

SPECTROSCOPIC STUDIES OF ALKALI INDUCED REACTIONS AT CEMENT CARBONACEOUS AGGREGATE INTERFACES

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ABSTRACT

Reactions between alkaline solutions and carbonaceous aggregates have traditionally been studied by the measurement of the expansion of rock cylinder specimens and by observing length changes in concrete or mortar prisms containing the aggregate and stored in different environments.

In this study data has been obtained from reactive and nonreactive rock core specimens using surface analytical techniques to assess the extent of reaction involved and to detect compositional changes. Two sets of samples were examined. These were prepared from limestone from various locations within the UK. The surface of these samples was investigated before and after exposure to alkaline solutions and compared with identically treated reference argillaceous dolomitic limestone from Kingston, Canada. The latter is known to be highly reactive when used in concrete. The change in reactivity was measured and images of the surface obtained using scanning electron microscopy (SEM) to identify differences in topography between treated and untreated samples.

Elemental analysis of areas of interest was carried out using energy dispersive X-ray analysis (EDX) and the chemical changes induced by alkali-aggregate reaction were determined using X-ray photoelectron spectroscopy (XPS) and secondary ion mass spectrometry (SIMS) to indicate potentially non-reactive formulations.

XRD-powder diffraction was used to detect reaction products and the difference in mineralogical composition following the expansion reaction.

INTRODUCTION

Alkali-aggregate reactions (AAR) have been recognised for more than 50 years. However, the first reports could not distinguish the cause of deterioration of concrete (Stanton 1940). More recently, alkali aggregate reactions (AAR) have become an international research topic (Swenson & Gillott, 1960; 1964).

In general, AAR involves the chemical reaction between aggregates and the pore solution within concrete, leading to the deterioration and in severe cases to gradual collapse of concrete structures (Poole & Sotiropoulos, 1980). Improved materials may be obtained by a combination of scientific and industrial research to investigate the mechanism of alkali-carbonate reactions (Liang, 1994). Here we report studies using conventional petrographic and engineering methods together with new surface analysis techniques to identify the reaction mechanism, the process and location of expansive forces together with changes in composition.

MATERIAL

Unweathered rock specimens were collected from several British quarries. In

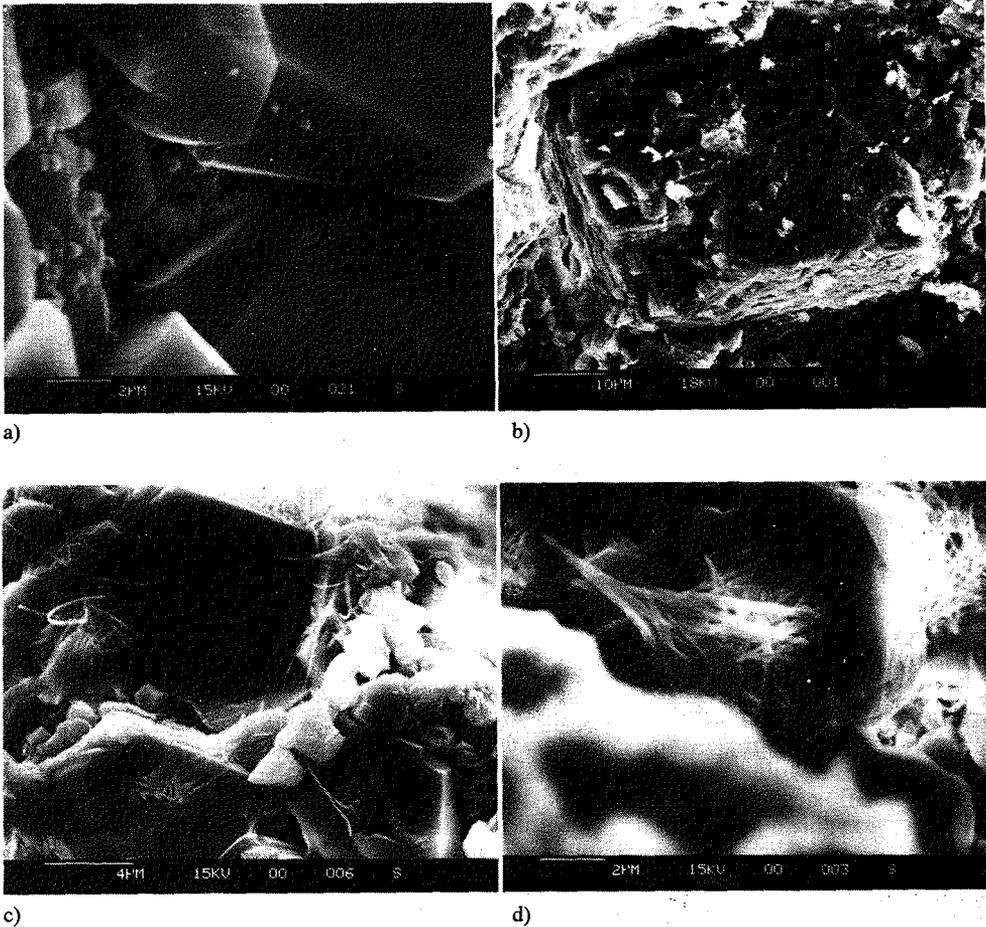
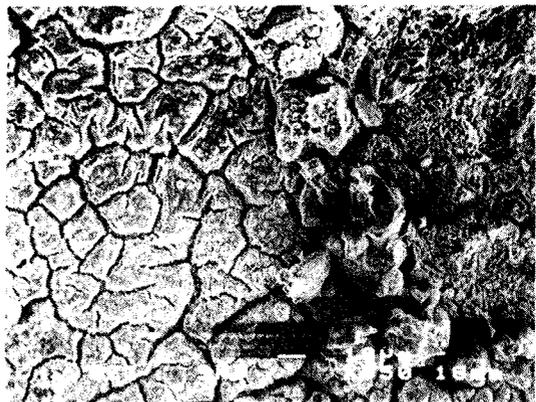


Fig. 1, SEM Micrographs; a) mineral grains within untreated rock sample; b) degraded dolomite crystal at the edge of the treated rock core; c & d) needle-like reaction products on the surface of calcite and dolomite grains.

addition samples from Canada which had previously been shown to undergo reactivity and expansion when used in concrete were used as reference material. The mineralogical composition of the samples was such that they varied from sound limestone and dolomite from the South West of England to a highly dolomitised altered limestone. Most samples were from the Carboniferous age with the exception of the highly porous Permian Mg-limestone and argillaceous dolomitic limestone of Ordovician age from Canada.

Preparation of Samples

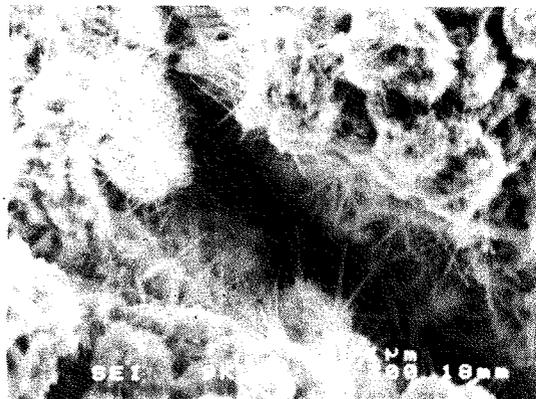
Samples for expansion measurements were prepared according to ASTM C-586 instructions. Cylinders of fresh rock were drilled to 9mm diameter, cut to a length of 35 ± 5 mm and the ends shaped to 120° angle. Samples were stored and



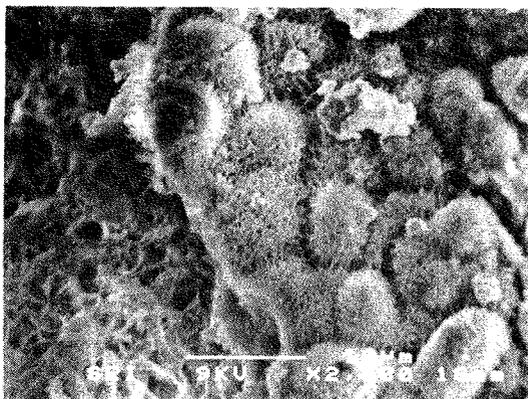
a) White gel deposits on the surface of the rock core after 2 years of exposure.



b) Plate-like minerals deposited within the cracks.



c) Needle-like minerals indicated by XRD analysis as thermonatrite $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$.



d) Left: pristine sample surface; right: gel-like formations which appear to grow out of 'map-cracks'.

Fig. 2. SEM micrographs of products deposited on the surface of the rock core through map cracking.

monitored according to ASTM-C586. A minimum of three specimens were taken from the various locations and from each source five rock cores were produced and immersed in 1N NaOH solution for 24 months at room temperature. For surface and microscopy analysis rock cores were cut to provide cross-section discs for depth profile measurements of elemental distributions.

EXPERIMENTAL

Samples were examined before and after immersion in NaOH using X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), microRaman spectroscopy, scanning electron microscopy (SEM) and X-ray diffraction (XRD) analysis.

XPS measurements were carried out using a Vacuum Generators ESCASCOPE photoelectron spectrometer with a MgK_{α} X-ray source operated at 400W, with a 3mm entrance slit. Wide scans were recorded at 50eV pass energy and regional scans at 30eV. For SEM measurements a Hitachi S2300 scanning electron microscope was used and microRaman spectra were recorded with a Renishaw Ramascope System 2000 with a He/Ne laser tuned to 623nm and operating at 25mW maximum power. SIMS studies employed a Vacuum Generators Ionex Time-of-Flight Mass Spectrometer with 30kV liquid metal gallium source. For XRD analysis, a Philips PW100 diffractometer was used with CuK_{α} radiation.

RESULTS

Geological data indicates that the British aggregates produced from dolomitic limestone would be susceptible to alkali attack under the experimental conditions used here, although their expansion was at a later stage and much slower rate.

The SEM images clearly identified the difference between fresh rock specimens and those treated with alkaline solutions. The physical changes wrought upon dolomitic grains were clearly apparent at the edges of crystals, (Fig. 1a, b). Particularly clear images of damaged dolomite grains were obtained after exposure to alkali (Taylor, 1990) and interesting features such as secondary minerals could also be seen on some grains, (Fig. 1c & d). Acicular and plate-like minerals were identified on the surfaces of primary grains. These were identified as reaction products, formed as a result of grain/pore solution interaction, and consisted mainly of silicon based materials containing some aluminium and magnesium.

EDX analysis also revealed a difference in composition between the edges of core specimens and their interiors, where only partial access was gained by the surrounding solution. XRD analysis supported these observations.

The difference in porosity between tightly packed limestone specimens and highly dolomitised, weathered limestones with large cavities was also investigated. Little difference in expansion behaviour was noticed despite the fact that the alkaline medium would be expected to have easier access to the aggregate grains in the latter material. Presumably the empty space in the cavities accommodated any reaction products formed, which supports that confined spaces only may be of importance for expansion. XPS spectra recorded from treated and untreated samples revealed little difference between exposed and unexposed aggregate surfaces. Here, the depth of analysis is 50Å, and the elements Ca, Mg, Na, O, Al and Si were detected and the relative intensities were similar before and after exposure to solutions. Even when surface deterioration was apparent, as shown in Figure 2, for example, little difference in surface composition could be detected in the XPS spectrum. This observation may be attributed to the fact that such measurements provide

SIMS DATA

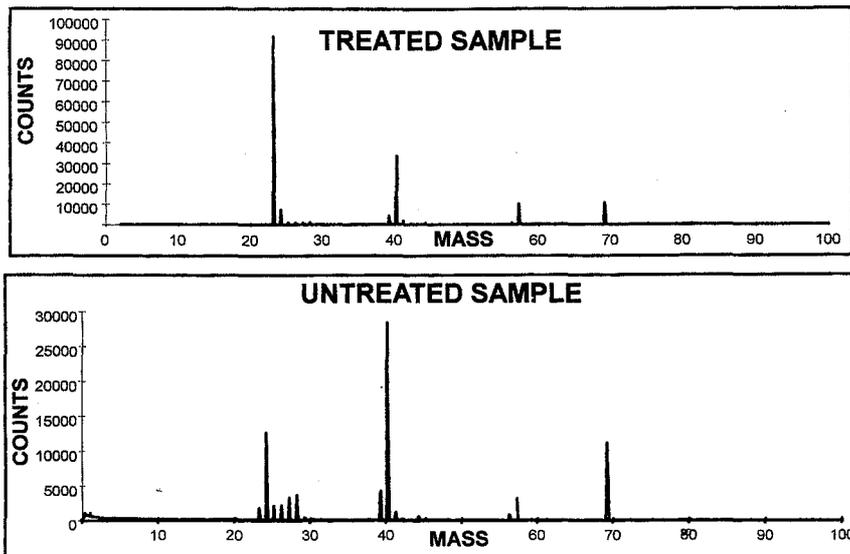


Fig. 3. SIMS data showing the difference in the amount of Na, Mg, Al and Si in treated and untreated samples. The main isotopes are at: Na(23), Mg(27,25), Al(27), Si(28,29) and Ca(40).

information from the uppermost monolayers of the surface and are influenced by the solid/liquid interface rather than the bulk changes produced by chemical reaction.

The results obtained using secondary ion mass spectroscopy were more informative since they offered a sensitive identification of certain elements which were difficult or impossible by other means. Thus useful information was obtained on the ratios of Si, Al, Mg and Ca at the surface of treated and untreated samples, where EDX results, for example, indicated the build up of magnesium and silicon at the periphery of aggregate grains. This may be a consequence of migration of these elements to the surface or leaching of former constituents. Not surprisingly incorporation of sodium from solution was also noted. Some typical spectra are shown in Fig. 3. Numerous attempts were made to record the distribution of important elements across the surface in the form of maps of ionic species at specific amu in the SIMS spectrum. Only moderate success was achieved since these measurements were often complicated by charging of the surface.

The same set of samples were used for XRD analysis. Samples of treated and untreated rock cylinders were crushed into fine powder. These samples were extracted from surface, edge and middle or bulk regions in order to establish the change in mineral composition brought about by interaction with the alkaline solution. Interesting observations were made in the diffraction patterns obtained from the edge regions of samples from Canadian and British sources. Results from fresh pristine samples were quite different but as Fig. 4 shows, those recorded from these samples after exposure to alkali were similar apart from differences in the intensity of the observed peaks. The treated samples therefore appeared to contain the same reaction products albeit in different proportions. By the same token patterns obtained from central regions of treated rock cylinders closely resembled

those obtained from fresh material. However there was a large difference between the surface composition of the treated sample and the edge regions. It may be concluded that the reaction deposits are unlikely to be responsible for rock expansion since they were more or less identical for the two samples with very different expansion properties, reactivity and composition it depends on where they form and how much forms.

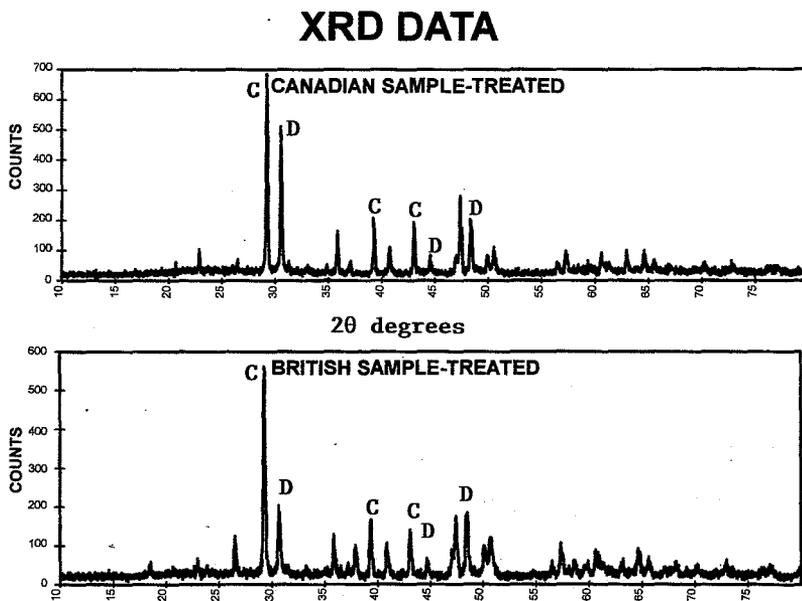


Fig. 4. XRD data showing the similarity in mineralogical composition between very expansive Canadian sample and non-expansive British sample

DISCUSSION

Measurements of the surface composition before and after exposure indicate that the reaction between alkaline solutions and carbonaceous aggregates is a complex reaction. Measurements on Canadian reference materials have shown that argilloseous dolomitic limestone of a given texture and origin may expand following exposure to alkaline solution. However, pure limestone and dolomite may behave similarly under the same experimental conditions and the influence of both clay minerals and silica may be important but the correlation between the rate of expansion and changes in composition is unclear.

Alkali-aggregate reactions (AAR) may take many forms but an interconnecting sequence of events appears to be common to them all. Thus the alkali-carbonate reaction once initiated continues until the ultimate deterioration of the matrix, and unlike ASR is unaffected by various admixtures. However important concurrent side reactions may modify the pathway and hence the rate of the deterioration. One such process is the alkali-silica reaction (ASR) which may expand the lattice through the formation of gel-like products. To obtain an understanding of the relationship between these processes further work is necessary using thermodynamic models to predict the importance of competing reactions (Reardon, 1990).

FUTURE WORK

The ability to image the surface of a polished aggregate grain under a thin layer of alkaline solution using atomic force microscopy (AFM) is particularly appealing (Hochella, 1995). This coupled with surface spectroscopic measurements would enable changes at the surface to be monitored on an atomic scale providing greater insight to the chemical processes taking place at the liquid/solid interface. Equally promising is the technique of environmental scanning electron microscopy (ESEM) which may also provide a visual record of changes occurring at these surfaces simulating in situ conditions, especially moisture.

The expansion behaviour of the Canadian and British aggregates may be further understood by considering the thermodynamics of the reactions involved. To some degree the use of analytical techniques applicable to solid state may assist this study by elucidating the mechanism of (ACR) correlating rock composition and the performance of aggregates in alkaline environments. However the influence of the presence of clay minerals and their role in dedolomitisation processes may also be important (Gillott, 1964).

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