Types of alkali–aggregate reactions and the products formed

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The alkali–aggregate reaction comprises the alkali–silica reaction (ASR) and the alkali–carbonate reaction (ACR). Reaction kinetics of the ASR depends on the grain size and crystalline structure of the reactive silicon dioxide. The reaction starts in the aggregates along the particle periphery and progresses inward. After cracking of the particle, larger amounts of reaction products are formed and are eventually extruded in the cement paste, where they fill cracks and voids. ASR products within aggregates predominantly consist of (hydrated) silicon, alkalis and calcium with characteristic atomic ratios of $(Na + K)/Si \sim 0{\cdot}25$ and $Ca/Si \sim 0{\cdot}25$. They take up additional calcium while releasing alkalis when extruded. Amorphous and crystalline reaction products occur and coexist. Expansion is the result of water adsorption by the reaction products. In ACR, harmless dedolomitisation is distinguished from deleterious reaction of fine-grained silica disseminated throughout the carbonate matrix. Further research is needed to gain more in-depth knowledge about the thermodynamics and kinetics of ASR products and the mechanisms of expansion. This should allow the establishment of a better link between concrete structures and both accelerated testing and models.

1. Introduction

This paper reviews the alkali–aggregate reaction (AAR). In the AAR, the alkaline pore solution of the concrete reacts with minerals present in the concrete aggregates, leading to the formation of reaction products. Depending on the reactive minerals present in the aggregates, two different types of AAR can be distinguished: the alkali–silica reaction (ASR) and the alkali–carbonate reaction (ACR). Additional types of deleterious aggregate reactions have been reported, but those are not considered here.

2. ASR

In the ASR, silicon dioxide (SiO_2) present in minerals is dissolved and subsequently precipitated as the ASR product that contains calcium in addition to silicon and alkalis. By taking up water, the ASR products exert mechanical stress that eventually leads to cracking of concrete. The silicon dioxide dissolution process, and the formation of a sol and a subsequent gel are described in detail in numerous publications (e.g. Gaboriaud *et al.*, 1999, 2005; Hench and West, 1990; Powers and Steinour, 1955a; Wijnen *et al.*, 1989, 1990). The current understanding of ASR mechanisms has recently been

summarised in Rajabipour *et al.* (2015). This paper focuses on aspects only marginally covered in that summary, notably the formation, composition and structure of ASR products and their spatial distribution in concrete.

2.1 Reacting minerals

The dissolution of 'silica' (silicon dioxide regardless of speciation) is related to the degree of crystallinity (Broekmans, 2004; Marinoni and Broekmans, 2013). Defects in the quartz crystalline structure facilitate dissolution. Such defects can be caused by mechanical deformation (e.g. mylonite, gneiss) or alternatively by chemical impurities incorporated during growth. The effect of deformed quartz from a fault zone on aggregate reactivity was shown by Monteiro *et al.* (2001). Overall, quartz is responsible for slowly developing ASR and leads to damage in concrete structures after one to a few decades.

Due to the rapid cooling rates involved in their formation, volcanic rocks often contain a glassy matrix. These glasses are susceptible to being dissolved in an alkaline environment and may cause ASR. Poorly crystalline silica species such as chalcedony and opal, and metastable polymorphs such as

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cristobalite and tridymite react relatively quickly with the alkaline pore solution of concrete and may cause expansion within a decade (Katayama, 1997).

Besides silica, alkalis present in reactive volcanic glasses (Katayama, 2012a) may be released into the concrete pore solution. Moreover, common rock-forming minerals such as feldspars, micas, nepheline, clays and zeolites may release alkalis especially when weathered, thus contributing to deleterious ASR (Bérubé et al., 2002; Constantiner and Diamond, 2003; Van Aardt and Visser, 1978).

2.2   ASR products

2.2.1   Formation
Hydroxyl, alkalis and calcium diffuse from the cement paste into the aggregate provoking the dissolution of reactive minerals. Initial reaction products usually form a rim inside the aggregate periphery (Katayama, 2012a; Saouma et al., 2015). Thermodynamic modelling shows that supersaturation of the ASR product is first attained inside the aggregate adjacent to the cement paste (Guthrie and Carey, 2015), after which the interior gets affected. Initial, very fine-grained ASR products are deposited interstitially between mineral grains, and are difficult to identify. Only when stress generation has led to the cracking of the aggregate, are larger deposits formed in these newly created cracks, first within the aggregate (Figure 1) and later as extruding products in the cement paste (Figure 4;

Katayama, 2012a; Katayama et al., 2004; Leemann and Lura, 2013).

2.2.2   Chemical composition
The tiny volume of ASR product poses challenges for its chemical analysis. Interstitial ASR products between mineral grains may be detected by line scans showing the presence of alkalis and calcium (Figure 2). However, as the volume of ASR products only represents a small fraction of the volume activated by the electron beam, reliable quantification is not possible.

Deposits of ASR products with dimensions larger than a few micrometres, usually formed after crack formation, can be analysed reliably with energy-dispersive X-ray spectroscopy (EDS) or wavelength-dispersive X-ray spectroscopy. Prerequisites are instrument set-up minimising analytical artefacts and the use of carefully polished specimens.

The ASR product within aggregates consists of silicon (Si), sodium (Na), potassium (K) and calcium (Ca), often with minor contents of aluminium, iron and magnesium (Fernandes, 2009, 2015; Katayama, 2012a). The typical (Na + K)/Si ratio and Ca/Si ratio are both approximately 0·2–0·3 (e.g. Çopuroğlu, 2013; Katayama, 2012a; Leemann and Lura, 2013; Leemann and Merz, 2013; Peterson et al., 2006; Thaulow et al., 1996). Towards the edge of the aggregate, the calcium content of ASR products increases whereas the alkali content often decreases (Fernandes, 2015; Katayama,
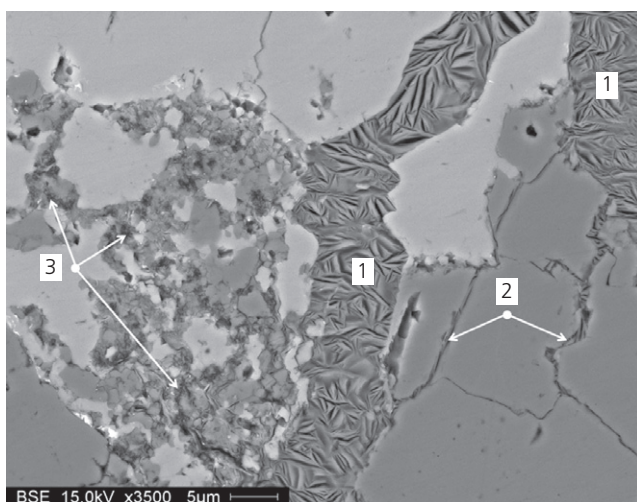

Figure 1. Crystalline ASR product in an aggregate within cracks (1), along mineral grain boundaries (2) and together with partially dissolved quartz (3). The medium grey mineral is quartz and the light grey one is calcite. Concrete from a retaining wall
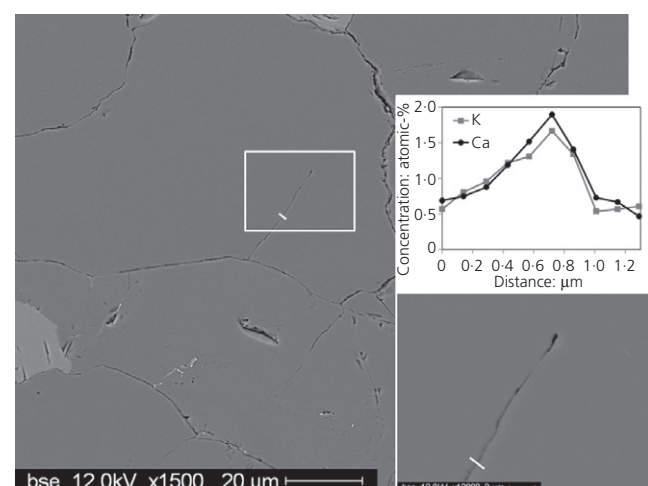

Figure 2. Location of an EDS line scan between two adjacent quartz grains in gneiss aggregate. The white rectangle in the larger image indicates the location of the smaller image, on which the EDS line scan and the measured calcium and potassium distributions are shown. Concrete from a dam
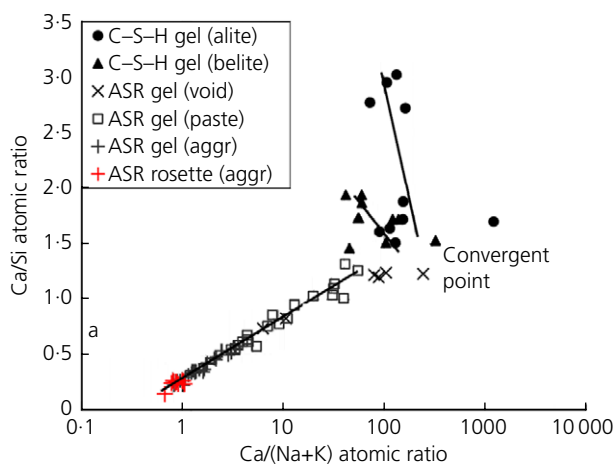
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Figure 3. Atomic Ca/Si ratio against atomic (Ca/(Na + K) ratio of ASR products within the aggregate and in the cement paste compared with C–S–H formed by the hydration of ordinary Portland cement as analysed in a concrete produced with reactive volcanic rock (Katayama, 2012a)
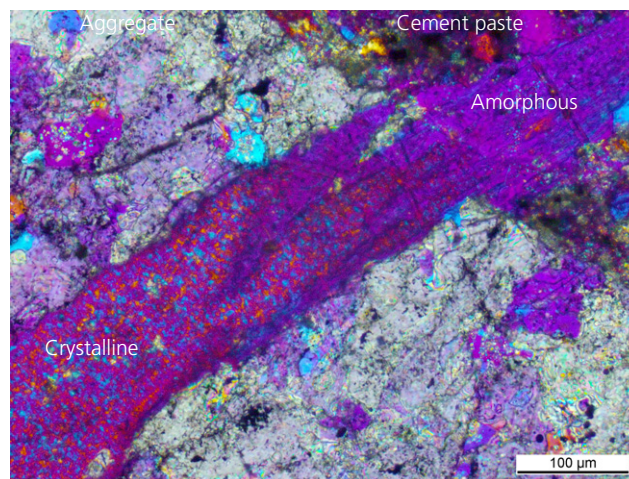

Figure 4. Transition between crystalline ASR product in a cracked aggregate and amorphous ASR product in the cement paste. Thin section analysed with crossed polarisers and inserted gypsum plate. Concrete from a bridge

2012a; Katayama and Bragg, 1996; Leemann and Lura, 2013; Thomas, 1998, 2001). Calcium uptake is even more pronounced in extruded reaction products, and shifts towards the composition of calcium–silicate–hydrate (C–S–H) (Figure 3). There are exceptions to this general trend, for example, ASR products of similar composition are occasionally formed in air voids close to the aggregate. Unfortunately, in many publications containing analyses of the ASR products it is not clearly stated where the analysed products are located, complicating their interpretation.

With regard to the formation (see previous paragraph) and the composition of the reaction products, it has to be pointed out that they are different from those model systems where silicon dioxide and portlandite (calcium hydroxide ($Ca(OH)_2$)) are mixed with alkaline solutions. As first reported by Hou *et al.* (2004) and later confirmed by others (Kim and Olek, 2014; Kim *et al.*, 2015; Leemann *et al.*, 2011), calcium–silicate–hydrate forms first and only when portlandite is depleted are ASR-type products formed. This sequence should not be confused with the formation and composition of ASR products in concrete as described above.

2.2.3 Crystalline structure
Two main types of ASR products are found. Reaction products in the interior of an aggregate particle are predominantly crystalline, whereas reaction products along particle edges and in paste cracks and voids are mostly amorphous (ASR gel). Optical microscopy allows easy distinction between the two as

the crystalline product is refractive and the amorphous is isotropic (Figure 4). However, exceptions occur in both types.

The crystalline material is sometimes interpreted as an aged amorphous product (e.g. Peterson *et al.*, 2006; Šachlová *et al.*, 2010). However, this seems contradicted by the observation of crystalline products in specimens exposed to only a few days of accelerated testing conditions. Nevertheless, an amorphous precursor cannot be entirely precluded.

The crystalline ASR product has a platy morphology (Figure 5) and a distinct X-ray diffraction (XRD) pattern (e.g. Cole and Lancucki, 1983; Cole *et al.*, 1981; Katayama, 2012a; Marfil and Maiza, 2001; Peterson *et al.*, 2006). Due to their small dimensions, in situ characterisation of crystalline ASR products can only be performed by micro XRD (Dähn *et al.*, 2016; Marinoni *et al.*, 2015).

On the basis of the chemical compositions determined by SEM-EDS or an electron probe micro-analyser, a number of mineral names have been assigned to crystalline reaction products – for example, okenite (Cole and Lancucki, 1983), mountainite and rhodesite (De Ceukelaire, 1991), okenite and nekoite (Peterson *et al.*, 2006), cryptophyllite and shlykovite (Katayama, 2012a, 2012b). Benmore and Monteiro (2010) determined the crystalline structure of surface-extruded reaction products. However, as these gels have been in contact with cement paste and were exposed to carbon dioxide, causing carbonation, they are likely not representative of ASR products causing expansion. A recent analysis with synchrotron-based
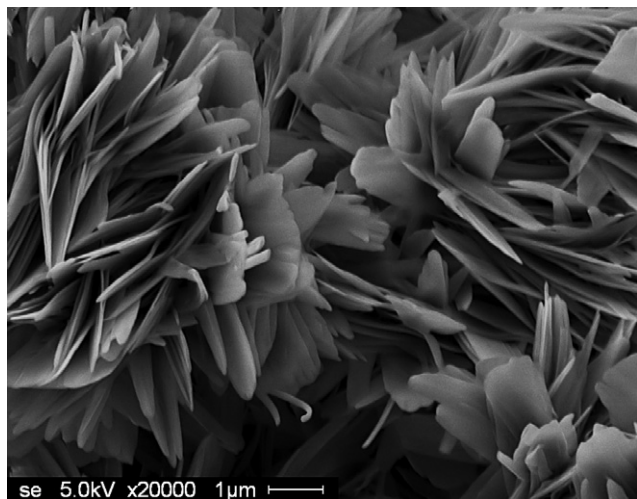
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Figure 5. Morphology of crystalline AAR product in an air void.
Concrete from a bridge

micro XRD shows that the crystalline product within aggregates is a new layer of silicate similar to mountainite and rhodesite (Dähn *et al.*, 2016). Its structure consists of an ($Si_{20}O_{48}$)-layered framework with wide channels and large interlayer spaces, enabling incorporation of molecular water and potassium, sodium and calcium. The analysed structure helps to explain the intrinsic properties of the ASR product, such as its variable Na/K ratio, stability in an alkaline environment and cation exchange and swelling capabilities.

2.3 Mechanism of expansion

Observations regarding field structures and laboratory tests reveal that deleterious ASR is controlled by availability of moisture (Kurihara and Katawaki, 1989; Nilsson, 1983; Olafsson, 1992; Poole, 1992; Poyet *et al.*, 2006), which is attributed to water uptake of the reaction products. Synthetic amorphous ASR products are known to be able to take up substantial amounts of water at high relative humidity (RH) (Kirkpatrick *et al.*, 2005; Krogh, 1975; Leemann *et al.*, 2011; Vivian, 1950), thereby expanding and exerting stress (Struble and Diamond, 1981). Imbibition has been attributed to capillary suction and osmosis (Foster, 1932; Glasser, 1979; Helmuth *et al.*, 1993; Hench and Clark, 1978; Katayama, 2012a; Powers and Steinour, 1955a, 1955b). Non-bridging oxygen and silanol groups present in amorphous reaction products appear to bond alkalis or water more effectively compared with crystalline material (Katayama, 2012b; Kirkpatrick *et al.*, 2005).

The exchangeability of water and/or cations in kanemite (e.g. Apperley *et al.*, 1995; Kirkpatrick *et al.*, 2005; Wieker *et al.*, 1998) appears very similar to the mechanisms known for clay

minerals (Anderson *et al.*, 2010; Fink and Thomas, 1964; Foster *et al.*, 1954; Wrangler and Scherer, 2008), changing lattice parameters and leading to swelling or contraction. The open crystalline structure of the ASR reaction product proposed by Dähn *et al.* (2016) also facilitates cation exchange and water uptake related to RH or temperature, causing volume changes.

Precipitation of a crystalline phase from a supersaturated solution can produce pressure (e.g. Flatt and Scherer, 2008; Winkler and Singer, 1972). To the best of the authors' knowledge, the crystallisation pressure of the crystalline ASR product has not yet been investigated.

To exert stress on its environment, a certain minimum viscosity or E-modulus of the ASR reaction product is required (Katayama, 2012a; Krogh, 1975). Highly expanding gels with low viscosity will simply be squeezed into the paste without exerting stress. However, the E-modulus of crystalline ASR products within aggregates ranges from 8 to 12 MPa (Leemann and Lura, 2013) and is thus able to exert stress.

Calcium is an essential constituent in the formation and expansion mechanism of ASR reaction products. Incorporation of (divalent) calcium reduces swelling potential compared with (monovalent) alkali varieties (Prezzi *et al.*, 1997; Rodrigues *et al.*, 2001; Wieker *et al.*, 1998), as previously observed in micas (Hazen and Wones, 1972), and clays (Kjellander *et al.*, 1988). Consequently, expansion can be expected to be reduced upon extrusion into the cement paste.

3. ACR

In ACR, dolomite (calcium magnesium carbonate ($CaMg(CO_3)_2$)) reacts with dissolved sodium and potassium in the alkaline pore solution, precipitating brucite magnesium hydroxide in pockets within the dolomite (Figure 6). Sodium, potassium and carbonate (CO_3) remain dissolved and react with portlandite (calcium hydroxide), precipitating calcite calcium carbonate forming haloes of calcite in the surrounding cement paste (Figure 7), while recycling sodium and potassium to the pore solution again. As such, this reaction is a dedolomitisation and can be regarded as an ACR in a narrower sense. In severe cases, it can negatively affect the soundness of the aggregate (Prinčič *et al.*, 2013). However, since it comprises a net volume reduction, it does not cause expansion.

By contrast, finely dispersed silica in carbonate (calcite, dolomite) aggregates has only recently been identified as the cause for expansion by deleterious ASR (Grattan-Bellew and Chan, 2013; Grattan-Bellew *et al.*, 2010; Katayama, 2004, 2010, 2012a). Earlier work wrongly attributed expansion to dedolomitisation as the finely dispersed silica remained undetected in
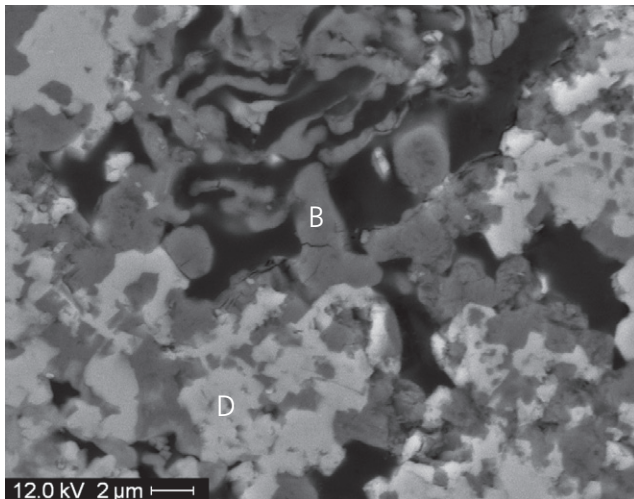
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Figure 6. Dedolomitisation rim: partially dissolved dolomite (D, bright grey) with newly formed brucite (B, medium grey) and pores (black). SEM image in backscattering mode
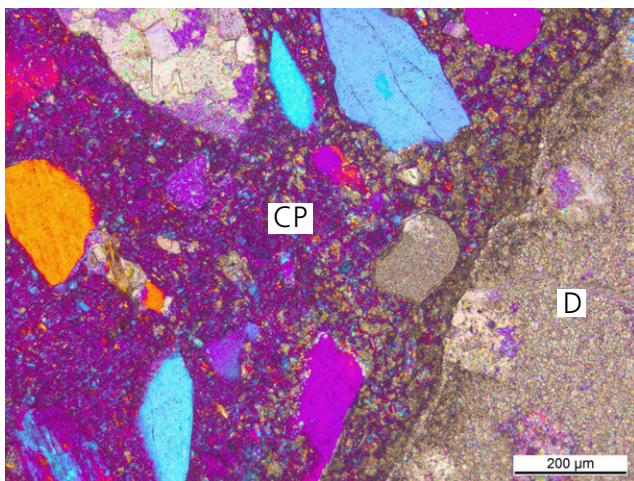

Figure 7. Carbonate halo: dolomite aggregate (D) with dedolomitisation resulting in calcite formation in the cement paste (CP) adjacent to the aggregate. Thin section, crossed polarisers and gypsum plate under optical microscope

the carbonate matrix (Swenson, 1957; Swenson and Gillott, 1960, 1964). However, the ASR caused by this type of silica is independent of dedolomitisation. Whether the ACR in this wider sense should be regarded as a combination of both processes (Katayama, 2004, 2010, 2012a) is addressed by Katayama *et al.* (2016) elsewhere in this issue.

4. Summary and outlook

This paper addresses selected aspects of the AAR, notably the reacting minerals, the formation, composition and structure of ASR products, and their mechanisms of expansion. Although the knowledge of AAR is continuously increasing, there are still gaps that need to be filled. They are given below.

- More in-depth knowledge is needed on the composition and structure of the ASR products leading to decisive stress generation. This has to be combined with the sequence of formation and the spatial distribution of the ASR products at different stages of the reaction.
- Although model systems are able to provide important data, it is essential to increase the amount of data acquired from concrete obtained from AAR-affected structures.
- Establishing thermodynamic and kinetic data on ASR products would make modelling possible. Consequently, some of the microstructural phenomena observed may be better explained.
- Data on the effect of temperature on the physical properties of ASR products should improve the transferability of the results obtained in accelerated tests to concrete structures.
- The ultimate goal of understanding the mechanisms of the ASR is to prevent damage in new concrete structures and enable efficient repair of damaged concrete structures.

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