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IMAGING OF ASR GEL BY SOFT X-RAY MICROSCOPY

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ABSTRACT

The soft x-ray transmission microscope XM-1 was used to examine alkali-silicate reaction (ASR) gel morphology in an experimental investigation of the alkali-aggregate reaction (AAR). The XM-1 microscope is operated by the Center for X-ray Optics on beamline 6.1 of the Advanced Light Source, a third generation synchrotron radiation facility operated by the Ernest O. Lawrence Berkeley National Laboratory. The instrument is unique as samples can be observed wet, with high resolution (43 nm), over time, as chemical reactions proceed. Soft x-ray microscopy was used to examine the in situ reaction of ground ASR gel, obtained from a large dam, and solutions of sodium hydroxide, calcium hydroxide, and combined sodium and calcium hydroxide.

From this investigation, it appears that ASR gel combines with alkalis present in pore solution to produce a reaction gel capable of swelling, while the reaction of the ASR gel in the presence of calcium hydroxide and no alkalis results in the formation of a structure resembling C-S-H. It is theorized that the formation of C-S-H or a related compound will decrease the degree of swelling that would otherwise result from the formation of an alkali-aggregate reaction product. The C-S-H-like structure may also contribute strength. These hypotheses are currently under investigation. © *1998 Elsevier Science Ltd*

Introduction

In concrete, alkali metal ions and hydroxyl ions contributed principally by the cement and reactive silica present in aggregate can participate in a destructive alkali-aggregate reaction (AAR). The product of this reaction is an alkali-silicate reaction (ASR) gel that tends to imbibe water found in the concrete pores, leading to swelling of the gel and eventual cracking of the affected concrete member. Episodes of alkali-aggregate reaction have been reported in concrete structures in nearly every country, but its occurrence is not common, considering that the great majority of existing concrete structures remain unaffected. By a recent

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assessment, alkali-aggregate reaction is active in 104 dams and spillways around the world (1). However, when the reaction does occur, the damage to the structure can be extensive. Because no method presently exists to arrest the expansive chemical reaction and because many features of AAR continue to be poorly understood, the reaction remains the subject of much interest and study.

Currently, little is known about the gel structure and the influence of the product morphology on the gel's capacity for expansion. In particular, microscopic examination of the reaction over time and characterization of its product morphology could lead to greater understanding of the reaction kinetics and the mechanisms of expansion. Observation has been limited by the constraints imposed by currently available microscopy techniques. Most existing techniques available for the examination of concrete microstructure and related reaction products, including AAR products, demand that samples be dried and exposed to low pressure during the observation period. These sample preparation requirements present a major disadvantage for the study of the alkali-aggregate reaction. Given the nature of the reaction and the effect of water on its products, it is likely that the removal of water will affect the morphology, creating artifacts in the sample.

The purpose of this research is to observe and characterize the alkali-aggregate reaction in situ at high resolution without introducing sample artifacts. Unconditioned samples were observed over time by soft x-ray microscopy without drying and at standard pressure conditions. Thus, the microstructure of the sample is unaffected and can be observed and recorded intact.

The purpose of this paper is to present new research concerning the effect of pore solution cations, namely sodium and calcium, on the product formed as a result of alkali attack. The alkali-silicate reaction gel studied in this investigation was obtained from a large dam experiencing distress from the AAR. After a brief review of the chemistry of the reaction, results of in situ observation of the reaction will be reported and characterization of the reaction products will be discussed.

Alkali-Aggregate Reaction in Concrete

Alkali-aggregate attack of the siliceous aggregate is initiated at aggregate surfaces exposed to the alkaline pore solution in concrete. As a result, a crystalline, densely structured silica network, such as quartz, is more resistant to attack as compared to an open-structured silicate, such as opal. Mehta and Monteiro (2) have listed silicates in a decreasing order of reactivity as: opal, obsidian, cristobalite, tridymite, chalcedony, cherts, cryptocrystalline volcanic rocks (andesites and rhyolites), and strained or metamorphic quartz.

Ions present in the pore solution, including hydroxyl, sodium, potassium, and calcium ions, can more freely penetrate a poorly crystalline structure as compared to a dense, ordered silicate structure. The attack is initiated by hydroxyl ions that rupture Si-O-Si bonds, loosening the network and producing Si-O^- species. Cations abundant in the pore fluid are attracted to these sites of negative charge and become incorporated into the alkali-aggregate reaction gel. In addition, calcium ions react with silica species in solution to form calcium silicate hydrate (C-S-H) (3,4). It should be noted that the solubility of silica has been found to increase sharply at a pH greater than 10 (5–7). The high alkalinity of the concrete pore solution (pH typically measures 12.5–13.1 when produced with low alkali cement and may measure 13.5–13.9 when produced with high alkali cement) suggests that silica dissolves to a discernible degree in the concrete environment, and the dissolved species are available for further reaction with species present in solution. Silica dissolution and the reaction of silica with pore solution cations will described in greater detail in subsequent sections of this paper.

Thus, four distinct reactions comprise alkali-aggregate attack of siliceous aggregates in concrete (3):

1. dissolution of silica in the aggregate by hydroxyl attack;
2. reaction of surface silanol (Si-OH) groups with hydroxyl ions $(OH)^-$ in the solution to further promote dissolution;
3. binding of the alkali cations (Na^+, K^+) and calcium cations (Ca^{2+}) at negatively charged sites on the silicate surface; and
4. reaction of silicate species in solution with calcium ions in solution to form calcium silicate hydrate (C-S-H).

ASR gel capable of expanding is believed to be produced by Reactions 1–3 listed above (8,9). The gel formed by the reaction of silica and alkalis tends to imbibe water and swell, generating expansive strains. In the presence of a sufficient amount of water, the induced strains will surpass the tensile capacity of the concrete, and the affected members will crack. As a result of this damage, the member will experience a loss of strength, particularly in flexure, and a decrease in stiffness—material properties essential to ensure the integrity and performance of the structure under service loads.

Pessimum Proportion

It has been established that hydroxyl attack promotes the dissolution of silica (3,5). Once the saturation concentration of dissolved silica in a local environment has been reached, repolymerization of dissolved silica into a gel, containing silica as well as water and alkalis, begins. The gel is much less dense than the structure from which the silica was originally dissolved. Thus, the ongoing processes silica dissolution and repolymerization in the presence of a sufficient amount of water will produce expansion associated with ASR.

Dent Glasser and Kataoka (3) have identified a ratio of silica gel concentration to volume of 0.05 M or 0.7 M NaOH solution (SiO_2/Na_2O) where gel expansion reaches a maximum. This research demonstrated the existence of a "pessimum proportion" for expansion associated with ASR. At the pessimum proportion, the ratio of silica to alkali concentrations is optimized to produce the greatest expansion through silica dissolution and repolymerization where alkalis are incorporated into the product gel which tends to imbibe water.

The influence of mole ratio of SiO_2 to K_2O or Na_2O on the degree of connectivity, or polymerization, of potassium silicate solutions was investigated by Zanni et al. (10) using ^{29}Si nuclear magnetic resonance (NMR) spectroscopy. At a mole ratio = 0.3 of SiO_2 to K_2O, which is below the pessimum proportion, monomeric, dimeric, and cyclic silica species, along with chains of silica tetrahedra and tertiary networks, were identified. At higher molar ratios, quaternary silica networks were identified. As the ratio of SiO_2 to K_2O is increased from 0.1 to 4.5, the transition from the ionic state to the colloidal state of the potassium silicate solution was found to progress with the mean degree of connectivity increasing sharply at ratios greater than 2.0.

Effect of Calcium Cations

The effect of calcium cations on the alkali-aggregate reaction, as described above as Reaction 4, has been the subject of much scrutiny. Powers and Steinour (8,9) have postulated that the ratio of calcium ion to alkali ion concentrations in the concrete controls the expansion produced by the gel. If the calcium ion concentration is high as compared to the alkali ion concentration, Powers and Steinour (8,9) expect a non-swelling lime-alkali-silica complex to result from the reaction of the silica and calcium cations. Conversely, according to the Powers-Steinour theory, when the ratio of calcium to alkali ion is low, a swelling alkali-silica complex will result. In a similar vein, Prezzi et al. (11) have proposed a model based on Gouy-Chapman double layer theory to explain the expansion caused by alkali-aggregate reaction in concrete. According to the theory, ions with a larger valence will result in a thinner double layer, causing comparatively smaller gel expansion. This suggests that the greater the concentration of bivalent calcium species, relative to monovalent sodium and potassium species, the smaller the expansion in concrete. Wang and Gillot (12) have supported the Powers-Steinour theory that the lime-alkali-silica gel is non-swelling, but argue that the presence of excess calcium hydroxide promotes the alkali-aggregate reaction. The authors suggest that calcium ions may replace alkalis in the product gel, essentially releasing the alkalis into solution to attack reactive silica at additional sites, resulting in further expansion. While the precise effects of each cation species on the gel product remain speculative, it appears that relative concentrations of cation species present in concrete pore solution are expected to affect the expansion of the alkali-aggregate reaction gel in some way.

Spectroscopic examination of the gel product may provide information about the effect of cations on the gel structure and expansion. Cong and Kirkpatrick (13) have conducted ^{29}Si magic angle spinning NMR spectroscopy that has shown that the gel produced by the reaction of silica gel in alkaline solution is amorphous, while the gel produced by the reaction of silica gel in alkaline solution in the presence of calcium hydroxide contains calcium-bearing polymerizations of silica similar to C-S-H. These findings are in agreement with Reaction 4 (above) described by Dent Glasser and Kataoka (3,4).

Experiment

The behavior of alkali-silica reaction (ASR) gel exposed to alkaline solutions is examined by x-ray microscopy. By observing the product morphology, information concerning the role of pore solution cations, specifically sodium and calcium, on the reaction and the product's potential for expansion will be gained.

Sample Preparation

Samples consisted of finely ground particles of ASR gel obtained from the FURNAS dam, located in Minas Gerais, Brazil on the Rio Grande. Construction of the concrete dam was begun in 1958 and completed in 1963. Symptoms of alkali attack on the quartzite aggregate were first documented in 1995. The ASR gel was sampled from three different locations in the galleries of the FURNAS dam. A chemical analysis of the ASR gel from each site is presented in Table 1. The ASR gel samples used in this investigation were transparent and

TABLE 1
Composition by mass of alkali-aggregate reaction gel.

	Site 1 (%)	Site 2 (%)	Site 3 (%)
Loss on Ignition	26.63	17.11	10.92
SO_3	0.01	0.28	—
MgO	0.15	0.10	2.63
SiO_2	56.40	61.18	68.72
Fe_2O_3	0.40	0.22	0.31
Al_2O_3	0.48	0.35	7.72
CaO	0.56	1.64	1.62
MnO	0.02	0.01	0.01
Na_2O	0.81	1.00	1.44
K_2O	14.06	16.82	16.32
Alkali Equivalent	10.06	12.07	11.52

originally ~1 cm long each. The ASR gel acquired from the dam was ground by hand to a mean size of 300 sieve.

To study the influence of calcium ions and alkalis on the ASR gel, the ground gel was exposed to three solutions: a) saturated calcium hydroxide solution, b) 0.05 M sodium hydroxide solution, and c) saturated calcium hydroxide solution + 0.01 M sodium hydroxide. Results obtained by Dent Glasser and Kataoka for the reaction of silica gel in 0.05 M NaOH (3) and in saturated $Ca(OH)_2$ + various concentrations of NaOH (4) were used as guidelines for the selection of the above solutions and concentrations.

All solutions were made from deionized, low resistivity (17.8 MΩ·cm) water and reagent-grade chemicals and were stored in sealed nalgene flasks until used. The calcium hydroxide solutions were discarded after 8 h to avoid carbonation. The saturated calcium hydroxide solution was used to study the exclusive effect of calcium cations on the ASR gel. The pH of the saturated $Ca(OH)_2$ solution measured 12.4. The sodium hydroxide solution was used to study the exclusive effect of alkalis on the ASR gel. The pH of the 0.05 M NaOH solution measured 12.6. Finally, the combined effects of calcium cations and alkalis were examined by introducing the gel to a solution of saturated $Ca(OH)_2$ + 0.01 M NaOH. The pH of this combined solution was 12.6. Solutions were filtered to 0.2 μm prior to introduction to the ASR gel.

Finely ground particles of the ASR gel were dusted across a silicon nitride (Si_3N_4) observation window. Wet samples were prepared by placing a 2 or 3 μL drop of solution onto the window containing the ASR gel particles. A second silicon nitride window was placed on top of wet samples, and the chamber was sealed to prevent leakage.

In addition, other samples were prepared by adding pessimum proportion (SiO_2/Na_2O = 3) of the ASR gel to prepared 0.05 M sodium hydroxide solution. The pessimum proportion samples were prepared with 0.05 M solution instead of the 0.7 M solution (an alkali concentration more representative of concrete pore solution) because excessive surface tension between the brittle silicon nitride windows was generated when drops of the higher molarity solution were placed between the windows. The pessimum proportion samples were stored in sealed polyethylene vials. Samples were observed periodically by placing a 2 or 3 μL drop of the ASR gel/solution suspension onto a silicon nitride window, and wet chambers were prepared in the manner described above.

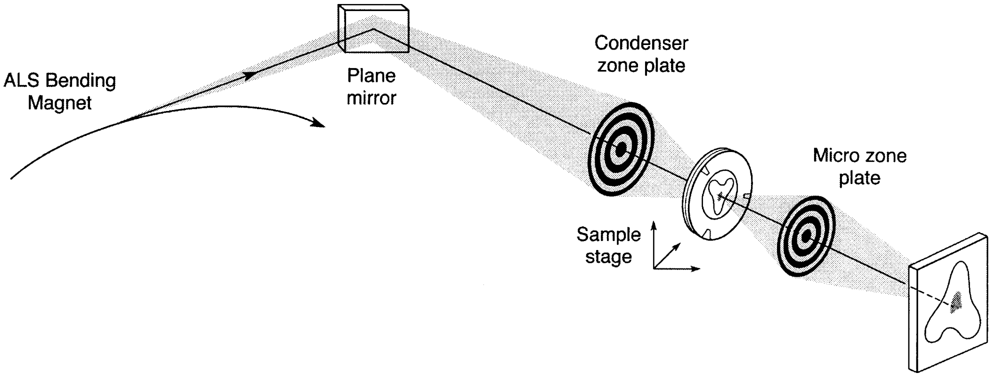

FIG. 1.
Schematic of the soft x-ray transmission microscope XM-1 used for these studies.

It should be noted that the solid/solution ratio used in these studies was much greater than would be typically found in concrete. Such a large ratio was necessary to produce samples that were highly penetrable by x-rays.

Observation Technique

Experiments were conducted at the soft x-ray transmission microscope XM-1, which is built, operated, and maintained by the Center for X-ray Optics (CXRO) at the Advanced Light Source (ALS) at the Ernest O. Lawrence Berkeley National Laboratory. The instrument uses a condenser zone plate lens to focus bending magnet radiation in the soft x-ray regime through a monochromator pinhole onto the sample (14). A schematic representation of the instrument in depicted in Figure 1. After passing through the sample, the x-rays are focused by a micro-zone plate lens onto a CCD camera which takes images of the sample. The instrument achieves a resolution of 43 nm and allows imaging of samples up to 10 μm thick in water (15).

Samples were observed at a wavelength of 2.4 nm and at a magnification of 2400×. Exposure times measured 1 to 180 s. Samples were observed dry and after the addition of the alkaline solution. The effect of the solution on the samples was documented over time, from 5 min. after adding the solution to 2 weeks after adding the solution to the ground ASR gel.

Results of Experiment

X-ray microscopy images of the dry, ground ASR gel show that the particles are of irregular shape, with clearly defined edges (Fig. 3a). No evidence of crystalline structure was apparent from the examination of the dry ASR gel. The amorphous nature was confirmed by X-ray diffraction under CuKα radiation of a mixture of the three samples where sharp peaks were absent from the diffraction pattern of the ASR gel (Fig. 2). The diffraction pattern and chemical composition of the ASR gel did not appear to correspond to those of any substance described in the literature.

A suspension of ASR gel in 0.05 M NaOH solution was prepared according to the

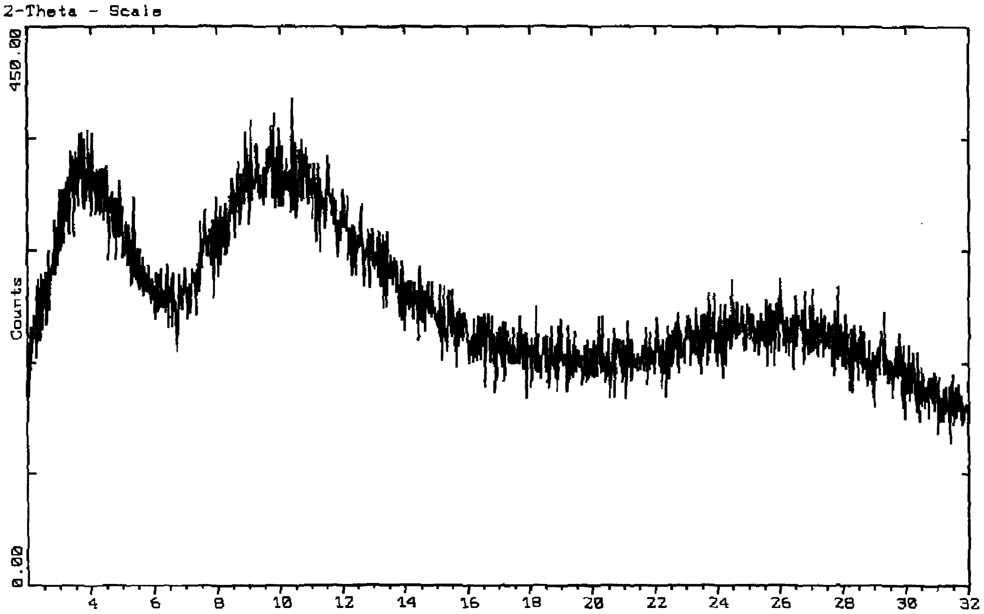

FIG. 2.
X-ray diffraction of ground ASR gel from FURNAS dam, Brazil.

pessimum ratio $SiO_2/Na_2O = 3$ described by Dent Glasser and Kataoka (3). X-ray microscopy images taken 1 h after mixing show the gel sample to be dispersed in the solution across the silicon nitride sample-window. Gel particles remain irregular, but the edges are not as clearly defined as when dry (Fig. 3f). While the interior or central regions of the original particle remains dense, edges of the of the particle are more transparent to x-rays. In addition, the area near the center of the original particle appears to have no discernible internal structure, while the cloud-like forms around the perimeter of the particle appear to have regions of varying density. A qualitative examination of these images suggests that the particle has begun to dissolve at its surface and to repolymerize while exposed to the sodium hydroxide solution.

To examine the effect of calcium cations on the gel in solution, the ASR gel was dusted across a silicon nitride window and a drop of saturated calcium hydroxide solution was introduced. Reaction products were visible 3 to 5 min. after the saturated calcium hydroxide solution was added to the ASR gel. The reaction appeared to stabilize in about an hour, with no changes in the reaction products visible after that time. The products were characterized by dendritic growth of lath-like structures in a spherulitic pattern, exhibiting symmetry about two axes. Structures recorded in Figures 3b and 3c exhibit such symmetry with fine, lathlike structure visible within the distinctive “sheaf of wheat” morphology. Over time, the individual sheaf of wheat structures tended to aggregate into clusters in the presence of calcium hydroxide solution. Such a cluster is shown in Figure 3d.

Again, the ASR gel was dusted across a silicon nitride window. A drop of saturated calcium hydroxide solution containing 0.01 M sodium hydroxide was introduced. The reaction product appeared to be a combination of the products observed in the previous

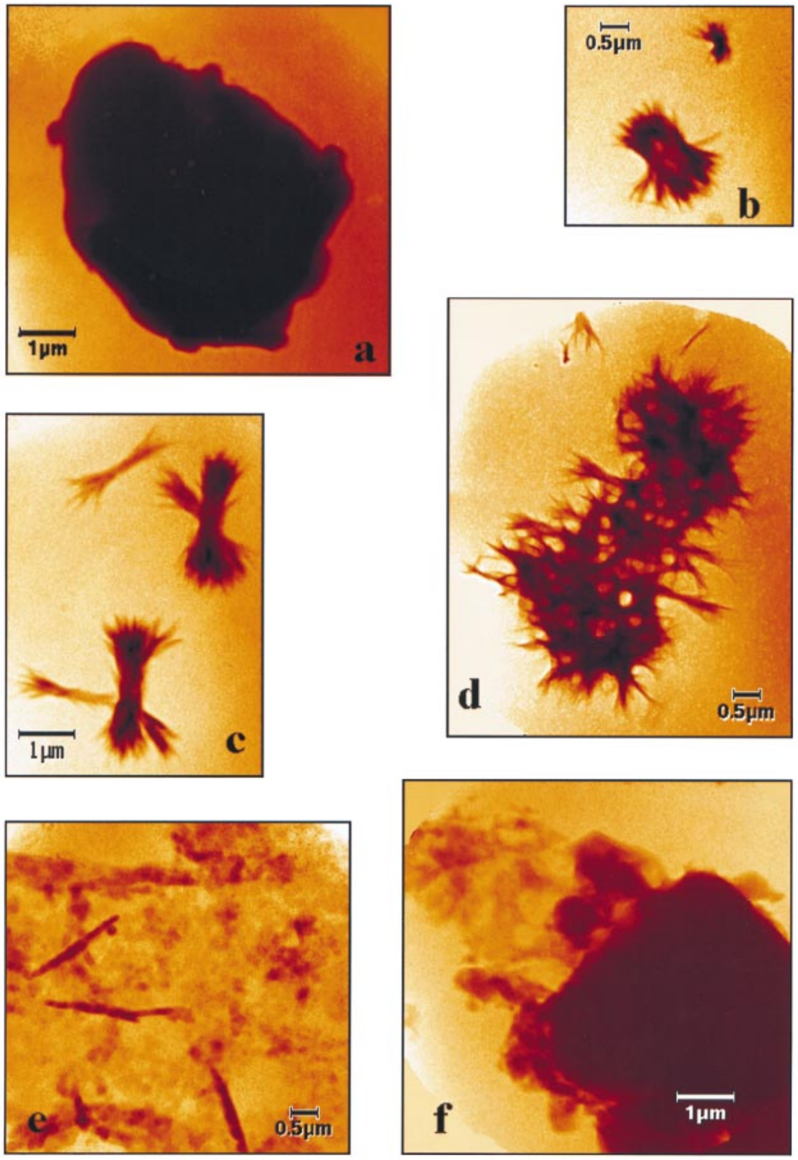

FIG. 3.
(a) X-ray image of dry, ground ASR gel from FURNAS dam, Brazil. (b) X-ray image of ASR gel in saturated $Ca(OH)_2$ solution after 30 minutes. (c) X-ray image of ASR gel in saturated $Ca(OH)_2$ solution after 30 minutes. (d) X-ray image of ASR gel in saturated $Ca(OH)_2$ solution after 2 hours. (e) X-ray image of ASR gel in saturated $Ca(OH)_2$ + 0.01M NaOH solution. (f) X-ray image of ASR gel in 0.05M NaOH solution after 1 hour.

solutions (Fig. 3e). The product appeared to be less dense than when dry and contained dispersed slender lath-like structures. This product morphology suggests that the silica dissolved to some extent, reacted to some degree with the aqueous calcium cations to form the lath-like structures, and repolymerized and aggregated.

Discussion

Indications of dissolution and repolymerization are consistent with the mechanisms described in Reactions 1–2 described previously. Dissolution is initiated at the surface, as suggested by comparing Figure 3a of the dry, ground ASR gel with Figure 3f of the ASR gel reacting in the sodium hydroxide solution. Areas of decreased density located at the perimeter of the particle (Fig. 3f) suggest that the silica network, originally dense and less pervious, has become less ordered, allowing the ions in the surrounding solution to permeate more freely into the silicate network. As described previously, the solubility of silica increases greatly at pH values greater than about 10. However, because of low diffusivity in the sample (as in concrete), the area near the site of dissolution may reach its saturation concentration for a given pH value. As a result, the silica repolymerizes, incorporating sodium and potassium cations into the alkali-silica reaction gel. The repolymerized gel appears to be significantly less dense than the original silicate. Dent Glasser and Kataoka identified a pessimum mole ratio of SiO_2/NaO for chemical grade silica gel where the expansion associated with ASR reaches a maximum (3). At ratios slightly less than and slightly greater than this pessimum amount, the expansion is less. Samples included in this investigation were prepared according to this proportion, and the dissolution and repolymerization of the ASR gel can be interpreted as an expansion due to attack by alkalis.

The highly structured products formed in the calcium hydroxide solution contrast greatly with the unstructured products formed in the sodium hydroxide solution. Largely, the products resulting from the reaction of the silica species and the calcium ions alone (Figs. 3b, 3c, and 3d) in this investigation resemble structures described by Rashed (16) and Williamson (17). Rashed reported similar microstructure while examining the reaction of silica fume in concrete by scanning electron microscopy (SEM), supporting Taylor's (18) theory that the pozzolanic reaction and the alkali-aggregate reaction may be similar. In addition, the spherulitic sheaf of wheat morphology was found to form during bottle hydration of dicalcium silicate (C_2S) and tricalcium silicate (C_3S) (17). This characteristic microstructure appears to result from the reaction of silica species and calcium cations in the presence of water in locations of relative emptiness, which would allow such extensive crystal growth. The samples prepared for this investigation were of high solution-to-solid ratio, which would provide ample space for product growth. It is not certain whether the reaction product is formed by a through-solution or topochemical reaction, but a through-solution process is indicated. The ASR gel particles dissolved completely in the calcium hydroxide solution, and products formed freely (i.e., not on the surface of an existing solid) and were initially well dispersed. In fact, no particles of the ground gel were observed after the addition of calcium hydroxide solution.

The branched structure is thought to be a precursor to calcium silicate hydrate (C-S-H). The effect of the formation of a C-S-H or its precursor is not certain. However, it has been theorized that this product would not produce swelling (8,9). In addition, it is uncertain if such a reaction product could provide additional strength to a concrete member experiencing alkali-aggregate reaction. If this hypothesis is confirmed, it could provide a basis for a methodology to control the expansive alkali-aggregate reaction in concrete.

Reaction between the ASR gel and the sodium hydroxide solution did not result in the formation of highly ordered structures with a tendency to flocculate, as seen with the reaction of the gel in calcium hydroxide solution. Instead, reaction with sodium hydroxide produced relatively less dense, cloud-like forms, which remained widely dispersed. This suggests that of the cations studied in this investigation, it is the alkalis in concrete pore solution that produce the expansive ASR gel, while reaction with calcium ions does not result in expansion. This is consistent the theories presented by Powers-Steinour (8,9), and Prezzi et al. (11).

Conclusions

The research presented here is an attempt to integrate surface chemistry and concrete technology to gain a greater understanding of the alkali-aggregate reaction. Four fundamental reactions which comprise the alkali-aggregate reaction were examined. These reactions can be summarized as the dissolution of silica in alkaline solution, the adsorption of alkalis onto silica gel, and the reaction of aqueous silica species with calcium ions to form C-S-H.

A novel x-ray microscopy technique, using the XM-1 transmission microscope operated by CXRO, was used to examine the reaction of ground ASR gel, obtained from a Brasilian dam, and sodium hydroxide, calcium hydroxide, and combined sodium and calcium hydroxide solutions. Reaction of the ASR gel in sodium hydroxide solution resulted in surface dissolution and repolymerization of the ASR gel. Reaction of the ASR gel with calcium hydroxide solution produced spherulitic structures resembling the distinctive "sheaf of wheat" morphology. Reaction of the ASR gel with the combined solution produced dissolution and repolymerization of the gel with some lath-like formations resulting from the reaction of calcium cations and dissolved silica. From this investigation, it appears that reactive silica combine with alkalis present in pore solution to produce a reaction gel capable of swelling, while the reaction of the silica in the presence of calcium hydroxide and no alkalis results in the formation of a structure resembling C-S-H. The effect—beneficial or detrimental—of the growth of this reaction product is under investigation.

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