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Raman microscopy of alkali-silica reaction (ASR) products formed in concrete

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ABSTRACT

Recently, the structure of the crystalline alkali-silica reaction (ASR) product formed in affected concrete has been identified based on μ-XRD measurements. However, the data were obtained from a single aggregate. In this study, Raman microscopy is applied on crystalline ASR products formed in several aggregates and concrete mixtures, enabling a comparison of their spectra and with it their structure. In a first step, samples from the same concrete used for μ-XRD measurements are analyzed and compared. In a second step, samples from a second structure and from a concrete prism test are measured. In addition to Raman microscopy, SEM with EDX is used to characterize the microstructure. The Raman spectra of the crystalline ASR product are practically identical in all studied aggregates and concrete mixtures, showing it is the same phase. This conclusion is further supported by the microstructural data.

1. Introduction

Alkali-silica reaction (ASR) leads to damage in various concrete structures worldwide. The internal stresses that lead to cracking are caused by the formation and swelling of the ASR products within the aggregates of the concrete. The increasing stress developing in affected aggregates eventually leads to their cracking, with further cracks proceeding into the cement paste. The mechanism leading to expansion in ASR is still not well understood. The main reason is the insufficient characterization of the ASR products. Although its chemical composition can be easily analysed using energy-dispersive X-ray spectroscopy (EDS) in a scanning electron microscope (SEM) [1–8], the small volumes of ASR products formed in aggregates make an analysis of their structure very challenging. As a result, little data are available. In a few studies, XRD patterns have been presented [2,9–11]. However, the structure of the crystalline ASR product present in aggregates has been identified only recently using synchrotron-based micro X-ray diffraction (XRD) [12]. The crystalline ASR product is a previously-unknown silicate, consisting of a layered framework with wide channels and large interlayer spaces. Consequently, the SiO_2 tetrahedra are mainly configured as layers of SiO_2 tetrahedra with three bridging oxygens (Q_3). Additionally, a smaller amount of SiO_2 tetrahedra is present as chains with two bridging oxygens (Q_2) surrounding channels and interlayer space. Both channels and interlayers permit the incorporation of potassium, sodium, calcium and water. However, this analysis was performed on the crystalline ASR products in only one aggregate, as the process of analysis is very complex and requires equipment of restricted access. Therefore, a method allowing an easier identification of the structure of the ASR products would permit to assess the representativeness of the identified silicate.

A method that has the potential to reveal information about the structure of ASR products is Raman spectroscopy. It is based on inelastic scattering of monochromatic light, usually provided by a laser, and gives information about the vibrational modes of the investigated material resulting in a phase-specific “fingerprint”. It has been applied in studies on cement hydration, carbonation and sulfate attack [13–18]. In layer silicates with similarities to the crystalline ASR product, e.g., magadiite or kanemite, the combination with nuclear magnetic resonance (NMR) or XRD has permitted to assign specific bands of the Raman spectrum to structural features of the investigated materials [19–25]. Recently, first efforts have been made to apply it on natural [26] and synthetic [27] ASR products. Raman microscopy allows not only the analysis of bulk samples, as those performed in the majority of studies referenced above, it enables also in-situ analysis with a lateral resolution of a few micrometres [15,28,29]. As such, Raman microscopy is expected to allow the characterization of small amounts of ASR products formed in affected concrete. If the technique can be applied successfully, it should make it possible to compare the ASR products formed in different aggregates of a concrete, in concrete from different structures in the field and in concrete subjected to accelerated tests in the laboratory.

This study aims to assess the representativeness of the results presented in [12] by exploring the potential of Raman microscopy to characterize ASR products formed in concrete. In a first step, the ASR

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products formed in different aggregates of the same concrete used for the μ-XRD analysis in [12] are studied. In a second step, the obtained Raman spectra are compared with the ones obtained from the ASR products formed in another concrete damaged by ASR. Then, the analysis is extended to ASR products formed in a concrete tested in a concrete prism test. The ASR products are additionally studied with SEM combined with EDS.

2. Materials and methods

2.1. Materials and mix designs

Concrete from a bridge (built in 1969, concrete CS-1) and a retaining wall (built in 1980, concrete CS-2), both damaged by ASR [30], were used for analysis. Concrete CS-1 was the same one used for the μ-XRD analysis in [12]. Information on the concrete composition is given in [5]. In both cases ordinary Portland cement (OPC) was used. Their Na_2O-equivalent is not known, but Swiss cements typical have values in the range of 0.7–0.9 kg/m^3. The cement content in concrete CS-1 is between 300–350 kg/m^3, water-to-cement ratio (w/c) between 0.45 and 0.50. The aggregates mainly consist of limestone with detritic quartz occasionally incorporating a dolomitic component. The cement content and w/c in concrete CS-2 is about 400 kg/m^3 and 0.43–0.45. The aggregates are dominated by limestone with detritic quartz and siliceous limestone. The aggregates present in these two structures are slow-reacting, as it is the case as well for the concrete used for the accelerated test described below. The samples from the structures were sealed in plastic bags immediately after coring. In the laboratory, discs were cut from the cores and studied in an optical microscope to identify aggregates containing ASR products. After identifying locations of interest, the samples were ground with silicon carbide coated papers (P240 and P600). Following quick flushing with acetone and additional cleaning with pressurized air, the samples were stored in airtight plastic bags until analysed by Raman microscopy. The third concrete was produced with slow-reacting silicates consisting of sandstones and cataclasites with crypto- and microcrystalline quartz as the reactive phase, a cement content (high alkali OPC) of 440 kg/m^3 resulting in a Na_2O-equivalent of 5.5 kg/m^3 and a w/c of 0.45. It was subjected to the Norwegian 38 °C concrete prism test [31] and reached an expansion of 0.22% after two years. Samples were prepared as described above. Samples of concrete CS-1 and CPT were prepared for the SEM analysis after they were analysed by Raman microscopy. This allowed an investigation of identical locations with both methods. The samples were dried for three days at 50 °C, impregnated, polished and carbon coated.

2.2. Methods

Two different SEM were used for sample analysis. The ESEM-FEG XL30 was operated in the high vacuum mode (3.0–6.0 × 10^{-6} Torr) with an accelerating voltage of 12 kV and a beam current of 200–220 μA. The chemical composition was determined with energy dispersive X-ray spectroscopy (EDS) using an EDAX 194 UTW detector, a Philips digital controller and Genesis Spectrum Software (Version 4.6.1) with ZAF correction. The Nova NanoSEM 230 FEI was used in the high vacuum mode (3.0–5.0 × 10^{-6} Torr) with an acceleration voltage of 12 kV, a spot size of 4.5 and a beam current of 90–100 μA. An Qxford SSD detector (80 mm^2) and INCA Energy software with ZAF correction were used for the EDS analysis. Between 30 and 60 EDS point analysis were conducted per aggregate to measure the chemical composition of the ASR products.

The Raman spectra were acquired using a Raman Bruker Senterra microscope equipped with a Peltier-cooled CCD detector and operated with the software Opus 6.5. A laser with a wavelength of 532 nm was operated with a power of 20 mW using a lens with a magnification of 50 ×. Integration time was 20 s with two accumulations. Spectrum resolution was 3–5 cm^{-1}. The diameter of the laser beam was about 1 μm. However, the diameter of the area irradiated by the laser beam is about 2–3 times larger depending on focusing accuracy and surface roughness. Several spectra were acquired for each investigated location, placing the measured spots at a distance of a few micrometres from each other. The mean was calculated for each location and the resulting spectrum was smoothened with a running mean of 10 to decrease noise. The spectra were background corrected and normalized. In the concrete of the bridge, between 10 and 30 Raman spectra were collected from the crystalline ASR product present in cracks within six different aggregates. Due to the small rock fragments present in veins filled with ASR products, a background signal of quartz and/or calcite was sometimes recorded, as for example in concrete CS-2. Such rock fragments are a common feature in ASR-affected concrete. They are produced by the initial cracking of the aggregates due to ASR and are embedded at a later stage by ASR products filling the cracks. In addition to the spectra from the ASR products, measurements were conducted on calcite and quartz to facilitate the identification of background signals. The absolute Raman intensities of these two minerals were 10–20 times higher than the intensity of the ASR products.

3. Results

3.1. Morphology and chemical composition

The majority of the cracks in aggregates of concrete CS-1 and CS-2 are filled with ASR reaction products. They display domains with a layer-like texture in cracks within the aggregates and are smooth and untextured in the interface with the cement paste (Figs. 1 and 2). As shown in [12,26] the textured ASR products are crystalline, while the untextured are amorphous. As crack-fillings in the cement paste itself, ASR products often display layering parallel to the crack edges (Fig. 3).

The cracks caused by ASR in aggregates of concrete CPT are mainly empty. Only in the periphery of cracked aggregates within a distance from the interface with the cement paste of about 1–3 mm, larger amounts of ASR products are present (Fig. 4). Right at the interface, they are amorphous (locations L2 and L3 in Fig. 4). However, further away from the interface (> 0.2 mm) they are crystalline and structured in layer-like domains identical to the products in concrete CS-1 and CS-2 (locations L1 in Fig. 4). Sometimes, amorphous products are present as thin layers (1–5 μm) at the edge of cracks accompanied by crystalline ASR products that are filling part of the crack in the middle (Fig. 5).

The chemical composition of the crystalline ASR product in cracks

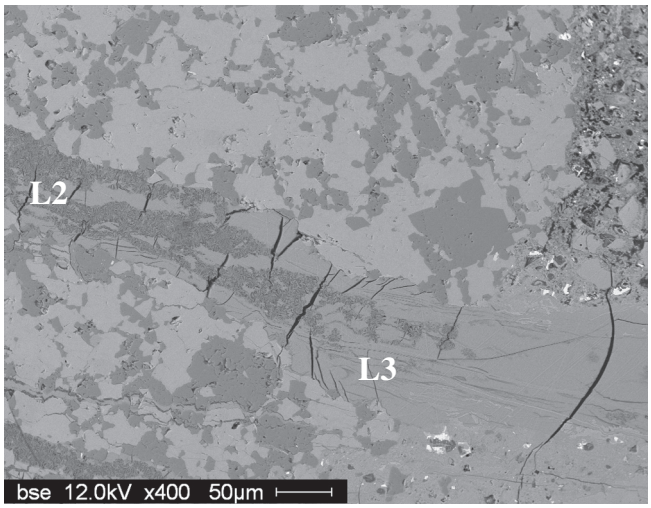

Fig. 1. Vein in aggregate of concrete CS-1 with locations L2 (crystalline and amorphous ASR products) and L3 (amorphous ASR product) indicating the location where the Raman spectra shown in Fig. 7B were obtained. Location L1 is further to the left in the vein, where only crystalline ASR product occurs.