Piersanti, Matthew and Shehata, Medhat H. "The Presence of Ettringite in Concrete Affected by alkali-silica Reaction and its Potential use as Recycled Aggregate." *Journal of Microscopy (Oxford)*. doi:10.1111/jmi.13093.

THE PRESENCE OF ETTRINGITE IN CONCRETE AFFECTED BY ALKALI-SILICA REACTION

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Abstract

Samples were collected from a 20-year-old concrete suffering alkali-silica reaction for examination using scanning electron microscopy. The concrete was also exposed to cycles of freezing and thawing in service. The study shows that backscattered electron imaging, energy dispersive x-ray analysis, and x-ray mapping are helpful tools to identify the type of aggregate used in concrete and the presence of alkali-silica reaction products. X-ray mapping was found a helpful tool to confirm the presence of reaction products in cases where the products or the cracking are not very clear in the collected image. The study shows the presence of crystalline ettringite in the air voids of the concrete. The formed ettringite is believed to have no direct effect on the deterioration as they form in an empty space without causing swelling pressure on the concrete. However, the presence of these crystals might have reduced the efficacy of the entrained-air system to resists freezing/thawing cycles leading to more deterioration, although the study did not confirm that this was the case in the investigated concrete.

Keywords: Durability, scanning electron microscopy, alkali-silica reaction, freezing and thawing, ettringite, air void system.

Introduction

Alkali-silica reaction (ASR) is a deterioration mode in concrete in which a reaction takes place between reactive silica in some aggregates and the alkaline pore solution in concrete[1]. The reaction produces an alkali-silica gel which absorbs water and expands, causing cracking and disruption to the affected concrete elements. Evaluating concrete affected by ASR is carried out using non-destructive tesing[2] or microscopy methods such as the Damage Rating Index[2-4] to evaluate the level of damage. The level of damage, along with lab testing and other parameters such as concrete composition and environmental conditions, can be used to estimate the potential for further expansion in affected concrete[5.7]. One of the tools used to evaluate the mechanisms and level of damage in deteriorated concretes is microscopy, including scanning electron microscope (SEM)

In most cases, concrete deterioration in service occurs due to more than one mechanism, such as freezing/thawing coupled with ASR[8,9]. The presence of one mode of deterioration might accelerate another. For example, cracking due to ASR can promote water to penetrate concrete and cause more damage due to freezing and thawing[9].

Interestingly, it has been reported that ettringite is found in lab concrete suffering different deterioration modes and not exposed to sulphate environment[10]. It has been explained that the formation of this secondary ettringite occurs due to the movement of calcium, alumina, and sulphate ions towards nucleation sites followed by recrystallization. For concrete suffering ASR, the reaction and the formation of ASR gel provide a concentration gradient that promotes the movements of the Ca, Al, and SO_4 ions to nucleation sites[10]. However, it was thought that this type of secondary ettringite is formed in cracks or voids within the concrete and does not contribute to the damage[10].

In this paper, SEM was used as a tool to study the modes of deterioration in 20-year-old concrete samples suffering ASR and were exposed to cycles of freezing and thawing.

Experimental Investigation

Materials

ASR-affected concrete bridge barriers were obtained from a bridge in Sudbury, Ontario, Canada, after 20 years of service. The barriers were used to carry out a comprehensive research project that involves monitoring the remaining expansion of the barriers in an outdoor exposure site and evaluating the expansions of extracted cores under different laboratory conditions[7]. Moreover, some barriers were crushed and used as recycled concrete aggregate (RCA) in new concrete and tested for ASR[7]. In the current study, samples were collected from the barriers and examined using SEM to help evaluate the damaging mechanisms. Some barriers were taken from the northeast ramp, which suffered a high level of deterioration, and others from the northwest side with less cracking and signs of deterioration. The barriers were made with a reactive aggregate from the same region - called Sudbury aggregate - which is reactive gravel containing argillite, greywacke, and quartz-wacke.

Experimental procedure

Samples Preparation for SEM

Concrete chunks were obtained from the barriers of high deterioration for examination using SEM and Energy Dispersive X-Ray analysis (EDS). The samples were dried by incubation in acetone solution to remove the water gently, without causing specimen shrinkage. After that, the samples were placed under vacuum for five days at 38ºC. The samples were then impregnated with epoxy and polished with a diamond grade of 0.3 µm. The polished specimens were sputtered with carbon using Edwards Vacuum Coating System Model #306A. The polished sections were studied in a JEOL JSM6380 LV - SEM operated at 20 kV in backscattered electron imaging mode (BSE).

Experimental Results and Discussion

Figure 1 showed a Backscattered Electron (BSE) image in one of the examined samples showing a coarse aggregate particle surrounded by mortar. EDS spectra collected on the coarse aggregate particle show the composition of locations of argillite composed of silica, alumina, and alkalis in the form of potassium (Spectra 26 and 27), and locations of silica (Spectra 13 and 15). The spectra show that the detected elemental composition matches that of Sudbury aggregate, confirming the presence of the reactive aggregate Sudbury in the sample.

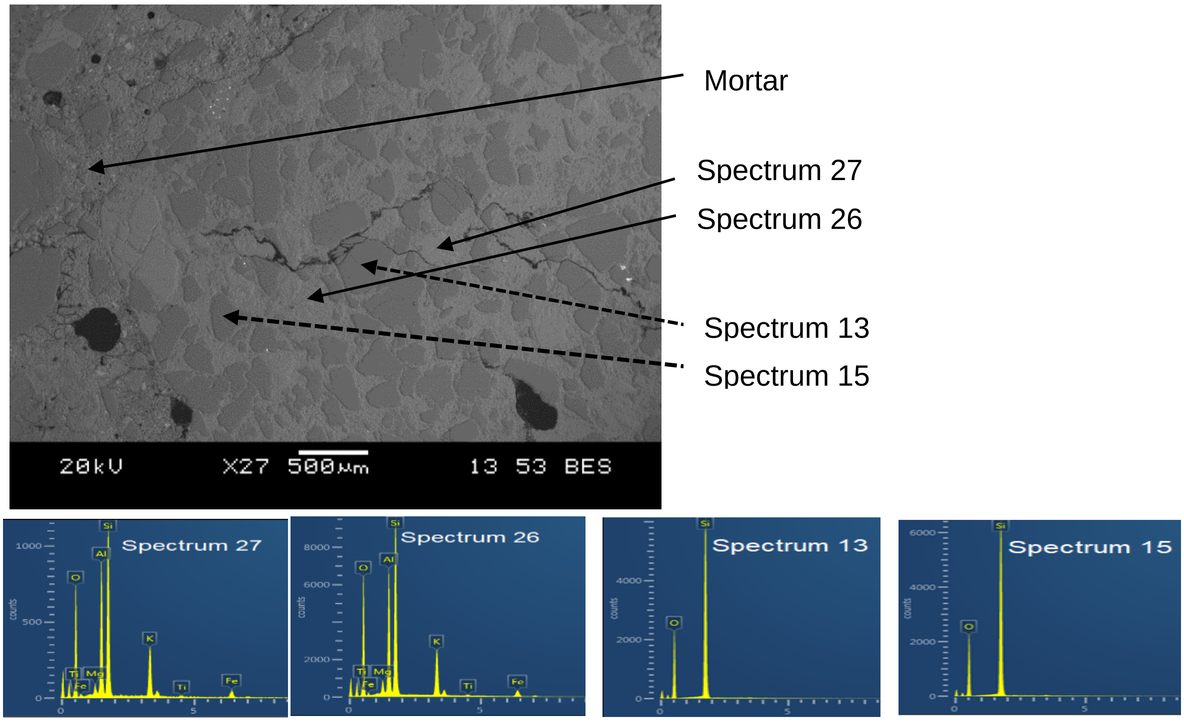

Figure 1. Backscattered Electron Image (BSE) in sample showing original stone with empty cracks and surrounded by mortar.

Figure 2 shows a reactive aggregate with a crack filled with silica gel as evidenced by the collected EDS spectrum. A typical elemental composition of ASR gel includes silica, alkalis, and calcium, with a Ca/Si ratio much lower than that of calcium silicate hydrates (CSH). In CSH, the Ca/Si is usually > 1.0, while in the case of ASR gel, the Ca/Si is much lower than 1.0, as found here. The alkali cation present in the gel is potassium (K) since most of the alkalis in Portland cement produced in Ontario are in the form of K_2O.

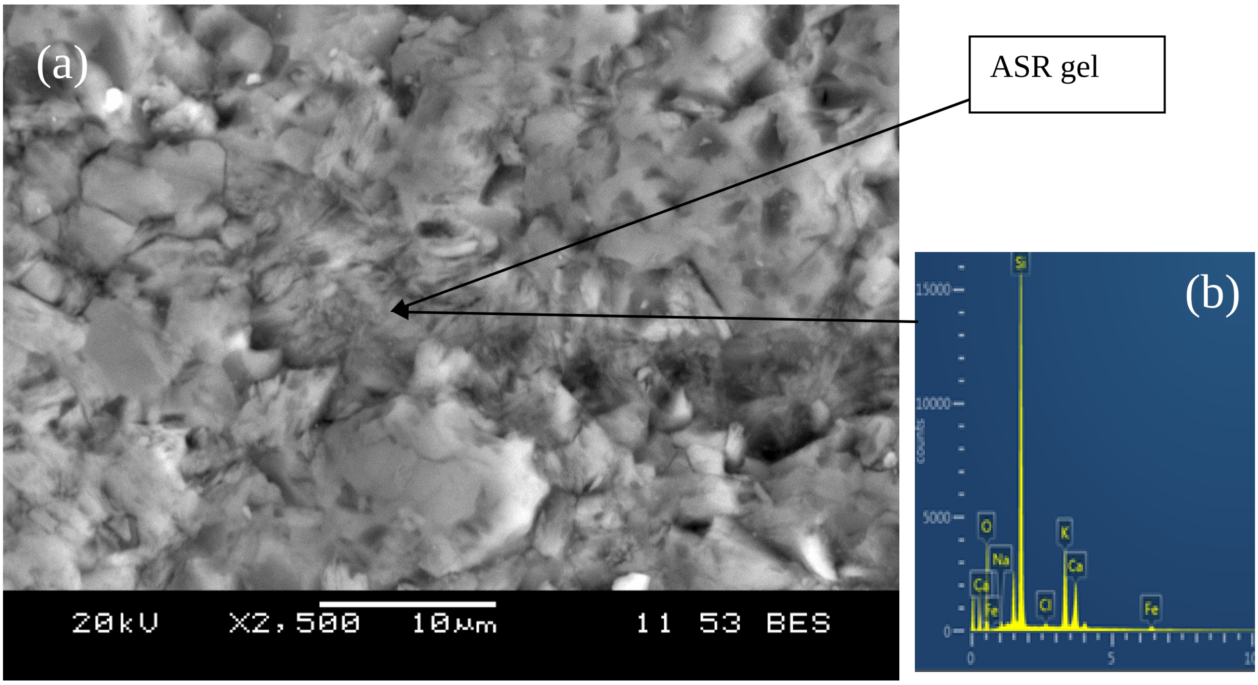

Figure 2: (a) Backscattered Electron Image (BSE) in reactive aggregate showing ASR gel as demonstrated by the EDS spectrum (b).

Another way to assess the presence of an ASR product is to carry out an EDS X-ray mapping of the image to show the distribution of particular elements within the image. This exercise becomes more useful if the presence of ASR produce is not very clear in the collected BSE image. In this process, each element is assigned a color, and the concentration of the element is detected in the whole window or image. A brighter shade of color indicates a higher concentration of the element represented by that color. Figure 3 shows the application of the method on a coarse aggregate particle. Figure 3 (a) shows a BSE image within the coarse aggregate with a possible crack in the middle. Figures 3 (b), (c), and (d) show the distribution of silicon in red, potassium in blue, and aluminum in green. Since silicon and potassium (two main components of ASR gel) are readily available in the stone as well, it is hard to confirm whether or not ASR gel is present. However, when the three mapping windows are placed on top of each other to form the layered image in Figure 3 (e), it is clear that the relative concentration of K (blue) is much higher in the middle of the image, confirming the presence of a gel-filled crack within the aggregate. It should be noted that silica is still present in the gel, as represented by the red dots.

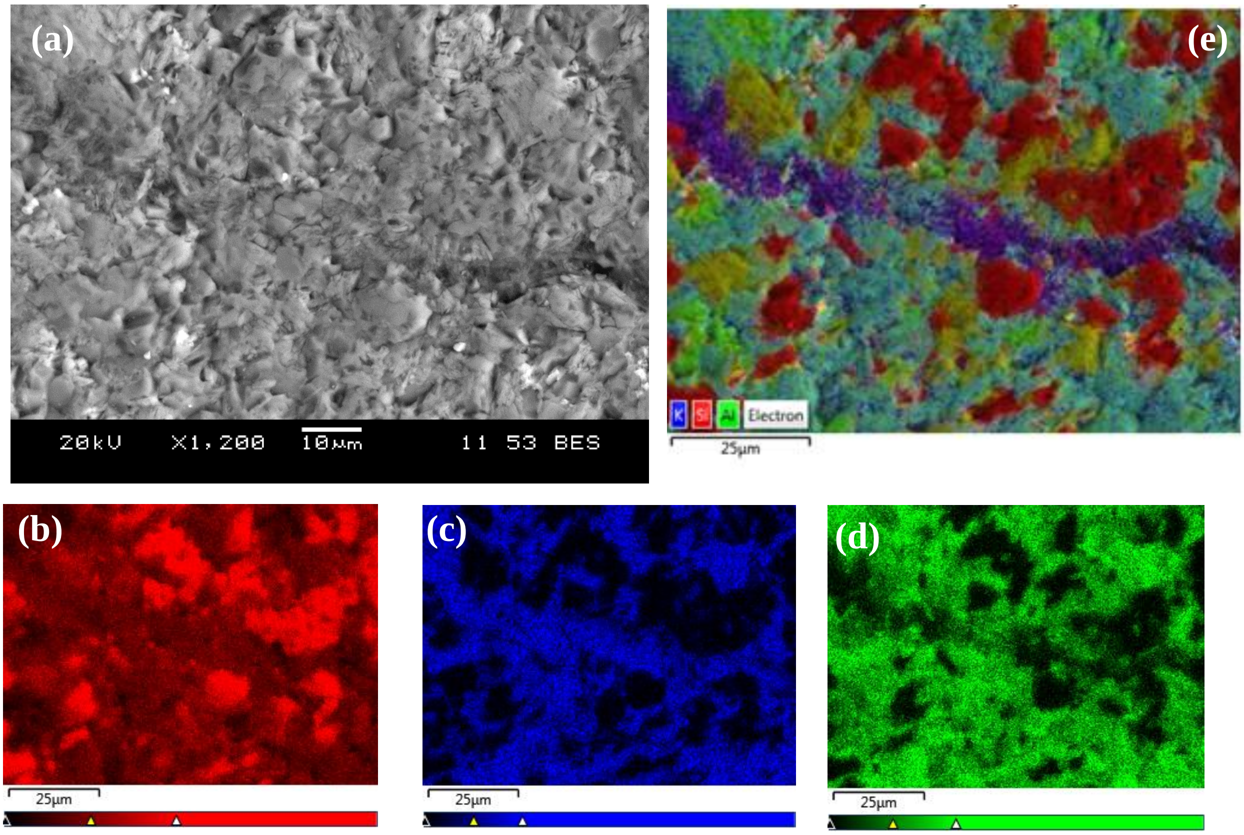

Figure 3: (a) BSE image of cracked aggregate; (b,c,d): X-Ray mapping of the aggregate showing the individual distribution of Si (red), K (blue), and Al (green); and (e) layered image showing the combined distribution of the elements Si, Al, and K.

In examining the collected concrete samples, crystals of ettringite were detected in air voids, as shown in Figure 4. The collected spectrum confirms that the detected material is ettringite. Ettringite within air voids or crakes in deteriorated concrete has been detected and reported in earlier works in lab samples[10]. These crystals are unlikely to contribute directly to the damage as they form in a relatively large space without causing cracking or disruption to the concrete elements. However, having these crystals filling an entrained air void can reduce the capacity of the concrete to resist freezing and thawing cycles leading to more deterioration. Although not confirmed in the current study, it is quite possible that the recrystallization of ettringite in entrained air voids could have contributed - indirectly - to the damage found in the ASR-affected barriers by reducing resistance to freezing and thawing.

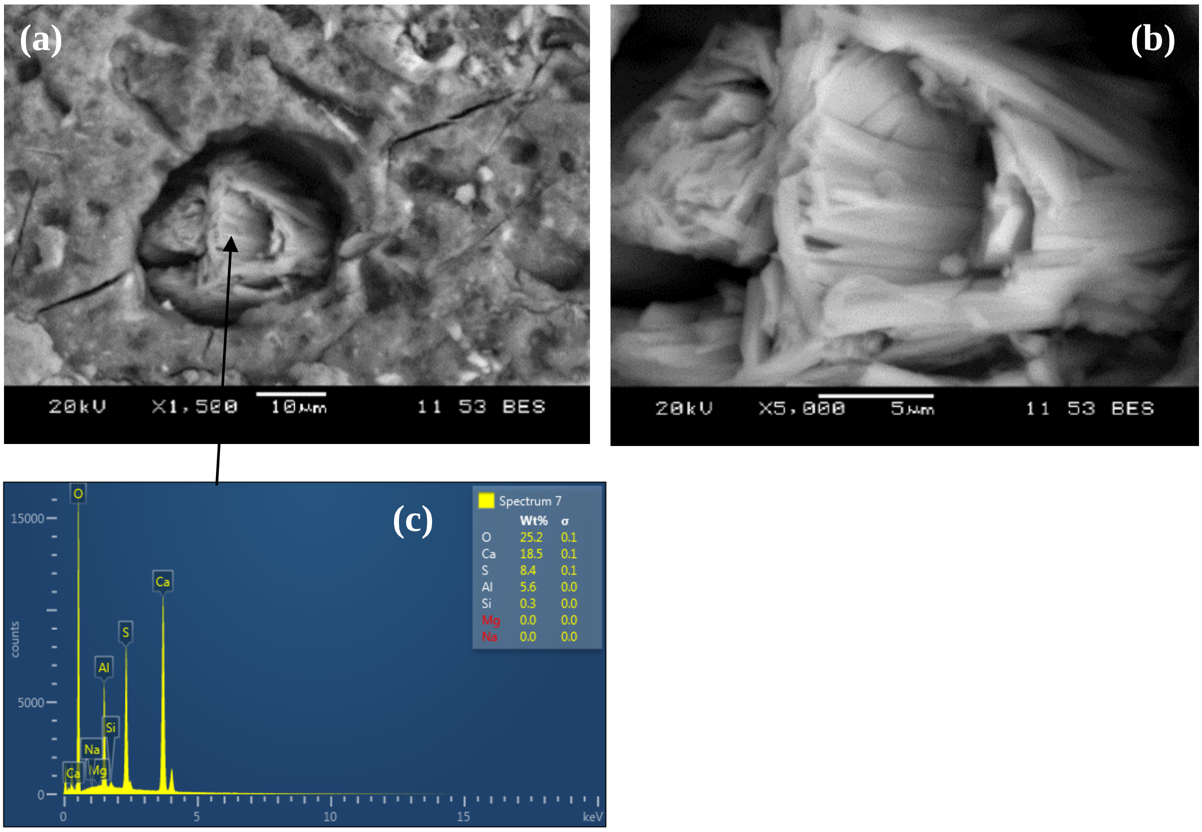

Figure 4: (a) BSE image showing crystals of ettringite in an air void; (b) high magnification BSE of the same location showing the crystals of ettringite, and(c) EDS analysis of the crystal.

CONCLUSIONS

For the materials investigated in this study, the following conclusions are drawn:

1. The SEM and EDS analysis are useful tools to help identify aggregates in concrete by comparing the obtained EDS elemental composition to the aggregate phase composition.

2. The presence of ASR products could be detected by BSE combined with spot EDS analysis. In cases where the presence of gel is not clear in the BSE image, elemental mapping by EDS and the creation of a layered image can be helpful.
3. Using SEM, ettringite was found as crystals in air voids in deteriorated concrete suffering ASR. This type of ettringite formation in air voids indicates that ettringite is not a direct cause of the damage. However, its presence in air voids could have a role in reducing the concrete capacity to withstand freezing/thawing cycles.

ACKNOWLEDGMENT

Funding for this research project is obtained through a discovery grant from the Natural Sciences and Engineering Research Council of Canada (NSERC) and the Ministry of Transportation, Ontario (MTO) Highway Infrastructure Innovation Fund. The financial support of NSERC and MTO is highly appreciated. Opinions expressed in this paper are those of the authors and may not necessarily reflect the views and politics of MTO.

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