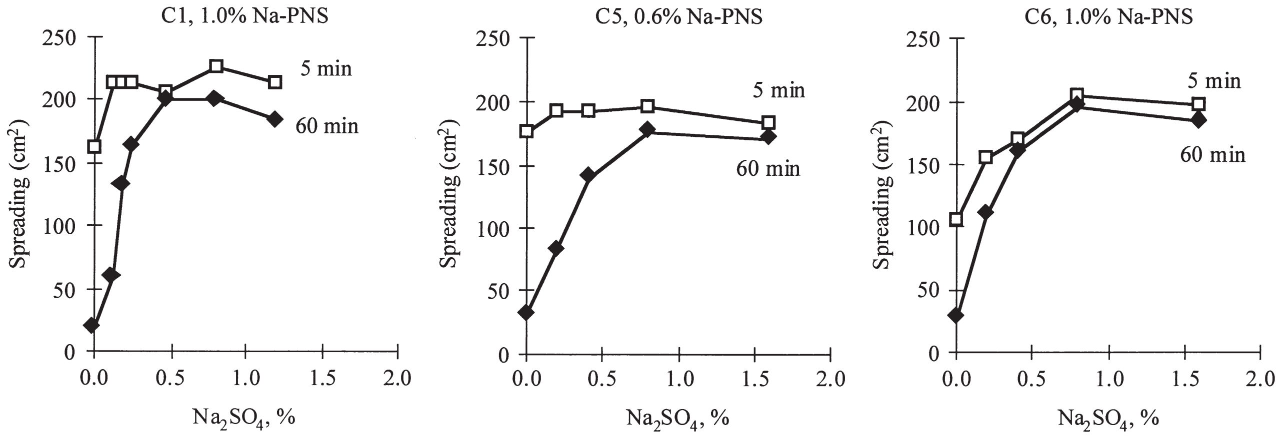

Fig. 7. Effect of Na_2SO_4 addition on slump loss of the cement pastes with w/c = 0.35.

To determine the optimal alkali content, the soluble alkalis contained in the clinker and the soluble alkalis added in the cement mixture must be taken into consideration. The mini slump values at 60 min were plotted vs. the total soluble alkali content represented by the soluble Na_2O equivalent. Fig. 8 left panel shows the results for cement pastes C1 and C6 containing 1.0% superplasticizer. Fig. 8 right panel presents results for cement pastes C2 to C5 containing 0.6% superplasticizer. From the curves in Fig. 8, the following conclusions can be drawn:

- There is an optimum soluble alkali content with respect to fluidity and fluidity loss, which was found to be 0.4–0.5% Na_2O soluble equivalent. At this optimum soluble alkali content, initial fluidity is maximum and fluidity loss is minimum.
- Adding Na_2SO_4 significantly improved fluidity in cements with less than the optimum soluble alkali content, while slightly decreasing fluidity in the cements with more than the optimum content. Therefore, the existence of adequate soluble alkali in the solution during the first few minutes after mixing is of primary importance in ensuring cement/superplasticizer compatibility. In other words, inadequate soluble alkalis in solution during the first few minutes of hydration is more likely to render a cement/superplasticizer combination incompatible than excessive soluble alkalis.
- This optimum alkali content is independent of the superplasticizer dosage and cement type for the cements and superplasticizer tested.
- The soluble alkali content is one of the major parameters controlling fluidity and fluidity loss in cement paste containing superplasticizer. In cement with an optimum amount of soluble alkalis, the C_3A content has practically no effect on fluidity loss.

2.4. Validation on concrete

To confirm that adding alkali sulfate to low-alkali cement can effectively reduce the slump loss of high-perfor-

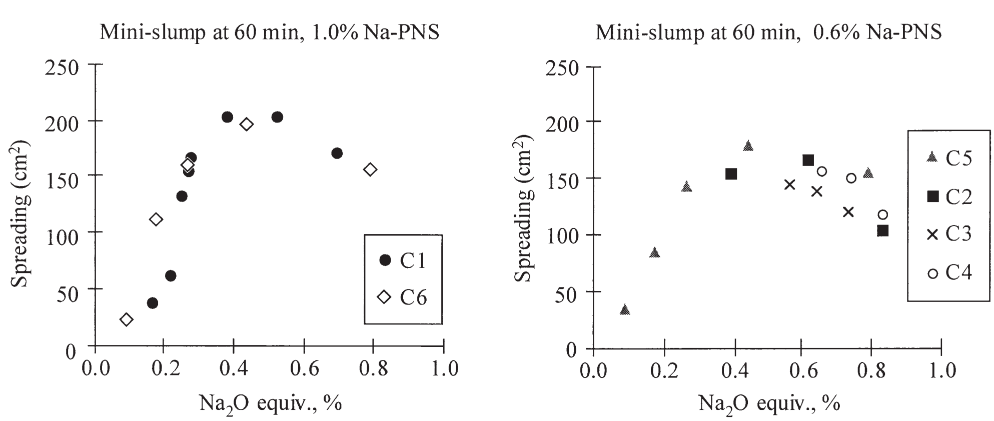

Fig. 8. Relation between the mini-slump test and soluble alkali content.

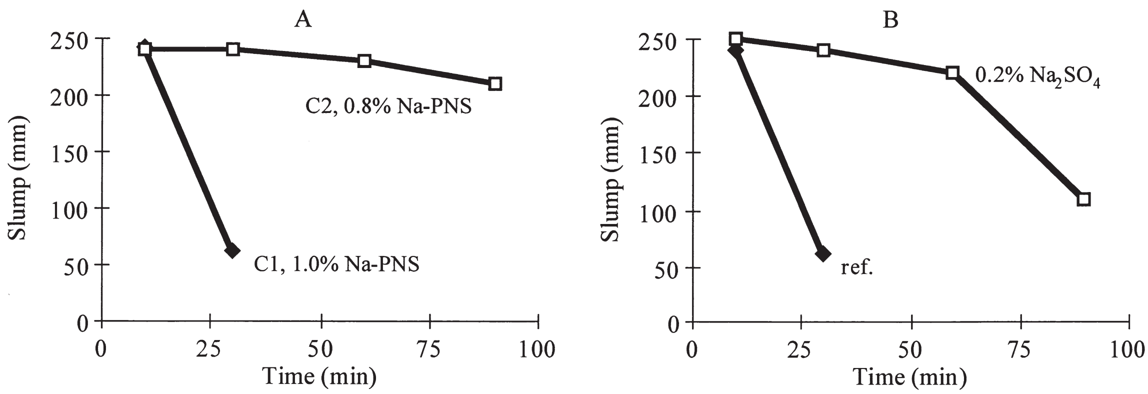

Fig. 9. Concrete slump of cements C1 and C2 with w/c = 0.30. (A) With no Na_2SO_4 added; (B) with Na_2SO_4 added into cement C1.

mance concrete, tests were carried out on concrete made with cements C1 and C2. These mixes had a w/c ratio of 0.30 and comprised 470 kg/m^3 of cement, 810 kg/m^3 of sand, and 1050 kg/m^3 of coarse aggregate. The superplasticizer dosage was adjusted to achieve a constant slump of 220 $\pm$ 20 mm after mixing. For cement C1, 1.0% superplasticizer was added to the mixing water, whereas only 0.8% superplasticizer was needed for cement C2.

Slump loss is compared in Fig. 9A, which shows that cement C1 produced a rapid slump loss at 30 min, whereas cement C2 had practically no slump loss over 90 min. The addition of 0.2% Na_2SO_4 to cement C1 considerably reduced the slump loss during the 90 min, as shown in Fig. 9B. Moreover, the Na_2SO_4 addition to the mixture even positively affected the mechanical strength of the concrete, as shown in Table 4.

3. Conclusions

The importance of soluble alkali in ensuring the compatibility of cement with a PNS superplasticizer has been established. The soluble alkali content was determined during the first few minutes of hydration in a solution extracted from the cement paste with a w/c of 0.35.

There exists an optimum soluble alkali content with respect to the fluidity and fluidity loss, which was found to be 0.4–0.5%Na_2O equivalent. At this optimum alkali content, the initial fluidity is maximum and fluidity loss is minimum. This optimum soluble alkali content is independent of the superplasticizer dosage and cement composition.

Table 4
Compressive strengths of concrete made with cement C1, w/c = 0.30, 1.0% Na-PNS

	24 h	7 days	28 days	91 days
With no Na_2SO_4	41.3	69.7	77.8	85.9
With 0.2% Na_2SO_4	41.6	72.5	80.6	86.8

Cements with less than the optimum soluble alkali content showed significant increases in fluidity when Na_2SO_4 was added. Cements with more than the optimum soluble alkali content showed slightly decreased fluidity with the addition of Na_2SO_4. Therefore, adequate soluble alkali content in the solution during the first few minutes after mixing is of primary importance to ensure cement/superplasticizer compatibility. In other words, if there is not an adequate supply of soluble alkalis in solution, the cement/superplasticizer combination may not be compatible in terms of rheology.

The soluble alkali content is one of the major parameters controlling fluidity and fluidity loss in cement paste containing superplasticizer. In cement with an optimum amount of soluble alkalis, the C_3A content has practically no effect on fluidity loss.

Adding Na_2SO_4 to optimize the soluble alkali content in an incompatible cement/superplasticizer pair is simple and effective in controlling the slump loss of the superplasticized concrete without negatively affecting the initial and final compressive strengths.

The mechanism of action of the soluble alkalis on the initial fluidity and the fluidity loss of superplasticized cement paste or concrete is under study, and our results will be published soon.

Acknowledgments

The authors would like to thank the Association Technique de l'Industrie des Liants Hydrauliques in France and Kyunggi Chemicals Ind. Co. Ltd. in Korea for their financial support.

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