

A MICROSTRUCTURAL STUDY OF ASR INDUCED BY ALKALI ACETATE AND FORMATE DEICERS

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Abstract

ASR can be induced if concretes or mortars containing ASR-susceptible aggregates are exposed to certain concentrated organic salt solutions now commonly employed as airfield pavement de-icers. Mortars with an ASR reactive aggregate exposed to such solutions at 80°C undergo rapid expansions exceeding those of companion mortars exposed to the 1N NaOH used in conventional ASR testing at 80°C. An SEM study is provided to document the microstructural changes accompanying the expansions of the mortars. The aggregate used was an ASR reactive quartzite of comparatively straightforward mineralogy; and the deicers included potassium acetate, sodium acetate, potassium formate, and sodium formate in concentrations reflecting their use in the field. Most of these solutions produced significantly more extensive ASR-induced cracking and visible deterioration than did the 1N NaOH used in conventional ASR testing. Other ASR reactive aggregates produced similar, and in some cases even more severe results. Concretes exposed to these deicer solutions at 38°C showed similar (but slower) ASR responses.

Keywords: alkali silica reactions, microstructure, airfield pavement de-icers, alkali acetates, alkali formates

1 INTRODUCTION

In response to environmental and other concerns, a new generation of de-icers and anti-icers is being used on concrete pavements primarily at commercial airports. These formulations are based on alkali acetates and formates. They are used either as highly concentrated solutions applied directly to pavements surfaces (“anti-icers”) or in solid form as pellets applied on snow or ice to induce melting (“de-icers”). 50% wt. solutions of the potassium salts are usually applied as anti-icers, and pellets of the sodium salts are used as de-icers. For simplicity, we will henceforth refer to all of these substances as “deicers”.

It has recently become apparent that use of these deicing materials has been associated with alkali silica reaction (ASR) on concrete pavements in a number of airports in North America and elsewhere. Various investigations have been carried out to provide information on the nature and mechanism of the responses [1-4].

It appears that even highly concentrated or saturated solutions of most of these substances have only modestly alkaline pH levels by themselves; measured values are between pH 8.4 and 11 for all but saturated sodium formate, which is somewhat more highly alkaline (pH 12.9). It appears, however, that on contact with calcium hydroxide (or concrete containing calcium hydroxide) the modestly alkaline solutions show an almost immediate jump in pH as measured by conventional glass electrode pH instruments. Measured pH levels as high as pH 15 (with potassium acetate) appear to be rapidly generated by such contact. However in these extremely concentrated solutions the relation between measured pH and actual OH⁻ ion activities remains in some doubt [4].

In the present paper we illustrate the results of trials in which mortar bars prepared with a straightforward quartzite ASR reactive aggregate were exposed at 80°C to 1N NaOH in the conventional ASTM C 1260 procedure and to concentrated solutions of these deicers (potassium and sodium acetate and potassium and sodium formate) under the same test conditions. Expansion measurements and scanning electron microscopy (SEM) were used to document the ASR responses generated.

Similar trials, reported elsewhere [1], were carried out with other reactive aggregates, and ASR responses were also documented with them. However in some cases other interactions

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besides ASR may have taken place as well.

2 EXPERIMENTAL

The ASR-reactive aggregate whose response is described in the present paper is a quartzite rock derived from a quarry located in Sioux Falls, South Dakota, U.S.A. This aggregate has an established history of ASR reaction in concrete pavements in Minnesota and South Dakota [5]. It is composed of strained quartz grains cemented with interstitial secondary quartz, and additionally contains very small amounts of microcrystalline quartz, kaolinite, and hematite. While ASR expansions recorded with this aggregate on exposure to the deicers are not as severe as those obtained with certain other reactive aggregates, they apparently are not to be complicated by other effects that may have been induced in some of the mineralogically more complex aggregates.

The mortars reported here were prepared using an ASTM Type I cement with an alkali content of 0.82 % $\text{Na}_2\text{O}_{\text{equiv}}$. A second set of mortars was prepared with a different cement, a low alkali cement of 0.31 % $\text{Na}_2\text{O}_{\text{equiv}}$. These mortars were found to show only slightly smaller expansions than the present set, suggesting that the alkali content of the cement used is not of great importance in these tests.

The mill analysis provided with the cement used here was as follows: CaO:61.8%, SiO₂:19.7%, Al₂O₃:5.0%, Fe₂O₃:3.1%, MgO:2.5%, SO₃: 4.2%, K₂O:0.84%, Na₂O:0.27%, LOI:1.90%.

The mortars, produced in accordance with the ASTM C 1260 specification, had a sand:cement ratio of 2.25 and a water:cement ratio of 0.47. The sand was carefully prepared by crushing, sieving, and washing the quartzite rock to meet the specified gradation.

The various deicer solutions used were as follows (note that concentrations are specified at room temperature):

- potassium acetate, 50% by wt., as used in field practice (6.40 molar)
- potassium formate, 50% by wt., as used in field practice (7.84 molar)

Both the potassium salts have extremely high solubilities. The sodium salts have somewhat lower solubilities, and since they are ordinarily applied in pellet form the concentrations used here were the concentrations of the saturated solutions at room temperature, which were as follows:

- sodium acetate, % by wt, 4.66 molar
- sodium formate, % by wt, 5.92 molar

Measurements of expansion of the various mortars were carried out at intervals in the usual manner.

The microstructural examinations were carried on specimens prepared after 28 days exposure at 80C. SEM examinations were carried out on flat polished specimens in the backscatter mode, using an Aspex Personal SEM equipped with an energy-dispersive x-ray analysis system. The specimen preparation procedure involved gentle drying, followed by impregnation and with an extremely low viscosity epoxy resin, and hardening. A smooth surface was cut in the hardened specimen using precision slow speed diamond blade saw lubricated by propylene glycol. The surface so produced was polished with diamond paste of progressively finer sizes, and finally sputter coated with a thin layer of a gold-palladium alloy. No water was allowed to contact the specimen during sample preparation, all polishing steps being carried out with non-aqueous liquids.

3 RESULTS

3.1 Mortar bar expansions and associated responses

The mortar bar expansions experienced by the mortar bars exposed to the various solutions at 80°C are shown in Figure 1.

It is evident that with all of the solutions the quartzite aggregate generates expansions far beyond that needed to qualify for an ASR-reactive aggregate in the standard ASTM C 1260 test (0.1% at 14 days). As seen in the figure, expansions continued beyond 14 days and reached (and in most cases vastly exceeded) 0.4% at 28 days.

All of the deicer solutions produced higher expansions than the standard 1N NaOH solution. The 28-day expansion measured with potassium acetate only slightly exceeded that obtained with NaOH; this level was exceeded by a factor of 2 for sodium acetate and by factors of more than 4 with both potassium and sodium formate solutions.

Not shown in Figure 1, but worthy of note, is that for both potassium-bearing deicers, mortar bars containing Ottawa silica sand (prepared as 'controls') underwent small but definite

expansions of the order of 0.03 – 0.05 %; SEM examinations indicated that even this normally inert sand exhibited some ASR response with these solutions.

3.2 Visual and SEM examinations

Visual examination of the various mortar bars whose expansions are documented in Figure 1 showed the usual evidences of ASR; severe cracking, bending, and exudation of gel was commonly found to accompany the expansions. The SEM examinations documented here were all secured from specimens that had undergone 28 days of exposure at 80°C.

Mortar bars exposed to 1 N NaOH solution (in the standard ASTM 1260 test)

An illustration of the degree of ASR reaction and associated microcracking undergone by the quartzite-bearing mortar in exposure to 1 N NaOH in the standard ASTM 1260 test is provided in Figure 2.

As expected, many of the sand grains are cracked, and partly filled with gel; at higher magnification it can be seen that many of the cracks extend into the surrounding paste. The ASR gel deposits show the usual energy dispersive x-ray spectroscopy (EDS) indications for Na-bearing ASR reaction products, including small peaks for Ca and Na and the major peak for Si., as seen for example in Figure 3.

Note that Figure 3 and other similar figures contain three elements: a relatively low magnification image of a general area, a higher magnification image of a selected area within it; and a feature of interest with respect to local chemistry marked by a small white square. The EDS spectrum displayed below the two images was secured at the spot indicated by the small white square.

Mortar bars exposed to potassium formate solution

Exposure to the mortar bars to the potassium formate solution results in not only much greater expansion than that generated with NaOH, but also in visually much more severe indications of ASR. As seen in Figure 4, the ASR-induced cracks in the sand grains are significantly more pronounced, and partial dissolution of some of the silica appears to have taken place. Most of the cracks extend into the surrounding cement paste, and bond cracks are prominent. While many of the cracks appear empty, local areas with significant gel contents can be seen within some of the sand grains.

In Figure 5, a “river” of ASR gel is seen to cut across the long, narrow sand grain. The EDS spectrum indicates that the alkali component of the ASR gel produced here is potassium, reflecting the fact that the solution to which the mortar was exposed is a solution of a potassium salt, rather than sodium hydroxide.

The rough-textured, slightly darker area above the siliceous portion of the sand grain is kaolinite, but this component takes no part in the ASR reaction.

Mortar bars exposed to sodium formate solution

In Figure 1 it was seen that the sodium formate-induced expansion was even higher than that induced by potassium formate. As can be seen in Figure 6 it appears that the intensity of the overall ASR response visible in SEM was also more or less comparable, especially within the larger sand grains.

In Figure 7 we provide an illustration of ASR gel deposited within a paste crack in this mortar. Here the alkali component of the gel is sodium, since the mortar was exposed to a solution of sodium formate, rather than potassium formate.

Mortar bars exposed to sodium acetate solution

As seen in Figure 1, mortar bars exposed to the acetate-based deicers exhibited somewhat less expansion at 80°C than did those exposed to the formates. Sodium acetate produced significantly higher expansion than did the potassium acetate.

An indication of the overall extent of the ASR reaction induced by exposure to sodium acetate is provided in Figure 8. It is seen that this mortar is also severely and extensively cracked; however, unlike the crack pattern exhibited by the mortars exposed to the formate solutions, the cracks across the paste matrix are as prominent (if not more so) than the cracks within the aggregate grains.

Figure 9 provides an indication of partial gel filling in one of the cracks within a quartzite sand grain. The gel appears not to contain any calcium in this location.

Mortar bars exposed to potassium acetate solution

In Figure 1 it was indicated that the 28-day expansion induced by potassium acetate with this quartzite aggregate was substantially less than the 28-day expansions induced by the other deicers. This is not the case with ASR reactive aggregates in general; very severe effects with this solution have been noted for other reactive aggregates [1].

The SEM image of Figure 10 is quite consistent with the relatively moderate expansion recorded here, and the degree of distress appears to be similar to that shown in Figure 2 for the mortar exposed to NaOH. The cracks are much narrower than those seen with the other deicers, and obvious cracking seems mostly to take place around the perimeters of the aggregate. However, close examination indicates that many of the larger sand grains have white "rivers" running across them that appear to consist of cracks locally filled with deposits of light-colored material. As indicated in Figure 11, the crack filling material has the composition expected for potassium-bearing ASR gel, but within the aggregate grains the gel has only small component of the calcium, which is often present in larger proportion closer to the surrounding cement paste.

Careful examination indicates that many of the filled cracks extend as narrow empty cracks into and frequently across the surrounding cement paste.

4 DISCUSSION

The SEM examinations of mortars with a reactive aggregate exposed to various alkali formate and acetate solutions at 80°C in the manner modeled on the ASTM C 1260 test procedure confirms that the extraordinary expansions recorded for them are indeed consequences of ASR attack. Crack patterns, evidences of silica dissolution, and reaction product gel composition are all indicative of such response.

Similar responses, somewhat more complicated in some cases, were seen with other reactive aggregates. The expansions achieved with some of them significantly exceeded even the extraordinary values exhibited by the quartzite-bearing mortar bars exposed to potassium and sodium formate as documented here. In particular, very severe and extremely rapid expansions (of the order of 1.5% or more) were observed with a rhyolite-bearing gravel aggregate from Las Placitas, New Mexico, U.S.A. for all of the deicer solutions. Indeed, for this aggregate the mortar bars were so badly cracked and distorted that in some cases expansion measurements had to be abandoned during the first week or two after the start of the exposure.

The obvious question arises as to the extent to which the reactions observed at 80°C reflect merely an acceleration of ASR responses that would occur more slowly at normal field exposure temperatures, or whether the high temperature was required to induce the reactions. In trials with concrete prisms exposed to the same solutions at 38°C (in the manner of ASTM C 1293 standard tests, but with the prisms immersed in the various deicer solutions) it was evident that the former was the case. Substantial expansions were detected at 6 months and a year. The early expansions were generally greater with high alkali cement than with low alkali cement, suggesting that effective penetration of the deicer solutions took some time. However, by 1 year at 38°C cracking and gel formation confirmed that ASR was taking place on exposure to all of the deicer solutions, although to different degrees with different reactive aggregates [1]. In some cases the ASR may have been complicated by other effects induced by the deicer solutions.

5 CONCLUSIONS

Mortars prepared with a mineralogically uncomplicated ASR reactive aggregate (a quartzite from South Dakota, U.S.A.) showed clear evidences of conventional ASR responses after having been exposed to various concentrated alkali acetate and formate deicer solutions at 80°C, under conditions identical with those of the standard ASTM C 1260 test. Measured expansions in most cases very substantially exceeded those obtained with the standard 1N sodium hydroxide exposure, and SEM evidence of reactions with the deicer solutions were generally severe, and in most cases far more severe than with the standard sodium hydroxide solution. Other experiments carried out with concrete prisms at 38°C indicated that the reactions occurred at lower temperatures and did not require exposure at 80°C.

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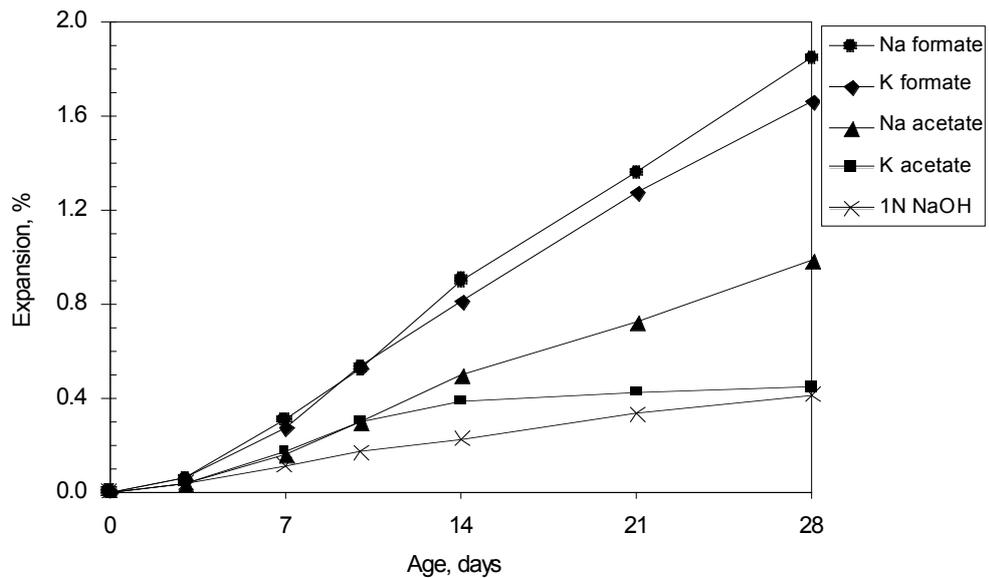


Figure 1: Expansions measured for quartzite – bearing mortar bars on exposure to 1N NaOH solution and to solutions of alkali acetates and formates.

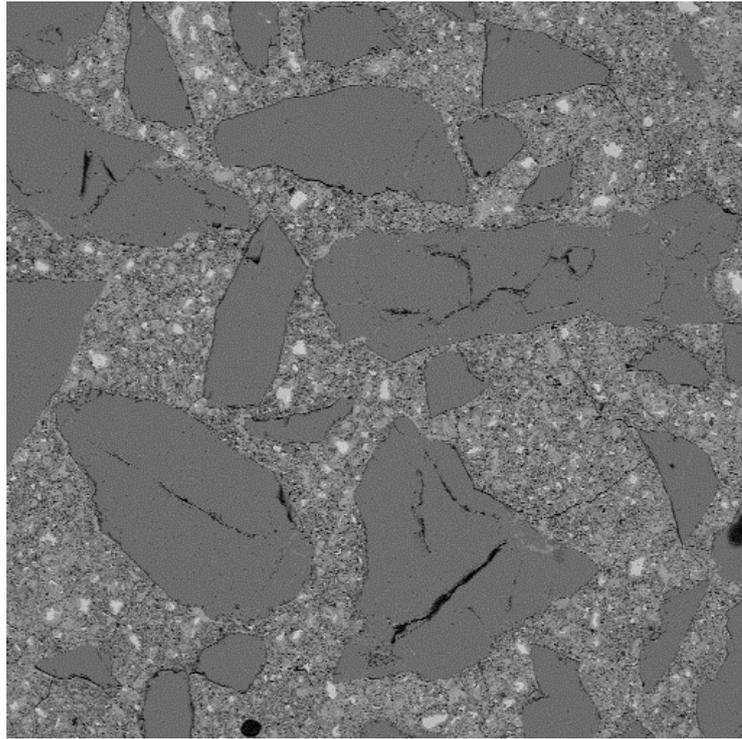


Figure 2: Indications of ASR in the quartzite mortar exposed to 1N NaOH solution.

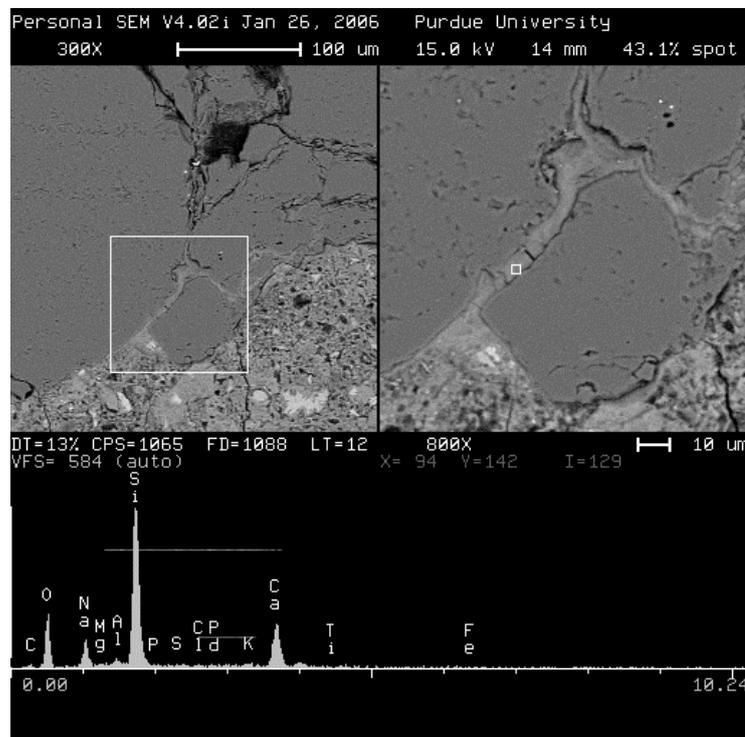


Figure 3: Area in NaOH-exposed mortar showing crack with ASR gel.

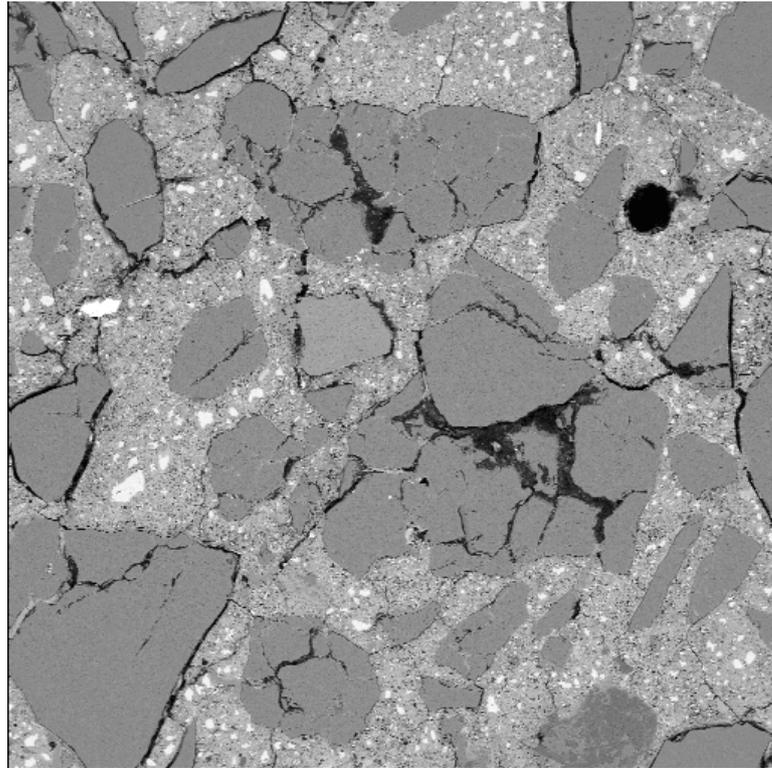


Figure 4: Evidences of severe ASR in the quartzite mortar exposed to potassium formate solution.

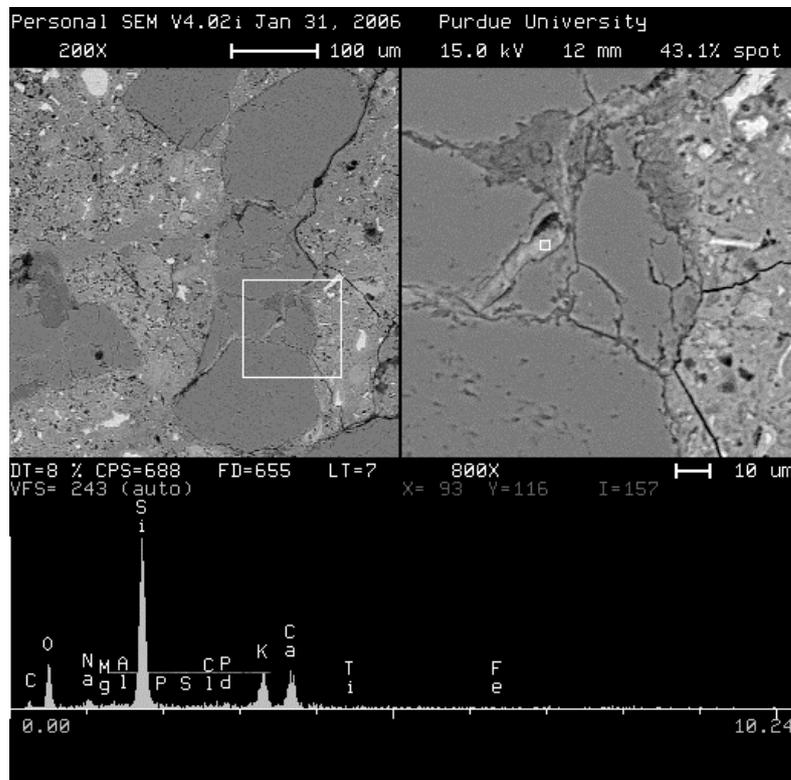


Figure 5: Area in potassium formate-exposed mortar showing crack filled with ASR gel.

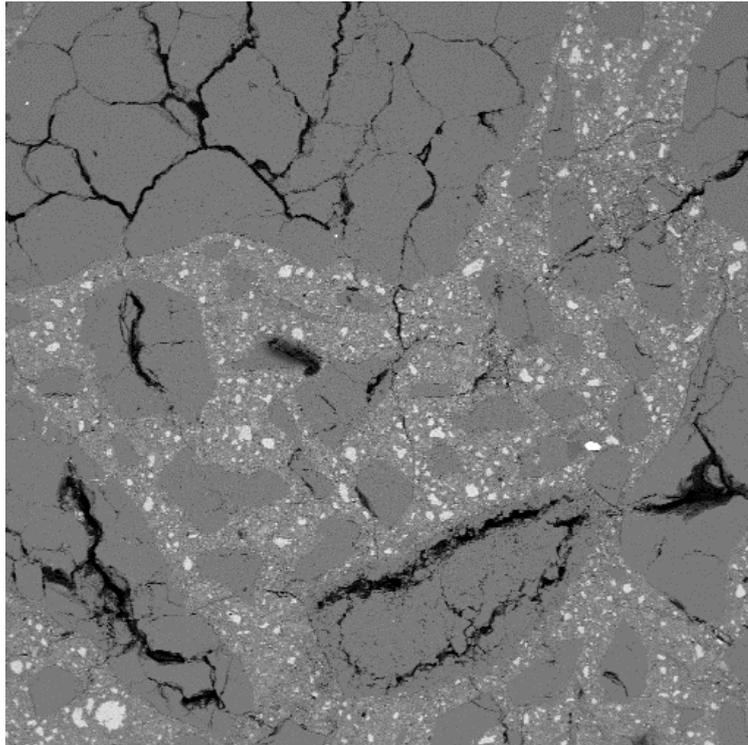


Figure 6: Evidences of severe ASR in the quartzite mortar exposed to sodium formate solution.

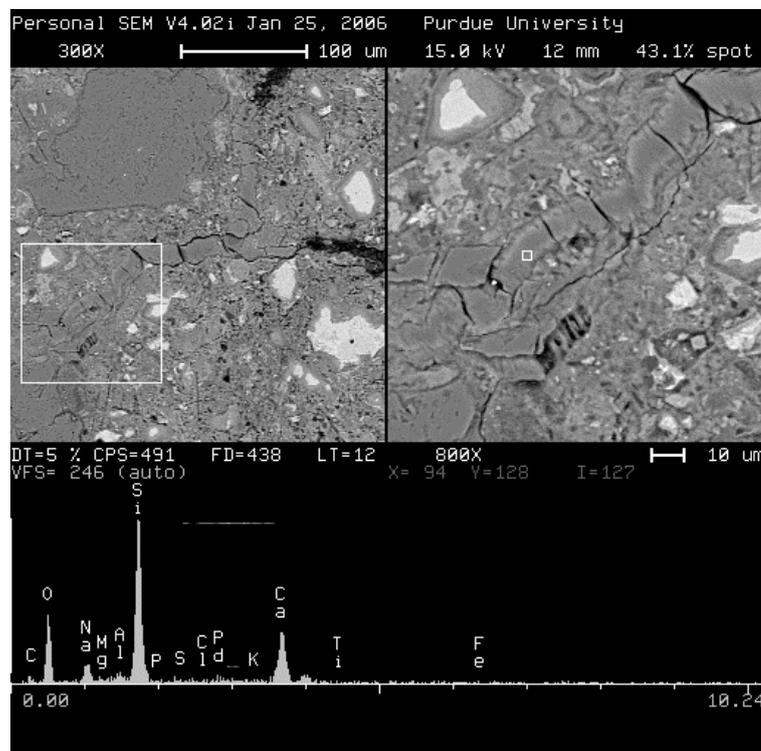


Figure 7: Na-bearing ASR gel deposited within, and locally filling, a paste crack in the mortar exposed to sodium formate solution.

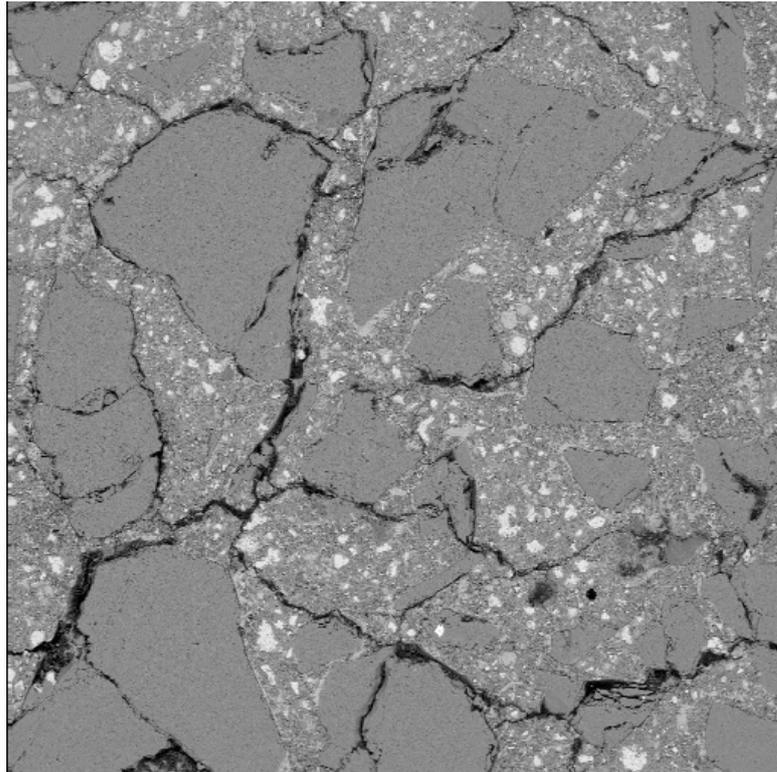


Figure 8: Evidences of severe ASR in the quartzite mortar exposed to sodium acetate solution.

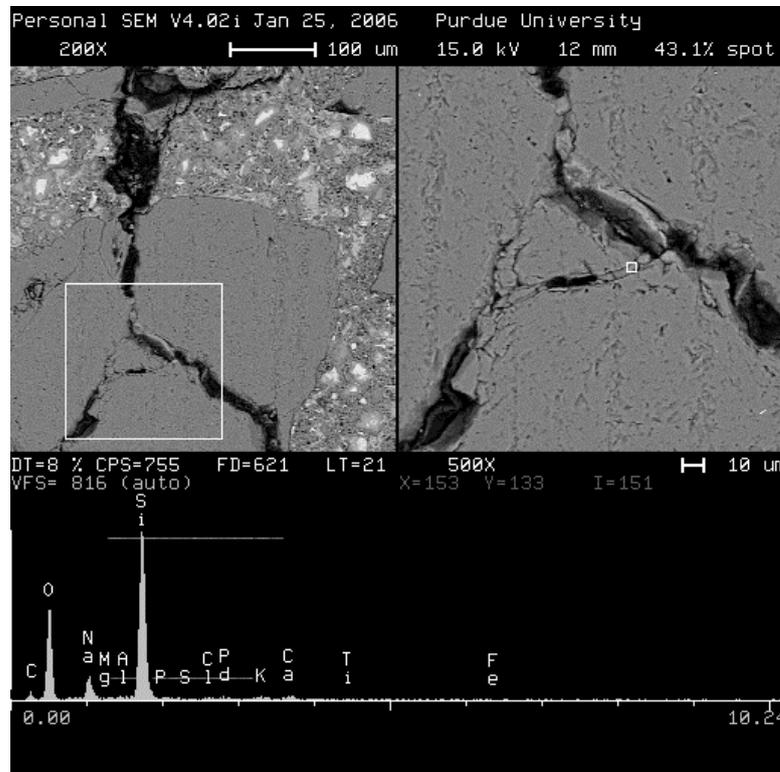


Figure 9: Gel deposit within a crack in the central part of a reacting sand grain in the mortar exposed to sodium acetate solution.