Microstructural Studies of Alkali-Silica Reaction in Fly Ash Concrete Immersed in Alkaline Solutions

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This article presents expansion and microstructural data for a series of concrete mixes containing reactive flint aggregate, with a range of fly ash levels, exposed to various alkaline salt solutions. This study was undertaken to determine whether fly ash has any influence on alkali-aggregate reaction beyond changes in pore solution chemistry; in these tests the external source of alkalis should neutralize pore solution effects. Fly ash was found to be effective in reducing expansion even after extended periods (44 months) of exposure in 1N NaOH at 80°C, notwithstanding the presence of abundant reactive silica and an inexhaustible supply of alkali hydroxides. Higher levels of ash (40%) prevent damaging expansion and cracking in this environment despite considerable evidence of reaction. In some cases, flint grains had been completely removed by dissolution. The addition of $Ca(OH)_2$ *at the mixing stage was found to increase the expansion of all the concretes; the effect on concrete with 40% ash was most marked, the expansion increasing by nearly 20 times. The most noticeable difference between deteriorated control specimens (no ash) and concrete with 40% ash was the formation of a calcium-alkali-silica rim on certain flint grains in concrete without ash. Such particles were invariably sites of expansive reaction with cracks emanating from them. The absence of such a feature in concrete with 40% ash is probably linked to the reduction in* $Ca(OH)_2$ *at the cement-aggregate interface. It is possible that the formation of this reaction rim produces expansive forces itself or acts as a semi-permeable membrane preventing diffusion of alkali silicate solution from the reaction site, thereby leading to osmotic pressure generation. Regardless of the actual mechanism, the presence of* $Ca(OH)_2$ *appears to be critical for the development of expansion due to alkali-silica reaction. It was observed that the alkalis of the reaction product were distributed in bands. In the Portland cement concrete specimens, the distribution of the gel consisted of a high calcium reaction rim at the aggregate-cement interface with a sodium-rich silica gel adjacent to it, followed by a potassium-rich silica gel. The potassium-rich silica gel appears to have a crystalline, needle-like structure, whereas the sodium-rich silica gel is amorphous. In fly ash concrete specimens in which the formation of calcium-rich reaction rim was prevented, it was observed that the sodium-rich gel had diffused into the surrounding cement matrix, and the potassium-rich gel had remained within the original aggregate boundary.*

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It is well established that the use of fly ash as a partial replacement for Portland cement in concrete is an effective means for controlling expansion due to alkali-silica reaction (ASR). However, the precise mechanisms by which fly ash suppresses expansion are poorly understood, and the role of ash has been variously attributed to the following: (1) reduction in pore solution alkalinity, (2) reduced availability of calcium, and (3) refined pore structure leading to reduced ionic mobility and water permeability.

Pore solution studies have shown the effect of fly ash on the alkalis available in solution to vary depending on the composition of the ash, level of replacement, age of sample, and alkali content of the cement. Diamond [1–3] demonstrated that the Class F ash generally reduces the pore solution alkalinity in proportion to its level of replacement, i.e., the ash acts as an inert diluent. However, other work [4,5] has shown fly ash to have a positive effect (on reducing alkalinity) beyond that of mere dilution, especially at later ages and when blended with high alkali cement.

Pore solution composition is a critical parameter in alkali-aggregate reactions, but there is evidence that many other factors influence the resulting expansion in concrete containing supplementary cementing materials such as fly ash. Fly ash has been shown to be effective in controlling the expansion of concretes (and mortars) immersed in alkaline salt solutions [6–9], where the effects of pore solution alkalinity are apparently neutralized by the external source of alkalis. It has been demonstrated that the addition of CaO can induce expansion in concretes containing fly ash [10] or silica

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TABLE 1. Chemical analyses of cementitious materials

	SiO_2	Al_2O_3	Fe_2O_3	CaO	SO_3	K_2O	Na_2O	Na_2O_e
OPC	20.6	5.10	3.10	64.5	2.53	0.73	0.15	0.63
Fly ash	53.8	27.8	8.84	2.49	3.60	3.54	1.13	3.46

fume [11]. Alternatively, Chatterji [12] showed that expansion could be prevented by either leaching $Ca(OH)_2$ out of Portland cement concrete or by use of a very low cement content (and thus low $Ca(OH)_2$ content) prior to storing in alkaline solutions. In the latter case, silica gel was observed oozing out of concrete without evidence of any expansion. He also found the use of a highly reactive pozzolan equally effective in alkaline environments.

Various mechanisms have been proposed to explain the dependence of damaging reaction on $Ca(OH)_2$. Chatterji [13] suggested that expansion occurs in concrete when the net amount of material entering a reactive silica grain (K^+, Na^+, Ca^{2+}, OH^-) exceeds the amount of material leaving the grain (Si^{4+}). The calcium concentration in the pore solution surrounding the grain controls the rate of diffusion of silica away from the reactive site, and at high levels of calcium the migration of silica is prevented leading to expansion. Wang and Gillott [11] suggested that $Ca(OH)_2$ acts as a "buffer" to maintain a high concentration of OH^- ions in solution, but also provides Ca^{2+} ions that exchange for Na^+ and K^+ ions in expansive alkali-silica gels to produce nonexpansive calcium-alkali-silica gels. The Na^+ and K^+ ions are thus liberated to produce further damaging reaction.

In an earlier study by Thomas et al. [14], alkali-silica gel was found in fly ash concretes with no associated expansion or cracking. The composition of this gel was found to be different from the gel found in cracks in comparable Portland cement concretes (without fly ash). It was postulated that the gel formed by the reaction between cement alkalis and reactive silica in the aggregate was initially low in calcium and high in alkali. This gel is relatively fluid and readily disperses into the cement paste. In plain concrete the alkali in the gel may be replaced by calcium, producing a more viscous product that is less able to dissipate when it swells on contact with water. Hence, the swelling of the high calcium gel may lead to tensile stresses developing in the concrete, leading to disruption. The lower availability of calcium in the fly ash concrete, due to reduced $Ca(OH)_2$ content, prevents the formation of the damaging form of gel. Consequently, the gel remains in a fluid state and disperses through the pore structure rather than creating internal stresses.

There is conflicting evidence in the literature concerning the effect of chemical composition on the swelling characteristics of calcium-alkali-silicate gels. Powers and Steinour [15,16] postulated that the ratio of lime to alkali determined the type of reaction product formed. At low concentrations of $Ca(OH)_2$ an expansive alkali-silica product is formed, but if sufficient $Ca(OH)_2$ was present, a nonexpansive calcium-alkali-silica complex is formed. Struble and Diamond [17,18] suggested that this explanation was an oversimplification and produced synthetic gels containing calcium that were shown to be swelling. Conversely, gels without calcium varied in free swelling behavior.

This study examines the effect of fly ash on the expansion and microstructure of concrete containing reactive aggregate after immersion in various alkali-salt solutions for extended periods of time (up to 3 years).

TABLE 2. Concrete mix details and expansion results

Mix	Lime Content[1] (kg/m^3)	TV Content[2] (% agg.)	Fly Ash Content[3] (%)	Final Expansion at 2–3 Years (%) 1M NaOH at 80°C (a)	3M NaCl at 50°C (c)	1M Na/KOH at 38°C (b)
L1	0	25	0	1.233	0.027	0.889
L2	90			1.690	0.012	1.266
L3	0	25	25	0.430	0.023	0.004
L4	90			0.960	0.022	0.118
L5	0	35	0	1.683	0.012	0.883
L6	90			2.715	0.010	1.533
L7	0	0	0	−0.007	0.004	−0.015
L8	90			−0.012	0.021	−0.014
L9	0	25	40	0.031	0.000	0.004
L10	90			0.582	0.042	0.060
L11	0	100	0	0.120	0.007	0.017
L12	90			0.934	0.005	0.737

Note: [1]Lime > 95% $CaOH_2$ (by TGA); [2]reactive Thames Valley aggregate blended with "inert" carboniferous limestone; [3]cementitious material content (OPC + fly ash) = 450 kg/m^3.

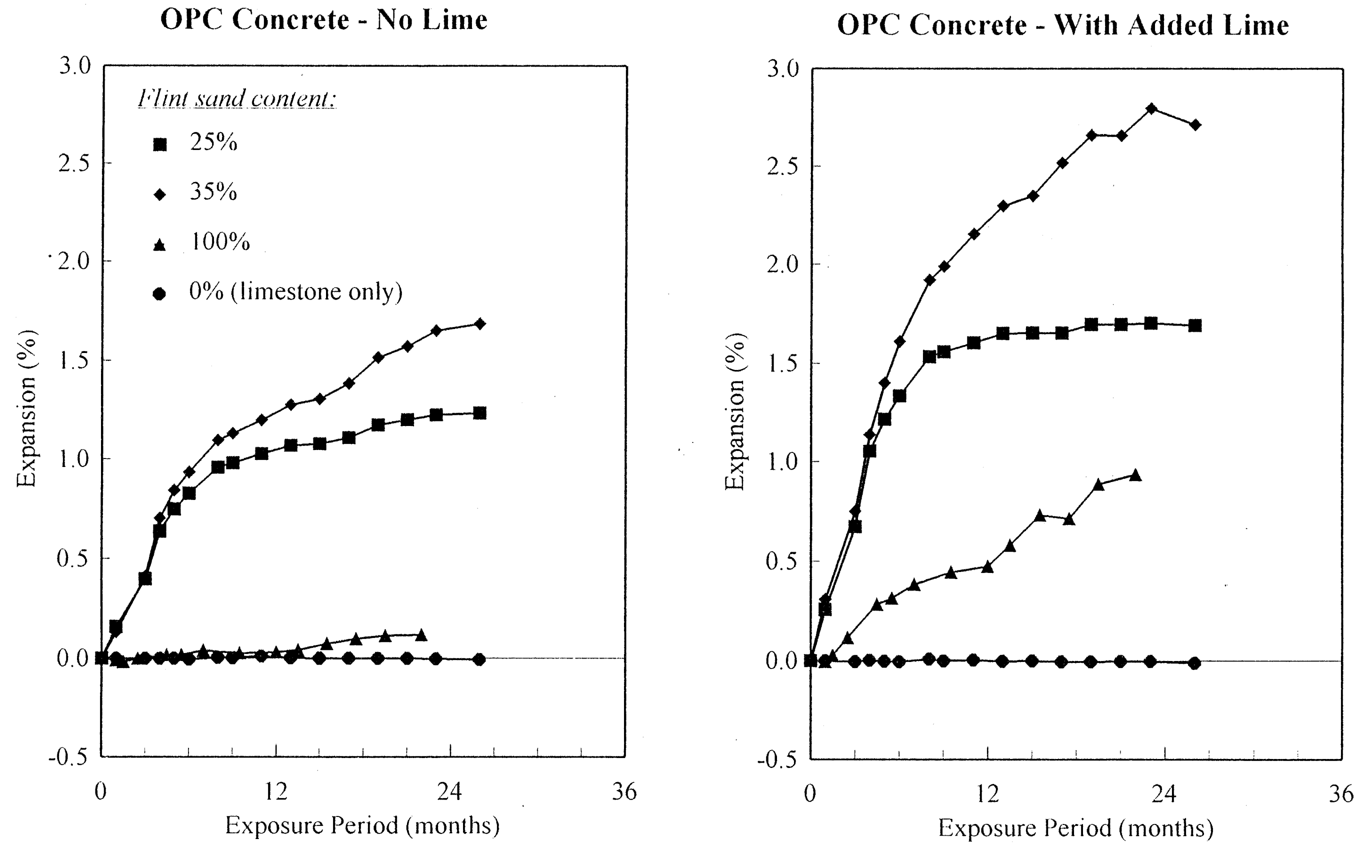

FIGURE 1. Effect of lime on the expansion of ordinary Portland cement (OPC) concrete stored in 1M NaOH at 80°C.

The use of alkaline host solutions was intended to neutralize any pore solution effects due to the presence of fly ash, thereby allowing other effects to be examined.

Experimental Methods

Materials

Concretes were cast using a low alkali Portland cement (0.63% Na_2O_e) and a low lime, bituminous fly ash; chemical analysis data are given in Table 1. A reactive sand from the Thames River valley was used. This sand was composed of 50% flint with lesser amounts of quartz, meta-quartzite, and carbonates. Previous experience has shown that maximum concrete expansion occurs when the flint content is approximately 10–15% of the total aggregate [19]. For most tests, the sand was blended with a carboniferous limestone (coarse and fine aggregate) such that the "pessimum" proportion of Thames Valley sand was achieved (i.e., 25% sand or 12.5% flint by mass of total aggregate). The total silica content of the limestone was less than 1.0% and the material is considered to be nonreactive. In some cases, the reactive sand was combined with reactive gravel from the same quarry to make up 100% of the concrete aggregate.

Concrete Mixes and Curing

Twelve concrete mixes were cast with 450 kg/m^3 cementitious material (ordinary Portland cement [OPC] + fly ash) and a water/cementitious material ratio of 0.6. Selected mixes were cast with 90 kg/m^3 of calcium hydroxide in addition to the cementitious material. Details of mixes are given in Table 2.

From each mix, concrete prisms (50 × 50 × 200 mm) were cast with stainless steel inserts for expansion measurements and cylinders (50 × 100 mm) for chemical and microstructural analysis. After demolding for 24 hours, concrete specimens were sealed in polyethylene bags and stored at 38°C.

Exposure Conditions

After 28 days of curing, specimens were placed in one of the following exposure conditions:

(a) 1M NaOH at 80°C
(b) 0.5M NaOH + 0.5M KOH (i.e., 1M OH^-) at 38°C
(c) 3M NaCl at 50°C.

Solution (a) was selected to represent the conditions used in the NBRI [20] accelerated mortar bar test.

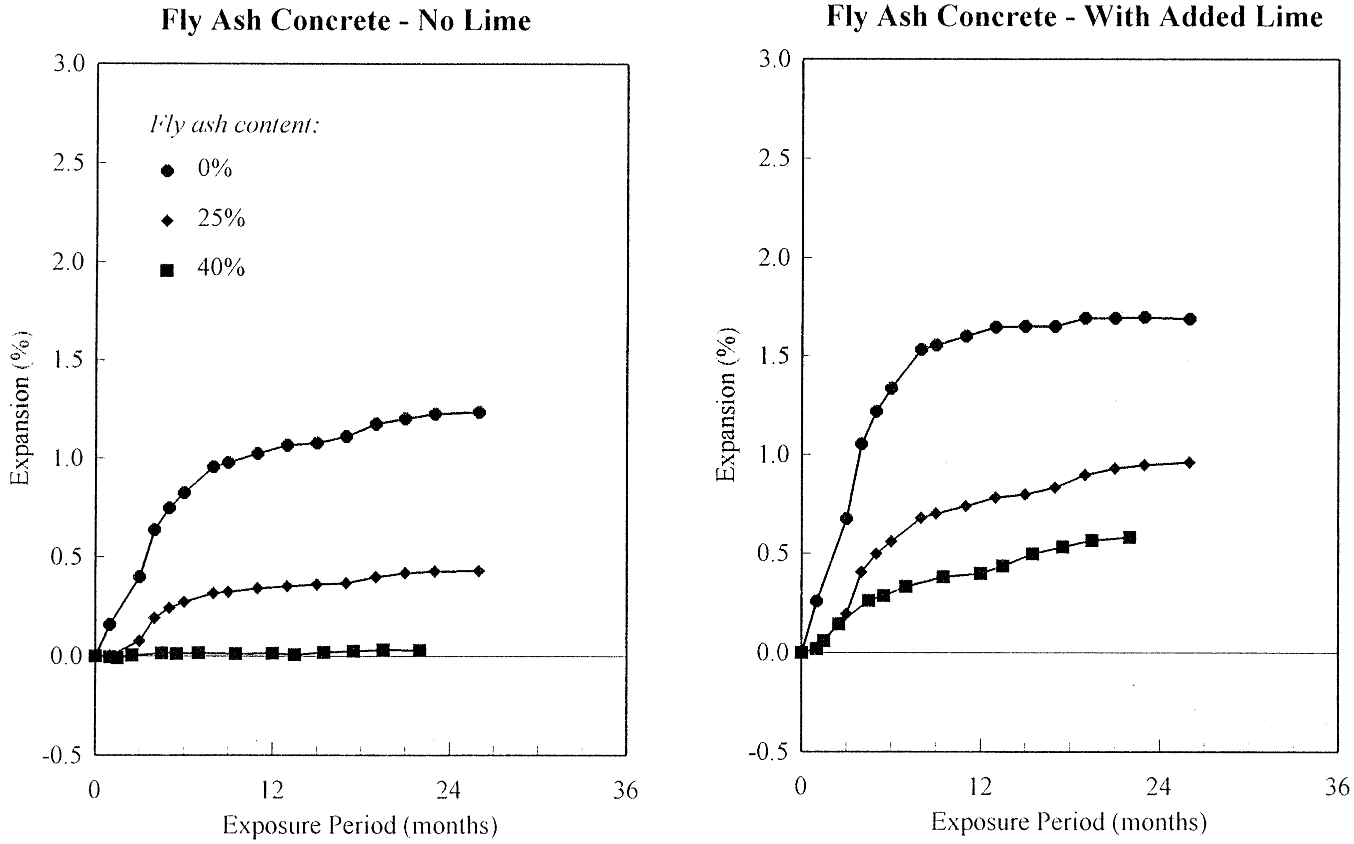

FIGURE 2. Effect of lime on the expansion of fly ash concrete with 25% flint sand stored in 1M NaOH at 80°C.

Solution (b) was selected to represent a highly alkaline concrete pore solution. Storage condition (c) was selected as it has been reported [21] that immersion in NaCl solution may produce greater concrete expansion than immersion in alkali hydroxide solution; immersion of mortar bars in 3N NaCl is the basis of the Danish Mortar Bar Test, TI-B51, for assessing the reactivity of aggregates in Denmark [22].

Analysis

Concrete prisms were monitored for length change for periods up to 3 years (or more in some cases). Concrete cylinders were removed from the solutions at various periods for examination by scanning electron microscopy (SEM); both polished and fracture surfaces were examined. SEMs equipped with energy-dispersive X-ray (EDX) analysis, wavelength-dispersive X-ray (WDX) analysis, and qualitative X-ray mapping capabilities were the primary research tools used for this study. Backscatter electron (BSE) and secondary electron (SE) imaging were used for viewing and imaging. EDX analyses and mapping were performed using an accelerating voltage of 20 KeV and a probe current of 100 μA, whereas WDX analyses were conducted at 10 KeV and 300 μA. Emphasis was placed on the location, distribution, and morphology of ASR products.

Results

Expansion of Concrete Prisms

Table 2 presents the final expansion data for concrete specimens after approximately 2–3 years of storage in solution. As expected, the expansion was dependent on the conditions of exposure, and the reactive aggregate, lime, and fly ash content of the concrete. None of the concrete specimens expanded significantly when stored in 3M NaCl at 50°C, regardless of the material composition.

The effect of reactive aggregate content and lime on the expansion of OPC concrete (without fly ash) is shown in Figure 1. Concrete with 25% and 35% reactive sand expanded rapidly in 1M NaOH at 80°C, with final expansion values exceeding 1.0% at 2 years. However, concrete with 100% reactive aggregate (i.e., Thames Valley sand and gravel) showed considerably lower expansion. Thames Valley sand is known to exhibit pessimum behavior, and the reduced expansion when the sand and gravel are combined has been attributed to the high reactive SiO_2/Na_2O_e ratio in the concrete [19].

FIGURE 3. Specimen L1a (1M NaOH at 80°C/0% fly ash). BSE image showing disrupted sand-sized flint grains and gel-filled cracks. F = flint; G = gel; L = limestone.

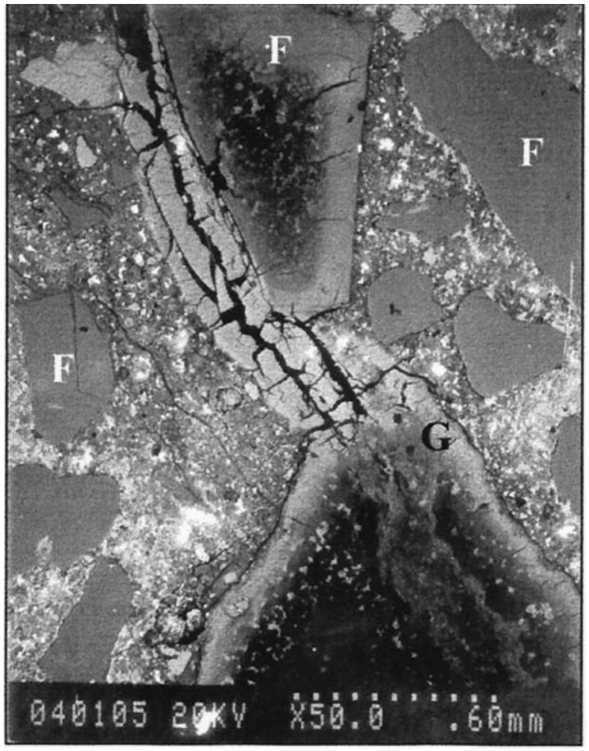

FIGURE 4. Specimen L1b (1M Na/KOH at 38°C/0% fly ash). BSE image showing disrupted flint grains and gel-filled cracks. F = flint; G = gel.

In these tests, the Na_2O_e is supplied by the external solution and pessimum behavior was not expected.

The addition of lime at the time of mixing increased the expansion of all the OPC concrete specimens containing reactive Thames Valley aggregate. The effect was most marked for the concrete with 100% Thames Valley, although the rate of expansion was clearly less than that for concrete with lesser amounts of reactive aggregate. Concrete without reactive aggregate (i.e., containing 100% carboniferous limestone) did not expand regardless of the presence of additional lime.

Figure 2 shows the effect of fly ash and lime on the expansion of concrete with 25% Thames Valley sand when stored in 1M NaOH at 80°C. The presence of 25% fly ash reduced the ultimate expansion by 65% (compared with the equivalent OPC concrete) and 40% ash almost eliminated expansion (97% reduction compared with OPC concrete). The addition of lime increased the expansion of the fly ash concrete significantly; an increase from 0.031% to 0.582% was observed for the concrete with 40% fly ash.

Microstructural Study

Five specimens were chosen for microstructural examination. Two of the specimens, L1a and L9a, were stored in solution (a) (1M NaOH) at 80°C for 44 months. These concretes contain 25% Thames Valley sand, no additional lime, and 0% and 40% fly ash replacement, respectively. Specimens L1b and L9b ("a" and "b" have been assigned to these specimens to differentiate their respective storage solutions), similar in composition to the previous specimens, were stored in solution (b) (1M Na/KOH) at 38°C for 44 months. Sample L10b is similar to L9b with the addition of 90 kg/m^3 of lime. All samples were epoxy impregnated, polished, and carbon coated to facilitate analysis by EDX.

OBSERVATIONS OF CONTROL SPECIMENS (0% FLY ASH). Inspection of the control samples L1a (expansion = 1.233%) and L1b (expansion = 0.889%) revealed abundant evidence of reaction and expansion. Common features of reaction include disruption of sand-sized flint grains, grains being almost completely replaced with gel in some cases (Figures 3 and 4), gel-filled cracks radiating perpendicularly from the aggregate-cement interface through the cement matrix linking other reaction sites (Figure 5), and air voids filled with alkali-silica gel (Figure 6). Evidence of expansion was apparent throughout the specimen. Large cracks filled with alkali-silica gel were found passing through inert limestone coarse aggregate particles (Figure 7).

A feature observed throughout these specimens was a distinct "banding" of the alkali-silica gel at the aggre-

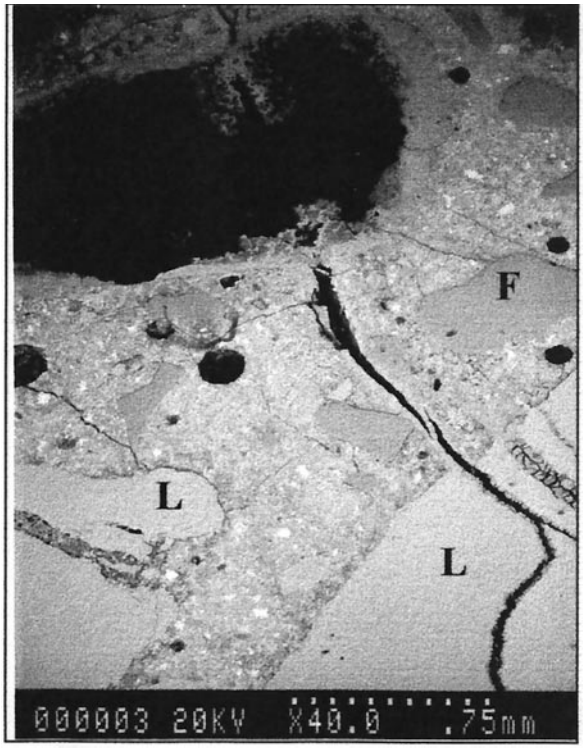

FIGURE 5. Specimen L1b (1M Na/KOH at 38°C/0% fly ash). BSE image showing reacted flint particle with crack radiating perpendicularly, damaging inert limestone aggregate. F = flint; L = limestone.

gate-cement interface at sites of expansive reaction. This banding consists of a two-layer calcium band at the aggregate-cement interface, followed by a high sodium silica band and high potassium silica band. This feature is best shown with the aid of an X-ray map (Figure 8). The individual frames show the BSE image and the relative concentration and distribution of calcium, sodium, silica, and potassium. The BSE image shows a completely reacted coarse aggregate particle containing alkali-silica gel in the lower two thirds of the image and cement matrix in the upper third. Of primary interest is the well-defined, continuous high calcium band, or reaction rim, at the aggregate-cement interface. This feature has been observed by other researchers [12,15,16,26,27]. Comparison of the BSE image and the elemental distributions shows two distinctive layers to this high calcium band. The layer closest to the interface clearly contains the greatest concentration of calcium yet the smallest concentration of silica. Conversely, the inner layer contains a lower concentration of calcium yet a higher concentration of silica. EDX analysis confirms this observation; spot analyses show the Ca/Si ratio to be approximately 1.0 or slightly greater at the interface (first layer) and to decrease to about 0.25 toward the center of the reacted particle away from the interface.

FIGURE 6. Specimen L1b (1M Na/KOH at 38°C/0% fly ash). BSE image showing air void filled with gel.

Worthy of note is the location and distribution of the alkalis in the reaction product. Again a banding is observed with a concentrated sodium band closest to the interface next to the double-layer calcium band, followed by a concentrated potassium band. This banding is apparent in the BSE micrographs, but is even more apparent by investigation with X-ray maps (Figure 8). Close inspection of these bands shows a difference between the morphology of the gels. The potassium-rich silica gel appears to have a crystalline, needle-like structure. This structure differs from typical ASR gels reported by other workers; however, similar products have been documented by Davies and Oberholster [23], Thomas [26], and Buck and Mather [28]. The sodium-rich silica gel has a more amorphous composition.

Concern was expressed as to the true nature of the reaction product distribution in dried, polished SEM samples as compared to actual concrete microstructure. Investigation of fresh, wet fracture surfaces on an environmental SEM at low vacuum confirmed that the distribution pattern of reaction products observed in the polished surfaces did not occur due to sample preparation (i.e., vacuum drying).

OBSERVATIONS OF FLY ASH SPECIMENS (40% FLY ASH). Inspection of fly ash specimens without additional lime, L9a (expansion = 0.031%) and L9b (expansion = 0.004%), showed extensive evidence of reacted aggregate parti-

FIGURE 7. Specimen L1a (1M NaOH at 80°C/0% fly ash). BSE image showing large gel-filled crack causing distress to inert limestone particle and partially reacted flint particle. C = crack; F = flint; G = gel; L = limestone.

cles and, subsequently, alkali-silica gel; however, little or no indication of expansive reaction was found. Coarse aggregate particles were discovered in varying degrees of reaction, from localized and partial reaction (Figure 9) to complete reaction and dissolution of the particle (Figure 10). At these sites little or no cracking was observed despite evidence of extensive reaction. The peripheral microcracking observed in Figures 10 and 11 is not characteristic of expansion of aggregate (which produces radial cracks), but rather indicates shrinkage of the reacted particle perhaps during the drying and specimen preparation. The absence of significant cracking is consistent with the expansion data obtained from the prismatic specimens.

Examination of the location of the reaction products revealed that alkali-silica gel was not found within cracks as typically found in the control specimens; instead it was observed that the alkali-silica gel had permeated into the surrounding cement matrix (Figures 10 and 11). Indeed, "rivers" of alkali-silica gel were found flowing from reacted aggregate particles through the cement paste (Figure 12).

The distribution of the reaction products around the aggregate-cement interface also differed in comparison with the control samples. The distribution pattern encountered in the control specimens of three distinct bands (high calcium, high sodium, high potassium) was not found in the fly ash concrete specimens. Instead, it was discovered that the high calcium reaction rim was no longer apparent, the high potassium silicate gel band was located within the aggregate void not crossing the interface, and the high sodium silicate gel had infused into the surrounding cement matrix. This phenomenon is documented in Figure 11 and the corresponding x-ray map in Figure 13.

Inspection of specimen L10b (expansion = 0.060%), with 40% fly ash and 90 kg/m^3 of additional lime, revealed evidence of partially reacted coarse aggregate particles. The absence of expansive cracking, the formation of reaction rims at the aggregate-cement interface, and alkali-silica gel banding were noted. A distinguishable feature is the concentration of reaction at the center of the particle. An interesting feature found on some of the reacted particles is the presence of a thin, light-colored (calcium) rim inside the reacted particle separating the apparent internal reacted phase from the external nonreacted phase. A micrograph showing these reactions features is shown in Figure 14.

Discussion

The expansion data clearly indicate that the availability of Ca(OH)$_2$ influences the development of expansion due to alkali-aggregate reaction. Indeed, the consump-

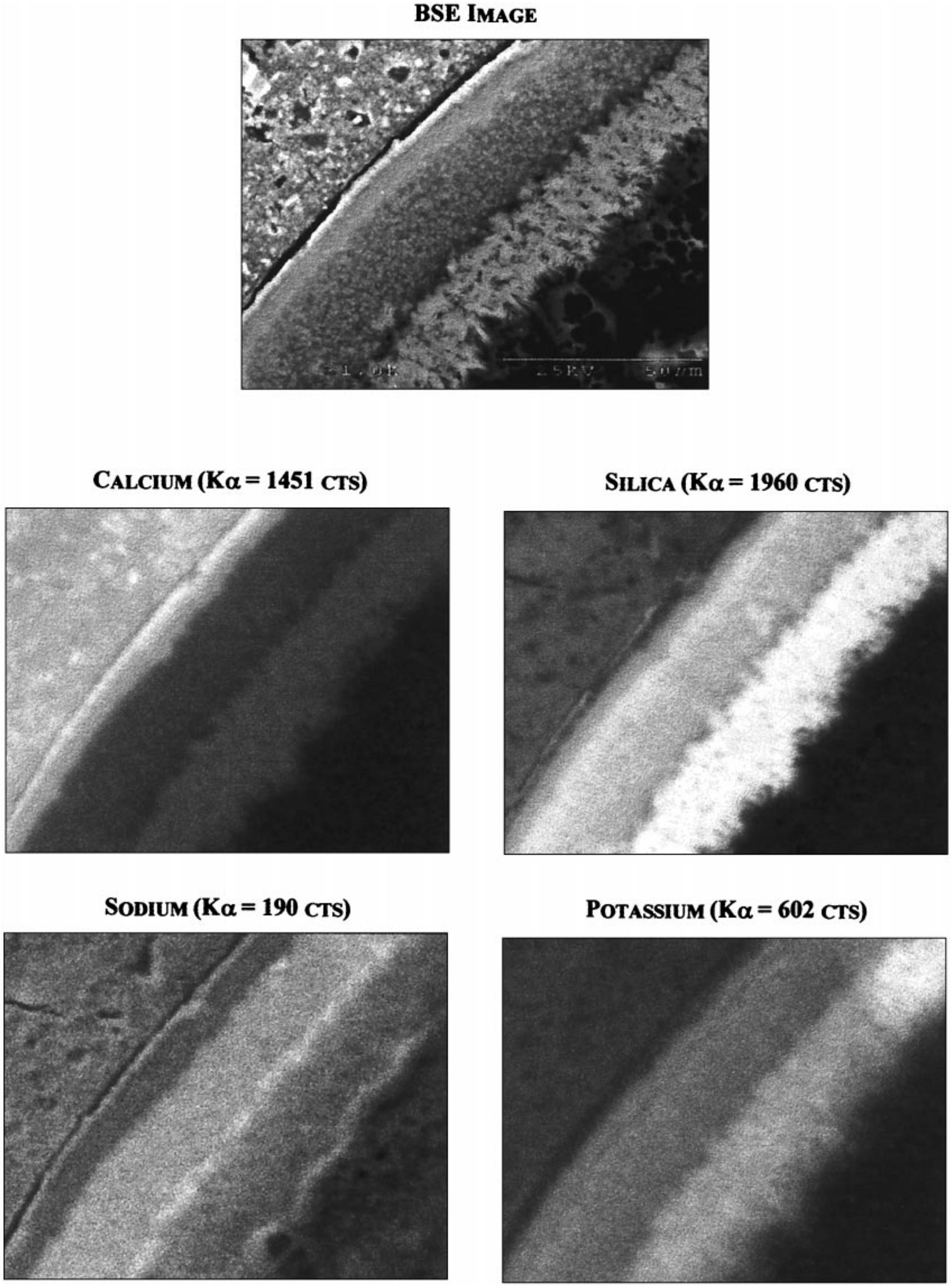

FIGURE 8. Specimen L1a (1M NaOH at 80°C/0% fly ash). X-ray map of aggregate-cement interface. Reacted particle with reaction product on the right, cement matrix on the left.

tion of $Ca(OH)_2$ by fly ash appears to reduce damaging expansion regardless of the supply of reactive silica and alkali hydroxides. Observations made on concretes with 40% fly ash indicate that reactive silica (flint) may be removed from its original site due to reaction with highly alkaline pore solution without the generation of expansive forces. The silica probably goes into solution and is eventually leached away (i.e., silica ions diffuse

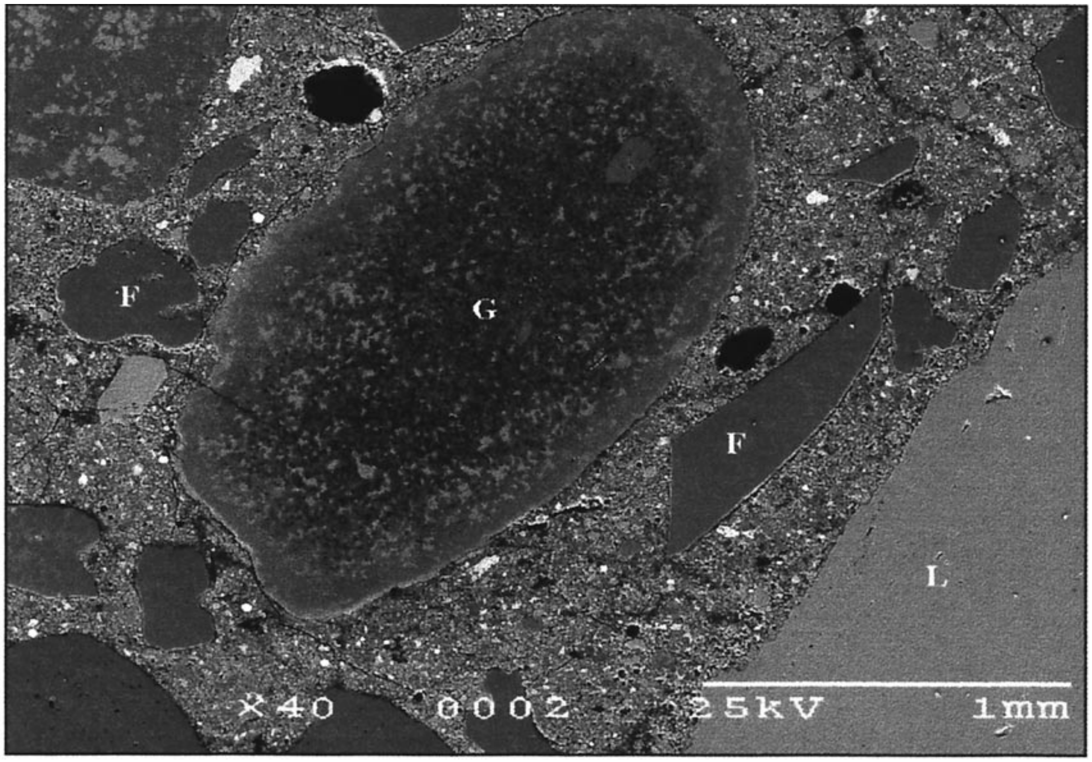

FIGURE 9. Specimen L9a (1M NaOH at 80°C/40% fly ash). BSE image showing partially reacted flint particle. Gel is identified in the interior of the particle. F = flint; G = gel; L = limestone.

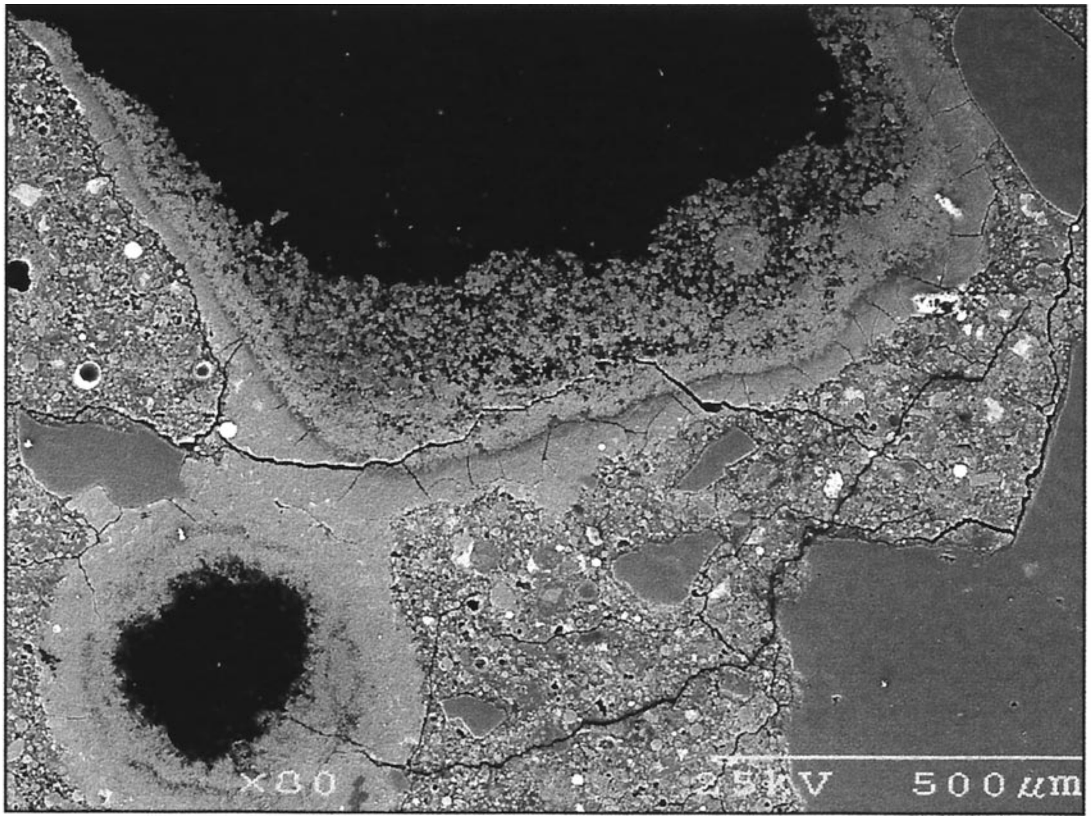

FIGURE 10. Specimen L9a (1M NaOH at 80°C/40% fly ash). BSE image showing reacted flint particles without a calcium rim and sodium-rich gel diffused into the surrounding cement matrix.

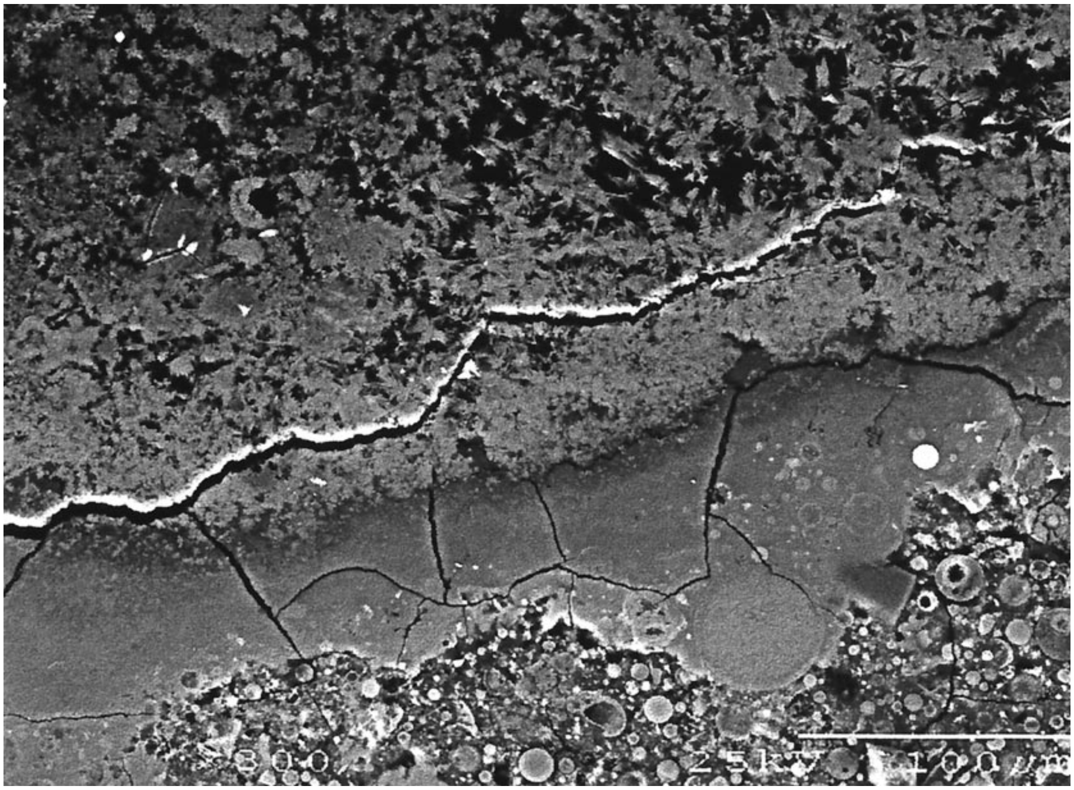

FIGURE 11. Specimen L9a (1M NaOH at 80°C/40% fly ash). BSE image showing close-up of aggregate-cement interface and amorphous sodium-rich gel diffused into cement paste, whereas crystalline high potassium gel is contained within reaction site. X-ray map available (Figure 13).

through concrete into the host solution). Struble [24] demonstrated that significant quantities of silica (2M) can remain in solution with alkali hydroxides in the absence of cement hydration products (e.g., $Ca(OH)_2$).

Microstructural examination revealed the presence of three distinct gel compositions: high calcium, high sodium, and high potassium silica gels. The distribution of these gels is characteristic of the concrete (plain OPC or fly ash concrete) and alludes to the mechanisms involved in alkali-silica reaction.

In Portland cement concretes, it was observed that the reaction product was contained within aggregate boundaries, air voids, and cracks. The high calcium gel was found to form at the periphery of reactive aggregate particles. The formation of this high calcium reaction rim at the aggregate-cement interface reflects the relative abundance of $Ca(OH)_2$ in the interfacial zone. Amorphous high sodium silica gel was found on the interior of this high calcium layer, followed by a crystalline high potassium silica gel. This "banding" distribution was observed in all specimens without ash (including fracture surfaces) regardless of the storage conditions during testing, and such particles were invariably sites of expansion as indicated by perpendicularly radiating cracks.

The fly ash concrete specimens (40% ash) yielded a very different reaction product distribution. The high calcium, silica gel reaction rim observed in the Portland cement concrete was not apparent in the fly ash concretes. The other gel compositions were still detected; however, the location of these reaction products had changed. In the absence of the high calcium rim, the amorphous high sodium gel was found to have diffused beyond the aggregate-cement interface into the immediately surrounding cement matrix. Indeed, in some cases "rivers" of gel were observed to flow through the cement paste. The crystalline high potassium silica gel did not exhibit this fluid behavior; this gel composition was found exclusively within the original aggregate boundary.

These observations are consistent with the findings of Struble and Diamond [17,18], who showed that synthetic calcium gels behaved in a manner similar to gels without calcium with respect to swelling properties, but that the calcium gels remained solid after testing, whereas some sodium-silicate gels became fluid.

It would appear that the formation of the high calcium reaction rim prevents the flow of sodium-rich gel into the matrix. It is possible that this high calcium gel, acting as a semi-permeable membrane, permits the diffusion of alkali hydroxides into the silica particle but resists the counterdiffusion of the resulting aqueous

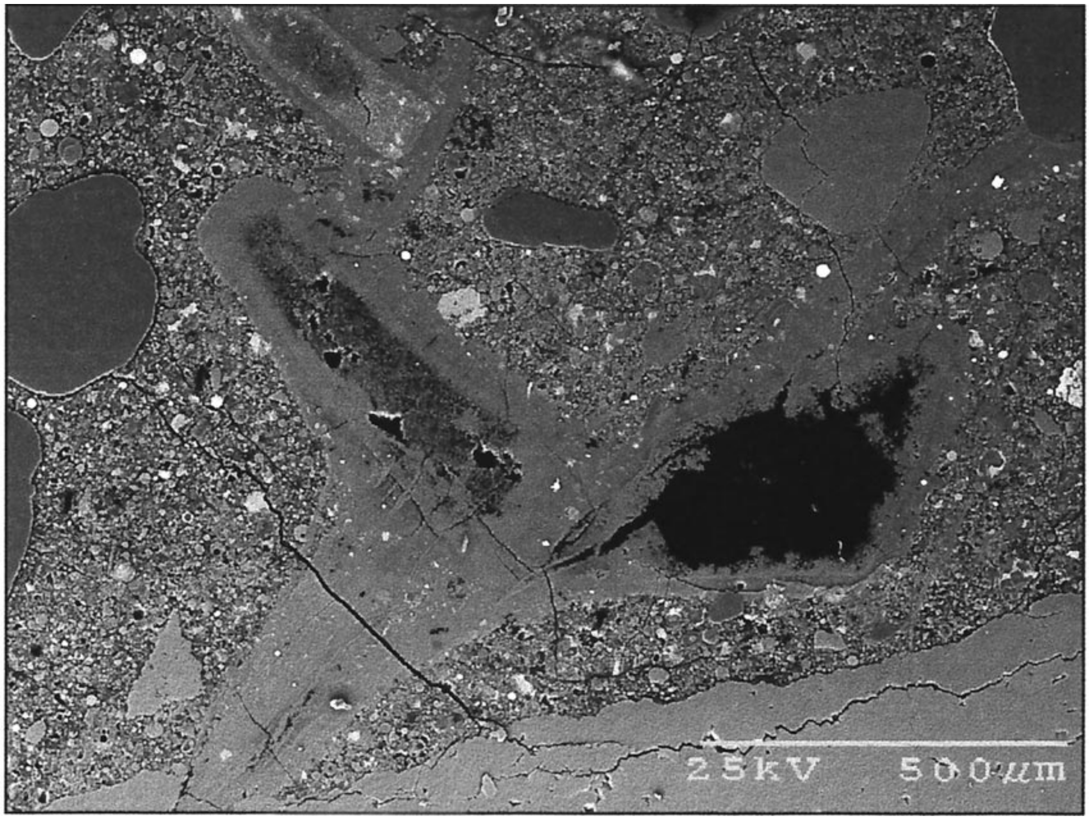

FIGURE 12. Specimen L9a (1M NaOH at 80°C/40% fly ash). BSE image showing "river" of alkali-silica gel flowing through cement paste from reacted flint particles.

alkali-silica. This results in the development of expansive forces by the formation of an osmotic pressure cell between the alkali-silica solution and pore water in the surrounding cement paste. This mechanism is similar to Hansen's osmotic pressure theory [25], expansion resulting from hydraulic pressure (due to osmosis), except that the calcium-alkali-silica reaction rim provides the semi-permeable membrane as opposed to the cement paste in Hansen's model. Such a mechanism also bears similarities to that put forth by Chatterji [13], in which high calcium concentrations in the pore solution prevent the diffusion of silica away from the reactive site and lead to expansive forces.

Alternatively, the calcium gel itself may be expansive. This premise opposes the hypothesis proposed by Powers and Steinour [15,16], who postulated that a high lime to silica ratio ($Ca/Si \approx 1$) is required to produce "safe" nonexpansive reaction product provided the calcium reaches the reaction site at a sufficient rate. Their hypothesis is difficult to reconcile with the findings of this study, since fly ash will not only reduce the availability of calcium but will also reduce its diffusivity. In this study, reaction products with $Ca/Si > 1$ were found in the high calcium reaction rim, and concrete expansion studies indicate that significant expansion had occurred.

Further study is required to elucidate the role of $Ca(OH)_2$ in alkali-aggregate reactions and the influence of gel composition on its expansive nature and viscosity. However, there is considerable evidence that $Ca(OH)_2$ plays an important role in alkali-aggregate reaction and controls the degree of damaging expansion that occurs. Expansion that occurs in fly ash concrete may be due to insufficient consumption of $Ca(OH)_2$ due to: (1) alkali-silica reaction proceeding more quickly than pozzolanic reaction (where highly reactive forms of silica are present), (2) low pozzolanicity of fly ash, (3) high calcium content of fly ash, or (4) insufficient quantity of fly ash. Although significant levels of $Ca(OH)_2$ are still present in most fly ash concretes, the distribution is affected, especially at the aggregate/cement interface where substantial reductions occur due to the presence of fly ash.

Conclusions

1. Fly ash was effective in reducing the expansion due to alkali-silica reaction in concrete immersed in alkaline salt solutions for extended periods of time (more than 3 years).

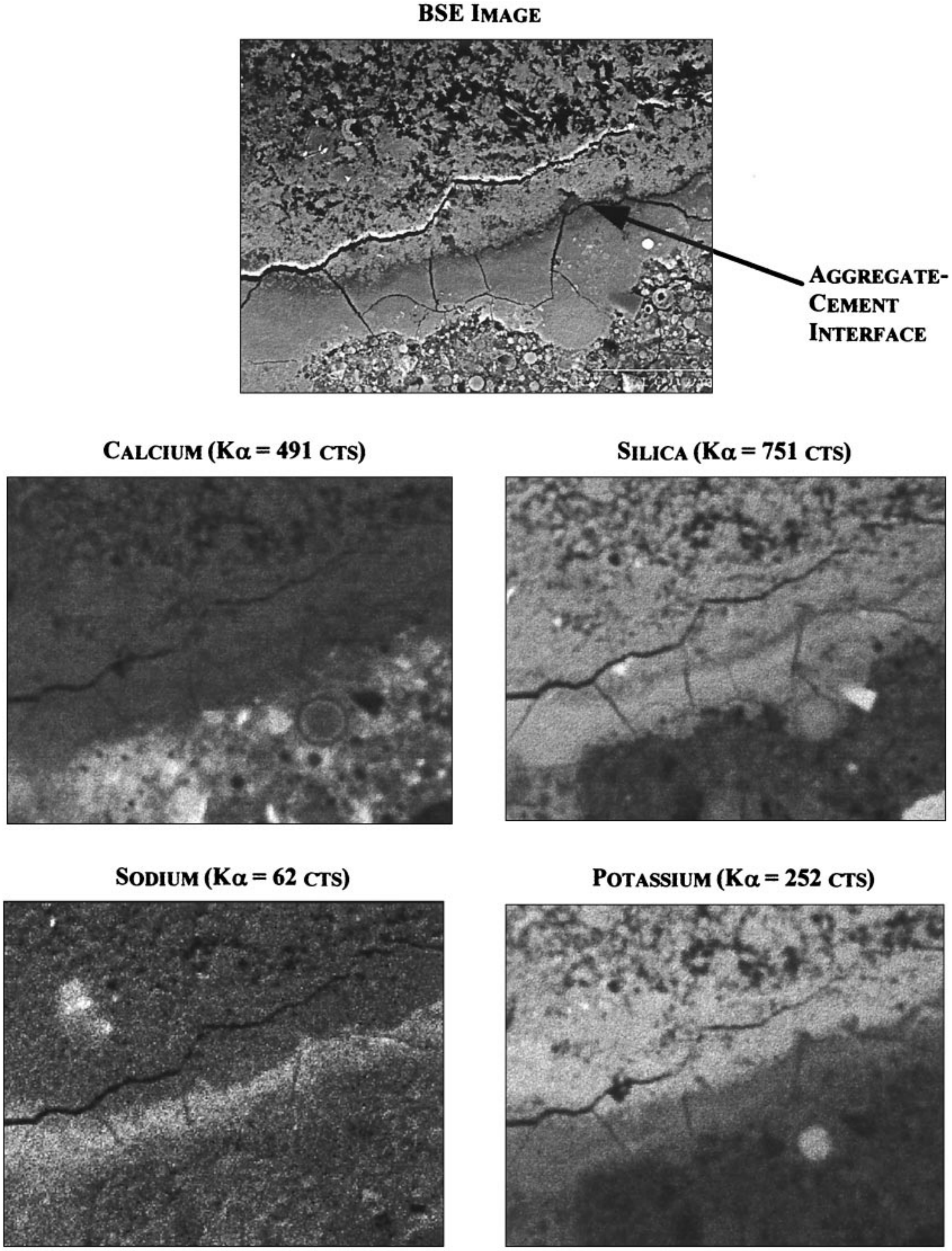

FIGURE 13. Specimen L9a (1M NaOH at 80°C/40% fly ash). X-ray map of aggregate-cement interface. Reacted particle with reaction product on bottom of frame, cement matrix on top of frame.

2. At higher levels of replacement (40% ash), deleterious expansion was prevented despite evidence of considerable reaction of flint particles within the concrete. In many cases, flint grains were found to have been completely removed by dissolution without associated damage.
3. The addition of $Ca(OH)_2$ at the mixer was found to promote expansion in fly ash concretes.
4. A calcium-alkali-silica reaction rim was observed to form at the periphery of some reactive flint grains in Portland cement concrete. This feature was not observed in concrete with 40%

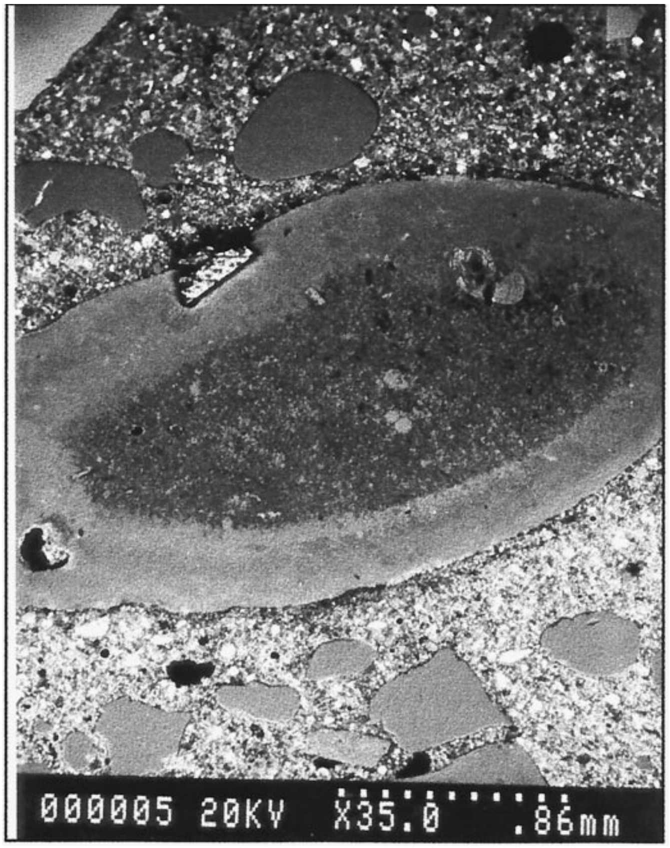

FIGURE 14. Specimen L10b (1M Na/KOH at 38°C/40% fly ash/90 kg/m^3 CaO). BSE image showing flint grain with partial reaction at center of particle. Light-colored calcium band is beginning to form within the particle.

ash, probably due to the reduced $Ca(OH)_2$ at the cement-aggregate interface.

5. The distribution pattern of low calcium alkali-silica gels differ in Portland cement concretes as compared to fly ash concretes. It was observed that a distinctive "banding" occurred within this gel, characterized by an amorphous high sodium silica gel and a crystalline needle-like high potassium silica gel.
6. It was observed in the fly ash concrete that in the absence of a high calcium reaction rim, the high sodium gel could easily disperse through the pore structure of the cement matrix, alleviating internal stresses.

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