Chemical Changes Associated with Expansion due to Alkali Silica Reaction: Results from Room-Temperature Mortar Bar Experiments

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Abstract

Recent research concerning the alkali silica reaction in our group has provided significant new insight into the sequence of chemical reactions that occur during the alkali silica reaction (ASR) and the structure of the alkali-silica gel. The relationship between gel formation and expansion and cracking of concrete and mortar, however, is still poorly understood. We describe here experimental results for mortar bars made with silica glass aggregate monitored under ASTM C1260 conditions but at room temperature rather than 80°C. For these specimens, substantial expansion occurred well before alkali-silica gel was observed using XRD, optical microscopy, and ^{29}Si MAS NMR. Detailed SEM-EDS analysis, however, revealed the presence of a Na-Ca-Si gel in progressively developing crack-like features in the aggregate. The results confirmed the association of gel and expansion, demonstrate that significant expansion can occur prior to extensive reaction of the cement paste with silica released by alkali attack on the aggregate, and suggested that under these conditions the rate of transport of alkalis, water and calcium to the gel is much faster than transport of silica away from the site of aggregate dissolution. SEM observations confirmed the depletion of portlandite and chemical variation of Ca/Si ratio at the interface of alkali-silica gel and cement paste in some places in the mortar, indicating the applicability of the chemical model proposed previously by our group for ASR occurring in mortar.

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1. Introduction

The alkali silica reaction (ASR) is one of the most important mechanisms of concrete deterioration and causes severe infrastructure damage worldwide. Damage due to ASR is the result of the complex interaction of chemical and mechanical processes. The traditional view is that ASR involves the reaction of metastable forms of silica in the aggregate with the alkaline pore solution in the hydrated cement paste to form a hydrous alkali (K,Na) silicate gel that may imbibe water and expand to such an extent that it cracks and destroys the concrete. Earlier work by Hou et al. in our group based on reactions of aggregate and alkali solution provided significant new insight into the sequence of chemical reactions and the structure of the ASR gel [1,2], although the relationship between development of ASR gel in mortar and concrete and expansion and cracking is still poorly understood. This earlier work included a chemical reaction model involving ASR gel formation only after dissolved silica has reacted fully with any CH to form C-S-H and after C-S-H has converted to a Si-rich form. To verify the applicability of this chemical model in mortar and also investigate chemical and microstructural relationships in ASR, we set up mortar bar experiments at room temperature using the ASTM C1260 protocol with silica glass aggregate that showed significant early (<60 days) expansion correlated with only small amounts of gel detectable by SEM-EDX but not by XRD or ^{29}Si MAS NMR. The silica glass was chosen because it does not have the internal porosity of other highly reactive aggregates (e.g., opal), allowing for somewhat greater resolution of gel and aggregate by SEM-EDX and thus better understanding of its microstructural development.

2. Experimental Methods

2.1 Sample Preparation

The expansion experiments were carried out according to the ASTM Standard Test Method for Potential Alkali Reactivity of Aggregates (Mortar-Bar Method) (ASTM C 1260), but were done at room temperature instead of 80°C in order to reduce the reaction rate and more effectively simulate field conditions. Companion mortar specimens were used for chemical and microstructural studies: x-ray diffraction (XRD), optical microscopy, scanning electron microscopy (SEM), and ^{29}Si MAS NMR. Because Fe in ordinary portland cement can significantly degrade the ^{29}Si NMR signal, a type I white cement (Lehigh cement company) with 0.15% total alkali (as Na_2O equivalent) was used. The mortars contained either silica glass (Vycor glass from Corning Glass Co.) as a reactive sand or crystalline quartz (Ottawa sand from US Silica Co.) as a non-reactive sand.

For each mortar, about 440 g of cement were mixed with 990 g of sand in a paddle mixer. To produce the required water/cement ratio of 0.47, 206.8 g of deionized water were introduced along with 3.73 g of solid NaOH to increase the alkali content from 0.15% to 0.8%. Each mortar was mixed for several minutes and then cast into standard bars.

Six bars were made, three with Vycor glass and three with Ottawa sand. The mortar bars were pre-cured in their molds at 100% relative humidity for one day, demolded, and cured in deionized water for one additional day. The bar lengths were measured, and they were then immersed in 1N NaOH solution at ~23°C. Samples for chemical and microstructural examination were cut from one bar of each type at selected time intervals. The samples for NMR and XRD were ground to a powder, immersed in acetone overnight to stop hydration, and then stored in a desiccator over calcium sulfate until they were analyzed. Samples for optical thin sections and SEM were heated at 105°C for 24 hours, stored in a vacuum for several weeks, and then vacuum-impregnated with epoxy and polished. The lengths of the other two bars of each type were measured during this time to obtain expansion data. At each time each bar was measured twice and the results averaged.

2.2 Sample Examination

Powder XRD patterns of mortar samples were recorded using a Rigaku Rotaflex diffractometer under the following conditions: 40 kV, 40 mA, Cu-Kα radiation (λ=1.5406 Å), and graphite crystal monochromator. The samples were scanned in steps of 0.02° (2θ) in the range from 3° to 50° using a count time of 3 s per step under ambient conditions of temperature and relative humidity.

The ^{29}Si MAS NMR spectra were obtained using a General Electric GN300WB spectrometer (H_0 = 7.05 T) and a 7-mm Chemagnetics MAS probe. The single pulse spectra were obtained at room temperature with 90° pulse durations of 5.5 μs, relaxation delays of 50 s, MAS frequency of ~6 kHz, and 500 transients. The ^{1}H-^{29}Si cross polarization (CP) MAS NMR spectra were obtained at room temperature using the same instrument with 90° pulse durations of 6 μs, relaxation delays of 2 s, contact times of 5000 μs, MAS frequencies of ~5.5 kHz, and 500 transients. In all cases the chemical shifts were referenced to external tetrakistrimethylsilane (TTMS) at -9.9 ppm. After acquisition, the free induction decays were treated following standard procedures using the NMR Utility Transform Software (NUTS, Acorn NMR software).

SEM-EDX examination was performed using a JEOL 6060LV scanning electron microscope with an energy-dispersive X-ray spectrometer (EDX). The working distance was 10 mm, optimized for EDX. The accelerating voltage was 20-30 kV and the diameter of the interaction volume was nominally ~4 μm. Optical microscopy used a Nikon Labophot-pol microscope equipped with both transmitted and reflected light optics and a digital image capture system.

3. Results and Interpretation

3.1 Expansion Data

The Vycor mortar bars showed significant expansion beginning at 4 days and increasing to ~0.5% at 60 days (Fig.1). Vycor is known to be highly reactive to ASR, and the observed expansion is expected even at room temperature due to the continuous supply of Na^+ from the external NaOH solution. In contrast, the reference mortar bars made with Ottawa sand aggregate showed almost no expansion up to 60 days (0.01%).

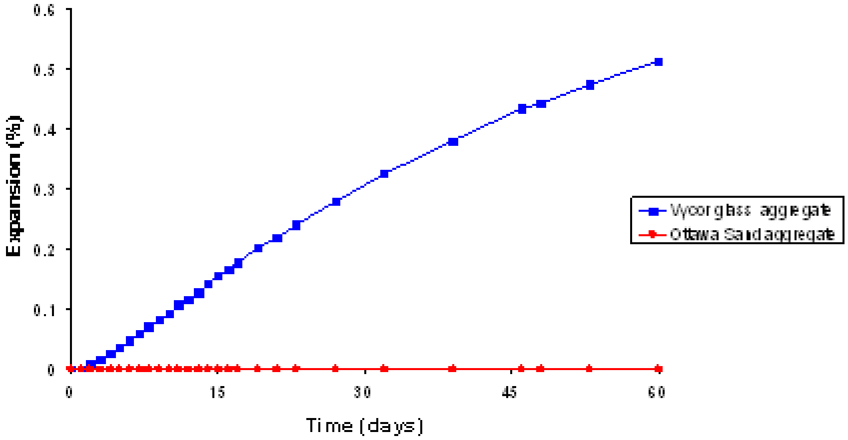

Figure 1. Expansion of mortar bars

3.2 XRD

The XRD patterns of the mortars containing Vycor glass (Fig. 2) show the expected changes due to cement hydration, but no detectable loss of Portlandite (CH) that would indicate its consumption due to reaction with dissolved silica from the aggregate [1]. The 2-day sample shows the presence of CH at ~18° 2θ and 34° 2θ, unhydrated cement (alite and belite) at ~32° 2θ, AFt at ~9° 2θ, AFm at ~10.5° 2θ, and Vycor glass indicated by the broad peak centered at ~22° 2θ. The small peak at ~29° 2θ may indicate the formation of C-S-H. With increasing reaction time, the relative intensity for CH did not change significantly, whereas the peaks for unhydrated cement decreased and the peak attributed to C-S-H increased due to progressive hydration. The XRD patterns of the Ottawa sand mortar bars were essentially the same, except that peaks for quartz replaced the broad glass peak centered at ~22° 2θ (data not shown).

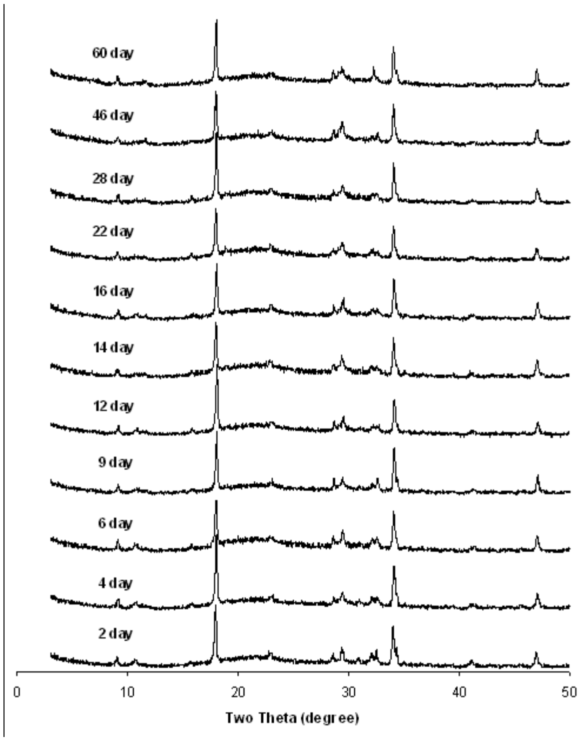

Figure 2. XRD patterns of Vycor mortar bars

In summary, the XRD patterns demonstrated deceasing unhydrated cement, formation and increase of C-S-H, and the consistent presence of CH, AFt and AFm with increasing reaction time. Based on reactions of aggregate and alkali solution, Hou et al. [1] proposed that ASR gel does not form until local pozzolanic consumption of portlandite is complete. The absence of CH consumption in conjunction with significant expansion in the current study appears to be inconsistent with the proposed model.

3.3 ^{29}Si NMR Spectroscopy

The ^{29}Si MAS NMR spectra of the Vycor mortar (Fig. 3) showed little evidence for changes in C-S-H polymerization or a Q^3 resonance for ASR gel, consistent with the XRD results. Only the spectrum of the 60 day sample showed a resolvable increase in the relative intensity of the C-S-H Q^2 resonance, indicative of increased average polymerization, and a small, poorly resolved shoulder near –90 ppm that might be attributable to ASR gel. As in previous studies, the resonances at about –72 (narrow and broad components), -79, -84 and -110 ppm can be readily assigned to the unhydrated cement, Q^1 and Q^2 of C-S-H, and Vycor glass, respectively (Fig.3A) [3]. With increasing reaction time, the relative peak intensities showed the well-known sequence of consumption of the Q^0 sites of unhydrated cement phases and production of the Q^1-dominated C-S-H. However, no change was observed to indicate conversion of Q^1- to Q^2-dominated C-S-H, except perhaps at 60 days.

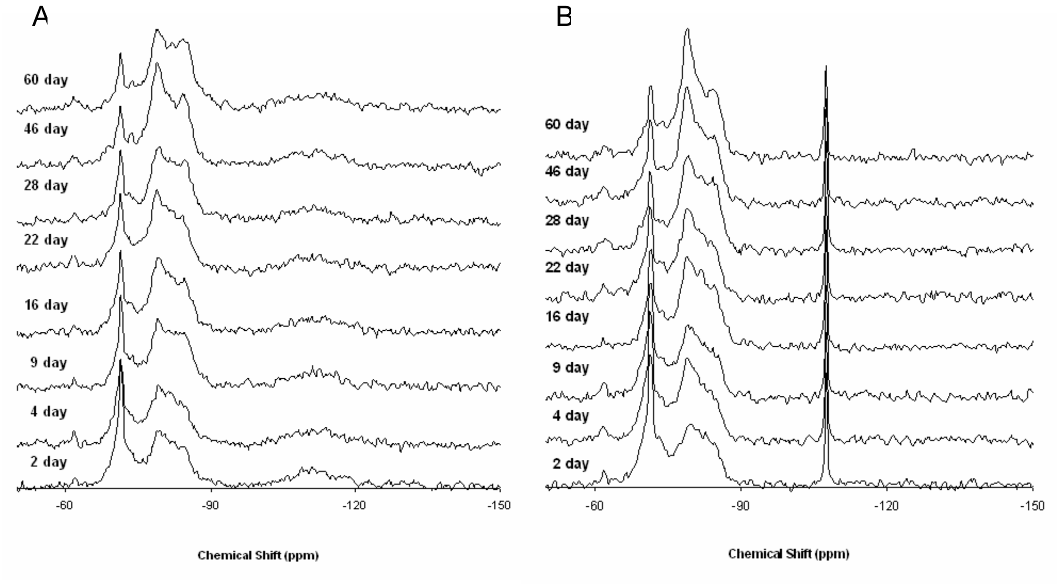

Figure 3. ^{29}Si NMR spectra of Vycor (A) and Ottawa sand (B) mortar bars

The relative intensity of the broad peak centered near -110 ppm due to the Q^4 sites of Vycor glass decreased with increasing reaction time, suggesting progressive ASR attack of the glass. The intensity of this peak cannot be quantified due to its extremely long T_1 relaxation time. None of the samples yielded a well-resolved resonance near -90 to -95 ppm that would represent Q^3 Si sites in ASR gel [1,2], even though there has been significant expansion. Similarly, the ^{1}H-^{29}Si cross polarization (CP) MAS NMR spectra (not shown) did not show a resolvable Q^3 peak near –95 ppm for ASR gel. As for the XRD results, the absence of a Q^3 resonance for ASR gel and changes in the C-S-H polymerization in the current study appears to be inconsistent with the proposed model [1] that ASR gel does not form until conversion of high-Ca- C-S-H to low-Ca C-S-H is complete.

The ^{29}Si MAS NMR spectra of the Ottawa sand mortar bar samples are very similar to those of the Vycor glass samples, except that the broad Q^4 peak for glass is replaced by a narrow Q^4 peak for quartz at –107 ppm and the Q^1/Q^2 ratio of the C-S-H at 60 days is higher. (Fig.3B). The absence of a Q^3 peak for ASR gel in the Ottawa sand mortars is expected due to the non-reactivity of this aggregate.

3.4 Optical and SEM-EDS Examination

Taken together, the absence of clearly observable consumption of CH in the XRD patterns and the lack of an increase in the Q^2/ Q^1 ratio in the C-S-H and final Q^2 dominated structure in C-S-H and a Q^3 resonance for ASR gel in the NMR spectra, suggest either that the amount of ASR gel was below the detectability limits of these methods or that our ability to analyze the gel is more limited in mortar than in aggregate-solution mixtures. It is interesting to note that in work not yet published, we have observed that in mortars cured at 80°C considerably more gel is produced than observed here and that expansion is roughly coincident with gel formation as observed by NMR. Detailed optical microscopy and SEM-EDS examinations (described below) showed that ASR gel was present within Vycor glass grains but not in the cement paste, that the amount of ASR gel increased with increasing expansion, and that the gel contained Na and considerable Ca even though it was confined to the interior of the glass. Thus expansion was in fact related to formation of gel, but under the conditions here the gel was present in small amounts and was confined to the interiors of the aggregate grains. Optical and SEM examination of the Ottawa sand mortar bar samples did not show the presence of ASR gel or other features associated with expansion, as expected.

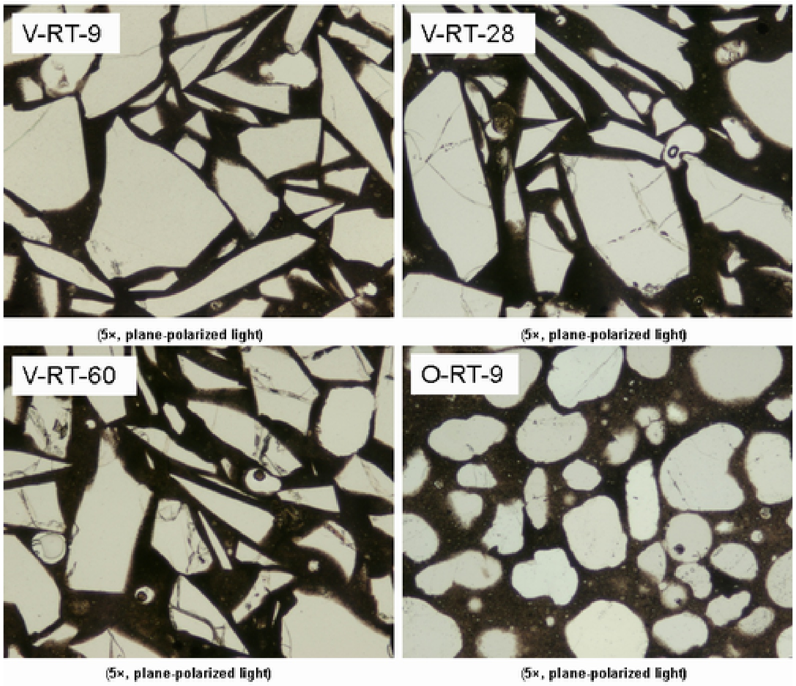

Figure 4. Optical micrographs of mortar bar samples: Vycor 9 days, Vycor 28 days, Vycor 60 days and Ottawa sand 9 days

Optical microscopy of the Vycor mortar showed progressive development of curved, crack-like features within the Vycor grains from 9 to 60 days (Fig.4), although clear resolution of ASR gel within these features was not possible with method. The crack-like features in the Vycor grains were about 1 to 7 μm wide, and the width increased with increasing reaction time. We use the term crack-like feature, rather than crack, because we argue below that these features do not appear to be the result of fracturing by mechanical stress but are more likely to be due to chemical attack of the glass, perhaps in combination with mechanical stress. As expected, the Ottawa sand mortar showed no features that can be related to cracking or expansion (Fig.4).

Examination by SEM-EDS provides more detailed microstructural and chemical information at higher magnification and resolution, and for our samples provided much more detailed information about the ASR gel and its development than the other techniques used. The SEM-EDS analysis of the Vycor mortar clearly confirms the formation of ASR gel within the crack-like features in the Vycor grains and shows that the gel contained both Na and Ca. In the 9-day sample, crack-like features ~1-2 μm across were present in some Vycor grains. Many of these individual features varied in width, and some were associated with cavities up to approximately 3 μm across (Fig. 5). In many places, especially where they were thinner, the crack-like features were empty; but in other places they contained gel that EDS showed to contain Na and Ca (Fig.5). Often the gel did not fully fill the opening, suggesting significant loss of volume due to drying.

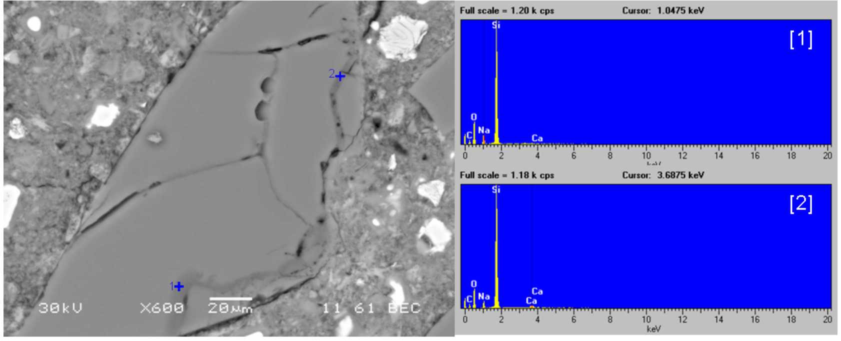

Figure 5. SEM micrograph with EDS spectra showing ASR gel in the 9-day Vycor glass mortar

At higher magnification, very small cracks, about 1 μm wide, were observed in the cement paste. Some of these cracks were parallel to external surfaces of Vycor grains, but some were at a high angle to the Vycor surface and were closely associated with the ASR gel in Vycor grains. No ASR gel was found in the cement paste. The cracks not obviously associated with ASR gel were probably due to drying shrinkage.

With increasing reaction time, more crack-like features developed in the Vycor grains, and the largest widths increased from approximately 2 μm at 9 days to 7 μm at 60 days (Fig.6).

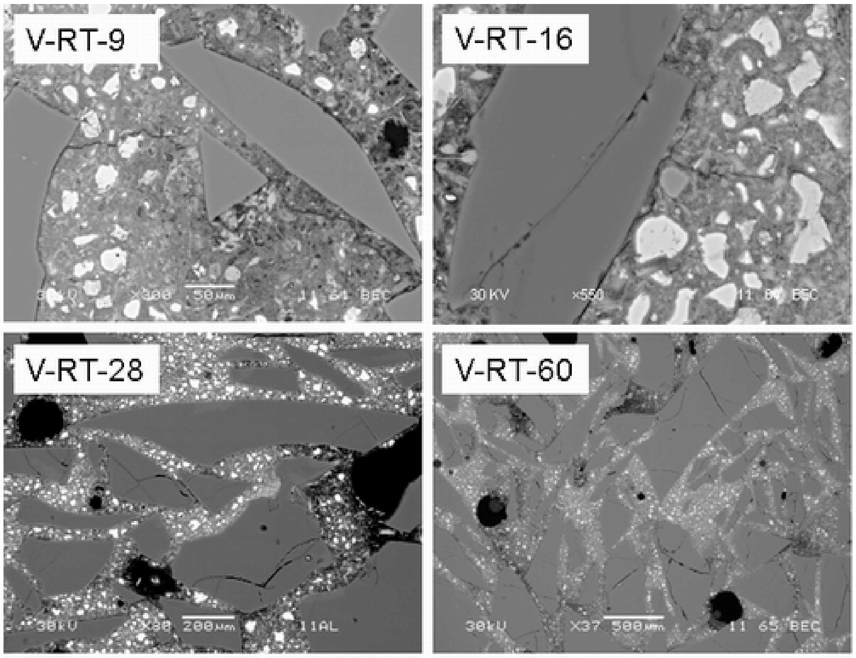

Figure 6. SEM BSE images of Vycor mortar bar samples at 9, 16, 28, and 60 days

For the 60-day sample, the relative intensities of the Na and Ca peaks in the EDS spectra suggest increasing incorporation of these elements in the gel compared with that in younger samples (Fig. 7). The EDS data also show that the Ca content of the ASR gel is consistently higher close to the paste than deeper into Vycor grain interiors.

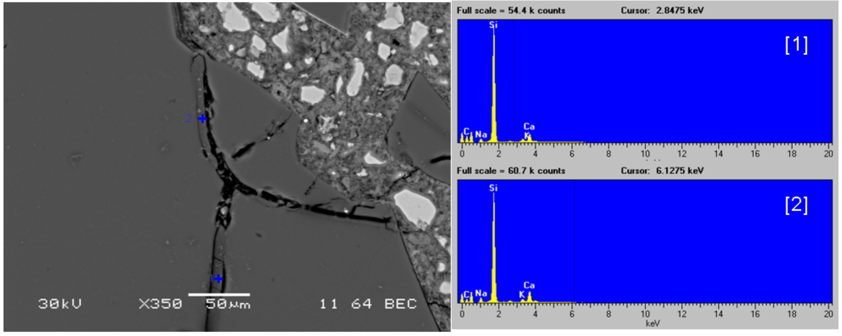

Figure 7. SEM micrograph with EDS spectra showing ASR gel in the 60-day Vycor glass mortar

In contrast with the XRD and NMR results, SEM micrographs of some samples clearly showed local consumption of CH and decreasing Ca/Si ratio in C-S-H moving away from the Vycor surface where ASR gel was in contact with the cement paste. At some positions, CH had been consumed locally in paste that was in contact with ASR gel (Fig.8 and 9). In other cases, EDX analyses of paste showed that the C-S-H near ASR gel had a relatively lower Ca/Si ratio than that in the bulk paste, suggesting local reaction with silica released by alkali attack of the aggregate (Fig. 10 and 11).

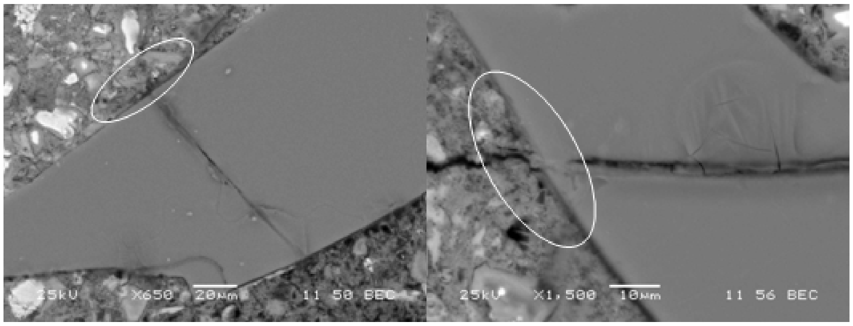

Figure 8. SEM micrograph of the 28-day Vycor glass mortar bar showing the depletion of CH (circled area)

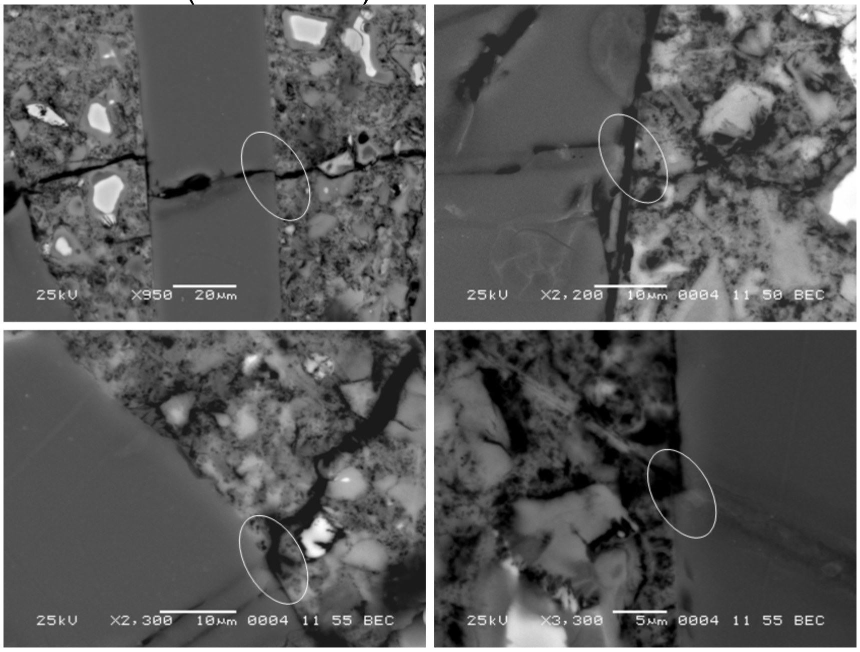

Figure 9. SEM micrograph of the 60-day Vycor glass mortar bar showing the depletion of CH (circled area)

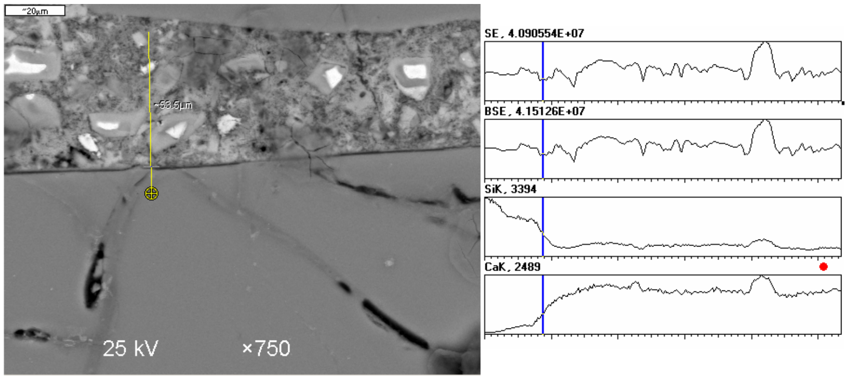

Figure 10. SEM micrograph of Vycor 28-day sample showing the line scanning results of C-S-H phase

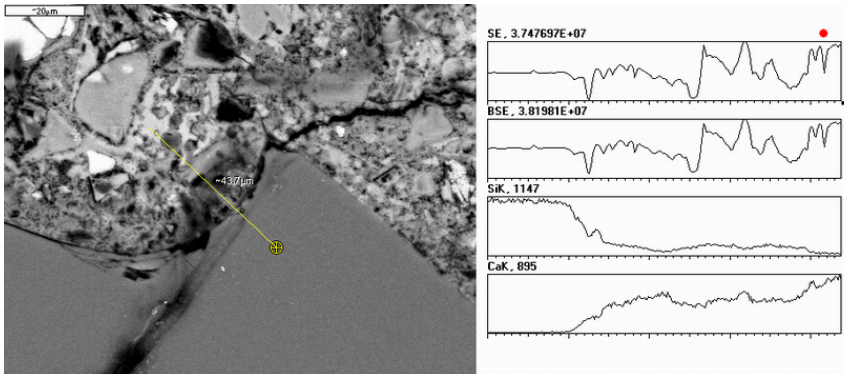

Figure 11. SEM micrograph of Vycor 60-day sample showing the line scanning results of C-S-H phase

4. Discussion

In the ASR chemical reaction sequence proposed by Hou et al. [1], ASR gel does not form until the silica in solution generated by alkali attack on the aggregate first reacts fully with any CH with which it is in chemical communication to form C-S-H and any C-S-H with which it is in chemical communication is first converted to a Si-rich C-S-H. At the ambient conditions here, the results show that sufficient gel can be generated to cause significant expansion without evidence of extensive reaction with the cement paste. However, the presence of Ca in the ASR gel and its general increase with increasing reaction time do indicate reaction with the paste and migration of Ca from the paste, and support the idea that Ca plays very important role in the formation of expandable gel [1,4-6]. The increase in the Q^2/Q^1 of the C-S-H at 60 days also suggests detectable reaction of C-S-H with released silica by that time. More importantly, the SEM observations clearly show local reduction in both the amount of CH and the Ca/Si ratio of C-S-H, which were not indicated by the bulk XRD and NMR analyses. Those results are consistent with the proposed chemical model of Hou et al [1]. and in turn may indicate its applicability in mortar system.

On the other hand, the overall results demonstrate that it is possible to have significant mortar expansion due to relatively small amounts of ASR gel confined in the aggregate grains. Detailed microstructure-based transport, chemical reaction and mechanical modeling are needed to fully understand the complex interplay of alkali and calcium migration, water migration, silica dissolution and migration, CH and C-S-H reaction, ASR gel formation and expansion, and deformation of the cement paste. Our observations provide a basis for this modeling using a well-constrained model system. Qualitatively, the results suggest that the rate of transport of Na, water and Ca to the site of gel formation within the aggregate grains is significantly faster than transport of dissolved silica away. However, the reasons for this observation remain incompletely understood.

5. Conclusions

The progressive increase in number and width of the crack like features in the Vycor glass aggregate, their weak association with cracks in the cement paste, their irregular widths, and the larger pits on many of them, all in the absence of an applied external load, suggest that they are not due to fracturing under stress but to chemical attack of the glass. Their widening and propagation may be aided by expansive stresses within the aggregate grains due to incorporation of water into the gel. The results demonstrated that significant ASR expansion can occur prior to extensive reaction of the cement paste with silica released by alkali attack of the aggregate, and suggested that under these conditions transport of alkalis, water and calcium to the gel is much faster than transport of silica away from the site of aggregate dissolution. The detailed SEM-EDS analysis confirmed the local consumption of CH and reduction in Ca/Si ratio at the interface of ASR gel and cement paste, indicating the applicability of previously proposed chemical model in a more complex mortar system.

Acknowledgments

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