

# Interfacial transition zone of cement paste-reactive aggregate in cement-zeolite mortars

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**Abstract.** Alkali-aggregate reaction is an expansive chemical reaction between the alkalis present in cement paste and minerals contained in aggregates. Mineral admixtures can mitigate the detrimental processes caused by this reaction. One of the minerals that reduce the effects of the alkali-aggregate reaction is natural zeolite. This study attempts to explain the process that takes place in the zone surrounding reactive gravel in the cement mortar made with an addition of natural zeolite. Mortar bar expansion tests were performed and a scanning electron microscope equipped with an energy-dispersive X-ray spectrometer was used to observe the paste-aggregate interfacial zone. The results confirmed the influence of the zeolite on the reduction in reactive aggregate-based mortar expansion. The microstructure of the aggregate-paste interfacial region was described and particular sub-zones varying in terms of calcium, sodium, potassium and silicon contents were determined.

**Key words:** alkali-aggregate reaction, SEM-EDS, mortar expansion, zeolites.

## 1. Introduction

High alkali cements contribute to the distress of concrete due to alkali-aggregate reaction (AAR), also known as internal corrosion. Two types of AAR are commonly recognized: alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR). Both induce swelling and deterioration of concrete. An increasing body of research is suggesting that the phenomena of AAR are in fact based on the ASR mechanism [1–3] and that the differences between the reaction types are associated with various forms of reactive silica [4–6] and the presence of other minerals.

Applying natural pozzolans, such as clinoptilolite from the zeolite group, can mitigate the deleterious effects of AAR, as has been proven in [7–10]. Both pozzolanic reaction and ion-exchange reaction are responsible for the effectiveness of this mineral admixture [7, 10]. Clinoptilolite captures and immobilizes sodium and potassium ions into the nanochannels of its structure, thereby reducing the amount of alkalis available for the reaction with aggregates.

This paper attempts to describe the mechanism of AAR in mortars containing clinoptilolite, viewed through the changes occurring in the microstructure of reactive aggregate-cement paste interfacial region. The observations of the mortar microstructure were carried out with the use of a scanning electron microscope (SEM) integrated with an energy dispersive x-ray spectrometer (EDS). The microstructure of cement mor-

tars with reactive aggregates and cement-zeolite binder was compared with that of zeolite-free mortars.

## 2. Materials and methods

The mortars were made with postglacial gravel [11] mechanically crushed to particles finer than 4 mm and divided into fractions, Portland cement CEM I 42.5R with  $\text{Na}_2\text{O}_{eq} = 0.66\%$ , and zeolite containing 83% potassium clinoptilolite. Chemical compositions of the cement and the zeolite are presented in Table 1. Considering that cements made in Poland contain more potassium than sodium,  $\text{K}_2\text{SO}_4$  was added to ensure alkali content sufficient to initiate AAR to value of  $\text{Na}_2\text{O}_{eq} = 1.10\%$ .

The mortar samples were manufactured to ASTM C 1260 [12]. Two batches of mortars were prepared, each including five mortar bars with dimensions  $25 \times 25 \times 250$  mm. Cement was used as a binder in one batch (batch C); In the other, 30% cement was replaced with zeolite (batch 3Z). After demoulding at 1 day, the samples were stored in water for 24 hours at  $80^\circ\text{C}$ . Following 48 hours of hardening, the samples were immersed in 1 M sodium hydroxide solution and stored for 47 days at  $80^\circ\text{C}$ . Length change of mortar bars was measured every day for 16 days. From day 17 the expansion was measured once per week. At 49 days fracture surfaces of the mortar bars were observed under the scanning electron microscope.

Table 1  
 Cement and zeolite compositions, [%]

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	LOI	Cz. n.r.
Cement	20.20	4.80	3.00	61.70	1.80	2.70	0.78	0.15	0.45	–	–	3.00	1.00
Zeolite	67.07	12.40	0.90	2.09	0.72	–	2.80	2.05	0.19	0.04	0.014	–	–

LOI – loss on ignition; Cz.n.r. – HCl insoluble parts

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### 3. Discussion of the results

**3.1. Mortar expansion.** The results of the expansion measurements conducted for cement mortar and cement-zeolite mortar samples are presented in Fig. 1. In this test method, the mortar bar expansion that exceeds 0.2% classifies the aggregate as deleterious material due to alkali-aggregate reaction, whereas expansions from 0.1 to 0.2% indicate the potential for damage in concrete [11].

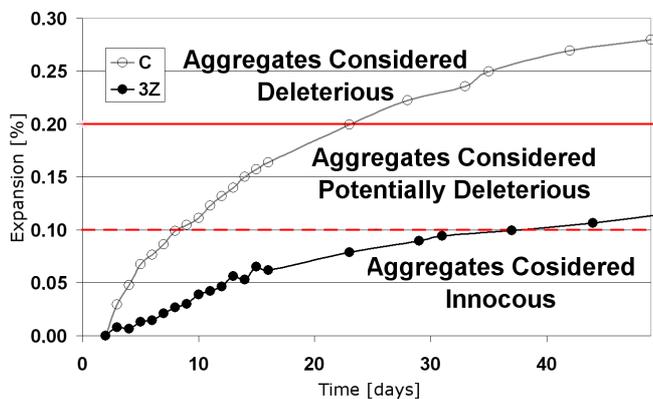


Fig. 1. Comparison of expansions of mortar bars made with and without the zeolite admixture

The application of clinoptilolite as a 30% replacement of the cement resulted in a significant reduction in reactive aggregate-based mortar expansion. During the first 16 days of expansion measurements, the average length increase recorded for mortar bars with cement was approximately 0.164%, which suggested the potential risk of damage due to alkali-aggregate reaction. The value of this parameter for the mortars with zeolite replacement was only 0.062%, which indicated no potential for AAR-induced damage. No inhibition of expansion was observed in both mortar types during the 16-day period. The 49-day expansions classified the cement mortar as exposed to damage due to AAR (0.280%) and the cement-zeolite mortar as exposed to potential damage (0.116%). The recorded expansion confirms the progress of alkali-aggregate reaction in mortars.

**3.2. Mortar microstructure.** The SEM study of the fracture surfaces of the cement-zeolite mortar bars revealed the presence of alkali gel on the aggregate grain surfaces in the form lamellar particles and the grains that debonded from the cement matrix (Fig. 2). The AAR products were detected at the aggregate-paste interfaces.

In cement mortars, the reaction products were observed at the debonding sites and had the needle-like forms (Fig. 3a). The chart in Fig. 3b shows that this phase is rich in sodium whose peak exceeds the peak characteristic of calcium.

Five sub-zones of the aggregate/cement zeolite paste interfacial transition region were differentiated in the analysis (Fig. 4a). The results of the x-ray microanalysis of these sub-zones are presented in Fig. 4b. Sub-zone I is the C-S-H phase (Type III product in Diamond's classification [6]) that surrounds the aggregate grain.

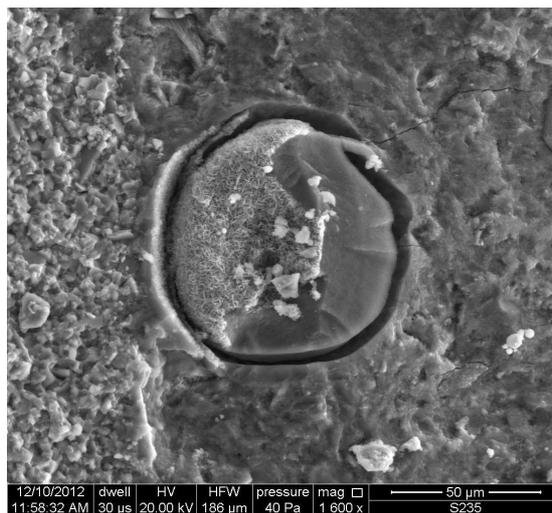


Fig. 2. Silica gel-covered aggregate debonded from the cement-zeolite matrix

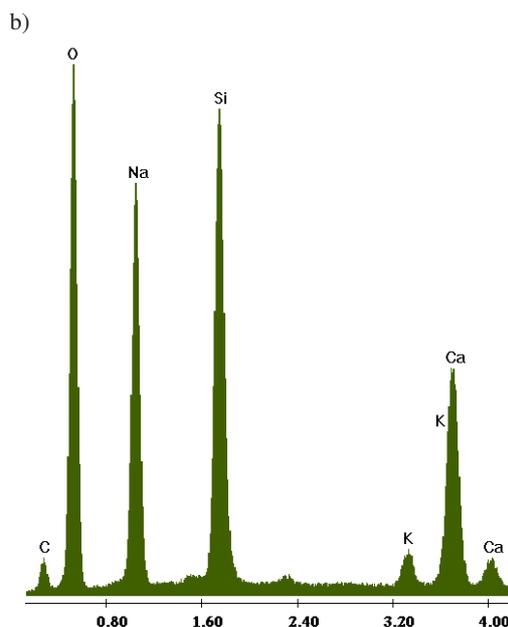
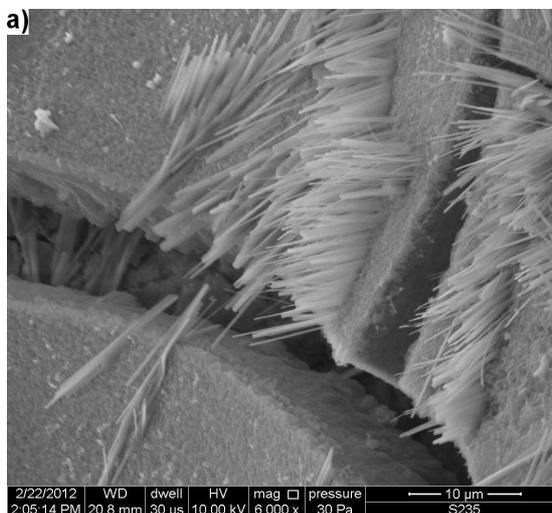


Fig. 3. AAR products in the cement mortar

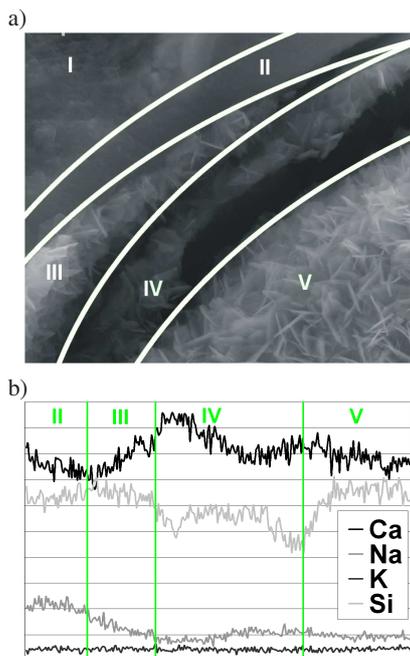


Fig. 4. a) The division of the paste/aggregate contact zone into sub-zones, b) mass contents of Ca, Na, K and Si in sub-zones II-V

The sub-zone II is the closely packed C-S-H phase that lies in the area of increased sodium content, as seen in Fig. 4b. Subsequent sub-zones, III, IV and V, are AAR products. Alkali gel formed on the C-S-H builds sub-zone III. Between this gel and the gel formed on the aggregate (sub-zone V) there is a separated from them layer of AAR products classified as sub-zone IV. This may be a reaction rim that detached from the aggregate as a result of the alkali gel accumulating and swelling under it. The structure of this sub-zone corresponds to the area of increased concentrations of calcium, as seen in Fig. 4b.

No cracks running through the aggregate were observed in the investigated area. Cracking initiated along the boundary separating the aggregate from the paste and propagated in the form of smaller cracks through the paste, as seen on the right-hand side in Fig. 2. Formed in the paste-aggregate contact zone, AAR products with the increased calcium content (sub-zone IV) can be identified as the reaction rim [13, 14]. The location of this sub-zone, between the alkali gel sub-zone (II) settled on the C-S-H phase and the gel sub-zone (V) settled on the aggregate may be regarded as the result of its detachment from the aggregate grain due to the build-up of pressure from the swelling gel. This may indicate that the strength of the reaction rim (sub-zone IV) is lower than that of the reactive aggregate. The alkali gel generates tensile stresses [15, 16] causing the damage to the reaction rim before it reaches the value necessary to damage the aggregate. The damaged rim may release the gel accumulated under it (sub-zone V) and make access for the pore solution. With the progression of the AAR the reactive rim can redevelop and the process repeats. It also suggests that rich in calcium products of subzone IV are characterized by a less expansionary than subzone V.

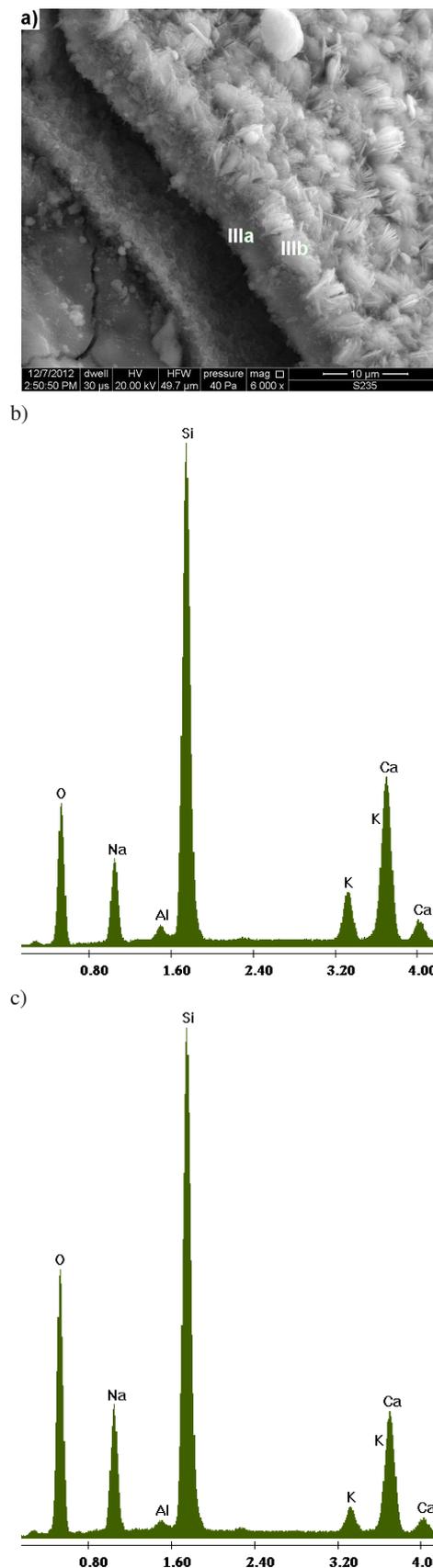


Fig. 5. a) sub-zone III, b) microanalysis of the densely packed layer, c) microanalysis of the loosely packed layer

The alkali-aggregate reaction products cover only part of the aggregate observed in Fig. 2, which may be evidence for their separation from the aggregate grains. This may be due to the fact that, contrary to the findings reported by Ichikawa and Miura [13, 14], a gravel aggregate grain is not entirely composed of reactive silica. The reactive silica may occur in the aggregate more or less uniformly, as for example chalcedony in the carbon binder [11]. In the case of granite aggregate, the reaction products will form on the strained quartz responsible for the aggregate reactivity.

Figure 5 shows another area of the paste-aggregate boundary zone, aggregate debonding site. Sub-zone III of the gel formed on the paste comprises two layers. The external layer is composed of densely packed crystalline products IIIa (Fig. 5b) and has the potassium content higher and sodium lower than that in the internal layer made of loosely packed reaction products IIIb (Fig. 5c).

Analysis of alkali-aggregate reaction products (Figs. 3 and 4) revealed considerable amounts of sodium ions in their compositions, as opposed to the amount of potassium ions, which may be due to the supply of sodium ions from NaOH solution surrounding the samples. AAR products had a form of lamellar particles in the cement-zeolite mortars, whereas in the plain mortars they had a needle-like form.

#### 4. Conclusions

The results of this study have shown that:

- natural zeolite used as 30% cement replacement in the mortar reduces expansion due to alkali-aggregate reaction, which may result from different compositions of the AAR products on the aggregate grain surface;
- alkaline gel formed between the aggregate and the hardened cement paste constitutes the boundary zone composed of sub-zones with varying contents of calcium and sodium. One of the them is the tight reaction rim composed of alkali calcium silicates in the sub-zone IV;
- alkali gel that surrounds the reactive aggregate, poor in sodium in cement-zeolite mortars, debonds from the reaction rim causing no aggregate cracking;
- increased content of potassium in the mortars in relation to the sodium content does not play a significant role in the AAR product formation. The amount of potassium present in the alkali gel is similar to that in C-S-H. Sodium ions from the solution surrounding the samples are incorporated in the alkali-silica gel forming in the contact zone.

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