The addition of caesium to concrete with alkali-silica reaction: implications on product identification and recognition of the reaction sequence

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Abstract

The formation of alkali-silica-reaction (ASR) products in concrete aggregates generates stress leading to the formation of cracks proceeding from the aggregates into the cement paste. However, there is little knowledge on the initial ASR products formed in aggregates before the cracking occurs, as their small volume considerably complicates analysis. In this study, a new approach for identification and visualisation of ASR product formation leading to concrete damage is presented. Caesium is added as a tracer during concrete production. Because it is mainly incorporated in ASR products, their backscattering contrast in the scanning electron microscope is considerably increased. This makes it possible for the first time to follow the temporal and spatial progression of ASR with resolution in the nanometre scale, thereby delivering a coherent reaction sequence.

Keywords: concrete, alkali silica reaction, microstructure, caesium, reaction sequence

1. Introduction

Alkali-silica reaction (ASR) in concrete causes stress and expansion leading to substantial damages of vital infrastructure worldwide. Expansive ASR products are formed due to the reaction between metastable SiO₂ present in aggregates and the alkaline pore solution in concrete. Although ASR is in the focus of cement and concrete research since decades, various aspects are still only poorly understood [1]. One major reason making the reaction difficult to follow are the dimensions of the initial ASR products formed before aggregates crack. Apparently, these products form at nanometre scale between mineral grains within reactive concrete aggregates [2,3]. This size range complicates the identification of the first or initial ASR products with scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS). With respect to SEM, the situation is further impeded by the fact that the ASR products and the reactive SiO₂ have very similar backscattering coefficients. It is evident that the formation of ASR products yields mechanical stress leading to cracking of the aggregates. But it is not known how initial ASR products are distributed in the aggregates and how their distribution changes with ongoing reaction. After aggregates have been cracked, relatively large volumes of secondary ASR products are forming in cracks of several micrometres width proceeding from the aggregates into the cement paste. They can easily be identified and analysed with SEM and EDS [4-9]. However, these secondary ASR products form after the first essential damage has already occurred. In order to establish clarity about the progress of ASR before cracking, the distribution of initial ASR products in aggregates and their time course has to be further examined.

To effectively enable the identification of initial ASR products formed before the cracking of the aggregates, the use of a tracer is suggested. Such a tracer needs to fulfil two requirements. Firstly,

it has to be mainly incorporated in the ASR products rather than in the cement hydrates. Secondly, as the backscattering coefficient in the SEM is dependent on the atomic number of the investigated material [10-12], such tracer requires an atomic number distinctly exceeding the one of major components of ASR products (oxygen, silicon, calcium, sodium and potassium). Hereby, a high backscattering contrast of ASR products in favour of SEM and EDS imaging shall be enforced. Candidates fulfilling these requirements are the earth alkali rubidium and caesium with the atomic numbers 37 and 55, respectively. Due to the higher atomic number, caesium is preferable. Additionally, the radii of hydrated potassium and caesium ions are in the same range [13-15].

In this study, the addition of CsNO_3 as an approach to identify initial ASR products by means of SEM is explored as a novel approach. Three concrete mixtures are produced using aggregates susceptible to ASR. Apart from the reference concrete mixture without any addition, one mixture was doped with CsNO_3 and another one with the equivalent amount of KNO_3 as a second reference. The objective of the second reference concrete with KNO_3 is to assess whether ASR reactions provoked with caesium behave similarly as conventional ASR reactions affected by potassium. The concrete was exposed to accelerating test conditions for ASR. Subsequently, its microstructure was investigated using SEM and EDS at different test stages.

2. Materials and Methods

2.1 Materials

Concrete C-Ref was produced with 440 kg/m^3 of Portland cement (CEM I 42.5 N, see Table 1) and a water-to-cement-ratio (w/c) of 0.45. The used aggregate originates from an alluvial deposit in the Southwest of Switzerland consisting of gneiss and quartzite. A mass of 1790 kg/m^3 in four different grain size fractions was added (0/4 mm: 40 mass-%, 4/8 mm: 15 mass-%, 8/16 mm: 20 mass-%, 16/22 mm: 25 mass-%). The production of concrete C-Cs and C-K additionally included 7.83 kg/m^3 of CsNO_3 and 4.06 kg/m^3 of KNO_3 , respectively. These additions result in a molar ratio of $\text{Cs}/(\text{Na}+\text{K})$ of 0.38 in concrete C-CS and in an increase of the Na_2O -equivalent from 0.79 to 1.09 kg/m^3 in both concrete mixtures.

Oxides [mass-%]	SiO_2	Al_2O_3	Fe_2O_3	Cr_2O_3	MnO	TiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O	SO_3	LOI
CEM I 42.5	20.14	4.56	3.25	0.013	0.05	0.368	0.24	63.0	1.9	0.96	0.16	3.25	2.06

Table 1: Composition of the CEM I 42.5.

Three prisms ($70 \times 70 \times 280 \text{ mm}^3$) were produced with each concrete mixture. The prisms were demoulded after 24 h, followed by the procedure for the concrete prism test (CPT).

Samples from one of the prisms per mixture were taken after 4 weeks, 8 weeks and 16 weeks. They were cut to appropriate size for microscopy, dried in an oven for three days at 50°C , epoxy impregnated, polished and carbon coated.

2.2 Methods

The CPT according to the Swiss guideline SIA 2042 [16] was used. The test requires storage of the prisms ($70 \times 70 \times 280 \text{ mm}$) at 60°C and 100 % relative humidity (RH) for 20 weeks with measurements every 4 weeks. The limit value of expansion is 0.2 ‰.

The microstructure of the concrete was analysed with a scanning electron microscope (SEM) FEI Quanta 650 using a pressure between 3.0 and 5.0×10^{-6} Torr. Chemical analysis was performed

by energy-dispersive X-ray spectroscopy (EDS) with a Thermo Noran Ultra Dry 60 mm² detector and Pathfinder X-Ray Microanalysis Software. An acceleration voltage of 12.0 or 12.5 kV was used for imaging and EDS point analysis or line scans and 15 kV for the element maps. About 400 EDS point analyses were conducted to measure the composition of the ASR products in the aggregates of concrete C-K and C-Cs.

The identification of ASR products and their spatial distribution was mainly investigated with SEM backscattering images. Additionally, EDS element mappings were performed. Along with the visual investigation of ASR revealed by the high contrasting caesium tracer, the data allows quantitative assessment of element distribution. For this purpose, two aggregates were chosen. Phase identification was performed with the help of thresholding of the SEM image values. Thresholding of the caesium and potassium element maps was also the method for identification of locations where ASR products occur. Likewise, empty cracks or void pockets have been identified by using thresholding of the SEM images. Small isolated regions below a defined size, being manifested due to electron noise, have been removed. The procedures have been accomplished by using ImageJ and its “Segment Phases 3D” tool [17]. Thereby, local masks of the phases “ASR products”, “cement paste”, “aggregate”, and “cracks/pores in aggregate” have been realized.

Both, potassium and the tracer caesium are the decisive indicators for the presence of ASR products. Hence, their distribution in aggregates is a convenient measure for the progression of ASR. In particular, the penetration depth and thereby the radial concentration is of interest. For this purpose, binary masks of aggregates as achieved by thresholding from SEM are subjected to a peeling process [18]. Hereby, shells of constant width are stripped from the aggregate surface up to its centre. Subsequently within the scope of each shell, the average amounts of K and Cs are calculated by considering the respective map data.

3. Results

3.1 Expansion

The expansion of concrete C-Ref is about two times higher than the limit value defined in SIA 2042 (Figure 1A). The addition of the alkali results in an increase of expansion to 1.22 % and 0.91 % for concrete C-K and C-Cs. The relative increase in mass during the test is related to expansion showing the highest values for concrete C-K and lowest values for concrete C-Ref (Figure 1B).

3.2 Scanning electron microscopy

3.2.1 Backscattering contrast

Obviously, caesium has been incorporated into the ASR products, as they can be easily detected due to their increased backscattering contrast compared to quartz in concrete C-Cs. This applies to both, ASR products present in aggregates as well as in the cement paste. The ASR products in the aggregates form thin layers between adjacent minerals resulting in the formation of a connected network as well as partial or complete filling of cracks or voids. In order to demonstrate the impact of caesium on the backscattering contrast, the thin layers of ASR products between adjacent mineral grains are displayed for both, concrete C-K and C-Cs (Figure 2). In concrete C-K, the ASR products between adjacent quartz grains cannot be unambiguously recognized even at high magnification. EDS line scans across quartz grain boundaries confirm their presence only, by showing peaks at calcium, potassium and sodium (Figure 3A). In contrast to concrete C-K, the

thin layers are easily and reliably identifiable in concrete C-Cs due to the strong impact of caesium on the backscattering contrast. EDS line scans confirm the presence of ASR products containing caesium (Figure 3B). An easy assessment of their distribution is feasible (see paragraph 3.2.3) even in a spatial range where ASR products are hardly detectable in samples without caesium addition despite of highly elaborate analysis.

3.2.2 Morphology and composition

The ASR product present in the aggregates of concrete C-K is typically homogenous and non-structured at a distance to the surface of the aggregate $< 10 \mu\text{m}$. Towards the interior of aggregates, the ASR product becomes finely structured, showing plate-like features (Figure 4A). In contrast, the ASR product in concrete C-Cs is mainly homogenous and non-structured (Figure 4B) in the entire aggregate. Less plate-like features occur compared to concrete C-K.

EDS point analysis shows the presence of caesium in the ASR products located in aggregates of concrete C-Cs. Its concentration is lower than the one of potassium but higher than the one of sodium. Apart of the presence of caesium, the main difference to the ASR products formed in concrete C-K is the lower average calcium content, resulting in an average molar Ca/Si-ratio of 0.18 compared to 0.26 in concrete C-K (Figure 5 and Table 2). Although the majority of the analysed points overlap with the composition determined for the ASR products in concrete C-K, a larger number of points display values below 0.15, lowering the average Ca/Si-ratio. ASR products in concrete C-Cs with low Ca/Si-ratio occur in two different situations. Firstly, they can be present in the interior of the aggregates at the head of the ingressing front of ASR products (see paragraph 3.2.3). Secondly, they can be linked to cracks running from the aggregates into the cement paste. Thereby, the products fill cracks at the edge of aggregates and propagate as crack-filling extrusions into the cement paste. This particular situation was observed only a few times and stands in contrast to the usual composition of the ASR products present in cement paste, which typically shows an increased Ca/Si-ratio of 0.4 up to 1.3. It typically comes along with a decreased (Na+K+Cs)/Si-ratio.

element	O	Na	Mg	Al	Si	S	K	Ca	Fe	Cs	Ca/Si	(Na+K+Cs)/Si
	[mol-%]										molar ratio [-]	
concrete C-K	65.2 ± 4.1	1.4 ± 0.5	0.0 ± 0.1	0.3 ± 0.2	21.7 ± 2.2	0.0 ± 0.0	5.7 ± 1.3	5.7 ± 1.4	0.1 ± 0.1	- -	0.26 ± 0.06	0.33 ± 0.06
concrete C-Cs	65.2 ± 6.5	1.1 ± 0.5	0.1 ± 0.4	0.3 ± 0.4	22.0 ± 3.8	0.0 ± 0.0	2.8 ± 1.2	3.9 ± 3.1	0.1 ± 0.2	2.4 ± 0.9	0.18 ± 0.10	0.31 ± 0.09

Table 2: Chemical composition of the ASR products present in aggregates of concrete C-K and C-Cs.

3.2.3 Distribution of the ASR products in concrete C-Cs

The high backscattering contrast of the Cs-containing ASR products allows easy identification and assessment of their distribution in aggregates and in the cement paste. In order to capture a relatively early stage of the reaction, the following description mainly focuses on the 4 and 8 week old samples of concrete C-Cs.

Summarizing the observations, three different situations can be classified with regard to Cs-containing ASR products in aggregates: i) no ASR products present, ii) ASR products present in uncracked aggregate, and iii) ASR products present in cracked aggregate.

The most conspicuous feature in situations ii) and iii) is the thin layers of ASR products between adjacent mineral grains (Figure 2) forming a connected network. Layer thickness is in the range of nanometres, at the limit of the resolution power of SEM at the used settings (acceleration voltage, spot size), up to a few micrometres. These layers start close to the surface of the aggregates and proceed inwards reaching varying depth. In some aggregates, mostly sand grains with diameters below 2 mm, this ingressing front of ASR products may reach the centre of the aggregates. In larger aggregates, ASR products are usually absent in the central part. These layers form independently of the mineralogy of the adjacent grains and occur not only between quartz grains but also between feldspar or mica grains (Figure 6). In the case of situation iii), ASR induced cracks extending from the aggregates into the cement paste occur independently of the depth that the front reaches in an aggregate. These newly-formed cracks are often empty in the aggregate with ASR products only present at the edge of the aggregates. At the age of 16 weeks, the degree of filling is increased. Like in the case of the thin layers of ASR products between adjacent mineral grains, the filling of the cracks starts at the edge of the aggregates moving inward. This applies as well for the ASR products filling such cracks in concrete C-K.

This inward-moving front of thin layers and fillings of ASR-induced cracks lead to the observation that more ASR products are present close to the edge of the aggregates compared to the centre of the aggregates. In order to make this characteristic visible, EDS element mappings are performed on two aggregates. The first one (aggregate 01) is from concrete C-Cs at the age of 4 weeks. Aggregate 01 has not been cracked yet and reveals ASR products along mineral grain boundaries and along gaps $> 1 \mu\text{m}$ between mineral grains. The other aggregate (aggregate 02) is from concrete C-Cs at the age of 8 weeks. It contains all typical features observed in reacting aggregates: ASR products along mineral grain boundaries, in small ASR-induced cracks and few minor extrusions of ASR products into the ITZ. Pixel size of the two mappings is $1.9 \mu\text{m}$ (aggregate 01) and $1.6 \mu\text{m}$ (aggregate 02), respectively. Veins or layers below these widths are not resolved. Consequently, the network formed by the thin layers of ASR products along mineral grain boundaries is not resolved. Figure 7 shows aggregate 02 with a segmentation of the Cs-containing ASR products, Figure 8 the distribution of the Cs-containing ASR products in relation to the distance of the surface of the aggregates 01 and 02. The quantitative analysis clearly shows a decreasing amount of ASR products with increasing distance from the surface of aggregates. One particular feature is the sharp decrease of Cs-containing ASR product close to the surface. It is caused by uptake of calcium and simultaneous release of alkali as observed in several studies [5,7,8].

Figure 9 focuses on a particular location of the aggregate shown in Figure 7 below the resolution provided by the element maps. Here both, thin layers between adjacent quartz grains and an intact quartz grain still exhibiting its original crystal habitus enclosed by ASR products precipitated in pore space generated by dissolution are present.

Two different situations occur in regard to extrusions of ASR products into the cement paste. Firstly, ASR products may extrude into relatively large cracks running from the aggregates into the cement paste. Secondly, ASR products may only extrude into pores of the cement paste at the

interfacial transition zone (ITZ), if the cracks formed in the aggregates do not extend into the cement paste. Qualitatively judged, the amount of extruding ASR products is considerably larger in concrete C-Cs than in concrete C-K.

4. Discussion

4.1 Backscattering contrast

The EDS analysis shows that caesium is indeed incorporated into the ASR product. This results in an increased backscattering coefficient with higher brightness in the SEM, which facilitates the identification of the ASR product.

4.2 Morphology and composition

The caesium-containing ASR product displays a lower average Ca/Si-ratio compared to the one formed in concrete C-K. This may result in a generally lower viscosity and stiffness [8, 19-22] that could explain the higher amount of ASR products extruded into the cement paste and the lower expansion in the concrete performance test compared to concrete C-K. Possible reasons for the lower Ca/Si-ratio are a higher SiO₂ dissolution rate or an inherent property of the Cs-containing product. Additionally, the ASR product in concrete C-Cs differs in its morphology, as it is mainly amorphous and does usually not form the finely-structured, plate-like forms observed in concrete C-K.

4.3 Sequence of ASR

Taking into account the observations in regard to the distribution of ASR products described above, the following sequence on the formation of ASR products can be deduced. Alkali diffuse into the aggregates by starting to dissolve reacting minerals. Thin layers of ASR products start to form within small pre-existing gaps between adjacent mineral grains at the edge of the aggregates. Based on reactive-transport calculations [23], ASR product formation starts there as a result of the gradients in pH, dissolved silica, alkali and calcium present. With ongoing reaction, the front of ASR products successively moves towards the interior of the aggregates. Consequently, sodium, potassium, caesium and calcium have to diffuse from the cement paste to the head of the reaction front by passing the already-formed ASR products. Such diffusion must be driven by a concentration gradient of these ions between the cement paste and the aggregate generated by ASR product formation. Alkali and calcium are bound in similar quantities within the ASR products formed in concrete aggregates [4-9]. However, the calcium concentration in the pore solution of the cement paste is considerably lower compared to the one of the alkalis [24,25]. Consequently, the availability of calcium in reacting aggregates is restricted compared to the more abundant alkalis and calcium has to diffuse from the cement paste into the aggregates. Moreover, if a saturated alkali-silica solution is present in aggregates, the inward diffusion of calcium ions leads to supersaturation of this solution with respect to alkali silicates and the precipitation of ASR products as shown experimentally and by thermodynamic modelling [26]. Therefore, it can be stated that the limiting factor for the formation of the ASR products at the ingressing front is the inward diffusion of calcium leading to supersaturation. This is supported by the low Ca/Si-ratio of the ASR products as it is observed directly at the head of the ingressing front.

The point of cracking is reached at varying penetration depths of the ingressing ASR front. Apart of the depth reached, the point of cracking is likely dependent on aggregate-specific parameters, its size, shape, cleavage, pre-existing cracks, porosity and mechanical properties. If crack widths are > 10 µm, the cracks usually extend into the cement paste. If they are smaller, they stop at the

ITZ. Yet in both cases, crack formation leads to the extrusion of ASR products. Obviously, cracking provides a pathway for the extrusion of ASR products and highly concentrated alkali-silica solution. Initially, these extrusions have a low Ca/Si-ratio as indicated by EDS analysis of a few extrusions that must have occurred shortly before sample preparation. Consequently, their viscosity must be relatively low during the extrusion compared to the products with a higher Ca/Si-ratio [8,19-21]. After reaching the cement paste they take up calcium resulting in the high Ca/Si-ratio observed in various studies [4-8]. The cracks formed in the aggregates start to fill with ASR products from the edge of the aggregate inwards in the same manner as observed for the thin layers between adjacent mineral grain as described above.

In order to crack, stress must be generated in the aggregates. Stress generation has to be linked to the ASR product formation in the confined space along the ingressing front. In the literature, different mechanisms for expansion of ASR products and stress generation are proposed, like osmotic pressure [27,28], double-layer repulsive forces [29,30], or surface forces between alkali-silicate particles [31]. As ASR products form in confined space due to supersaturation caused by calcium ingress, crystallization pressure may be an additional mechanism of stress generation.

5. Conclusions

The paper presents a new approach for identifying and visualizing ASR product formation leading to concrete damage. For the first time, it enables a reliable and coherent understanding of the temporal and spatial progression of ASR reactions down to the nanometre scale. The procedure is based on SEM and EDS on concrete doped with caesium as tracer. Caesium is bound in the ASR products, which increases the backscattering contrast in SEM. This enables the easy and unambiguous identification of the ASR products and allows to comprehend the reaction sequence of ASR at different stages:

- The first ASR products are formed as thin layers adjacent to mineral grains close to the surface of the aggregate. Their thickness ranges from the nanometre scale up to few micrometres.
- With ongoing reaction these layers move towards the interior of the aggregates as a front forming a connected network.
- The formation of these layers induces mechanical stress leading to cracking of the reactive aggregates.
- Aggregate cracking occurs at various penetration depths of the front. Likely, the point of cracking additionally depends on aggregate-specific properties like size, shape, cleavage, pre-existing cracks, porosity and strength.
- Whenever cracking of aggregates occur, extrusion of ASR products into the cement paste is observed, which fills either cracks in the cement paste or pores in the ITZ.
- The extrusion products initially have low Ca/Si-ratio and presumably low viscosity, but take up calcium within days, increasing the Ca/Si-ratio from < 0.15 to > 0.4 .
- The cracks formed in the aggregates are initially empty and then start to fill with ASR products from the surface inward.

The comparison with two reference concrete mixtures, one with no addition and the other one with KNO_3 addition of identical molarity to the one of CsNO_3 , demonstrate that caesium does not change ASR and the studied samples can be regarded as representative:

- Both the addition of KNO_3 and CsNO_3 increase expansion of concrete C-K and C-Cs compared to concrete C-Ref without addition.
- The majority of EDS point analysis show the same Ca/Si and (Na+K+Cs)/Si-ratios of the ASR products in concrete C-K and C-Cs. The lower average Ca/Si-ratio of 0.18 in concrete C-Cs is caused by a higher number of points with values <0.15 .
- The filling of cracks generated in aggregates of concrete C-K and C-Cs starts at the surface of the aggregates and proceeds inwards in the same way. While mainly finely-structured ASR product is present in such cracks of concrete C-K, mainly structure-less ASR products are formed in concrete C-Cs.

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7. References

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Figure 1: Expansion (A) and mass change (B) of concrete C-Ref, C-K and C-Cs a function of time. The dashed line shows the SIA 2042 expansion limit.

Figure 2: Boundaries between three adjacent quartz grains in concrete C-K (A), and six quartz grains in concrete C-Cs (B) with easily identifiable thin layers of ASR products. The lines indicate the locations of the EDS line scans shown in Figure 3.

Figure 3: EDS line scan across the boundary of two adjacent quartz grains in concrete C-K (A, line 1) and C-Cs (B, line 2) at the locations shown in Figure 2.

Figure 4: Cracks in gneiss aggregate of concrete C-K filled with ASR products (denoted by white arrows) (A) and partly filled crack in gneiss aggregate of concrete C-Cs (B). Note the fine plate-like structure partly present in (A) compared to the unstructured ASR products in (B).

Figure 5: Molar $(\text{Na}+\text{K}+\text{Cs})/\text{Si}$ -ratio as a function of the molar (Ca/Si) -ratio of ASR products formed in aggregates of concrete C-K and C-Cs.

Figure 6: Bright Cs-containing and aluminium-free ASR product between K-feldspar and mica in a gneiss aggregate.

Figure 7: Aggregate in concrete C-Cs (A) with phase segmentation based on EDS element mapping (B): ASR products (white), cement paste (light grey), aggregate (dark grey) and cracks/pores in aggregate (black). White arrow in (A) indicates the location of the feature shown in Figure 9.

Figure 8: Relative area of Cs-containing AAR products in aggregates as a function of the distance to the aggregate surface. Aggregate 01 is identical to the one shown in Figure 7.

Figure 9: ASR products in quartzite along mineral grain boundaries, small cracks and porosity created by dissolution with single, undissolved quartz grain (Q). The location of the single quartz grain (Q) is indicated by the white arrow in Figure 7.