DISCUSSION

In general the addition of 2 % accelerator reduces the set time of the control cement paste to about 1 minute, but when 2 % SP is present in the paste, the accelerated setting is dramatically weakened. In order to attain the same set time, a larger quantity of accelerator is required. The results show that the addition of 5 % accelerator significantly reduces the setting of the paste in the presence of 2 % SP. On the other hand, the presence of the accelerator reduces the retardation of the setting of the paste caused by the SP.

According to reference 9, the reactions which take place immediately after mixing the cement with water are of decisive importance with regard to setting. These reactions mainly refer to the hydration of C_3A phase in the cement. The heat release for the first 30 minutes hydration shows that the rate of reactions in the accelerator containing sample is greater than the control sample. A large amount of foil-like CAH phases is formed besides the ettringite. In the previous work (5) it has been concluded that the CAH phases are the hydration products not only from the C_3A hydration but also from the reaction of the added aluminate in the accelerator. These foil-like CAH phases cover and connect the cement grains, resulting in the rapid setting of the cement paste. In addition it is noticeable that the concentration of the sulphate-ions is largely enhanced in the accelerator containing sample. This is probably due to the reaction of the gypsum with alkali hydroxide in the solution at an elevated pH over 13 to form calcium hydroxide and alkali sulphate.

The influence of SP on the cement hydration is widely discussed. It is known that this low adsorbing PC type SP enhances the C_3A hydration but retards the dissolution of the bassanite. Therefore the PC type SP induces linear growth of the ettringite crystals. The high content of aluminate-ions in the liquid phase of SP+accelerator sample found in this study indicates that the formation of the hydrate phases which consume aluminate-ions, such as the ettringite crystals and CAH phases, is restrained.

It can be concluded from the above that the presence of the $NaAl(OH)_4$-accelerator is beneficial to the formation of CAH phases. The quantity of the ettringite crystals depends on the calcium content in the liquid phase and the sulphate supply that results from set regulation. The SP is most probably to restrain the formation of ettringite crystals and CAH phases and to change the morphology of the two hydrate phases. It is, therefore, reasonable to conclude that the most important factor that governs the effects of the two chemical admixtures is how intensive they can exert their effect on the cement hydration, especially the C_3A hydration. This means the added quantity of SP and accelerator is critically important.

ESEM micrographs show that a combined application of SP and $NaAl(OH)_4$-accelerator causes growth of long prismatic ettringite crystals and foil-like calcium aluminate hydrate phases. The amount of the hydrate phases in the

SP+accelerator sample is higher than the sample where the SP is the sole admixture. Furthermore the morphology of the ettringite crystals and the CAH phases in the SP+accelerator sample is different from the other samples, especially the CAH phases. In the SP+accelerator containing sample, the CAH phases agglomerate surrounding the cement grains spherically. They are not homogenously distributed and large enough to connect the grains with each other. In that way the accelerated setting of the paste is inhibited and more accelerator is needed. Similar agglomerated CAH phases have been described in reference 8, there the modified CAH phases have been considered as organo mineral complexes (OMC) because of the assumption that the sulfonate group of the investigated SP may replace sulphate ions in the $CA\bar{S}H$ phases. As far as the SP molecule in this study does not comprise of sulfonate groups, this interpretation remains uncertain for our findings. Further work is needed to be emphasized on the verification of the constitution and the stability of the modified CAH phases.

CONCLUSIONS

The investigation reveals that due to the addition of SP the effect of the $NaAl(OH)_4$-accelerator is suppressed. This includes the set time, the progress of cement hydration and the formation of the CAH phases. Conversely the retarding effect of the SP is suppressed by the accelerator influence. The composition of the liquid phase displays the excess supply of aluminate-ions in the case of the accelerator containing samples.

The rapid setting caused by 2 % set accelerator in the cement paste is due to the formation of a large quantity of foil-like CAH phases which cover and connect the cement grains.

A combined application of SP and $NaAl(OH)_4$-accelerator causes growth of long prismatic ettringite crystals and foil-like CAH phases. These CAH phases merely agglomerate surrounding on the surfaces of the single cement grain. They are not homogenously distributed over the grains and not large enough to cause the rapid setting.

The most important thing for the combined effect of the SP and the $NaAl(OH)_4$-accelerator on the very early hydration of the cement is considered how intensive they can exert their effect in the cement to influence the C_3A hydrating reaction.

More research work is needed to verify the formation mechanism and stability of the CAH phases in the cement paste in the presence of SP.

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Table 1 Chemical composition of the normal portland cement (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3
20.2	5.25	3.07	64.4	1.19	0.53	0.11	2.8

Table 2 Phase composition of normal portland cement (%)

C_3S	C_2S	C_3A	C_4AF	Na_2O-eq.
58.4	13.9	8.7	9.3	0.47

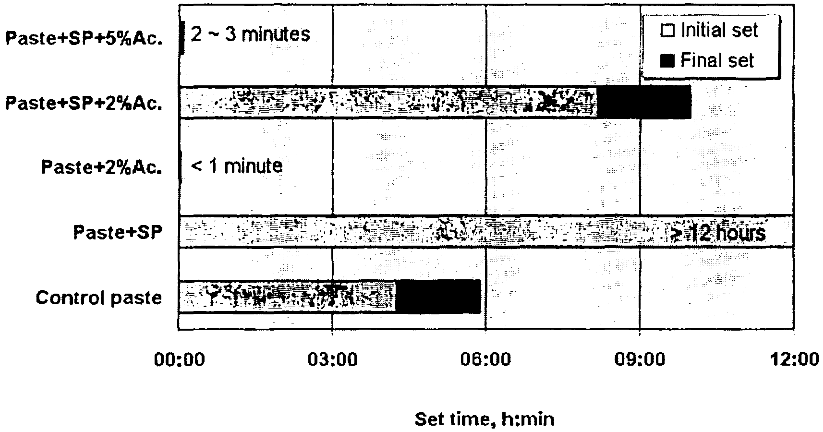

Fig.1 Effect of accelerator and superplasticizer on the set time of cement pastes

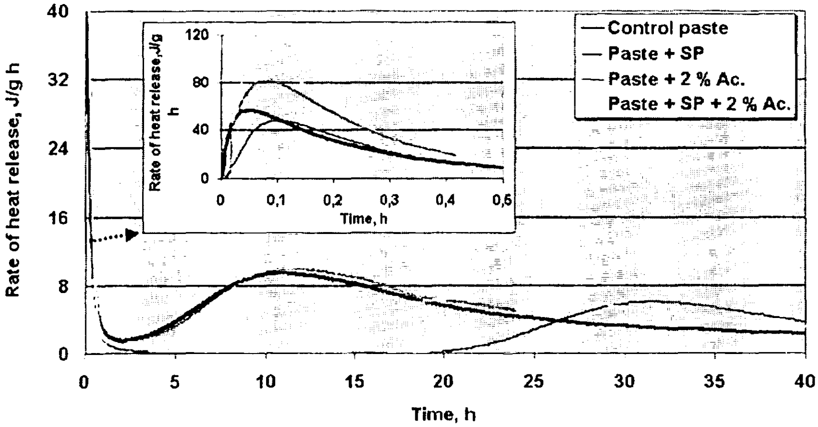

Fig. 2 DCA diagram of the early hydration of the cement (Ac.: accelerator)

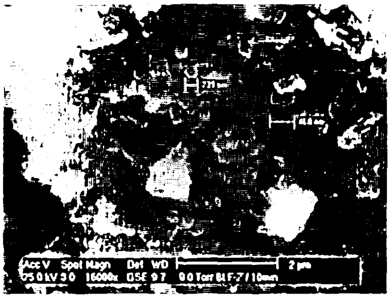

Fig. 3 Control cement paste(× 16000), 10 minutes hydration

Fig. 4 Paste with 2 % SP (× 16000), 10 minutes hydration

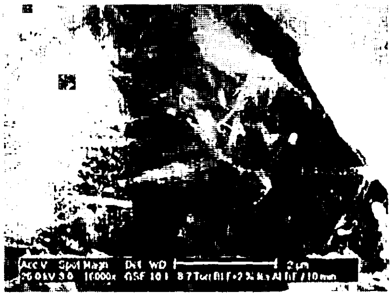

Fig. 5 Paste with 2 % accelerator (no SP, × 16000), 10 minutes hydration

Fig. 6 Paste with 2 % accelerator (no SP, × 16000), 10 minutes hydration

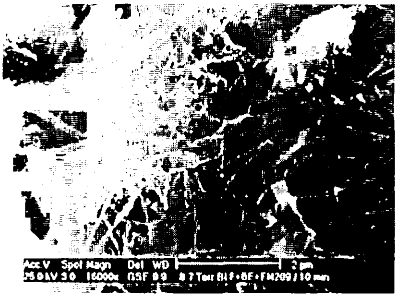

Fig. 7 Paste with 2 % accelerator and 2 % SP (× 16000), 10 minutes hydration

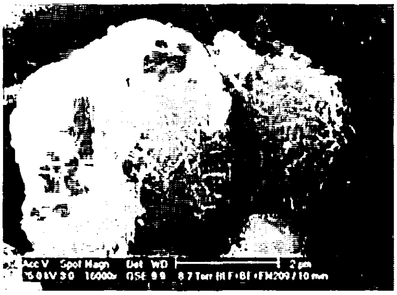

Fig. 8 Paste with 2 % accelerator and 2 % SP (× 16000), 10 minutes hydration

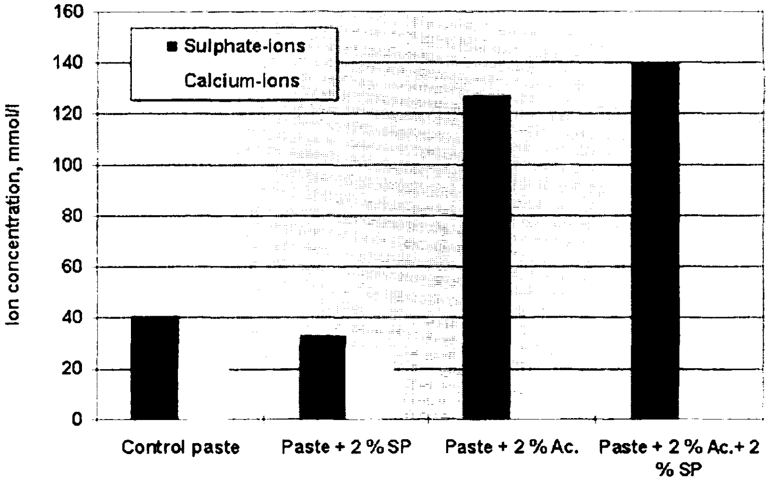

Fig. 9 Calcium- and sulphate-ions concentrations in the liquid phase (pore solution) of the cement paste after 10 minutes hydration

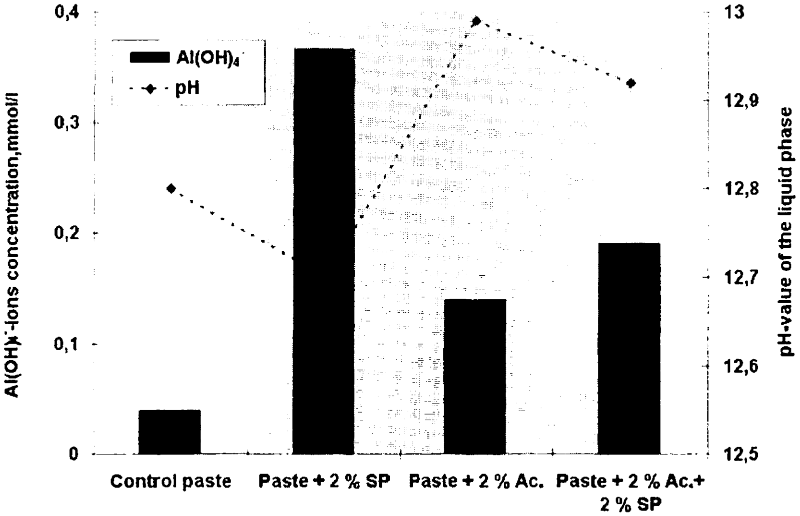

Fig. 10 $Al(OH)_4^-$-ions concentration and pH values in the liquid phase (pore solution) of the cement paste after 10 minutes hydration

SP-217—28

A New Rapid Test Method to Predict $LiNO_3$ Dosage for Controlling ASR Expansion

by C.-S. Shon, D. G. Zollinger, and S. L. Sarkar

Synopsis:

A test apparatus called "dilatometer" has been developed to predict the dosage of lithium nitrate ($LiNO_3$) required to control ASR expansion as a function of the alkali level and aggregate reactivity. The dilatometer is instrumented so as to monitor within a short period of time the volumetric expansion of the siliceous gel produced by a siliceous aggregate. The rationality of this test procedure was explored from comprehensive laboratory experiments related to the effects of temperature, normality of NaOH test solution, and $LiNO_3$ dosage. Determination of the level of expansion within 30 hours, using this method enables one to predict the dosage of $LiNO_3$, which is now being used as an ASR mitigating agent, needed for a particular aggregate to control expansion due to ASR. Based on the test results, it is anticipated that this test method will be useful for predicting the optimum dosage of $LiNO_3$ required for a particular aggregate type and source.

Keywords: alkali-silica reactivity; dilatometer; lithium nitrate ($LiNO_3$); normality of NaOH; temperature

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INTRODUCTION

Damage to concrete due to alkali silica reactivity (ASR), first reported by Stanton in 1940 (1), has become internationally recognized as a major source of deterioration of concrete structures such as bridges and pavements. Ever since ASR was first recognized, voluminous research has been conducted on the mechanism of this deleterious reaction, and several test methods either developed or proposed to measure expansion due to ASR (2).

The Strategic Highway Research Program (SHRP) initiated a major research effort to find a better test method for ASR (3). This research effort also looked on the role of lithium in preventing ASR in