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Cement & Concrete Composites 27 (2005) 796–801

Cement & Concrete Composites

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Alkali-aggregate reaction—identifying reactive silicates in complex aggregates by ESEM observation of dissolution features

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Received 8 March 2004; accepted 8 March 2005

Abstract

A petrographic examination can only be used to qualify a concrete aggregate in regard to its potential for AAR when the reactivity of the corresponding lithologies and minerals are known. In this study, two complex Swiss aggregates with polished surfaces were immersed in an alkaline solution in order to identify reactive minerals. Afterwards, dissolution and precipitation phenomena were investigated by environmental scanning electron microscopy.

In general, quartz is the most reactive mineral in both aggregates. Feldspar, biotite and chlorite exhibit dissolution phenomena, and liberate alkalis and calcium. Various morphological types of gels are formed as precipitates on the polished surface: thin calcium silicate hydrate structures exhibiting card house morphology; small agglomerates (2–20 μm) with a smooth surface; and large agglomerates (20–500 μm) characteristic of common ASR reaction products. These gels mainly consist of Si and Ca with variable amounts of Na, Mg, Fe and Al.

Keywords: Alkali aggregate reaction; Identification; Reactive silicates; Feldspar; Mica

1. Introduction

The first published case of alkali-aggregate reaction (AAR) in Switzerland dates from 1995 [1]. In recent years, several cases of AAR have been reported [2,3]. These studies document that in the past damages caused by AAR have erroneously been attributed to independent processes like frost, leaching or sulphate attack. Fast reacting minerals like amorphous or cryptocrystalline silica are rare in Swiss aggregates. Therefore, the reactions in concrete seem to proceed at a relatively slow pace. As typically rapid reactive minerals are rare, the question arises whether there are other silicate components causing the AAR. The answer is especially important concerning the petrographic examination. An aggregate can only be classified with respect to AAR when the reactive aggregates and minerals are known [4].

The goal of this study is to develop a method to identify rock components responsible for AAR in concretes containing these aggregates. A case study is presented from two complex aggregates quarried from two different alluvial deposits. Both are classified as reactive by the AFNOR P 18-588 test and have shown to be able to produce damages in concrete due to AAR [5,6]. On a microscopic scale, AAR is characterised by the dissolution of reactive minerals, the formation of gel and the cracking of the reactive aggregates. This study is concerned with the dissolution of silicates in an alkaline solution and subsequent precipitations. The phenomena are investigated by environmental scanning electron microscopy (ESEM) after immersing polished aggregates in an alkaline solution.

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doi:10.1016/j.cemconcomp.2005.03.007

2. Method

One of the aggregates studied is quarried from the alluvial deposit of the Reuss river in central Switzerland. The other one comes from a quarry close to Lake Brienz. The overwhelming part of the source for both aggregates was subjected to greenschist facies metamorphism during the Alpine orogenesis.

The complex Reuss aggregate incorporates a large variety of sedimentary and igneous rocks which is typical for aggregates used in Switzerland. Most of the Brienz aggregate origins from the Aar-massive, a geological unit consisting of metamorphic igneous rocks.

The petrographic examination of the aggregates was carried out according to SIA 162/1 [7]. Additionally, their texture and mineralogy was investigated with thin sections under a polarisation microscope.

The investigation of the reactivity of single components in the aggregates was carried out by the following procedure: Particles (4–8 mm) were embedded in epoxy, cut and polished. For each type of aggregate, two samples with a combined surface area of approximately 40 cm^2 were prepared. They were immersed in 1000 ml of 2 M NaOH solution (pH $\sim$ 14) at a temperature of 38 °C in a calibrated heater without stirring. NaOH was used to produce the alkaline solution because it is employed in various accelerated test methods to determine aggregate reactivity (e.g. [8]). The relatively high concentration and temperature of the solution were chosen in order to accelerate the dissolution of silicates. The composition of the solution was analysed before and after the experiment using plasma emission spectrometry (ICP-OES). The liquid samples taken from the solution were immediately diluted with HNO_3, at a ratio of 1 + 9 to prevent any precipitation. Dissolution and precipitation phenomena on the polished surfaces were studied with an environmental scanning electron microscope (ESEM-FEG XL30). The samples were not coated and the operating conditions of the ESEM were between 15–20 kV and 0.5–1.5 Torr. The chemical compositions of reactive minerals and of precipitates were analysed with energy dispersive X-ray spectroscopy (EDX) using point spectra. An EDAX 194 UTW detector, a Philips digital controller and EDAX Microanalysis System Software (Version 3.0) for ZAF quantifications were used.

3. Results

3.1. Petrography

The petrography of Reuss and Brienz aggregate are shown in Tables 1 and 2 respectively. The quartz in the gneiss and schist often shows undulary extinction. This can also be observed for some of the quartz in granite and sedimentary components. About two third of the feldspars in the granite, gneiss and schist of both aggregates are hydrothermally altered. Some of the biotite in the igneous rocks is altered to chlorite.

Table 1
Petrography and silicate mineralogy of the Reuss aggregate

Rock type	Percent by number	Amount of silicates	Main silicates
Greenstone	1.0	>95	Pyroxene, amphibole, feldspar, chlorite
Gneiss/schist	11.0	>95	Quartz, feldspar, muscovite, biotite, chlorite, amphibole
Pegmatite	4.5	>95	Quartz
Chert	3.0	>95	Quartz
Various sandstones	21.5	~90	Quartz, feldspar, various mica
Siliceous limestone	5.5	~25	Quartz
Limestone	20.0	<5	Quartz
Siliclastic limestone	11.5	~10	Quartz, feldspar, various mica
Dolomite	20.0	<5	Quartz
Calcareous shale	2.0	~60	Quartz, mica
Sum	100		

Table 2
Petrography and silicate mineralogy of the Brienz aggregate

Rock type	Percent by number	Amount of silicates	Main silicates
Granite/gneiss	85.0	>95	Quartz, feldspar, muscovite, biotite, chlorite, amphibole
Sandstone	4.5	~85	Quartz, feldspar, various mica
Siliceous limestone	5.0	~25	Quartz
Siliclastic limestone	11.5	~10	Quartz
Sum	100		

3.2. Dissolution phenomena

The dissolution features are very similar in both aggregates. Overall quartz shows the highest degree of etching (Fig. 1). Moreover, it is the most abundant silicate present. The mineral grains dissolve from their grain boundaries inward. The degree of etching appears to be independent of the grain size. Large grains and microcrystalline grains show similar dissolution phenomena.

Quartz within schist, gneiss and deformed granite is affected much stronger by etching than it is in the sandstone. On two gneiss particles from the Reuss deposit, an increased degree of etching of quartz was observed along cleavage planes. Nevertheless, in some sandstone particles and siliceous limestone particles strongly etched quartz was observed.

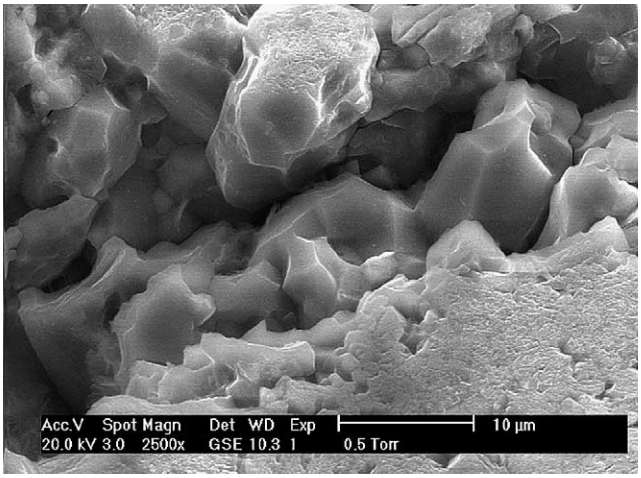

Fig. 1. Etching phenomena involving several quartz minerals. Polished surface of a gneiss particle from Reuss aggregate, after two weeks immersion in 2 M NaOH at 38 °C.

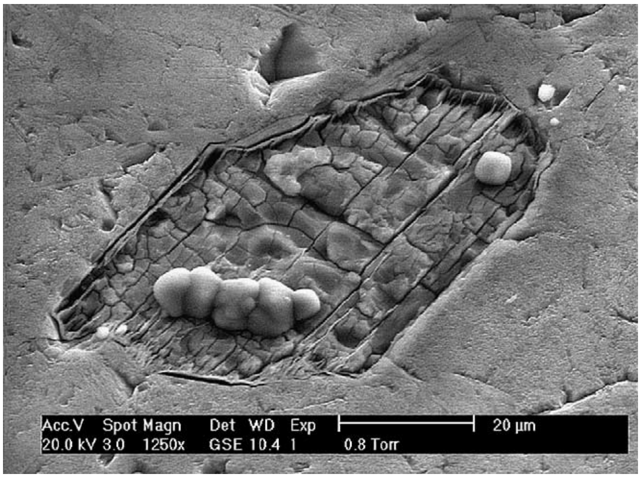

Fig. 2. Etched biotite and gel precipitates on the polished surface of a schist particle. Reuss aggregate, after two weeks immersion in 2 M NaOH at 38 °C.

In addition to quartz also feldspar (albite and orthoclase), biotite, and chlorite exhibited indications of dissolution (Figs. 2 and 3). They often display a rough surface texture that appears to be caused by a preferred etching along specific planes. These planes either represent crystallographic cleavages or compositional zonations in the case of feldspar (growth zonations or perthite-exsolutions).

Depending on the lithology there are differences in the way the minerals are dissolved. In sedimentary rocks, dissolution is usually limited to one silicate at a time. In contrast, larger pits with widths of up to 0.5 mm in granite, gneiss and schist document intense dissolution affecting several minerals simultaneously.

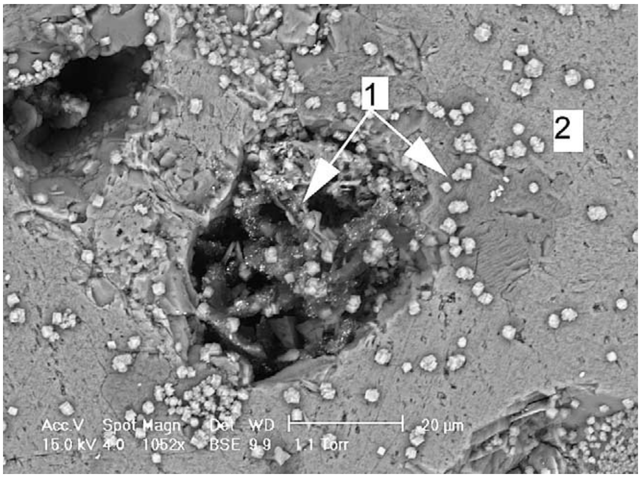

Fig. 3. Etched orthoclase (1, darker grey) embedded in anorthite (2) on the polished surface of a granite particle. The small isometric minerals are calcite crystals (altered portlandite). Brienz aggregate, after two weeks immersion in 2 M NaOH at 38 °C.

Table 3
Concentration of ions dissolved from samples into the NaOH solution

Element	Ca	Si	K	Li	Al
[mmol/l]	0.47	1.07	0.10	0.05	0.26

Quartz with dissolution phenomena was observed in all lithologies except for the greenstone. Dissolved feldspars were present in granite, gneiss, schist, sandstone and siliclastic limestone whereas etched biotite and chlorite was only observed in granite, gneiss and schist.

After immersing the samples for two weeks, the recovered NaOH solution showed an enrichment of Ca, Si, K, Li and Al (Table 3).

3.3. Precipitation phenomena

The number of the precipitates is significantly less than the number of the etched minerals found, there are no precipitates on or near the majority of the etched minerals in both aggregates.

Three different types of gel precipitates can be distinguished by their morphology: thin-layer deposits with a card house structure (Fig. 4), small agglomerates with a diameter between 2 and 20 µm (Fig. 2) and large agglomerates with a diameter between 20 and 500 µm (Fig. 5). Transitions between these morphological types can be observed. The surface of small agglomerates is generally smooth while the surface of the large agglomerates often displays a card house like structure. The large agglomerates are cracked (Fig. 5). The thin layers and the large agglomerates are mostly located at the edges of etched minerals, while the small agglomerates occur directly on them. The occurrence of large agglomerates on the inner areas of the polished aggregates is linked to microcracks in the aggregate.

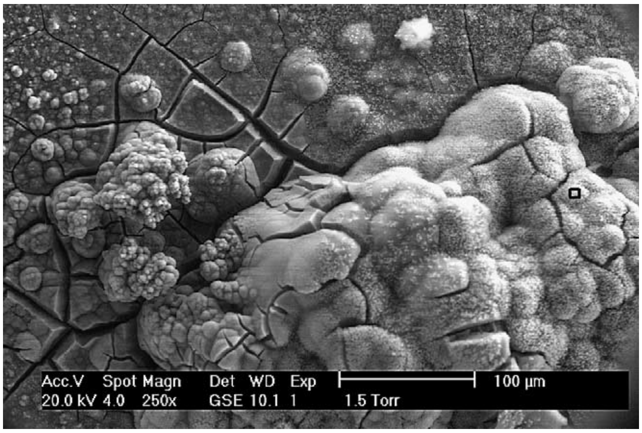

Fig. 4. Large agglomerate of gel on the surface of a gneiss particle. EDX analysis on right side of agglomerate (black square). Reuss aggregate, after two weeks immersion in 2 M NaOH at 38 °C.

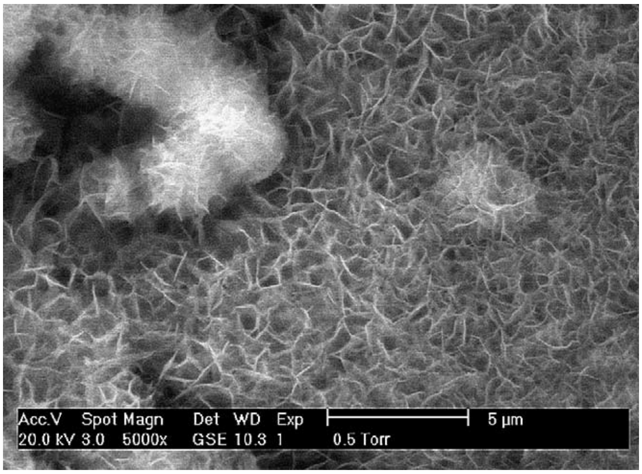

Fig. 5. Thin layer of gel with card-house morphology on the surface of a schist particle. Reuss aggregate, after two weeks immersion in 2 M NaOH at 38 °C.

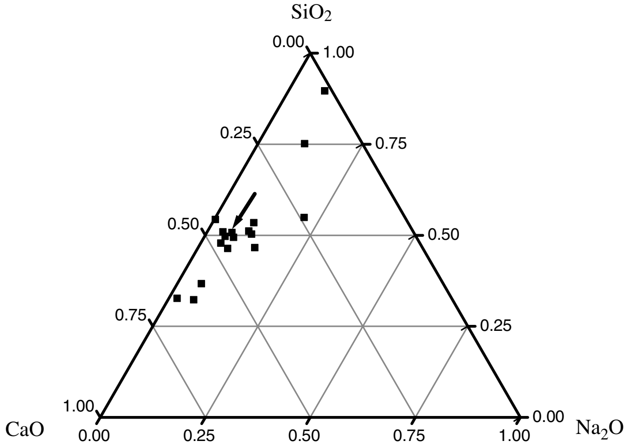

Fig. 6. Composition of the large gel agglomerates in percent by weight. The arrow points at the composition of the agglomerate shown in Fig. 4.

The analysis of the large agglomerates with EDX shows that they are mainly composed of SiO_2 (average of 46% by weight) and CaO (average of 36% by weight) with varying minor concentrations of Na_2O (average of 7% by weight), K_2O, $Al2O_3$ and Fe_2O_3 (Fig. 6).

Locally precipitation of portlandite was observed in addition to the gel precipitates. Mostly, the portlandite formed directly on aggregates with etched calcite.

4. Discussion

4.1. Dissolution phenomena

Silicates with dissolution phenomena are described as "reactive" in this study, because they are not stable in an alkaline solution, and may therefore influence the AAR.

Quartz is the most frequently etched mineral in both aggregates studied. There is no connection between the size of the quartz minerals and the degree of dissolution. However, highly deformed quartz exposed in cleavage planes of schist, gneiss and granite seems to display a higher reactivity. Obviously, there is a relationship between the degree of deformation and the reactivity [9].

Two feldspars (albite and orthoclase) are identified as further reactive dissolvable components. In general, no differences are observed between the dissolution of the feldspars in the different lithologies. Although the degree of alteration of the feldspars was not determined, it appears that hydrothermally altered feldspars are more reactive. In the literature, feldspars are mentioned as sources for alkali ions repeatedly (e.g. [10,11]). The release of alkali ions from feldspar bearing aggregate has been demonstrated indirectly by hot water extractions [12]. Recently, measurements of pore solutions of mortars containing crushed feldspars have shown that significant amounts of alkali ions can be released and that they can actively take part in the AAR [13]. Additionally, the ratio of Ca to Na and K in the pore solution may be changed by feldspar dissolution. This may influence the development of pressure within the reactive aggregates [14,15].

Mica has to be considered as another source for alkali ions. In both aggregates, biotite flakes with considerable dissolution phenomena are observed. In contrast, etched chlorite is not a source for alkali ions. In this study, muscovite with signs of dissolution has not been found. However, it has been shown previously by similar experiments that muscovite may be reactive in a NaOH solution as well [16]. It has also been demonstrated that phlogopite can release K ions in cement paste and in mixed Ca–Na solutions [17]. Furthermore, the presence of detrital mica and interstitial clay in sandstone used as concrete aggregate seems to enhance the solubility of quartz due to the release of alkali ions [18]. Clay minerals can even produce C–A–S–H and C–S–H types when mixed with lime [19].

The dissolution of different silicates observed in this study correlates to observations made in the microstructure of 21 year old tunnel linings produced with the Reuss aggregate; quartz, feldspar and biotite all show dissolution features [20].

The presence of K, Li, Al and Si ions in the NaOH solution at the end of the test reflects the dissolution of silicates. These elements are found in various feldspars and mica minerals [21].

The relative degree of etching found suggests that feldspars and biotite react somewhat slower than quartz. When the AAR proceeds at a relatively slow pace, alkali release from silicates may prevent a depletion of alkali ions in the pore solution. It has not been shown so far that feldspar and mica can directly cause expansion. But it is evident that feldspar and mica can be partly dissolved in alkaline solutions. Therefore, they are able to support the AAR by the release of alkali ions and prove to be at least indirectly reactive.

Often low alkali cement is chosen to decrease the risk of AAR [22]. But the addition of silica fume, fly ash or furnace slag to the concrete has proven to be more effective in AAR prevention reducing the content of OH^- ions in the pore solution [23,24]. These admixtures should especially be preferred to reduce the risk of AAR when there is a possibility that alkali ions are released into the pore solution by reactive silicates.

The identification of reactive minerals and rock components in aggregates by the method presented here complements the petrographic examination and increases its reliability. Usually an aggregate is classified in regard to its potential reactivity only based on the various forms of quartz present (e.g. [25,26]). Considering the importance of the release of alkali ions such a possibility should be taken into account as well. Although a majority of the etched minerals can be identified with an optical microscope, the use of an ESEM or a SEM allows a more precise identification of reactive minerals.

4.2. Precipitation phenomena

The large agglomerates of gel on the polished surface of the samples are always cracked although the samples were not dried before examination. Obviously, these gels contain a fair amount of water. Concerning their morphology, they strongly resemble gels observed in mortar specimen tested for AAR under lab-conditions or the amorphous C–S–H gel of early cement hydration [27,28]. The size of the large agglomerates and their locations at the edge of aggregates and in areas of the aggregates with cracks indicates that minerals are not only being dissolved on the polished surfaces. Dissolution takes place in the interior of aggregates as well, and the gel is precipitated where the dissolved ions reach the polished surface.

5. Conclusions

Based on the results of this study the following conclusions are drawn:

- Potentially reactive minerals in complex aggregates can be identified by the immersion of polished aggregates in a NaOH solution, and subsequent examination with an electron microscope.
- The method can complement the petrographic examination and tests determining the potential reactivity of aggregates.
- Mica and feldspars in the aggregates studied dissolve less frequently than quartz; feldspars dissolve more frequently than mica, and are a common source for alkali ions. Therefore, they may influence the chemistry of the pore solution and subsequently the progress of the AAR.

Acknowledgement

The authors would like to thank Ralf Kägi for the support in the EDX analysis and Claudia Schreiner for analysing the NaOH solution.

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