

# Microscopic investigation of building materials affected by alkali-silica reaction

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## Abstract

*The alkali-silica reaction (ASR) is a harmful process, which can occur in concrete. As product of this chemical reaction a swellable alkali-silica gel can exert pressure leading to cracking of the material. The damages induced by ASR can differ in their magnitude, and to assign certainly that ASR is the main damage mechanism a microscopic investigation is necessary. Therefore this article presents a study on concrete affected by ASR with the purpose of assessing the degree of damage and evaluating various alkali-sensitive aggregates.*

*For texture analysis thin section petrography is the major tool. Optical microscopy offers the best way to analyse ASR-affected concrete samples for damage classification by visualising the gel and the crack formation. The chemical investigation of the gel enables a precise determination of the involved amounts of the major oxides SiO<sub>2</sub>, CaO, Na<sub>2</sub>O and K<sub>2</sub>O. The proportions of these components of the gel are decisive with regard to its ability to swell. For this analysis scanning electron microscopy coupled with energy dispersive X-ray spectroscopy was utilised. Furthermore micro X-ray fluorescence analysis showed elemental distributions, especially the depletion or enrichment of elements involved in ASR.*

*Keywords: alkali-silica reaction; concrete; damage analysis; materials characterisation; preparation of thin sections*

## I. INTRODUCTION

Concrete is the most applied building material in modern times. It is present in all kinds of structures and no other material seems to replace concrete as the most selected building material in the near future. The prime advantages are the high performance, the easy production and a facile processability. The sustainability and durability are important requirements to concrete. Even if concrete is significantly less susceptible against factors promoting a damage, compared to other materials, there are still mechanisms affecting it. In particular, high-ways and hydraulic structures made of concrete worldwide show cases of alkali-silica reaction (ASR) damages.

This article refers to experience at BAM Federal Institute for Materials Research and Testing for several decades to ASR research and damage assessment. ASR is a severe damage mechanism that can occur in concrete, when certain conditions related to composition and exposition arise in a critical combination.

The chemical reaction is based on the alkalis and the silica in the concrete and was first identified by Stanton in highway structures in California (Stanton, 1940). Actually three components are needed to initiate ASR: alkali-sensitive siliceous aggregates, alkalis coming from internal (cement or other com-

ponents) or external sources (de-icing salt or sea water) and water. If all of these components are sufficiently present an alkali-silica gel could be formed (Hobbs, 1988). This gel itself needs additional space when it is formed. Furthermore it is able to swell in the presence of humidity, both processes generating an expansion pressure inside the concrete. As a consequence of intensive expansion, cracks can occur, which significantly lowers the strength of the material. Parameters like amount and chemical composition of the gel as well as the pattern and width of cracks can help to classify the ASR damage (Swamy, 1992).

The objective of this article is to demonstrate the microscopic work on ASR affected concrete samples, carried out to assess the damaging process or to evaluate various alkali-sensitive aggregates. It will explain the approach of ASR investigation from the macroscale to microscale, starting briefly with the condition assessment, over treatment and investigations of samples in the laboratory, to the use of different microscopical and analytical techniques. In the main part the characteristic features for identifying ASR in concrete are presented by using microscopic images. Especially the emphasis lies on the role of the aggregate. Different kinds of aggregates and varying damage patterns are shown and explained. The formation and resulting characteristics of the gel are discussed more detailed.



Figure 1: ASR affected concrete construction showing extensive cracks and the escape of the alkali-silica gel. As the gel reacts with the atmosphere, a characteristic white carbonated efflorescence remains on the surface of the construction.

Especially the amount and properties of the gel are known to deliver important information relating to the damage process. Ongoing research is aimed to reveal interrelationships between the chemical composition of the gels and its damaging potential. Examples for these investigations, carried out with scanning electron microscopy coupled with energy dispersive X-ray (SEM/EDX) spectroscopy and micro X-ray fluorescence ( $\mu$ -XRF), are presented in the last chapter.

## II. METHODOLOGY

A common investigation due to ASR begins with a broad assessment of the affected structure and ends with a specific sample being studied microscopically at high magnification. Structures suffering from ASR damages typically show extensive macroscale cracks, even on the surface. An escape of the alkali-silica gel out of the material is typical, but it reacts quickly with the carbon dioxide from the atmosphere. This causes a carbonated efflorescence, which deposits as a characteristic white pattern on the surface of the concrete (Figure 1). In addition, expansion of single aggregates located near the surface can result in pop-outs, which represent conical fragments leaving a sinkhole in the concrete.

The distinct presence of cracks at the surface simplifies the consideration, where to take samples out of the concrete construction for further laboratory tests. If an estimation of the risk for the further damage development is needed, the storage of concrete samples under ASR provoking conditions (e.g. slightly elevated temperature, increased alkali and water supply) for a specific time is a frequently

used tool (Chatterji, 2005). All these accelerated ASR tests are conceptualised to evaluate mainly the ASR sensitivity of aggregates for classification before using it in concrete production. As a result of ongoing ASR, the concrete sample expands, which is observed by measuring length changes. The length change is used to classify if the sample is either sensitive due to ASR or not. Examples for often used tests are the accelerated mortar bar method ASTM C 1260 or the concrete prism test ASTM C 1293. In Germany a special guideline for the classification of aggregates related to ASR by the 'German Committee for Reinforced Concrete' specifies the slightly modified way of testing (DAF-Stb, 2013).

The following detailed description of ASR in this article is based on microscopic work. For this purpose the combination of optical microscopy and SEM/EDX offers a comprehensive method to acquire the following essential information. Three major aspects can be taken into consideration. First of all the petrographic analysis offers the best way to describe the present aggregates and moreover to classify the ASR sensitivity of these aggregates. The second focus lies on the visualisation of cracks and the alkali-silica gel, even for microscale formations. Finally the quantification of the chemical composition can be obtained by measuring the gel. All aspects together contain important information for the precise identification of ASR and a potential risk for further damage.

To gain representative results, a special thin section preparation is necessary. Normally ASR damaged samples show a weak cohesion. Therefore the preparation process is based on the solidification of the sample by using a specific resin. In addition

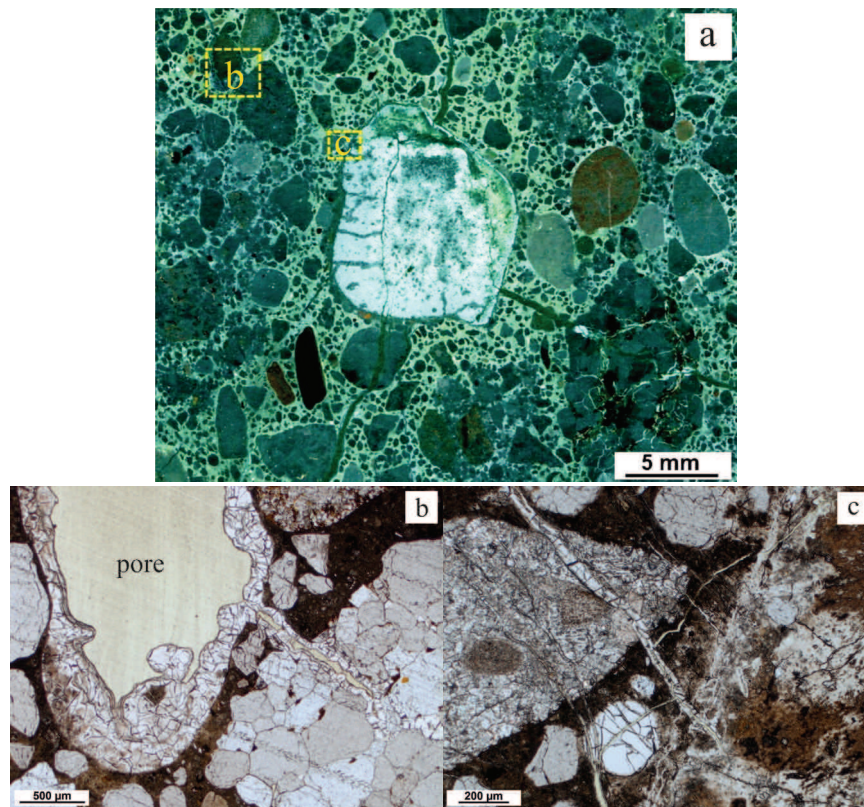


Figure 2: ASR damaged concrete of a hydraulic structure. a) Macroscopic overview of a thin section in which the opal in the centre shows strong ASR induced cracks spreading in different directions through the hardened cement paste and the aggregates. b) Enlarged PPL-Image of the same sample showing massive alkali-silica gel accumulating in a pore. c) Enlarged PPL-Image of the same sample showing alkali-silica gel filled cracks spreading from the big aggregate at the right side into the hardened cement paste and through other aggregates.

this prevents the sample from further deterioration during the preparation steps. After drying at moderate temperatures and a vacuum-pressure impregnation the resin penetrates the whole sample and after curing it obtains the sample material in a fixed state. In this way the alkali-silica gel, which is very sensitive to leaching and drying, is conserved in the resin with as small as possible alteration. A fluorescent coloured pigment is added to the resin, which offers a unique way to discern those finer resin-filled areas in detail by its colour and by irradiating with UV light. In consequence of the size of the aggregates of the concrete, special dimensioned thin sections in the order of 60 x 90 mm are commonly produced to include a sufficiently large area to analyse. Water is an involved factor of ASR. The whole preparation process has to be carried out completely anhydrous. The replacement of water with petroleum prevents changes of the reaction products and the leaching of the gel. For this publication optical microscopic images were acquired by using the polarising microscope Zeiss Axioskop 40 and the stereo microscope Olympus SZX16 both using transmitted illumination in plane-polarised light (PPL) and cross-polarised light (XPL). In addition, both microscopes are equipped with UV light.

The chemical composition of the gel can be determined by using the SEM Leo Gemini 1530 VP and the  $\mu$ -XRF EDAX Eagle III. Those allow fast simultaneous EDX-multi-elemental analysis for mappings and point analysis.

### III. ASR INDUCED DAMAGE IN CONCRETE

The presence of an alkali-silica gel is not always resulting in a deterioration of the concrete. Basically it is decisive how much sensitive aggregate is contained in the concrete and how it is distributed. Furthermore, the reactivity of the used aggregates is important and how much gel can possibly be formed. The concrete could also offer enough pores for the gel to spread out. This will inhibit or delay an expansion pressure leading to cracking. The chemical composition can vary leading to the generation of swellable or non-swellable gels. However, with the incorporation of water by the gel it increases the probability of expansion and will likely damage the concrete microstructure. The absorption of water is reversible, which results in a recurring mechanism of wetting and drying. Indeed the absence of gel cannot exclude ASR as the main trigger for the damage. For example precip-

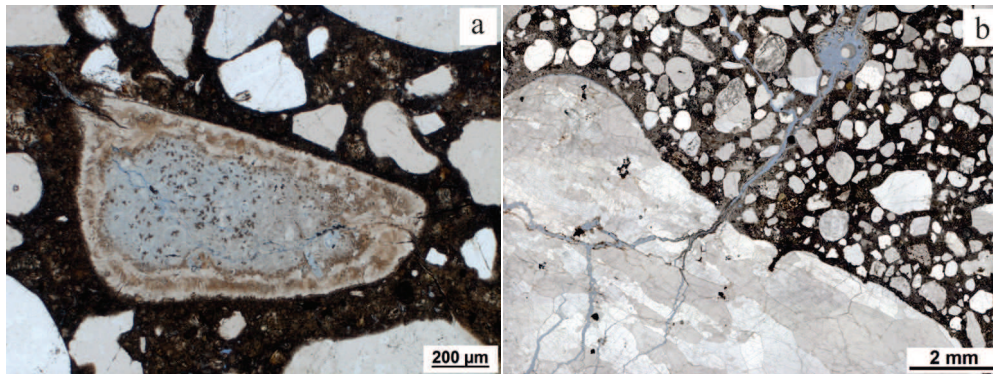


Figure 3: PPL-images of different ASR affected aggregates: a) Microcrystalline quartz shows a uniform reaction rim due to dissolution of the silica at the whole surface. b) Gneiss shows crack progression following the boundaries of the distorted quartz minerals.

itations could leach out all of the damaging gel remaining just the unfilled cracks in the building material. Therefore the microscale view is even more important to possibly see a few tiny remnants of the alkali-silica gel.

The main ASR induced damages in concrete are attributed to cracks emanating from aggregates. These can occur through all components of the concrete, through the hardened cement paste or through the aggregates as well as along the interface of them. Those typical patterns are mainly influenced by the mineralogy of the aggregates. It can take many years until the ASR damages can be observed on a concrete construction (Blight and Alexander, 2011). Structures close to sea are subjected to additional alkali ingress of the salt water. Also de-icing salts used for highways supply alkalis to the concrete. An ASR damaged sample of a hydraulic structure is indicated in Figure 2a. This macroscopic overview of a thin section shows the widespread deterioration due to cracks, but the alkali-silica gel is not clear identifiable. To certify that ASR is the trigger of the cracks, an enlarged microscopic view is necessary. Figure 2b and Figure 2c refer to the gel accumulation inside pores

and cracks by using optical microscopy.

### Role of the aggregate

In all cases the ASR damage depends on the presence of alkali-sensitive siliceous aggregates, which is in turn connected to the mineralogical structure of the aggregate. The crystallinity of an aggregate is of essential importance (Dron and Brivot, 1992). ASR on highly crystalline aggregates made primarily of silica just takes place at the exterior surface of the aggregate. This process is slow and dissolves little amounts of silicate ions. Therefore those aggregates (e.g. quartz) are approximately inert (Broekmans, 2004). In comparison to that, amorphous or poorly crystalline forms of silica (e.g. opal or glass) are prone to attack by hydroxyl and alkali ions into its interior (Dent Glasser and Kataoka, 1981). Especially for porous aggregates the hydroxyl ions can penetrate easily, which increases the ASR intensity compared to denser aggregates. In general aggregates consisting of micro and crypto crystalline quartz varieties afford more surfaces for ASR and hence show higher sensitivity.

Besides different mineralogical structures, var-

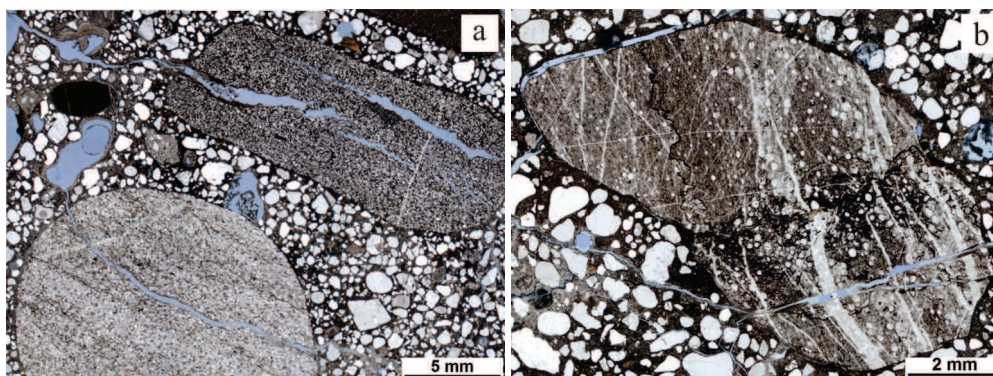


Figure 4: PPL-images of the cracking patterns of different aggregates: a) Aggregates, containing fine grained quartz, show cracks through the whole particle due to ASR. b) Siliceous rock shows an ASR induced crack penetrating straight through the highly crystalline quartz veins.

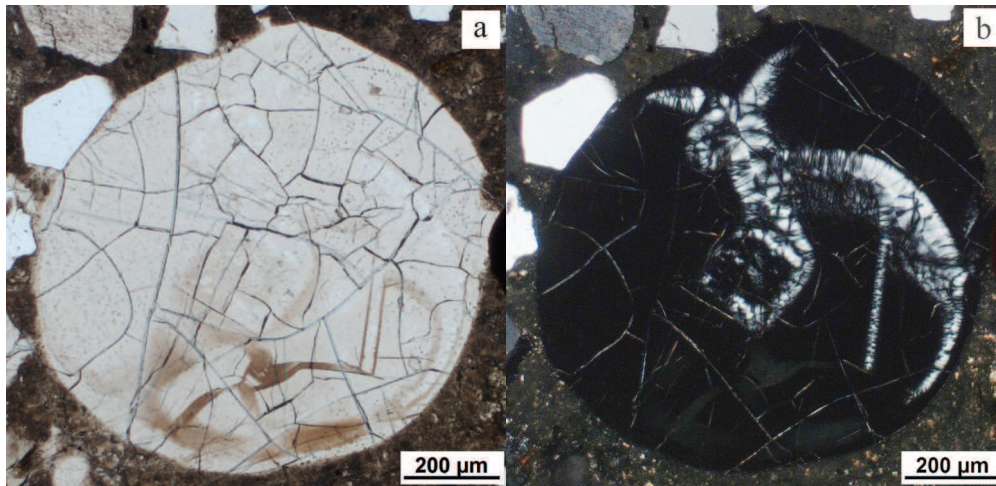


Figure 5: Microscopic images of a completely with alkali-silica gel filled pore. Amorphous and crystalline parts are visible. a) PPL-image. b) XPL-image.

ious aggregates differ in the appearance of their damages (Ferraris, 1995). The dissolution and crack initiating of an aggregate depends on the position of the most weak silica parts. For an aggregate built up just by amorphous SiO<sub>2</sub> the entire particle can dissolve and will show a uniform reaction zone on the whole surface (Figure 3a). In comparison to that a polymineral aggregate (e.g. granite or greywacke) can consist of pure silica (mainly quartz) with differing crystal structures and other minerals like mica, feldspar or pyroxene. This specifies the path of cracks inside polymineral aggregates along the most sensitive silica phases. As indicated in Figure 3b, one gneiss aggregate, containing thoroughly distorted quartz due to tectonic distortions (often called stress quartz), shows a crack accumulating and branching out at these areas. Aggregates consisting of fine grained quartz (e.g. flint or chert) typically show a uniform texture of interlocking grains. These kinds of aggregates show single and almost linear cracks (Figure 4a). Siliceous rocks, as shown in Figure 4b, may contain a lot of different sized and oriented quartz veins. In this example

the ASR induced crack penetrates the aggregate regardless of the orientation of those veins. That is because the quartz veins represent no distorted silica phases and thus don't affect the propagation of the crack.

### Texture characteristics of the alkali-silica gel

Under PPL the amorphous alkali-silica gel appears mainly transparent (white) and often shows a characteristic mud-cracked structure because of shrinkage effects due to desiccation (Figure 5a). This could either originate during the life time of the concrete construction or caused from the sample preparation. The gel is isotropic, showing full extinction under XPL (Figure 5b). Usually it fills out the available space, already existing cracks and the pores. When there is no further space for the gel to spread out, a pressure on the surrounding material is applied and with increasing pressure cracking will probably be enhanced. Hence the air pore content in concrete is an important parameter, as it

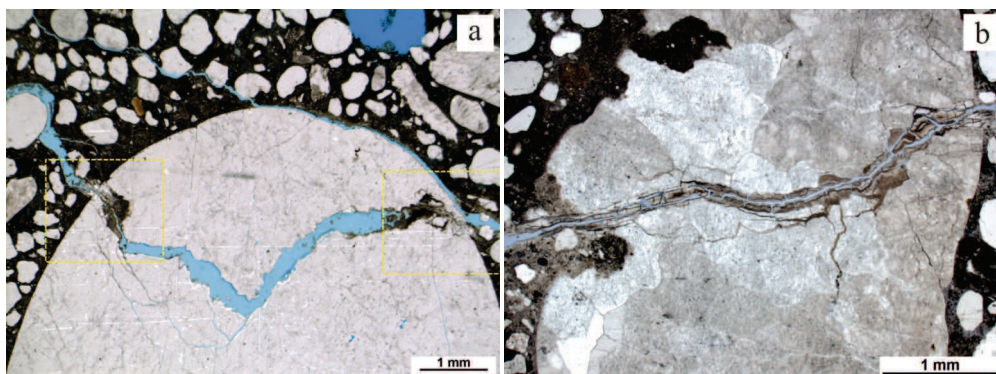


Figure 6: a) PPL-image of an ASR induced crack through a quartzitic rock fragment showing alkali-silica gel accumulation at the endings of the crack. b) PPL-image of another quartzitic aggregate showing alkali-silica gel deposition completely along the crack walls.

Table 1: General chemical composition of alkali-silica gels and certain ratios to develop a swelling pressure in wt%.

	SiO <sub>2</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O
General composition(Helmuth et al., 1992)	40 - 83	1 - 48	0 - 23	0 - 24
Necessary composition for swelling(Kawamura and Iwahori, 2004)			Both alkalis not more than 25	
Necessary composition for swelling(Mansfeld, 2008)		5 - 30		

offers more space for the gel.

The alkali-silica gel in cracks or air voids is not always a pure gel, since crystallisation can take place. Areas of much gel often show a mix of amorphous and crystalline parts, where typical interference colours from white to brownish can be visualised using XPL (Figure 5b).

As already mentioned, ASR induced cracks can be filled entirely (Fig 2c) or only partially with gel or even no gel can be present. In Figure 6 two quartzitic rock grains show different gel accumulations. In the first case (Figure 6a) it is accumulated just at both ends of the crack and in between it is unfilled. This remaining 'unfilled' area is filled just with the blue resin based on the sample preparation. The other example (Figure 6b) shows an aggregate in which the walls of the crack are consistently filled with gel. The narrow unfilled range is probably a result due the drying by the sample preparation process.

#### IV. THE CHEMISTRY OF ALKALI-SILICA GEL

The alkali-silica gel mainly consists of SiO<sub>2</sub>, CaO, Na<sub>2</sub>O, K<sub>2</sub>O and H<sub>2</sub>O. The amounts of all of these oxides can considerably vary, as indicated in Table 1. This depends primarily on the initial pa-

rameters (e.g. source of alkalis, aggregates and water), the sensitive aggregate for the gel formation and the age of the gel. The proportion of these ingredients affect the physical parameters (e.g. the viscosity) and of course the microstructure. The amount of alkalis and calcium is prior responsible for the swelling capacity and thus for the potential damage (Tab. 1). Above an alkali content of 25 wt% no great expansions are expected (Kawamura and Iwahori, 2004). Additionally when the gel is high in calcium no swelling occurs (Ferraris, 1995). To evoke the swelling ability, the amount of CaO has to be between 5 and 30 wt% (Mansfeld, 2008). Without CaO no swelling pressure will be build-up and too much CaO results in the formation of non swellable C-S-H phases.

For a comprehensive investigation of ASR affected structures the analysis of the chemical composition of the reaction products is advisable to affirm if alkali-silica gel is present.

#### Analysing alkali-silica gel via SEM/EDX

SEM/EDX is the commonly used tool to detect the quantitative chemical composition of an alkali-silica gel. Two samples were chosen for the SEM-investigation, which are shown by PPL- and XPL-

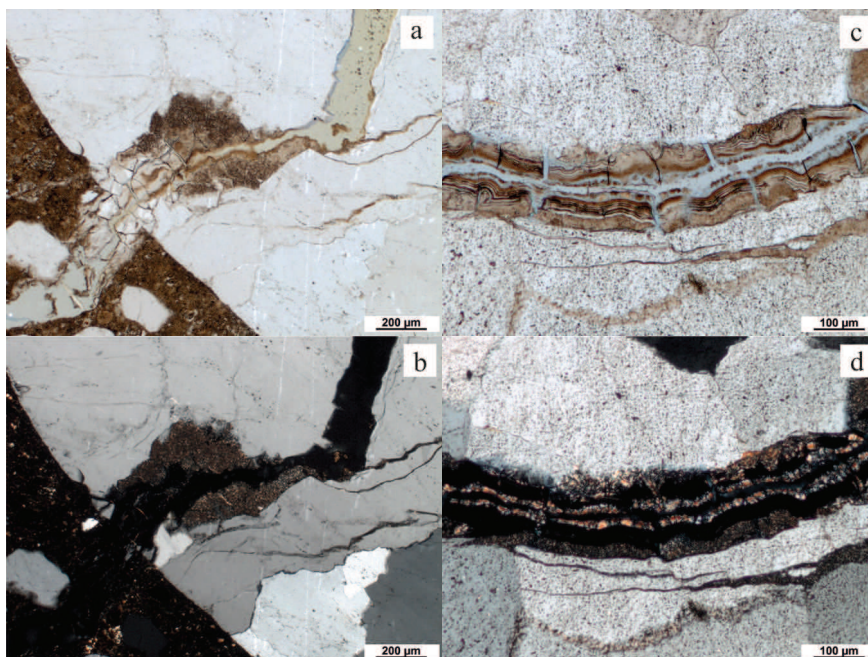


Figure 7: Amplified views of the two quartzitic aggregates as indicated in Figure 6 using PPL (a, c) and XPL (b, d)

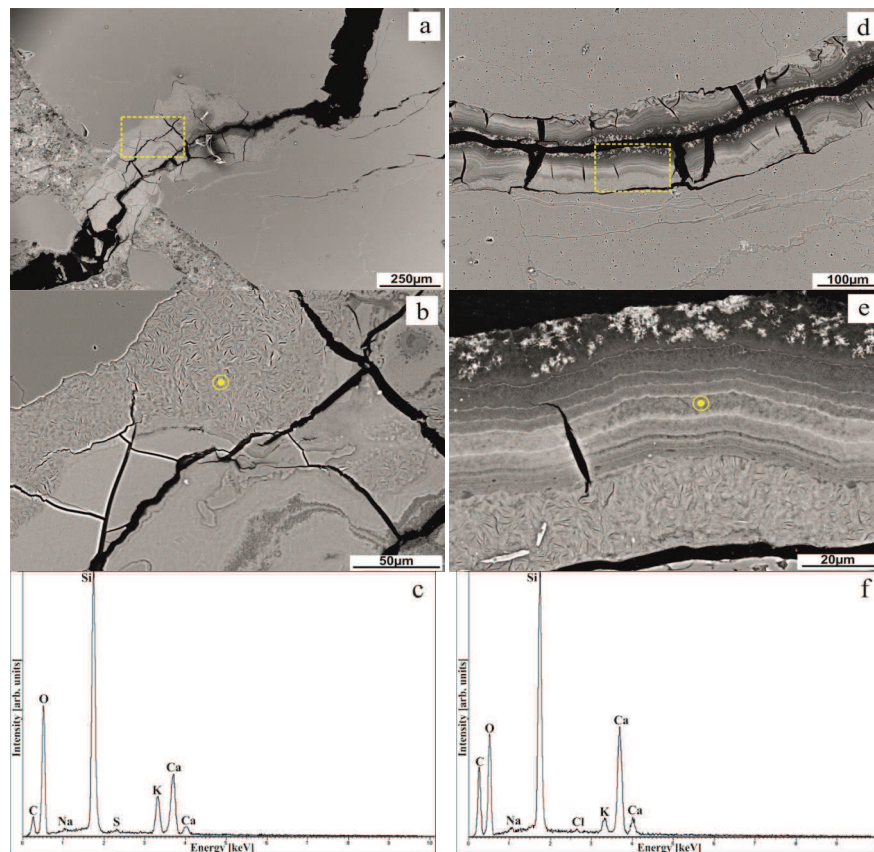


Figure 8: a) BSE-image of the same quartzitic rock grain showing in Figure 7 (left). b) BSE image of the highlighted area showing the position of EDX-analysis. c) EDX result of the chemical composition of the measurement spot. d) - f) Same procedure using the quartzitic aggregate of Figure 7 (right) with focus on the layered structure of the alkali-silica gel.

images in Figure 7. In these figures the presence of amorphous and crystalline reaction products are both clearly visible.

Figure 7 (left) shows a crack perpendicular to the contact zone between the aggregate and the hardened cement paste. Remarkably just the area close to the contact zone contains gel, which reveals with higher magnification a typical mud-cracked structure. Obviously this very small reaction zone and low amounts of gel was sufficient to form the whole crack. This can be explained by the dense structure

of the quartzitic grain. Figure 7 (right) shows an ASR affected crack inside another quartzitic rock grain. The gel in this example fills the entire crack and shows a characteristic layered structure with mud-cracks and a brownish colour. In both cases gel is present next to crystalline reaction products.

By using SEM the Back-Scattered-Electron (BSE) images contain information about the distribution of different elements in the sample (Figure 8). Upon a higher magnification the gel gets even better visualised (Figure 8b and 8e) and offers a very good

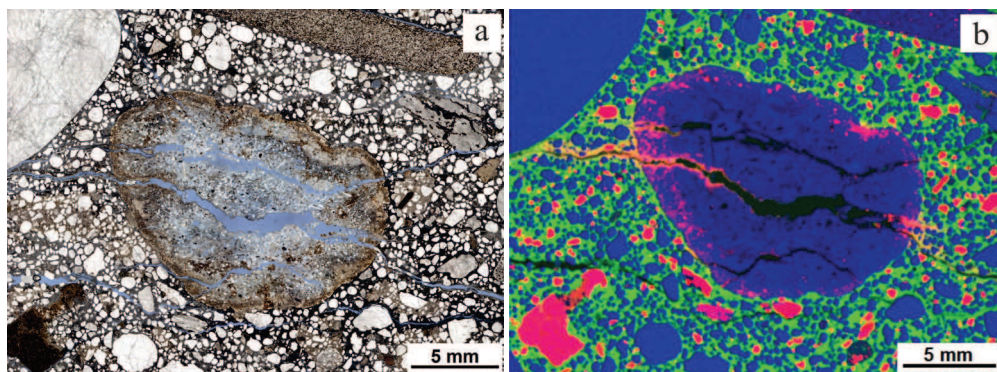


Figure 9: a) PPL-image of an ASR damaged opal sandstone. b)  $\mu$ -XRF acquired RGB-image showing the element distribution of potassium (red), calcium (green) and silicon (blue).

setting of the measurement points (spotsize of 5  $\mu\text{m}$  resp. 2  $\mu\text{m}$ ). The results of the EDX analysis are shown in Figure 8c and 8f. In both cases the EDX-spectra show a characteristic alkali-silica gel pattern with high silicon, calcium and potassium peaks. Minor amounts of sodium are present in both EDX-spectra. The carbon content in both samples is attributed to the resin used for the sample preparation.

### Analysing alkali-silica gel with $\mu$ -XRF

The use of  $\mu$ -XRF offers another opportunity to gain the chemical composition of ASR affected structures and identifying the alkali-silica gel. Besides measuring single spots, the elemental mapping of a specific surface area is a very useful tool to analyse for instance an entire aggregate. An elemental mapping of an ASR affected region can offer information about chemical changes in the vicinity of the alkali-silica gel formation, e.g. a depletion of calcium inside the hardened cement paste or silicon inside the aggregate as well as an enrichment of alkalis inside the crack.

One ASR affected sample is shown in Figure 9. The aggregate shows heavy damages with several cracks (Figure 9a). The  $\mu$ -XRF-image, indicated in Figure 9b, illustrates the elemental distribution of this area (spotsize of 50  $\mu\text{m}$ ). By overlaying of three elements RGB-images can be acquired, showing potassium in red, calcium in green and silicon in blue. This exemplifies the depletion or enrichment of these three elements in detail. The concrete in Figure 9 shows cracks with distinct potassium enrichments at the contact zone between aggregate and hardened cement paste. Especially at the crack walls potassium accumulations are visible. The further inside of the aggregate, the cracks contain less of the alkali-silica gel, which is explicable with the presence of the blue resin caused by the sample preparation indicated in Figure 9a.

## V. CONCLUSION AND PERSPECTIVES

This article shows that the combination of different microscopic devices offers a suitable methodology to evaluate the material properties and to determine the damage potential due to ASR. In the last decades a huge number of studies were published worldwide concerning ASR, but there are still questions e.g. about the exact reaction mechanism and related to testing the ASR damaging potential of aggregates and also concrete in the most reliable and fast way.

The division 'Building Materials' of the BAM Federal Institute for Materials Research and Testing carries on intensive work with ASR. In many cases materials from potentially ASR affected buildings

are examined and evaluated. Beyond that ongoing ASR research work is reflected to different aspects. One finished PhD thesis considered the natural pozzolana 'Rhenish trass' and its effect on ASR in concrete (Bürgisser, 2011). Additional topics among others are the sampling and laboratory investigations of motorway sections with different ASR damage classes, the effect of hydrophobizing of concrete surfaces to reduce the ASR damage. Furthermore the range of topics includes investigations of ASR in structural concrete elements under simultaneous dynamical loading and external alkali supply.

The PhD project of the main author of this article is focused on the grain size dependence of the damaging ASR potential. The aim is to study the relationship between the aggregate properties (grain sizes and geometry) of different aggregate types and the ASR mechanism based on mineralogical and microstructural characterisation of the reaction products. In particular, differences of the amount and the chemical composition of the reaction products, based on the chosen grain geometry, are the major concern.

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