MICROSTRUCTURE, CRYSTALLINITY AND COMPOSITION OF ALKALI-SILICA REACTION PRODUCTS IN CONCRETE DETERMINED BY TRANSMISSION ELECTRON MICROSCOPY

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Abstract

Several aspects of alkali-silica reaction (ASR) are still poorly understood, for example the formation of ASR products occurring before significant aggregate cracking. This study focuses on the analysis of these products and the comparison with the products formed after crack formation. A novel approach for the characterisation of ASR products was used combining different electron microscopy techniques. This combination allows analysis of the ASR products present in small gaps and cracks with a width below 1 µm present between adjacent mineral grains of aggregates. In the three samples studied, the products in thin grain boundaries show no distinct morphology and they are amorphous. They were defined as untextured ASR products. The products present in larger veins form fibrils and platelets, called platey products, and are mainly crystalline. In spite of the differences in morphology, untextured and platey ASR products are of similar composition.

1. Introduction

Alkali-silica reaction (ASR) is a critical problem worldwide [1] leading to long-term degradation of affected structures. ASR occurs between aggregates containing reactive forms of silica, alkalis originating from the cement and moisture. It can affect all types of concrete structure like walls, pavements, bridges and dams. As an example, more than 400 structures suffer from this deleterious reaction in Switzerland [2]. More than a third of Swiss dams show expansion likely attributable to ASR [3]. In most cases, where moisture cannot be excluded, there is no possibility to stop the expansion caused by the reaction and repair is very expensive. Dams for example may have to be cut vertically (slots of 1-2 cm large) to release stresses [3].

The mechanisms behind the expansion caused by ASR are still not fully understood. But according to current knowledge, the reaction proceeds as follow [4]. In an alkaline environment (pH ≈ 13), the silica structure of the aggregates is dissolved by hydroxyl ions breaking siloxane bridges and attacking terminal silanol groups ≡Si-OH (here “≡” does not indicate a triple bond but the fact that Si is connected to three other atoms) which are present at the silica-water interface, according to Eq. 1:

OH⁻ ions also hydrolyse the siloxane bonds ≡Si-O-Si≡ (Eq. 2):

Sodium and potassium ions provided by the cement balance the negative anion charges in the silica network (Eq. 3):

This product can absorb water, resulting in swelling, expansion and cracking of concrete.

The first ASR products are formed along mineral grain boundaries or in pre-existing cracks within the aggregates [5, 6, 7]. Their width is generally in the range of a few hundredths of micrometer to one micron at most. When the stress originating from the formation of these ASR products exceeds

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the tensile strength of the aggregates, new cracks are generated. They start in the aggregates and propagate into the cement paste. They are considerably wider (typically $> 10\ \mu\text{m}$) than the gaps between adjacent mineral grains or than the pre-existing cracks. Eventually, these cracks are filled with new ASR products [5].

The characteristics of the ASR product firstly formed in boundaries or narrow cracks are insufficiently understood. The small amount of ASR product formed makes it very challenging to analyse as it is below the spatial resolution ($1\text{-}3\ \mu\text{m}$) of energy-dispersive X-ray spectroscopy (EDS) as used in conventional scanning electron microscopy (SEM).

Although ASR products are generally reported as being a gel, *i.e.* amorphous, it has been shown in a few publications (*e.g.* [8, 9, 10, 11, 12, 13, 14]) that the secondary ASR product present in large cracks within the aggregates can also be crystalline. Typically, there is a change to an amorphous phase at the edge of the aggregate as it was already shown by Leemann [15] and as it can be seen in Fig. 1. In the cracks propagating into the cement paste the product is amorphous [16].

Fig. 1: SEM-BSE image of a crack running from an aggregate into the cement paste illustrating ASR products with two different microstructures, the crystalline phase (C) in the aggregate and the amorphous gel (A) at the edge of the aggregate and in the cement paste in concrete C1.

The composition of ASR products filling $10\text{-}100\ \mu\text{m}$ cracks in aggregates has been extensively studied (for example [17, 18, 19, 20]), as they are easy to analyse with techniques such as conventional SEM-EDS. The results in regard of the ASR products within aggregates vary to a certain degree but always contain Si, K, Na and Ca with approximate atomic ratios of $0.15\text{-}0.25$ for Ca/Si and $0.20\text{-}0.35$ for (Na+K)/Si (*e.g.* [18, 20]).

Several crystal structures for ASR products have been proposed in the literature; they are all layered silicates independently of concrete mix design and type of aggregate in which it is formed as indicated in [15]. For example Dähn et al. concluded that mountainite $\text{KNa}_2\text{Ca}_2[\text{Si}_8\text{O}_{19}(\text{OH})]\cdot 6\text{H}_2\text{O}$ or rhodesite $\text{KHCa}_2[\text{Si}_8\text{O}_{19}]\cdot 5\text{H}_2\text{O}$ can fit to the crystal structure of the ASR product observed in a 50-year old bridge [8], which was already stated by de Ceukelaire from the analysis of ASR product coming from a Belgian bridge [10].

At the edge of the aggregate particles and in the cement paste the calcium concentration of the amorphous ASR product increases and the alkali concentration decreases to give a composition similar to C-S-H [13, 14, 18, 21].

Transmission electron microscopy (TEM) offers a higher spatial resolution for imaging and chemical analysis compared to SEM-EDS, because the problem posed by the interaction volume of the electron beam with the sample can be significantly reduced due to the thickness of the TEM lamella (approximately 100 to 150 nm) [22]. Moreover, with selected area electron diffraction (SAED) in TEM it can be determined whether the analysed material is crystalline or amorphous, which cannot be done in a SEM.

An improved knowledge on the ASR products formed in narrow spaces of aggregates is a key issue to understand the mechanism of ASR, the goal of this study is to characterize these ASR products with techniques which have the required spatial resolution. First, locations of interest are identified with SEM-EDS. TEM lamellae are cut in these locations with focused ion beam (FIB) followed by an analysis in the TEM using both scanning transmission electron (STEM) mode, STEM-EDS and SAED. To the knowledge of the authors, this is the first approach combining these techniques for characterising ASR products.

2. Materials and methods

2.1. Materials preparation

Three different specimens were studied. The first one came from an accelerated mortar prism test (M1) and the two others from two different concrete structures in Switzerland (C1 and C2), both affected by ASR.

Mortar M1 was produced with 580 kg/m³ CEM II/A-LL 42.5N (Portland cement blended with 15 wt% limestone powder), a water-to-cement ratio of 0.50 and ASR-reactive gneiss aggregates with a grain size of 0-4 mm. Bars with dimensions 40 x 40 x 160 mm³ were exposed to a temperature of 60 °C and a relative humidity of 100 % for 20 weeks (following the Swiss guideline SIA 2042 [23]) resulting in an expansion of 0.25 ‰. More experimental details about this accelerating procedure can be found in [24].

After the test, this mortar was prepared for SEM analysis: a 2-cm-thick slice was cut from the middle of one of the prisms, dried in an oven at 50 °C for three days, epoxy impregnated, polished down to 1 µm and carbon coated.

Concrete C1 originated from the abutment of a concrete bridge built in 1969 and damaged by ASR. The concrete was produced with CEM I and aggregates consisting mainly of limestone with detritic quartz and sandstone with minor amounts of gneiss, quartzite, schist and granophyre [13].

Concrete C2 was collected from an ASR-affected gravity dam constructed in the 1950s. It was produced with CEM I and aggregates consisting mainly of gneiss and minor amounts of limestone containing detrital quartz.

After cutting, C1 and C2 samples were prepared for SEM analysis in the same way as described above.

2.2. Methods

The samples were first investigated with a scanning electron microscope (Nova Nano SEM 230, FEI) at a pressure of $2.0\text{--}4.0 \times 10^{-6}$ Torr at an accelerating voltage of 12 kV and a beam current of 80-88

113 μA . A SSD detector (80 mm^2) from Oxford and INCA Energy software with ZAF correction were
 114 used for the EDS analysis.
 115 In each sample, ASR products were identified by SEM imaging, using backscatter electrons (BSE)
 116 detector and EDS line scans performed across the boundaries of adjacent quartz grains in an
 117 aggregate, as shown in Fig. 2. Here, the values of concentrations are not considered, only the fact that
 118 alkalis and calcium concentrations are increasing in the gap between 2 aggregates. Multiple SEM
 119 images at different magnifications were taken in order to easily recognize the working areas during
 120 milling in the FIB.
 121

122 *Fig. 2: Example of a) SEM-EDS line scan (red arrow) performed across a crack and b) corresponding concentration profiles for different elements along the crack, especially calcium, sodium and potassium which show peaks indicating that the crack is filled with ASR product.*

123 Each sample was then transferred to a focused ion beam microscope (NVision40 FIB, Zeiss) in order
 124 to produce TEM lamellae. The dual-beam column of this device allows the isolation and milling of
 125 the exact area of interest. First a carbon protective layer was deposited to preserve the surface. The
 126 sample was then milled to produce a $15 \times 10\text{ }\mu\text{m}^2$ lamella: thinning down to $1.5\text{ }\mu\text{m}$ was done at 30
 127 kV with progressively decreasing currents ranging from 27 nA down to 1.5 nA, in order to optimize
 128 the time and to keep the ASR product undamaged. Subsequently, the lamella was extracted by a
 129 piezo-controlled micromanipulator (Kleindiek) and transferred onto a TEM copper grid by carbon
 130 welding. In the next step, its thickness was reduced to about 150 nm (corresponding to electron beam
 131 transparency) by a final milling using decreasing voltages from 30 to 5 kV and decreasing currents
 132 from 1.5 nA to 80 pA.
 133 A transmission electron microscope (Tecnai Osiris TEM, FEI) equipped with an EDS detector (Nano
 134 XFlash, Bruker) was used for TEM and EDS analyses, operating with an accelerating voltage as low
 135 as 80 kV and a low current density (corresponding to a very small spot size) in order to limit the
 136 extent of potential beam damage and as such to preserve the structure of the ASR products.
 137 For investigation, STEM was chosen from the different modes of analyses available in the TEM. In
 138 this mode, the electron beam is focused into a small probe and scanned over the sample. The generated
 139 signal is detected at any point of the specimen. Two different detectors were used to generate images:

bright field (BF) and high angle annular dark field (HAADF). SAED was also used in order to check the crystallinity of the investigated ASR products, using a selected area (SA) aperture of 250 nm of diameter.

Finally, for chemical analysis, STEM-EDS hypermaps were recorded, *i.e.* a single EDS spectrum is collected for each scanned point. Quantification can then be done on a single spectrum (*i.e.* in a single point of the map) or on a defined area, with averaging of the EDS spectra contained in this area. The choice of the quantified area is done on the STEM-BF or the STEM-HAADF image eventually combined with elemental mapping. Especially the Na and/or K maps are considered as they can help to localize ASR products.

3. Results

3.1. Morphology and crystallinity of ASR products

Fig. 3 shows part of a gneiss aggregate consisting entirely of quartz grains in the chosen location of mortar M1. Several gaps between adjacent quartz grains are present, some of them seem to be empty and others are filled with ASR product. Among them, a boundary between two adjacent quartz grains supposedly filled with ASR product and a larger crack clearly filled with ASR product (namely M1-1 and M1-2 indicated in Fig. 3) were chosen by SEM to be milled by FIB and analysed by TEM. Corresponding STEM images are shown in Fig. 4a and b at different magnifications.

Crack M1-1 is very thin, between 150 and 200 nm in width. ASR product is present, and the observed “particles” have dimensions in the same order of magnitude, between 50 and 150 nm. The corresponding SAED pattern is shown in Fig. 5: a diffuse ring is observed around the transmitted beam (*i.e.* the big luminous point at the centre of the diffraction pattern) showing that the material is completely amorphous.

Sample M1-2 is located in an approximately 6-8 μm wide crack partly filled with ASR product. In this crack, the ASR product displays relatively large fibrils or platelets becoming larger in the centre of the crack. Here, they form well defined, relatively large platelets (in the red circle of Fig. 4b). SAED reveals the structure of the ASR products: the fibrils near the aggregate edges are amorphous (their diffraction pattern looks the same as in Fig. 5), whereas the platelets in the middle of the vein are crystalline, as shown by the SAED pattern (Fig. 4b) which is composed of points corresponding to reflections of crystallographic planes. As the quantity of ASR product is low, only one sharp SAED pattern was collected and it was not possible to index it. It was observed that the intensity of the diffraction spots decreased with increasing exposure time to the electron beam, until these spots completely disappeared, after which a diffraction pattern characteristics of an amorphous material (like the one of Fig. 5) was observed. This clearly indicates that the electron beam damages the sample during exposure, which was already studied by Roessler et al. on crystalline C-S-H [25]. It was concluded by these authors that at cumulative electron doses higher than $6.4 \times 10^3 \text{ e}/\text{\AA}^2$, the crystalline parts of C-S-H are turned into amorphous ones. In this study, even if the cumulative electron dose was kept largely lower ($\leq 5 \times 10^2 \text{ e}/\text{\AA}^2$), the crystalline structure was observed to progressively turn into an amorphous one.

Fig. 3: SEM image showing the two analysed locations (cracks M1-1 and M1-2) in a gneiss aggregate of the M1 sample.

SEM image of Fig. 6 locates one analysed area of the concrete C1 (namely sample C1-1). The studied aggregate consists of calcareous sandstone, containing quartz and a substantial amount of calcite. Sample C1-1 was chosen in an area consisting of quartz, where the authors considered grain boundaries to be present, in order to maximise the probability to find ASR product. The selected crack is approximately 500 nm and is filled with ASR product (checked by SEM-EDS with the same method as described in paragraph 2.2 and Fig. 2).

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Fig. 4: STEM images (BF detector) of (a) M1-1 (b) M1-2 cracks filled with ASR product. The red circle indicates the area of crystalline ASR product with associated SAED diffraction pattern.

Fig. 5: SAED pattern of ASR product of Fig. 4a showing a diffuse ring and no distinct diffraction spots.

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The corresponding STEM images are shown in Fig. 7 (left and centre images). The morphology of the product found in C1-1 crack is of similar contrast as the adjacent minerals and appears structureless. Its dimensions are so small that it is difficult to distinguish it from the mineral grains. It was not possible to use SAED on this product with the selected area aperture of 250 nm due to its tiny size (diffraction signal intermixed with those of neighbouring minerals). In order to make it easier to localise the ASR product on the image, potassium elemental distribution measured by STEM-EDS is

198 shown in Fig. 7 (right image). Note that a mica grain (containing O, K, Al and Si) was also identified
 199 and must not be mistaken for ASR product.
 200

201 *Fig. 6: SEM image of Concrete C1 showing the location of sample C1-1. The studied aggregate consists of calcite (light grey) and quartz (medium grey).*

202 The location of sample C1-2 in an aggregate containing quartz and calcite is shown on SEM image
 203 of Fig. 8, whereas Fig. 9 shows STEM images of this sample. The microstructure of the ASR product
 204 included in this large crack (50-70 µm) is comparable to the one of the central area of the crack in
 205 sample M1-2, with even larger platelets. Additionally, they are also crystalline as confirmed by
 206 SAED. A diffraction pattern of one of these platelets is shown at Fig. 10 as an example: the pattern
 207 is composed of individual reflections (bright points) which are seen within diffuse rings similar to
 208 rings of Fig. 5. This indicates that the material excited by the electron beam in the analysed area does
 209 not consist of one single crystal, but of an assemblage of small crystals (smaller than the size of the
 210 aperture, *i.e.* here 250 nm). D-spacings were calculated from the rings determined in Fig. 10 and were
 211 compared to calculated d-spacings of crystallographic structures proposed in the literature for ASR
 212 products, as mentioned in the introduction (Table 1). The manufacturer of the TEM claims the
 213 determination of d-spacings with an error of 5 to 10 %. In Table 1, precisions were calculated with a
 214 5% error. It can be seen that the d-spacings determined experimentally are close from the ones of
 215 okenite, mountainite, rhodesite and structure determined by Dähn et al. [8], with a better agreement
 216 with okenite structure.
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Table 1: *D*-spacings calculated from SAED pattern of Fig. 10 compared with the closest ones of ASR candidate phases from the literature.

<i>d</i> -spacings	Determined in this study with a 5% error	Okenite [26]	Mountainite [27]	Rhodesite [28]	Structure determined by Dähn et al. [8]
d_1 (Å)	4.53 ± 0.23	4.43	4.40	4.37	4.36
Plane		(-2 0 2)	(3 0 0)	(4 1 0)	(0 0 2)
d_2 (Å)	3.58 ± 0.18	3.56	3.56	3.53	3.57
Plane		(1 -1 5)	(-2 1 3)	(0 0 2)	(1 1 2)
d_3 (Å)	3.18 ± 0.16	3.17	3.15	3.15	3.17
Plane		(2 -2 2)	(-1 2 1)	(2 2 0)	(2 2 0)

Fig. 7: STEM images (BF detector) of C1-1 sample (left and centre images). Right image shows the TEM-EDS elemental distribution of potassium, facilitating the locating of ASR product.

Fig. 8: SEM image of location of sample C1-2, in an aggregate containing quartz (medium grey) and calcite (light grey).

Fig. 9: STEM images (BF detector) of C1-2 sample.

Fig. 10: SAED pattern of one of the platelets forming ASR product of Fig. 9.

Fig. 11: SEM image locating samples C2-1 and C2-2 in a quartz aggregate of concrete C2.

Fig. 12: STEM images (BF detector) of corresponding cracks of Fig. 11: (a) C2-1 and (b) C2-2.

223 In Fig. 11 the locations in concrete C2 are indicated where the samples C2-1 and C2-2 were obtained.
 224 Two thin cracks were chosen on purpose. The crack in sample C2-2 is approximately 1 μm wide and
 225 in sample C2-1 it is about half of this width. Presence of ASR product was first verified by SEM-
 226 EDS as reported above in paragraph 2.2 and Fig. 2.

227 The morphology of the ASR products in samples C2-1 and C2-2 looks similar to that observed by
 228 STEM (Fig. 12a and b). They seem to consist of platelets or bundles of platelets more or less oriented
 229 parallel to the walls of the crack. For C2-2 the thickness of the platelets is about 200 nm, which is
 230 less than in the case of platelets in sample C1-2 (500 nm). Consequently, their microstructure is
 231 similar to the one of the crystalline ASR products in M1-2 and C1-2. However, their SAED pattern
 232 is similar to the one shown in Fig. 5 indicating an amorphous phase.

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234 3.2. Composition of ASR products

235 An example of STEM images combined with K elemental map measured by STEM-EDS is shown
 236 in Fig. 13, where three areas containing ASR product were quantified (in green).

237 For each sample, at least ten different areas were analysed, except for sample C1-1 whose crack is
 238 too narrow to permit such a high number of analysed areas (4 areas only). The results were then
 239 averaged. Only Si-, Ca- and (Na+K)-contents were considered (and normalised to 100%), as other
 240 elements excluding oxygen are only present in the ASR products as traces. They are summarised in
 241 Table 2.

Fig. 13: Examples of STEM(-EDS) images (sample M1-1): a) BF image; b) HAADF image; c) BF image combined with K elemental map; d) HAADF image combined with K elemental map; showing the same 3 areas (in green) used for the quantification of EDS spectra.

4. Discussion

The characteristics of the analysed ASR products are summarised in Table 2. The ASR products can be separated in two types regarding morphology, crystallinity and volume of the products present.

- *Untextured* ASR products: Products in samples M1-1 and C1-1 formed between adjacent quartz grains are present as thin layers (typically $< 1 \mu\text{m}$) and display no distinct morphology. Although analysis by SAED was only possible in the case of sample M1-1 and showed amorphous materials, it is likely that the ASR products in sample C1-1 are amorphous as well.
- *Platey* ASR products: ASR products found in the four other samples are present as filling of larger cracks with a width higher than $1 \mu\text{m}$. They all have a similar morphology and consist of platelets. The only difference is the presence of some fine fibrils in sample M1-2 that is not observed in the three other samples, but the appearance of fibrils instead of platelets can also be due to the two-dimensional view of the STEM images. The similarity of morphology of samples M1-2, C1-2, C2-1 and C2-2 indicates that the differences in the boundary conditions during the formation of the secondary ASR products, 60°C and 100 % relative humidity during several weeks in case of sample M1-2 and natural exposure for decades in case of field samples, have little impact. Nevertheless, although their morphology is similar, crystallinity of platey products can be different: samples C2-1 and C2-2 were shown to be amorphous, whereas SAED showed that C1-2 is crystalline. As for M1-2 sample, both crystalline and amorphous platelets were found in the same crack. Here, the possible effects of lamella preparation by FIB and analysis by TEM on ASR products have to be pointed out. In principle, sample damage by the ion beam in FIB is possible [29, 30, 31], however it was checked that this was negligible. Exposure to the electron beam in TEM can cause damage as well [25, 32, 33]. As mentioned in paragraph 3.1 it was observed that a cumulative electron dose as low as $5 \times 10^2 \text{ e}/\text{\AA}^2$ was sufficient to turn the crystalline structure into an amorphous one. It could be possible that the damage in a sample which was found amorphous occurs before SAED

patterns are obtained. This possibility cannot be ruled out in the analysis of samples C2-1 and C2-2. This issue will be studied in more depth in the future.

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The composition of these two types of ASR products is plotted in a ternary diagram in Fig. 14, also distinguishing between amorphous and crystalline platey ASR products. It can be seen that the composition of all analysed ASR products is comparable, despite the observed differences in morphology and crystallinity. Possible reasons could be kinetics of formation or space available for growth. While the untextured ASR products form in narrow gaps restrained by adjacent pore walls, the platey ASR products start to grow in larger cracks. Nevertheless, the composition of both products is very similar and agrees with the composition of ASR products formed within aggregates reported in other studies [13, 18, 34, 35].

Table 2: Summary of characteristics of the analysed ASR products. The concentrations values are in at%, normalised, excluding oxygen and trace elements, with ± 0.2 at% precision.

<i>Sample</i>	<i>Approx. thickness of the crack</i>	<i>Morphology of ASR products</i>	<i>Crystallinity of ASR products</i>	<i>Type of ASR products</i>	<i>Ca</i>	<i>Si</i>	<i>(Na+K)</i>
M1-1	150-200 nm	Globular “particles”	Amorphous	Untextured	18.6	62.1	19.3
M1-2 (edges)	6-8 μm	Large fibrils, small platelets	Amorphous	Platey	17.0	60.6	22.4
M1-2 (centre)	6-8 μm	Large platelets	Crystalline	Platey	15.3	63.9	20.9
C1-1	500 nm	Structure-less	Amorphous	Untextured	12.9	72.0	15.1
C1-2	50-70 μm	Large platelets	Crystalline	Platey	15.3	64.1	20.6
C2-1	500 nm	Platelets, bundle of platelets	Amorphous	Platey	18.2	65.7	16.1
C2-2	1 μm	Platelets, bundle of platelets	Amorphous	Platey	21.7	61.9	16.4

Fig. 14: Ternary plot of Si, Ca and (Na+K) normalised concentrations measured in untextured and platey ASR products.

5. Conclusions

Combining SEM, FIB, TEM and EDS is a novel approach for the analysis of ASR products in concrete. The results obtained from a mortar exposed to an accelerated laboratory test and concrete from two different structures allows to draw the following conclusions:

- The approach is well-suited to study the morphology, crystallinity and composition of ASR products even in small volumes present in cracks with a width $< 1 \mu\text{m}$.
- The untextured ASR product present in gaps and sub-micrometre cracks along mineral grain boundaries seems to be amorphous based on the results of SAED.
- The platey ASR products formed after cracking of the aggregates and present in relatively large volumes are composed of platelets or occasionally fibrils. They can be either crystalline or amorphous.
- The composition of studied ASR products is very similar in spite of the differences in morphology and crystallinity.
- The short lifetime of the crystalline ASR product under the beam can be an issue, making its analysis difficult, at least in regard to SAED where the sample is exposed to a high electron dose. Low cumulative electron doses have to be used in order to keep the crystallinity of the products intact.

302 The results of this pilot study have to be confirmed by the analysis of additional samples.

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