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EFFECT OF CHEMICAL ADMIXTURES ON THE EXPANSION OF SHRINKAGE-COMPENSATING CEMENT CONTAINING A PRE-HYDRATED HIGH ALUMINA CEMENT - BASED EXPANSIVE ADDITIVE

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ABSTRACT

The effect of chemical admixtures on ettringite formation and expansion of expansive cement containing a pre-hydrated high alumina cement - based additive (H-HAC) is discussed. Nine chemical admixtures including surfactants, accelerators, retarders and a bonding agent were investigated. Compacted samples were used to study the effect of chemical admixtures on relevant hydration reactions. Normally mixed paste samples were also used to study chemical and surface - chemical effects. The effect of admixtures on ettringite formation and reaction of gypsum at early hydration times was followed by XRD analysis of high w/c wet samples containing large amounts of expansive additive. Suggestions are given for the control of ettringite formation and expansion in expansive cement - based systems.

INTRODUCTION

It is well known that drying shrinkage contributes to cracking and corrosion in concrete elements. Suggested solutions include the use of expansive cement (ACI 223-90). The role of expansive cement in North American construction is likely to increase due to renewed emphasis on repair and rehabilitation of urban infrastructure. New expansive additives may become attractive, if they can be easily produced or manufactured. Effective application at concrete batch plants or at the job site is desirable. Compatibility with other chemical admixtures is required. The development of a pre-hydrated high alumina cement - based expansive additive (H-HAC) appears to satisfy many of the above requirements [1]. This innovative material made from commercial cementitious materials can be added to Portland cement concrete on site and produce a pre-determined amount of expansion without significantly affecting the engineering properties of concrete. In this study, chemical admixtures, including selected surfactants, accelerators, retarders and bonding agents, were investigated to determine their effect on the expansion behavior of expansive cement containing H-HAC - based expansive additive. The system OPC - HAC - $C\bar{S}H_{0.5}$ - CH - H_2O has received little previous interest, probably due to limitations imposed by its rapid setting behavior [2]. Some retarders e.g. tartaric acid and sulfite liquors were studied; they all reduced expansion dramatically. It was also reported that ASTM Type D admixtures could improve the setting behavior of similar mixtures [3]; these however also resulted in a significant decrease of expansion. Previous work by the authors indicated that an SNF-type superplasticizer accelerates the formation of ettringite in fresh expansive cement paste, depletes expansive reagents and results in a lower ultimate expansion [4]. Reduced setting time and expansion in presence of superplasticizer was also observed when expansive cement containing H-HAC - based expansive additive was used [1].

In this work, the effect of admixtures on the expansion of expansive cement containing H-HAC - based expansive additive was investigated using compacted specimens and normally mixed paste specimens. Compacted specimens were used to monitor chemical reactions. The mixes were used to study the effect of admixtures on chemical and surface chemical reactions. XRD analysis was employed to determine the effect of chemical admixtures on ettringite formation and depletion of gypsum at early hydration times.

EXPERIMENTAL

Techniques

The chemical admixtures used in this study comprised four groups: surfactants; accelerators; retarders; and a bonding agent. The effect of the different chemical admixtures on expansion of compacted and normally mixed specimens was determined. XRD analysis was used to monitor their effect on ettringite and gypsum formation.

Expansion of compacted samples:

Compacted samples provide a fixed cement paste structure before hydration, effectively eliminating dispersion and other surface chemical effects on the expansion of expansive cement. The solution concentration can be considered to be relatively constant during the hydration, as the solution to solid volume is sufficiently large (e.g. solution : solid volume = 1000 : 1 in the present test). A sample thickness less than 2 mm minimizes gradients and facilitates uniform diffusion of chemical species into the entire specimen. Relative expansion effects due to the presence of admixtures can be readily determined.

Expansion of normally mixed samples:

Surfactants can disperse cement particles, increase the effective reaction surface and accelerate the chemical reaction rate during the period the mixture remains in the plastic state. Initial length measurement is usually taken after 24 hours. During this period ettringite formation has depleted some of the reactants responsible for formation of expansive product. Subsequent expansion is the result of surface effects and further chemical reaction. The influence of admixtures on chemical reactions at later ages is reduced as the early interaction with cement consumes most of the admixtures. Leaching of residual admixture at later ages may also reduce its concentration in pore solution. Expansion of the samples at later ages may be similar to that of plain expansive cement if the nature of the hydration products is not significantly altered.

XRD analysis of the expansive cement paste:

Samples having a very high water-cement ratio and expansive additive to Portland cement ratio were used for XRD analysis. The major peaks associated with the ettringite phase (d=9.8 Å), and the formation of gypsum (d=7.6 Å) from hemihydrate were monitored for all the samples. The test was designed for the comparison of parallel samples. The comparison is based on the significant difference between parallel samples. A high speed mixer was used to mix the expansive cement formulation. Mixes were then prepared by combining the expansive cement formulation with the specific admixture of interest. Bleeding and segregation were minimized by the high content of hemihydrate in the formulation, high speed mixing and continuous rolling of the pastes in the sample bottles to the time of analysis by XRD. The wet sample taken from the bottle was quickly scanned by XRD in about one minute. The effect of chemical admixtures on the formation of ettringite and the change in gypsum content during hydration was determined by comparing differences in the area of corresponding characteristic peaks.

Materials and Mixtures

Nine chemical admixtures were used in this study. These included: three surfactants, sodium lignosulfonate (SLS), sodium sulfonated napthalene formaldehyde (SNF) and sodium sulfonated melamine formaldehyde (SMF); three accelerators, NaCl, $CaCl_2$, and Na_2SO_4; two retarders, sodium citrate and sucrose; and one SBR latex bonding agent. The expansive additive was made from a combination of commercial cementitious materials: Ciment Fondu, Plaster and Hydrated Finishing Lime. The Al-bearing material in the expansive additive was prepared by hydrating Ciment Fondu for about 24 hours followed by drying and grinding to the desired fineness. The components of the expansive additive were in the following proportions: H-HAC (0.6), hemihydrate (0.3) and hydrated lime (0.1). Type 10 Portland cement had the following chemical composition (wt.%): SiO_2=19.83; CaO=61.21; Fe_2O_3=3.20; Al_2O_3=4.18; MgO=4.09; SO_3=3.93; Na_2O=0.45 and K_2O=0.82. The H-HAC based expansive additive had the following oxide composition (wt.%): Al_2O_3=16.6; CaO=34.4; SiO_2=1.9; Fe_2O_3=1.7; SO_3=15.7. These percentages were calculated on the basis of the starting materials including the water content of H-HAC. The sum was therefore less than 100%. The mixture for compacted and normally mixed specimens had the OPC - expansive additive ratio: 1/0.2; the mixture for XRD analysis had the OPC - expansive additive ratio: 3/7. The admixture concentrations of solutions in which the compacted specimens were immersed and the admixture contents of normally mixed specimens expressed as the wt. % of CH saturated water and expansive cement respectively were as follows: SLS - 0.5%; SNF - 1%; SMF - 1%; $CaCl_2$ - 2%; NaCl - 2.1%; $Na_2SO_4{\cdot}10H_2O$ - 5.8%; sodium citrate - 0.1%; sucrose - 0.03%; SBR latex - 6%. The SBR latex emulsion with solid content 53% by weight was supplied by Sternson Inc.

Specimen Preparation

Compacted systems:

Compacts were made by compacting dry H-HAC -based expansive cement at a pressure of 240 MPa. The dry cement mixture was rotated in a plastic bottle for 48 hours. Five grams of dry sample were placed in a 32 mm diameter circular steel mould and compacted. Compacts were stored for 24 hours and then placed in distilled water for about one hour to adsorb the water. Prism shaped specimens, 30 x 5 x 2 mm, were cut from the compacted discs and mounted on specially designed Tuckerman optical strain gages (sensitivity 2 x 10^{-6} mm/mm); initial readings were taken immediately. The gauge length was 20 mm. Samples were then immersed in solutions containing saturated calcium hydroxide and selected admixtures. Compact samples were immersed in a latex - lime water solution to demonstrate the effect of the latex solution itself on expansion characteristics of expansive cement (The content of solid latex in the latex-lime water solution was 3.18% by wt.). The same Cl^- molarity in $CaCl_2$ and NaCl solutions and same Na^+ molarity in NaCl and Na_2SO_4 solutions were employed, i.e. 0.36 mol/l. Length change readings were made at various hydration times.

Paste mixes:

Paste mixes were prepared by mixing portland cement with 20% expansive additive for 1 minute using a high speed mixer. The w/c was 0.5. Each admixture was dissolved in a pre-weighed amount of water before mixing. The Cl^- and Na^+ molarities were the same for solution prepared with $CaCl_2$ and NaCl as well as NaCl and Na_2SO_4. The water - cement ratio of latex - modified paste samples was determined by accounting for the water content of the latex solution. The latex solution was integrally mixed with the cement paste but not with the compacted material. Most cement paste samples were cast in plastic bottles and cured at 23 °C and 100% R.H. for 24 hours. Samples containing retarders were cured for 48 hours to provide sufficient strength during cutting. The samples were cut into 30 x 5 x 2 mm prism specimens at 24 hours. Prisms were mounted on Tuckerman optical strain gages for length change measurements. Initial readings were taken at about 24 - 25 hours for most samples and at about 48 - 49 hours for samples containing retarding admixtures. The samples were immersed in calcium hydroxide saturated distilled water at 23 - 25 °C in a desiccator to avoid carbonation. Length change measurements were made at various hydration times.

XRD analysis:

The paste samples for XRD analysis were prepared by mixing Portland cement with H-HAC - based expansive additive (OPC/expansive additive = 3/7) in a high speed mixer for 1.5 minutes. The w/c was 1.5. The mixes were cast into plastic bottles, containing pre-weighed amounts of admixture in accordance with test requirements. Each bottle contained about 40 grams of cement paste. The bottles were put on a rolling machine after filling. The wet samples were continuously rotated at 25 °C. At selected hydration times, samples were removed from the bottles and placed on glass slides. The coating on glass slides for all the samples had similar thickness. The XRD spectra were obtained in about 1 minute by scanning in the 2θ range of 6 to 15 degrees. A Rigaku X-ray Diffractometer System Geigerflex D/Max -B was used. Copper Kα radiation was employed. The peak width and height were calculated using Rigaku Standard Data Processing software.

RESULTS

The results of experiments designed to assess the effect of several admixtures on the expansion behavior of cement containing H-HAC - based expansive additive are reported. The results are presented in four groups according to admixture class .

Surfactants

The effect of surfactants on the expansion of compact samples is illustrated in Fig.1. It is apparent that SLS and SMF significantly reduced expansion of the expansive cement. SNF appeared to promote the increase in expansion. SLS reduced expansion of the compact sample more than SMF.

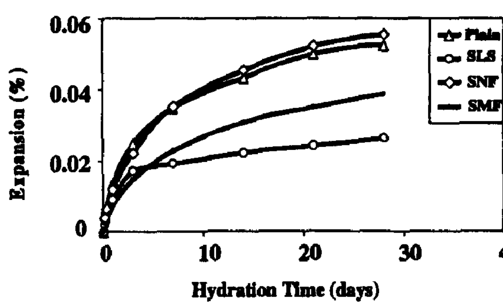

Fig. 1. Effect of surfactants on the expansion of compacted expansive cement samples.

The relative order of the expansion in mixed paste samples is markedly different (Fig.2.). The sample with SLS showed highest expansion while those with SNF and SMF had much lower expansion.

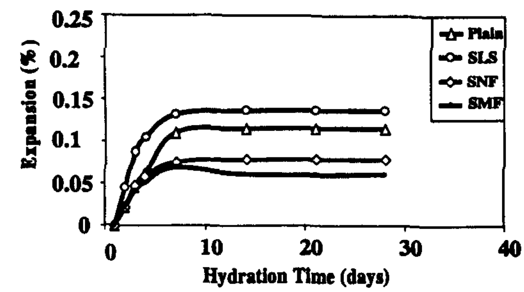

Fig. 2. Effect of surfactants on the expansion of paste mixes containing expansive cement.

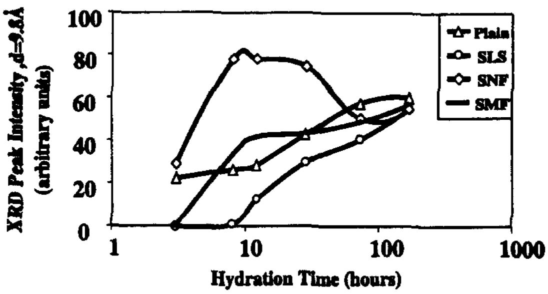

Fig. 3. Effect of surfactants on ettringite formation in expansive cement systems.

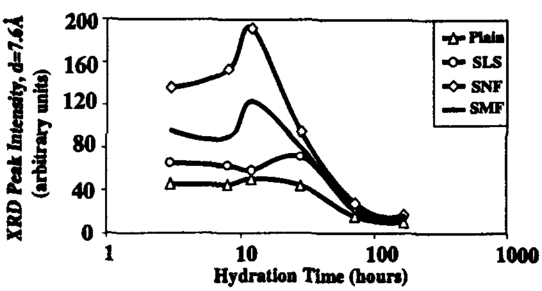

Fig. 4. Effect of surfactants on amount of gypusm in expansive cement systems.

The effect of surfactants on ettringite formation is shown in Fig.3. The XRD intensity of the ettringite peak in the sample with SNF was much higher than that of the plain sample. The amount of ettringite in the system containing SNF increased in first 8 hours, remained essentially constant up to 12 hours and then decreased. The reason is not clear and further study is required. It is apparent that ettringite started to form before 3 hours hydration in the plain and SNF sample, after 3 hours in the SMF sample and after 8 hours in the SLS sample. This would appear to indicate that both SMF and SLS would delay the formation of ettringite in the expansive cement. The ettringite peak intensity values of all samples approached similar values at 3 days, even though the development of the ettringite peak in the SLS sample was slower than the others.

The effect of surfactants on the amount of gypsum present during hydration of expansive cement is shown in Fig.4. The XRD intensity of the gypsum peak (d = 7.6Å) was much higher when surfactants were used. SNF appears to effectively accelerate the formation of gypsum from hemihydrate. SMF and SLS accelerated gypsum formation to a lesser extent. The major increase of the gypsum peak intensity in SNF and SMF samples occurred before 12 hours. The peak intensity subsequently decreased. At 28 hours, the peak intensities of the three samples containing surfactant approached a common value. At 3 days, the content of gypsum in all the samples was similar and relatively low.

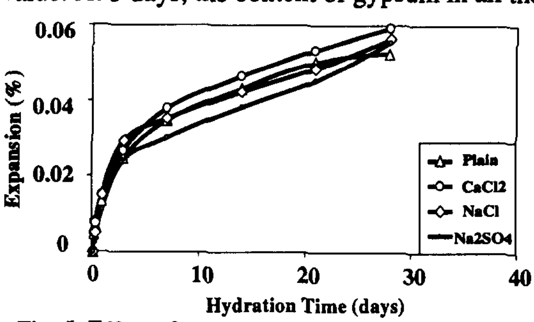

Fig. 5. Effect of accelerators on the expansion of compacted expansive cement samples.

Accelerators

The effect of three inorganic accelerators on the expansion of compacted samples is shown in Fig.5. In general, three different salts had little effect on the expansion of compacted samples. The expansion of the NaCl sample was similar to that of plain sample, while the sample with $CaCl_2$ had a slightly higher expansion than the plain sample. Na_2SO_4 reduced

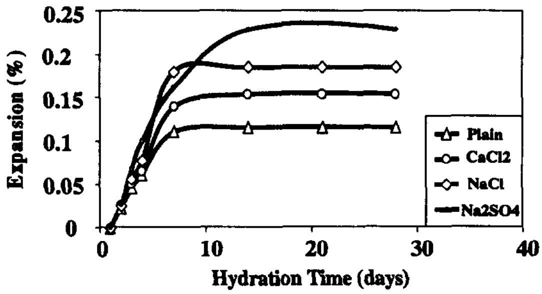

Fig. 6. Effect of accelerators on the expansion of paste mixes containing expansive cement.

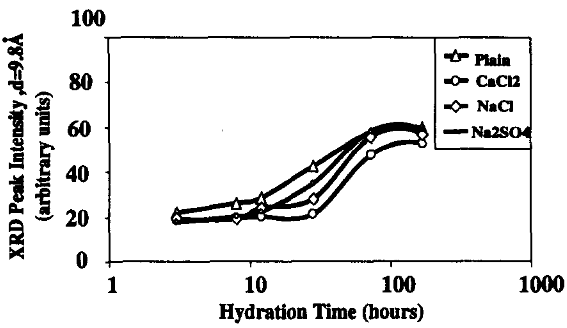

Fig. 7. Effect of accelerators on ettringite formation in expansive cement systems.

expansion during 3 - 20 days but after 28 days the expansion exceeded that of the plain sample.

The effect of these salts on the expansion of paste mixes illustrated in Fig.6. was more significant than for compacted samples. The use of the salts in mixed expansive cement generally results in higher expansion. The major effect generally occurred from 3 to 7 days. The sample containing Na_2SO_4 had the highest ultimate expansion after 14 days. The sample with $CaCl_2$ had a lower expansion value which was slightly higher than that of the plain sample. NaCl specimens had greater expansion than corresponding specimens containing Na_2SO_4 at 7 days. Subsequently the expansion of the sample with NaCl approached a constant value while that with Na_2SO_4 continued to increase.

The effect of accelerators on ettringite formation is shown in Fig.7. All the samples containing accelerators displayed a lower rate of ettringite formation than the plain sample indicating that other factors in addition to ettringite formation are responsible for larger expansions in expansive cement systems containing H-HAC. These salts retarded ettringite formation relative to the reference system. The intensity of the ettringite peak in the $CaCl_2$ sample remained the same at 28 hours as that at 3 hours; the ettringite peak of the sample with Na_2SO_4 and NaCl continued to grow at a low rate. The ettringite peak intensity for all the samples approached a similar value after 3 days.

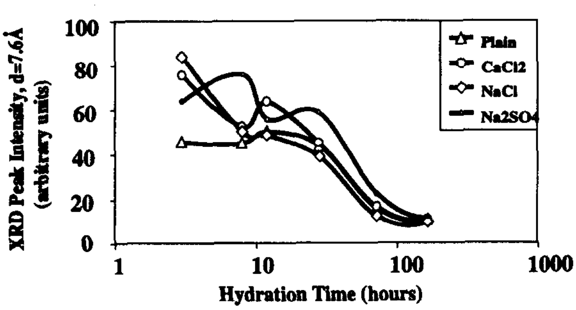

Fig. 8. Effect of accelerators on amount of gypusm in expansive cement systems.

The effect of accelerators on the amount of gypsum present is shown in Fig.8. These accelerators enhanced the formation of gypsum at early ages up to 8 hours. Then the peak height of all the samples became similar. It was difficult to attribute any significance to the differences in gypsum content resulting from addition of these salts. The gypsum content in all the samples was small after 3 days.

Retarders

The effect of retarders on the expansion of compacted samples is shown in Fig.9. A large reduction in expansion resulted when retarders were added to the expansive cement system. Two retarders, sodium citrate and sucrose, had a similar effect on the expansion. The expansion of the sample containing sucrose approached constant value after only 3 days hydration while expansion of that containing sodium citrate developed slowly and continuously. After about 10 days hydration, the expansion of the sodium citrate sample exceeded that of sucrose sample.

Addition of retarders had a different effect on mixed pastes as shown in Fig.10. Sucrose addition still resulted in a strong reduction of the expansion; shrinkage actually occurred after 7 days hydration. The sample containing sodium citrate had reduced expansion up to 4-5 days; it then exceeded the expansion of the plain sample.

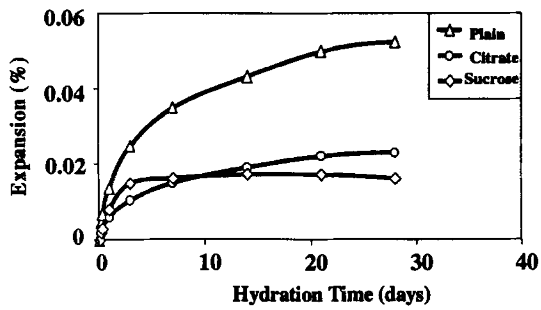

Fig. 9. Effect of retarders on the expansion of compacted expansive cement samples.

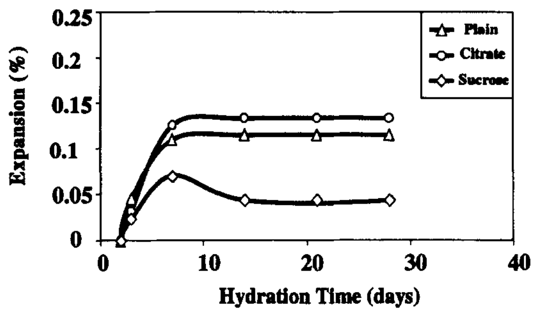

Fig. 10. Effect of retarders on the expansion of paste mixes containing expansive cement.

The effect of retarders on ettringite formation is shown in Fig.11. A strong retardation effect was observed before 3 hours hydration; there was no evidence of ettringite formation. Ettringite was detected between 3 and 8 hours, and then the amount increased very slowly. The ettringite peak heights of the retarded sample were always less than that of the plain sample. A greater amount of ettringite formed in the sucrose sample than in the sodium citrate sample before 28 hours. The intensity value of the ettringite peaks in all the samples was about the same at 3 days.

The effect of retarders on the amount of gypsum formed is shown in Fig.13. The retarders slightly increased the intensity of the gypsum peak at all ages. No significant difference

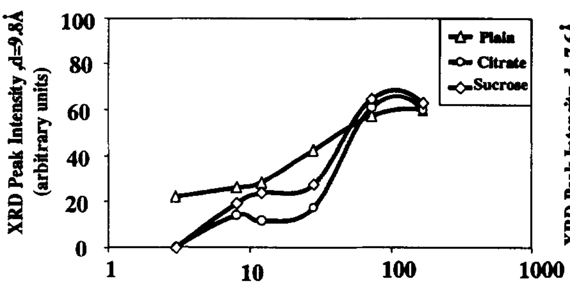

Fig. 11. Effect of retarders on ettringite formation in expansive cement systems.

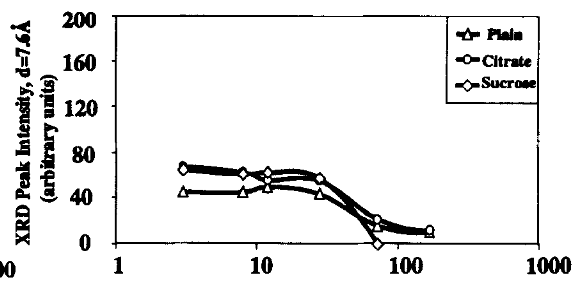

Fig. 12. Effect of retarders on amount of gypusm in expansive cement systems.

of the effect of their addition on gypsum content was observed. The gypsum content of all the samples was very small at 3 days.

Bonding Agent

The effects of an SBR latex bonding agent, on the expansion of compacted and mixed paste samples are shown in Fig.13 and 14, respectively. Latex addition resulted in a decrease in expansion of compacted samples and increased expansion of mixed paste samples. The effects of latex on ettringite formation and gypsum content are shown in Fig. 15 and 16, respectively. Ettringite formation was only slightly reduced in the first 72 hours. Gypsum formation was initially accelerated in the latter sample during the first 8 hours hydration. The peak intensity values were then similar to those of the plain sample. In practice latex - modified cement systems are generally subjected to a drying period in order to facilitate formation of a latex film. In these experiments the specimens were continuously moist cured in order to assess the effect of the latex solution itself on the expansion characteristics of the systems studied.

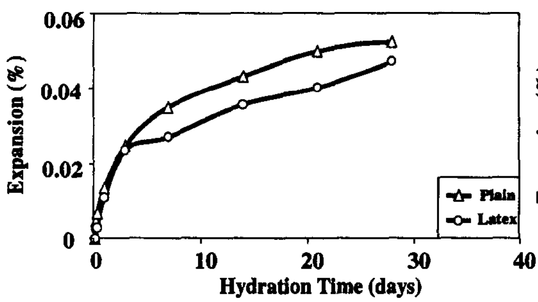

Fig. 13. Effect of a latex bonding agent on the expansion of compacted expansive cement sample.

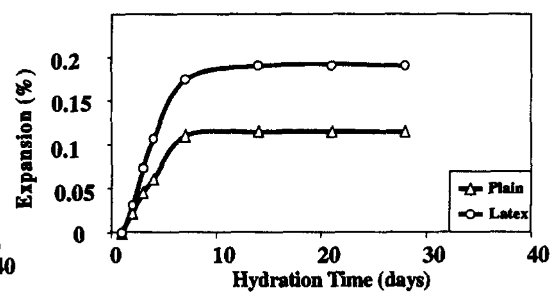

Fig. 14. Effect of a latex bonding agent on the expansion of paste mixes containing expansive cement.

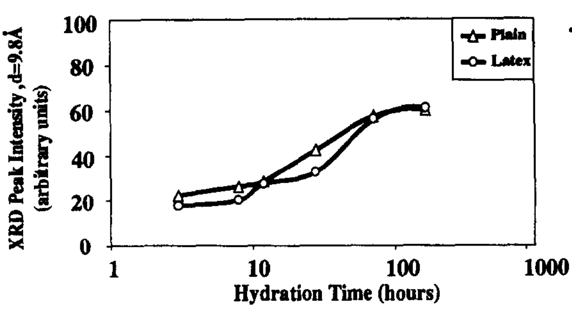

Fig. 15. Effect of a latex bonding agent on ettringite formation in expansive cement systems.

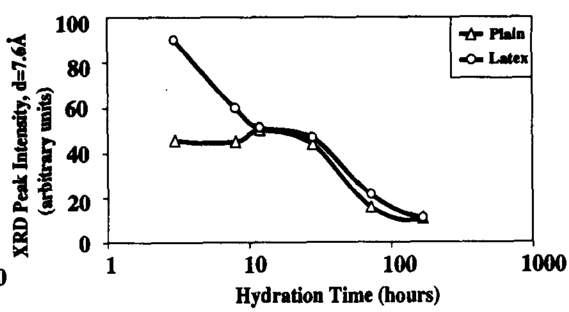

Fig. 16. Effect of a latex bonding agent on amount of gypusm in expansive cement systems.

DISCUSSION

Chemical Interaction and Ettringite Formation

It is apparent from Fig.1, 5, 9 and 13 that only two of the admixtures studied, SNF and $CaCl_2$, have a positive effect on the expansion of compacted systems. This is likely a result of chemical reaction processes involving ettringite formation. SLS, sucrose and sodium citrate retard hydration and reduce expansion, possibly resulting from chemical interaction between the admixtures and expansive cement. Other hydration products in addition to ettringite may form and contribute to the expansion process. These were not identified. The rate of ettringite formation is also affected by presence of admixtures and is likely a factor affecting the amount of expansion. It is known that sodium citrate reacts with calcium hydroxide to form insoluble products e.g. calcium citrate. This reaction lowers the concentration of calcium hydroxide and slows down the formation of ettringite and expansion. Ultimate expansion is not only dependent on the amount of ettringite but also the process of ettringite formation. It also results in formation of a dense coating on expansive components and decreases the hydration rate. SMF also retards ettringite formation but to a less extent than the other retarders. SNF , latex and some inorganic salts ($CaCl_2$, NaCl and Na_2SO_4) appear to have little effect on expansion as a result of chemical reaction and ettringite formation, indicating that the interaction between these admixtures and expansive additives may not significantly affect ettringite formation.

Surface Interaction and Ettringite Formation

The relative expansion of paste mixes and compacted expansive cement systems indicates that different mechanisms of expansion are operative in these two types of samples. Samples containing superplasticizer had the highest expansion for the compacted samples and the lowest expansion for the paste mixes. A possible explanation is attributed to surface interaction. At very early hydration times before setting, the surfactant disperses cement particles resulting in increased reaction surface, accelerated dissolution of Al-bearing materials and SO_3-bearing materials and an apparently elevated rate of ettringite formation. This accelerated ettringite formation consumes a great deal of expansive material at early ages leading to a reduction in the amount of available expansive material at later ages. The total amount of ettringite at later ages is similar for all the samples. A lower ultimate expansion value may be attributed to early formation of ettringite prior to rigid network formation in the paste microstructure. The reduced amount of ettringite subsequently produced would be expected to have a less significant effect on expansion of the system.

Temporary Suppression of Ettringite Formation

Some admixtures that suppress ettringite formation in compacted samples (e.g. SLS and sodium citrate) produce higher expansion in paste mixes. Temporary suppression of ettringite formation prevents expansive material from forming under conditions that induce internal stress in fresh and weak cement paste i.e. prior to continuous structure formation. Thus delayed hydration can help generate expansion effectively. Selection of a suitable retarder and optimum dosage is required.

CONCLUSIONS

1. SNF - type superplasticizer can be used to reduce ultimate expansion in cement containing H-HAC expansive additive by accelerating early ettringite formation and expansion.
2. SMF - type superplasticizer can also be used to reduce expansion in expansive cement containing H-HAC expansive additive by accelerating early ettringite formation and expansion at very early hydration times. Early suppression of expansion through chemical interaction may possibly result in a higher ultimate expansion by addition of an optimum amount of superplasticizer.
3. Sodium lignosulfonate and sodium citrate can be used to control expansion through suppression of ettringite formation at very early hydration ages. Optimization of dosage is required.
4. Sucrose significantly reduces expansion because it restricts the formation of ettringite so effectively that even a very low concentration will result in minimal expansion.

5. Inorganic salts, eg. $CaCl_2$, NaCl and Na_2SO_4, can be used to promote expansion of cement containing H-HAC - based expansive additive. The role of chemical interaction of these salts on the expansion process is not clear. A possible expansion mechanism would attribute increased ultimate expansion to the slight delay of ettringite formation in fresh and weak cement paste.
6. SBR latex - based bonding agents can increase the expansion of cement containing H-HAC - based expansive additive possibly through chemical interaction effects at early ages. Optimization of dosage is required.

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