Influence of cement and plasticizer type on the heat of hydration

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Abstract
The influence of interactions between different cement and plasticizer types on heat of hydration has been investigated. Six cements with different dosages of naphtalene, lignosulphonate and polyacrylate based plasticizers were used. The admixtures were found to alter the hydration sequence as well as prolong the induction period of the cements. Cement fineness and content of cubic C_3A were found to be of particular importance concerning initial heat rate and duration of the induction period. The duration of the induction period decreased, moreover, with increasing content of easily soluble alkali in the cements.

1. Introduction
Rheology of cementitious pastes depends on the adsorptive behaviour of the admixtures and their interaction with the cement [1,2]. Rheological parameters can only give indirect measures of the cement-admixture interactions. This work investigates, therefore, the influence of cement and plasticizer type on the reactivity of paste by isothermal calorimetry.

2. Materials
Three different categories of plasticizers have been studied namely
- Sodium lignosulphonate (LS) sugar reduced and molecular size enriched by ultra filtration. The molecular weight of the polymer was 51,000.
- Sodium naphthalene sulphonate – formaldehyde condensate (SNF) in water solution with 42 % solids. The number of structural units (n) in the SNF molecule was presumably between 10 and 20. The molecular weight is 2,350 for n = 10 and 4,700 for n = 20.
- Polyether grafted polyacrylate (PA) water solution containing 18 % solids and a viscosifying agent. The molecular weight of the polyacrylate was 220,000.

Table 1 shows the mineralogy of the six cements in the study determined by multicomponent Rietveld analyses of XRD profiles, specific surface determined by the Blaine method and content of easily soluble alkalis determined by plasma emission spectrometry.

Table 1: Mineral composition (%) and alkali content of Portland cements obtained by QXRD and plasma emission spectrometry

Cement no.	1	2	3	4	5	6
Cement Type	CEM I 42.5 RR	CEM I 42.5 R	CEM II A-V 42.5 R	CEM I 52.5 R-LA	CEM I 42.5 R-LA	CEM I 42.5 N
Alite	64.7	66.0	60.3	65.0	61.9	51.6
Belite	14.8	9.4	7.1	12.9	19.7	17.3
Ferrite	7.5	8.7	7.1	9.6	12.0	5.4
Cubic Aluminate	5.9	3.4	3.1	0.5	0.4	3.6
Orthorhombic Aluminate	1.1	1.7	3.4	3.0	1.7	8.7
Lime	1.0	1.2	0.2	0.6	0.7	0.4
Periclase	1.6	1.2	1.7	0.3	0.4	0.9
Gypsum	0.0	0.2	0.0	1.4	1.3	3.2
Hemihydrate	1.8	2.0	2.1	1.5	0.4	1.2
Anhydrite	0.6	0.5	0.4	0.4	0.4	0.8
Calcite	0.5	4.6	0.6	4.0	0.7	4.3
Portlandite	0.3	0.4	0.5	0.3	0.2	0.4
Quartz	0.0	0.4	1.5	0.4	0.2	0.4
Arcanite	0.3	0.4	0.1	0.0	0.0	1.8
Mullite	-	-	2.6	-	-	-
Amorphous	-	-	9.3	-	-	-
Blaine	546	360	467	364	447	308
K (%)	0.92	0.88	0.58	0.32	0.36	0.42
Na (%)	0.22	0.17	0.12	0.74	0.84	0.04
Na_{eqv} (%)	0.76	0.69	0.46	0.26	0.30	0.29

3. Heat of hydration measurements

An 8 channel TAM Air Isothermal Calorimeter from Thermometric AB, Sweden was used for the heat of hydration measurements. The temperature was set to 20°C and data points were recorded every 30 seconds. The initial hydration peak was measured separately from the main peaks. Pastes for initial heat of hydration measurements were prepared by weighing 5 grams of cement into glass ampoules which were loaded into the calorimeter. Solutions of the three plasticizers SNF, LS and PA were added to the cements in a dosage of 0.32% by cement weight. The w/c was 0.4 for all measurements. The samples were mixed internally in the calorimeter for one minute with a stirrer produced by Thermometric AB. The heat of hydration was logged until the start of the induction period which appeared approximately 1 hour after water addition.

Cements 1-4 and 6 were used for measurements of the main heat of hydration peaks. Cement number 5 was not studied since it was not available at the time of measurement. 6 grams of cement were weighed

into glass ampoules. The dosages of superplasticizers were 0.0, 0.32% and 0.80% of cement weight and the w/c was 0.4 for all pastes. The samples were mixed in a motorized stirrer (IKA-WERK, RM 18 (60 Watt)) from Janke & Kunkel KG, for two minutes. The ampoules were sealed with aluminium caps and inserted into the calorimeter. The heat of hydration was logged until 72 hours after water addition.

4. Results and discussion

Examples of measured initial heat of hydration peaks are depicted in Figure 1. The endothermic peaks occurring in the first minute after mixing are probably caused by dissolution of potassium sulphate in the mixing water [3]. The figure shows that the rate of heat development depends on the superplasticizer type: Pastes with LS have a lower maximum hydration rate than pastes with PA and SNF and they hydrate over a longer time span. The shapes of the initial heat peaks were similar for all cement types tested.
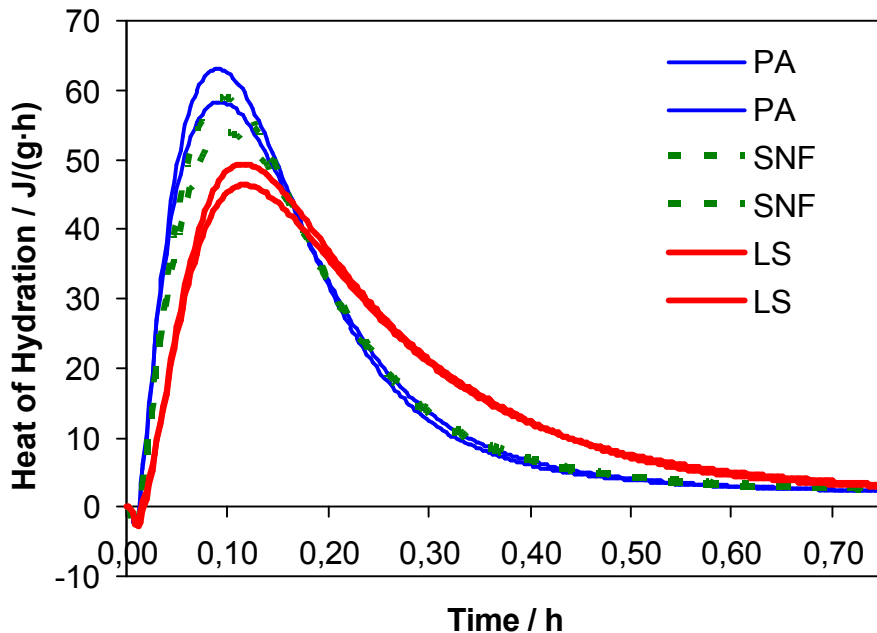

Figure 1: Initial heat of hydration peaks for Cement 2 with 0.32% PA (top), SNF(middle) and LS (bottom) . Two parallels are performed for each measurement.

Table 2 recites the time of occurrence of the maximum heat rate for the different cement and plasticizer combinations. The data illustrate that the time of the maximum initial hydration occurs within the first few minutes for all plasticizer and cement combinations. Cement 3 was strongly retarded with all plasticizer types compared with the other cements. Some of the retardation might be caused by the 16.3% inter-ground fly ash in this cement. It has been reported that fly ash might result in a retarding effect

for C_3A [4]. The effect of fly ash on the hydration of C_3S has, however, been debated [4,5]: The discrepancies found in literature may be caused by different origin of the fly ashes used since they may have even more variable chemistry than cements. Fly ash might, moreover, inhibit different plasticizer adsorption capacity than cement [2,6]. A low adsorption capacity leaves more plasticizer for the cement compared to the unblended cements which in turn might lead to a more retarded cement hydration.

Table 2: Times of maximum heat rate development for all cement and plasticizer combinations.

Cement number	Time of peak (min)		
	PA	SNF	LS
1	4.3	4.0	5.3
2	5.5	6.2	7.1
3	12.7	11.8	15.7
4	7.7	7.7	13.7
5	6.0	6.0	7.1
6	3.4	3.4	3.8

The heat of hydration curves were used to investigate if any correlations could be found between the initial heat of hydration peak and cement characteristics. Integration of the heat evolution curves proved to be difficult since it was hard to define an end point of the initial hydration curve. The maximal rate of heat evolution (top point of the curve) was therefore chosen as a correlation variable.

As expected, no correlations were found between the maximal rate of heat evolution and the silicate phases alite and belite. Correlations between maximal heat rate and the single cement variables C_4AF and total amount of C_3A were also poor. There was, however, a correlation between the product of the cement fineness and C_3A content if the fly ash cement was left out of the plot as illustrated for pastes with LS in Figure 2 (see the discussion about the influence of fly ash above). This finding illustrates that cement cannot be treated as a univariable material. Similar correlations were found for pastes with PA and SNF, but the correlation coefficients were somewhat poorer (0.87 and 0.81 respectively). The unfavorable regression coefficients ($R^2 < 0.9$) may partly be caused by agglomerates which remained undispersed after mixing the pastes internally in the calorimeter. This mixing method makes measurement of the initial hydration peak possible, but prevents visual control of the fresh paste.
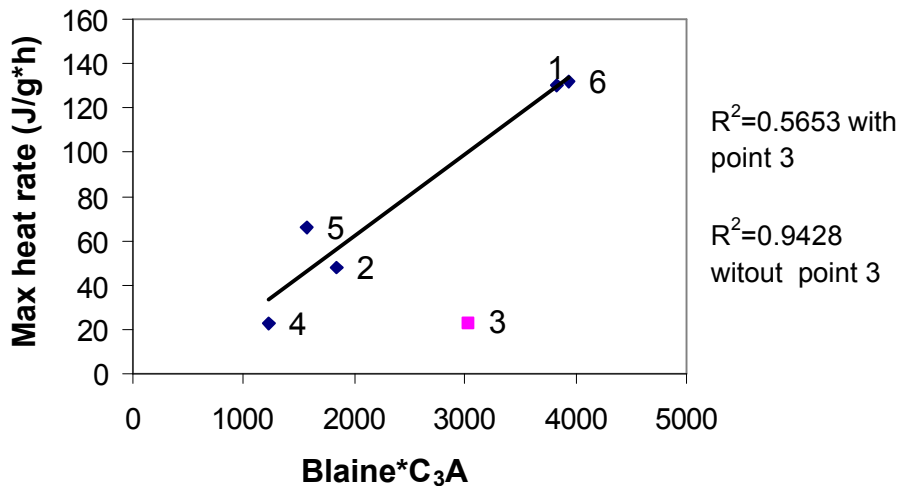
Figure 2: Correlation between maximum heat rates at the initial peak of hydration against the product of the cement fineness (Blaine) with the total amount of C_3A for the cements 1-6 with 0.32% LS.

The admixtures prolonged the dormant period and changed the hydration sequence as illustrated by PA and SNF in Figure 3. The shape of the calorimetric curves of Cement 6 with LS and PA resembled each other even though LS prolonged the duration period to a much higher extent than PA (see Figure 4). SNF had the least effect on the duration of the dormant period and thus more overlapping heat of hydration curves than pastes with PA and LS at the given plasticizer concentrations. Figure 3 illustrates that the heat of hydration curve for Cement 6 has three main peaks when no superplasticizer is added. The first peak is normally interpreted as CSH and CH formation, while the origin of the second peak has been associated with renewed AFt formation [3,7]. The third peak has been connected with hydration of the ferrite phase [8] or with the conversion of AFt to AFm (sulphate depletion peak) [9]. Taylor states, however, that the principal exothermic component for all these reactions involving the aluminate or ferrite phases, probably is the reaction of the anhydrous compound with water and not the precipitation or subsequent reactions of hydrated compounds [7].

The second and third peaks were generally not as easily detected for the other cements as for Cement 6 probably because their C_3A contents were markedly lower. A small AFt shoulder could however be distinguished. Increasing amounts of SNF, LS or PA seemed to increase the second peak while the third peak broadened considerably or disappeared as illustrated for cement 6 with PA and SNF in Figure 3. Thus, the overall heat evolution might be increased even thought the second heat peak is delayed. Bensted found similarly that the first peak of a retarded cement paste was increased in comparison with that of a neat cement slurry [10]. Sandberg and Roberts [11] reported, moreover, that the aluminate reactivity increased while the silicate hydration was retarded as LS was

added to Portland cement pastes at increasing dosages. As a consequence, the third peak appeared closer and closer to the maximum of the main silicate hydration peak. Eventually, the third peak appeared before the strongly retarded silicate hydration peak.
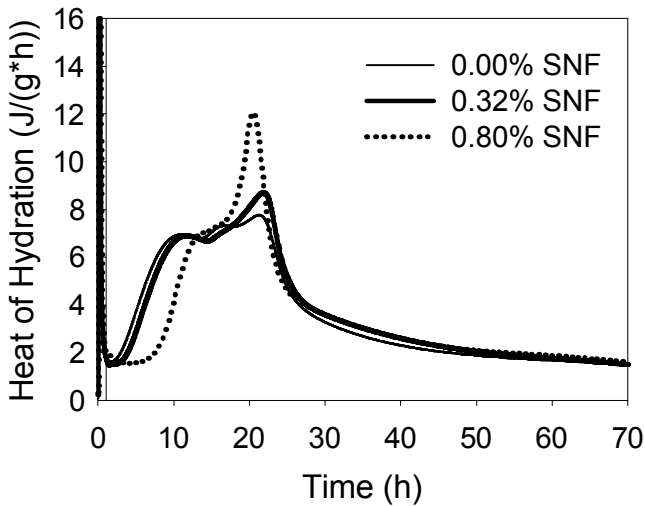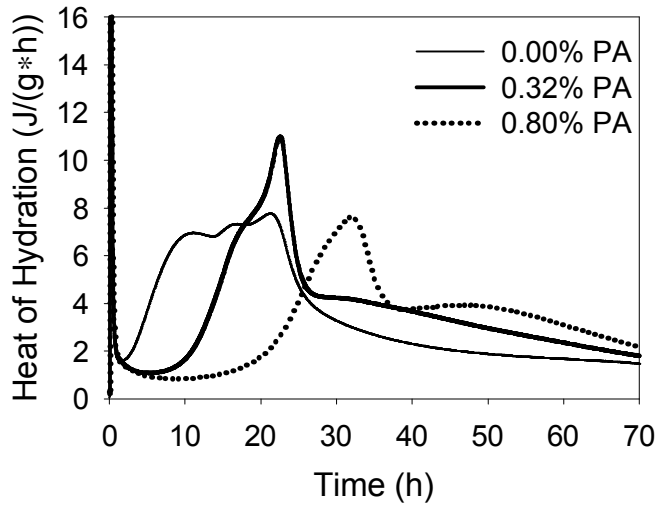

Figure 3: Heat of hydration curves for Cement 6 with 0%, 0.32% and 0.80% PA (above) and SNF (below).

4.1 Influence of cement characteristics on the induction period

The end of the induction period was defined as the first occurring minima in the heat rate curve added 0.25 J/(g·h) to ensure that the onset of the accelerated hydration had been reached. The duration of the induction period depended on plasticizer type and dosage as illustrated by Figure 4. LS was the strongest retarder of the three plasticizers while SNF had the least effect on the duration of the dormant period. SNF and LS has been

found to have similar saturation dosages on the cements under study while PA had markedly lower [1]. The relatively strong retarding effect of LS is thus probably not only caused by adsorption onto active hydration sites on the cement surface. A possible explanation for the retarding behaviour of LS is that it produces a complex salt with Ca^{2+} in a higher degree than SNF and PA [12]. Such Ca-complexation results in delayed occurrence of $Ca(OH)_2$ supersaturation and thus prolonged induction period. Figure 4 shows, furthermore, that the shape of the induction period curves for pastes with PA differ from the curves of pastes with LS and SNF. This difference might be caused by PA having a much lower saturation point and different adsorption characteristics than SNF and LS. These differences might partly be caused by the PA molecules being markedly larger than SNF and LS and thus being able to block a higher amount of active nucleation sites simply by surface coverage. PA is, moreover, not known to intercalate into the hydration products as SNF and LS [1].

An interesting feature of Figure 4 is that SNF at low dosages increased the reaction rate and thereby reduced the duration of the induction period as seen for Cements 1 and 4. This effect was probably caused by improved dispersion of the cement particles due to the superplasticizer [13].

No correlations between the end of induction period and cement characteristics such as cement fineness, aluminate and alkali content could be found for pastes without plasticizer. This might be caused by the narrow distribution of setting times for these pastes and thus high uncertainty of the induction period readings. Some correlations were, however, found for plasticized pastes as illustrated by Table 3 and Figure 5. The correlations seem even to include the fly ash cement which might indicate that the fly ash does not have as strong influence on the main heat of hydration as on the initial.

Table 3 illustrates that the end of induction period did not correlate with the cement fineness (Blaine), C_3S or C_3A content introduced as single parameters. The end of the induction period did, however, correlate with the content of cubic C_3A and the product of Blaine and cubic C_3A. The cubic modification of C_3A seemed thus to have a stronger influence on the duration of the induction period than the sum of orthorhombic and cubic aluminate. This finding indicates that the cubic aluminate modification was more reactive than the orthorhombic as found by others [14,15].
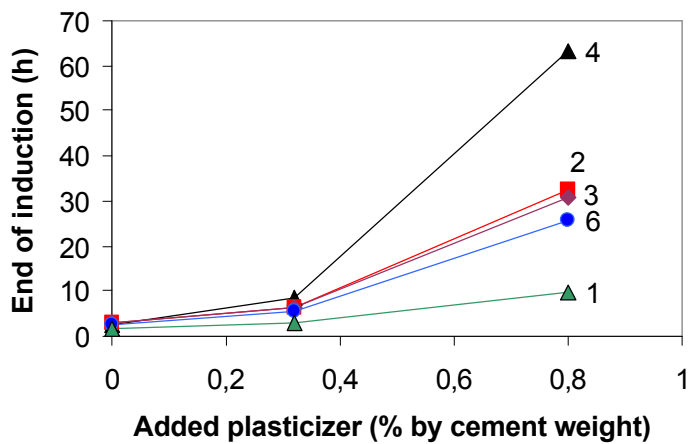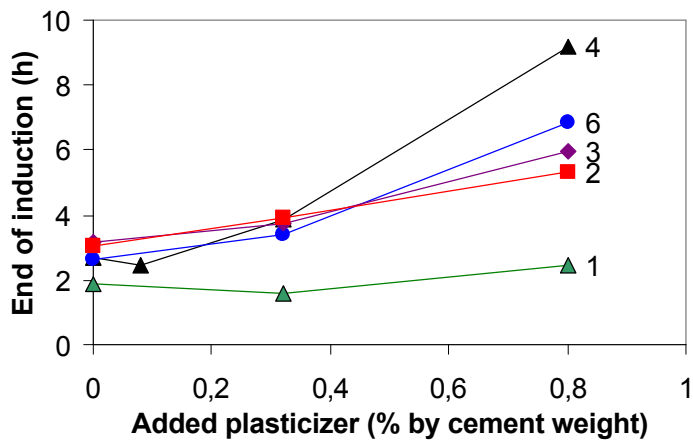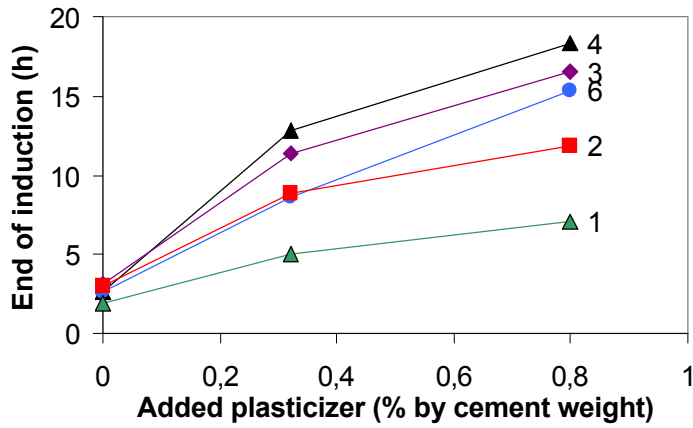
Figure 4: End of induction period for Cements 1-4, 6 with added PA (top), SNF (middle) and LS (bottom).

The end of the induction period is associated with the hydration of C_3S to CSH. It might therefore seem surprising that the content of C_3S has a lower correlation factor than cubic C_3A. The induction period appears, therefore, to be governed by interactions between the cements and

plasticizers: Plasticizers are known to be preferentially adsorbed onto the aluminate phases and free lime [12]. The silicate hydration is thus dependent on the aluminate-plasticizer interactions since a low content of aluminate leaves a high amount of plasticizer for the silicates which in turn result in a prolonged induction period. Work done by Mollah et al.[16] has indicated that plasticizers adsorb onto silicate surfaces via calcium ions formed during the initial hydration reactions. This adsorbed bi-layer of plasticizer and calcium ions prolong the duration of the induction period in a twofold manner: Firstly by covering the silicate surface and secondly by removing calcium ions from the solution. Uchikawa et al.[12] have, moreover, found that plasticizer adsorption on active hydration sites can cause retardation and altered morphology of the hydration products formed by reducing growth or by intercalation in the hydration products. The superplasticizer might thus decrease the dissolution rate of anhydrite and create a diffusional barrier at the surface of the reacting constituents.

The experimental results indicate that the end of the induction period decreases with increasing content of water soluble alkali in the cements. Figure 5 illustrates how the length of the induction period decreases with increasing $K \cdot cC_3A$ factor. Alkali sulphates are known to accelerate the hydration of Portland cement in the acceleration period and increase the rate of heat evolution towards its peak [17]. The increased hydration rate has been linked to accelerated rate of ettringite formation [18], but the alkali sulphates are not known to alter the progress of C_3S and C_3A hydration [19].

Table 3: Regression coefficients for correlations between cement characteristics and end of induction period.

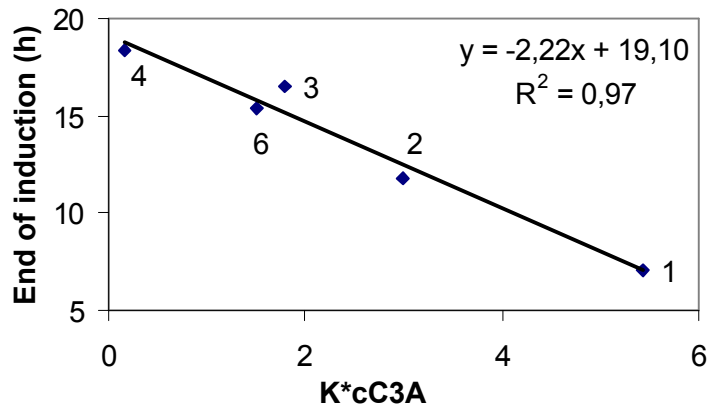| Characteristic	R^2			
	No plasticizer	0.80% SNF	0.80% LS	0.80% PA
C_3S	0.01	0.04	0.05	0.09
C_3A	0.13	0.03	0.30	0.01
Blaine	0.13	0.58	0.33	0.40
Blaine$\cdot C_3S$	0.13	0.54	0.22	0.43
Blaine$\cdot C_3A$	0.40	0.40	0.75	0.23
$Na_{eqv} \cdot cC_3A$ [1]	0.51	0.45	0.11	0.62
$Na_{eqv} \cdot C_3S$	0.70	0.73	0.35	0.77
$K^+ \cdot C_3S$	0.48	0.73	0.38	0.77
Na_{eqv}	0.20	0.80	0.44	0.81
K^+	0.19	0.81	0.49	0.81
cC_3A	0.44	0.92	0.97	0.80
Blaine$\cdot cC_3A$ [1]	*0.55*	0.94	0.80	0.81
$K^+ \cdot cC_3A$ [1]	0.50	0.96	0.72	0.97

[1] cC_3A = cubic C_3A

Figure 5: End of induction period a function of easy soluble potassium times the cubic C_3A content for cements 1 - 4 and 6 with 0.80% PA.

5. Conclusions

The maximum heat of hydration rate of the first heat of hydration peak correlated with the product of the cement fineness and C_3A content. The cement containing fly ash had to be excluded due to its relatively low initial heat of hydration.

SNF, LS and PA were found to change the hydration sequence as well as prolong the induction period of the cement pastes. The hydration seemed thus to be governed by interactions between the cements and plasticizers.

The duration of the induction period decreased with increasing values of easily soluble alkali, cubic aluminate, Blaine·cC_3A and K^+·cC_3A. The results indicated that the cubic aluminate modification was more reactive than the orthorhombic.

The duration of the induction period did not depend as strongly on the silicate phases as on the aluminates. This effect is probably caused by the plasticizer's affinity for the aluminate phases which rules the silicate - plasticizer interactions.

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