PART II

QUANTITATIVE ANALYSIS OF INTERACTIONS BETWEEN PORTLAND CEMENTS AND SUPERPLASTICIZERS
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ABSTRACT

A new approach to studying interactions between chemical admixtures and cements has been developed in this research. Features include repeated analyses at short intervals of physico-chemical parameters important in admixture effects including the sulfate-bearing phases of the cement (gypsum, hemihydrate, and insoluble anhydrite), ettringite, and concentrations of the admixture and of inorganic ions in the paste solution. The gypsum, hemihydrate, and ettringite analyses are made by DSC; anhydrite is analyzed by QXRD; admixture concentrations are measured by UV spectroscopy; and inorganic ion concentrations are measured by conventional methods. The physical behavior of the paste is also monitored.

Studies have been carried out using both naphthalene sulfonate and melamine sulfonate superplasticizer admixtures. The methods developed can be applied for any chemical admixture.

Two different conventional portland cements and a special white cement have been used. The white cement has a very low alkali content, and anhydrite is the single form of calcium sulfate present.
The effectiveness of the superplasticizer has been found to depend on maintaining a reasonable concentration of it in solution. Cement mixes that do not were found to stiffen and set prematurely. This response was found to be associated with a low concentration of sulfate in the paste solution. Adding sulfate reduces the early uptake of superplasticizer and allows the admixture to function properly.

In all cases it has been found that the presence of the superplasticizer modifies the early pattern of ettringite development.

\[ \text{Na}^+ \] ions balancing the negative sulphonate sites in the superplasticizers are immediately detected in the paste solution. As the dissolved polymer is incorporated into the hydrating cement, the sulphonate sites are replaced by \( \text{OH}^- \) ions, leading to a permanent increase in the \( \text{OH}^- \) ion concentration.

The early absorption of superplasticizer by the hydrating cement was found to be reversible under some circumstances.

When excessive amounts of alkali hydroxides were added to superplasticized white cement, premature stiffening of a variant kind was developed.
CHAPTER ONE
INTRODUCTION

1.1 General

Admixtures generally have become of major importance in concrete construction recently. Due to multiple purposes of the concrete structure and various restrictions on the construction environments, the requirements for the performance of the concrete have become more varied, and more specific for every construction. In order to satisfying the various demands for concrete, new and different kinds of chemical admixtures have been developed and recently made available. These newer chemical admixtures, such as superplasticizers, offer distinctive advantages over older systems, and appropriate use has been shown in many cases to provide major benefits in terms of both strength development and durability.

However, these benefits of chemical admixtures come at some cost in chemical complexity and possible interaction problems when incompatibilities with certain cement types, mutual incompatibilities among several chemical admixtures, or incompatibilities with other concrete components arise. Chances are higher for these deleterious interactions to take place, because using a variety of cements along with multiple kinds of admixtures at the same time in concrete is not unusual nowadays.
Although research needs for these interaction problems are high, the number of basic studies to investigate the mechanisms of the problem is smaller than that of the practical studies on admixture performance in specific concretes.

Furthermore, the methodologies for studying the effects of chemical admixtures are still to be developed. The additions of chemical admixtures result in various changes in the cement hydration processes, and affect the chemistry of pore solution and solid hydration products. Those changes taking place in time series are visualized by analyzing both organic and inorganic species in the pore solution, and by time-series analyses to show changes in the solid phases. Information obtained by those different analyses are to be integrated and evaluated properly.

Among the various chemical admixtures, benefits of the superplasticizer have become particularly apparent. Since superplasticizers were introduced to the market in 1970's, their excellent performance in obtaining better workability and higher strength in concretes have been widely acknowledged, and the use of superplasticizers become indispensable in advanced concrete construction. Some incompatibility problems with cements have been observed for certain type of superplasticizers, and are considered to be high priority research topics. Superplasticizers are thus considered to be suitable material for an application of the analytical approach.
1.2 Objectives and Scope of Work

The objectives of the research are as follows. First, a comprehensive analytical approach which is suitable for evaluating the interactions between cements and chemical admixtures quantitatively is to be established. This includes the analytical method for determining the admixture concentration levels and their changes with time in cement paste solution, using UV spectrum analysis. Subsequently, the effects of the superplasticizer on the solution phase and the solid phases need to be evaluated in time series by several analytical methods. Especially the analysis of the solids by differential scanning calorimetry (DSC) seemed promising.

In the present work, this analytical approach was applied to the study of two popular types of superplasticizers, naphthalene sulfonate and melamine sulfonate, with three cements. Two of them are ordinary portland cements used in major amounts for concrete constructions in Indiana. Another cement is a white cement, with which a cement-superplasticizer incompatibility problem was observed. The interaction phenomena between these particular cements and superplasticizers were investigated. Finally, the effectiveness and limitations of this experimental approach, and those of the component analytical methods were assessed.

This report consists of nine chapters. An introduction, and the scope of the study are presented in Chapter 1. In Chapter 2, the previous work reported in the literature concerning the interaction between the constituents of cements and admixtures is reviewed and summarized.
The materials used in this research are described in Chapter 3. Chapter 4 provides information on experimental work carried out and on methods used. This includes a summary of the paste mixes prepared and details of the experimental methods used for analyses of the solution and the solid.

In the subsequent three chapters, the experimental results are presented, and discussed. Chapter 5 covers the results on the white cement. In Chapter 6 and Chapter 7, the results on two different ordinary portland cements are presented separately.

In Chapter 8, the previously presented results on three different cements, and those on experimental method itself, are comprehensively discussed. Chapter 9 contains the detailed findings and the overall conclusions.

1.3 Terminology

Some of the terminology used in this study is clarified as follows:

1. Superplasticizers

The term "superplasticizer" is used in this study, as a synonym for the somewhat more clumsy term "high-range water-reducing admixture" preferred by some authorities.

The two types of superplasticizers used in this study have been called by different names by different researchers. The first type has been called variously "naphthalene sulfonate-formaldehyde condensate", "formaldehyde condensate of beta-naphthalene sulfonate", or "sulfonated naphthalene formaldehyde".
However, the term "naphthalene sulfonate" or "naphthalene sulfonate superplasticizer" is used for this type of superplasticizer throughout this study.

The second type has been called "melamine sulfonate-formaldehyde condensate", or "sulfonated melamine formaldehyde" by various authors. However, the name "melamine sulfonate" or "melamine sulfonate superplasticizer" will be used for this type of superplasticizer in this study.

2. Units

The units used in this study are basically SI units, or the units used conventionally in cement chemistry field.

The concentration of all inorganic ions is expressed in milliequivalent per liter, abbreviated as meq/L. 1000 meq/L equals to 1 normality (N). In contrast, the concentration of all superplasticizers is expressed in gram/liter (g/L).
3. Symbol of Oxides

The following abbreviations of the common oxides in the cement chemistry are used throughout the text.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Symbol</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>A</td>
</tr>
<tr>
<td>CaO</td>
<td>C</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>F</td>
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<td>H₂O</td>
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<td>Na₂O</td>
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<td>K₂O</td>
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</table>
2.1 Cement Paste without Admixture

Prior to discussing superplasticizer performance, some of the literature on hydration of plain cement (without admixtures) is reviewed in this section. Since chemical analysis of the solution phase is one of the primary experimental approaches used in this study, and early responses involving the solid phases containing CaSO₄ is another, these two topics were the focus of the review.

2.1.1 Solution Phase Analyses

With respect to solution phase analysis, an early and comprehensive study was performed by Lawrence [1]. He showed that the major dissolved species were Ca²⁺, K⁺, Na⁺, SO₄²⁻, and OH⁻, and that relatively high concentrations of these ions were observed early in the hydration. He observed that concentration changes were small for all the ions for the first several hours.

In the solution prior to setting, the concentrations of calcium have been a great concern, especially in relation to the precipitation of the calcium hydroxide phase and thereafter to the hardening. The approach taken frequently was to calculate the degree
of saturation in terms of calcium hydroxide. Hansen and Pressler [2] showed experimental data on the solubilities of Ca(OH)$_2$ and CaSO$_4$·2H$_2$O in alkali solution conditioned by different concentrations of KOH and NaOH. At equilibrium, they measured Ca$^{2+}$ and SO$_4^{2-}$ ion concentrations along with those of K$^+$ and Na$^+$. The results show that the Ca$^{2+}$ ion concentration slightly decreases with increasing alkali concentration in the low alkali concentration region. In higher alkali concentration range (higher than about 0.2 N), the Ca$^{2+}$ concentration was not affected by the alkalis. The SO$_4^{2-}$ concentration increases with increasing alkali ion concentrations.

However, Diamond [3] pointed out the importance of the correction for the activities of the ions. With consideration of the activity coefficient and recognizing the importance of the existence of complex ion CaOH$^+$ in the solution, Gartner et al. [4] indicated that the liquid phase of most cements were supersaturated with respect to CH by a factor of 2 to 3. With respect to gypsum, the degree of supersaturation did not exceed 1.3 in the cases studied.

Bailey et al. [5] tried to develop a computer program to calculate the concentrations of the varies species found in the solution and to obtain the ionic activity products of the solutions. They attributed the sudden drop in the ion product of Ca$^{2+}$ and SO$_4^{2-}$ ions observed within the first several minutes of hydration to the formation of secondary gypsum from more soluble forms of calcium sulfates, rather than to the formation of ettringite.
After several hours, the concentration of both the Ca$^{2+}$ and SO$_3^{2-}$ ions decrease suddenly from their plateau levels. Taylor [6] mentioned that this sharp fall corresponded to the renewed growth of ettringite observed in SEM and to the shoulder of the heat evolution curve.

Pore solutions after setting were first expressed in an apparatus described by Longuet et al. [7], and Barneyback and Diamond [8] described the methodology of expressing pore solutions using the apparatus in detail.

Taylor [9] tried to predict the increasing alkali concentration of the pore solution in a long term from the water:cement ratio, total and water-soluble alkali contents of the cement.

2.1.2 Role of CaSO$_4$ in Cement Paste Hydration

The primary purpose for the addition of CaSO$_4$ to cements is to slow down the reactions of C$_3$A, especially when alkalis are present [10]. In calorimetry measurements, the heat evolution curve of pure C$_3$A hydration in the presence of CaSO$_4$ shows a pattern similar to that of cement, which shows an intense first peak, an induction period and a second peak of heat evolution. Jawed et al. [11] explained the reason for induction period in this system of hydrating C$_3$A-CaSO$_4$2H$_2$O system as follows. They stated that ettringite is usually experimentally detected at the surface of the C$_3$A rather than on the gypsum particles. They considered that ettringite initially forms a coating on the reacting C$_3$A surface, which slows down the diffusion of inor-
ganic ions (SO$_4^{2-}$, OH$^-$, Ca$^{2+}$), and resulting in slowing down the reaction.

Mehta [12] considered that ettringite formed via a through-solution mechanism rather than via a topotactic mechanism because ettringite formed indiscriminately throughout the system, according to his SEM work.

Tadros et al. [13,14] presented a view on the retardation of C$_3$A hydration by the sulfate ion. Using C$_3$A dissolution data, they concluded that the retardation was not primarily the result of formation of an ettringite film on the C$_3$A surface but by the adsorption of sulfate ions onto the positively charged C$_3$A particles. This was said to result in reduction of the number of dissolution sites which would otherwise be available for the hydroxide ions to catalyze the dissolution.

Collepardi et al. [15] did not confirm the idea that retardation of C$_3$A hydration occurs as results of SO$_4^{2-}$ ion absorption, by showing that Na$_2$SO$_4$ did not retard C$_3$A hydration.

Though the results reported in the literature are contradictory in many cases, the conditions of the experiment were different from each other and different from those of the real cement systems. Some of the experiments were carried out in diluted suspensions, although others were closer to the real conditions of cement use.

Locher et al. [16] extensively investigated the mechanism of set of cement paste and the role of calcium sulfate in it. They considered that recrystallization of ettringite played a major part in setting. A thin ettringite layer was said to form rapidly on the surface of cement particles but did not reduce the workability of the paste.
Recrystallization of this microcrystalline ettringite into large needlelike crystals was then said to bridge the spaces between adjacent particles and cause setting. Locher et al. also considered that the reactivity of the specific C₃A present modifies the formation of ettringite, and consequently the setting time. Formation of the thin layer of ettringite and recrystallization of ettringite were accelerated when C₃A is highly reactive.

In contrast, Jawed et al. [11] had a different view on set, and considered that it depended primarily on the alite hydration rather than on ettringite formation. The beginning of the second heat evolution peaks was generally considered as the start of the rapid period of calcium silicate hydration, and the resulting rapid C-S-H formation was said to coincide with the initial set. Microscopic investigations on the solid phase, for example by Scrivener [17] also supported the idea that the set was caused by accelerated formation of CSH (and CH), rather than by the secondary growth of ettringite crystals.

Uchikawa et al. [18] considered that the set mechanism was related to both ettringite formation and alite hydration. They stated that differences in the amount and the morphology of ettringite formed resulted in different set times, especially for the case of well burnt clinker. For poorly burnt clinker however, vigorous hydration of alite and formation of C-S-H gel contributed more to the setting time.

Uchikawa et al. [18] also measured the concentration of the Ca²⁺ and OH⁻ and SO₄²⁻ ion in suspension (water:cement ratio = 4.0) of clinker with three different
forms of the CaSO\textsubscript{4}, i.e., gypsum, hemihydrate, and insoluble anhydrite. Influences of the form of CaSO\textsubscript{4} were observed on the concentration of the Ca\textsuperscript{2+} ion and the SO\textsubscript{4}\textsuperscript{2−} ion, but not on that of the OH\textsuperscript{−} ion. The CaSO\textsubscript{4} saturation ratio observed increased in the order of anhydrite, gypsum, and hemihydrate added to clinker. When hemihydrate was used, there was a sudden decrease in the CaSO\textsubscript{4} saturation ratio due to the secondary gypsum formation.

Odler et al. [19] examined the effects of the different forms of the calcium sulfate and found that the rate of ettringite formation was reduced and the beginning of its conversion to the monosulfate was delayed if anhydrite was used as the CaSO\textsubscript{4}, compared to the hemihydrate or gypsum.

Tang and Gartner [20] showed that the chemical and physical form of the calcium sulfates as well as the amount added were very important factors in governing the characteristics of early cement paste hydration. They examined mixtures of a clinker and a various sources of the sulfate ion, including calcium sulfates as gypsum, hemihydrate, and insoluble anhydrite; alkali calcium sulfates as calcium langbeinite (2CaSO\textsubscript{4}·K\textsubscript{2}SO\textsubscript{4}) and syngenite (CaSO\textsubscript{4}·K\textsubscript{2}SO\textsubscript{4}·H\textsubscript{2}O); and alkali sulfates as aphthitalite (3K\textsubscript{2}SO\textsubscript{4}·Na\textsubscript{2}SO\textsubscript{4}). The presence of relatively soluble sulfates retarded the initial C\textsubscript{3}A hydration (for the first 2 minutes) and the rate at which C\textsubscript{3}A was dissolved and converted to ettringite varied significantly with the form of the sulfate added. They also found that increasing physical distribution of gypsum by intergrinding resulted in a smaller initial extent of C\textsubscript{3}A hydration.
These authors summarized a mechanism of sulfate phase reactions in a series of chemical reactions of different velocities as follows:

1. Initial dissolution of the calcium aluminate (rapid, very exothermic)

   \[ C_x A_y F_z + H_2 O = x' Ca^{2+} + 2y' AlO_2^- + (2x - 2y)' OH^- + z' FH_3 \]

2. Formation of initial protective hydrate layer (rapid)

   \[ n' Ca^{2+} + 2m' AlO_2^- + 2p' OH^- + (n - m - p)' SO_4^{2-} = C-A-S-H \]

3. Initial dissolution of sulfate phases (at various rates)

   \[ C_S, C_2 S_2 H, C_S H_2, K_S, K_3 N_S_4, K(CS)_2 H, K(C_2 S)_3 = Ca^{2+}.SO_4^{2-}.K^+.Na^+(aq.) \]

4. Initial dissolution of CaO and calcium silicates (at various rates)

   \[ CaO, C_3 S, C_2 S = Ca^{2+} + 2OH^- (+ C-S-H) \]

5. Establishment of gypsum equilibrium (fairly rapid)

   \[ Ca^{2+} + SO_4^{2-} = CSH_2 \]

6. Establishment of syngenite equilibrium (fairly rapid)

   \[ 2K^+ + Ca^{2+} + SO_4^{2-} = KCS_2 H \]

7. Steady consumption of CaSO_4 to form ettringite (slow)

   \[ C_x A_y F_z + (6y - x)' Ca^{2+} + 3y' SO_4^{2-} + (6y - 2x)' OH^- = y' Ca_6 A_3 S_3 H_{32} + z' FH_3 \]

Tang and Garner considered that the step 2 reaction is formation of protective layer onto the calcium aluminate surface which retards the calcium aluminate dissolution (step 1) and this layer may well be amorphous. The step 7 reaction is a slow pre-
cipitation of ettringite which is probably limited by diffusion of one of the components through the protective layer. After the step 7, when the sulfate supply is almost completely exhausted, that is, the sulfate near the calcium aluminate surface becomes insufficient to continue the reaction in the step 7, the ettringite layer becomes unstable and decomposes into the AFm phase.

Tang et al. [20] also considered that the secondary gypsum or syngenite formation from hemihydrate or calcium langbeinite, respectively, reduced the fluidity of the paste, or caused "mild false set'. Locher [16] observed the same phenomena.

Penko [21] tested a low alkali content clinker with addition of gypsum or alkali sulfate or both, and found that the dissolution rate of gypsum controlled the rate of formation of ettringite and the time of the conversion from the SO$_4^{2-}$ ion to the OH$^-$ ion in the liquid phase. If alkali and gypsum were overdosed in the cement system, gypsum remained undissolved longer and thus the SO$_4^{2-}$ ion concentration did not drop within a day.

Penko concluded that the undissolved solid gypsum in the cement system is the source of the slowly dissolving SO$_4^{2-}$ ion, and the limitation on its conversion to ettringite. The alkali sulfate on the other hand, dissolved quickly in the liquid system, provided the SO$_4^{2-}$ ion needed for initial ettringite formation, and caused the alkalinity resulted from hydrolysis.
2.2 Performance of Superplasticizers

An overview of research on cement paste with superplasticizer is provided in this section, which incorporates certain features in the hydration of cement free of admixture.

2.2.1 Mechanism of Superplasticizer Adsorption

There are a number of variations in the superplasticizers with regard to their chemical structure, but the two widely used have as their main component either naphthalene sulfonate or melamine sulfonate. Purified lignosulfonates are also used as superplasticizers, but to a lesser degree.

Naphthalene sulfonate based superplasticizers were developed in Japan, and the pioneering research work was summarized in a paper by Hattori [22]. Melamine sulfonate superplasticizer was developed in Germany [23]. The molecular structure of these superplasticizers are shown in Fig. 3.2-1. Both polymer structures are of reasonably long chains on which electric charge donor groups such as \(-\text{SO}_3^-\text{-M}^+\) are attached.

The actions of the two types of superplasticizer are basically the same. Generally speaking, the superplasticizer chains are adsorbed on the cement particles and thereby introduce strong negative charges on the particles at their interfaces with the solution; this results in an electrostatic repulsion between particles. This causes the dispersion of particles and reduces the viscosity of the cement paste. However, this view is too
general, and it will be discussed further.

The zeta potential of the cement particles is a key parameter to understand the performance of the superplasticizer, since the electrostatic force between particles is considered to be the essential driving force for the adsorption of the superplasticizer and for the fluidification of the paste.

Tattersall and Banfill [24] explained that the cement particles can obtain a charge either as a result of imperfections in the crystal structure near the surface (disorders), or through the preferential adsorption of specific ions on the surface.

When the superplasticizer is pre-dissolved in the mix water, the hydration of the cement grain and the adsorption of the superplasticizer onto the cement particles take place simultaneously in the first few minutes after the contact. However it is difficult to differentiate, in real cement hydration, whether the adsorption is on the anhydrous cement particles or on their early hydration products.

Nawa et al. [25] cited the work of Mascolo and Marroccoli [26], who investigated the reactivity of calcium aluminate hydrates. Based on the idea that the structure of $C_4A\cdot nH$ is a complex salt that consists of positively-charged $[Ca_2Al(OH)_6]^+$ balanced by negatively-charged interlayers of composition $[OH^-\cdot mH_2O]$, they concluded that the interlayer $OH^-$ anion of the $C_4A\cdot nH$ could be easily exchanged with various anions, and that its selectivity of anions in exchanging were determined primarily by the valence of the anion. Then Nawa et al. [25] suggested that the sulfate ion or the sulfonate group of the superplasticizers could be exchanged with the $OH^-$ ion in the
calcium aluminate hydrate phases. This was suggested as another interpretation of the adsorption phenomena.

2.2.2 Mechanism of Cement Particle Dispersion

According to Tattersall and Banfill [24], the concepts of interparticle forces, based on the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory would be explained as follows. The electric double layer consists of a layer of charged particle surface and counterions electrostatically attracted to the surface but exponentially diffuse away toward the bulk solution. When two particles approach each other in a suspension, their diffuse double layers begin to repel each other. Simultaneously, there is a force of attraction between particles due to van der Waals forces, which decreases with distance of the particles. By adding these repulsion and attraction, it is found that the resultant potential energy curve for particle interaction has a minimum value at a distance where an equilibrium is achieved. As the electrolyte concentration increases, the electrical double layer is compressed and the energy barrier decreases to nothing so that colliding particles can fall into the every minimum and stick together, and thus flocculate.

However, there are criticisms for treating flocculation in cement paste by the usual DVLO equations of colloid chemistry. Diamond [27] presented several reasons, including the large size of most of the ground clinker particles, the multitude of chemical phases that are exposed on the cement particle surfaces, the high volume concentration of the particles in paste of normal water:cement ratio, and the fact that
chemical reactions are occurring on the surface even during the dormant period.

Tattersall and Banfill [24] described that the condition of a cement-water suspension can be modified in three ways that will prevent the formation of a flocculated structure as follows.

i. Expansion or contraction of the electrical double layer around the particles.

ii. Generation of electrical repulsive forces between particles by adsorption of ionized compounds.

iii. Build-up of protective steric barriers to flocculation.

They considered that the mechanism of deflocculation induced by the superplasticizers was a mixture of both effects ii. and iii. listed above.

The steric effect is such that when adsorbed molecules form multilayer structure around the particle, the particles cannot physically approach each other so closely as the equilibrium potential distance. This skin of adsorbed molecules is also called a steric barrier. Taylor [6] considered that this steric effect is not a major action induced by superplasticizer. He considered the evidence convincing that uptake was mainly by the hydration products, and that significant amounts of the superplasticizer were absorbed as well as adsorbed. He supported the idea of an increase in zeta potential being the primary force.

Daimon et al. [28] added another possible mechanism of decreasing flocculation, which was an increase in solid-liquid affinity, but they considered the contribution of
this mechanism to be small.

The state of the superplasticizers adsorbed at the interface are usually modeled as long chains consisting of polymer mingled and attached loosely on the surface at relatively small numbers of negative sites [29]. Kondo et al. [30] acknowledged this adsorbed state as "loop" adsorption in contrast to "train" adsorption, in which the adsorbed polymer is stuck closely to the adsorbent. In "loop" adsorbed state, most of the active negative sites on the chains are in the neighborhood of the particle, but not neutralized by the charge on the cement surface. Andersen [31] considered that this gives more negative charges or the zeta potential onto the particle, which could also compress the electric double layer.

The fluidizing effect of the superplasticizer depends on its molecular weight. It has been generally considered that the higher the molecular weight, the more fluidity is imparted to the paste [15]. However, Hattori [22] stated that maximum superplasticizer performance was obtained for naphthalene sulfonate polymers with a degree of polymerization of about 10.

Andersen et al. [32] investigated the effect of the molecular weight of sulfonated polystyrene superplasticizer, and found that the optimum molecular weight to give the maximum adsorption onto a ordinary portland cement was 16,000 g/mole; superplasticizers of larger molecular weights were less adsorbed onto the cement, but gave a larger negative zeta potentials.
Experimental techniques usually used in investigating the effect of degree of polymerization include gel permeation chromatography (GPC) to determine the molecular weight distribution of the polymer, and an ultrafiltration process (UF) to remove the low molecular weight fraction [33, 34].

2.2.3 Absorption Characteristics

The adsorption of the superplasticizer at the first stage of hydration has been considered as the adsorption of organic molecules onto the solid. This topic has been investigated from the interest of the mechanism of organic retarders which are usually smaller molecules. In 1972, Young [35] carried out an extensive review on the mechanism of retardation. He stated that the admixtures in general were preferentially adsorbed onto the aluminate phases in the very early stage of the cement hydration, and were largely removed from the liquid phase.

The adsorption of salicylic acid was investigated by Blank et al. [36], and their results showed that the amount of adsorption onto the different cement minerals were in the order of $\text{C}_3\text{A} > \text{C}_4\text{AF} > \text{C}_3\text{S}$, but adsorption were measured in organic solution.

Diamond [37-39] studied the suspension of $\text{C}_3\text{A}$ and $\text{C}_4\text{AF}$ in the solution of salicylic acid. He observed a precipitation of a largely amorphous hydration product containing significant amount of salicylate, and considered that this phase is mainly due to removal of the salicylic acid from solution. Then he suggested that the interaction
between aluminum-bearing cement and hydrating cement compounds and salicylic acid is different from the simple physical adsorption.

As with other organic compounds, it is known that the amount of the superplasticizer adsorbed on different cement minerals are different. Adsorption onto pure C₃A and C₄AF are much larger than onto pure C₃S and C₂S, and are larger than overall adsorption onto ordinary portland cement [40, 41].

But again, there is a complication in that the adsorption onto the anhydrous or hydrated phases are not differentiated by adsorption experiments in an aqueous suspension. Massazza et al. [42, 43] examined the suspension of C₃A, ettringite, monosulfate in a non-aqueous solution of dimethylsulphoxide (DMSO) and obtained adsorption isotherms of superplasticizers showing considerable adsorption on calcium sulfoaluminate phases but little adsorption on C₃A.

Ramachandran [44] also obtained the similar results by examining C₃A-gypsum-H₂O system with superplasticizers. In addition, he diluted the aqueous suspension and did not detected any desorption of superplasticizer (naphthalene sulfonate and melamine sulfonate) which adsorbed on the surface of hydrated aluminate or sulfoaluminate phases. Taylor [6] cited several works which studied the anhydrous and hydrated compounds in aqueous and non-aqueous media and quoted that calcium lignosulphonate and superplasticizers were adsorbed by CSH, AFm phases or CH but not by C₃S, C₃A, or C₃AH₆.
Suzue et al. [40] compared the adsorbed amount of the superplasticizer in the suspension of each cement mineral separately for the cases with and without the presence of gypsum. Where there was no gypsum, the adsorption onto C₃A and C₄AF was about ten times as much as with gypsum present. They also showed that the adsorption of superplasticizer pre-dissolved in the mix water onto C₃A and C₄AF was significantly higher than that when the superplasticizer was added after the contact with water, which tends to explain the advantage of the late addition of the superplasticizer.

Chiocchio et al. [45] claimed that the optimum time to add the superplasticizer was at the beginning of the induction period. They remarked that a large portion of admixture added before the intense first C₃A hydration period was over, was taken up by the early hydration product of the aluminate phase and immediately covered by the subsequent hydration product. Thus the dispersing action was inefficient.

Andersen et al. [46] found that the average negative zeta potential of cement particles in the presence of naphthalene sulfonate superplasticizer decreased with increasing degree of CaSO₄ saturation. They attributed this to the compression of the electric double layer in a stronger ionic solution which also caused the less adsorption of the superplasticizer.

The effects of the alkali sulfate in cement is also important to the adsorption behavior. Nawa et al. [47] found that the adsorption of the naphthalene sulfonate superplasticizer on C₃A was greatly reduced in the presence of Na₂SO₄. The pres-
ence of the sulfate ion derived from either calcium sulfate or alkali sulfate decreased the adsorption of naphthalene sulfonate on C₃A and C₄AF, but increased the adsorption on C₃S.

In order to investigate this compositional difference in adsorption characteristics, attempts were made by many researchers to determine the zeta potential of each cement mineral separately. Tadros et al. [14] showed that the zeta potential of C₃A was initially positive, but it went down to zero due to the adsorption of the sulfate ions derived from either hemihydrate or K₂SO₄. Zelwer [48] concluded that the zeta potential of C₃S and of cement particles were negative in the absence of admixtures. That of C₃A particle was reported to be positive. Nawa et al. [25] also confirmed that in pure water, the zeta potential of C₃A and C₄AF was positive, whereas it was negative for C₃S. In addition, the zeta potential of C₃A and C₄AF changed from positive to negative when either the sulfate ion or naphthalene sulfonate superplasticizer were added to the suspension.

Thus they concluded that fresh cement paste suspension consists of particles having different values of zeta potential, and that since the naphthalene sulfonate and the sulfate ion are both negative they tend to be adsorbed competitively on the C₃A or C₄AF surfaces which initially have positive zeta potentials.
2.2.4 Effects of Superplasticizer on Early Hydration

The addition of superplasticizer to cements results in a more dispersed state of the cement particles. This exposes a larger surface area, and thus the cement hydration is promoted. However, the addition of the superplasticizer also leads to retardation by an inherent mechanism, in which the adsorbed long chain polymer coats the surface of the cement particles and hinders further hydration.

Odler and Becker [49] found that the hydration of C3S was retarded by all three types of superplasticizers (naphthalene sulfonate, melamine sulfonate, and lignosulfonate).

Massazza et al. [42, 43] investigated effects of the superplasticizer on C3A hydration. He found that both naphthalene sulfonate and lignosulfonate slowed down the rate of ettringite formation. He also noticed a damage of morphology of the ettringite associated with the incorporation of superplasticizer, in that the size of the ettringite was smaller with the admixture.

Ramachandran [44] found in a suspension of C3A-gypsum-H2O that the rate of hydration at very early age to form ettringite was accelerated by the superplasticizers (naphthalene sulfonate and melamine sulfonate), but conversion to monosulfate, corresponding to the second heat evolution, was retarded.

Aitcin et al. [50] classified cement particles into three fractions by size i.e. coarse, medium, and fine, and compared the degree of retardation caused by the naphthalene based superplasticizer on each fraction. The medium fraction (30μm -
4μm) was the most retarded, whereas the fine fraction (< 4μm) showed almost no retardation. Chemical analysis showed an increase in SO₃ and alkali contents in the finer fraction compared to the others.

Nawa et al. [47] showed that the retardation effect of naphthalene sulfonate superplasticizer increased with increasing alkali sulfate content of the cement. They suggested that the alkali sulfate hindered the adsorption of the admixture onto the aluminate phases, permitting larger adsorption on the silicate phases such as C₃S and C₂S, which delayed the overall hydration.

The calcium salt of naphthalene sulfonate superplasticizer has been generally considered as non-retarding. However, whether the hydration was retarded or not by the calcium salt depended on the chemical composition of the cement, as shown for example by Basile et al. [51].

2.2.5 Effects of Superplasticizer on Rheological Characteristics

The rheology of the cement paste has been investigated for long time but general agreement has not been reached, probably because the experimental results were highly dependent upon the experimental methods used including the apparatus and the mixing procedure. In this section, the review is limited to those papers which examined the effect of superplasticizer on rheological properties.
Banfill [52] cited the work by Petrie [53] who found that, as the dosage of a naphthalene based plasticizer increased, the flow behavior changed from Bingham to reversible Newtonian, i.e. the width of the hysteresis loop and the yield value decreased. A similar result was found by Banfill [54], in that a naphthalene sulfonate reduced both the yield value and the hysteresis loop area almost to zero.

Daimon and Roy [28,55] carried out an extensive study on the rheology of the paste relating with the adsorption characteristics of superplasticizers and the zeta potential generated thereby in the suspension. They found that the zeta potential obtained was proportional to the amount of superplasticizer adsorbed, and to the fluidity of the paste, and concluded that zeta potential was the cause of improved dispersion.

Banfill [52] studied the effect of both naphthalene sulfonate and melamine sulfonate superplasticizers on the flow properties of a cement paste of 0.35 water:cement ratio. The yield value of the cement paste decreased virtually to zero at high dosage, whereas the plastic viscosity decreased about 40% to a minimum value and then increased slightly with further increase in the concentration of the admixture. He also stated that both yield value and plastic viscosity of the paste were affected more by the melamine sulfonate than by the naphthalene sulfonate at equal dosage.

Not much work has been reported with regard to the mechanism through which the adsorption causes an improvement in the workability of the paste. Massazza et al. [56] examined suspensions of C\textsubscript{4}AH\textsubscript{13} and C\textsubscript{3}AH\textsubscript{6} in lime water with superplasticiz-
ers, and reported poor correlation between the zeta potential value of calcium aluminate hydrates in those suspension and the apparent viscosity of the paste.

Researcher such as Ramachandran [44] considered that the viscosity of the paste depends on the amount superplasticizer adsorbed on the silicate phases. Suzue et al. [40] reasoned that the effectiveness in increasing fluidity of late addition of the superplasticizer is due to a larger adsorption on the silicate phases. With early addition some superplasticizer is removed from the liquid almost immediately by the rapidly hydrating aluminate phase. Nawa et al. [47] measured zeta potentials of calcium silicate particles and of calcium aluminate particles in superplasticized cement systems, and found that both kinds of particles were charged negatively. However, they found that the aluminate particles had a higher absolute potential than the silicate particles. They suggested that this reflects greater uptake of the superplasticizer by the aluminate particles. Since the viscosity of the suspension is governed mainly by the repulsion between silicate particles, this effect was considered to result in larger viscosity than would have been produced by the superplasticizer of aluminate particles had not been present.

The form of the calcium sulfate present in a given cement has several effects on the rheology of superplasticized cement paste. The rate of the dissolution of free calcium sulfate is generally considered to decrease in the series, hemihydrate > gypsum >> anhydrite. Basile et al. [51] tested the effect of the CaSO₄ form on the rheology of cement paste using the mini slump cone. Two clinkers, each with either gypsum or hemihydrate were examined with and without the addition of naphthalene sulfonate
(calcium salt) superplasticizer. The fluidity of the superplasticized paste was always higher with gypsum than with hemihydrate.

The same result was obtained by Nawa et al. [47]. They compared the effects of the three forms of calcium sulfate (gypsum, hemihydrate, anhydrite) on the viscosity of superplasticized cement paste as measured by a coaxial cylinder viscometer. They found that pastes with low alkali clinker and anhydrite always showed extremely high viscosity regardless of the dosage of the superplasticizer. For a medium and a high alkali clinker, the viscosity of the paste was found to decrease in the order of hemihydrate, anhydrite, and gypsum.

2.2.6 Superplasticized Concrete

The rheological behaviors of superplasticized concrete have been associated with the characteristics of the pastes discussed so far. Rixom and Waddicor [57] measured the rheological parameters of a superplasticized concrete as a function of the dosage of the admixture, by using special apparatus capable of measuring the torque when mixing. They found that the yield value was significantly reduced by the admixture but the plastic viscosity was not much reduced. Tattersall and Banfill [24] reached the same conclusion.

Slump loss is one of the major problems for concrete with superplasticizer. The stiffening rate depends greatly on the specific cement composition, especially the relative proportions of sulfate and C₃A. Meyer and Perenchio [58] stated that the rate of
slump loss increased as $C_3A$ content of the cement increased, and Khalil and Ward [59] stated that the rate of slump loss decreased with increasing $SO_3$ content. Basile et al. [51] stated that the rate of slump loss of concrete with superplasticizer appeared to be higher in concrete with cement containing hemihydrate than with cement containing gypsum.

2.2.7 Admixture - Cement Incompatibility Problems

A few cases of admixture-cement incompatibility problems are described for reference. It is well known that lignosulfonate admixture sometimes causes abnormal quick setting. Some work such as that of Coulon [60] suggested that the sulfate and $C_3A$ contents were important in this regard. He concluded that lignosulfonate admixture inhibited the dissolution of sulfate from the cement for a limited time so that free hydration of $C_3A$ could take place, giving flash set. Dodson et al. [61] tested the effects of different forms of calcium sulfates and reported that natural anhydrite with portland cement clinker could produce flash set in paste in presence of calcium lignosulfonate admixture. The rate of dissolution of natural anhydrite in lime water is slower than those of gypsum or hemihydrate, as other researchers have pointed out [16, 62, 63], but in addition, Dodson et al. showed that the dissolution rate of natural anhydrite was significantly reduced where lignosulfonate admixture was present. They considered that this was probably caused by the adsorption of lignosulfonate onto natural anhydrite particles, which retarded their dissolution.
Other instances of admixture-cement incompatibility involve the results of delayed conversion of hemihydrate to gypsum. When this process, normally completed during the mixing cycle, is delayed, false set may be exhibited. Adsorption of lignosulfonate (or other organic admixtures) onto hemihydrate surfaces may, in a few cases, delay its conversion to gypsum and so induce tendencies toward the occurrence of false setting.

Tattersall [24] reported a particular case that the yield value measured for concrete was about 3 times as high when a calcium lignosulfonate admixture was used. This kind of difficulty could be overcome by late addition of the lignosulfonate after a few minutes' mixing.

This importance of the mixing sequence was early discussed for the set-retarding admixture by Bruere [64], who found that about several minutes late addition of lignosulfonate had remarkably extended the induction period compared to the case where admixture was predissolved.

Grutzeck [65] reported a case of potential incompatibility between salt and superplasticizer. Mixing of saturated NaCl solution with the naphthalene sulfonate superplasticizer caused extreme foaming.
CHAPTER THREE
MATERIALS

3.1 Cement

Two different kinds of ASTM Type I ordinary portland cement and one white cement were used for the study. The mill analysis of each cement was provided by the cement manufacturers, and is shown in Table 3.1-1. In addition, the SO$_3$ content determined in this laboratory by the author is also shown in the table. The physical data of each cement provided by the cement manufacturers is shown in Table 3.1-2.

The first cement, designated cement "L", was produced by Lone Star Industries at Greencastle, IN. This particular cement has been used in the Materials Area Concrete Laboratory at Purdue University as a standard laboratory cement (Laboratory No. 326), and considered to be representative of cements in northern and central Indiana.

The second cement, designated cement "S", was produced by Southwestern Portland Cement Co. in Fairborn, OH. This particular cement has also been used in prior studies at Purdue University, and is considered as representative of cements used in southern Indiana.

The white cement "W" is a sulfate resisting ASTM Type I portland cement, produced by Aalborg Portland A/S, Denmark, and supplied through the Lehigh Portland
### Table 3.1-1 Mill analysis and Bogue composition of cements

<table>
<thead>
<tr>
<th>Chemical Analysis (%)</th>
<th>Type of Cement</th>
<th>Cement &quot;L&quot;</th>
<th>Cement &quot;S&quot;</th>
<th>Cement &quot;W&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.98</td>
<td>20.6</td>
<td>23.88</td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.38</td>
<td>4.0</td>
<td>1.94</td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.46</td>
<td>3.1</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>64.34</td>
<td>61.36</td>
<td>70.03</td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>1.09</td>
<td>4.9</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>3.03</td>
<td>2.8</td>
<td>1.82</td>
<td></td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.09</td>
<td>0.25</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>0.72</td>
<td>0.90</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Alkalis, Na₂O equiv.</td>
<td>0.56</td>
<td>0.85</td>
<td>0.083</td>
<td></td>
</tr>
<tr>
<td>Loss on Ignition</td>
<td>1.40</td>
<td>1.9</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>Insoluble Residue</td>
<td>0.23</td>
<td>0.28</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>SO₃ (analyzed by author)</td>
<td>3.17</td>
<td>-</td>
<td>3.13</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Bogue Composition (%)</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>54.14</td>
<td>54.0</td>
<td>74.2</td>
</tr>
<tr>
<td>C₅S</td>
<td>19.39</td>
<td>18.36</td>
<td>12.5</td>
</tr>
<tr>
<td>C₃A</td>
<td>10.10</td>
<td>5.35</td>
<td>4.4</td>
</tr>
<tr>
<td>C₄AF</td>
<td>7.47</td>
<td>9.43</td>
<td>1.3</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>5.15</td>
<td>4.76</td>
<td>3.1</td>
</tr>
</tbody>
</table>
Table 3.1-2 Physical data of cements

<table>
<thead>
<tr>
<th>Physical Data</th>
<th>Type of Cement</th>
<th>Cement &quot;L&quot;</th>
<th>Cement &quot;S&quot;</th>
<th>Cement &quot;W&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blaine Fineness (cm²/g)</td>
<td></td>
<td>3275</td>
<td>3720</td>
<td>-</td>
</tr>
<tr>
<td>Fineness (#325, % passing)</td>
<td></td>
<td>83.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Soundness</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Autoclave Expansion (%)</td>
<td></td>
<td>0.011</td>
<td>0.18</td>
<td>-</td>
</tr>
<tr>
<td>Normal Consistency (%)</td>
<td></td>
<td>25.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Time of Setting</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gillmore Initial (hr:min)</td>
<td></td>
<td>1:55</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Gillmore Final (hr:min)</td>
<td></td>
<td>3:50</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Vicat Initial (hr:min)</td>
<td></td>
<td>1:25</td>
<td>2:27</td>
<td>-</td>
</tr>
<tr>
<td>Vicat Final (hr:min)</td>
<td></td>
<td>3:00</td>
<td>4:00</td>
<td>-</td>
</tr>
<tr>
<td>Air Entrainment (% by volume)</td>
<td></td>
<td>9.7</td>
<td>7.6</td>
<td>-</td>
</tr>
<tr>
<td>Compressive Strength (psi):</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(2 inch Mortar cubes)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Day</td>
<td></td>
<td>2140</td>
<td>1780</td>
<td>-</td>
</tr>
<tr>
<td>3-Days</td>
<td></td>
<td>3430</td>
<td>3090</td>
<td>-</td>
</tr>
<tr>
<td>7-Days</td>
<td></td>
<td>4290</td>
<td>4190</td>
<td>-</td>
</tr>
<tr>
<td>28-Days</td>
<td></td>
<td>5380</td>
<td>5360</td>
<td>-</td>
</tr>
</tbody>
</table>
X-ray diffraction patterns of those three cements are provided in Fig. 3.1-1 to Fig. 3.1-3.

Cement L has a relatively high $C_3A$ content. It has 5.15% of CaSO$_4$ according to the Bogue calculation, and the mineral form of the CaSO$_4$ is hemihydrate.

Cement S contains an unusually high MgO content, 4.9%. The alkali content is 0.85% Na$_2$O equivalent, somewhat higher than that for cement L. The form of CaSO$_4$ is a mixture of hemihydrate and gypsum.

The white cement was selected for use in this study because of its very low alkali content (0.083% Na$_2$O equivalent). It also has low contents of both aluminum and iron. The SO$_3$ content by the author's analysis is in the normal range, 3.13%, in contrast to the mill analysis data, which indicated only 1.82%. The XRD pattern shows that the calcium sulfate is completely in the form of natural anhydrite (insoluble anhydrite), and DSC analysis does not show any dehydration peak.

3.2 Superplasticizer

The two most popular superplasticizer types, based respectively on naphthalene sulfonate and melamine sulfonate were studied in this research. The molecular structure of the repeating unit of each of these polymeric types is shown in Fig. 3.2-1.
Fig. 3.1-1 X-ray diffraction pattern for cement "L."
Fig. 3.1.3 X-ray diffraction pattern for white cement "W"
Fig. 3.2-1 Molecular structure of superplasticizers
3.2.1 Naphthalene Sulfonate Superplasticizers

Two commercial superplasticizers, classified into the category of sodium beta-naphthalene sulfonate formaldehyde condensate, were used in this adsorption study. The first superplasticizer, designated superplasticizer "A", was supplied by the W.R. Grace Co. It is a dry solid product and was used in the study reported by Burk et al. [66] of W.R. Grace Co. (their designation "Admixture A1"). The second superplasticizer, designated superplasticizer "B", was a commercially-available solution form of "Mighty 150", produced by Kao Corporation.

Both superplasticizers are not simple materials, but mixtures of monomers, polymeric species of various degree of polymerization (chain lengths), and some inorganic salt impurities. In Table 3.2-1, chemical analysis data and physical properties of superplasticizers are summarized. A breakdown of the molecular species present in superplasticizer A was obtained from the paper by Burk et al. There are no similar data available for superplasticizer B or the melamine sulfonate superplasticizer.

The solid content of the superplasticizer B was determined by drying the sample of known volume in oven at 105°C, and it was found to be 52%.

To determine the inorganic components quantitatively, the original mixing water containing the specified amount of pre-dissolved admixtures was chemically analyzed. The contents of each element in the original admixture were calculated, and are also shown in Table 3.2-1. The inorganic salt impurity contents of each admixture were calculated from the contents of SO₄ in solution, assuming that the SO₄ in the original...
Table 3.2-1 Chemical and physical data on superplasticizers

<table>
<thead>
<tr>
<th>Chemical Analysis Data (%)</th>
<th>Napthalene Sulfonate</th>
<th>Melamine Sulfonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superplasticizer</td>
<td>A</td>
<td>B</td>
</tr>
<tr>
<td>Solid Components (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Monomer</td>
<td>8.18</td>
<td>-</td>
</tr>
<tr>
<td>Nonadsorbables</td>
<td>10.49</td>
<td>-</td>
</tr>
<tr>
<td>(mostly dimer &amp; trimer)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Higher Polymers</td>
<td>68.03</td>
<td>-</td>
</tr>
<tr>
<td>Na3SO4</td>
<td>13.3</td>
<td>-</td>
</tr>
<tr>
<td>Inorganic composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(by analysis) (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na</td>
<td>11.6</td>
<td>8.6</td>
</tr>
<tr>
<td>K</td>
<td>0.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Ca</td>
<td>0.2</td>
<td>0.7</td>
</tr>
<tr>
<td>OH</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SO4</td>
<td>3.2</td>
<td>0.7</td>
</tr>
<tr>
<td>NaOH estimated</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na2SO4 estimated</td>
<td>4.7</td>
<td>1.0</td>
</tr>
<tr>
<td>organics composition</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(by subtraction) (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>85.0</td>
<td>89.9</td>
<td>86.1</td>
</tr>
<tr>
<td>organics charge density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(meq/g)</td>
<td>5.26</td>
<td>4.45</td>
</tr>
</tbody>
</table>

Physical Properties

| Solid content (kg/L):   | solid | 0.518 | 0.333 |
admixture was derived from Na$_2$SO$_4$ impurity. Then the organic fraction of each admixture was estimated by subtraction of all inorganic elements.

For superplasticizer A, the Na$_2$SO$_4$ content is calculated as 4.7 %, which is much less than 13.3% obtained by Burk et al. However, the organics content of 85.0 %, estimated by subtraction is similar to the sum of the monomer, nonadsorbable, and higher weight polymers reported in Burk et al.'s data. These percentages do not include the alkali ions associated with the polymer. The apparent inorganic impurity level in superplasticizer B was somewhat less than that of superplasticizer A, the estimated Na$_2$SO$_4$ content being only about 1%. The organic content of the solids (less the associated alkali contents) was 89% as compared to 85% in superplasticizer A. This compositional comparison of the two superplasticizers will be discussed further in Chapter 5.

3.2.2 Melamine Sulfonate Superplasticizer

The melamine sulfonate superplasticizer used was a commercial product, Melment, obtained from Gifford Hill Co. The admixture was supplied as a solution, and no molecular composition data was available. The solids content was 33%, and the results of chemical analyses are also shown in Table 3.2-1.

A considerable content of sodium found by the chemical analysis, is mostly the counter cation to the negatively charged sulfonic acid site of the polymer. Though the sulfate ion was the largest anion impurity, a significant amount of OH ion was
detected in the original admixture solution, whereas other naphthalene sulfonate admixtures were conditioned almost neutral or slightly acidic.
CHAPTER FOUR
EXPERIMENTAL WORK AND METHODS USED

4.1 Summary of Mixes and Analyses

Table 4.1-1 summarizes the cement paste mixes designed in this study and the elemental analyses done for each mix. The mix code is defined such that the first capital letter refers to the kind of cement, the second capital letter refers to the kind of superplasticizer, and the third and fourth letters refer to either the kind of alkali sulfates added or the dosage of the added alkali hydroxide where used.

The first capital letter is either W, L, or S, which signifies that the paste is of the white cement W, the ordinary portland cement L, or the other ordinary portland cement S, respectively.

The second capital letter is either A, B, or M, which is designated as naphthalene sulfonate superplasticizer A, or naphthalene sulfonate superplasticizer B, or melamine sulfonate superplasticizer M, respectively. The capital letter O means a control paste without any superplasticizer.

The third letter is either a number 0 thru 5, or a capital letter K, or N. When KOH is added to the mix water, a number is used to signify the level of dosage. (0 means no addition of KOH.) The letter K or N means that either $K_2SO_4$ or $Na_2SO_4$ is added to
### Table 4.1-1 Summary of mixes and analyses

<table>
<thead>
<tr>
<th>Mix no</th>
<th>WD</th>
<th>WA5</th>
<th>WA1</th>
<th>WA2</th>
<th>WA3</th>
<th>WA4</th>
<th>WA5</th>
<th>WB1</th>
<th>WB2</th>
<th>WB3</th>
<th>WB4</th>
<th>WB5</th>
<th>WB6</th>
<th>WSN</th>
<th>LD</th>
<th>LB</th>
<th>LM</th>
<th>SO</th>
<th>SB</th>
<th>SM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cement</td>
<td>W</td>
<td>W</td>
<td>W</td>
<td>W</td>
<td>W</td>
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<td>W</td>
<td>W</td>
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<td>W</td>
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<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>L</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>Design, ft</td>
<td>3.0</td>
<td>3.0</td>
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the mix water.

There were two mixes prepared with addition of different dosages of Na₂SO₄. One mix was dosed with 0.6% of Na₂SO₄, and the other mix with only 0.03%. To distinguish those mixes, the fourth supplemental code element was used, the latter mix was designated as WBNO.

In this research, the following parameters of the various cement pastes were determined by the analytical methods specified.

1. Loss on ignition by igniting a previously oven dried sample to 950°C for 15 minutes.

2. Amounts of ettringite and of calcium sulfate hydrates in the solids by Differential Scanning Calorimetry (DSC).

3. Amount of insoluble anhydrite in the solids by Quantitative X-ray Diffraction (QXRD).

4. Relative fluidity of paste by increase in area using the mini-slump cone.

5. Time of set of paste by Vicat apparatus.

6. Rate of heat evolution by the conduction calorimetry.

In addition, the following solution parameters were determined in paste solutions separated from the solids by pressure assisted filtration, or by use of a high pressure die, as appropriate:
7. Superplasticizer concentration in solution by UV spectroscopy.

8. K\(^+\), Na\(^+\), Ca\(^{2+}\) ion concentration of the liquid phase by atomic absorption spectroscopy.

9. OH\(^-\) ion concentration of the liquid phase by titration with HCl.

10. SO\(_{4}^{2-}\) ion concentration of the liquid phase either by BaSO\(_4\) gravimetric method, or by ion chromatography.

For the pastes of the white cement W, the control paste WO without superplasticizer was investigated first. The inorganic ion concentrations in the pore solution were determined and the solids were analyzed by DSC and QXRD. The set time, mini-slump, and the heat of hydration were also measured.

The mix series WAX and WBX (X signifies a "wild card" character) were designed to investigate the effects of alkalis added to the mix water on this almost alkali-free cement. In this series, the effect of alkali hydroxides was specifically investigated by the mix series WAX. KOH was used as the alkali hydroxide added in the mix water, and its dosage was controlled to 0.3%, 0.45%, 0.6%, 0.9%, and 1.2% Na\(_2\)O equivalent of the cement weight (samples coded WA1, WA2, WA3, WA4, WA5, respectively). WA0 is a control mix without addition of KOH. The superplasticizer used in these mix WAX was the naphthalene sulfonate superplasticizer A and its dosage was 2% by solid weight of the cement. The residual superplasticizer concentration was analyzed.
In a subsequent series of mixes WBX, naphthalene sulfonate superplasticizer B was used, and its dosage was fixed as 1.55%. The mix WB0 was a control mix without any addition of alkali, and the same analyses done for the first blank mix WO were carried out and their results were compared.

The effects of added KOH were further investigated with superplasticizer B. The mix WB3 and WB5 are parallel mixes to WA3 and WA5, with addition of KOH in the mix water at the dosage of 0.6% and 1.2% Na2O equivalent, respectively. The mix WB3’ is a repeat of the mix WB3. The OH⁻ and SO₄²⁻ ions in solution and the CaSO₄ bearing phases in solids were determined for these mixes, as well as residual superplasticizer concentration.

The effects of added alkali sulfates were also investigated here. Two different kinds of alkali sulfates, K₂SO₄, and Na₂SO₄ at the equal dosage of 0.6 % Na₂O equivalent were added in the mix water for the mix WBK and WBN. The inorganic ion concentrations and the superplasticizer concentration in pore solution were analyzed for these mixes. The mini slump measurement was also carried out. Their results can be also compared to those of the mix WB3, at the same 0.6% addition, and the different effects of KOH and alkali sulfates were discussed.

The mix WBN0 also contains Na₂SO₄ in the mix water but its amount was only 0.03% Na₂O equivalent. This mix was designed to investigate the effect of Na₂SO₄ impurity in the superplasticizer. The OH⁻, SO₄²⁻ ion concentrations in solution, and CaSO₄ bearing phases were determined for this mix.
The sampling of the paste W series were continued for several hours; additional samples at 24 hours were taken only for the mix WO and WBO.

In the mix series LX, and SX, the effects of two kinds of superplasticizers on both solids and solution of the pastes of ordinary "gray" portland cement L, and S, respectively, were investigated. These cements contained different forms of calcium sulfate.

With ASTM Type I cement L, three mixes were designed; the control mix LO without superplasticizer; the mix LB with naphthalene sulfonate superplasticizer B at 1.55 % dosage; and the mix LM with melamine sulfonate superplasticizer M at 0.5 % dosage. For each of these, a complete set of analyses were carried out. Sampling was at reasonably close intervals during the first day, and then at 3 days, 7 days, and 14 days.

In the mix series SX, using ASTM Type I cement S, the mix SB (with 1.55 % naphthalene sulfonate superplasticizer B), and the mix SM (with 1.55 % melamine sulfonate superplasticizer M) were compared to the admixture-free mix, SO. Both the parameters analyzed and the duration of the sampling were almost the same as for mix series LX.

4.2 Mixing and Sampling

All cement pastes were mixed using a standard Hobart mixer, in accordance with the ASTM C 305 mixing procedure for cement paste. Where used, the superplasticizer and alkalis were pre-dissolved in the mix water. The water:cement ratio was kept as
0.50 throughout the research. A considerable volume of each paste was stored in a large container, and additional smaller portions placed in small ointment jars and sealed.

For analyses prior to set, the large mass was used as the sample source. At each sampling the container was opened and the sample stirred to insure homogeneity. A portion of about 50 g was then removed and the mix solution was recovered from the fresh paste by a pressure filtration system, illustrated in Fig. 4.2-1. Nitrogen gas pressure of 40 - 80 psi and the use of a membrane filter of 0.45 μm nominal diameter were found to be effective in recovering solution for analysis.

After set, individual portions set aside in sealed ointment jars were removed at appropriate intervals and subject to pore solution expression using the high pressure die system described by Barneyback and Diamond [8], and illustrated in Fig. 4.2-2. The specimen was set in the bore of the die body, followed by the teflon seal and the piston unit. Specimens were loaded in a testing machine at up to 80,000 psi. Around 5 ml pore solution were obtained easily from even the oldest specimen examined, 14 days old.

For each sample from which pore solution was removed, the solids were recovered by flushing the paste with acetone for later solid phase analyses.
Nitrogen Gas
40 - 80 psi

Pressure Chamber

Cement Paste

Filter Membrane

Plastic Container

Fig. 4.2-1 Schematic drawing of pressure filtering system
Fig. 4.2-2 Schematic drawing of steel die
4.3 Analyses of Solution Phase

4.3.1 Naphthalene Sulfonate Superplasticizer Measurement by UV Spectroscopy

The naphthalene sulfonate concentrations were determined by UV analysis procedure described by Diamond and Struble [67]. The instrument used was Varian DMS 200 UV-visible spectrophotometer. The UV scanning speed was 50 nm/sec and the slit width was 2.0 nm. The original pore solution was diluted with de-ionized water by usually 1:1000. The UV absorption spectra of the naphthalene sulfonate superplasticizers A and B are shown in Fig. 4.3-1. The concentrations of two superplasticizers used to obtain these spectra correspond to 1:2500 dilutions of 2.0% dosage for superplasticizer A and 1.55% dosage for superplasticizer B.

The absorbance A of the diluted solution was measured directly in the absorbance mode of the instrument. The equation ordinarily applied for calculation is Beer-Lambert Law written as,

\[ A = ε \cdot l \cdot c \]

where:

- \( ε \) is the extinction coefficient (absorptivity) of a particular compound in a particular solvent at a particular wavelength in L/g/mm.
- \( l \) is the light path length, 10 mm for this study.
- \( c \) is concentration in g/L.

The UV spectrum of the naphthalene sulfonate superplasticizers consists of two peaks, an intense absorption peak at approximately 228 nm and a much weaker peak in the
Fig. 4.3-1 UV absorption spectra of naphthalene sulfonate superplasticizers A and B
range between 270 nm and 294 nm, as shown in Fig. 4.3-1. Since the extinction coefficient of the monomer naphthalene sulfonate and that of the polymeric species at 228 nm peak are quite different, the calculation using the shorter wavelength absorbance requires correction for the proportion of the residual monomer. However, the extinction coefficient by using the peak at the longer wavelength do not vary with different degrees of polymerization for naphthalene sulfonate. Thus the complication of the monomer composition can be avoided when the unique value of the extinction coefficient at 270 - 294 band peak is used.

The average extinction coefficient of naphthalene sulfonate species at the long wavelength was determined as 2.20 L/g·mm from the known concentration cases of the superplasticizer A. The figure for the identical admixture was reported as 2.08 by Burk et al. [66], 2.26 by Diamond and Struble [67], and 2.18 by Struble and Rossington [68].

4.3.2 Melamine Sulfonate Superplasticizer Measurement Method

Melamine sulfonate concentration was also determined by UV analysis. The pore solution was diluted to 1:2000 with de-ionized water. The UV spectrum of the original admixture M is shown in Fig. 4.3-2. It has only one characteristic peak of absorption, which appears in the range between 210 and 220 nm.

This UV light absorption peak at 210 - 220 nm band is interfered with by OH⁻ ion, as pointed out by some researchers such as Massazza et al. [43], or Yilmaz et al. [69]. The absorbance in the range shorter than 220 nm is enhanced by the OH⁻ ion,
Fig. 4.3-2 UV absorption spectrum of melamine sulfonate superplasticizers M (0.02g/L)
and the peak is unable to be recognized in stronger alkaline solutions. To avoid this interference, the paste solutions were neutralized prior to the UV spectroscopy measurement with sulfuric acid. Sulfuric acid was found to exhibit less interference on absorption in this range than did hydrochloric acid or nitric acid. Fig. 4.3-3 illustrates the effect of neutralization by these three kinds of acid on a trial superplasticizer concentration determination in the pore solution of 1-day old sample. HNO₃ had a strong characteristic absorption over this range. HCl caused some enhancement of the absorption at 195 nm or lower wavelength. However, H₂SO₄ had no detectable interference on the absorption peak of the superplasticizer.

4.3.3 Determination of Inorganic Ion Concentrations

The major inorganic ions in the pore solutions, K⁺, Na⁺, Ca²⁺, OH⁻, and SO₄²⁻, were determined by various methods. The details of each measurement are described below.

(1) Na⁺ and K⁺

The flame emission mode of an atomic-absorption - flame-emission spectrophotometer (Varian SpectrAA-20) was used for these alkali ions. In these determinations, the original pore solution was usually diluted 1:1000 to bring these alkali ion concentrations within the calibration range, below 10 ppm for the Na⁺ ion, and below 20 ppm for the K⁺ ion. The operational conditions of the spectrophotometer for the element measurement are outlined in Table 4.3-1. Although Na and K are somewhat
Fig. 4.3-3 Effects of the OH\(^{-}\) ion and neutralization with acids on UV absorption spectrum of melamine sulfonate superplasticizer M
subject to mutual ionization, common calibration standards for both ions without any 
additional reagent were used, according to the method of Barneyback [70].

(2) Ca$^{2+}$

The atomic absorption mode was chosen for Ca$^{2+}$ using a N$_2$O–C$_2$H$_2$ flame. The 
operational parameters used are also listed in Table 4.3-1. The optimum working 
range for those operational conditions was 1-5 ppm. Prior work done by the author 
[71] showed some interference (to a maximum of about 15%) could be produced by 
varying matrices of different pore solutions. Since the Ca$^{2+}$ concentration of pore 
solutions in this study did not exceed a maximum of 100 meq/L and this low values 
did not seem to affect the overall result, a single calibration standard solution con­
tained only CaCO$_3$ was used.

(3) OH$^-$

OH$^-$ was determined by reaction with excess HCl and methyl red was used as an indicator. After the solution reaches the first end point, it was boiled to expel 
CO$_2$, and the titration was resumed to the second end point.
Table 4.3-1 Analytical condition used for elements measurement

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</table>
(4). $\text{SO}_4^{2-}$

The sulfate ion was determined by two methods, direct $\text{BaSO}_4$ precipitation gravimetric method and ion chromatography. Indirect determination of $\text{SO}_4^{2-}$ with the $\text{Ba}^{2+}$ ion using atomic absorption was discarded due to the interference by naphthalene sulfonate remaining in the solution.

The $\text{BaSO}_4$ gravimetric method used was based on the ASTM C114 SO$_3$ determination procedure. This was mainly used in the early stages of this study, before the ion chromatography equipment became available. The contamination of $\text{BaSO}_4$ precipitate with naphthalene sulfonate was hardly avoidable when the residual polymer concentration was high, and its brownish color was frequently observed in the precipitate. Thus the method required monitoring of the residual naphthalene sulfonate concentration between each experimental operation, described as follows.

Two or three ml of the original pore solution was diluted to 250 ml, acidified with HCl, and digested for 15 minutes at a temperature just below boiling. Ten ml of $\text{BaCl}_2$ (100g/L) were added slowly to the solution, while was then heated for 15 minutes more. The solution was then left for 12 -18 hours to complete the precipitation of $\text{BaSO}_4$. It was then filtered through a medium speed glasswool filter, and the precipitate was oven dried at 105°C and weighed. At the same time, the concentration of naphthalene sulfonate in the filtrate was determined by UV spectroscopy.

The $\text{BaSO}_4$ precipitate consumed all the sulfate ion, and also a part of the naphthalene sulfonate polymer anion. An analysis for the latter was obtained by the
subtraction of the final concentration in the filtrate from the initial concentration. The calculation algorithm for the actual SO\textsuperscript{2-} ion concentration is illustrated on the following page. The result of a trial determination of a known SO\textsuperscript{2-} ion concentration in a synthetic pore solution with superplasticizer added was reasonably accurate with only ±0.3% difference.

In the later stages of this study, an ion chromatography method was applied for analysis of SO\textsuperscript{2-} concentrations. This method provides for a direct determination of SO\textsuperscript{2-} ion concentration regardless of the remaining superplasticizer in the solution. The instrument used was a Dionex 2000i/SP ion chromatography and equipped with an automatic integrator for the peak area calculation. The parameters of the instrument for this study are summarized in Table 4.3-2.

The calibration standards used contained 5 ppm and 10 ppm of the SO\textsuperscript{2-} ion in Na\textsubscript{2}SO\textsubscript{4} solution. The original pore solution was diluted to the SO\textsuperscript{2-} ion calibration range, usually by 1:1000 or 1:2500. The electrical conductivity was measured and automatically recorded as a function of time. The retention time for the sulfate ion under this particular settings of the instrument was around 6 minutes. Other than the SO\textsuperscript{2-} ion, the pore solution contained the OH\textsuperscript{-} ion, and the naphthalene sulfonate polymer anion as well. Neither anion is responded to by this chromatography system. The peak area of the conductivity is thus proportional to the SO\textsuperscript{2-} concentration, which was automatically calculated by the integrator.
\[ W_{[\text{NS}]} = (C_0 - C_T) \times V_s \]

\[ W_{\text{Ba}[\text{NS}]} = W_{[\text{NS}]} \times (1 + \frac{\text{cd}_{\text{NS}}}{1000} \times [\text{Ba equiv.}]) \]

\[ W_{\text{BaSO}_4} = W_{\text{prep}} - W_{\text{Ba}[\text{NS}]} \]

\[ C_{\text{SO}_4} = \frac{W_{\text{BaSO}_4}}{[\text{BaSO}_4 \text{ equiv.}]} \times \frac{1000}{V_s} \]

where:

- \( W_{[\text{NS}]} \): weight of naphthalene sulfonate in precipitate (g)
- \( C_0 \): original concentration of naphthalene sulfonate anion in pore solution (g/L)
- \( C_T \): residual concentration of naphthalene sulfonate anion after filtration (g/L)
- \( V_s \): pore solution sample quantity (L)
- \( W_{\text{Ba}[\text{NS}]} \): weight of Ba-[naphthalene sulfonate] in precipitate (g)
- \( \text{cd}_{\text{NS}} \): charge density of naphthalene sulfonate (meq/g)
- \([\text{Ba equiv.}] \): weight of Ba equivalent (137.33/2 g/eq)
- \( W_{\text{BaSO}_4} \): weight of BaSO\(_4\) (g)
- \( W_{\text{prep}} \): weight of total precipitate (g)
- \( C_{\text{SO}_4} \): concentration of \( \text{SO}_4 \) in pore solution (meq/L)
- \([\text{BaSO}_4 \text{equiv.}] \): weight of BaSO\(_4\) equivalent. (116.7 g/eq)

SO\(_4\) calculation procedure by BaSO\(_4\) gravimetric method
Table 4.3-2 Parameters for ion chromatography instrument

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion Separator</td>
<td>Flow Rate</td>
</tr>
<tr>
<td></td>
<td>Flow Pressure</td>
</tr>
<tr>
<td></td>
<td>Eluent</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Regenerent</td>
</tr>
<tr>
<td></td>
<td>Sample Volume</td>
</tr>
</tbody>
</table>
The reproducibility was such that the fluctuation of the peak area was within a 3% coefficient of variation. In comparisons made between the two methods of SO₄²⁻ analysis, it was found that the means of results by the BaSO₄ gravimetric method and by ion chromatography corresponded to each other within 4.0%. However, the ion chromatography method is recommended because of the much simpler experimental procedure.

4.4 Analyses of Solids

4.4.1 Loss on Ignition

The loss on ignition of the cement solids was determined according to ASTM C114. One gram of cement paste was ignited in a crucible in the muffle furnace at 950 ± 50°C for 15 minutes. Then it was cooled to the room temperature and reweighed. The ignition loss data for the solids with superplasticizers were corrected for the weight of the superplasticizer absorbed at each time of sampling.

4.4.2 Differential Scanning Calorimetry (DSC)

The instrument used was Du Pont 910 thermal analysis system. The DSC mode was chosen among other thermal analyses methods because of the greater sensitivity of the enthalpy measurement, and because the smaller sample size gives more facility to the experimental procedure. Quantitative analysis was carried out for ettringite (C₃A·3C₅S·32H), calcium sulfate hemihydrate, and gypsum by measuring the areas of
the respective dehydration peaks. Other hydrated compounds in cement pastes such as C-S-H gel were also observed in the DSC curve.

A synthetic ettringite for calibration was made by the following method described by Struble [72]. A stoichiometric amount of Al$_2$(SO$_4$)$_3$ solution was added to a saturated calcium oxide solution, upon which a white precipitate of ettringite appeared immediately. The ettringite was filtered and dried under flowing of nitrogen gas to avoid carbonation. An x-ray diffraction pattern of this synthetic ettringite showed no peaks other than those expected for ettringite.

The calibration material for calcium sulfate hemihydrate was obtained in ground form from Texas Industries Inc. Originally this sulfate was natural gypsum mined by the U.S. Gypsum Corp. in Sweetwater, Texas. The hemihydrate was apparently synthesized by heating the gypsum. Its purity was assured by its x-ray diffraction pattern, which showing diffraction peaks only for hemihydrate, and by a thermogravimetric analysis (TGA), which showing weight loss equivalent to an approximate half mole of water.

Reagent grade of gypsum was used for gypsum calibration. This gypsum is 99.99% pure.

Another common form of CaSO$_4$ is soluble anhydrite (γ-CaSO$_4$). It has only a trace of combined water and its crystal structure is almost identical to calcium sulfate hemihydrate. X-ray diffraction patterns of these two compounds are hardly distinguishable from each other. It was found here by DSC analysis that a soluble anhydrite
synthesized by heating gypsum to over 120°C, rehydrated to hemihydrate immediately in an atmosphere at the normal level of humidity (ca. 50% R.H.). This rehydration phenomenon has been generally observed for example by McAdie [73], Gay [74], and Hansen et al. [63]. Soluble anhydrite may exist in unhydrated cement as a result of dehydration of gypsum during the grinding operation. However, this soluble anhydrite in cements is considered to be mostly converted to hemihydrate. From these reasons, soluble anhydrite was not determined in this study.

The DSC analysis procedures used were as follows. The acetone dried solid sample was passed through a No. 325 sieve (0.045 mm), and ca. 4.0 mg of the sieved solids was placed in the aluminum pan of the instrument. The weight of the specimen used was reduced to about 1.5 mg when higher resolution was needed for separation of close peaks. The sample pan was then placed in the sample chamber along with the empty reference pan. Both pans were left open. It was found by extensive prior investigation that either crimping or hermetically sealing caused poor reproducibility of the dehydration peak temperatures.

It was found that the water content of the purging gas passed into the sample chamber affected the temperature of the dehydration peak. Air of 10% relative humidity at room temperature was chosen as the purging gas. Its flow rate was set at 140 mL/min. It was found that these conditions of the purging gas gave the best separation of the dehydration peaks of calcium sulfate hemihydrate, gypsum, and ettringite, and this was used. The relative humidity was controlled by bubbling the air through a glycerine-water solution, by which a constant relative humidity was maintained as
described in ASTM E 104-51.

A heating rate of 10°C/min was chosen as providing the best resolution of adjacent dehydration peaks.

Some of the solid samples analyzed contained all three compounds: ettringite, hemihydrate, and gypsum. The DSC curve for one of them, paste LB at age of 16 minutes, is shown in Fig. 4.4-1 to provide an example. The three peaks in the figure are characteristic DSC dehydration peaks for ettringite, calcium sulfate hemihydrate, and gypsum, respectively. These were observed in increasing order of temperature under these particular conditions of the purging gas, the sample preparation, and the heating rate.

The ettringite synthesized here had its DSC dehydration peak between 40°C and 50°C, in approximate agreement with the temperature range found by Struble et al. [72], which ranged from 30° to 55°C. Ettringite found in actual solids cement pastes at early ages started its dehydration approximately 35°C. As hydration proceeds or if large specimen weights were used, the dehydration peak tends to shift to higher temperature, ranging in this case from 40°C to 80°C.

The calcium sulfate hemihydrate used for calibration had its dehydration peak at approximately 80°-90°C, between which a half mole of combined water was released. Hemihydrate found in actual unhydrated or hydrated cements exhibited its dehydration peak at about the same temperature.
Fig. 4.4-1 DSC curve of paste LB at age of 16 minutes
The dehydration peaks of both pure gypsum and gypsum in actual cement and cement paste solids were observed in the range between 110°C and 120°C. Under the experimental conditions used, the entire two moles of its combined water were removed at once, in a single step.

The calibration curve for ettringite was obtained by a series of mixtures of the synthesized ettringite and a cement matrix, which does not have a peak in the corresponding temperature range. The three mixes containing 5%, 10%, and 14% of ettringite, along with 100% ettringite were used for this calibration curve determination. Fig. 4.4-2 shows the calibration curve obtained.

The calibration curves for hemihydrate and for gypsum were obtained similarly. For hemihydrate calibration, a series of mixtures contained 3%, 5%, and 6% of hemihydrate, plus 100% pure hemihydrate were used. For gypsum calibration, the gypsum contents of the mixtures used were 5%, and 6%, and 100% pure sample was also used. These curves are shown in Fig. 4.4-3 and Fig. 4.4-4.

According to the results of those calibrations, the average areas of the dehydration peaks of pure ettringite, hemihydrate, and gypsum under the particular settings of the instrument corresponded to about 810, 180, and 630 joules/g, respectively. The contents of these compounds in each solid sample were determined by normalizing the areas of corresponding dehydration peaks to those calibration numbers for pure compounds.
Fig. 4.4-2 Calibration curve for ettringite content by DSC dehydration peak area
Fig. 4.4-3 Calibration curve for hemihydrate content by DSC dehydration peak area
Fig. 4.4-4 Calibration curve for gypsum content by DSC dehydration peak area
The starting point and end point of the dehydration peak on the DSC curves were defined generally as the points where the gradient of the curve changes abruptly. These points were determined by inspection, or sometimes with some help from derivative curves provided by the instrument. The peak area under the straight line between those two points was calculated automatically by a computer program attached to the instrument.

A major hydration product of cement, C-S-H gel, loses its combined water at relatively low temperatures. A trial run of a synthetic C-S-H gel produced by hydration of a pure C₃S exhibited a broad DSC dehydration peak ranging from 40°C to 180°C. This temperature range overlaps the peaks of ettringite, hemihydrate, and gypsum. However, peaks of these target compounds are much sharper, so that they can be differentiated from the broad hump of the baseline caused by C-S-H gel.

Another source of complication is the formation of AFm phases in the cement pastes after several days. X-ray diffraction analysis was carried out for all specimens made with cement L and cement S aged between 1 day and 14 days. In none of these was an x-ray diffraction peak for calcium monosulfoaluminate hydrate (C₃A·C₅S·12H₂O) observed. However, in some of the pastes, small and poorly defined x-ray diffraction peaks at about 7.9 Å were developed typically starting at 3 days. These are likely to be due to C₄AH₁₃ or sometimes in part to a partly carbonated phase of similar structure (C₄A(C₀.₅H₁₂).
With respect to DSC, the author has examined a pure specimen of the calcium monosulfoaluminate hydrate under the same experimental conditions and found that it has a complex response; broad complex peaks between about 40°C and 110°C, and a well defined peak between about 130°C and 180°C. Thus if this compound were present in the experimental pastes, the first peak would contribute to the peak normally attributed to ettringite. However, the absence of any indication of an x-ray diffraction peak at or near 9.0 Å, it must be concluded that it is absent.

The author has also examined the DSC response for old reference samples of C₄AH₁₃. Unfortunately, these were carbonated to some degree, shown peaks for vaterite, aragonite, and calcite as well as the 7.9 Å peak characteristic of C₄AH₁₃. The DSC response for these samples involved small peaks between 80°C and 130°C and a much larger response at high temperature (230°C to over 300°C). The normal limits of the ettringite DSC peak with the technique used is about 40°C to 90°C; hence these could have produced same slight augmentation of the ettringite peak by the low temperature peaks here. However, all runs of actual solid samples were carried out at least to 300°C and there was no indication of the large expected second peak. Thus the situation is ambiguous, the assay of ettringite at later ages in those pastes may have included a very small contribution from the C₄AH₁₃ indicated to be present by x-ray diffraction.

The DSC peaks for some specimens, notably those for cement S with naphthalene sulfonate (SB) and melamine sulfonate (SM) admixtures, and for cement L with melamine sulfonate admixture (LM) show distinct shoulders on the high temperature
side of the peak, ca. 90°C. However, the existence of those shoulders does not correlate with the existence of the previously mentioned 7.9Å x-ray diffraction peak, and the shoulders are thought to represent primarily the effects of absorbed superplasticizer.

4.4.3 X-ray Diffraction Analysis

The instrument used was a Siemens D500 diffractometer using Cu-Kα radiation. The goniometer speed ordinarily used was 2° 2θ/min.

All the dry powdered sample material used was passed through a No. 325 sieve (0.045 mm) and either packed in a McCreary mount, or sprinkled onto a quartz crystal mount when the sample amount was limited.

4.4.4 Quantitative X-ray Diffraction Analysis

A quantitative x-ray diffraction analysis procedure was applied for insoluble anhydrite (α-CaSO₄, or natural anhydrite) in pastes made with the white cement (cement W). This cement contains only insoluble anhydrite as the calcium sulfate present, and no other quantifiable method of analysis is available.

The instrument used and all the parameter settings were as described previously. The internal standard method was applied using CaF₂ as the internal standard and soluble starch \((C₆H₁₀O₅)_X\), as the matrix. The insoluble anhydrite, CaF₂, and \((C₆H₁₀O₅)_X\) used for calibration were all reagent grade.
The insoluble anhydrite diffraction peak of d-spacing 3.499 Å (2θ of 25.4°) and the CaF$_2$ diffraction peak of d-spacing 3.155 Å (2θ of 28.3°) were used. Both diffraction peaks were strong and were found to be the least interfered by other peaks of cement compounds or hydrated cement products. CaF$_2$ at a uniform 20% by weight was added to each dry powdered sample. The combined powders were mixed in a plastic vial by shaking manually, and the mixture was passed through a No.325 sieve (0.045 mm) before being packed in a McCreary mount. Three replicate runs were carried out for each mixture.

The intensity ratio, that is, the ratio of the height of the specific peak of insoluble anhydrite to that of the CaF$_2$ peak is proportional to the weight composition of insoluble anhydrite. The calibration curve was obtained by a series of samples of CaF$_2$:matrix weight ratio of 1:99, 3:97, and 5:95, and yielded a regression coefficient $R = 0.971$.

4.4.5 Tests on Physical Characteristics of Pastes

Physical characteristics of the cement pastes were monitored by the mini-slump test and by determination of the setting time based on ASTM C 191 procedure.

(1) Mini-Slump Test

The mini-slump cone test was described in detail by Meyer and Perenchio [58], and by Kantro [75]. Cement paste is transferred to the mini-slump cone and the cone is lifted smoothly and quickly. The area of the paste spread on a polyethylene sheet is
measured and the slump value is expressed as the ratio of the spread area to the original inner area of the cone, expressed in percentage terms.

(2) Setting Time

The setting time of various pastes was measured using the Vicat needle apparatus. The procedure complied essentially with ASTM 191. The actual penetration test was performed on paste in the ointment jars.

4.4.6 Conduction Calorimetry

The heat evolutions at early ages for the mix series WX, LX, and SX, were determined calorimetrically. The instrument used was a conduction calorimeter made by Wexham Developments Limited. The specimen used consisted of a hand mixed cement paste of 5 g cement and 2.5 ml of liquid contained in a polyethylene bag. The bag was positioned around the thermal sensor of the instrument in an aluminum can filled with non-conducting oil. This aluminum can, covered with thermal insulator, was assembled and placed in a sealed acrylic cylinder, which was there immersed in the water bath used as a constant temperature heat sink.

The electrical output from the thermal sensor, $E$ (mV), was recorded by the plotter as a function of time. The relation between $E$ and the heat evolution rate of the sample, $W$ (mW) is written in the following Tian-Calvet equation.

$$W = K_1 E + K_2 \frac{dE}{dt}$$
Both $K_1$ and $K_2$ are constants of the instrument, and those constants were determined as

\begin{align*}
K_1 &= 29.05 \\
K_2 &= 5.55
\end{align*}

for the particular instrument of this study by Dr. D. Bonen of this laboratory. The results were expressed in units of mW/g of cement. The measurement was continued until the second peak of the heat of hydration was completed, usually by one and a half days.
In this chapter, effects of naphthalene sulfonate superplasticizers on cement pastes prepared with ASTM type I white cement (Coded cement W in this report) were investigated. This white cement has a very low alkali content, a low content of C₃A, and almost no C₆AF. Thus it is suitable as a "blank" material, since those parameters were considered to affect the interaction between dissolved superplasticizer and hydrating cement.

In Section 5.1, the results of a comprehensive study of (a) the control mix without superplasticizer (coded W0), and (b) a mix coded WBO, incorporating 1.55% naphthalene sulfonate superplasticizer B by weight of cement, are presented. Effects of naphthalene sulfonate are examined on various aspects of the paste including hydration, calorimetry, rheology, solution chemistry, and solid phase compounds formed.

In Section 5.2, specific effects of different alkali salts on absorption behavior of naphthalene sulfonate superplasticizers in cement W pastes were investigated. Two different naphthalene sulfonate superplasticizers (A and B) were used. Various kinds
and dosages of alkali hydroxides and alkali sulfates were dissolved in the mix water along with the naphthalene sulfonate superplasticizers. These series of mixes were coded WAX or WBX, depending on whether superplasticizer A or B was used. X is a wild card character which stands for the kinds or the dosage of the dissolved alkali. In this portion of the work, the main focus was to determine the effects of various treatment plus combination on the amount of superplasticizer remaining in solution after various periods. UV analysis of the residual naphthalene sulfonate in solution is the main analytical method.

In Section 5.3, some peculiar experimental findings in the previous series of pastes with superplasticizer A are re-investigated using superplasticizer B. Three pastes with cement W and 1.55% superplasticizer B were designed: one with 0.6% KOH, a second with 1.2% KOH, and a third with 0.03% Na$_2$SO$_4$. For those pastes, the concentrations of remaining superplasticizer, the OH$^-$ ion, and the SO$_4^{2-}$ ion in pore solution were determined prior to set, and analyses of CaSO$_4$-bearing compounds in the solids were also carried out.

In Section 5.4, based on the results of experiments described in the previous three sections, the superplasticizer interactions with the various pastes of this white cement W are discussed and explanations attempted. Differences in results with the two different naphthalene sulfonate superplasticizers are also discussed.

In Section 5.5, results of an experiment on the paste with melamine sulfonate superplasticizer M are reported. Effects of the melamine sulfonate superplasticizer on
the white cement was investigated to a limited extent, so the experimental results presented here are only for reference.

5.1 White Cement Systems with and without Superplasticizer B

5.1.1 Effect of Superplasticizer on Hydration

Fig. 5.1-1 shows the ignition loss data of the control mix WO and mix with superplasticizer WB0. All data for superplasticized pastes were corrected for the loss on ignition of the superplasticizer incorporated with the solids. With superplasticizer B, the loss on ignition (LOI) at the first measurement was a little higher than the control paste. However, it remained approximately constant for about 6 hours, while the LOI of the control pastes increased steadily; the control paste LOI overtook that of the superplasticized paste at about 3 hours and it was significantly higher by 6 hours.

Fig. 5.1-2 shows the conduction calorimetry results of both pastes. For the paste with superplasticizer, the start of the second heat evolution peak was delayed by 3 hours and the area under the peak was considerably reduced. This indicates that the superplasticizer retarded the overall hydration of cement W.

The rheological characteristics of the two pastes, as measured by the mini-slump cone percentage increase in area (or "spread") are shown as functions of time in Fig. 5.1-3. With this cement, it appears that the superplasticizer actually reduced the fluidity of the cement paste, the initial values of mini-slump spread being about 350%
Fig. 5.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement W without superplasticizer (WO) and with 1.55% naphthalene sulfonate (WB0)
Fig. 5.1-2 Conduction calorimetric curves showing heat evolution vs. time for mixes WO and WB0.
Fig. 5.1-3 Area of spread in mini-slump test vs. time for mixes WO and WB0
without the superplasticizer and only about 140% with it. Furthermore with the superplasticizer the spread was rapidly reduced to the base level (100%) while the cement paste without superplasticizer retained the ability to spread for up to 3 hours. It was observed that the superplasticized paste became gelatinous after only about 15 minutes in an initial "watery" state. No bleed water was detected.

Separate initial set time measurements for these pastes yielded a value of 5.5 hours for the control paste, and 6.5 hours for the superplasticized paste.

5.1.2 Control Paste Without Superplasticizer (WO): Solution and Solid Phase Analysis

5.1.2.1 Inorganic Ion Concentrations in the Paste Solution

Fig. 5.1-4 shows the concentrations of $K^+$, $Na^+$, $Ca^{2+}$, $OH^-$, and $SO_4^{2-}$ ions in the solution phase as functions of time over the first 24 hours. For ages before 5.5 hours, the solution phases was separated from the solid by pressure-assisted filtration. As indicated in the figure, for ages of 5.5 hours and beyond, separation was accomplished using the high pressure die.

The sum of the inorganic ion concentrations in the pore solution was significantly smaller than that found in ordinary portland cement systems. It is an unusual observation that the $Ca^{2+}$ ion was most concentrated of all the ionic species for the first 5 hours of hydration. These are reflections of the cement having a very low alkali content.
Fig. 5.1-4 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (WO)
The sulfate ion concentration decreased monotonically throughout this period; it
did not maintain constant concentration for some hours, as is usually found with ordi­
nary portland cement pastes. The OH⁻ ion concentration was also low.

5.1.2.2 Solid Phase Analyses

Fig. 5.1-5 shows the results of analysis for calcium sulfate-bearing phases in the

Fig. 5.1-5 shows the results of analysis for calcium sulfate-bearing phases in the
corresponding solids for the control paste WO, as functions of time over the first 24
hours. The y-axis expresses the concentration of each of the specific compounds
corresponding solids for the control paste WO, as functions of time over the first 24
(ettringite and anhydrite) in terms of its SO₄ content normalized to the ignited weight
of the cement paste, so that these numbers are directly comparable each other. The
content of anhydrite (insoluble or "natural" anhydrite) was determined by QXRD, and
of the cement paste, so that these numbers are directly comparable each other. The
the ettringite content was determined by DSC. Details of the analytical methods used
content of anhydrite (insoluble or "natural" anhydrite) was determined by QXRD, and
were presented in the previous chapter. The content of these compounds in the start­
the ettringite content was determined by DSC. Details of the analytical methods used
ting cement are indicated by filled-in data points. An analogous convention will be
were presented in the previous chapter. The content of these compounds in the start­
followed throughout this report.

The initial form of CaSO₄ in cement W is considered to be entirely insoluble
followed throughout this report.

The initial form of CaSO₄ in cement W is considered to be entirely insoluble
anhydrite from the following indications. For the DSC curve of the unhydrated
anhydrite from the following indications. For the DSC curve of the unhydrated
cement, there was no dehydration peak up to 300°C. From the X-ray diffraction pat­
cement, there was no dehydration peak up to 300°C. From the X-ray diffraction pat­
tem, peaks of calcium sulfates other than insoluble anhydrite were not observed. Dif­
tem, peaks of calcium sulfates other than insoluble anhydrite were not observed. Dif­
fraction peaks for alkali calcium sulfates were not recognized either. From the
fraction peaks for alkali calcium sulfates were not recognized either. From the
hydrated paste sample, only insoluble anhydrite and ettringite were the CaSO₄-
hydrated paste sample, only insoluble anhydrite and ettringite were the CaSO₄-
bearing phases detected up to one day.
Fig. 5.1-5 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste W0
(Percentage of each solid phase re-expressed in terms of its $SO_4$ content.)
The anhydrite content in the control paste WO was hardly reduced at the first contact with water. However, it decreased monotonically between 1 and 6 hours, and there was virtually no anhydrite detected by 24 hours. No plateau period was evident in the anhydrite content pattern with time.

The content of ettringite, starting at zero, exhibited an immediate rise, evident by the analysis at 10 minutes. Then it continued to increase at a somewhat slower rate, and it reached about 2\% equivalent SO$_4$ at 24 hours.

Table 5.1-1 shows the balance of the sulfates accounted for at each age. The SO$_4$ content of the original cement W is 3.76\% by chemical analysis carried out by the author, whereas the initial anhydrite content determined by QXRD was around 2.5\% of SO$_4$ equivalent. Some of this difference could be attributed to the sulfate forms in unhydrated cement which were not accounted for, such as alkali sulfate or alkali calcium sulfate. However, the alkali content of the cement W is only 0.083\%, equivalent to 0.13\% SO$_4$ if all alkali exists as a form of sodium sulfate. Thus it seems that the anhydrite amount calculated is somewhat low due to some complication of QXRD method.

The sum of the sulfates measured for sulfate-bearing compounds in the solid plus the sulfate ions in solution increased after the contact with mixing water and reached maximum of 3.23\% SO$_4$ content at 2 hours. It then decreased. After the dormant period, considerable sulfate is incorporated into amorphous C-S-H gel, which was not quantified in this analysis. The decrease in the sum of the sulfates after 2 hours seems
Table 5.1-1 Total balance of sulfate-bearing phase for mix WO*

(Percentages expressed in terms of equivalent $\text{SO}_4$ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Anhydrite (%)</th>
<th>Ettringite (%)</th>
<th>$\Sigma$ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.47</td>
<td>0.0</td>
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<td>2.47</td>
</tr>
<tr>
<td>0.17</td>
<td>2.35</td>
<td>0.62</td>
<td>2.97</td>
<td>0.09</td>
<td>3.06</td>
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<td>1.62</td>
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<td>2.76</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6.00</td>
<td>1.04</td>
<td>1.55</td>
<td>2.59</td>
<td>0.03</td>
<td>2.62</td>
</tr>
<tr>
<td>24.83</td>
<td>0.01</td>
<td>2.01</td>
<td>2.03</td>
<td>0.00</td>
<td>2.03</td>
</tr>
</tbody>
</table>

* The total $\text{SO}_4$ content of the cement, separately determined, was 3.76% as $\text{SO}_4$. 
to be due to this effect.

5.1.3 Paste with Naphthalene Sulfonate Superplasticizer B (WB0): Solution and Solid Phase Analysis

5.1.3.1 Removal of Superplasticizer from Solution

Fig. 5.1-6 indicates the concentration of superplasticizer remaining in solution as a function of time up to 1 day for the paste with 1.55% naphthalene sulfonate superplasticizer B (WB0). Almost all the absorbable portion of superplasticizer B was removed from the solution by 3 hours, and the solution concentration remained low indefinitely.

5.1.3.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 5.1-7 shows the changes in the inorganic ion concentrations up to one day for the mix WB0. In contrast to the control paste, the sum of the inorganic ion concentrations in the solution here was significantly higher. This was due to an additional 120 meq/L of the Na⁺ ion derived from the superplasticizer, and to the OH⁻ ion that was found to balance this extra Na⁺. The sodium cation had previously been balanced by polymer anion groups (sulfonate groups) of the superplasticizer.
Fig. 5.1-6 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (WBO) up to 1 day
Fig. 5.1-7 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (WB0)
The Ca\(^{2+}\) ion concentration here was much lower than in the control paste over the entire period of 1 day. The initial Ca\(^{2+}\) ion concentration was only 18 meq/L and it rose to a maximum of 35 meq/L at 16 minutes, before subsequently declining.

The SO\(_4^{2-}\) ion concentration was also found to be very low; it was less than 10 meq/L for the whole period of analysis, which was much lower than the control case for the first few hours.

5.1.3.3 Solid Phase Analysis

Fig. 5.1-8 shows the corresponding figure to Fig. 5.1-5 for the superplasticized paste WBO. Again insoluble anhydrite and ettringite were the only CaSO\(_4\)-bearing phases detected. The peculiar quick setting behavior of the paste WBO reported earlier, was not a false set, because the formation of gypsum was not observed either by X-ray diffraction or by DSC analysis.

The anhydrite content reduced almost by half at about 2 hours, and then it remained approximately constant from 2 hours to 6 hours. Then it was reduced significantly between 6 and 12 hours and virtually disappeared by 24 hours.

The ettringite formed at the initial contact with water was greater than with the control mix, but its subsequent increase was relatively slow. The amount of ettringite was constant at 2\% equivalent SO\(_4\) content after 12 hours.

Table 5.1-2 shows the balance of the sulfate phases for the paste with superplasticizer. The sulfate in the original mix water was negligible, as seen in the table. The
Fig. 5.1-8 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (WB0)
(Percentage of each solid phase re-expressed in terms of its $\text{SO}_4$ content.)
Table 5.1-2 Total balance of sulfate-bearing phase for mix WBO

(Percentages expressed in terms of equivalent SO₄ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Anhydrite (%)</th>
<th>Ettringite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>2.47</td>
<td>0.0</td>
<td>2.47</td>
<td>0.01</td>
<td>2.48</td>
</tr>
<tr>
<td>0.37</td>
<td>1.71</td>
<td>1.21</td>
<td>2.91</td>
<td>0.02</td>
<td>2.93</td>
</tr>
<tr>
<td>2.33</td>
<td>1.31</td>
<td>1.68</td>
<td>2.99</td>
<td>0.01</td>
<td>3.00</td>
</tr>
<tr>
<td>4.12</td>
<td>1.48</td>
<td>1.59</td>
<td>3.06</td>
<td>0.01</td>
<td>3.07</td>
</tr>
<tr>
<td>6.37</td>
<td>1.43</td>
<td>1.73</td>
<td>3.17</td>
<td>0.02</td>
<td>3.19</td>
</tr>
<tr>
<td>11.67</td>
<td>0.68</td>
<td>1.98</td>
<td>2.66</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>24.37</td>
<td>0.03</td>
<td>2.04</td>
<td>2.06</td>
<td>0.01</td>
<td>2.07</td>
</tr>
</tbody>
</table>
sum of the sulfates in the solids plus the sulfate ion in the pore solution was found to be 2.9% at the first measurement. It increased slightly to 3.2% by 6 hours, and then decreased by 24 hours. This overall change in the total sulfates detected is similar to the pattern found for the control pastes.

5.2 Effects of Alkalis on Naphthalene Sulfonate Superplasticizer Absorption on White Cement W

In this section, experimental results of the mix series coded WAX and WBX are covered. The WAX series mixes were designed first to examine the effect of the alkali hydroxide in the mix water on the adsorption of naphthalene sulfonate superplasticizer for the white cement W. Using a 2% dosage of superplasticizer A, different amounts of KOH were dissolved in the mix water. The dosages used were 0.3%, 0.45%, 0.6%, 0.9%, and 1.2%, expressed as equivalent Na₂O content in the cement. The individual mixes were coded as mix WAO (for the control without KOH addition), and WA1, WA2, WA3, WA4, and WA5, respectively. The removal of the admixture from solution prior to set was monitored.

Then a series of mixes coded WBX was prepared. This series was designed to investigate the effect of different alkali salts on the removal of naphthalene sulfonate superplasticizer from the cement paste solution. A constant 1.55% dosage of superplasticizer B was used. In this series, KOH, K₂SO₄, and Na₂SO₄ were added to the mix water in amounts equivalent to 0.6% Na₂O in the cement. These mixes were coded WB3, WBK, and WBN, respectively. The control mix for this series was WB0,
results for which have been previously described.

5.2.1 Effects of KOH Addition to Paste with Superplasticizer A (Mix Series WAX): Solution Phase Analysis

5.2.1.1 Removal of Superplasticizer from Solution and Physical Characteristics of Pastes

Fig. 5.2-1 shows the concentration of the naphthalene sulfonate superplasticizer A remaining in solution as a function of time for the pastes of the white cement W with different amounts of KOH addition. The dosage of the superplasticizer A was 2% by weight of cement for all pastes. However, the initial concentration of naphthalene sulfonate in the mix water was only 34 g/L, equivalent to only 1.7% by weight of cement in the mix water; the sodium sulfate impurity of the admixture referred in Chapter 3 was subtracted from the gross solid weight.

For the paste without KOH addition (WA0), a little more than a half of the superplasticizer was removed from solution (i.e. taken up by the hydrating cement) in the first 10 minutes. The concentration then remained almost constant thereafter. The rheological condition of the paste was such that the paste was watery and it segregated internally so that the larger particles formed a segregated layer at the bottom, with much bleeding evident at the top. This segregation was obviously due to the heavy dosage of superplasticizer.
Fig. 5.2-1 Concentration of residual superplasticizer A in mix water and pore solution vs. time for pastes W with different KOH addition (WAX)
It has been shown previously (Section 5.1.1) that an addition of a heavy dose of naphthalene sulfonate superplasticizer B (1.55%) resulted in an early stiffening and an almost complete removal of the admixture. Here, no such early stiffening effect was found.

For the pastes with 0.3% or 0.45% KOH additions (WA1 and WA2, respectively), the initial amounts of superplasticizer removed from solution were approximately the same as for the mix without KOH addition. However, here some of the initially removed superplasticizer was released back into the solution progressively over several hours, and then was re-absorbed. This phenomenon was more significant as the level of the KOH addition increased. For the paste with 0.6% KOH dosage (WA3), a large portion of the admixture went through this cycle of release to the solution and then subsequent removal from solution.

The addition of KOH also changed the physical characteristics of the cement pastes. For low and intermediate dosages of KOH addition (0.3% to 0.6% Na₂O equivalent), the paste characteristics changed to more homogeneity and segregation and bleeding were not observed. Furthermore at such dosage levels, setting was slow enough that separation of solution for analysis would be done by filtration over the full 8 hour period covered.

For pastes with heavier dosages of KOH, i.e. 0.9% (WA4) and 1.2% (WA5), both the solution concentration responses and the overall paste physical characteristics changed. For these pastes, nearly all of the superplasticizer was removed from solu-
tion immediately, and it was never fed back to the solution. The physical characteristics of the pastes appeared to change significantly with time. Initially they were unsegregated, fluid pastes, similar to those at lower KOH dosages, but by 1 hour they had changed to stiff gels. This change was followed by progressive stiffening and early setting. By 5 hours, this solution could no longer be filtered off from the paste, and it needed to be recovered by the high pressure die method.

5.2.1.2 Inorganic Ion Concentrations in the Solution for Paste WA3

The paste with 0.6% KOH addition (WA3), which exhibited the peculiar reversible removal of the superplasticizer from solution most significantly, was selected and its pore solutions were analyzed further. Fig. 5.2-2 present the concentrations of $K^+$, $Na^+$, $Ca^{2+}$, and $OH^-$ ions of two replicate runs on different days as functions of time. For technical reasons, the sulfate ion concentrations were not measured.

The concentrations at time zero (filled symbols) are those in the mix water prior to contact with cement, in which the superplasticizer and additional KOH were already dissolved.

The concentrations of the cations ($K^+$, $Na^+$, and $Ca^{2+}$) were found to be constant throughout the this 8-hour period of measurement. It is noticed from the figure that the $OH^-$ ion concentration in solution decreased progressively for the first 3 hours or so, and then remained approximately constant.
Fig. 5.2-2 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 2% naphthalene sulfonate superplasticizer A and 0.6% KOH addition (WA3)
5.2.2 Effects of KOH Addition to Paste with Superplasticizer B (WB3): Solution Phase Analysis

5.2.2.1 Physical Characteristics of Paste

For comparison with the previous results, similar experiment carried out using naphthalene sulfonate superplasticizer B instead of superplasticizer A. The actual dosage of superplasticizer B used here was selected so as to exhibit the same response of UV absorbance for the long wavelength band (290 nm) of naphthalene sulfonate as the superplasticizer A did at a dosage of 2.0%, as was previously shown in Fig. 4.3-1. KOH was added at 0.6% Na₂O equivalent by weight of cement. Control paste for this series (without KOH) was WB0.

The physical characteristics of this paste with superplasticizer B and a 0.6% KOH dosage were similar in all respects to those of the corresponding paste made with superplasticizer A. The mini-slump spread values with time for this paste are plotted in Fig. 5.2-3. The fluidity is modest for the first hour, but seems to increase substantially by 2 hours to a mini-slump spread level of 500%. However, this increase in fluidity is temporary, and by 4 hours the spread was again reduced to a low value. The increase in the mini-slump value corresponds approximately to the time of release of naphthalene sulfonate superplasticizer into the solution.

The pastes behaved as uniform fluid pastes without exhibiting segregation, and setting was delayed so that separation of solution for analysis could be done by filtra-
Fig. 5.2-3 Area of spread in mini-slump test vs. time for mixes WB3 and WBO
5.2.2.2 Removal of Superplasticizer from Solution

Fig. 5.2.4 shows the time pattern of superplasticizer concentration in the solution of this paste (WB3), and of the two runs of the previously discussed corresponding paste with superplasticizer A (WA3). The initial absorption and the subsequent release of the naphthalene sulfonate superplasticizer B was observed to be entirely equivalent in its magnitude and duration to that seen previously in the corresponding paste with superplasticizer A. This indicates that the desorption re-adsorption phenomenon cannot be attributed to a particular brand of naphthalene sulfonate superplasticizer.

5.2.2.3 Inorganic Ion Concentrations in the Solution Phase

Fig. 5.2.5 presents the concentrations of $K^+$, $Na^+$, $Ca^{2+}$, $OH^-$ and $SO_4^{2-}$ ions as functions of time for the paste WB3. The $SO_4^{2-}$ concentrations here were determined by the BaSO$_4$ gravimetric precipitation method.

It was found that the concentration of the $Na^+$ ion was constant at approximately 130 meq/L for the whole period. This concentration level is lower than that found with the equivalent paste with superplasticizer A. Most of the $Na^+$ ion is obviously derived from the superplasticizer in either case. This indicates that superplasticizer B contains less sodium than superplasticizer A, even though the UV absorption response of those
Fig. 5.2-4 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer A or B and 0.6% KOH addition (WA3, WB3)
Fig. 5.2-5 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55% naphthalene sulfonate superplasticizer B and 0.6% KOH addition (WB3)
two superplasticizers are similar. The concentrations of the other cations (K⁺ and Ca²⁺) were constant with time, at around the same levels as those for the pastes WA3.

The SO₄⁻² ion, which was not present in the mix water, dissolved massively into the solution phase from the cement immediately after its initial contact with water. It then stayed at around 230 meq/L for the rest of the measurement period. The OH⁻ ion concentration was at about 400 meq/L in the mix water, due to the added KOH. It then decreased at first, then stabilized at a level of about 230 meq/L and remained approximately constant. Aside from the difference in Na⁺ ion level, the results are similar to what was previously exhibited in Fig. 5.2-2 for the corresponding paste with superplasticizer A.

5.2.3 Effects of Alkali Sulfate Addition to Paste with Superplasticizer B (WBK, WBN): Solution Phase Analysis

In this section, results are reported for pastes similar to those in Section 5.2.2 except that alkali were added as alkali sulfates (K₂SO₄ and Na₂SO₄) instead of as alkali hydroxide. Superplasticizer B was again used, and the addition level of the alkali sulfates was again 0.6% Na₂O equivalent by weight of cement. The superplasticizer addition level was again 1.55%. The paste with K₂SO₄ was coded WBK; that with sodium sulfate was coded WBN.
5.2.3.1 Physical Characteristics of the Pastes

The initial physical characteristics of both pastes WBK (with $K_2SO_4$) and WBN (with $Na_2SO_4$) were similar to each other. In contrast to pastes with a corresponding level of KOH, these pastes remained watery and exhibited a high level of segregation and bleeding, and remained so for 6 hours or more.

Fig. 5.2-6 shows the results of the mini-slump test series with time of four pastes. Paste WB0 shows the response for the control paste with this superplasticizer, but without other additions; WB3 shows the changed response with 0.6% $Na_2O$ equivalent KOH added; and WBK and WBN show the changed responses with 0.6% $Na_2O$ equivalent $K_2SO_4$ and $Na_2SO_4$ added, respectively. As shown previously, the superplasticized white cement paste showed initially no fluidity and was stiffened rapidly. Addition of the KOH increased the fluidity somewhat, but only temporarily.

The patterns of the the mini-slump value for the superplasticized pastes with the two alkali sulfates were basically the same. The fluidity in both cases were much higher than with KOH, with spread percentages well over 1000%. This extreme fluidity persisted for about 7 hours for the $Na_2SO_4$-treated paste, 9 hours for the $K_2SO_4$-treated paste. Subsequently the fluidity rapidly decreased and set occurred rapidly thereafter.
Fig. 5.2-6 Area of spread in mini-slump test vs. time for mixes WBK, WBN, WB3, and WB0
5.2.3.2 Removal of Superplasticizer from Solution

Fig. 5.2-7 shows a comparison of the residual concentrations of superplasticizer B in the paste solution as functions of time for pastes WB3, WBK, and WBN.

The pattern of removal of superplasticizer from solution was different for the KOH-treated paste than for the two alkali sulfate treated pastes. As previously noted, in the presence of the KOH, the superplasticizer was nearly completely removed initially, then some of the previously removed superplasticizer was returned to the solution after about 1 hour, and it was subsequently again removed later.

In contrast, for the alkali sulfate treated pastes, the initial removal from solution of the superplasticizer was only about one third of that for the paste with KOH. Thereafter, the superplasticizer concentration decreased gradually; the rate being a little faster for the Na₂SO₄-treated paste. For neither paste was the phenomena of temporary return of superplasticizer to solution observed. Nevertheless, at any age, the concentration of superplasticizer remaining in solution was always much higher with the alkali sulfates than with the KOH.

5.2.3.3 Inorganic Ion Concentrations in the Solution Phase

Fig. 5.2-8 and Fig. 5.2-9 show inorganic ion concentrations as a function of time for the superplasticized pastes with K₂SO₄ and Na₂SO₄ respectively. Again the SO₄⁻² ion concentrations were determined by the BaSO₄ gravimetric precipitation method.
Fig. 5.2-7 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B and 0.6% addition of K$_2$SO$_4$, Na$_2$SO$_4$, and KOH (WBK, WBN, WB3)
Fig. 5.2-8 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55% naphthalene sulfonate superplasticizer B and 0.6% K$_2$SO$_4$ addition (WBK)
Fig. 5.2-9 Concentration of inorganic ions in mix water and pore solution vs. time in paste with 1.55\% naphthalene sulfonate superplasticizer B and 0.6\% Na₂SO₄ addition (WBN)
For the paste with K$_2$SO$_4$, the cation changes were similar to those for the paste with KOH, except for the Ca$^{2+}$ ion. The Ca$^{2+}$ ion concentration for the paste WBK increased immediately over 50 meq/L and remained nearly constant at this level, which was significantly higher than the paste with KOH.

For the anions, the SO$_4^{2-}$ ion concentration was initially high in the mix water and decreased only a little. The OH$^-$ ion rose up to 130 meq/L after the initial contact then increased gradually.

Next for the paste with Na$_2$SO$_4$ (Fig. 5.2-9), the Na$^+$ ion remained at the highest level (about 500 meq/L) for the whole period of analysis due to its extra addition plus from the superplasticizer. There was almost no K$^+$ ion detected. The Ca$^{2+}$ ion concentration rose to 90 meq/L at one hour then gradually decreased to a level around 30 meq/L, which is also higher than that for the paste WB3.

The anion patterns were quite similar to those patterns for the paste with K$_2$SO$_4$, and both the OH$^-$ and the SO$_4^{2-}$ ion concentrations were stabilized at approximately the same levels as those for the paste WBK. It should be noted that in both cases the SO$_4^{2-}$ concentration level remained high, at least during this eight-hour period.
5.3 Effects of the Sulfate and Hydroxide Ions on Removal of Superplasticizer from Solution

5.3.1 Objectives of the Experiment

The results of experiments described in the previous section raise some questions with respect to the effects of alkalis on the removal of the naphthalene sulfonate superplasticizer from solution.

First, the study on the effects of alkali hydroxide on superplasticizer A showed that initial removal of the superplasticizer from solution increased with increasing dosage of KOH. In addition, the rheological behavior changed with increasing additions of KOH.

It was noticed that the removal pattern of the superplasticizer for the paste WB0 shown in Fig. 5.1-6, was significantly different from that of the paste WA0 shown in Fig. 5.2-1, although both are control pastes of the same cement without alkali addition. Superplasticizer B was almost completely removed from solution in the first 16 minutes, but an initial removal of superplasticizer A was only about half the amount added. Table 5.3-1 shows the inorganic ion concentration in the mix waters of pastes WA0 and WB0 as analyzed by atomic absorption and ion chromatography. The results indicate that superplasticizer A contains significantly more Na₂SO₄ impurity than the superplasticizer B; the corresponding SO₄²⁻ ion concentrations in the mix water were about 27 meq/L and 5 meq/L respectively. Actually, the total ionic con-
Table 5.3-1 Concentrations of inorganic ions and superplasticizer in the mix water for the paste WA0, WB0, WBNO

<table>
<thead>
<tr>
<th>Mix Code</th>
<th>WA0</th>
<th>WB0</th>
<th>WBNO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Superplasticizer (g/L)</td>
<td>34.0</td>
<td>31.8</td>
<td>31.8</td>
</tr>
<tr>
<td>Inorganic composition (by analysis) (meq/L):</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na⁺</td>
<td>201.0</td>
<td>116.1</td>
<td>120.3</td>
</tr>
<tr>
<td>K⁺</td>
<td>0.0</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>3.4</td>
<td>11.6</td>
<td>10.5</td>
</tr>
<tr>
<td>OH⁻</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>26.5</td>
<td>4.5</td>
<td>25.0</td>
</tr>
</tbody>
</table>
centrations of the solution of cement W without superplasticizer is so small that even a modest difference in the amount of $SO_4^{2-}$ added in the mix water may affect the removal of superplasticizer from the solution considerably.

In order to further investigate the effects of the anions concerning the points mentioned above, three more superplasticized paste mixes were examined in a supplemental study. All three pastes were dosed with 1.55% naphthalene sulfonate superplasticizer B. The first is a repeat of the paste mix WB3, i.e. water:cement ratio 0.5 white cement with the superplasticizer and incorporating a 0.6% KOH addition. This paste is coded WB3'. The second paste was a similar white cement paste with 1.2% KOH added in the mix water, coded WB5. This paste is comparable to WA5, previously described. Third mix is a similar white cement paste with 0.03% $Na_2SO_4$ addition in the mix water, coded WBN0. This amount of $Na_2SO_4$ is equal to the sulfate impurity of superplasticizer A, as was shown in Table 5.2-1. For these three pastes, the residual superplasticizer concentration in solution, the $OH^-$ ion concentration, the $SO_4^{2-}$ ion concentration, and the $CaSO_4$ bearing phases of the solids were analyzed as functions of time until the time of set.
5.3.2 Effects of KOH and Sulfate Additions on Residual Concentration of Superplasticizer B, on Anion Concentrations, and on Solid Phases Present

5.3.2.1 Removal of Superplasticizer from Solution

Fig. 5.3-1 shows the remaining concentration of superplasticizer in solution as a function of time for the pastes WBNO, WB3', and WB5. The pattern for the paste without any alkali addition, previously examined as the mix WBO, is also presented in the figure for reference.

For the paste with a small amount of Na2SO4 added (WBNO), the removal of superplasticizer from solution immediately after the contact with water was reduced to about half of the initial concentration, in contrast to the almost complete removal for the paste WBO. The subsequent decrease in concentration was small. Paste WBNO was found to be extremely fluid and it exhibited extreme segregation and bleeding, similar to the behavior of paste WAO, but quite different from that of paste WBO. It should be recalled that the latter was stiff, exhibited no segregation or bleeding.

For the paste with 0.6% KOH addition (WB3'), the pattern of the initial removal and the subsequent "desorption" of the superplasticizer previously reported for paste WB3 was repeated. However, for this mix, the amount of superplasticizer released back to solution was a little smaller than for the previous paste WB3.

For the paste with 1.2% KOH addition (WB5), almost all the superplasticizer was removed from solution within 10 minutes and there was no subsequent "desorption" of
Fig. 5.3-1 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B (WBO) and with 0.03% addition of Na$_2$SO$_4$, 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5)
superplasticizer observed. This adsorption pattern is the same as that previously seen with paste WA5. The present paste was found to stiffen actually within 6 minutes. However, there was a noticeable difference in this stiffening from the rapid solidification previously observed for the paste WB0. Here the cement particles seemed to be flocculated and small aggregations were found during the first 6 minutes while the paste was still fluid. For the previous paste without KOH (WB0), the cement particles had remained well dispersed in the fluid mass.

5.3.2.2 Anion Concentrations in the Solution Phase

Fig. 5.3-2 summerizes the SO$_4^{2-}$ ion concentrations of the three pastes vs. time. The pattern for the paste WB0 is also shown in the same figure. The SO$_4^{2-}$ ion concentrations were determined here by ion chromatography. By comparing the patterns for pastes WB0, WB3', and WB5, it is evident that the initial dissolution of the sulfate was greater as the alkalinity of the mix water increased. The sulfate ion concentrations for the pastes WB3' and WB5 increased rapidly at first, and then more slowly. For the paste WBN0, there was a small peak in the sulfate concentration to about 50 meq/L at 10 minutes, but it decreased again and stayed around the level of 30 meq/L for the rest of the period.

Fig. 5.3-3 exhibits the OH$^-$ ion concentration of the three pastes and the paste WB0 as functions of time. For the paste WBN0, the mix water did not contain any hydroxide ion; the OH$^-$ concentration of the paste increased to about the same concentration as that of paste WB0 (90 meq/L) in the first 14 minutes. It did not change
Fig. 5.3-2 Concentration of the \( \text{SO}_4^{2-} \) ion in mix water and pore solution vs. time for pastes \( W \) with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of \( \text{Na}_2\text{SO}_4 \), 0.6%, and 1.2% addition of KOH (WBNO, WB3', WB5)
Fig. 5.3-3 Concentration of the OH⁻ ion in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer B (WB0) and with 0.03% addition of Na₂SO₄, 0.6%, and 1.2% addition of KOH (WBNO, WB3', WBS)
For the pastes WB3' and WB5, the initial high concentrations of the OH⁻ ion in the mix water were not maintained in the pastes. Rather they decreased progressively as hydration proceeded. This decrease was mainly a response to the rapid increases in the SO₄²⁻ ion concentration by dissolution of the anhydrite. The net result was that the excess of the Na⁺ ions released from the superplasticizer was here balanced by an increase in the SO₄²⁻ ion concentration, rather than by increase in OH⁻ ion concentration.

5.3.2.3 Solid Phase Analyses

The CaSO₄-bearing phases observed in the solids separated from these three pastes were insoluble anhydrite and ettringite only, as were the cases for the pastes WO and WBO. Fig. 5.3-4 shows the changes of anhydrite contents (expressed as equivalent SO₄ content) as functions of time for the three pastes and the paste WBO. For the paste WBN0, the decrease of the anhydrite within the first 14 minutes was almost the same as that for the paste WBO. Subsequently the anhydrite content remained almost constant, before again starting a progressive decline at about 2 hours. The anhydrite content of paste WBO did not show an early constant period; however, it did remain approximately constant after 2 hours.

The patterns for the paste WB3' and WB5 were similar to each other, but very different from those described above. The anhydrite content declined immediately to
Fig. 5.3-4 Content of anhydrite in paste solids vs. time for pastes W with naphthalene sulfonate superplasticizer B (WBO) and with 0.03% addition of Na$_2$SO$_4$, 0.6%, and 1.2% addition of KOH (WBN0, WB3', WB5)
(Percentage of anhydrite re-expressed in terms of its SO$_4$ content.)
around 1.2% equivalent SO\text{4}^{2-}; it then continued to decline rapidly for both paste:
reaching essentially zero at 4 hours for the paste with 1.2% KOH addition.

Fig. 5.3-5 shows the ettringite content in the separated solid vs. time for the same
three pastes and the paste WB0. Although the paste WBN0 is identical to the paste
WB0 except for the small addition of Na\text{2}SO\text{4}, the amount of the ettringite formed in
the first 10 minutes was cut in half, from 1.2% to 0.6% equivalent SO\text{4}. This
significant difference in the ettringite produced was maintained with age over the
period investigated. It is thus considered that this difference in the ettringite forma-
tion may have contributed to the different rheological behaviors of two pastes.

For the paste WB3\text{',} the initial ettringite formation at 10 minutes was around 1%
but it rose to 1.6% at 1 hour and continued to increase to higher levels at a given age
than did the paste WB0.

An unusual response was found for the paste WB5. No ettringite had formed for
almost the first 2 hours of the hydration period; thereafter, ettringite started to form,
and the amount present increased fairly rapidly. This paste was stiffened quickly,
within 15 minutes; subsequently it remained in a gelatinous condition until it set.

Table 5.3-2 shows the balance of the SO\text{4}-bearing phases in pastes WBN0, WB3\text{',}
and WB5.

For paste WBN0, the sum of the sulfates allocated in the solids plus the SO\text{4}^{2-} ion
in the pore solution remained essentially constant for the 2 hours, then decreased
slightly. It should be recalled that the corresponding total percentages for the control
Fig. 5.3-5 Content of ettringite in paste solids vs. time for pastes W with naphthalene sulfonate superplasticizer B (WBO) and with 0.03% addition of Na$_2$SO$_4$, 0.6%, and 1.2% addition of KOH (WBNO, WB3', WB5) (Percentage of ettringite re-expressed in terms of its SO$_4$ content.)
Table 5.3-2 Total balance of sulfate-bearing phase for mix WBNO, WB3', and WB5

(Percentages expressed in terms of equivalent $SO_4$ content)

<table>
<thead>
<tr>
<th>Mix #</th>
<th>Age (hr)</th>
<th>Anhydrite (%)</th>
<th>Ettringite (%)</th>
<th>$\Sigma$ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
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<tr>
<td>WBNO</td>
<td>0.00</td>
<td>2.47</td>
<td>0.00</td>
<td>2.47</td>
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<td>2.53</td>
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<td></td>
<td>0.23</td>
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<td>0.75</td>
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<td>0.09</td>
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<td>0.08</td>
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<tr>
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<td>0.00</td>
<td>2.47</td>
<td>0.01</td>
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<td>0.24</td>
<td>2.36</td>
<td>2.60</td>
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<td>-</td>
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<tr>
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<td>0.00</td>
<td>2.47</td>
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<td>2.47</td>
<td>0.01</td>
<td>2.48</td>
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<td>1.32</td>
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<td>-</td>
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</tr>
</tbody>
</table>

* The total $SO_4$ content of the cement, separately determined, was 3.76% as $SO_4$. 
mix with superplasticizer free from sulfate impurity (WB0) were generally higher, increasing to around 3.0% by 6 hours (Table 5.1-2).

For paste WB3', the sum of the sulfates in the solids and the sulfate ions increased significantly to 3.2% for the first 1 hour, and then declined to around 2.7% by 4 hours. These total percentages were higher than those for the previous paste WBN0.

In contrast to these effects, the total sulfates accounted for in paste WB5 decreased at the first measurement to 1.8%, the decrease reflecting obvious dissolution of anhydrite without precipitation of identifiable ettringite. It then fluctuated in a range between 1.7% and 2.1%, lower total allocated sulfate contents than for any other mix of WBX series. The decrease in the total sulfates in the solids for the first 2 hours was larger than the increase in the sulfate ion concentration.

5.4 Discussion

5.4.1 Analyses for Control and Superplasticized White Cement Pastes (WO and WB0)

In the control paste, ettringite formation at early ages was moderate, probably because the rate of dissolution of insoluble anhydrite was slow. Considering that the anhydrite content was continuously reduced during the first 6 hours, it appears that the rate of anhydrite dissolution controls the rate of ettringite formation.

When the superplasticizer was added, the initial formation of ettringite and the consumption of insoluble anhydrite were both accelerated by the presence of the
superplasticizer. Both phenomena occurred probably because the cement particles were more dispersed by the action of the superplasticizer during the first 20 minutes of hydration. In solution, both the calcium ion and the sulfate ion were low from the early stage of hydration, probably as a result of the intense ettringite formation.

The peculiar quick stiffening of paste WBO, which was not a false set, can be attributed to the intense ettringite formation and the almost complete removal of the superplasticizer in the early stages of hydration. The ettringite content reached as high as 1.7% of SO₄ equivalent by 1 hour. This ettringite formation itself could cause filling and bridging the interparticle spaces, and lead to a quick setting of the paste. It is believed that the superplasticizer was preferentially incorporated with this ettringite, and was removed from the solution during the first 20 minutes of hydration. Thus the solution phase lacking residual superplasticizer, did not have any potential of dispersing the solid particles; this also appeared to assist this quick setting.

5.4.2 Effects of the OH⁻ ion on Hydration of Cement W and on Removal of Superplasticizer from Solution

From the results of the pastes with superplasticizer A and additional KOH (the WAX pastes), it appears that the higher hydroxide ion concentration in the mix water promoted the initial removal of the naphthalene sulfonate from the paste solution as shown in Fig. 5.2-1. But the picture is not simple. Based on the rheological feature of the pastes and the results of calcium sulfate phase analysis for analyses of WBX series, the early hydration pattern of the white cement W seems to be altered both by
mix water with dissolved alkali hydroxide, and by the action of the superplasticizer.

The form of the calcium sulfate in the white cement W is entirely composed of "insoluble" anhydrite. A higher OH\(^-\) concentration in the original mix water accelerates the rate of anhydrite dissolution. This results in a faster depletion of the anhydrite, and increases of the SO\(_4^{2-}\) ion concentration in solution. This increased dissolution of calcium sulfate releases an equivalent additional amount of the Ca\(^{2+}\) ion into the solution.

The effect of the OH\(^-\) ion was evident in the extreme case of a large addition of KOH in the mix water. For the paste WB5, although the SO\(_4^{2-}\) ion concentration in pore solution was markedly high, ettringite was not formed at all for the first 2 hours. Nevertheless the paste was stiffened within 15 minutes. In solutions of higher alkalinity than that of saturated Ca(OH)\(_2\) solution, the equilibrium

\[
\text{Ca(OH)}_2 \leftrightarrow \text{Ca}^{2+} + 2\text{OH}^- 
\]

shifts strongly to the precipitation side and the amount of Ca(OH)\(_2\) remaining dissolved in solution is reduced. It would seem that in the presence of high OH\(^-\) ion concentrations, the calcium sulfate would tend to dissolve rapidly to make up the "shortage" of Ca\(^{2+}\) ions. As more calcium sulfate is dissolved, the Ca\(^{2+}\) ions are progressively incorporated in additional Ca(OH)\(_2\) but the SO\(_4^{2-}\) ions remain in solution. In the WB5 paste, a prompt Ca(OH)\(_2\) precipitation occurred and may have caused the quick set. The loss on ignition data for the paste WB5 was as high as 3.01% at 10 minutes, and 3.22% at 1 hour, compatible with the existence of a large content of calcium hydroxide. The same pastes had very low evaporable water contents, as low as
0.38% and 0.55% at 10 minutes and 1 hour, respectively, so a large amount of cement hydration had not taken place.

The lack of ettringite formation may be explained by the possibility that the rate of the Ca(OH)$_2$ precipitation is so fast that the calcium ion selectively precipitates as calcium hydroxide in this high pH solution. As hydration continues, the increase of the SO$_4^{2-}$ ion concentration and the calcium ion consumption might reduce the OH$^-$ ion concentration and slow down the rate of Ca(OH)$_2$ precipitation. When the OH$^-$ ion concentration is reduced to around 0.45 N, i.e. after 2 hours of hydration, the rate of ettringite formation becomes relatively fast. It can be hypothesized that ettringite formation is hindered in solutions of OH$^-$ ion concentrations higher than around 0.5N.

Thus for the paste WB5, a combination of the rapid precipitation of Ca(OH)$_2$ and the almost complete removal of superplasticizer from solution within 10 minutes was responsible for this quick set. However, this may be only applicable to this white cement because of its peculiar properties. The superplasticizer removal from solution is obviously related to this Ca(OH)$_2$ precipitation, but the crystals of calcium hydroxide rarely incorporate foreign organic species; the mechanism is not clear.

For the paste WB3, the superplasticized pastes with KOH added to the mix water at 0.6% Na$_2$O equivalent by weight of cement, this rapid Ca(OH)$_2$ formation seemed to occur to a limited degree only. The removal of the superplasticizer from solution might thus be due to the incorporation by poorly-crystalline ettringite. The formation of ettringite was not limited in this paste of lower OH$^-$ ion concentration; the percen-
tage formed in the first 10 minutes was as high as 1.0% SO$_4$ equivalent in the solids
and increased thereafter to a larger percentage than in the paste WB0.

For the pastes without the OH$^-$ ion addition (WB0 and WBNO), the initial super-
plasticizer uptake and the hydration behavior are more influenced by other factors, as
will be discussed later.

Thus, it appears that the early removal of superplasticizer from solution may
involve different uptake mechanisms, depending on any addition made to the mix
water. Most of the superplasticizer is immediately taken up by the solids in the
absence of any such addition, and also in the presence of a high dosage of added
KOH, but the two responses are different in cause and character. Again, it is partially
due to the peculiar properties of the white cement.

Finally, it was noticed that in the mix water containing naphthalene sulfonate
superplasticizer and the 0.6%, 0.9%, and 1.2% KOH treatments, a fine white precipi-
tate was observed. A similar white precipitation was reported to develop in melamine
sulfonate superplasticizer when concentrated alkali hydroxide solution was added, in
research by Yilmaz et al. [76]. They considered the precipitate to be the result of
"denaturation" of the admixture in such solution. However, in the present paste, the
UV adsorption spectra of naphthalene sulfonate superplasticizer in the solutions with
the white precipitate was identical to that of the original superplasticizer. Thus it does
not appear that the plasticizing action would be affected by the response to the addi-
tion of the alkali hydroxide.
5.4.3 Effects of Sulfate Ions on Removal of Superplasticizer From Solution

Effects of the sulfate ions dissolved in the mix water on the initial adsorption of naphthalene sulfonate superplasticizer are reasonably apparent. Fig. 5.4-1 compares the time-dependent changes of the superplasticizer concentration remaining in solution for the pastes of the white cement W with different concentrations of the sulfate ion in the mix water. These pastes are WBO, WA0, WBN0, WBK, and WBN. The mix water of pastes WBO contained 5 meq/L of $SO_4^{2-}$ ion, those of the pastes WA0 and WBN0 contained around 25 meq/L, and those of pastes WBN and WBK contained around 400 meq/L. It is seen that the superplasticizer concentration remains approximately constant with time for each of these pastes, but that the actual concentration levels vary considerably.

Fig. 5.4-2 shows the time-dependent changes of the $SO_4^{2-}$ ion for the same pastes. The results of Fig. 5.4-2 indicate that the level of $SO_4^{2-}$ retained in solution are approximately 0, 40, 330, and 360 meq/L for pastes WBO, WBN0, WBN, and WBK, respectively. These levels are approximately proportional to the dosage of $SO_4$ added in the mix water, but for the pastes with the higher $SO_4$ addition (WBN and WBK) the concentration level maintained in the cement paste solution was actually a little less than was originally present in the mix water.

It is clearly seen that the higher concentrations of sulfate ions in the mix water somewhat hinder the initial uptake of the naphthalene sulfonate superplasticizer. Judged from the results for the pastes WBK and WBN, little difference occurs
Fig. 5.4-1 Concentration of residual superplasticizer in mix water and pore solution vs. time for pastes W with naphthalene sulfonate superplasticizer A and B (W0, WB0), and pastes W with superplasticizer B and 0.03%, 0.6% addition of Na₂SO₄, and 0.6% addition of K₂SO₄ (W0, WB0, WBK)
Fig. 5.4-2 Concentration of the SO$_4^{2-}$ ion in mix water and pore solution vs. time for pastes WBO, WBN0, WBN, and WBK.
between effects of sodium and potassium as the cation of the alkali sulfate on the adsorption characteristics of the superplasticizer.

The pastes WA0, WBN0, WBK, and WBN were all fluidized well, and the residual naphthalene sulfonate concentration in the paste solutions stayed high. Again, it is found that the residual concentration of the superplasticizer is strongly associated with the physical characteristics of the pastes. In addition, well-fluidized pastes appeared to show retardation in hydration compared to the control paste WO.

The patterns of superplasticizer adsorption of paste WA0 and WBN0 were almost identical, and the rheology of the two pastes were also similar to each other, but different from that for the paste WB0. The difference of two superplasticizers A and B in initial absorption behavior are probably explained by the amount of the sodium sulfate impurity.

The polymer anion of the naphthalene sulfonate superplasticizer and the \( \text{SO}_4^{2-} \) ion both have negative charges. Both may tend to be absorbed by positively charged surfaces of early C\(_3\)A hydration products, or incorporated into such products, almost immediately after the beginning of hydration. The white cement W has a very low alkali sulfate content; the sulfate present appears to be in the form only of anhydrite. Because of the low rate of dissolution of anhydrite, the sulfate ion concentration that is derived quickly from the cement itself is also low, as seen for the control paste WO. In this low range of sulfate ion concentration of the paste solution at very early ages, even a small amount of dissolved sulfate "impurity" apparently causes significant
interference with the removal of naphthalene sulfonate from solution.

However, this system of white cement paste W plus naphthalene sulfonate superplasticizer was so sensitive that its hydration behavior can be significantly affected by its mixing procedure. The author found that the small hand mixed specimen of WB0 remained well dispersed and showed bleeding for hours exactly like the paste WBNO, when the hand mixed WB0 paste was mixed in such a way that the mix water wet the cement slowly. The comparison hand mixed WB0 paste exhibited the quick set response usually seen for WB0 pastes when mixed vigorously in a short time.

The difference in early hydration behaviors of these superplasticized pastes with paste solutions of few sulfate ions present, are also observed in the amount of ettringite formed. Early ettringite formation (10 minutes) for the paste WB0 was 1.2% and that for the paste WBNO was only 0.6% equivalent of SO$_4$ content. This difference can be partially attributable to the sulfate ion concentrations in the solution phase.

The initial removal of superplasticizer from solution was about nearly complete for paste WB0, and only about a half for paste WBNO. Consequently, the paste WB0 exhibited a peculiar quick stiffening. In contrast, WBNO paste was completely dispersed and showed extensive bleeding for several hours. It is considered that ettringite formation itself can absorb and incorporate the naphthalene sulfonate.

For this particular white cement, the presence of naphthalene sulfonate admixture coupled with the lack of the sulfate ion in the paste solution at very early ages frequently resulted in quick premature stiffening. Adding sulfate ions along with the
superplasticizer seems to prevent this peculiar early hydration behavior. If sulfate ions are added, the amount of ettringite formed immediately is reduced, and the amount of naphthalene sulfonate superplasticizer removed from solution is also reduced; in consequence, a well-fluidized paste is produced. A possible explanation is that the initial hydration products contain more $SO_4^{2-}$ ions and fewer absorbed superplasticizer molecules. It may be that these initial products develop a less reactive surface for ettringite crystal growth, or that they act as a kind of the coating layer. In either case, the amount of ettringite formed quickly is reduced. This response may be specific to this white cement whose gypsum is entirely in the form of slowly-dissolving anhydrite.

5.4.4 Mechanism of "Desorption" of Superplasticizer

For the superplasticized pastes with 0.6% KOH addition (WB3), the phenomenon of the temporary release of the polymer previously removed from solution was observed.

In some circumstances, the naphthalene sulfonate superplasticizer is probably incorporated unstably with the amorphous early hydration products. Thus the changes in the ionic concentrations in the paste solution could cause "desorption" of these polymers from the solid surfaces.

With melamine sulfonate superplasticizer, Yilmaz et al. [76] considered that the "adsorption" of superplasticizer at early stage of hydration is controlled by ettringite or its precursor, and that the desorption of admixture occurs as this amorphous
precursor crystallizes to ettringite. However, no actual evidence to relate the crystallinity of ettringite and the superplasticizer adsorption was given in this paper.

5.4.5 Solid Phases

From the solid phase analyses, no crystallization of gypsum from anhydrite was detected regardless of the presence of the superplasticizer, or the concentration of the $\text{SO}_4^{2-}$ or the $\text{OH}^-$ ions in solution.

The paste systems to which the alkali hydroxide was intentionally added preserve a high $\text{OH}^-$ ion concentration in the pore solution, which increases the solubility of calcium sulfates in general, thus hindering the formation of any hydrous calcium sulfate phases. As long as the $\text{OH}^-$ ion concentration is high, gypsum is not able to form even in the presence of some sulfate ions.

For the normal pastes without an addition of KOH, the absence of gypsum or hemihydrate phases is probably explained by the fact that in the actual absence of alkali sulfates, the slow rate of dissolution of anhydrite keeps the CaSO$_4$ level in solution below the saturation level. In addition, the ettringite formation process constantly consumes the sulfate ion from the liquid phase. Therefore it is not unexpected to observe such direct conversion to ettringite without a transient state of gypsum, when the initial form of calcium sulfate in cement is insoluble anhydrite.
5.5 Effects of Melamine Sulfonate Superplasticizer on White Cement "W" Pastes: Physical Characteristics of Pastes and Removal of Superplasticizer from Solution

In the course of this research program, the study on white cement paste with melamine sulfonate superplasticizer was carried out to a limited extent. The results of the preliminary experiment are reported here for reference. The paste examined was a plain mix of white cement W with 2% dosage of melamine sulfonate superplasticizer B by weight of cement. The superplasticizer was dissolved in the mix water, and no inorganic ion was added to it.

--- Physical Characteristics of the Paste

The physical characteristics of the paste was peculiar, and it had not been similarly observed in any pastes of the white cement with naphthalene sulfonate superplasticizers. The hydration of the paste was very severely retarded due to the heavy dosage of the melamine sulfonate superplasticizer. The paste had been watery, and completely segregated for 2 days.

Fig. 5.5-1 shows the mini-slump spread values with time for this paste. The heavy dosage of the melamine sulfonate superplasticizer produced an entirely fluidized state (mini-slump value of over 1000%) for the first 3 hours. Then the spread value declined to 800% by 6 hours, however, it decreased only to 700% during the subsequent 18 hours. By 45 hours, the mini-slump value was dropped to 280%, and the paste was solidified several hours later. The initial set was at 54 hours.
Fig. 5.5-1 Area of spread in mini-slump test vs. time for paste W with 2% melamine sulfonate superplasticizer M
143

— Removal of Superplasticizer from Solution

Fig. 5.5-2 shows the concentration of melamine sulfonate remaining in solution as a function of time over 2 days. The dosage of the superplasticizer M used here was 2%, equivalent to weight concentration of 40 g/L in the mix water. Three fourth of the admixture was initially removed from solution, and its concentration was reduced to about 10 g/L. However, this remaining concentration of the superplasticizer had been maintained up to 45 hours. The paste solution at 45 hours was still able to be recovered by the pressure filtering method.

As the experiment was carried out in the early stage of this research project, the interference on the melamine sulfonate determination by UV analysis due to the OH\(^-\) ions in the paste solution was not handled properly yet. The concentration of melamine sulfonate was determined without neutralizing the solution sample. Therefore the actual concentration of the polymer must be lower than the values indicated in the figure by approximately 15%. However, the time-dependent pattern of the absorption for this paste is considered to be figured out properly.

5.6 Findings

The findings from the experimental work on white cement W are summarized as follows.

1. The white cement used shows a peculiar chemical composition which is reflected in somewhat peculiar hydration characteristics. Cement W is described as a
Fig. 5.5-2 Concentration of residual superplasticizer in mix water and pore solution vs. time for paste W with 2% melamine sulfonate superplasticizer M
cement of very low alkali content, low aluminate phase content, almost no iron content, and having insoluble anhydrite as the only form of calcium sulfate present. The solutions within the control paste WO have low ionic strength and low alkalinity.

2. Pastes of this white cement mixed only with a relatively pure naphthalene sulfonate superplasticizer exhibited rapid stiffening. This behavior is associated with the formation of a large amount of ettringite within about 15 minutes of the start of hydration, coupled with an almost complete removal of the superplasticizer from solution.

3. Two different naphthalene sulfonate superplasticizers produced significantly different early behaviors with the white cement. Pastes mixed with a less pure superplasticizer (superplasticizer A), that contains significant sodium sulfate impurity, did not stiffen but remained dispersed indefinitely. This behavior was reproduced using the pure superplasticizer (superplasticizer B) when an identical dosage of Na₂SO₄ impurity was added to it.

4. KOH added to the mix water affects the uptake of the naphthalene sulfonate from solution. With the less pure superplasticizer, the initial uptake increased as the amount of added KOH increased. The hydration reaction pattern of the pastes altered differently with different dosages of KOH, and the uptake of superplasticizer cannot be explained by one comprehensive mechanism.

5. Introduction of SO₄²⁻ ions into the mix water reduces the initial removal of
naphthalene sulfonate by the white cement. The presence of the sulfate ion in solution thus appears to lead to better performance by the superplasticizer.

6. Superplasticized pastes to which similar dosages of $\text{K}_2\text{SO}_4$ and $\text{Na}_2\text{SO}_4$ were added exhibited only slight differences in removal patterns of the naphthalene sulfonate from solution.

7. The cement paste mixed with naphthalene sulfonate and 0.6% KOH addition exhibited peculiar behavior. The polymer initially removed from solution by the solid phases was released back into solution, and then subsequently absorbed again.

8. As the dosage of KOH was increased, the rate of dissolution of insoluble anhydrite in the white cement was accelerated. With a high dosage (1.2%) of KOH, the superplasticized paste exhibited a different kind of quick solidification. From various items of evidence, such as the rapid formation of calcium hydroxide coupled with a complete lack of ettringite formation for the first two hours, the enhanced rate of insoluble anhydrite dissolution was attributed to the observed rapid precipitation of Ca(OH)$_2$ immediately after the start of the hydration. This precipitation was considered to be due to the high initial pH of the mix solution.

9. No hydrated form of calcium sulfate was found at any time in any of the hydrated pastes of the white cement. This was true regardless of the presence of superplasticizer or of added amounts of $\text{SO}_4^{2-}$ or $\text{OH}^-$ ions. For the pastes of moderately alkaline solution (i.e. with little or no added KOH), the slow rate of dissolution of anhydrite appears to restrict the sulfate ion concentration to values less than the
saturation level of calcium sulfate (80 meq/L). For the pastes of higher initial OH⁻ ion concentration, i.e. those with substantial amounts of added KOH, gypsum did not precipitate despite the increased level of sulfate in solution.

10. A heavy dosage (2% by weight of cement) of a melamine sulfonate superplasticizer severely retarded the hydration of the white cement. The paste had been completely dispersed with bleeding for almost two days. The residual concentration of the admixture in paste solution remained reasonably high during the corresponding two day period.
In this chapter, broader effects of superplasticizers on cement pastes prepared with ASTM Type I cement L were investigated. This is a type I portland cement of moderate alkali content and typical chemical composition. Pastes examined included (a) the control mix (LO), (b) the mix LB, incorporating 1.55% naphthalene sulfonate superplasticizer B by weight of cement, and (c) the mix LM, incorporating 0.5% melamine sulfonate superplasticizer M. Analyses of both paste solution and solid specimens were carried out for specimens sampled periodically during the first day, and also at 1, 3, 7, and 14 days after mixing. All specimens were kept in sealed containers up to the time of sampling.

The lower concentration of melamine sulfonate used here was selected because of the very strong effect of this superplasticizer on the white cement described in the previous chapter. It was found that with a 2% dose setting of the white cement was delayed for two days and the amount remaining in solution at two days was still high. In consequence, in the work with cement L, the dosage of melamine sulfonate was reduced to 0.5%.
6.1 Result

6.1.1 Effects of Superplasticizers on Hydration

Fig. 6.1-1 illustrates the loss on ignition over the first day of hydration for the three mix series, LO, LB, and LX, and Fig. 6.1-2 shows the pattern of Fig. 6.1-1 extended to 14 days. The loss on ignition data have been corrected for the superplasticizer absorbed by the solids. Results of conduction calorimetry analysis for these three mixes up to two days are shown in Fig. 6.1-3.

The loss of ignition data and calorimetry measurement for mix LB indicate the existence of a severe retarding effect of this heavy dosage of the superplasticizer B. The melamine sulfonate superplasticizer M, used at a much lower dose level, caused only modest retardation. From the longer term loss on ignition data, it is found that the retardation effect by superplasticizer B, appears to be converted to a permanent reduction in loss on ignition. This permanent reduction in ignition loss may be a reflection of a change in the composition of the hydration product, rather than of a permanent reduction in the amount of cement that will hydrate. For mix LM, loss on ignition was about the same as the control case at one day and became higher thereafter.

In Fig. 6.1-4, the mini-slump value is plotted as a function of time for the three series of mixes. Both superplasticizers greatly increased the spread, to an early level of about 1100% as compared to a level of the order of 300% - 400% without super-
Fig. 6.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement L without superplasticizer (LO), with 1.55% naphthalene sulfonate (LB), and with 0.5% melamine sulfonate (LM)
Fig. 6.1-2 Loss on ignition of pastes for periods extended to 14 days
Fig. 6.1-3 Conduction calorimetric curves showing heat evolution vs. time for mixes LO, LB, and LM
Fig. 6.1-4 Area of spread in mini-slump test vs. time for mixes LO, LB, and LM
plasticizer. The initial set time without superplasticizer was 5.5 hours, and after about 2 hours there was a progressive reduction in spread (fluidity). For the paste with a high dosage of naphthalene sulfonate the initial set time was delayed to 12.5 hours; the available data in Fig. 6.1-4 show that the high initial level of spread was maintained for at least 6 hours. In contrast, the lower dosage of melamine sulfonate produced only a modest retardation (initial set increases from 5.5 hours to 8.5 hours), and the spread percentage decreased rapidly from the starting level of over 1100% to only about 200% by 6 hours.

6.1.2 Control Paste Without Superplasticizer (LO): Solution and Solid Phase Analysis

6.1.2.1 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-5 shows the concentrations of K⁺, Na⁺, Ca²⁺, OH⁻ and SO₄²⁻ as functions of time over the first 24 hours of the control paste. The results of two replicate runs on different days are plotted, and are reasonably consistent. The pattern was that predicted for a low alkali cement paste from prior work, as presented recently by Diamond and Penko [77].

The concentrations of the alkali ions, Na⁺ and K⁺, were stabilized quickly at levels of about 300 meq/L and 30 meq/L respectively. The concentration of Ca²⁺ rose immediately to about 40 meq/L, maintained almost constant for several hours, and then diminished to near zero between 12 and 24 hours.
Fig. 6.1-5 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (LO)
For the anions, the $\text{SO}_4^{2-}$ concentration was maintained at a plateau of about 220 meq/L, then progressively decreased to about 20 meq/L after 12 hours. There was an increase in the $\text{OH}^-$ ion concentration from 150 meq/L to 350 meq/L, corresponding in both time and magnitude to this decrease of $\text{SO}_4^{2-}$.

Fig. 6.1-6 provides the same information as Fig. 6.1-5, but extended to 14 days. As expected, the $\text{Ca}^{2+}$ and $\text{SO}_4^{2-}$ ion concentrations were practically zero after the first day. The ions remaining in solution were $\text{K}^+$, $\text{Na}^+$, and $\text{OH}^-$; for all of these, the concentration rose significantly between 1 and 3 days, and increased slightly thereafter. This uniform increase after 3 days is presumably due to reduction of solvent water caused by cement hydration.

Table 6.1-1 shows the sum of the cation concentrations and the sum of the anion concentrations for duplicate 1 day determinations and for three longer-time determinations for these LO control cement pastes. Each value of the algebraic difference between the sum of the anions and the sum of the cations seems to be within a range of reasonable experimental error. There are approximately equal numbers of net positive and net negative values, and the mean algebraic difference of the set is only +0.6 meq/L. This is only about 0.2% of the mean concentration of either cations or anions, strongly indicating that the analyses were correct and that no ion other than those reported was present in appreciable concentration.
Fig. 6.1-6 Concentration of inorganic ions in pore solution vs. time for extended periods up to 14 days in control paste (LO)
<table>
<thead>
<tr>
<th>Age</th>
<th>Σ Cations (meq/L)</th>
<th>Σ Anions (meq/L)</th>
<th>Difference (meq/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Run 1 (hr)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>282.7</td>
<td>280.8</td>
<td>+1.9</td>
</tr>
<tr>
<td>0.50</td>
<td>368.1</td>
<td>358.8</td>
<td>+9.3</td>
</tr>
<tr>
<td>1.00</td>
<td>363.6</td>
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</tr>
<tr>
<td>2.23</td>
<td>361.9</td>
<td>357.9</td>
<td>+4.1</td>
</tr>
<tr>
<td>3.83</td>
<td>368.7</td>
<td>373.5</td>
<td>-4.9</td>
</tr>
<tr>
<td>5.95</td>
<td>371.2</td>
<td>368.1</td>
<td>+3.1</td>
</tr>
<tr>
<td>23.17</td>
<td>364.9</td>
<td>372.9</td>
<td>-8.0</td>
</tr>
<tr>
<td><strong>Run 2 (hr)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.17</td>
<td>315.4</td>
<td>336.3</td>
<td>-20.9</td>
</tr>
<tr>
<td>0.98</td>
<td>355.3</td>
<td>344.1</td>
<td>+11.2</td>
</tr>
<tr>
<td>2.02</td>
<td>345.8</td>
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</tr>
<tr>
<td>4.47</td>
<td>349.4</td>
<td>346.6</td>
<td>+2.8</td>
</tr>
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<td>5.82</td>
<td>359.8</td>
<td>365.4</td>
<td>-5.6</td>
</tr>
<tr>
<td>12.00</td>
<td>372.2</td>
<td>364.5</td>
<td>+7.7</td>
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<tr>
<td>23.92</td>
<td>377.6</td>
<td>375.0</td>
<td>+2.5</td>
</tr>
<tr>
<td><strong>Run 2 (day)</strong></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.88</td>
<td>439.4</td>
<td>431.8</td>
<td>+7.6</td>
</tr>
<tr>
<td>7.00</td>
<td>455.9</td>
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</tr>
<tr>
<td>14.00</td>
<td>469.2</td>
<td>473.8</td>
<td>-4.5</td>
</tr>
</tbody>
</table>
6.1.2.2 Solid Phase Analyses

Fig. 6.1-7 exhibits the results of analyses for CaSO₄-bearing phases carried out in the corresponding solid samples over the first 24 hours. The initial form of calcium sulfate in cement L was found to be entirely calcium sulfate hemihydrate. The CaSO₄-bearing solid phases detected throughout the experiment were all in the hydrous forms, specifically hemihydrate, gypsum, and ettringite. Those compounds were quantified by DSC analysis, and the quantity of each compound found was re-expressed in terms of the ratio of its SO₄ content to the ignited weight of the compound. In this way the amount of each compound can be visualized in terms of the fractional content of the total sulfate originally present in the cement. The results of two replicate runs on different days are presented on the figure. It is seen that ettringite determinations are highly reproducible as a function of time, and that the residual gypsum determination are reasonably so.

The calcium sulfate hemihydrate found in the original cement corresponded to 1.3% SO₄ content (compared to a total SO₄ analysis of 3.76% for the cement). This hemihydrate analysis was done several times on different days with the same result. No other form of calcium sulfate was detected either by x-ray diffraction or by DSC analysis. However, soluble anhydrite (γ-CaSO₄) may be present in an unknown amount; this phase contains only a trace of water and would escape detection by both DSC and x-ray diffraction, since its crystal structure is virtually identical to that of hemihydrate. Its quantitative assessment by x-ray diffraction in the presence of hemihydrate is extremely difficult and was not attempted. Additional sulfate may have
Fig. 6.1-7 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste LO
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)
been present in the clinker as alkali sulfate, alkali calcium sulfate, and in solid solution in some of the cement components.

Within the first 10 minutes it was found that the hemihydrate had completely disappeared. Gypsum had formed equivalent to 1.5% SO₄ content (as compared with the 1.3% SO₄ equivalent content of hemihydrate). The gypsum content was maintained at the 1.5% SO₄ level until about 4 hours and then it progressively decreased. Gypsum was not detected in the solid at 12 hours but it might have been completely gone at any time after the previous determination at 6 hours.

An initial formation of ettringite in the first 15 minutes was detected, amounting to around 0.5% SO₄. Then the ettringite content continued to increase rapidly to around 12 hours, and then more slowly to 24 hours.

The relationship of ettringite formation to the heat evolution curve (Fig. 6.1-3, mix LO) was not entirely clear. However, the onset of rapid ettringite formation at about 2 hours seems to coincide with the second peak of the heat evolution curve. This second major peak of hydration of the control mix LO had a small shoulder around 12 hours. Some researchers, such as Taylor [6], considered such a shoulder to be caused by the onset of secondary ettringite formation, rather than to conversion of ettringite to monosulfate. Since ettringite formation has been continuous and rapid since about 2 hours and the shoulder appears at 12 hours, the results rule out the former hypothesis in this case. The latter hypothesis is also obviously incorrect, since no monosulfate was detected.
Fig. 6.1-8 shows the same patterns extended to 14 days. The ettringite did not seem to increase during the longer term period and was constant at an equivalent $SO_4$ content of around 2.2%. No calcium aluminate monosulfate hydrate was found over the entire 14 days.

Table 6.1-2 illustrates the total balance of sulfate accounted for at each age. The initial hemihydrate content was determined by DSC using as a calibration mixtures of well crystallized hemihydrate with another cement having anhydrite. Any soluble anhydrite would not have been tallied. After hydration began, the sum of the $SO_4$ content in the solid phases accounted in the analysis (ettringite, gypsum, and hemihydrate) plus that in the solution phase increased from about 2.5% $SO_4$ to almost 3% $SO_4$ at about 5 hours. It then began to be progressively reduced, reaching about 2-1/4% at 1 day and then being maintained at about this level.

Some of the sulfate present is not accounted for due to the difficulty of quantitative analysis. Any alkali sulfate, alkali calcium sulfate, and soluble anhydrite present in the original cement are not accounted for in the calculation; thus the hemihydrate sulfate content of 1.38% at time zero obviously does not represent the total sulfate in the system. Alkali sulfates and alkali calcium sulfates dissolve very rapidly; thus the sulfate in the solution phase at early stages is mostly derived from these phases. It is also known that the sulfate ion is later incorporated to some extent by amorphous C-S-H gel as it develops. This is not easily quantified, and is believed to be responsible for the reduction of the sum of sulfate contents determined after the rapid cement hydration has begun.
Fig. 6.1-8 Content of sulfate-bearing phases in paste solids vs. time for extended periods up to 14 days for control paste LO
Table 6.1-2 Total balance of sulfate-bearing phase for mix LO*
(Percentages expressed in terms of equivalent SO₄ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Etrangite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.38</td>
<td>0.0</td>
<td>0.0</td>
<td>1.38</td>
<td>0.0</td>
<td>1.38</td>
</tr>
<tr>
<td>0.20</td>
<td>0.0</td>
<td>1.40</td>
<td>0.46</td>
<td>1.87</td>
<td>0.58</td>
<td>2.44</td>
</tr>
<tr>
<td>1.02</td>
<td>0.0</td>
<td>1.63</td>
<td>0.66</td>
<td>2.28</td>
<td>0.48</td>
<td>2.76</td>
</tr>
<tr>
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<td>0.74</td>
<td>2.43</td>
<td>0.47</td>
<td>2.90</td>
</tr>
<tr>
<td>4.52</td>
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<td>1.11</td>
<td>2.51</td>
<td>0.47</td>
<td>2.97</td>
</tr>
<tr>
<td>5.87</td>
<td>0.0</td>
<td>0.67</td>
<td>1.24</td>
<td>1.90</td>
<td>0.51</td>
<td>2.41</td>
</tr>
<tr>
<td>12.38</td>
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<td>0.0</td>
<td>1.79</td>
<td>1.79</td>
<td>0.49</td>
<td>2.28</td>
</tr>
<tr>
<td>24.26</td>
<td>0.0</td>
<td>0.0</td>
<td>2.21</td>
<td>2.21</td>
<td>0.04</td>
<td>2.26</td>
</tr>
<tr>
<td>(day)</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>2.90</td>
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<td>0.0</td>
<td>2.10</td>
<td>2.10</td>
<td>0.01</td>
<td>2.11</td>
</tr>
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<td>0.0</td>
<td>2.25</td>
<td>2.25</td>
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<td>2.25</td>
</tr>
<tr>
<td>14.02</td>
<td>0.0</td>
<td>0.0</td>
<td>2.29</td>
<td>2.29</td>
<td>0.01</td>
<td>2.31</td>
</tr>
</tbody>
</table>

* The total SO₄ content of the cement, separately determined, was 3.76% as SO₄.
With regard to the SO$_4^{2-}$ ion concentration in solution, this was found to be approximately constant at a plateau level (corresponding to about 0.5% SO$_4$) until 12 hours. The progressive drop of the sulfate ion from this plateau level occurred after the secondary gypsum was consumed totally. At the same time the hydroxide ion concentration started a corresponding increase to higher levels. The timing of this sudden drop of the sulfate concentration was not until much after the peak of heat evolution (7 hours), which implies that the phenomenon is not associated with hydration but is initiated by the depletion of solid gypsum. It is evident that additional crystalline ettringite is formed between 12 and 24 hours, even after the gypsum content has been exhausted (Fig. 6.1-7). The SO$_4^{2-}$ ion for this additional ettringite came from the existing stock of dissolved SO$_4^{2-}$ at 12 hours, as seen in Fig. 6.1-5.

6.1.3 Paste with Naphthalene Sulfonate Superplasticizer (LB): Solution and Solid Phase Analysis

6.1.3.1 Removal of Superplasticizer from Solution

Fig. 6.1-9 indicates the concentration of superplasticizer remaining in solution as a function of time up to one day, and the results of three replicate runs on three different days. About one quarter of the heavily dosed superplasticizer was removed from solution immediately; then the concentration was maintained at a constant level for about 6 hours. Most of the residual naphthalene sulfonate was then removed from solution between 6 and 14 hours, which corresponds to a major rise in the loss on ignition as
Fig. 6.1-9 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (LB) up to 1 day
indicated in Fig. 6.1-1, and to the major peak of the heat evolution curve in Fig. 6.1-3. The removal of the admixture from the liquid phase is attributed probably to either adsorption on or incorporation in the hydration products being produced. As illustrated in Fig. 6.1-10, only a low concentration of superplasticizer remained in solution by 1 day, and this low level persisted until 14 days.

6.1.3.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-11 shows the changes in inorganic ion concentrations until 24 hours for the mix LB. Again the results of three replicate runs on different days are shown.

The original mix water with the dissolved superplasticizer contains considerable concentrations of inorganic ions (shown as filled symbols in Fig. 6.1-11). The ion with the highest concentration was 120 meq/L of Na+. There was a concentration of 20 meq/L of Ca\(^{2+}\), about 5 meq/L of SO\(_4^{2-}\), and a very little K\(^+\) (2 meq/L). The OH\(^-\) ion is not found in measurable concentration. These ions are derived from the superplasticizer.

Paste solutions recovered at early ages with the admixture show a large difference in the Na\(^+\) ion concentration. This is seen to be maintained at about 150 meq/L with superplasticizer present, much higher than previously found for the mix LO without superplasticizer, which was only about 40 meq/L. The additional sodium is derived from the admixture, as will be discussed later.
Fig. 6.1-10 Concentration of residual superplasticizer in pore solution of LB pastes for extended periods up to 14 days.
Fig. 6.1-11 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (LB)
The K⁺ ion concentration followed approximately the same pattern for the present data as was previously seen without superplasticizer, both being close to 300 meq/L at first, and trending slightly upward. The Ca²⁺ ion concentrations showed were slightly higher than those previously found, but showed a similar decreasing trend with time.

There was a significant difference in the two patterns for the SO₄²⁻ ion. The SO₄²⁻ ion was released to an initially higher concentration with the superplasticizer present (270 meq/L compared with about 230 meq/L). Then it was gradually reduced to the plateau over the first 12 hours but its plateau concentration level was higher with the admixture. There was even a small increase in SO₄²⁻ concentration at around 14 hours before the expected decline. The residual concentration at 24 hours for the paste with admixture was significantly higher than that in the control paste.

The OH⁻ ion concentration pattern with time was similar for both the superplasticized and control pastes.

Fig. 6.1-12 shows the longer term pattern for the superplasticizer-bearing paste. All the concentrations for the ions remaining in solution were approximately stabilized by 3 days and the increases in alkali ions and OH⁻ ion concentrations thereafter were much slower. The K⁺ ion concentration level was about 50 meq/L higher for the control paste than for the superplasticized paste. For the Na⁺ ion, the plateau concentration level was about 120 meq/L higher with the naphthalene sulfonate than without. The OH⁻ ion concentrations leveled off by 3 days to about a 50 meq/L higher level with the superplasticizer. Both SO₄²⁻ and Ca²⁺ ions were negligible after 3 days.
Fig. 6.1-12 Concentration of inorganic ions in pore solutions of naphthalene sulfonate bearing pastes (LB) vs. time for extended periods up to 14 days.
Table 6.1-3 shows the sum of cations and anions for these pastes with superplasticizer. It is apparent that the balance previously found in the control pastes (Table 6.1-1) is not present here. Rather there were a large excess of cations present throughout the experiment, staying over 100 meq/L for the first 4 hours, and then dropping down progressively to around 20 meq/L at 24 hours. For pastes older sample than one day, only a small excess of cations was observed.

This lack of balance is apparently due to the residual concentration of the superplasticizer in the solution. While the separate inorganic ions have been accounted for, the negative $-\text{SO}_3^-$ (sulfonate) sites on the naphthalene sulfonate polymer chain remaining in solution have been neglected in the calculation. The naphthalene sulfonate superplasticizer B is a mostly sodium salt of what should be regarded as polymerized naphthalene sulfonic acid, i.e. a polymer bearing ionizable $-\text{SO}_3^-$Na$^+$ sites. This was confirmed by the previous analysis of the original mix water for the superplasticized paste. This Na$^+$ ion was released into the paste solution and was taken account into the sum of the cations, whereas the residual sulfonates associated with the dissolved polymer chains have not been considered yet. This "polymer anion" should be included to the charge balance.

Table 6.1-3 also shows the superplasticizer concentration in the solution phase. Assuming that all of the $-\text{SO}_3^-$ sites are fully neutralized by the cations determined, and that they are 100% ionized, the "polymer anion" concentration in the solution phase can be approximately equated to the excess cation concentration. If this is so, one should be able to estimate the charge "density" (meq/g) of the dissolved polymer.
Table 6.1-3 Experimental cation-anion balance in solutions for mix LB

<table>
<thead>
<tr>
<th>Age</th>
<th>Σ Cations</th>
<th>Σ Inorganic Anions</th>
<th>Difference</th>
<th>Polymer Conc.</th>
<th>Calculated Charge Density*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(meq/L)</td>
<td>(meq/L)</td>
<td>(meq/L)</td>
<td>(g/L)</td>
<td>(meq/g)</td>
</tr>
<tr>
<td>Run 1 (hr)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.00</td>
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<td>6.2</td>
<td>+ 113.7</td>
<td>31.5</td>
<td>3.61</td>
</tr>
<tr>
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<td>368.4</td>
<td>+ 112.0</td>
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<td>4.73</td>
</tr>
<tr>
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<td>376.9</td>
<td>+ 109.3</td>
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<td>4.51</td>
</tr>
<tr>
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<tr>
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<td>4.26</td>
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<tr>
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<td></td>
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<td></td>
<td></td>
</tr>
<tr>
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<td>3.0</td>
<td>6.77</td>
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<td>Run 2 (day)</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>+ 18.4</td>
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<td>(12.28)</td>
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<td>+ 10.8</td>
<td>1.4</td>
<td>(7.94)</td>
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<tr>
<td>14.00</td>
<td>533.7</td>
<td>529.2</td>
<td>+ 4.5</td>
<td>1.5</td>
<td>(3.11)</td>
</tr>
</tbody>
</table>

* of residual superplasticizers in solution.
by dividing the surplus cation concentration (meq/L) by the weight concentration of superplasticizer (g/L) at the same time. Such estimates are shown in the rightmost column of Table 6.1-3. These values are almost constant, at an average value of 4.8 meq/g over the first day.

Fig. 6.1-13 shows a combination plot of (a) remaining weight concentration of naphthalene sulfonate in the liquid phase vs. time and (b) the excess cation charge difference calculated vs. time. The left and right y-axis are excess cation concentration and superplasticizer weight concentration respectively. The two axes are aligned by the average charge density calculated for the "polymer anion" in solution over the first day, as 4.8 meq/g. The correlation of these two parameters is evidently high.

6.1.3.3 Solid Phase Analyses

Fig. 6.1-14 shows the data corresponding to Fig. 6.1-7 for the present superplasticized cement pastes. The results of two replicate runs and one partial run on different days are plotted.

The compounds detected were the same as for the control cement pastes. However the deviation of the data points in replicate runs seems to be larger, probably because the polymer adsorption affects the crystallization process and results in slightly different amounts of combined water of the hydration products.

In the presence of the superplasticizer, the rate of the conversion from hemihydrate to gypsum was slowed down. Hemihydrate was still observed in the 10 minute
Fig. 6.1-13 Association of superplasticizer concentration and apparent excess cation charges in liquid phase for mix LB
Fig. 6.1-14 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (LB) (Percentage of each solid phase re-expressed in terms of its SO₄ content.)
sample, but it was fully converted to gypsum by 1 hour. However, the actual amount of gypsum produced in this period was reduced with the superplasticizer. The amount of gypsum produced immediately after the mixing was not as high as in the control mix, being only around 0.8% (expressed in terms of the SO$_4$ content), while it was around 1.5% for paste without superplasticizer. It seems that the superplasticizer is absorbed by hemihydrate particles, as well as by the hydrating clinker phases and their products, and this may retard their dissolution and subsequent formation of gypsum.

The gypsum content gradually increased to a maximum of 1.5% SO$_4$ content at around 10 hours. Then it decreased gradually and reached zero sometime between 16 and 22 hours. This gypsum depletion preceded the start of the drop of the sulfate ion concentration in the solution phase, as was previously observed in the control case.

Ettringite was found in the 15 minute sample at about 0.5% as SO$_4$, and its concentration was constant for next 4 hours. This is different from the time pattern of ettringite production when no superplasticizer was present (Fig. 6.1-7). In that case there was a continuous increase in ettringite content and no plateau. At approximately 4 hours with the superplasticizer, the ettringite content started to increase, and it increased almost linearly and reached about 1.95% SO$_4$ content at one day.

Fig. 6.1-15 shows the same patterns for times extended to 14 days. The CaSO$_4$-bearing compound detected throughout this period continued to be entirely ettringite; no monosulfate was found. Though there was some variation, the trend was such that
Fig. 6.1-15 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for naphthalene sulfonate bearing pastes (LB)
the ettringite amount reached a maximum of about 2.6% \( \text{SO}_4 \) content at 3 days. It then appeared to decrease to about 2.1% \( \text{SO}_4 \) content and remained constant from 7 days onward.

Table 6.1-4 shows the balance of the sulfate phases for the superplasticized paste. The combined \( \text{SO}_4 \) contents determined in recognized phases are somewhat lower than the corresponding totals for the paste without admixture. Between 1 hours and 4 hours, the total sulfate accounted for averaged 1.9% \( \text{SO}_4 \) as compared to almost 3% previously (Table 6.1-2). A much smaller amount of secondary gypsum is the main reason for the smaller total value here. It is presumed that some of the calcium sulfate at this stage existed in an amorphous phase, perhaps associated with absorbed layers of the polymer. Subsequently, the total \( \text{SO}_4 \) increased to around 2.8% at 6 and 12 hours reflecting in part a significant increase in the gypsum content. At later ages the total then decreased, presumably reflecting incorporation of some \( \text{SO}_4 \) with the C-S-H hydration products.

6.1.4 Paste with Melamine Sulfonate Superplasticizer (LM): Solution and Solid Phase Analysis

6.1.4.1 Removal of Superplasticizer from Solution

Fig. 6.1-16 illustrates the concentration of the melamine sulfonate superplasticizer M remaining in solution as a function of time for 24 hours. The dosage of the superplasticizer M used here was 0.5%, leading to an initial concentration of about 10 g/L.
Table 6.1-4 Total balance of sulfate-bearing phase for mix LB

(Percentages expressed in terms of equivalent $\text{SO}_4$ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Ettringite (%)</th>
<th>$\Sigma$ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.38</td>
<td>0.0</td>
<td>0.0</td>
<td>1.38</td>
<td>0.01</td>
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<td>1.05</td>
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<td>0.51</td>
<td>1.33</td>
<td>0.58</td>
<td>1.91</td>
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<td>0.47</td>
<td>1.25</td>
<td>0.53</td>
<td>1.79</td>
</tr>
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<td>0.89</td>
<td>2.28</td>
<td>0.56</td>
<td>2.83</td>
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<tr>
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<td>0.0</td>
<td>1.18</td>
<td>1.01</td>
<td>2.20</td>
<td>0.58</td>
<td>2.78</td>
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<tr>
<td>24.38</td>
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<td>1.89</td>
<td>0.26</td>
<td>2.15</td>
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</tr>
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<td>2.64</td>
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<td>2.67</td>
</tr>
<tr>
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<td>2.18</td>
<td>0.01</td>
<td>2.19</td>
</tr>
<tr>
<td>14.02</td>
<td>0.0</td>
<td>0.0</td>
<td>2.25</td>
<td>2.25</td>
<td>0.01</td>
<td>2.27</td>
</tr>
</tbody>
</table>
Fig. 6.1-16 Concentration of residual superplasticizer in mix water and pore solution for melamine sulfonate bearing pastes (LM) up to 1 day
Due to this light dosage, the proportion of the admixture initially removed by the cement was higher than for the mix LB. However, the pattern of the absorption with time is the same as was found with naphthalene sulfonate: a sequence of immediate absorption, plateau, second-stage absorption, and retention of a residual low concentration were observed in the pattern. For pastes older than 1 day, the residual concentration of the superplasticizer was only about 0.4 g/L, as shown in Fig. 6.1-17.

6.1.4.2 Inorganic Ion Concentrations in the Paste Solution

Fig. 6.1-18 shows the time dependent concentration of the inorganic ions up to 1 day. The general pattern is similar to the control mix case shown in Fig. 6.1-5, presumably because the light dosage did not appreciably interfere with early cement hydration, or delay its heat evolution peak very much.

However, similar to the effect found for the naphthalene sulfonate superplasticizer in the LB series, it was found here that the initial concentration level of the Na⁺ ion was higher than without admixture, this time about 40 meq/L higher. This Na⁺ concentration remained almost constant for the first 24 hours. This lesser enhancement in Na⁺ concentration here as compared with LB pastes was proportional to the lesser dosage of the superplasticizer used.

It was found that the sulfate ion concentration here was a little higher at the plateau than was that for the control paste. The residual concentration of sulfate at 24 hours was also a little higher than that in the control case. The other inorganic ions,
Fig. 6.1-17 Concentration of residual superplasticizer in pore solution of LM pastes for extended periods up to 14 days
Fig. 6.1-18 Concentration of inorganic ions in mix water and pore solution vs. time in paste with melamine sulfonate superplasticizer (LM)
K\(^+\), Ca\(^{2+}\), and OH\(^-\), exhibited almost the same concentration-time patterns as those for the control mix without superplasticizer.

Fig. 6.1-19 shows the longer term pattern for the mix LM, for period up to 14 days. Differences from the control mix LO were shown, in that both Na\(^+\) and OH\(^-\) ion concentrations are about 50 meq/L higher than those in the control mix without superplasticizer. This implies that the additional sodium introduced by the superplasticizer was converted into NaOH in the pore solution and remained as such. In contrast, the K\(^+\) ion concentration was about the same as that for the paste without superplasticizer.

The same analysis of cation-anion-polymer balance was applied for the melamine sulfonate superplasticizer paste as previously applied for naphthalene sulfonate paste. Table 6.1-5 shows the same calculations as Table 6.1-1 for the mix LM. The trends of the residual excess cation and of the residual melamine sulfonate superplasticizer are similar for the first 24 hours of hydration, but there is much more scatter than was found previously for naphthalene sulfonate. The "charge density" calculated for the melamine sulfonate increased significantly over the first half day or so. However, subsequent calculations are essentially meaningless probably because of the low concentration of the residual melamine sulfonate.
Fig. 6.1-19 Concentration of inorganic ions in pore solutions of melamine sulfonate bearing pastes (LM) vs. time for extended periods up to 14 days.
Table 6.1-5 Experimental cation-anion balance in solutions for mix LM

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Σ Cations (meq/L)</th>
<th>Σ Inorganic Anions (meq/L)</th>
<th>Difference (meq/L)</th>
<th>Polymer Conc. (g/L)</th>
<th>Calculated Charge Density* (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
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<td>+28.1</td>
<td>10.0</td>
<td>2.81</td>
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<td>0.20</td>
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<td>297.5</td>
<td>+14.8</td>
<td>4.4</td>
<td>3.35</td>
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<td>3.99</td>
</tr>
<tr>
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<td>+14.1</td>
<td>2.6</td>
<td>5.48</td>
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</table>

<table>
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<tr>
<th>Age (day)</th>
<th>Σ Cations (meq/L)</th>
<th>Σ Inorganic Anions (meq/L)</th>
<th>Difference (meq/L)</th>
<th>Polymer Conc. (g/L)</th>
<th>Calculated Charge Density* (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.25</td>
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<td>494.3</td>
<td>-3.0</td>
<td>0.4</td>
<td>(-6.66)</td>
</tr>
<tr>
<td>7.03</td>
<td>502.1</td>
<td>503.2</td>
<td>-1.1</td>
<td>0.4</td>
<td>(-3.14)</td>
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<tr>
<td>13.16</td>
<td>544.1</td>
<td>523.7</td>
<td>20.4</td>
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<td>(55.19)</td>
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</tbody>
</table>

* of residual superplasticizers in solution.
6.1.4.3 Solid Phase Analyses

Fig. 6.1-20 shows the patterns of CaSO₄-bearing phase for the mix LM until one day. Even with this lighter dosage of melamine sulfonate superplasticizer, the initial dissolution of hemihydrate was slowed, and residual hemihydrate was detected even at 15 minutes. The production of gypsum was also slowed somewhat. However, similar to the control paste, the gypsum was gone sometime between 6 and 12 hours. The reduced superplasticizer dosage as compared to the mix LB obviously resulted in much less retardation; in consequence, the gypsum disappeared far more quickly than in the LB pastes. Again a decline of the sulfate ion concentration was initiated after the total consumption of gypsum phase, i.e. starting after 12 hours.

The content of ettringite was increasing non-linearly in this period. Its formation rate was slower than that for the control mix LO for the first 6 hours. Then the rate of formation of ettringite increased rapidly, resulting in almost the same content as that for the control mix between 6 and 12 hours, and an excess over the control case at 24 hours.

Fig. 6.1-21 shows the time patterns up to 14 days for sulfate-bearing solids. Ettringite was the only calcium sulfate solid detected after 1 day. The ettringite concentration appeared to be almost constant at around 2.7% SO₄ after 2 days. It was found that the shape of the peak of ettringite in DSC for this mix LM made it harder to differentiate ettringite from C-S-H gel than was the case with mix LB. Experimental errors in this determination will be discussed later.
Fig. 6.1-20 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for melamine sulfonate bearing pastes (LM).
(Percentage of each solid phase re-expressed in terms of its SO$_4$ content.)
Fig. 6.1-21 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for melamine sulfonate bearing pastes (LM)
Table 6.1-6 shows the balance of the detected sulfate phases for the mix LM. The total sulfate accounted for rose during the first 2 hours to about 2.7% as $SO_4^-$, and then fluctuated around this value. This total of detected $SO_4^-$-containing phases was rather high, especially in later ages, due to the high content of ettringite detected.

6.2 Discussion

6.2.1 Nature of Residual Naphthalene Sulfonate Remaining in Solution

As pointed out in Chapter 3 and Chapter 4, the molecular weight composition of the naphthalene sulfonate superplasticizer can be estimated by the difference in UV light absorbance at two characteristic wavelengths. The actual naphthalene sulfonate concentration was determined throughout this study by using the extinction coefficient at the longer characteristic wavelength around 290 nm, designated $\varepsilon_1$, because the absorbance at this wavelength is little affected by the degree of polymerization. The extinction coefficient at the shorter characteristic wavelength (218 nm), designated $\varepsilon_s$, alters with the composition of the monomer, and can also be estimated by the Beer-Lambert law,

$$
\varepsilon_s = \frac{A_s}{c \cdot l}
$$

where $A_s$ is the observed absorbance at the shorter wavelength, $c$ is the concentration of the naphthalene sulfonate estimated by the absorbance at the longer characteristic wavelength, and $l$ is the length of the light path. Here, the $\varepsilon_s$ can be obtained for the
Table 6.1-6 Total balance of sulfate-bearing phase for mix LM

(Percentages expressed in terms of equivalent SO₄ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Ettringite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.38</td>
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<td>0.0</td>
<td>1.38</td>
<td>0.01</td>
<td>1.39</td>
</tr>
<tr>
<td>0.23</td>
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<td>0.21</td>
<td>0.97</td>
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<tr>
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<td>1.97</td>
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<td>2.60</td>
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<td>2.81</td>
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<td>2.93</td>
</tr>
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<td>2.57</td>
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</table>
naphthalene sulfonate remaining in solution at any given time, and then the ratio of the \( e_s \) to \( e_t \) can be calculated. Fig. 6.2-1 illustrates this ratio \( e_s/e_t \) as a function of time for the mix LB.

Burk et al. [66] stated that the ratio of two extinction coefficients is linearly correlated to the percentage of monomer species in the naphthalene sulfonate superplasticizer. By using the equation of Burk et al., the data in Fig. 6.2-1 was also expressed in terms of the calculated percentage of monomer in the naphthalene sulfonate remaining in solution. The scale for this percentage is indicated on the right y-axis of the figure. The results indicated that the initial low percentage of monomer (about 12%) rose only a little after the first contact to around 19% at 12 hours. Then it jumped up to a much higher level of nearly 50% between 12 and 16 hours, and was constant after that.

The indication is that the large proportion of polymeric species initially present in the superplasticizer remained in the solution phase for several hours prior to set, and served to maintain the fluidity of the paste by its dispersing action. At the surge of the hydration around 12 hours, the polymeric species were preferentially adsorbed onto the newly formed hydration products, mostly C-S-H gel, whereas monomer was not absorbed and stayed in the liquid phase.

At later ages, the ratio \( e_s/e_t \) was found to be high, that is, the proportion of monomer in the solution phase was very high. Furthermore, low molecular weight polymeric species such as dimer, trimer, etc., which may compose about the same weight
Fig. 6.2-1 Extinction coefficient ratio ($\varepsilon_n/\varepsilon_1$) and estimated corresponding percentage of monomers in residual naphthalene sulfonate found in paste solutions vs. time for LB pastes.
fraction as monomer in the original superplasticizer, are also not taken up by the solid phases according to Burk et al. [66]. Assuming that 50% of monomer plus about the same portion of dimer plus trimer are left in the solution phases older than one day, it appears that virtually no higher polymeric species exist in the older samples.

An attempt to convert the "polymer anion" concentration of naphthalene sulfonate to the equivalent inorganic anion at each age was shown at Table 6.1-3. It is noticed that the calculated charge density at time zero, i.e., that in the initial mixing water, is only about 3.6 meq/g. This is lower than the corresponding calculation for the early paste solutions, which seems to be fairly constant at approximately 4.7. The charge density measurement reflects the estimated number of sulfonate groups present per gram of polymer. This may vary considerably with chain length, and is only an average characteristic.

The apparent charge density became high irregular for the naphthalene sulfonate remaining in solution in paste samples older than 1 day. This is probably because the denominator of the calculation, the naphthalene sulfonate concentration, becomes so low that experimental error becomes unacceptably high. A direct measurement for dissolved sulfonate groups would obviously be a more appropriate alternative.

For the paste LM, a correlation between the polymer concentration and the excess positive charge were observed, but it was not as consistent, as seen by the variation in the apparent charge density of the melamine sulfonate in solution.
6.2.2 Effects of Superplasticizers on Inorganic Ion Concentrations in Solution

Significant effects of the superplasticizer were found for the early concentrations of SO$_4^{2-}$ ions, OH$^-$ ions, and Na$^+$ ions.

The increased level of SO$_4^{2-}$ concentration maintained for a while in the pore solution with both superplasticizers as compared to the control paste may have some significance in terms of early reaction. The increased SO$_4^{2-}$ level with superplasticizer can be attributed to smaller amounts of both gypsum first and then of ettringite formed in the dormant period, presumably due to absorption of the polymeric species on these crystals as they grow. This is clearly a transient effect; after a few days gypsum has been fully depleted and the sulfate concentration of superplasticizer-bearing and superplasticizer-free pastes are identically negligible.

It is confirmed from the analysis of pore solution after one day that the OH$^-$ ion concentrations were higher in the pore solutions containing superplasticizers than in the pore solution without admixture. The actual OH$^-$ ion concentration determined at 14 days were 460 meq/L without admixture, 520 meq/L with the naphthalene sulfonate, and the same 520 meq/L with the melamine sulfonate. This enhancement in alkalinity obviously due to the extra Na$^+$ ion derived from the superplasticizers. As was shown previously in Fig. 6.1-11, the concentrations of inorganic ions present in the original mix water for the superplasticized paste LB are 120 meq/L of Na$^+$, 20 meq/L of Ca$^{2+}$, 5 meq/L of SO$_4^{2-}$, and a trace amount of K$^+$. This extra Na$^+$ is brought into solution with the superplasticizer as the main cation, balancing the nega-
atively charged sulfonate group of the superplasticizer. As hydration proceeds, the polymer anions are absorbed to the solid phases, but the corresponding Na⁺ ions remain in solution. A corresponding amount of OH⁻ ion is dissociated by hydrolysis action to neutralize the positive Na⁺ ion charge. Presumably the same mechanism occurs in the melamine sulfonate pastes. When considering the use of alkali-bearing superplasticizer, higher pore solution alkalinity is thus to be expected. This may increase the susceptibility of the concrete to alkali-aggregate reaction.

6.2.3 Solid Phases

In all three cases, the commencement of the progressive decline of the sulfate ion concentration occurred independently to the general hydration process, but always followed the exhaustion of the secondary gypsum. This confirms the findings by Diamond [77] that this decay is triggered by approaching exhaustion of the residual gypsum. Retardation by superplasticizer absorption on the cement naturally postpones this condition.

The ettringite content in the two superplasticized pastes were smaller than that of the control paste up to 12 hours. As mentioned previously, it is considered that the superplasticizer interferes somewhat with the growth of the ettringite crystals that have incorporated some of the superplasticizer.

For all three pastes of cement L, the amount of ettringite leveled off after 3 days. This level of the ettringite concentration in mature pastes for mix LB was approxi-
mately 2.1% $SO_4$ equivalent, almost equal to the ettringite content of the corresponding control pastes. Thus the effect of the naphthalene sulfonate superplasticizer on the longer term ettringite content appears to be insignificant. For the paste LM, the long-term ettringite content (after 1 day) was 2.7% $SO_4$ equivalent, even higher than that for the control paste.

One of the most unexpected findings was that calcium aluminate monosulfate hydrate was not detected in any of the solid phases from mix L, even up to 14 days. The absence of monosulfate was confirmed both by checking the x-ray diffraction peak at d-spacing of 9.0 Å, and by DSC analysis as follows.

To begin with, monosulfate was synthesized by following the method described by Suzuki et al. [78]. In that method, previously synthesized ettringite is boiled for 4 hours in the form of a dilute suspension of water:solids ratio 200. Though it was found that the product contained a little ettringite impurity, the DSC curve generated for specimens in the special DSC environment described earlier in this study, showed endothermic peaks at 82°, 145°, and 220°C which correspond to the dehydration peaks of monosulfate at 120°, 180°, and 290°C according to Suzuki et al. The complete absence of monosulfate in all of these pastes was indicated by the fact that no endothermic peak was detected in the temperature range between 200°C and 300°C from any of the solid samples.

The normal partial conversion from ettringite to monosulfate at ages later than 1 day in cement pastes has been observed previously by many workers, for example by
Seligman et al. [79]. However, it was not observed here, even after the sulfate ion concentration in the pore solution had dropped to virtually zero later than 3 days. Some slight decreases in the ettringite contents were observed particularly in some superplasticized pastes, but those were not considered significant. Rather, the ettringite contents were nearly constant after 3 days for all three pastes of cement L.

This stability of ettringite appears to be attributable to the compositional characteristics of cement L. The cement L has only 5.38% of $\text{Al}_2\text{O}_3$ and 3.03% of $\text{SO}_3$ in the mill analysis; the proportion of $\text{SO}_3$ to $\text{Al}_2\text{O}_3$ is 0.56 by weight. This number suggests that the sulfate content compared to the aluminate content, is relatively high. This may promote the stability of the ettringite.

As is mentioned in the section 4.4.2, there is a complication in the quantitative determination of the ettringite in one day old and older samples for the cement L. As the paste hydrates, the overall DSC pattern shows a broad endothermic depression due to dehydration of C-S-H gel, so that the differentiation of ettringite from C-S-H gel becomes subject to some experimental uncertainty.

The basic rules for the differentiation were stated previously. However, the gradient of the DSC curve does not change abruptly in these older pastes. Thus the determinations of the starting point and end point become less distinctive than that for the younger pastes. Of the three pastes of cement L, the paste with melamine sulfonate exhibited the least sharp peak for ettringite, which was reflected in the larger variations of calculated ettringite contents for mix LM. Fig. 6.2-2 shows transition of the
Fig. 6.2-2 DSC curves of the paste LM samples at 1 day to 14 days
DSC curves of older samples for the mix LM. For practical purpose with the ambiguous later specimens, a representative value was obtained by selecting the peak area of ettringite so chosen that the separation line drawn approximately in the middle of the maximum and the minimum cases shown in Fig. 6.2-2. The percentage difference between these extreme cases for samples older than one day averaged 2.7% for mix LO, 4.0% for mix LB, and 7.8% for mix LM.

6.3 Findings

The findings resulting from the experimental work carried out with cement L are as follows.

1. Both naphthalene sulfonate and melamine sulfonate had a retarding effect on the hydration of cement L. The effect was observed in calorimetry, in loss on ignition, in time of setting, in mini-slump, in the solution phase chemistry, and in the solid phase compound formation.

2. A method of incorporating organic ions into the charge balance calculation between positive and negative species in solution was developed and applied to both naphthalene sulfonate and melamine sulfonate bearing pastes. The apparent "charge density" of the naphthalene sulfonate polymer remaining in the paste solutions was fairly consistently estimated; that of the melamine sulfonate polymer was more variable.

3. The proportion of monomeric naphthalene sulfonate superplasticizer remaining in
paste solution was estimated by analyzing two characteristic peaks in UV absorption spectrum as a function of time. It was confirmed that the polymeric species in the superplasticizer were mostly adsorbed by the period of second hydration peak.

4. The sulfate ion concentration in paste solution at its "plateau" level (before the sudden drop) was higher in the presence of superplasticizers. This was a transient effect, attributed to retardation.

5. Significant increases were found in the Na⁺ ion concentrations of pore solution with superplasticizers. These increases were due to Na⁺ ions initially neutralizing sulfonate groups on the polymer.

6. It was found that the OH⁻ ion concentrations increased at later ages for pore solutions with superplasticizers to balance the excess Na⁺ ions derived from the polymers.

7. It was found that the initial form of calcium sulfate in cement L was entirely hemihydrate. This was converted to gypsum almost immediately after the first contact with water. Gypsum stayed in the paste for about half a day. After that only detectable CaSO₄-bearing compound was the ettringite. This conversion pattern was basically the same for this cement system with or without superplasticizers.

8. It was found useful to express the total of the solid CaSO₄ phases detected and the sulfate ions in solution in terms of sulfate content, as a function of time. The total sulfate quantified in this method was less than the total cement sulfate analysis because alkali or other clinker borne sulfates were not accounted for in the early
stages, and sulfate incorporated in C-S-H gel was not accounted for in the late stages. Nevertheless, changes in the total CaSO₄ phase detected were of interest in following the progress of the reactions.

9. The progressive decay of the sulfate concentration in solution from the “plateau level” in the liquid phase was preceded by the complete depletion of solid gypsum. This was common with or without the admixture.

10. No calcium aluminate monosulfate hydrate was detected in any of the cement L paste samples up to 14 days of age, even though the sulfate concentration in the pore solution was virtually zero after one day.

11. Ettringite determination by DSC analysis in the more mature samples was subject to a complication because of increasing amounts of C-S-H gel. This difficulty was enhanced in the system with superplasticizers and resulted in experimental errors, since the characteristic dehydration peak of ettringite lost its sharpness.
In this chapter, results are reported for studies similar to those previously described for cement L, but here carried out on another ASTM Type I cement, cement S. Cement S is a somewhat higher alkali cement than the previously studied cement L (0.85% Na₂O equivalent as compared to 0.56% Na₂O equivalent), and has a high content of MgO. The calcium sulfate here is in the form of a mixture of gypsum and hemihydrate.

The mixes described here include the control mix SO without admixture; mix SB, with 1.55% naphthalene sulfoate superplasticizer B; and mix SM, with 1.55% melamine sulfoate superplasticizer M. Thus the dosages of melamine sulfoate and naphthalene sulfoate superplasticizers used here are on an equal weight basis, permitting direct comparison of their effects.
7.1 Results

7.1.1 Effects of Superplasticizers on Hydration

Fig. 7.1-1 shows the loss on ignition data vs. time until 24 hours for the pastes SO, SB, and SM, and Fig. 7.1-2 shows the same data of these pastes for times extended to 14 days. All data have been corrected for the ignition loss of the superplasticizer present in the solids. Fig. 7.1-3 shows the results of conduction calorimetry analysis for these three pastes over the first two days. Comparing the calorimetry curve for the admixture-free mix SO and the corresponding previous control mix LO, cement S is confirmed as being slower in hydration than cement L.

The loss of ignition curves for the first day for the two admixture-bearing pastes were similar to each other. The 24-hour data (Fig. 7.1-1) indicated a severe retardation of hydration for both admixture-bearing pastes compared to the control mix SO; between 6 and 24 hours the non-evaporable water contents for both mixes SB and SM were only about one third of that for mix SO.

The retardation effect (reduced non-evaporable water) by the superplasticizer persisted indefinitely (i.e. at least for 14 days) with the naphthalene sulfonate superplasticizer; but with melamine sulfonate superplasticizer it started to diminish after a few days. The loss on ignition value approached that of the control paste at 14 days. Thus the hydration process and resultant products at longer ages appear to be differently affected by the two different superplasticizers.
Fig. 7.1-1 Loss on ignition as a function of time up to 1 day for pastes of cement L without superplasticizer (SO), with 1.55% naphthalene sulfonate (SB), and with 1.55% melamine sulfonate (SM).
Fig. 7.1-2 Loss on ignition of pastes for periods extended to 14 days
Fig. 7.1-3 Conduction calorimetric curves showing heat evolution vs. time for mixes SO, SB, and SM
From the conduction calorimetry data, the times to peak maximum of the second hydration peak were 7 hours, 21.5 hours, and 22 hours for mixes SO, SB, and SM respectively. Thus both superplasticizers severely retarded hydration; of the two, the melamine sulfonate seems to have slightly less retardation effect.

Fig. 7.1-4 exhibits the mini-slump spread area values as functions of time for these mixes. The pastes with both superplasticizers were entirely fluidized (spread area 1200%), and segregation of the solids and extensive bleeding persisted almost up to set. The kind of segregation observed with the superplasticized pastes was not at all observed for the control pastes. The spread area percentage for the control paste started off only at 450% and steadily diminished with time.

Initial set occurred at 7 hours for the control paste, 19 hours for mix SB, and 20 hours for mix SM. Thus very prolonged delays of the initial set time were produced by both superplasticizers at this very high dosage level.

7.1.2 Control Paste without Superplasticizer (SO): Solution and Solid Phase Analysis

7.1.2.1 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-5 shows the concentrations of inorganic ions as functions of time over the first day. The data points between 14 and 22 hours were obtained from a separate run. The inorganic ion concentrations of the pore solution of this cement were generally lower than those for cement L during this 24-hour period.
Fig. 7.1-4 Area of spread in mini-slump test vs. time for mixes SO, SB, and SM
Fig. 7.1-5 Concentration of inorganic ions in mix water and pore solution vs. time in control paste (SO)
The concentrations of the alkali ions, Na\(^+\) and K\(^+\), were initially at 30 meq/L and 150 meq/L respectively. The Na\(^+\) concentration increased gradually over the first day of hydration. That for K\(^+\) was almost constant for 20 hours or so, then increased somewhat. The concentration of the Ca\(^2+\) ion was initially at 30 meq/L. It decreased progressively until 8 hours but then it underwent a peculiar jump to a maximum of 50 meq/L before again progressively reducing toward zero.

For the anions, the SO\(_4^{2-}\) ion concentration was initially at 120 meq/L. It gradually decreased to a plateau level at around 100 meq/L; subsequently it slightly increased. The maximum concentration was observed at 12 hours. Then the concentration progressively decreased to a residual concentration at 24 hours of around 50 meq/L. The OH\(^-\) ion concentration was reasonably stable at 130 meq/L between 1 and 8 hours. Subsequently it first decreased a little then progressively increased, mirroring (in reverse) the sulfate ion concentration changes.

Fig. 7.1-6 provides ion concentration data for this control paste to 14 days. The concentrations of the alkali ions and the OH\(^-\) ion rapidly increased between 1 day and 3 days, and continued to increase until 14 days, to a degree greater than the increments of the corresponding ions observed for cement L. At 14 days, the OH\(^-\) ion concentration was around 500 meq/L; for cement L, it was 470 meq/L. The Ca\(^2+\) and SO\(_4^{2-}\) ions were absent from the pore solution in pastes older than 3 days.

Table 7.1-1 shows the sum of the cation concentrations and the sum of the anion concentrations and its balance for the control paste SO. Until the age of 8 hours, 10 to
Fig. 7.1-6 Concentration of inorganic ions in pore solution vs. time for extended periods up to 14 days in control paste (SO)
Table 7.1-1 Experimental cation-anion balance in solution for mix SO

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>( \Sigma ) Cations (meq/L)</th>
<th>( \Sigma ) Anions (meq/L)</th>
<th>Difference (meq/L)</th>
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</table>
30 meq/L excess of anions are observed; this excess is larger than the numbers observed for the control paste of cement L. The anion-cation balances are more nearly equal for the rest of the hydration period.

7.1.2.2 Solid Phase Analyses

Fig. 7.1-7 presents the results of analyses of CaSO₄-bearing compounds in the solid phase for the control pastes SO₄ as functions of time for the first 24 hours. The initial form of CaSO₄ in the cement S was a mixture of hemihydrate and gypsum. Those two hydrated forms of CaSO₄ and ettringite were quantified by the DSC analysis. Again, the quantities of the CaSO₄-bearing compounds are expressed in terms of equivalent % SO₄ of the compound analyzed, based on the ignited weight of the pastes.

The initial SO₄ content in cement S was 1.5% SO₄ as hemihydrate and 0.8% SO₄ as gypsum. The rate of dissolution of hemihydrate and conversion to gypsum was quick, and no hemihydrate was detected in even the first hydrated cement paste sample. The observed gypsum content at 10 minutes was 1.8% SO₄ equivalent; this reflects the sum of residual original gypsum plus secondary gypsum produced immediately from the hemihydrate. The gypsum content remained at around this level until about 4 hours. It was then gradually consumed, diminishing to zero by 16 hours.

The observed ettringite content rose immediately to 0.8% SO₄ equivalent at 10 minutes. Then the ettringite formed increased progressively to about 1.7% SO₄
Fig. 7.1-7 Content of sulfate-bearing phases in paste solids vs. time up to 1 day for control paste SO
(Percentage of each solid phase re-expressed in terms of its SO\(_4\) content.)
equivalent at 24 hours.

This time-dependent pattern of the solid phases for cement S reflects a milder sulfate response than with the cement L. Both gypsum consumption and ettringite formation were not so abrupt.

Fig. 7.1-8 show the same patterns extended to 14 days. No calcium monosulfaloaluminate hydrate was detected by DSC during this period, and the ettringite content seems to be approximately constant. The actual DSC curves for specimens at 1 day and older are shown in Fig. 7.1-9.

The characteristic dehydration peak of ettringite was less sharp for the control paste SO than for the corresponding control paste LO. The ettringite peaks exhibited here are in the broad range between 40° and 110°C. Again the exact boundaries of the peaks are difficult to document with certainty. The two extensions of the baseline shown in the figure as bounding the area of dehydration peak represent the approximate minimum and maximum possibilities in each case. A representative value was selected in the middle of those, as explained in the previous chapter. The possible variation in ettringite content between the extremes was about 10%.

Table 7.1-2 shows the observed balance of sulfate-bearing forms in this paste as a function of time. The total sulfate content of cement S according to the mill analysis is equivalent to 3.36% as SO₄. In the cement itself, the sum of the sulfates accounted for by these analytical methods was only 2.2%; obviously some of the sulfate, such as alkali or alkali calcium sulfate or any soluble anhydrite present were not included in
Fig. 7.1-8 Content of sulfate-bearing phases in paste solids vs. time for extended periods up to 14 days for control paste SO.
Fig. 7.1-9 DSC curves of the control paste samples at 1 day to 14 days
Table 7.1-2 Total balance of sulfate-bearing phase for mix SO

(Percentages expressed in terms of equivalent SO$_4^-$ content)

<table>
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<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Ettringite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
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<td>0.00</td>
<td>1.81</td>
<td>1.81</td>
<td>0.12</td>
<td>1.93</td>
</tr>
</tbody>
</table>

* The total SO$_4^-$ content of the cement by the mill analyses was 3.36% as SO$_4^-$.
the analysis. After the hydration started, the sum of the analyzed sulfates (including the \( \text{SO}_4^{2-} \) ion in solution) increased to about 2.7% between 0.2 and 4 hours, and then it decreased to about 2%. After one day, the data showed some scatter. The progressive reduction with time in this parameter was attributed to incorporation of sulfate in increasing amounts in the C-S-H gel as it developed over time.

The \( \text{SO}_4^{2-} \) ion concentration in the paste solution reached a maximum and then decreased when the solid gypsum was almost exhausted around 12 to 14 hours. It is thus again confirmed that the solid gypsum controls the sulfate ion in the early pore solution.

7.1.3 Paste with Naphthalene Sulfonate Superplasticizer B (SB): Solution and Solid Phase Analysis

7.1.3.1 Removal of Superplasticizer from Solution

Fig. 7.1-10 indicates the concentration of naphthalene sulfonate superplasticizer B remaining in solution as a function of time until 24 hours, and the same plot is extended to 14 days in Fig. 7.1-11. The amount of the superplasticizer removed from solution immediately by the cement was approximately one half of the initial concentration. This is larger than the amount of naphthalene sulfonate initially removed by cement L.
Fig. 7.1-10 Concentration of residual superplasticizer in mix water and pore solution for naphthalene sulfonate bearing pastes (SB) up to 1 day.
Fig. 7.1-11 Concentration of residual superplasticizer in pore solution of SB pastes for extended periods up to 14 days.
The superplasticizer concentration in solution decreased slowly for a time up to 12 hours, and more drastically between 12 and 24 hours, to a residual concentration of about 3 meq/L. This low residual concentration did not change thereafter.

7.1.3.2 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-12 shows the changes in inorganic ion concentrations up to 24 hours for the mix SB. Reflecting the slow hydration of this cement and the severe retardation effect of the admixture, the inorganic ions concentrations changed only slightly over the first day of hydration.

The Na\(^+\) ion concentration was initially 120 meq/L. It increased quickly to 150 meq/L and maintained this approximate level for 24 hours. The corresponding level for the SO paste was only 120 meq/L. The K\(^+\) ion concentration here stayed at around 140 meq/L, slightly lower than the control case. The concentration level of the Ca\(^{2+}\) ion increased during the first few hours to 70 meq/L. The concentration-time pattern for Ca\(^{2+}\) here is much different from that of the control SO paste, and the level was generally higher; it stayed up at 40 meq/L even at 24 hours.

With respect to anions, much of the sulfate was immediately dissolved, and SO\(_4^{2-}\) reached a concentration of 170 meq/L at 10 minutes, much higher than the control samples. It decreased to 120 meq/L over the next 4 hours, and then increased again. Its concentration was always higher than the control paste during this period. Even at 24 hours, it was still as high as 150 meq/L.
Fig. 7.1-12 Concentration of inorganic ions in mix water and pore solution vs. time in paste with naphthalene sulfonate superplasticizer (SB)
The OH⁻ ion concentration increased gradually in the first 4 hours, and then stabilized at about 150 meq/L until 24 hours. Unlike the control case, no progressive increase in concentration was observed in this period.

Fig. 7.1-13 shows the same concentration patterns until 14 days. The Ca²⁺ and SO₄²⁻ concentrations had dropped to almost zero by 4 days. Again the alkali ions and the OH⁻ ion increased markedly between 1 day and 4 days, and only slightly thereafter. During the period from 4 to 14 days, the K⁺ concentration was about 40 meq/L lower and the Na⁺ concentration was higher by about 120 meq/L, than those of the control mix. The OH ion concentration was higher by 50 meq/L than the control mix at 14 days. These longer-term elevations of sodium ion concentration and corresponding OH⁻ ion concentration as a result of the addition of the naphthalene sulfonate, were seen to be similar to those produced with cement L.

Table 7.1-3 shows that the sum of inorganic cations and anions and their balance along with analyses on the residual polymer concentrations. The charge density for the naphthalene sulfonate polymer still in solution was calculated in the same way as was previously done for cement L.

In general, the results seemed similar to those for the mix LB, and the same analytical procedure on the polymer anions seemed to be applicable. The excess of cations balancing the residual polymer anions was seen at each age. The excess of cations was obviously very highly correlated with the residual polymer content for the first 12 hours, as indicated by the virtual constancy of the calculated charge density
Fig. 7.1-13 Concentration of inorganic ions in pore solutions of naphthalene sulfonate bearing pastes (SB) vs. time for extended periods up to 14 days.
Table 7.1-3: Experimental cation-anion balance in solution for mix SB

<table>
<thead>
<tr>
<th>Age  (hr)</th>
<th>Σ Cations (meq/L)</th>
<th>Σ Inorganic Anions (meq/L)</th>
<th>Difference (meq/L)</th>
<th>Polymer Conc. (g/L)</th>
<th>Calculated Charge Density* (meq/g)</th>
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<th>Σ Inorganic Anions (meq/L)</th>
<th>Difference (meq/L)</th>
<th>Polymer Conc. (g/L)</th>
<th>Calculated Charge Density* (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.95</td>
<td>494.2</td>
<td>481.9</td>
<td>+12.3</td>
<td>0.6</td>
<td>(21.85)</td>
</tr>
<tr>
<td>7.10</td>
<td>533.3</td>
<td>525.4</td>
<td>+7.9</td>
<td>0.7</td>
<td>(11.86)</td>
</tr>
<tr>
<td>14.00</td>
<td>566.5</td>
<td>546.5</td>
<td>+20.0</td>
<td>1.0</td>
<td>(19.10)</td>
</tr>
</tbody>
</table>

* of residual superplasticizers in solution.
offered as the ratio of these two parameters. However for 24 hours and later, the calculated charge density became large and inconsistent, due to the very small residual concentrations of the polymer at long ages.

As discussed in section 6.2.1, the calculated charge density at time zero, i.e. in the mix water before cement has been added, was 4 meq/g, lower than those in the paste liquids between the start of hydration and 12 hours. These are reasonably constant at about 5.30 meq/g. Thus from the observation in both mixes LB and SB, the naphthalene sulfonate polymers in the mix water, and that fraction of them that remains unadsorbed in the paste solutions in the early hours have different values of charge density.

7.1.3.3 Solid Phase Analyses

Fig. 7.1-14 shows the results of the CaSO\(_4\)-bearing phases determined for paste SB (with 1.55% naphthalene sulfonate superplasticizer) for the first day of hydration.

The heavy dosage of the superplasticizer B again resulted in severe retardation, as had been seen previously for mix LB. In the present results, the gypsum content for the first few hours was more constant, and the ettringite production rate was slowed down compared to the control mix data previously shown in Fig. 7.1-7. Here the content of the gypsum was almost constant for the first 6 hours at 0.9% SO\(_4\) equivalent, a lower level than the control case. It then decreased, and reached zero probably a little earlier than the 24 hours shown in the plot (no data being taken between 12 and 24.
Fig. 7.1-14 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for naphthalene sulfonate bearing pastes (SB).
(Percentage of each solid phase re-expressed in terms of its SO4 content.)
hours). At 24 hours, the sulfate ion concentration in the pore solution was still in the period of the "plateau" level before the sudden drop.

The ettringite content here was also almost constant for the first 12 hours at a comparatively low value of 0.9% $\text{SO}_4$ equivalent; however, it had increased to well over 2% $\text{SO}_4$ by 24 hours.

Fig. 7.1-15 shows the same patterns as Fig. 7.1-14 in the longer term until 14 days. The results of two replicate runs on different days are plotted. One of the points (at 4 days) in the first run was low, and is assumed to have been a deviant point and is not shown.

Again no calcium aluminate monosulfate hydrate was detected throughout the period of study. However, the ettringite content determination for this mix SB samples was subject to a different kind of complication. As is seen for example in Fig. 7.1-16, at one day the dehydration peak in the DSC curve has a complicated geometry at the higher temperature side. Three different inflection points are observed, two of which are points at which the derivative changes from higher to lower values, and an intermediate one at which the derivative changes from lower to higher values. The latter is not reasonable as a possible baseline-defining point. However, if the lower temperature higher to lower derivative inflection point were used as a baseline-defining point, the area included within the ettringite peak would be obviously too small. Thus the highest temperature inflection point was used as a baseline-defining point, as shown in the figure. This phenomenon was not observed for the paste LB.
Fig. 7.1-15 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for naphthalene sulfonate bearing pastes (SB)
Fig. 7.1-16 DSC curves of the paste SB samples at 1 day to 14 days
This phenomenon is believed to represent a shift in the dehydration process, i.e. a shoulder caused by the incorporation of the superplasticizer on or within AFt compounds. There was no sulfate-bearing compound other than ettringite detected in XRD, and the low hump indicative of C₄AH₁₃ was the same in intensity as seen previously in the control paste. Judging from the height of the XRD peak for ettringite, the amount of ettringite present at each age appeared to be in the same order as for the mix LB. From these indications, it appears that the proper end point of the ettringite dehydration peak was the one selected as indicated in Fig. 7.1-16.

The trend of ettringite content observed for samples older than one day seemed to indicate that ettringite was constant at about 2.2% SO₄ equivalent.

A shoulder similar to the shoulder on the DSC peak for ettringite was also observed on the corresponding DSC peak for gypsum in these naphthalene sulfonate-treated pastes. This shoulder may reflect the absorption of naphthalene sulfonate polymer on the surfaces of the gypsum crystals. Fig. 7.1-17 shows this effect.

Table 7.1-4 shows the balance in terms of sulfate for the mix SB. The total sulfate for the superplasticized paste was quite constant at a little over 2% SO₄ equivalent consistently over the 14 day period. The general level was lower than that for the control mix. As was reasoned similarly in the corresponding mix with cement L, with superplasticizer present, much of the sulfate appears to be present in phases not accounted for in the calculation.
Fig. 7.1-17 DSC curves of the paste SB samples at 4 hour to 12 hours
Table 7.1-4 Total balance of sulfate-bearing phase for mix SB
(Percentages expressed in terms of equivalent SO₄ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Ettringite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>1.52</td>
<td>0.77</td>
<td>0.00</td>
<td>2.29</td>
<td>0.01</td>
<td>2.30</td>
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<tr>
<td>0.30</td>
<td>0.00</td>
<td>1.09</td>
<td>0.89</td>
<td>1.97</td>
<td>0.42</td>
<td>2.39</td>
</tr>
<tr>
<td>1.00</td>
<td>0.00</td>
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<td>0.83</td>
<td>1.65</td>
<td>0.36</td>
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</tr>
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<td>0.90</td>
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<td>1.81</td>
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<td>2.12</td>
</tr>
<tr>
<td>11.50</td>
<td>0.00</td>
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<td>1.65</td>
<td>0.33</td>
<td>1.98</td>
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<td>24.02</td>
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<td>2.11</td>
<td>2.11</td>
<td>0.40</td>
<td>2.51</td>
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<tr>
<td>3.99</td>
<td>0.00</td>
<td>0.00</td>
<td>2.31</td>
<td>2.31</td>
<td>0.01</td>
<td>2.32</td>
</tr>
<tr>
<td>7.14</td>
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<td>2.21</td>
<td>2.21</td>
<td>0.01</td>
<td>2.22</td>
</tr>
<tr>
<td>14.02</td>
<td>0.00</td>
<td>0.00</td>
<td>2.17</td>
<td>2.17</td>
<td>0.02</td>
<td>2.19</td>
</tr>
</tbody>
</table>
7.1.4 Paste with Melamine Sulfonate Superplasticizer M (SM): Solution and Solid Phase Analysis

7.1.4.1 Removal of Superplasticizer from Solution

Fig. 7.1-18 illustrates the concentration of the melamine sulfonate superplasticizer M remaining in solution as a function of time until 24 hours in paste of cement S treated with 1.55% by weight of melamine sulfonate superplasticizer. The initial dosage here is the same 1.55% as for the naphthalene sulfonate admixtures in the pastes SB, so that the results are directly comparable. The absorption pattern was quite similar to that for the mix SB (shown by a dotted line in the same figure), except that the transient concentration of melamine sulfonate was about 3g/L lower than that of naphthalene sulfonate between 1 and 12 hours. After one day, the pattern was identical to the mix SB as only a trace amount remained in solution, as seen in Fig. 7.1-19.

7.1.4.2 Inorganic Ion Concentrations in the Solution Phase

Fig. 7.1-20 shows concentrations of inorganic ions found for the mix SM. The patterns for the first 24 hours look very similar to those for the corresponding naphthalene sulfonate-bearing paste SB, shown in Fig. 7.1-12.

Here again the Na⁺ ion and the K⁺ ion concentrations were stabilized in the 160-170 meq/L range (Na⁺) and at 150 meq/L (K⁺), both levels are almost equal to those for the paste SB. Here the Ca²⁺ jumped to 100 meq/L at the first measurement,
Fig. 7.1-18 Concentration of residual superplasticizer in mix water and pore solution for melamine sulfonate bearing pastes (SM) up to 1 day
Fig. 7.1-19 Concentration of residual superplasticizer in pore solution of SM pastes for extended periods up to 14 days
Fig. 7.1-20 Concentration of inorganic ions in mix water and pore solution vs. time in paste with melamine sulfonate superplasticizer (SM)
but then it went back to a constant level at around 50 meq/L and decreased to 30 meq/L between 12 and 24 hours, also considerably higher than the control paste.

The patterns for the $\text{SO}_4^{2-}$ ion was similar to that found for the mix SB but the concentration level was a little higher. The initial concentration was as high as 220 meq/L and went down gradually to a plateau at 150 meq/L which maintained for 24 hours. The $\text{OH}^-$ ion concentration plateaued at 170 meq/L, a little higher than the mix SB, in the first 6 hours. Again there was no sudden increase in concentration during the first 24 hours of hydration.

Fig. 7.1-21 shows the same data extended to 14 days for the mix SM. Again these are very similar to those for the paste SB. A few differences are that the $\text{OH}^-$ ion and the $\text{K}^+$ ion concentration were slightly higher than those for the mix SB. The $\text{OH}^-$ ion concentration here was about 580 meq/L at 14 days, 50 meq/L higher than the paste SB, and 100 meq/L higher than the control paste. For the $\text{K}^+$ ion, its concentration level up to 14 days was almost same as that of the control paste, around 300 meq/L at 14 days.

Table 7.1-5 shows the same calculations of the charge balance as Table 7.1-3 for the paste SM. This analysis of polymer anion seems to be also applicable to the melamine sulfonate superplasticizer. The correlation of the two parameters, the excess of the cations and the polymer concentration in pore solution, were significant. However, the concentration is not quite as exact as was the case for naphthalene sulfonate superplasticizer, as can be seen from the variation in the calculated charge den-
Fig. 7.1-21 Concentration of inorganic ions in pore solutions of melamine sulfonate bearing pastes (SM) vs. time for extended periods up to 14 days.
Table 7.1-5 Experimental cation-anion balance in solution for mix SM

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Σ Cations (meq/L)</th>
<th>Σ Inorganic Anions (meq/L)</th>
<th>Difference (meq/L)</th>
<th>Polymer Conc. (g/L)</th>
<th>Calculated Charge Density* (meg/g)</th>
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<td>0.00</td>
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<td>2.71</td>
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</tr>
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<td>+56.8</td>
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</tr>
<tr>
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<td>5.39</td>
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<td>+25.1</td>
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<td>(7.48)</td>
</tr>
<tr>
<td>(day)</td>
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<td></td>
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<td></td>
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<tr>
<td>2.97</td>
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</tbody>
</table>

* of residual superplasticizers in solution.
sity. The overall calculated charge density of the polymer before absorption was less than 3 meq/g. For the cement paste solutions, it progressively increased; to about 4 meq/g at 15 minutes, and to more than 5 meq/g by 12 hours. The calculated charge density values at later ages were considered to be unrealistic due to the very small values of the residual concentration used as the denominator in the calculation.

7.1.4.3 Solid Phase Analyses

Fig. 7.1-22 shows the patterns of CaSO₄-bearing phases for the mix SM up to 1 day. Generally, the results were analogous to the paste with naphthalene sulfonate superplasticizer. Again no calcium aluminate monosulfate hydrate was observed for the whole period. Hemihydrate was still detected at 16 minutes, but it was dissolved or converted to gypsum before 1 hour. The pattern for the gypsum content was similar in its magnitude and duration to that for the paste SB. The maximum formation of gypsum occurred at 1 hour and the content was 0.9% equivalent of SO₄, which was lower than the control paste. The gypsum content was constant around 0.6% from 4 to 12 hours, and it was entirely consumed sometime before 24 hours.

The pattern for ettringite was a little different either from that for the paste SB or the control paste SO. The ettringite content increased to 1.3% as equivalent SO₄ at 1 hour, but then remained almost constant until 12 hours. This quantity was the highest of three pastes of cement S, for the first 6 hours. Between 12 and 24 hours, ettringite increased significantly to 2.2% equivalent SO₄, which was higher than the control mix.
Fig. 7.1-22 Content of sulfate-bearing phases found in paste solids vs. time up to 1 day for melamine sulfonate bearing pastes (SM)
(Percentage of each solid phase re-expressed in terms of its SO₄ content.)
Fig. 7.1-23 is the same figure extended up to 14 days. There is an apparent downward trend on the ettringite content from 1 day to 7 days, followed by an apparent stabilization in ettringite content at about 2.5% SO₄ equivalent. No compounds other than ettringite that are considered to incorporate Ca and SO₄ were detected by XRD analysis. As mentioned in the section concerning the solid phases analysis of the paste SB, determination of the ettringite content by DSC for the samples after one day are subject to a complication associated with the shoulder of its dehydration peak. As shown in Fig. 7.1-24, the same complication exists here. The results of two replicate runs on different days are presented on the figure. One of the points at 14 days seemed unreasonable and was not included in the analysis. The same method for the baseline determination as the paste SB was also applied here, i.e. the shoulder was included.

The ettringite contents determined here are very much larger than for the control paste and the paste SB, which were only of the order of about 2.1% SO₄ equivalent.

Table 7.1-6 shows the combined data of all the CaSO₄-bearing phases determined over the 14 days period for paste SB. The sum of the total solid sulfate phases and the sulfate ion in solution was high at around 2.7% for 1 and 2 hours; it decreased to approximately 2.2% SO₄ equivalent before increasing again at ages of 1 day and later.
Fig. 7.1-23 Content of sulfate-bearing phases found in paste solids vs. time up to 14 day for melamine sulfonate bearing pastes (SM)
Fig. 7.1-24 DSC curves of the paste SM samples at 1 day to 14 days
Table 7.1-6 Total balance of sulfate-bearing phase for mix SM

(Percentages expressed in terms of equivalent SO₄ content)

<table>
<thead>
<tr>
<th>Age (hr)</th>
<th>Hemihydrate (%)</th>
<th>Gypsum (%)</th>
<th>Ettringite (%)</th>
<th>Σ Solid (%)</th>
<th>Solution (%)</th>
<th>Total (%)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>2.52</td>
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</table>
7.2 Discussion

7.2.1 Characteristics of Removal of Naphthalene Sulfonate Superplasticizers from Solution by the Two Gray Cements

The initial removal of the naphthalene sulfonate superplasticizer from solution by cement S was greater than that by cement L. Many factors can be taken into consideration as possible causes.

Examination of the properties of the two cements given with the mill analyses in Table 3.1-2 indicate that cement S has a significantly finer grind than cement L, the indicated Blaine fineness values being 3720 and 3275 cm$^2$/g respectively.

The SO$_4^{2-}$ ion concentrations in the paste solutions at early ages, were lower for cement S, and the release of the Na$^+$ or K$^+$ ion into solution were also lower for cement S. Those indications suggest that cement S has a smaller amount of alkali sulfate immediately soluble to the solution phase than does cement L. As was seen in Chapter 5, SO$_4^{2-}$ in solution interferes with the rapid uptake of naphthalene sulfonate which otherwise takes place.

7.2.2 Effect of Superplasticizers on Inorganic Ion Concentrations in Solution

It is confirmed in all pastes of cement S that gypsum depletion preceded the start of the drop of the sulfate ion concentration in the solution phase. This sequence of two events was clearly observed for the control paste SO, but the overall hydration
was so retarded for the two superplasticized pastes that the progressive decline of the \( \text{SO}_4^{2-} \) ion in pore solution took place only after 1 day.

The enhancement of the Na\(^+\) ion concentration due to the Na\(^+\) from both superplasticizers, and the subsequent corresponding increases of the OH\(^-\) ion concentration at later ages were also seen for both superplasticized pastes of cement S. In the period before set, the alkali ion concentrations were constant regardless of the absorption of the superplasticizers.

The Ca\(^{2+}\) ion concentrations were higher in pore solutions for both naphthalene sulfonate and melamine sulfonate superplasticized pastes than for the control mix. This effect was also previously found for the cement L with superplasticizer B. It was confirmed that the amount of gypsum formed immediately from hemihydrate was less in pastes with both superplasticizers. This effect is compatible with the high concentrations of Ca\(^{2+}\) produced in the early paste solutions. Generally, it can be interpreted as another symptom of the heavy retardation caused by both superplasticizers. The organics tend to coat the surface of both hemihydrate and cement particles, interfering with the recrystallization of the former to gypsum, and with the hydration of the cements.

For cement S, there seems to be little difference between naphthalene sulfonate superplasticizer B and melamine sulfonate superplasticizer M with respect to their effects on solution phase or calcium sulfate solids composition over time. The plots of the residual concentrations of the naphthalene sulfonate and of melamine sulfonate
over 24 hours were almost quantitatively identical to each other, and the inorganic ion concentration patterns were similar.

7.2.3 Solid Phases

There is a significant difference in the initial CaSO₄ forms of cement S and cement L, in that cement S has both gypsum and hemihydrate while cement L has only hemihydrate. Since hemihydrate converts to gypsum immediately, this difference does not appear to seriously affect the pattern of the CaSO₄-bearing phase changes. The initial ettringite formation was a little higher with melamine sulfonate than with naphthalene sulfonate, but this did not cause any major change in the rheology of the paste or the absorption of the admixtures from solution.

Again no calcium aluminate monosulfate hydrate was detected at later ages either from the control paste or from the superplasticized pastes of cement S, similarly to cement L. For cement S, the ratio of SO₃ to Al₂O₃ in the mill analysis was 0.70. It is higher than the corresponding ratio for cement L (0.56). Ettringite can be a stable form in a mature paste resulting from this chemical composition, which may be a part of reason for the absence of monosulfate.

From the XRD analysis of the solid samples at 1 day and older, a small broad peak was detected in the d-spacing range of 7.5Å to 8.2Å. This may be characteristic for several kinds of non-SO₄-bearing AFm type calcium aluminate hydrated compounds. The peak was significant in some samples. However, it is observed both in the control
pastes and the pastes with the two superplasticizers. Since the control pastes do not show the ettringite peak shoulder on DSC, formation of such phases is not responsible for the shoulder of the ettringite peak.

Between 1 day and 14 days, it appears that the ettringite content in the solid is approximately constant or slightly decreasing for both superplasticized pastes and the control paste of cement S. The apparent decrease may reflect the effect of the complicated figures of the DSC peaks at later ages, rendering the estimates subject to experimental errors. It should be noticed that the total area of the dehydration peaks for hydration products (including C-S-H gel) continues to increase after one day.

7.3 Findings

The following are listed as experimental findings from the experimental work on cement S.

1. Cement S was slower in hydration than Cement L despite its finer grind and higher alkali content. Heavy dosages of both naphthalene sulfonate and melamine sulfonate superplasticizers caused retardation more significantly than for the corresponding pastes of cement L. The degree of retardation founded with this cement hardly differs between the two superplasticizers (at the same dosage) up to 4 days. After that, the paste with melamine sulfonate showed greater hydration than did the paste with naphthalene sulfonate.

2. The time dependent patterns of the concentration of admixture remaining in solu-
tion were practically identical for both the naphthalene sulfonate and melamine sulfonate superplasticizers.

3. The analytical calculation to associate polymer anion concentrations with excess cation over anion charges of the inorganic species, developed in the previous chapter, was applied for the superplasticized pastes of cement S. It appeared to yield appropriate results, at least for the first day, when the amount of superplasticizer remaining in solution was large enough to be accurately measured. It was found that the calculated charge density of the residual dissolved patterns of both admixtures were not constant and increased as absorption of the superplasticizer proceeded, especially for melamine sulfonate.

4. The effects of the two superplasticizers on the solution phase ion concentrations were similar. Compared to the control paste SO, both produced Na⁺ ion enhancement derived directly from the superplasticizers, and subsequent corresponding OH⁻ ion enhancement at later ages; enhancement of the Ca²⁺ ion concentration in the period before setting; and enhancement of the concentration of SO₄²⁻ during the early plateau period.

5. Although the form of CaSO₄ in cement S was a mixture of gypsum and hemihydrate, and thus different from the entirely hemihydrate form in cement L, the results of the time-dependent solid phases analyses were similar for both cements; the hemihydrate in cement L had entirely converted to gypsum within one hour.

6. No calcium aluminate monosulfate hydrate was found in any solid sample for
7. The quantitative analysis of ettringite by DSC in older paste was found difficult again for the cement S, because of several effects. Non-sulfate-bearing AFm compounds, detected by x-ray diffraction, may be contributing to the ettringite DSC peak at later ages. Another feature at later ages is the progressively developed broad C-S-H peak from which the ettringite peak must be separated. Further, it was found that the characteristic dehydration peak of ettringite in many pastes exhibited a significant shoulder in a higher temperature side when either superplasticizer was present, which is probably attributable to incorporation of these admixtures into the ettringite phase. Consequently, the ettringite content determined by DSC becomes more variable at later ages.
8.1 Factors Affecting the Removal of Superplasticizer from Solution

8.1.1 General

The removal pattern of the superplasticizers from solution was similarly observed in all the superplasticized pastes. A large portion of the superplasticizer in the mix water is absorbed to the solids by the first measurement (usually about 15 minutes). Then the concentration of the remaining superplasticizer stays nearly constant or decreases very slowly for several hours depending on cement system. Subsequently, a rapid decline of the residual concentration of superplasticizer occurs at usually sometime between 12 and 24 hours, and only a small amount remains indefinitely thereafter.

The amount of the initially removed superplasticizer varies with the cement system, and probably with the inorganic ions present in the paste solution. In some cases with white cement W, almost all the superplasticizer was removed from the solution immediately. The pastes usually showed a rapid premature stiffening for these cases. The white cement has a peculiar chemical composition; it has a very low alkali con-
tent, a low aluminate content, a very low iron content, and the CaSO$_4$ contained is entirely "insoluble anhydrite". The immediate absorption of essentially all of the superplasticizer and the subsequent rapid stiffening of the pastes are considered to be an example of incompatibility problems between cements and admixtures.

Especially, it was observed in this particular white cement that the initial absorption of the superplasticizer could be changed by changing the mixing procedure, even for pastes of nominally identical compositions. No such effect was found for the other two cements, both of which were more nearly "normal" gray portland cement.

Not only can variation in the original mix procedure affect the superplasticizer response, but it was also found that remixing can cause additional removal or release of the superplasticizer by the solids with this sensitive white cement. It should be noted that the interaction between superplasticizer and hydrating solids are not simple, and are sensitive to slight changes of various factors. The white cement appears particularly sensitive to such effects.

The absorption of naphthalene sulfonate also varied considerably with addition of sulfate which will be discussed in detail later. The more nearly pure naphthalene sulfonate was absorbed by the white cement nearly completely with a few minutes; if sulfate ion in appreciable concentration was present, the immediate absorption was much reduced, with drastic consequences for the rheology of the paste.

The melamine sulfonate, which had some sulfate impurity content, underwent a considerable amount of initial absorption by the white cement, but left a substantial
residual concentration. This initial response resulted in phenomena quite different
from what was produced either by the nearly pure naphthalene sulfonate or by the
impure, sulfate-rich naphthalene sulfonate, specifically a complete retardation for two
days.

In comparing the response of the melamine sulfonate with naphthalene sulfonate
on the ordinary gray portland cements, no such drastic differences in behavior were
found. For example, with cement S, equal dosages of both superplasticizers produced
rapidly equal initial absorptions, and similar patterns of removal with time were found
thereafter. The rheological effects, and the time dependency of their effects were
quite similar.

8.1.2 Relation Between Ettringite Formation at Very Early Ages and Superplasticizer
Absorption

Fig. 8.1-1 shows that the amount of superplasticizer removed from solution by the
first measurement (usually about 15 minutes) expressed as the weight ratio normalized
to the original cement weight, and the ettringite formed during the same period for the
various mixes carried out in this study.

In the figure, it is clearly seen that the amounts of the ettringite formed (by the first
measurement at about 15 minutes) are linearly correlated with the amounts of the
superplasticizer removed from solution in the same period. The data include results
for three different cements with two different superplasticizers; even so, the fit of the
Fig. 8.1-1 The amount of superplasticizer removed from solution within the first 15 minutes of hydration vs. ettringite formed during the same period
regression line is quite good \((R = 0.908)\). This correlation between superplasticizer removed from solution and ettringite formed at the same time is taken as strong evidence that the removal process is primarily that of incorporation of superplasticizer into or with newly forming ettringite.

The regression line drawn in the figure is for all data secured in this research except one point. This single outlier point is for the paste of white cement with 1.2\% \(\text{Na}_2\text{O}\) equivalent of \(\text{KOH}\) added in the mix water (WB5). This paste exhibited rapid set and almost complete removal of the superplasticizer from solution, but no ettringite was observed for the first 2 hours of hydration. As discussed in Chapter 5, these phenomena were related to rapid \(\text{Ca(OH)}_2\) precipitation that was associated with the very high initial concentration of the \(\text{OH}^-\) ion in the paste solution. The removal of the admixture was considered to have occurred under very different conditions from all of the other cases.

**8.1.3 Sulfate Ion Effects in Paste Solutions**

Experimental work on white cement \(\text{W}\) in Chapter 5 appeared to indicate that the higher the \(\text{SO}_4^{2-}\) ion concentrations in the mix water, the less the initial uptake of the naphthalene sulfonate superplasticizer from solution. For the two gray cements \(\text{L}\) and \(\text{S}\), both of which showed higher early \(\text{SO}_4^{2-}\) ion concentrations, the initial removals of both superplasticizers from solution were much less than those for the white cement.
The removal of the admixture from solution can be affected by many factors other than the early sulfate ion concentration. The content of C₃A and C₄AF, and the fineness of the grind may both be significant in this respect. The two cements L and S both have much larger contents of the aluminate phases than the white cement dose. Despite this, the results were opposite to what may have been expected on this basis. While no data on the fineness of the white cement was provided, it gave indications of being considerably finer than the two gray cements. This presumed higher surface area might have contributed somewhat to the higher absorption.

Nevertheless, the main reason for the smaller initial absorption with the gray cements is considered to be the higher sulfate ion concentrations in solution. The alkalis in the clinker of both cement L and S mostly exist as alkali sulfates or alkali calcium sulfates, and they dissolve to the mix water quickly and release $SO_4^{2-}$ ions immediately. Also, the hemihydrate in these cements was found to dissolve fairly rapidly, also releasing a considerable amount of sulfate. Thus the sulfate ion concentration at the first measurement for the control pastes without superplasticizer for both gray cements were much higher than that for the white cement. This high initial $SO_4^{2-}$ ion concentration can be considered equivalent to the adding of the $SO_4^{2-}$ in the mix water for the previous experiments for the white cement.

It appears that in superplasticized systems, when a high concentration of $SO_4^{2-}$ ions is present in the early solution phase, the production of early, perhaps poorly crystalline, ettringite is reduced, and less of the superplasticizer is absorbed by the hydrating solids. In some cases also, the superplasticizer molecules taken up early by
the poorly crystalline ettringite are not necessarily permanently removed from solution. It is found for the white cement that an appreciable portion of this "absorbed" naphthalene sulfonate can be released back to the solution initiated by various causes, such as an addition of sulfate.

8.1.4 Hydroxide Ion Effects in Paste Solutions

Some pastes of the white cement were made with KOH dissolved in the mix water along with the naphthalene sulfonate superplasticizer. It is rare in real cement systems that the mix water is conditioned with alkali hydroxides. Some peculiar phenomena were observed in the superplasticized paste with large KOH additions (1.2% Na₂O equivalent). First, the calcium sulfate anhydrite phase was dissolved very quickly and released considerable amounts of both Ca²⁺ and SO₄²⁻ ions to the solution phase. Second, a vigorous precipitation of Ca(OH)₂ was observed and attributed to the limited amount of Ca(OH)₂ that can remain in solution in slightly alkaline systems due to the common ion effect, coupled with the large amount of Ca²⁺ dissolved from CaSO₄. Third, gypsum was not precipitated, and even ettringite was not observed for the first 2 hours. It is thought that these effects are not due to the special properties of the white cement or of the superplasticizer, but may be more general effects of a very high OH⁻ ion concentration in the solution phase.
8.1.5 Effects of the Form of Calcium Sulfate in the Cement

The three cements examined here contain calcium sulfate in forms different from each other. Cement L has only hemihydrate, and cement S contains both hemihydrate and gypsum. The white cement W contains only insoluble anhydrite as the initial form.

Comparing the two control pastes of the gray cements L and S, it was found that this difference in initial form of calcium sulfate did not significantly affect the hydration behavior as monitored by the analyses of solution phases and of the solid phases. The hemihydrate dissolved immediately after the initial contact with water, and converted to gypsum almost instantaneously. Thus the calcium sulfate observed to be present after 15 minutes was entirely gypsum for both of these control pastes.

When superplasticizer was introduced to the systems, a delay of this conversion from hemihydrate to gypsum was observed. In some superplasticized pastes, hemihydrate was formed to be still present between 15 minutes and 1 hour. It is considered that the superplasticizer was either adsorbed on or incorporated with the surface of the hemihydrate particle, and hindered its dissolution. This is the only difference found to originate from the difference between hemihydrate and gypsum as the initial form in the unhydrated cements, and its effect is considered to be small.

In contrast, the hydration behavior of the superplasticized pastes of white cement W were found to be very different from those for other ordinary portland cements L and S. Although other chemical and physical parameters of the white cement were
different from those for cement L or S, some of the characteristic effects observed can be specifically attributed to the insoluble anhydrite form of the gypsum.

It is possible that insoluble anhydrite absorbs some of the superplasticizer, and that the dissolution of anhydrite is thus delayed, similarly to the effect of superplasticizer on hemihydrate as seen previously. However, no such hindrance of dissolution was observed by the first measurement in any superplasticized paste of the white cement. Rather, the initial dissolution of insoluble anhydrite was somewhat promoted, compared to that found for the control paste, i.e. the reduction in the anhydrite content within the first 15 minutes was greater with superplasticizer. The reason is not clear. It may possibly be explained as an effect of greater wetting of the anhydrite due to the well dispersed state of the cement particles indicated by the action of the superplasticizer.

The rapid stiffening exhibited in some superplasticized white cement pastes did not occur for the superplasticized pastes with additional alkali sulfate in the mix water (WBN, WBK). The lack of the $\text{SO}_4^{2-}$ ion in the solution phase at very early ages is considered to be the primary cause for the rapid stiffening; almost all of the superplasticizer was immediately removed by the cement under these circumstances. The low $\text{SO}_4^{2-}$ ion concentration was a function in part of the very low content of alkali sulfate in this cement. It was further seen to be associated into the fact that only anhydrite, which has the slowest rate of dissolution of the $\text{CaSO}_4$ forms, was present. Even the alkali content in an original cement was low, the $\text{SO}_4^{2-}$ ion concentration would become reasonably high if the $\text{CaSO}_4$ in the cement were hemihydrate or gypsum.
forms.

8.2 Effects of Superplasticizer on Properties of Paste

8.2.1 Effects of Superplasticizer on Physical Characteristics of Pastes

It was found that the physical characteristics of pastes are associated with the superplasticizer concentration remaining in the solution phase. The fluidity of the paste (represented by the spread in area of the mini-slump cone test) was particularly closely related to the concentration of the superplasticizer remaining in the solution. When the residual concentration of the superplasticizer became so low that the residual superplasticizer was primarily monomer, the paste exhibited stiffening. There was no exception to this generalization.

Generally, the superplasticizer adsorbed on the surface of the particles is considered to provide a negative surface electric charge, leading to repulsion of particles of the same charges suspended in solution and effective dispersion. During cement hydration, the electric charges on the solid surface become ineffective by being covered with newly formed hydration products. Residual superplasticizer in solution is able to adsorb again to the new surface, and to maintain the dispersive state. Hence, an excess amount of superplasticizer in solution is considered to be necessary to maintain the fluidized state of the paste. In these pastes, the residual concentration of the superplasticizer was found to be generally an indicator of existing degree of fluidization of the paste.
8.2.2 Effect of Superplasticizer on Retardation in Hydration

All three superplasticizers A, B, and M exhibited a retarding effect. Since the dosage of the superplasticizers was high, the hydration of the well-fluidized pastes were considerably retarded. Even the superplasticized pastes of white cement W (WBO) that showed a stiffening at very early ages, showed delays in both the time of the second peak of heat evolution and in the time of set, as compared to the control pastes. However, the delay of the set time caused by the superplasticizer was shorter for the white cement than for the two gray cements.

The retardation effect may possibly be associated with an alteration of the hydration products formed, especially the ettringite. Ettringite formed in the presence of superplasticizer in solution appears to have absorbed significant contents of the superplasticizer molecule. This may modify the early ettringite and render it a more efficient barrier to further hydration of the unhydrated portion of the cement particles.

The two superplasticized pastes of the white cement batched with additional alkali sulfates in the mix water (WBN, WBK) exhibited considerable retardation, and otherwise behaved more normally like the superplasticized gray cements. Thus, even though the calcium sulfate was insoluble anhydrite, the cement behaved normally when a sufficient amount sulfate ion was made available in solution at very early stages of hydration. Without the added sulfate ion, the superplasticized white cement pastes behaved abnormally.
8.2.3 Effects of Superplasticizer on Solid Phase and on the Solution Phase

The analyses of CaSO₄ bearing compounds indicated that the time-dependent change of these compounds are basically the similar for the two ordinary portland cements. The hemihydrate in the unhydrated cements is converted to gypsum immediately at the beginning of hydration. The content of this "secondary" gypsum is gradually reduced toward zero, in the same way that "primary" gypsum is reduced when it is the only CaSO₄ constituent. After the gypsum is used up, the SO₄²⁻ ion concentration in paste solution starts to decline. Ettringite forms rapidly at very early ages, then continues to form at a slower rate.

For the white cement, the patterns are different from those for the other cements. The insoluble anhydrite content gradually diminishes as hydration proceeds, but the anhydrite does not convert to gypsum. The pattern of the ettringite formation is actually quite similar to that experienced with gray cements.

With introduction of either superplasticizer to the cement systems, some changes are observed in the solids. For the gray cement with hemihydrate, the amount of the gypsum formed in early stages is reduced compared to the paste without superplasticizer. For both gray cements, the gypsum stays longer than in the control pastes. For all three cements, the formation of ettringite after the end of the initial sudden ettringite production period is considerably slower with superplasticizers. Consequently, the period of constant ettringite content was much longer and was observed more prominently with superplasticizer. These outcomes are considered to be another retardation
effect due to the superplasticizer.

The important effects of the superplasticizer on the solution phases were the enhancement of the Na\(^+\) ion concentration, and the subsequent corresponding increases in the OH\(^-\) ion concentration at later ages. These phenomena were observed for all three cements.

8.3 Analyses of CaSO\(_4\)-Bearing Phases

The methodology applied in this study for quantitatively tracking SO\(_4\) in solids by using DSC, was shown to be practical. Its possibilities and limitations have been clarified. It is an strong advantage that ettringite, hemihydrate, and gypsum can be quantified simultaneously by a single run of the DSC, without complicated pre-treatment.

Even with the relatively facile experimental procedure, the contents of those three compounds as determined by the area of dehydration peaks, are fairly accurate. Those of the calcium sulfate hemihydrate and the gypsum are particularly accurate, since the characteristic dehydration peaks for these solid phases are reasonably distinct. However, discussed in Chapter 6 and Chapter 7, the determination of ettringite is complicated by increasing development of the C-S-H gel, the possible production of C\(_4\)AH\(_X\)-type compounds, and the incorporation of the superplasticizers, especially at older ages than 1 day. The ettringite measured here is probably much less crystalline than other calcium sulfates; thus the characteristic dehydration peak is observed at
lower temperatures.

The determination by DSC is considered to be more accurate than by methods such as QXRD. However, the anhydrite phase present must be determined by QXRD analysis, since no thermal analysis method can be used. This quantitative analysis is subject to larger deviations than those found in DSC analysis.

However, it must be recognized that the combination of the DSC analyses developed here and the x-ray diffraction analysis for insoluble anhydrite is still incomplete, even for the original unhydrated cement. The sum of the $SO_4$ contents of all the solid phases was less than the cement sulfate content reported in the mill analysis for all three cements. Alkali sulfates and alkali calcium sulfates were not accounted for, and the possibly presence of some soluble anhydrite along with the hemihydrate in cements L and S could not be taken into account. The systems after water was added, were also incompletely evaluated with respect to sulfate. It is well known that at later ages sulfate ions are captured by C-S-H gel. This sulfate cannot be quantified easily either.

In addition to those sulfates not accounted for, different quantitative analysis methods have different degrees of variations in results, so that the combined balances are not so accurate. However, it does appear that time-dependent changes of each CaSO$_4$-bearing phase determined by the DSC analysis is correctly monitored, even though the sum of all of the sulfate present cannot be completely apportioned.
9.1 List of Findings

The following is a list of detailed findings resulting from the experimental work carried out in this study.

1. At the high dose levels used, both naphthalene sulfonate and melamine sulfonate superplasticizers had a retarding effect on the hydration of all the cements examined. The retarding effect was observed in calorimetry, in measurement of non-evaporable water content with time, in measurements of the disappearance of gypsum and the appearance of ettringite with time, and in measurements of the pattern of changes in the solution phase diminishing with time.

2. The superplasticizers used also produced retardation in setting time for all three cements, except for certain cases with the white cement, in which premature setting occurred.

3. The white cement examined here is described as very low alkali content, low aluminate phase content with almost no iron content, and with insoluble anhydrite being the only form of calcium sulfate present. Due to this peculiar composition, this white cement was found to be very sensitive in interaction with the
superplasticizers. In addition to other admixture interaction effects, it was found that the degree of absorption of the superplasticizer by the hydrating cement can be even changed by changing the mixing procedure. This kind of sensitiveness is not observed for either of two ordinary gray portland cements used.

4. Pastes of this white cement mixed only with a relatively pure naphthalene sulfonate superplasticizer exhibited rapid stiffening rather than the expected dispersing effect. This is considered to be an incompatibility problem between the cement and the admixture. This stiffening is associated with formation of a large amount of ettringite at very early ages, coupled with an almost complete removal of the superplasticizer from solution.

5. Two different naphthalene sulfonate superplasticizers produced significantly different early behavior with the white cement. Pastes mixed with a less pure naphthalene sulfonate superplasticizer containing sodium sulfate impurity, did not undergo premature stiffening, but exhibited the expected dispersing effect. This normal behavior was reproduced using the pure naphthalene sulfonate superplasticizer when dosage of Na$_2$SO$_4$ "impurity" identical to that present in the less pure superplasticizer was added to it.

6. It was found that addition of the sulfate ions into the mix water reduces the initial removal of naphthalene sulfonate by the white cement. The presence of a reasonable concentration of sulfate ion in the mix solution results in maintaining a reasonably high residual concentration of naphthalene sulfonate in solution. This
appears to be necessary to prevent the premature stiffening. By itself, the insoluble anhydrite present in the white cement does not dissolve rapidly enough to maintain the needed sulfate in concentration.

7. While the removal of naphthalene sulfonate from solution by the hydrating white cement is affected by sulfate ion addition, similar dosages of K$_2$SO$_4$ and Na$_2$SO$_4$ exhibited only slight differences in the absorption patterns.

8. It is found that addition of OH$^-$ ions to the mix water also affected the absorption of naphthalene sulfonate from the mix solution of the superplasticized white cement paste. With the less pure superplasticizer, the initial uptake increased with increase in the initial OH$^-$ ion concentration of the mix water. However, the reaction pattern of the pastes altered differently with different dosages of KOH, and the differing uptakes of superplasticizer cannot be explained by one comprehensive mechanism.

9. It was found specifically that an 0.6% KOH addition to superplasticized white cement paste with either naphthalene sulfonate superplasticizer produced a peculiar response, such that most of the superplasticizer initially removed from solution by the solid phases, was subsequently released back into solution, and then absorbed again. This response was entirely reproducible. Similar, but weaker responses of the same kind were observed with slightly greater and with slightly smaller additions of KOH.

10. As the dosage of KOH was increased, the rate of dissolution of insoluble anhydrite
in the superplasticized pastes of the white cement was accelerated.

11. With a very high dosage (1.2%) of KOH, the white cement paste with the pure naphthalene sulfonate exhibited an unusual kind of quick setting behavior. Instead of the expected retardation effect with superplasticized pastes, this paste stiffened in about 10 minutes and set in about 5 hours. A large amount of Ca(OH)$_2$ was precipitated quickly, and ettringite did not form for the first 2 hours. These phenomena are related to the high initial pH of the mix solution.

12. No hydrated form of calcium sulfate was found at any time in any of the hydrated pastes of the white cement. This was true regardless of the presence of naphthalene sulfonate superplasticizer or of added amounts of SO$_4^{2-}$ or OH$^-$ ions. For the pastes of moderately alkaline solution (i.e. with little or no added KOH), the slow rate of dissolution of anhydrite appears to restrict the sulfate ion concentration to values less than the saturation level of calcium sulfate (80 meq/L). For the pastes of higher initial OH$^-$ ion concentration, i.e. those with substantial amounts of added KOH, gypsum did not precipitate despite the increased level of sulfate in solution.

13. A heavy dosage (2% by weight of cement) of a melamine sulfonate superplasticizer severely retarded the setting of the white cement. The paste remained fluid and completely dispersed, with bleeding evident, for almost two days. The residual concentration of the admixture in the paste solution remained quite high during the corresponding two day period.
14. The time dependent patterns of the concentration of admixture remaining in solution were studied for some of the materials examined. In studies with one of the ordinary portland cements used, it was found that these time-dependent absorption patterns were practically identical for both the naphthalene sulfonate and melamine sulfonate superplasticizers, dosed at the same weight concentration.

15. The sulfate ion concentration in paste solution at its "plateau" level (before the sudden drop) was higher in the presence of superplasticizers. This was a transient effect, since the existence of the constant $SO_4^{2-}$ ion plateau is limited in time, and eventually the $SO_4^{2-}$ ion concentration decreases to negligible amounts.

16. It is found that the $Ca^{2+}$ ion concentration in the pore solution of the superplasticized pastes is higher than that observed for the corresponding pastes without superplasticizer. This was true while the paste was well dispersed, and while the residual concentration of the superplasticizer was reasonably high. At older ages (usually after 1 day), the $Ca^{2+}$ ion concentration drops to near zero with the superplasticizer, as it does at an earlier age without the superplasticizer.

17. Both superplasticizers are thought to be made up of polymers of varying chain length. It is known that the less pure naphthalene sulfonate superplasticizer contains a significant content of monomer molecules, i.e., "polymer" of single molecular units, and that these are not absorbed by cements. The proportion of monomeric naphthalene sulfonate remaining in the paste solution as a function of time was studied by analyzing two characteristic peaks in the UV absorption spec-
trum. It was confirmed that when the dormant period had ended and the cement had started its rapid hydration phase marked by the second hydration peak, nearly all of the polymeric chain molecules were taken up by the hydrating cement, leaving mostly monomeric molecules in solution.

18. All of the cement pastes studied, regardless of the presence or absence of superplasticizer, produced ettringite as the only sulfate-bearing crystalline hydration product. No calcium aluminate monosulfate hydrate was detected in any sample of any of the three cements. This was true for hydrating pastes of the two ordinary portland cements studied up to 14 days, and was true even though the sulfate concentration in the pore solution was virtually zero after 3 day. This absence of detectable monosulfate was not expected.

19. At older ages (3 days and beyond), a small broad x-ray diffraction peak was sometime detected at the d-spacing of about 7.9Å in pastes of both ordinary portland cements studied. This was attributed to the formation of non-sulfate-bearing AFm compounds. It was observed in pastes both with and without superplasticizers.

20. A method was developed for studying the rates of dissolution of insoluble anhydrite, the conversion of hemihydrate to gypsum, and the rate of decomposition of the gypsum in the reacting cement pastes. This was applied throughout this study to secure information concerning the effects of the admixtures on these processes. The method was repeated DSC analysis of solids filtered from the cement pastes as a function of time.
21. The same method of DSC analysis was found to be suitable for the quantitative evaluation of the amount of ettringite being produced in the same pastes. However, several problems were associated with ettringite analysis by this method for older pastes.

22. It was found that the characteristic DSC dehydration peaks of both ettringite and gypsum in some pastes exhibited a significant shoulder on the higher temperature side when either superplasticizer was present, and not when superplasticizer was absent. These peak shoulders are thought to be due to absorption of admixtures by, or into the ettringite or gypsum, respectively.

23. It was found useful to express the total of the solid CaSO₄-bearing phases detected (including ettringite) and the sulfate ions in solution re-expressed in terms of equivalent sulfate content, as a function of time. The total sulfate quantified in this method was less than the total cement sulfate analysis because alkali or other clinker borne sulfates were not accounted for in the early stages, and sulfate incorporated in C-S-H gel was not accounted for in the late stages. Nevertheless, various interactions with the superplasticizers were pinpointed by changes produced in the sulfate systems as measured by this tally.

A number of findings related specifically to the analytical methods used or to their application can be summarized below.

a. The measurement of melamine sulfonate by UV analysis is interfered by the OH⁻ ion in the solution. This interference is found to be effectively eliminated by
neutralizing with sulfuric acid prior to the UV analysis.

b. It was confirmed in preliminary study that pure gypsum is dehydrated to soluble anhydrite by heating to 160°C, and that this soluble anhydrite is rehydrated instantaneously to hemihydrate under the normal humidity conditions at room temperature.

c. Synthesized calcium sulfoaluminate monosulfate hydrates showed several complicated dehydration peaks on DSC. However, the major peak always appeared in the temperature range between 200°C and 300°C. The complete absence of monosulfate in the experimental pastes reported in this work is confirmed by that fact that no peak was observed in this 200°C - 300°C temperature range with any of the samples studied.

d. A synthesized C$_4$AH$_{13}$ sample (with some carbonation) also analyzed by DSC, showed a strong response between 230°C and 300°C, which is considered to be characteristic of this calcium aluminate hydrate compound when well crystallized.

9.2 Conclusions

The conclusions established as a result of the study are as follows:

1. A new approach to the study of the interactions between superplasticizers and cements has been developed in this research. The new features include time-dependent analysis of the calcium sulfate-bearing phases by DSC and by x-ray diffraction, coupled with similar time-dependent analyses of both superplasticizer
and inorganic ions in the paste solutions. This approach was found to be very effective in studying the nature of superplasticizer effects, and the same methods can be adopted to the study of the interaction effects that may be produced by other kinds of chemical admixture.

2. A key element in this approach is DSC analysis of changes in the contents of gypsum and hemihydrate as the pastes react with water. The same DSC runs are also used to study the rate of formation of ettringite. The rate dissolution of insoluble anhydrite (where present in a given cement) cannot be studied by DSC, but requires quantitative x-ray diffraction analysis. The content of soluble anhydrite is not determinable, but experiments indicate that soluble anhydrite is not stable in laboratory air and converts immediately to hemihydrate. The quantitative analysis of ettringite for later age is complicated by increasing development of the C-S-H gel, the possible production of C₄AH₆-type compounds, and incorporation of the superplasticizer on or within ettringite.

3. The rheological effectiveness of superplasticizer appears to depend on maintaining a reasonable concentration of molecules of the proper chain length in solution. The tendency appears for the hydrating cement to preferentially absorb the effective polymeric molecules and leave a greater proportion of ineffective monomer molecules in solution as hydration proceeds.

4. The rheological effectiveness of naphthalene sulfonate superplasticizer also is associated with the content of sulfate ions in solution. Cement pastes lacking a
reasonable concentration of sulfate ions do not show the expected dispersive effect of the superplasticizer, and stiffen and set prematurely. This response is associated with rapid removal of nearly all the superplasticizer from solution by the hydrating cement, coupled with simultaneous formation of a very large amount of ettringite. When soluble sulfate is supplied to such cement systems, the early uptake of superplasticizer is reduced, the rate of ettringite formation is decreased, and the admixture produces its normal dispersing action on the cement.

5. In "normal" superplasticized cement pastes, the time pattern of ettringite development is different from that of corresponding admixture-free pastes. With the superplasticizer present, ettringite production during the first few minutes of hydration is very rapid. The content of ettringite then remains constant for some hours before again starting to increase. This behavior is very different from what is found in similar pastes without superplasticizer, in which ettringite production does not stop, but is continuous through at least the first day of hydration. This difference is considered to be in part an expression of the retardation effect produced by the superplasticizer.

6. The presence of superplasticizer strongly affects the nature of development of the sulfate-bearing compounds in the early stages of cement hydration. When the total of the crystalline sulfate-bearing compounds (gypsum, hemihydrate, insoluble anhydrite, and ettringite) is added to the total sulfate found in solution at each stage of the early reaction processes, it is found that the total amount detected is much reduced in the presence of the superplasticizer. This reduction is attributed
mostly to poor crystallinity of the solid products in which the superplasticizer is absorbed or incorporated.

7. Both naphthalene sulfonate and melamine sulfonate superplasticizer used in this study were primarily Na\(^+\) neutralized, as are most commercial superplasticizers. Use of such superplasticizers results in an immediate increase in the Na\(^+\) ion concentration of the pore solution, as the superplasticizer is dissolved and the balancing cation of the sulfonate groups is ionized. Subsequently, as the polymer is absorbed from the solution by the hydrating cement solids and its sulfonate groups correspondingly removed from the solution, they are replaced by OH\(^-\) ions, leading to a permanent increase in the OH\(^-\) ion concentration of the paste solution. This may produce a greater tendency to alkali aggregate reaction damage if susceptible aggregates are used.

8. In pore solutions of pastes incorporating superplasticizers, it was found that the sum of inorganic cations consistently exceeded the sum of inorganic anions. It was established that this apparent lack of charge balance was due to neglect of the anionic sites (exposed sulfonate groups) on the polymeric chains of the dissolved superplasticizers. As the superplasticizers were removed from solution by the hydrating cements, this apparent discrepancy was reduced.

9. An measurement of the apparent charge density (meq/g) of the overall superplasticizer was developed, involving paired measurement of the apparent discrepancy between positive and negative inorganic ions and weight concentration of dis-
solved polymer. This produced fairly consistent estimates of charge density of residual polymer in solution for naphthalene sulfonate (about 4.8 meq/g) and similar, but more variable estimates for melamine sulfonates. However, in the later stages when absorption of superplasticizer was more nearly complete, the calculations broke down because of inaccuracy in measurement of the content of the small amount of residual polymer remaining in solution.

10. It was found that conversion of hemihydrate to gypsum was completed by 15 minutes in the absence of superplasticizers, but that completion of this normally rapid process was appreciably delayed in the presence of superplasticizers. Subsequent to this conversion, no distinction was found between rates of dissolution of primary gypsum and secondary gypsum produced from hemihydrate.

11. In all cases examined with and without superplasticizer, the decline in sulfate ion concentration in the paste solution was preceded by the exhaustion of the solid gypsum.
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