

A case study of alkali-silica reactions: petrographic investigation of paving deterioration

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Abstract

Alkali-silica reactions are one of the most common causes of deterioration of concrete. This paper presents a petrographic study of a damaged paving situated in Bologna (North Italy) where alkali silica reactions produced diffused pop-out of cm-sized chips.

Siliceous limestone, chert and flint present in the aggregate did not show any reactivity; alkali-silica reactions developed only from fine-grained silica rich marls. Reactive grains show an evident zonation with fractured cores and more compact rims. ASR produced mobilization of alkalis towards the interior of reactive grains coupled with mobilisation of Ca²⁺ ions which re-precipitate and react with alkali-silica rich fluids to produce a hard rim. The final effect is the cracking of the grain due to accumulated gels inside. Alkali-silica reactions developed only on the flooring exposed to capillary rise of water. A further proof of the reactivity of these fine-grained marly grains is the late-stage formation on their surface of Na-carbonate.

Key words: Alkali-aggregate reaction; petrography; microstructure; SEM-EDX.

Introduction

Alkali-silica reactions (ASR) is a phenomena responsible for severely damaging concrete structures. ASR is caused by reactions between the alkali ions (Na, K) present in the cement and reactive amorphous to low crystalline silica components like chert, volcanic glass and siliceous limestones, accidentally present in the

aggregates. These reactions produces silica-rich gels capable of swelling and cracking the hardened concrete.

This paper presents the results of a petrographic study of a damaged flooring. Alkali-silica reactions (ASR) affected a concrete flooring shortly after construction. The ASR produced diffused damages at the surface with popping-out of centimeter-size chips. The

aggregates does not contain in appreciable amounts the well known components responsible of ASR like siliceous limestones, chert and flint. The ASR developed only from fine-grained sedimentary rocks. The aim of this paper is to identify the nature of reactive components by a petrographic study and to propose a reaction mechanism.

The area around Bologna (North Italy) is characterized by a thriving construction activity which needs large amounts of aggregates. The quality of aggregates is of paramount importance but environmental considerations impose the exploitation also from places in which this quality is not assured.

Geological setting

The aggregates were extracted from a quarry located near Pontecchio Marconi (Bologna) in the Reno river valley. They consist of mixed sand-gravel deposits of quaternary age. The lithological composition represents the geological formations outcropping in the medium-upper Reno valley (V.V. AA., 2003) and are mainly made up by micritic limestones (Jurassic to Cretaceous), partially silicified limestones (upper Jurassic) siliceous marls (Miocene), sandstones (Miocene to Pliocene).

Experimental

The flooring affected by ASR is located at the lower level of a large commercial building a few kilometers apart the centre of Bologna, North Italy. The flooring is underground and in contact with the ground. ASR affected exclusively this part of the building (Figure 1a).

The study started extracting 12 cores (94 mm diameter, 130-180 mm height; Figure 1b, c) collected both with evident surface damages and in places not damaged (Figure 1a, b).

The concrete contains aggregates ranging in size from 0.5-4 cm. The aggregate components

are mainly of flat morphology with rounded surfaces; these shapes are typical of gravels coming from fluvial deposits. The upper layer of the flooring is made up by a thin, red coloured quartz-cement mortar (3-5 mm). The surface is coated with a protecting thick paint (Figure 1a).

After recovery the cores were sealed wet in plastic bags stored at a mean temperature of 20 °C to monitor the onset of new ASR. After 12 months all the cores evidenced new damages on lateral surfaces. Reactive single components of the aggregate was sampled extracting 33 smaller (25 mm diameter; Figure 1d, e) side cores.

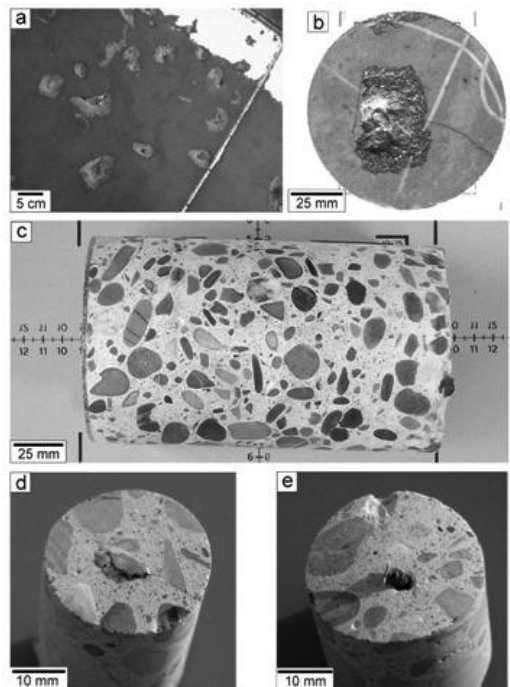


Figure 1. a) Surface of the flooring with pop-out of cm-size chips; b) top view of a core with evident damages; c) side view of a core. Notice the spherical to elliptical shape of the grains; d) new damages developed on lateral surfaces after 12 months. Fractured and uplifted grain; e) protrusion of wormlike ASR gel.

Methods

Samples were studied with polarizing light microscope, reflected light microscope, scanning electron microscopy (SEM) with energy dispersive X-ray analyzer (EDX; SEM Philips 515b / EDAX DX4) and Raman Probe (Micro Raman Renishaw).

Thirty reactive grains (from the extracted 25 mm cores) were prepared for SEM-EDX study making polished thin sections. Each grain was carefully examined with backscattered detector. EDX analyses were performed at 15 kV accelerating voltage and 2 nA beam current for 100 live second counting time. Measured concentrations were calculated with ZAF corrections. Natural silicates and oxides were used for calibration. The mean composition for reactive components of the aggregate was estimated scanning the beam over selected areas.

Analyses were recalculated assuming all CaO as CaCO₃ and recasting the analyses. This assumption is correct as the CaO content of clays and silicates in the clast is always low.

Macroscopic, thin section and SEM-EDX analyses

A typical reactive (Figure 2a) grain shows elongated rounded shape, evident concentric zonation with a homogeneous core and alternance of light and dark bands. The concentric bands are separated by fractures filled by epoxide resins used for making section (Figure 2b). At the optical microscope we recognize a fine-grained clastic sedimentary rock made up by small grains of calcite, quartz, mica set in a very fine matrix made up by clay, calcite, silica minerals. Are also present shell fragments and foraminifera (Figure 2c, d) filled with micrite and chalcedony. Characteristic is the presence of framboidal (globular) aggregates of pyrite (Figure 2d). The rock making up the clast may be classified as siliceous marl.

In some cores ASR produced emission of

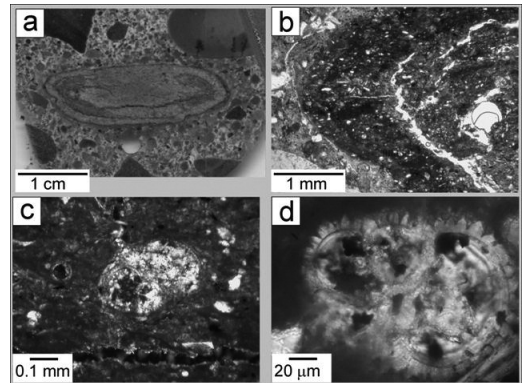


Figure 2. a) Typical elongated, rounded shape of a reactive grain, reflected light; b) reactive grain with concentric bands separated by fractures, thin section, transmitted polarized light microscope; c) and d) particular of a reactive grain with foraminifera filled by micrite, chalcedony and pyrite, thin section, transmitted polarized light microscope.

alkali-silica gels of which the most striking example is the worm-like protrusion in Figure 1e. SEM observations on fracture samples (Figure 3) testify the characteristic morphology of the gels coating the rough surface of concrete. On the right is reported the EDX spectra of gel with its composition (mean of 5 spot analysis). The morphology and composition are similar to those reported in literature (Thaulow et al., 1996; Samuel et al., 1984; Davies and Oberholste, 1986; 1998; Thordal et al., 1990; Fernandes et al., 2004).

The grains have almost always a rounded to elliptical morphology (Figure 4a, b). They display a fractured core separated from a more compact rim. Some grains show cores completely detached from rim due to vertical expansion (Figure 4b). The composition of the grain is shown in the EDX spectra of Figure 4e.

In some places inside grains are recognized alkali-silica gel (Figure 4c, d). The rounded magnified zone in Figure 4d is made up by a

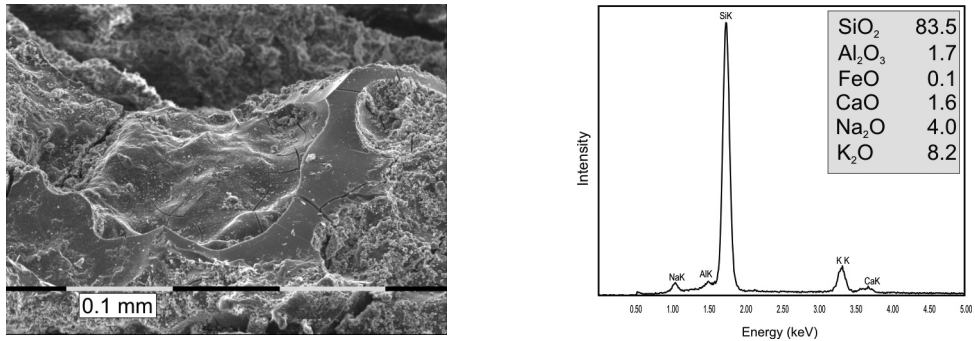


Figure 3. Alkali silica gels on the surface of a concrete. SEM image (left, secondary electron image; EDX spectra and composition of the gel, right).

central irregular calcite grains embedded by an alkali-silica gel whose spectra and composition are reported in Figure 4f. From the image it is evident the expansive character of gel with fractures extending across the grain.

Gel composition (Figure 3 and Figure 4f inset) were checked for reactivity following the method outlined by Bonakadar et al. (2010). Calculation of the R and Y parameter (equations 2 and 3) point out values for $R > 2$ and for $Y \sim 3.9$, values well in excess of the $Y=2$ value considered the limit which separate reactive from non reactive gels.

The most outstanding feature of the reactive grains is the presence of a fractured and less compact to porous core surrounded by a compact rim which “envelopes” the clast. SEM images (Figure 4a, b) illustrate this evidence. These visual characteristic are always coupled with substantial variations in the chemical composition (Figure 5). The EDX analyses (spectra in Figure 5, right side) point out a significant enrichment of CaO in the rim. All the 30 studied clasts presents this Ca enriched rim.

Very late stage reactions

The long-term reactive behaviour of studied grains was confirmed by an interesting late-stage reaction.

After SEM study polished sections were stored in a plastic thin-sections box and conserved in one of the author’s office. After about one year all the reactive grains covered with a thin white patina. Figure 6a, b illustrate one reactive clast before (6a) and after (6b) reaction. Figure 6c is a magnified image showing a continuous thin layer of acicular crystal which cover almost completely the surface. This layer of needle-like crystals is present only over the alkali-rich cores and absent on calcium enriched rims. SEM-EDX analyses (Figure 6d) pointed-out a Na-mineral, provisionally identified as a carbonate. To better characterize it 3 selected specimens were analyzed with Raman probe. The collected spectra (6d) allowed to identify the sample as a sodium carbonate (Edwards et al., 2007). This reaction emphasizes the reactivity of these particular grains active in presence of air.

Discussion

Alkali-silica reactions are described using various models (Dent Glasser and Kataoka, 1981; Wang and Gillott, 1991; Poole, 1992; Garcia-Diaz et al., 2006) all involving destruction of siloxane bonds by hydroxyl activity. One recent and interesting model for ASR is those proposed by Ichikawa and Miura (2007) which involves mobilization of alkalis

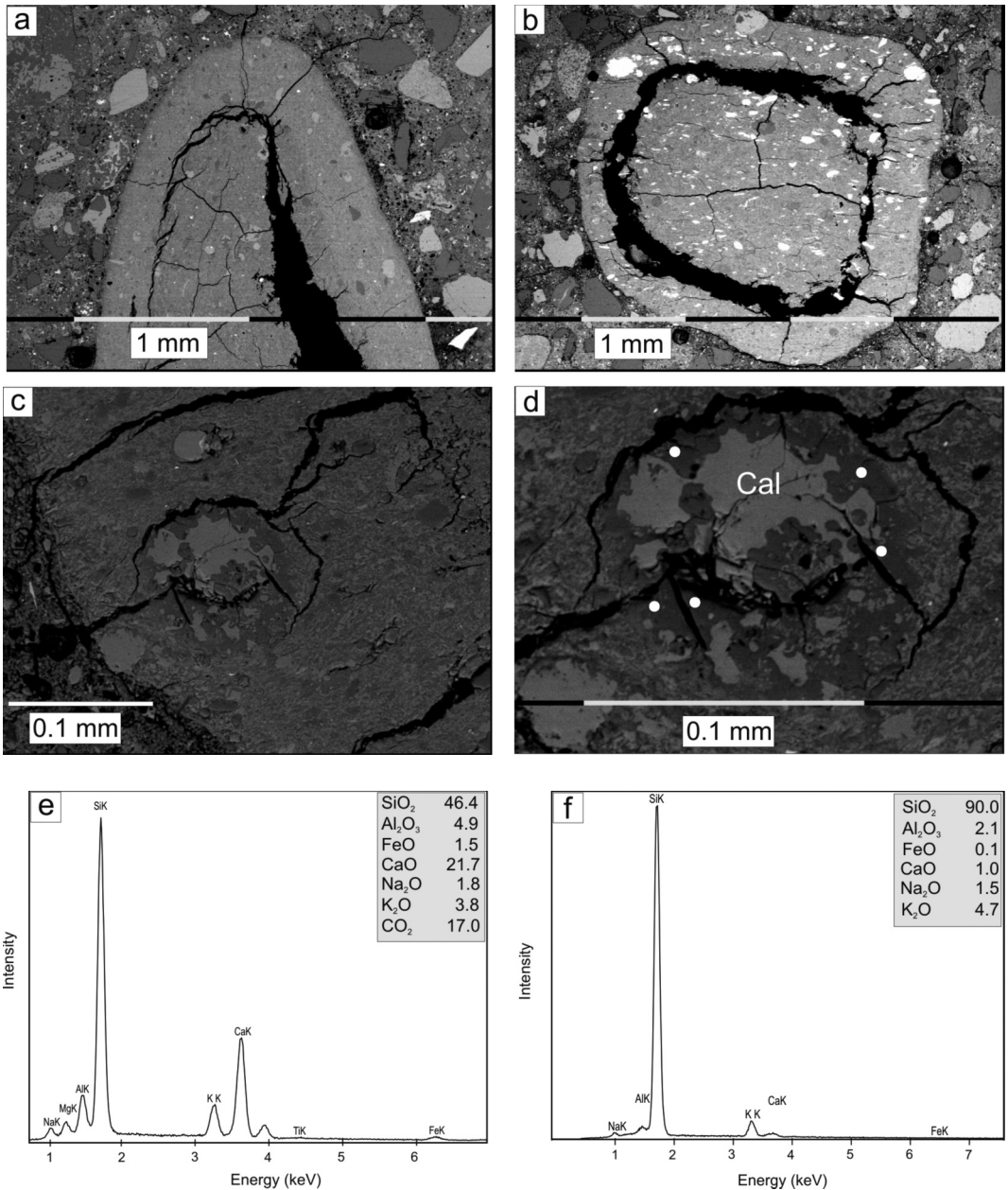


Figure 4. a), b) characteristic shape of two reactive grains. Rounded to elliptical shape, rim detached from the core, fractures extending to the surrounding concrete. c), d) fractured zone with concentration of alkali-silica gel. Notice the fracturing. e) EDX spectra and composition of a reactive grain. f) EDX spectra and composition of alkali-silica gel of Figures c, d. Cal = calcite, white spot are locations of analyses.

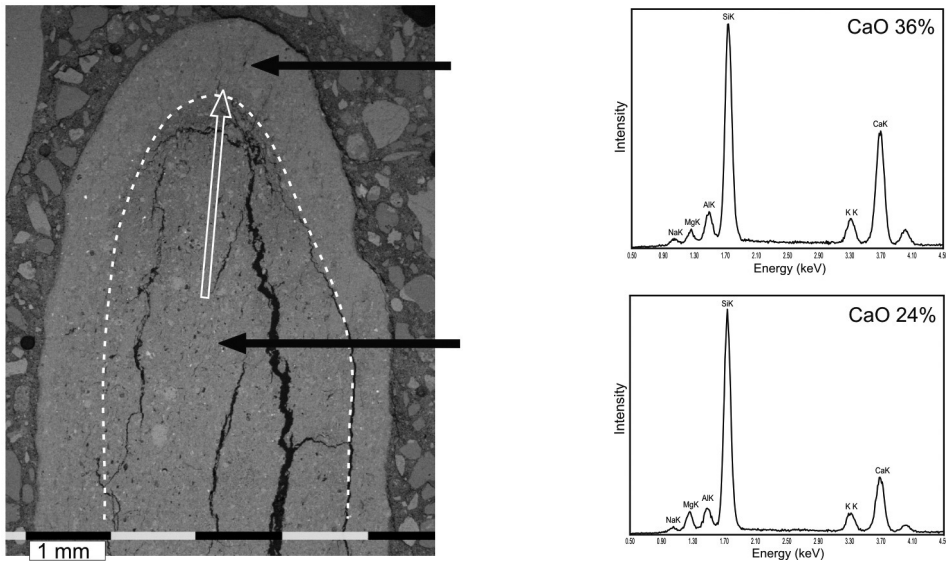


Figure 5. Reactive grain with fractured core and more compact rim. White arrow indicate the calcium enrichment. EDX spectra on the right indicate the compositions.

towards the interior of a reactive clast coupled with dissolution of Ca^{2+} ions which re-precipitate and react with alkali-silica rich fluids to produce a hard rim which subsequently traps alkali gels inside the grain to give an expansive pressure. The final effect is the cracking of the grain due to accumulated excess pressure.

Our observations fit well this model, in particular:

1) Evident zonation of grains with fractured cores and more dense, compact rims. The cracking (Figure 4a, b, c) radiates from the cores of clast and fractures the surrounding concrete. Silica rich gels does not preferentially segregate in veins but tend to impregnate (Figure 4c, d) the clast fracturing the surrounding zones.

2) EDX analyses indicate a systematic enrichment of calcium in the rims of grains. This evidence fit well the Ichikawa and Miura (2007) model of Ca^{2+} transport across the grain.

3) The development of silica-rich gels inside the clast induces a volume increase and fracturing starting from the reactive grain to

surrounding concrete.

4) Applying the equations proposed by Bonakdar et al. (2010), gels result reactive.

5) The reactivity of grains is testified by the late stage formation of Na-carbonates only on alkali rich cores.

Conclusions

The petrographic study of a damaged flooring allowed to identify unusual reactive rocks and made clear that siliceous limestone, chert and flint present as accidental components in the same concrete did not show any noticeable reactivity. ASR developed only from fine-grained rocks which, on the base of petrographic and micropalaeontological investigations, were classified siliceous marls probably belonging to the Anconella member of the Marne di Antognola Formation.

The model we suggest for ASR involves reactions of the fine silica components of reactive grains with formation of calcium

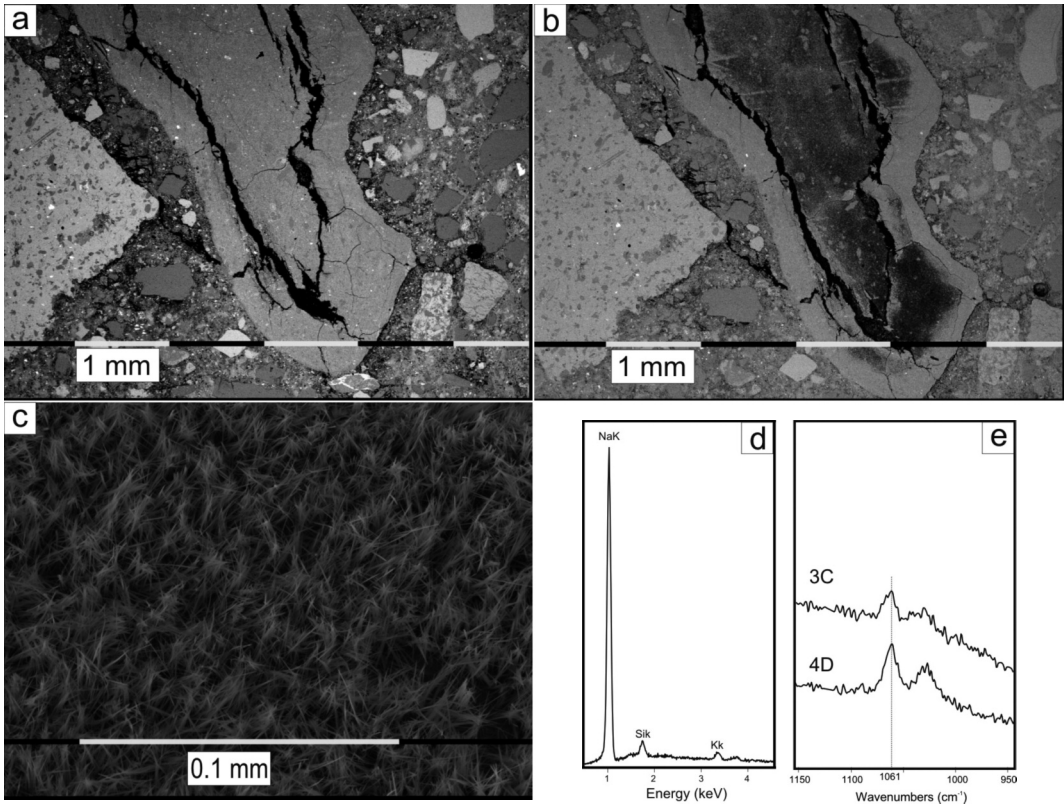


Figure 6. Reactive grain before (a) and after (b) crystallisation of Na-carbonate which cover the core. c) magnified image of the core with a continuous layer of needle-like crystal. d) EDX spectra and e) Raman spectra of the crystals in figure (c).

enriched hard rims which traps stresses according with the Ichikawa and Miura (2007) model. These stresses are at last so strong to produce the fracturing of grains which extends and damage the surrounding concrete. The triggering mechanism is the capillary rise of water from the ground at the base of the flooring.

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