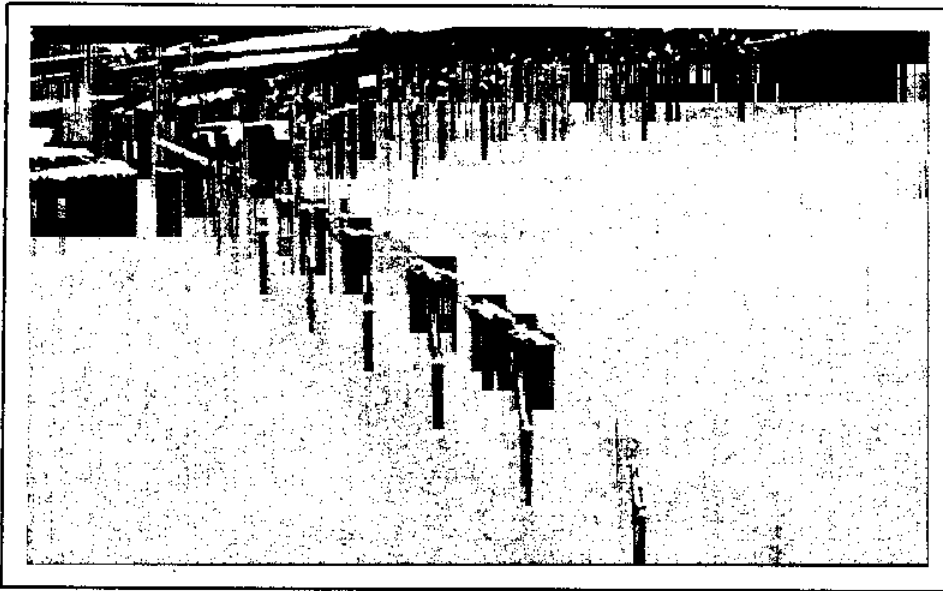


Unexpected Release and Re-Sorption of Superplasticizer**Mario Collepari Symposium**
on
Advances in Concrete
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Synopsis: An unusual interaction between naphthalene sulfonate superplasticizer and a low alkali white sulfate-resisting cement is described. At a reasonable dose rate, nearly all of the superplasticizer is sorbed and held indefinitely by the cement. Additions of potassium hydroxide (made to simulate the effects of a higher alkali content) resulted in a sequence of desorption of some of the previously sorbed superplasticizer over the first 4 hours of hydration, followed by resorption of most of it over the next few hours. The extent of desorption varied the amount of alkali hydroxide added, exhibiting a maximum at a dose equivalent to 0.6% Na₂O. At higher doses the desorption disappeared. The calcium sulfate present in this cement was anhydrite, and the added KOH stimulated rapid dissolution of the anhydrite. Gypsum was never formed, but at low and intermediate addition levels ettringite was formed quickly. At the higher KOH addition levels ettringite formation lagged, and high levels of dissolved sulfate remained in solution. The sorption-desorption phenomenon does not seem to be related to the much slower desorption and resorption of melamine sulfonate reported some years ago by Yilmaz and Glasser.

Keywords: Cement, superplasticizers, sorption, desorption, resorption, ions, XRD, alkali hydroxide, sulfate, ettringite.

P.K. Mehta
Editor

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INTRODUCTION

Superplasticizers have been used to control the rheological characteristics of concrete for many years, but detailed knowledge of their interactions with various cements remains incomplete. The present paper is a contribution reporting an unexpected case of such interaction, involving initial sorption of superplasticizer, return of much of the sorbed superplasticizer to the pore solution during the dormant period, and subsequent re-sorption.

MATERIALS AND METHODS

The superplasticizers used in this study were naphthalene sulfonates obtained from commercial sources. Superplasticizer "A" was supplied in dry form by the W.R. Grace Co.; it had an estimated impurity sodium sulfate content of about 5%, based on our analysis. Superplasticizer "B" was a commercial product of the Kao Soap Co., supplied as a 52% solids by weight solution. Our estimate of the impurity sodium sulfate level was much lower, about 1%. The desorption and resorption response we found was similar for both, suggesting that it is characteristic for the class of naphthalene sulfonates, rather than for any given formulation.

The cement on which the desorption-and resorption effect was displayed was a white, sulfate resisting ASTM Type I cement produced by Aalborg Portland A/S and marketed by Lehigh Cement Co., Allentown, PA. It had a very low alkali content; as a sulfate-resisting cement, it had a low aluminate content ; and as a white cement it had a low iron content. The mill analysis supplied by the manufacturer indicated the following oxide contents: CaO - 70.0%, SiO₂ - 23.9%, Al₂O₃ - 1.94%, Fe₂O₃ - 0.42%, SO₃ - 1.82%, Na₂O - 0.10%, K₂O - 0.02%. The corresponding Bogue composition was given as C₁S - 74.2%, C₂S - 12.5%, C₃A - 4.4%, and C₄AF - 1.3%. The SO₃ content of the

particular sample of the cement material used in this research was re-analyzed and found to be somewhat higher than indicated by the mill certificate, 3.13%. XRD indicated that the "gypsum" present was entirely in the form of anhydrite, which was confirmed by the lack of dehydration response for gypsum or hemihydrate on DSC.

Pastes were mixed at a water:cement ratio of 0.50 using the standard ASTM C 305 mixing procedure. The pore solutions were separated and the pore solution analyzed at frequent intervals. For the first few hours, separation was accomplished using a gas pressure filtration system in which N₂ gas at 40 to 80 psi was applied to a replicate portion of about 50 g of the paste. The pore solution as forced through a membrane filter containing nominally 0.45 μ m diameter pores and immediately recovered for analysis. At later stages after set, the pore solution was expressed using the high pressure die system described by Barneyback and Diamond (1). In either case, the leftover solids were stripped of the remaining pore solution by repeated flushing with acetone, and immediately dried for later solid-phase analysis.

As mentioned previously, two different naphthalene sulfonate superplasticizers were used in this work. The solid, relatively pure superplasticizer B where used, was dissolved in the mix water at a concentration of 32 g/L, corresponding to a dosage of 1.6% by weight of cement. Superplasticizer A , where used, was also predissolved in the mix water. The solids content of the dosage used with superplasticizer A was nominally slightly higher, 40 g/L or 2% by weight of cement. However, because of the relatively high (and not precisely established) impurity content, the actual starting concentration of naphthalene sulfonate was less than this. Our UV analysis indicated an actual starting concentration value of 34 g/L.

The analyses of the pore solutions for superplasticizer content were carried out by normal UV spectroscopic methods after appropriate dilution. The weaker of the two well-known UV bands for naphthalene sulfonate, centered near 282 nm, was used for analysis. The value of the extinction coefficient determined for this band using known solutions of superplasticizer A as the standard was 2.20 L/mm-g, in reasonable agreement with previous workers.

The inorganic ions were separately analyzed, using flame emission for Na and K and AAS for Ca. In some of the determinations SO₄²⁻ was determined by AAS; subsequently ion chromatography was used.. The OH⁻ ion concentrations were determined by titration with dilute HCl using the methyl red end point after boiling to expel CO₂.

In the separated solids, anhydrite was determined by QXRD and ettringite by DSC. In none of the samples examined was there any indication of gypsum, hemihydrate, or monosulfate in the DSC patterns.

RESULTS

The cement was found to rapidly sorb a little more than half of the applied dosage of superplasticizer A from the mix water in the first few minutes; very little additional sorption occurred subsequently. In contrast, nearly all of the added dosage of superplasticizer B was sorbed almost immediately. The sorption data for both are plotted in Fig. 1.

It was indicated by experiment that the relatively incomplete removal of superplasticizer from solution for superplasticizer A as compared to the nearly complete sorption with superplasticizer B was due to its high content of sodium sulfate impurity in the former. Separate additions of sodium sulfate (or potassium sulfate) to pastes mixed with the relatively pure superplasticizer B substantially reduced its initial sorption. Additions of either of the alkali sulfates at dosages equivalent to 0.6 % cement Na_2O reduced the initial sorption with superplasticizer A from over 90% to about 25% of the naphthalene sulfonate supplied.

The alkali and OH^- ion concentrations found in these pastes (without added alkali sulfate) were far below the usual range for portland cement pastes. This is a characteristic property of the particular very low alkali cement used. For the control cement paste prepared without any admixture at all, the combined alkalis were maintained in the pore solution at about 20 meq/L and the OH^- ion concentration at about 60 meq/L during the early hours of hydration. In the paste with superplasticizer B the alkali ion concentration was initially recorded as about 130 meq/L, the increase being almost entirely as sodium from the superplasticizer. The combined alkali concentration increased progressively to about 160 meq/l at 24 hours. The OH^- ion concentration was initially lower, but quickly rose to nearly match the sodium concentration. The very much increased OH^- ion concentration for the superplasticized paste compared to the non-treated paste is a consequence of the fact that sodium introduced by the superplasticizer is converted to sodium hydroxide when the polymer chains are sorbed and separated from the solution phase (2).

As mentioned, the cement has very little alkali of its own. It was considered of interest to "simulate" to some degree the effect of a higher level of alkalinity on the sorption of the superplasticizer. Accordingly, pastes were prepared with pre-dissolved additions of KOH as well as naphthalene sulfonate in the mix water, the KOH dosages being calculated in terms of equivalent percentages of Na_2O by weight of cement. The results of these treatments on the sorption of the superplasticizer A are shown in Fig. 2.

At low dosages (0.30%, and 0.45% equiv. % Na_2O) there was little effect of the added KOH on the initial naphthalene sulfate sorption, but at these levels

there was a discernible tendency for a little of the superplasticizer to be desorbed back into the solution at about an hour after mixing. The superplasticizer released was later re-sorbed.

Increasing the dosage of added KOH to the from 0.4% to 0.6% had a marked and highly significant effect. As seen in Fig. 2, the *initial* removal of superplasticizer from solution increased markedly, reducing the initial concentration to a level like that exhibited with the essentially sulfate-free superplasticizer B. This amplified initial sorption was quickly reversed, and major desorption occurred; by 2 hours the concentration of naphthalene sulfonate in solution had risen from 4 g/L to 12g/L, and by 4 hours to more than 17 g/L. This point marked a peak in the desorption effect; subsequently the previously desorbed superplasticizer was again removed from solution by the cement paste. The naphthalene sulfonate concentration dropped from over 17 g/L at 4 hours to about 6 g/L at 8 hours.

This amplified sorption-desorption-resorption effect seems to be restricted to a narrow dosage range of added KOH. Further increases in added KOH (to 0.9% and 1.2% equivalent % Na_2O , respectively) preserved the initial amplified sorption effect, but at these higher levels the amplified initial sorption seemed to be permanent; that is, all of the superplasticizer sorbed during the first few minutes remained sorbed.

The concentrations of the various inorganic ions present in the pore solution are given in Fig. 3 for the 0.60% treatment level, the KOH dosage exhibiting the most significant sorption reversal effect. Unfortunately, the SO_4^{2-} ion concentrations in these solutions could not be determined for technical reasons. Of the ions whose concentrations were analyzed, the only one that showed changes that appeared to correlate in time with the reversal of the naphthalene sulfonate sorption was the OH^- ion concentration. This concentration went through a shallow, but possibly suggestive minimum at 4 hours, the time of the peak desorption of naphthalene sulfonate. The implication that might be drawn is that perhaps the enhanced initial naphthalene sulfonate sorption is a function of enhanced OH^- ion concentration, and it reverses if the OH^- ion concentration is reduced. This suggestion is consistent with the more complete (and permanent) sorption exhibited at higher KOH treatment levels, which maintain higher OH^- ion concentrations throughout.

That the sorption reversal effect is not associated with any peculiar characteristics of superplasticizer A (or its sulfate impurity level) seems to be apparent from Fig. 4, in which naphthalene sulfonate concentrations vs. time are plotted for several pastes exhibiting the effect: two mixed with superplasticizer A and one with superplasticizer B. All had KOH addition at the 0.6% Na_2O equivalent level. The desorption and resorption effects are essentially identical for all.

In Fig. 5 we plot the inorganic ion concentrations found for the superplasticizer B trial plotted in Fig. 4, this time including sulfate analysis data. It should be recalled that superplasticizer B is essentially sulfate-free, so that here all of the sulfate found in solution is derived from the cement.

The sulfate concentrations found are on the order of 200 meq/L at the start, increasing rapidly and then more gradually to about 260 meq/L. The sulfate content of the cement appears to be about 3.1% SO_3 , which would correspond to a concentration of about 1,550 meq/L if all of the sulfate dissolved and remained in solution. The inference is either that the dissolution of the anhydrite is slow or that precipitation of gypsum or ettringite limits the concentration in solution at any given time. Actually both are true, as will be seen later.

The concentrations of K^+ and of Ca^{2+} ions are almost identical to those of Fig. 3, for the corresponding 0.6% KOH treatment with superplasticizer "A", but the concentration of Na^+ is here substantially lower, about 150 meq/L as compared to over 200 meq/L. Presumably this reflects a lower degree of sulfonation of the polymer of this superplasticizer, hence a reduced content of charge-balancing Na^+ cation.

In Fig. 5 there is again a significant reduction in the OH^- ion concentration during the period of naphthalene sulfonate desorption, as indicated in Fig. 3 for the corresponding data with superplasticizer A. However, here the subsequent increase in OH^- ion concentration during the re-sorption period is even less marked than previously found. Thus the simple hypothesis that naphthalene sulfonate might desorb in response to reduction in OH^- ion concentration and then resorbs as the OH^- ion concentration again increases seems untenable. The desorption effect might be indeed be induced by some simultaneous combination of temporary OH^- ion decrease and SO_4^{2-} ion increase, but it is difficult to relate the resorption to any observed changes in the ion concentrations.

OH^- ion concentrations for the paste mixed with superplasticizer B alone, and for corresponding pastes incorporating pre-dissolved KOH are shown in Fig. 6. These represent new determinations. The "plain" superplasticized paste showed a general OH^- ion concentration level of only about 100 meq/L throughout the relevant period. Incorporation of KOH in the mix water at the 0.6% dose level, which produces the most significant sorption reversal, raised the general level of OH^- ion concentration to about 400 meq/L initially, dropping to about 350 meq/L. The 1.2% dose level initially raised the OH^- ion concentration level to close to 800 meq/L but this was progressively reduced to about 400 meq/L over the first four hours.

The response of cements to added alkali hydroxides was investigated several years ago. It was shown (3) that alkali hydroxide predissolved in the mix water

reacted to immediately dissolve gypsum and precipitate an equivalent amount of calcium hydroxide. The net contribution to the pore solution is an immediately enhanced content of alkali sulfate rather than of alkali hydroxide. It was also found that if the cement was formulated with anhydrite instead of gypsum, the rate of dissolution of the calcium sulfate and the rate at which the alkali sulfate appeared in the pore solution was correspondingly reduced. This appears to be what is happening here.

The SO_4^{2-} ion concentrations corresponding to the pastes of Fig. 6 are shown in Fig. 7. Almost no sulfate is found in the pore solution of the "plain" superplasticized paste. The implication is that the anhydrite did not dissolve, or that ettringite is formed immediately from any dissolved anhydrite. For the 0.6% equivalent dosage, dissolved sulfate rises quickly at first, then more slowly to a level of about 200 meq/L. For the 1.2% equivalent dosage, dissolved sulfate rises very quickly to just under 300 meq/L, and reaches over 450 meq/L at about 4 hours. It is clear that introduction of KOH liberates sulfate over a period of hours, more or less in proportion to the dosage level introduced. This is consistent with the findings quoted previously.

It was considered that some light might be shed by following the various simultaneous changes in all of the sulfate-bearing components of the system. Accordingly, determinations were made of the parallel changes in anhydrite content (by XRD), of ettringite content (by DSC), and of the pore solution sulfate content (by solution analysis) over the time period concerned. These constituted the sum of the quantifiable sulfate-bearing phases; since no gypsum, hemihydrate, or monosulfate was detected in these pastes. The determinations were carried out for pastes mixed with superplasticizer B by itself, and with additions of KOH corresponding to 0.6% and 1.2% Na_2O equivalents. For comparison purposes, the phase compositional percentages were reduced to the equivalent percentages as sulfate (SO_4), assuming that both anhydrite and ettringite had the ideal stoichiometric sulfate content.

The original anhydrite content of the cement was estimated by quantitative XRD as being equivalent to approximately 2.5% SO_4 by weight. This may be an underestimate, and a reflection of the uncertainty in the QXRD determination. Analysis of the cement sample by a standard wet chemical procedure yielded 3.13% SO_3 , corresponding to a sulfate percentage (as SO_4) of 3.75%. Since the cement has such a low alkali content, there can be little alkali sulfate or calcium alkali sulfate, and as stated earlier, anhydrite is the only sulfate-bearing phase recorded by XRD.

Fig. 8 summarizes the phase changes of the sulfate-bearing components for the superplasticized paste without KOH addition. It appears that perhaps 40% of the anhydrite dissolves over the first hour or two, but ettringite forms so rapidly that the sulfate ion concentration in solution remains negligible. Little change seems to occur after the first 2 hours.

Fig. 9 provides the corresponding data for the KOH treatment equivalent to 0.6% Na_2O , the dosage that produces the prominent sorption-desorption-resorption effect. The KOH produces a significant increase in the amount of the quickly dissolved anhydrite. The rate of precipitation of ettringite is also increased, but not enough to prevent accumulation of dissolved sulfate in the pore solution.

With the 1.2% KOH treatment level, as seen in Fig. 10, half the anhydrite is almost immediately dissolved, but no ettringite at all is formed during the first two hours or so. This results in a substantial early accumulation of sulfate in the pore solution. This pore solution concentration increases with time since the rate of anhydrite dissolution remains high. Ettringite starts to form only after 2 hours, but even so, at 4 hours sulfate corresponding to about 40% of the by-now fully dissolved anhydrite remains in solution. It is thus seen that the effect of the added is to increase the dissolution of the anhydrite, and in consequence increase the general levels of both the OH^- and SO_4^{2-} ion concentrations; in addition, high dosages depress ettringite formation.

DISCUSSION

The solid phase transformation results are of particular interest in the light of a suggestion some years ago by Yilmaz and Glasser (5) concerning sorption of melamine sulfonate superplasticizer. They found that with the cement they used (a moderate alkali generally "normal" BS-12 cement), within 1 to 3 hours after mixing, the melamine sulfonate was removed "almost entirely" from the pore solution. Subsequently they found a strong reversion of nearly all of the melamine sulfonate back into solution. However, their time scale was much different from that exhibited here; the maximum desorption not being reached until about 24 hours, i.e. after much of the cement had hydrated. Still later, they recorded a slow decline in the melamine sulfonate concentration, taking place over a period of months, rather than a few hours as found here. The effect was observed without any alkali hydroxide addition to the mix water, and was considered by the authors to illustrate a normal response of cement to melamine sulfonate treatment.

Yilmaz and Glasser suggested that the bulk of the initial sorption they recorded took place on or within the a temporary gel-like "ettringite precursor"; that is, a hydrated calcium sulfoaluminate gel from which ettringite later supposedly crystallizes. It was suggested that this "ettringite precursor" releases much of the sorbed superplasticizer back into the pore solution when the ettringite is crystallized from it.

The pattern of dissolution of anhydrite, crystallization of ettringite, and accumulation of sulfate in the pore solution depicted in Figs. 8 to 10 do not seem to fit the Yilmaz - Glasser hypothesis very well. For the "plain" naphthalene sulfonate bearing paste, substantial initial absorption occurs and is maintained, even though the ettringite seems to crystallize as fast as the anhydrite dissolves, i.e. little "ettringite precursor" presumably exists. For the pastes with 0.6% equivalent dosage of KOH that undergo the sorption reversals, the data of Fig. 9 show sorption reversals without any large amount of simultaneous ettringite crystallization. With the highest-level KOH treatment (Fig. 10) ettringite crystallization begins at 2 hours and proceeds rapidly, but no desorption of superplasticizer is noted.

Finally, Yilmaz and Glasser (4) indicated that their late stage removal of melamine sulfonate from solution was not due to resorption by the cement paste, but rather to slow precipitation of denatured superplasticizer, rendered insoluble by prolonged reaction with alkali. This does not seem a likely explanation for the much faster resorption observed in the present case.

CONCLUSIONS

Studies of the sorption of dissolved naphthalene sulfonate in cement pastes prepared from an unusual white cement with anhydrite as the interground calcium sulfate revealed some surprising features. Initial sorption of naphthalene sulfonate is rapid and removes nearly all of the heavy dose of superplasticizer. In this case the sorbed material remains sorbed indefinitely. Impurity sulfate or added sulfate reduces the proportion of naphthalene sulfonate that is sorbed substantially.

Small dosages of KOH predissolved with the naphthalene sulfonate in the mix water generate a tendency to temporary return of some superplasticizer to the pore solution.

An optimum KOH dose for this effect, is equivalent to a borderline cement alkali content (0.6% Na_2O). Such a treatment induces a return of much of the initially sorbed superplasticizer to solution in a few hours. The liberated superplasticizer is subsequently re-sorbed over the next few hours. The sorption-desorption-resorption phenomenon is reproducible and was found to take place with two very different naphthalene sulfonate superplasticizers.

With a heavy dosage of added KOH, (equivalent to 1.2% Na_2O in the cement), strong initial sorption occurs regardless of sulfate impurity, but none of the sorbed superplasticizer is subsequently liberated.

In all of these pastes, the anhydrite is progressively dissolved without the precipitation of gypsum. Ettringite crystallization starts immediately with untreated and modestly KOH-treated superplasticized pastes, but is delayed for several hours with high levels of added KOH.

High dissolved sulfate levels are produced in the pore solutions of pastes prepared with high dosages of added KOH.

Studies of the ionic concentrations of the inorganic species in the pore solutions over time, were coupled with corresponding determinations of the dissolution of the anhydrite and the crystallization of ettringite. These were inconclusive in establishing a mechanism for the unusual sorption-desorption-resorption effect. The effect does not appear to be related to the much slower effect reported with melamine sulfonate by Yilmaz and Glasser.

ACKNOWLEDGMENTS

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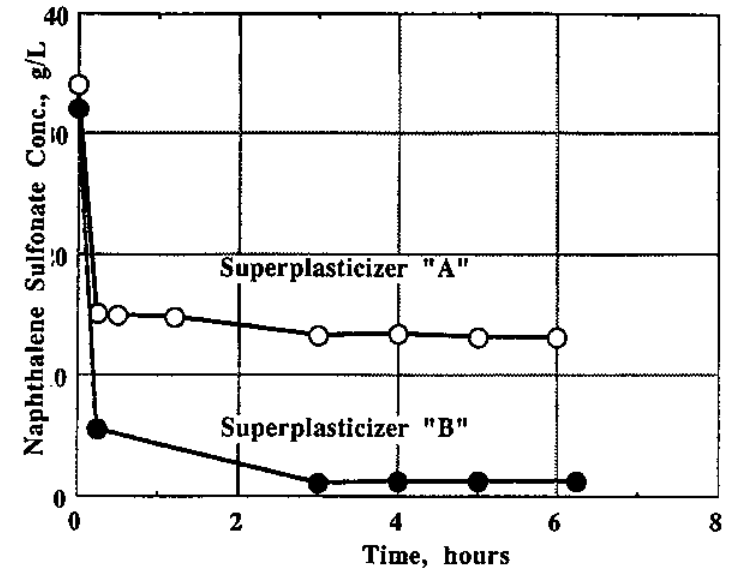


Fig. 1 Sorption of naphthalene sulfonate superplasticizers in cement paste.

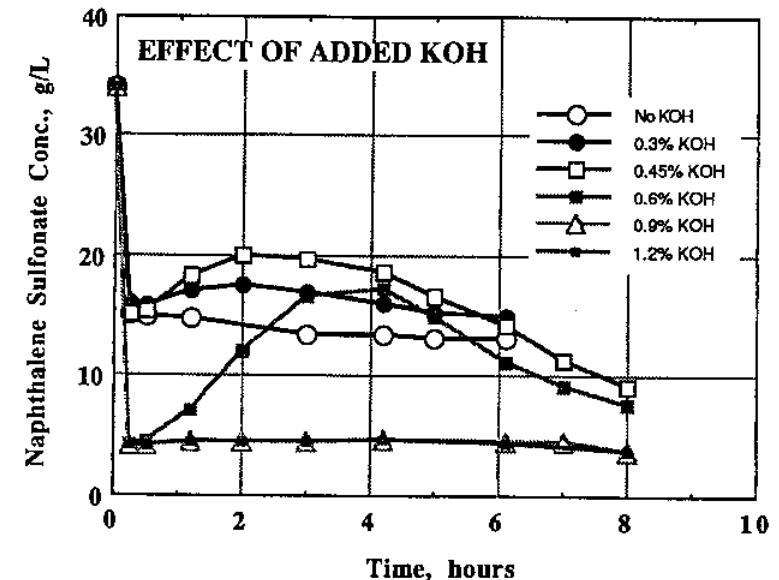


Fig. 2 Effects of KOH additions on sorption of naphthalene sulfonate superplasticizer "A".

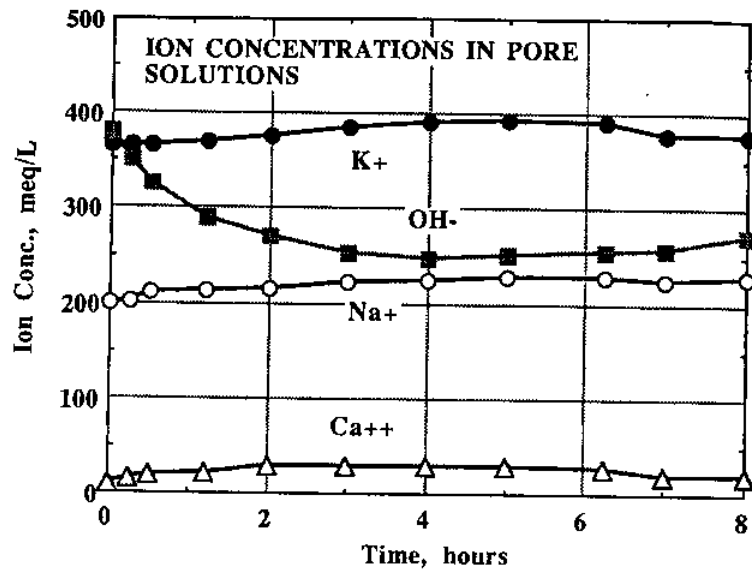


Fig. 3 Ion concentrations in pore solutions for paste with superplasticizer "A" and 0.6% Na₂O equivalent dosage of KOH

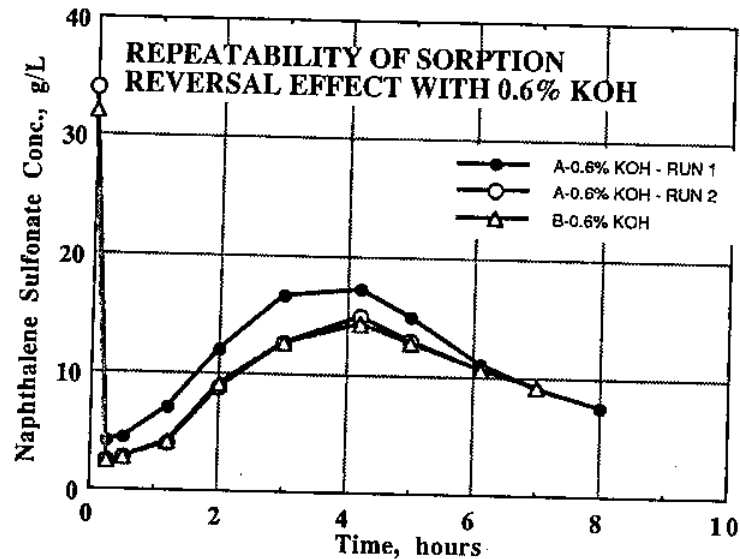


Fig. 4 Repeatability of the sorption reversal effects; results of two runs with superplasticizer "A" and one with superplasticizer "B".

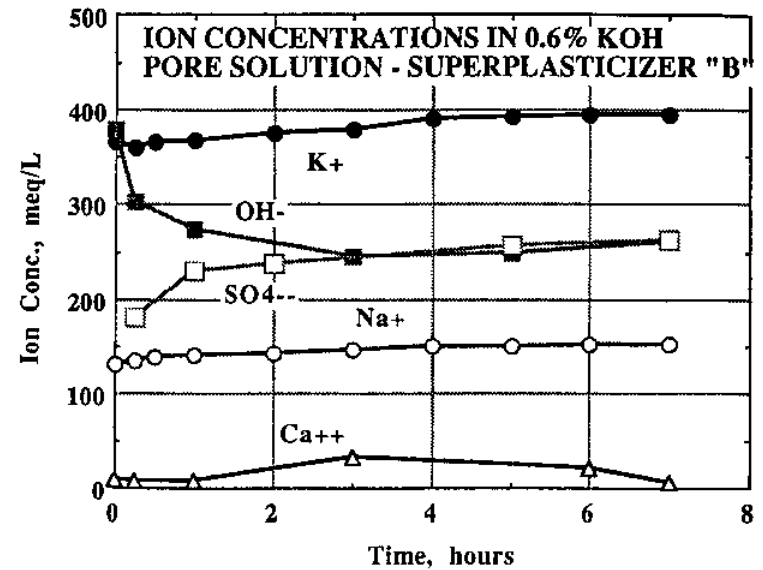


Fig. 5 Ion concentrations in pore solutions for pastes with superplasticizer "B" and 0.6% Na₂O equivalent dosage of KOH.

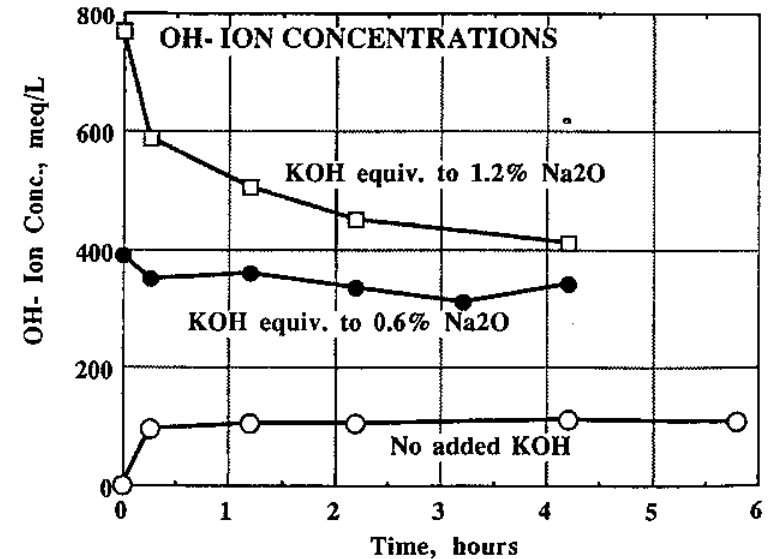


Fig. 6. OH⁻ ion concentration determinations for pastes with superplasticizer "B" at different levels of KOH addition.

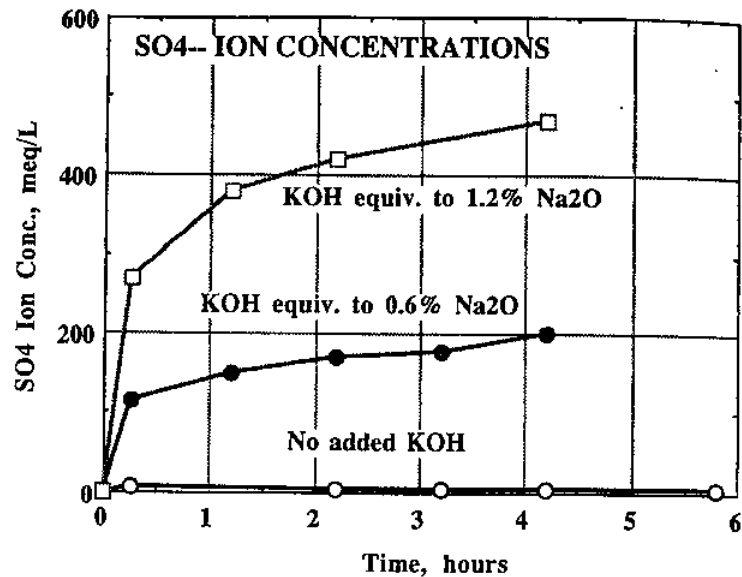


Fig. 7. SO₄²⁻ ion concentration determinations for pastes with superplasticizer "B" and different levels of KOH addition.

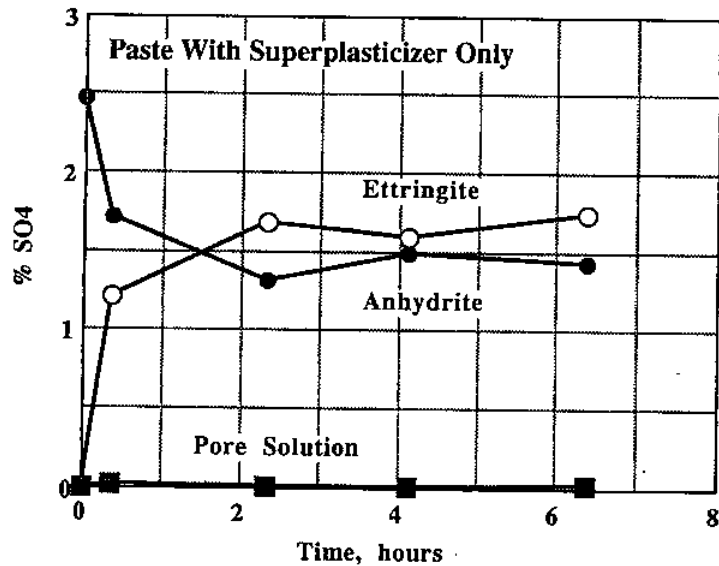


Fig. 8. Contents of anhydrite, ettringite, and sulfate in pore solution, expressed as equivalent % SO₄, in paste with superplasticizer "B" only.

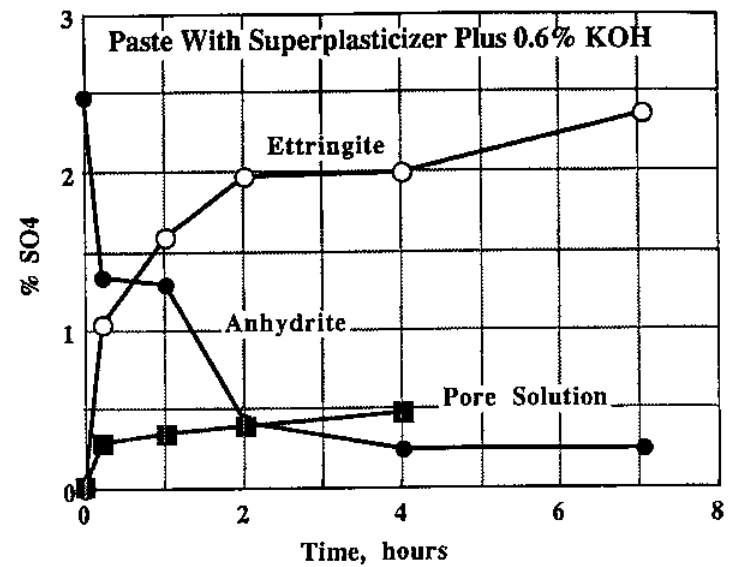


Fig. 9. Contents of anhydrite, ettringite, and sulfate in pore solution, expressed as equivalent % SO₄, in paste with superplasticizer "B" and 0.6% Na₂O equivalent dosage of KOH.

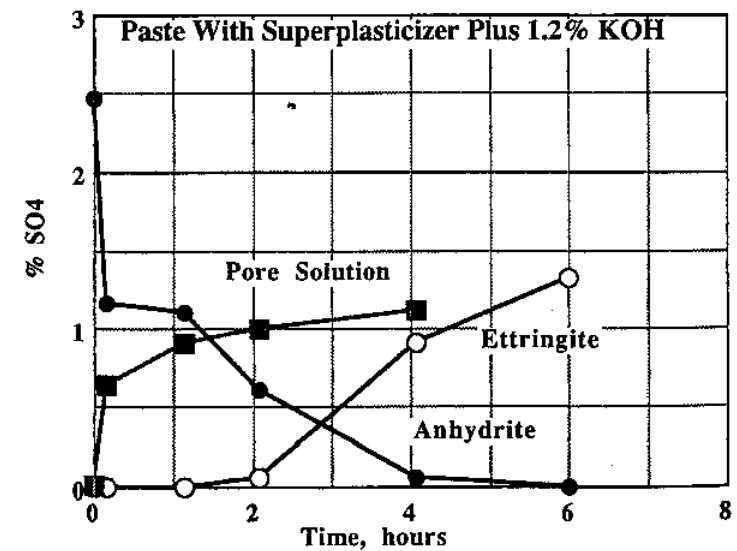


Fig. 10. Contents of anhydrite, ettringite, and sulfate in pore solution, expressed as equivalent % SO₄, in paste with superplasticizer "B" and 1.2% Na₂O equivalent dosage of KOH.