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THE SUPERPLASTICIZER ADSORPTION CAPACITY OF CEMENT PASTES, PORE SOLUTION COMPOSITION, AND PARAMETERS AFFECTING FLOW LOSS

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ABSTRACT

Studies are reported on the interaction of sodium salt of polynaphthalene sulfonate superplasticizer (PNS) with different cement types, its effects on the flow loss, and the chemistry of the pore solution at early time of hydration from mixing to presetting. Six commercial cements displaying a wide compositional range and fineness were selected. Results show that most of the superplasticizer is removed from the pore solution immediately after mixing. The adsorption capacity of the paste is mainly determined by the PNS molecular weight, cement fineness, and C_3A content. In turn, the rate of flow loss appears to be strongly governed by the ionic strength of the pore solution and marginally to C_3A content and ettringite formation. Oversulfating the cements by addition of up to 7% of gypsum, reduces the flow loss but within the range of data available, does not enhance the uptake rate of the superplasticizer by the cement constituents.

Introduction

The production of high strength concrete at a low w:c, requires the use of high-range water reducing admixtures (superplasticizers) to maintain adequate fluidity for placement. It is widely recognized that the improved fluidity mainly derives from a better particle dispersion as the superplasticizer is adsorbed on the cement particles, although other mechanisms, such as, releasing trapped water from cement floc and inhibiting surface hydration of cement particles may augment the fluidity. The negative electrical charge so produced prevents adhesion and flocculation of particles and prolongs setting time, e.g.[1-4] It was noted that the improved fluidity is accompanied by a retardation of the main peak of heat evolution and hydration of C_3S^*.[5,6]

Just as addition of various superplasticizers to the same cement yields different fluidities, the same superplasticizer affects differently various cements.[7,8] Basile et al.[9] showed that the

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higher the molecular weight of sodium salts of polynaphthalene sulfonate superplasticizer (PNS) the longer the dormant period and the later the occurrence of the main peak of heat evolution. In other words, the higher the molecular weight the greater the retardation. They also noted that the lower the monomer content, the higher the fluidity.

The initial greater fluidity of the superplasticized concrete is of short duration and followed by a slump loss.[10] The slump loss was attributed to the reactivity of the cement constituents, especially C_3A, C_4AF, and SO_3 content of the cement and its fineness.[10,11] It was also suggested that due to differences in the solubility rates of the calcium sulfate species, various reaction rates of C_3A with sulfate ions are recorded giving rise to variable slump losses.[12] In view of the practical importance of slump loss control at construction sites, the objectives of this investigation were to evaluate the parameters affecting the uptake of PNS and flow loss of superplasticized pastes, and the role of oversulfatization.

Materials and Method

Characterization of Materials

Table 1 shows the chemical and mineralogical composition of the cements and their fineness. Cement #1 and #2 are characterized by their low C_3A content and correspond to ASTM Type V cement. Cements #5 corresponds to Type I, #4 to Type III, and #6 is white cement. Material designated as #3 was originally Type II clinker that was ground in a laboratory mill to a specific surface of about 300 m^2/kg, and in other two mixtures it was blended manually with gypsum. The cements selected display a wide compositional range. Their C_3A content varies from a low of 2.8% for cement #1 up to 11.7 for the white cement, and their fineness ranges from about 300 to about 530 m^2/kg. A commercial gypsum that was ground in a laboratory mill to a specific surface of about 230 m^2/kg was used throughout. The gypsum contained in a decreasing order minor amounts of dolomite, quartz, and aluminous silicates. A commercial sodium salt of polynaphthalene sulfonate (PNS) was used. Its solid content was 42.1% on dry basis (100^0C) and approximately 65% of it has a molecular weight greater than 5000 g/mol, as determined by ion-pair chromatography.[13]

Differential dissolution was carried out in salicylic acid and the residue of each cement was X-ray diffracted and characterized for its C_3A and $CaSO_4$ polymorphs. Table 2 shows that the C_3A in cements #1, #2, #5, and #6 is cubic, and that in #3 and #4 orthorhombic. Gypsum was the preponderate calcium sulfate in #2 and #6, and hemihydrate in #4 and #5. Cement #1 contained gypsum, anhydrite, and some hemihydrate. Calcite was also detected in some of the cements. Its higher amounts in cement #2, #5, and #6 conformed with the relatively high LOI in these cements.

Paste Preparation and Pore Solution Expression

In order to obtain a measurable fluidity, pastes with and without PNS were prepared at two water to cement ratios of 0.35 for cements No. #1, #2, and #5 and 0.50 for #3, #4, and #6. Gypsum was added to the dry materials at two levels: 3 and 7% to clinker #3 by mass, and 1 and 7% to the other five cements. The PNS dosage was 1% "as is" of the cementitious materials by mass. Additionally, plain pastes (without gypsum addition) were superplasticized with 2% "as is" PNS, and cement #1 was also made with 0.5% "as is" PNS.

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[*] Cement nomenclature is used: C=CaO; $S=SiO_2$; $A=Al_2O_3$; $F=Fe_2O_3$. Thus, C_3S is Ca_3SiO_5, C_4AF is $Ca_4Al_2Fe_2O_{10}$ etc.

Table 1: Chemical and Physical Properties of Materials

No.	#1	#2	#3*	#4	#5	#6	Gypsum
CaO	66.42	65.07	63.19	64.24	62.07	65.69	30.45
SiO_2	23.75	20.56	22.46	21.51	21.16	21.40	6.78
Al_2O_3	2.64	3.56	5.54	4.30	4.31	4.47	1.38
Fe_2O_3	2.52	3.55	2.39	1.81	3.78	0.23	0.53
MgO	1.06	-	3.39	2.54	1.59	0.77	1.25
TiO_2	0.15	0.26	0.26	0.21	0.18	0.17	-
Na_2O	0.09	0.09	-	0.11	0.08	0.06	0.06
K_2O	0.28	0.68	0.81	0.51	0.52	0.27	0.12
SO_3	1.67	3.37	0.68	3.32	3.37	3.15	38.08
LOI	0.65	2.48	0.54	1.03	1.73	1.89	21.23
Bogue Normative Composition							
C_3S	64.3	64.7**	44.3	57.3	48.5	66.7	
C_2S	20.1	12.4	31.5	18.7	24.8	12.2	
C_3A	2.8	3.6	10.7	8.4	5.1	11.7	
C_4AF	7.7	11.2	7.3	5.5	11.6	0.7	
Blaine Fineness m^2/kg							
	305	389	308	530	357	492	230

* Clinker, ** corrected for $CaCO_3$ content.

Table 2 : XRD Analysis of Cementitious Materials (Salicylic acid treated)

	#1	#2	#3	#4	#5	#6
C_3A	cubic	cubic	orthorhombic	orthorhombic	cubic	cubic
Gypsum	present	high	-	trace	-	high
Hemihydrate	minor	-	-	present	present	-
Anhydrite	present	present	-	-	-	minor
Periclase	-	-	present	present	present	-
Calcite	possible	high	-	possible	present	-

Pastes were prepared by introducing the cement into the water within 30 s, manual mixing for one minute, and additional mixing at a high speed with a hand-held mixer for two minutes. Where superplasticizer was used, it was added to the mix water. Similarly, gypsum was manually premixed with the dry cement for two minutes until an apparent uniform mixture was obtained. The paste fluidity was measured by a mini-slump test at 10, 30, 60, 90, and 120 minutes. Evaporable (pore solution) water was expressed by pressure filtration device from a bed of about 75 g of paste that was placed in a pressure chamber at nitrogen pressure of about 50 psi. Membrane filter of 0.45 μm was found to provide the clearest filtrates. The yield of the filtrates ranged from 12 up to 62%. A part of the filtrates were immediately acidified with HCl, diluted 1:50 with deionized water and analyzed for Ca, S, Na, and K. The pH and PNS contents were analyzed on the rest of it.

Analysis Procedure and Instrumentation

The mineralogical composition of the cements and gypsum was carried out by XRD (Rigaku). The following analytical data were kindly provided by Prof. C. Jolicoeur and Mr. M-A Simard: cement composition by XRF (Kevex 0700); filtrate composition (Ca, S, Na, and K) and alkali content of the cements by ICP (ARL 3560 AES); PNS concentration in the filtrates as measured at the peak absorbance wavelength (usually near 276 nm) by Hewlett-Packard diode array UV-visible spectrometer, and the pH of the filtrate by Orion pH meter.

Results and Discussion

I. PNS Absorbance

Since the improved fluidity is related to the adsorption of the superplasticizer on the cement particles, its removal from the pore solution is of special interest. A wide range of uptake rates of PNS is reported in the literature. According to Matsukawa and Diamond,[14] about 25% of it was removed form the pore solution immediately after mixing, about 30% in less than 6 h, and about 90 % by 24 h. They suggested that the uptake rate of the PNS from the pore solution is parallel to the degree of hydration and can be interpreted as an effective removal of it by the hydrated phases. Luke and Aitcin reported another set of data: 30% < 5 minutes, 40% < 2 h, and about 90% after 2 days.[15] Higher removal rates ranging from 39 to 78% after mixing were given by Uchikawa et al.,[5] and still higher rates are presented in this study: 10 minutes after mixing about 51 to 94% of the PNS was absorbed.

It was noted that the degree of PNS uptake is related to the degree of polymerization. Monomer, dimer, and probably other low molecular weight polymers are more likely to remain differentially in the pore solution, while higher molecular weight polymers are absorbed on the cement particles.[16] Indeed, Figure 1 shows that the PNS peak is shifted from 294 nm for the "as is" material to about 276 nm as is measured in the pore solution of the superplasticized paste. In accordance with the above data, this shift corresponds to the presence of molecules of low degree of polymerization in the pore solution.

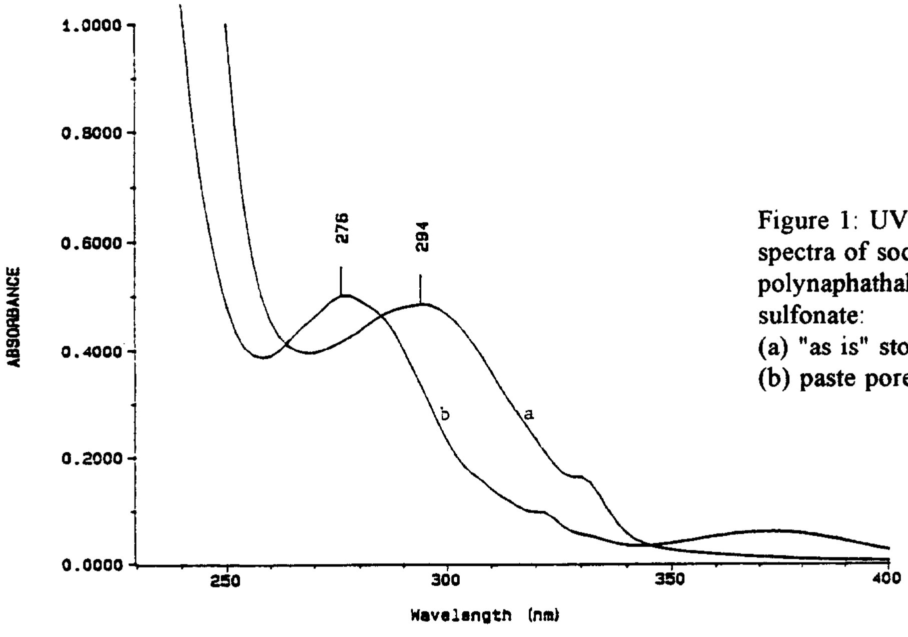

Figure 1: UV-absorption spectra of sodium polynaphathalene sulfonate:
(a) "as is" stock solution
(b) paste pore solution.

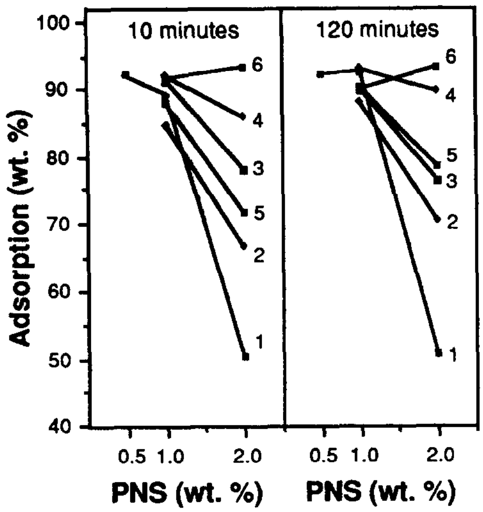

Figure 2. Adsorption vs PNS content. The cements are designated by numbers.

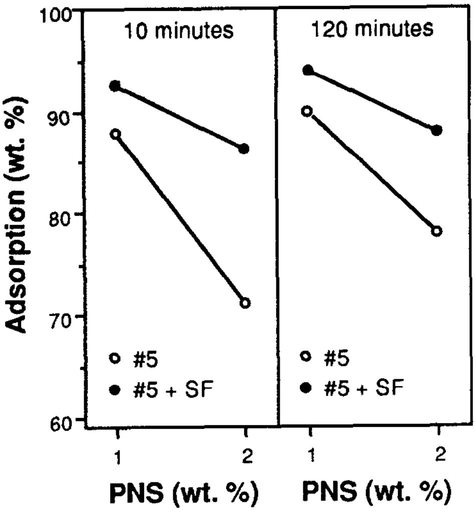

Figure 3. Adsorption vs PNS content on cement #5 with and without 10% silica fume.

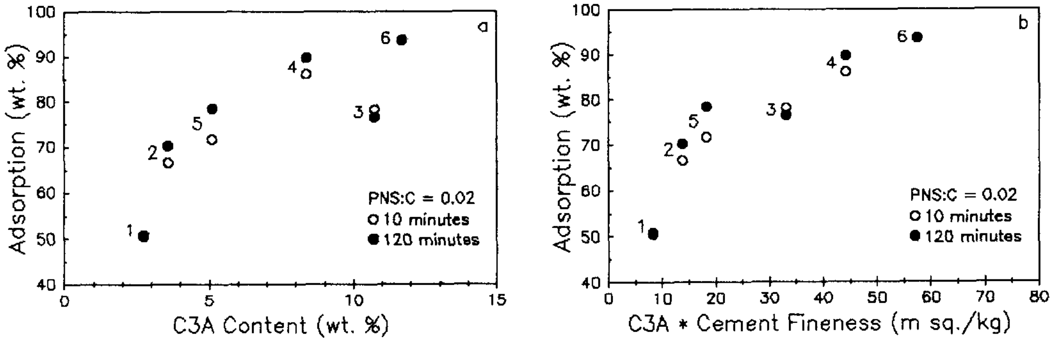

Figure 4: (a) Adsorption vs C_3A content. (b) Adsorption vs the product of C_3A fraction in the cement times cement fineness (m^2/kg). The cements are designated by their numbers.

Figure 2 shows the adsorption percentage of the PNS at 10 and 120 minutes after mixing. Several features can be seen: (a) The increase of the PNS dosage from 0.5 to 1% has little effect on the relative adsorption of the PNS on cement #1. However, by increasing the PNS content from 1 to 2%, a wide range of relative adsorption is displayed. (b) At 10 minutes and 1% PNS addition, the adsorption varies in a relatively small range from a low of about 85% for cement #2 to a high of 92% for cements #4 and #6. In turn, the corresponding range at 2% addition is from about 51 to 94%. (c) The adsorption tends to increase marginally from 10 to 120 minutes at both 1 and 2% PNS levels, otherwise the adsorption patterns are quite similar.

At PNS dosage of 2%, cements #4 and #6 display the highest relative adsorption, whereas cements #1 and #2 have the lowest values. The former are characterized by their high specific surface of about 500 m^2/kg and the latter by their lower C_3A content. It seems therefore, that both cement fineness and composition affect the degree of adsorption.

In another experiment aimed at evaluating the role of fineness, silica fume with a specific surface of about 20 000 m^2/kg replaced 10% of cement #5 by mass. As is illustrated in Figure 3, silica fume addition notably increased the PNS adsorption at both 10 and 120 minutes. Figure 4a depicts a definite correlation between the adsorption and C_3A content. A better correlation is yielded by plotting adsorption against the product of the C_3A fraction times the cement fineness (Fig. 4b). To be noted is that despite the distinct relations presented in Fig. 4a,b, a consistent and "universal" correlation between the C_3A content and PNS adsorption may not be attained, as the C_3A crystals in the cement neither appear as separate particles nor are they exposed preferentially on the surface of other polymineralic particles.[17] In contrast to Hanna et al.,[11] no obvious correlation of C_3A + C_4AF content and adsorption was observed. These results are in a partial accord with Uchikawa et al.'s study[5] suggesting a differential adsorption of PNS on the cement particles. Accordingly, the PNS forms a thick layer about 300 nm wide on the interstitial phases but only 50 nm wide on alite.

Based on these data, the mechanism of adsorption can be interpreted as follows: at low PNS dosage, the PNS is immediately absorbed on the cement particles, and the degree of PNS polymerization and cement fineness exert major control on the adsorption level. This initial level is maintained as long as the superplasticizer dosage is below a certain limit. Further increase of the PNS dosage (in this case from 1 to 2%) does not necessarily increase the total amount of PNS absorbed, but the adsorption is compositionally controlled: cements with low C_3A content, such as, #1 has a low adsorption capacity and the increase of the PNS content from 1 to 2% follows a marginal increase in the total adsorption (thus, it is relatively decreased by about 40%). On the other hand, cement #6 which is characterized by its high specific area and C_3A content has a large adsorption capacity (greater than 2% PNS) and maintains its relatively high adsorption level up to the PNS dosage used.

Attention is drawn to two more features. Oversulfating the cements with 1 and 7% gypsum does not affect the adsorption, and in the present study no direct correlation between the adsorption and C_3A type (e.g. cubic or orthorhombic) was established.

II. Evolution of Pore Solution Composition

Pore solution analyses have been carried out for a number of years by various workers. To be reiterated, the Ca, S, Na, and K content of the pore solution was measured by ICP, whereas the OH concentration was calculated from the measured pH. Since the pH is an activity measurement, one may postulate that the activity coefficient of the OH in high ionic strength solutions, such as, pore solutions is lower than 1. Thus, the actual OH concentration should be somewhat higher than the calculated one. With this reservation in view, the pore solution composition of the pastes is presented in Figure 5.

It is widely accepted that the pore solution is saturated with respect to $Ca(OH)_2$.[18] From thermodynamic considerations the solubility of $Ca(OH)_2$ should decrease as OH increases. But, apart from the difficulties involving the calculation of the ion concentration from the solubility product in solutions of high ionic strength,[19,20] the Ca ion concentration is affected by other ions. Rechenberg and Sprung[21] have shown that a higher Ca ion concentration always occurs in the presence of sulfate ions, but its concentration is depressed when the content of alkali and sulfate ions increases. This in turn increases the OH content.

As expected, Ca ions are inversely proportional to OH concentration, and their content

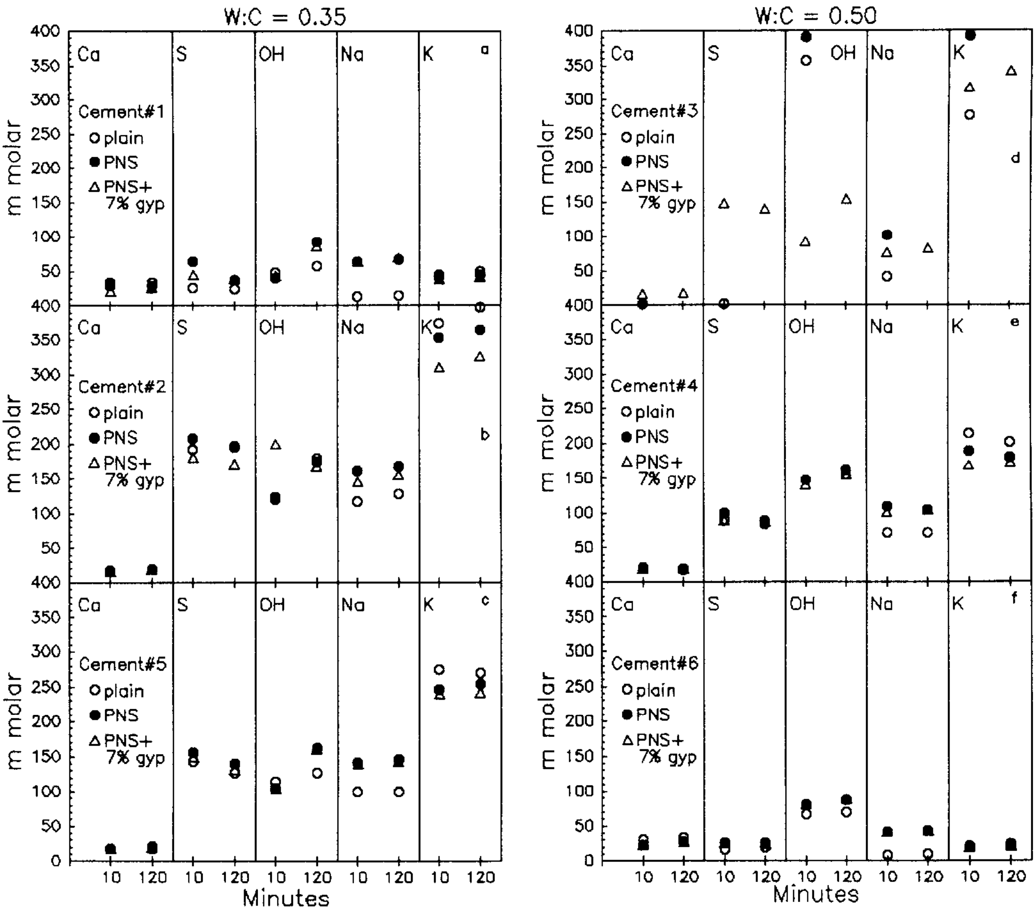

Figure 5. Evolution of pore solution composition at 10 and 120 minutes of hydration.

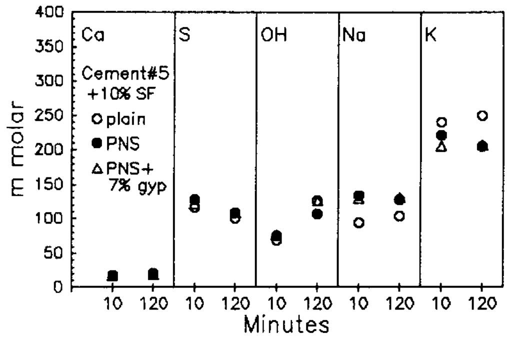

Figure 6. Evolution of the pore solution of cement #5 with 10% silica fume at 10 and 120 minutes of hydration.

is higher than that derived from the corresponding concentration in pure $Ca(OH)_2$ solution. In agreement with Moragues et al.,[22] the plotted points in a Ca^{2+} vs OH^- diagram lie above the theoretical curves for $Ca(OH)_2$ and sulfate-containing $Ca(OH)_2$ solutions. In addition, in the presence of soluble sulfate, it appears that in a cement system the OH concentration does not exceed 0.2 molar (~ pH 13.3). Only if no or small amount of sulfate is present (clinker #3), the OH approaches higher levels.

In the plain pastes, Ca ion concentration tends to slightly increase from 10 to 120 minutes along with an increase in Na, K, and OH concentrations, and a decrease in SO_4^- content. Incorporation of PNS and gypsum further complicates the pore solution chemistry. Presence of soluble alkali sulfate (syngenite was detected by TGA in cement #2) or hemihydrate (#4 and #5) results in a rapid build-up of sulfate ions in the pore solution. Addition of sodium PNS always increases the S and Na concentrations, whereas K and to a lesser extent, Ca decrease. Overdosing the superplasticized pastes with gypsum tends to suppress the concentrations of all the ions measured; especially that of the alkalies. A partial explanation to the latter effect may be related to the dilution effect. Interestingly, potassium reaches its highest levels in the plain pastes and it decreases as PNS and gypsum are added.

The ionic strength of the pore solution of the plain pastes varies widely from 0.15 molar for cement #6, 0.17 for #1, 0.35 for clinker #3 (0.59 with 7% gypsum), 0.43 for #4, 0.56 for #5 and up to 0.76 for #2. Evidently, the ionic strength is correlated neither to the C_3S nor to the C_3A content of the cements. Rather, it is primarily determined by the presence of alkali sulfate or soluble Ca sulfate and alkali. For example, the higher ionic strength of cement #2 can be attributed to the presence of syngenite. It was noted that silica fume addition to cement #5 reduces the ionic strength, and is especially effective in reducing sulfate, potassium, and OH concentrations (Figure 6).

III. Flow Loss of Superplasticized Pastes

Figure 7 depicts the fluidity of the pastes over time. The pastes are characterized by different initial flows and flow loss rates. The initial flow of heavily suspended solutions, such as, cement paste primarily depends on physical considerations, i. e., particle size distribution, shape factor, and the aspect ratio of the particles. Lack of this kind of information hinders a comprehensive comparison of the initial flow of the pastes. However, four distinct features are readily seen: (a) without PNS addition, pastes made with cements relatively low in C_3A and fineness (i.e., #1, #2, and #5) had greater fluidity for the same water to cement ratio than pastes made with cements high in C_3A and fineness (#4 and #6), (b) in all cases, 1% PNS addition improves the initial flow (as measured by the pat diameter) by 20 to 100%, (c) oversulfating the superplasticized pastes with 7% gypsum improves the flow, and (d) the pastes can be grouped into those that display sub parallel flow patterns (cements #1 and #6), and those exhibiting intercepting patterns (#2, #4,and #5). The latter group is characterized by a greater flow loss rate of the superplasticized and oversulfated pastes than that of the plain pastes. Clinker #3 displays a flash set, hence, cannot be directly compared, but it appears to belong to the second group.

By comparing Figs. 2 and 7 it can be seen that the initial flow is not directly related to the adsorption level. In part, this may be attributed to the narrow range of adsorption level when 1% PNS is added. It should be noted however, that the adsorption and flow loss are inversely proportioned over time, and that the increase of adsorption from 10 to 120 minutes does not prevent flow loss. This behavior illustrates the short-term repulsive forces generated by the superplasticizer.

The division of the flow patterns to sub parallel (cements #1 and #6) and intercepting one (all the others) neither corresponds to the water to cement ratio nor to C_3A content. Rather, these two groups are distinguishable by their ionic strength, being low for the former and relatively high for the latter. A plot of the flow and flow loss vs C_3A content (Fig.8) yields a poor correlation, especially as far as the flow loss is concerned. The flow loss can be regarded as a more sensitive indicator than the total flow since it records internal changes; in particular those

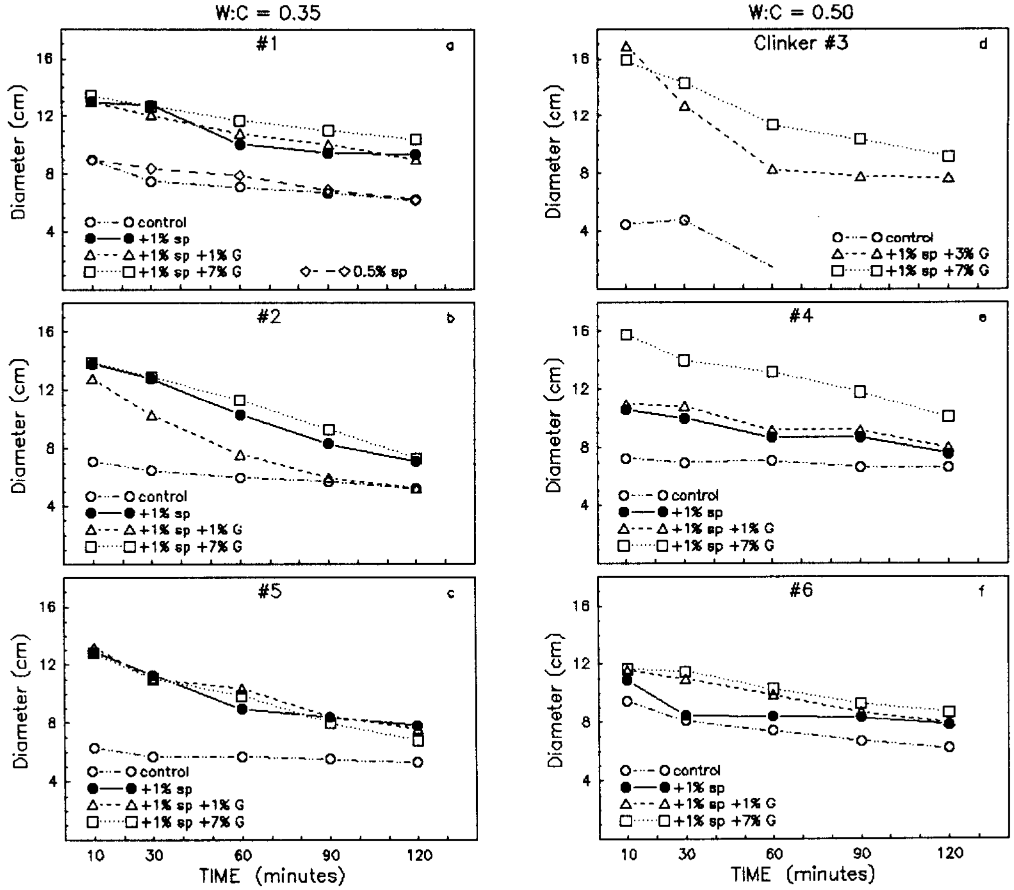

Figure 7: Fluidity of pastes vs time.

that take place after the rapid precipitation of ettringite that follows initial hydration. On the other hand, Figure 9 displays an obvious correlation between the flow and flow loss vs the ionic strength. The higher the ionic strength the greater the flow loss and the lower the flow at 120 minutes.

Since ettringite requires C_3A for its formation, a greater amount of it is expected to be formed in C_3A-rich cement. However, the flow loss appears to be closely related to the chemistry of the pore solution rather than the C_3A content. It suggests therefore, that the flow loss does not correspond to the amount of ettringite formed. This line of reasoning is in accord with the XRD data of the pastes. Figure 10 shows the diffraction patterns of the superplasticized pastes No. #1, #2, and #6 after 120 minutes of hydration. A notable ettringite peak appears in #6, traceable in #2, and questionable in #1. Pastes No. #1 and #6 have the lowest ionic strength and flow loss. Paste #2 has the highest ionic strength and high flow loss. This observation is in a good agreement with a recent study indicating that setting is related to C_3S hydration, but neither to ettringite formation nor to secondary ettringite recrystallization that may form a three dimensional network comprising large ettringite needles that arrest fluidity.[23]

Glasser et al.[24] have shown that in plain paste potassium is mainly concentrated in the

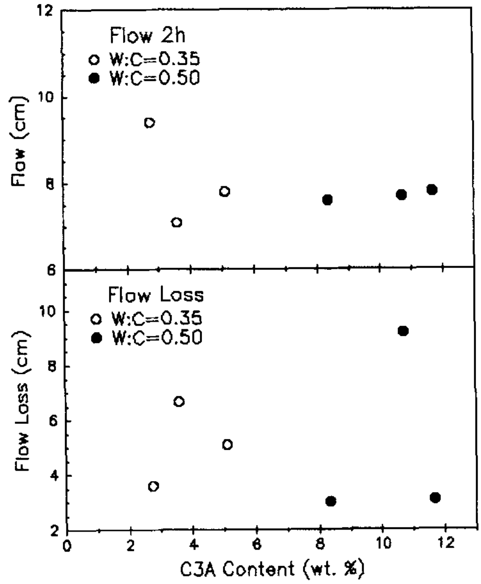

Figure 8. Flow and flow loss vs C_3A content.

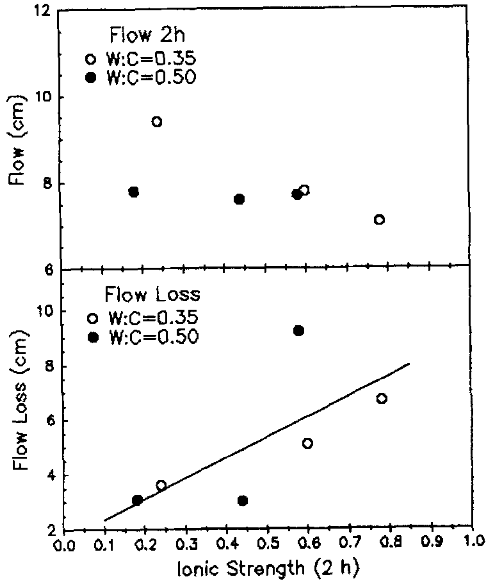

Figure 9. Flow and flow loss vs ionic strength.

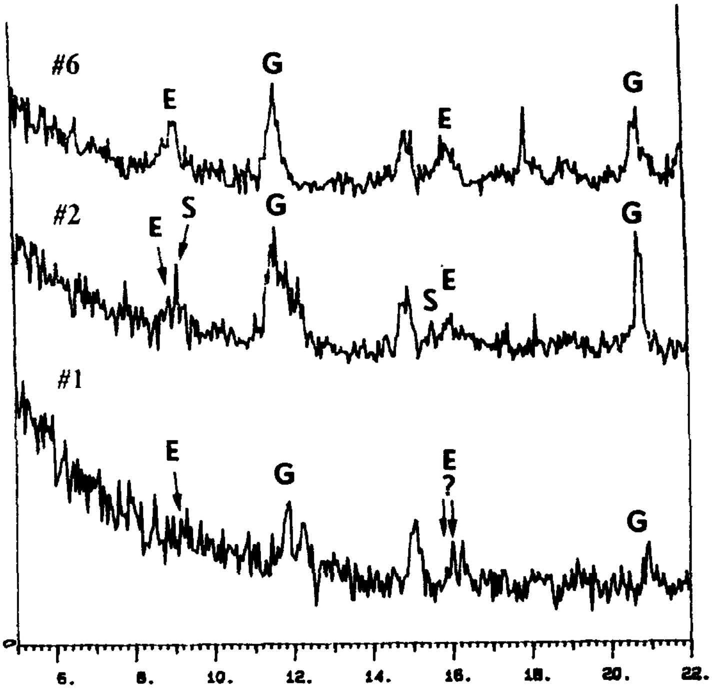

Figure 10. XRD patterns of the superplasticized pastes of cements No #1, #2, and #6 at 120 minutes of hydration.
E designates ettringite, G=gypsum, and S=syngenite. Figures on the abscissa are given in terms of $2\theta^0$ (Cu Kα).

pore solution. Nonetheless, the potassium concentration decreases as PNS is introduced, so do the ion concentrations of sodium, and sulfate when a distinct amount of gypsum is added. Potassium may substitute for Na in the superplasticizer, but the overall ion decrease suggests that at high ionic strength some alkali sulfate salts precipitate and remove the corresponding ions from solution. Several researchers noted a deposition of syngenite from the pore solution that may also lead to a rapid set.[21,25] The presence of syngenite could not be unambiguously established by the XRD patterns presented. If excessive amount of alkali sulfate does not deposit, does the flow loss observed relate to alkali sulfate deposition? One criticism of such an interpretation is that the fluidity of the oversulfated pastes is greater than that of the superplasticized pastes. It appears therefore, that similarly to ettringite deposition the alkali sulfate formation in the pastes studied did not effectively reduce the flow.

Another explanation for the flow loss concerns with the enhancement of C-S-H formation at high ionic strength environment. It is noteworthy to mention however, that the flow loss reported above took place significantly prior to the initial set of the cements as is determined by the Vicat test (ASTM C-191). Namely, most or all of it occurred during the dormant period where the heat evolution is minimum, thus limited precipitation can be anticipated. Alternatively, the slump loss may be related to the chemical properties of the fluid paste. It may be predicted that the negatively charged surfaces of the cement particles are more affected by a strong electrolyte in the pore solution rather than a weaker one. High strength pore solution will induces a greater polarization of the double surface layer formed around the particles and this in turn, would probably generate more electrostatic bonds that reduce fluidity. In this regard, the improved fluidity observed when gypsum was added is in line with the decease of the ionic strength of the pastes.

Conclusions

The flow behavior of superplasticized cement pastes, examined in conjunction with the pore solution evolution offers some interesting new insights on the adsorption mechanism of action and functional properties of polynaphthalene sulfonate superplasticizer. Amongst the observations and trends noted, the following appear significant:

1. The adsorption capacity of PNS is mainly determined by degree of polymerization of the PNS, cement fineness, and C_3A content.
2. In cement pastes prepared with the PNS used at concentration of 1% (0.4% solid), most of the superplasticizer is adsorbed (85-93%) on the cement particles, independently of the cement characteristics.
3. The ionic strength of the pore solution is mainly governed by the presence of alkali sulfate or soluble Ca sulfate and alkali. PNS addition increases the ionic strength.
4. Silica fume addition increases the amount of PNS adsorbed and decreases the ionic strength.
5. The initial flow is mainly governed by the fineness and C_3A content of the cement. Flow loss in turn, is best correlated with the ionic strength of the pore solutions. The C_3A and ettringite contents has a marginal effect on it. The greater rate of flow loss in high ionic strength pore solution is mainly attributed to a greater electrostatic attraction.
6. Oversulfatization reduce the ionic strength and improves fluidity.

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