# MICROSTRUCTURE OF ALKALI-SILICA REACTION PRODUCTS IN CONVENTIONAL STANDARD AND ACCELERATED TESTING

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Mortar bars with granite or chalcedonite aggregate have been tested under conventional standard testing, based on storage of specimens at at  $38 \pm 2^{\circ}$ C,  $RH \ge 95$  %. Aggregate of granite or chalcedonite and silica sand containing opal were used in mortar bars for expansion measurement under accelerated testing, based on storage of specimens in 1 N NaOH solution at  $80^{\circ}$ C. Scanning electron microscopy (SEM) equipped with an energy-dispersive X-ray analysis (EDX) showed that specimens that expanded in the conventional standard mortar bar test (after 30 months) contained alkali-silicate products and secondary ettringite. Specimens that expanded in the accelerated test (after 16 days) showed the same morphological and compositional alkali-silica gel only. The reaction products in the both methods appear to be the same, indicating that reaction mechanisms are the same but differ only in rates. The results of the conducted test show that the alkali content (especially potassium) in cement plays an important role in the process of expansion in the accelerated method.

### INTRODUCTION

The reaction between alkali and aggregate is a very slow process, whose results may become apparent inside the concrete construction, which contains the reactive components after many years. The applied petrographic or chemical methods of aggregate testing make possible to determine whether the aggregate is reactive. Yet whether the reaction between alkali and aggregate will cause concrete expansion and destruction is also dependent on other factors, including reactive material crushing, as well as the alkali content in the concrete pore solution. The reaction between alkaline hydroxides and aggregate is studied with the use of standard methods, in which mortar or concrete samples containing high alkali-content cement as well as the tested aggregate are stored in the temperature of 38°C and relative humidity exceeding 95 % [1-2]. If the aggregate is very reactive, expansion of the samples is observed after a relatively short time (less than six months). Less reactive aggregates need a much longer time for the expansion to occur. Consequently, accelerated tests are introduced to enable the detection of reactions between alkali and aggregate. In the 1980s, Oberholster and Davies [3] applied the accelerated method to detect alkali-silica reactions (the NBRI method).

The accelerated method of aggregate alkaline reactivity testing [4] is usually applied as a fast indicator of the sensitivity of aggregates, used in concrete, to potential destructive expansion, caused by the alkali-silica reactions. It is based on the papers published by Oberholster, and relies on expansion testing of mortar bars immersed in a normal sodium hydroxide solution at the temperature of 80°C over 14 days. The combination of the alkaline medium and high temperature causes fast, measurable expansion, even in case of low reactive aggregates [3]. This method's world/wide popularity has been confirmed by its application, described in several papers presented during the recent International Conference on Alkali-Aggregate Reaction [5]. In this method, the source of alkali are sodium ions, so the standard does not specify the alkali content in the cement used for mortar making, with the assumption that cementderived alkali little affect the expansion [6-7].

In the accelerated method, the increased alkali content and higher temperature in comparison with the standard method may cause the expansion mechanism to be different in both methods. The present paper presents the results of research on expansion and microstructure of mortars with granite and chalcedonite aggregates, performed with the use of the standard and accelerated methods. The influence of the alkali content in cement on the linear changes has also been investigated with the use of the accelerated method, as well as the microstructure of reactive silica aggregate mortars.

## EXPERIMENTAL

Granites, as a rule, produce good aggregate, but destruction of concrete with granite aggregate due to

alkali silica reactions is sometimes observed [8]. The reactive component of this aggregate is cryptocrystalline quartz, or quartz under strain. The main component of chalcedonite is chalcedony (88-92 %), quartz ca. 5 to 9 % and opal up to 3 %. Chemical composition of granite and chalcedonite is shown in table 1; chemical and mineral composition of cement (marked as Cement 1) - in table 2. In the experiments on the influence of the alkali content in cement on the course of the alkali-silica reaction in the accelerated method, silica sand containing 4 % opal was used as reactive silica aggregate. Size analysis of aggregates complied with the specifications of the ASTM C 1260 standard. In the experiment, industrial cement CEM I (marked as Cement 2), obtained through grinding clinker with gypsum (specific surface of 370 m<sup>2</sup>/kg) was used. Chemical and mineral composition of clinker is shown in table 2. An increase of the alkali content was obtained through the addition of  $K_2SO_4$  to the cement, the total content of  $SO_3$ in cements amounting to 3.5 %. In the cements manufactured in Poland, potassium oxide predominates over sodium oxide, hence the decision to increase the alkali content by means of adding potassium ions. In mortars, the water-to-cement ratio of 0.47 was used, and 24 25×25×285 mm bars were produced of each kind of mortar. After 24 hours of sample storage in the temperature of  $23 \pm 2^{\circ}$ C and relative humidity of  $\geq 95$  %, the bars were removed from their moulds, and a length measurement of 12 bars was taken. Next, they were placed in a climatic chamber in the temperature of  $38 \pm 2^{\circ}$ C and relative humidity exceeding 95 %. Deformation measurements were taken every 14 days. The remaining 12 bars were immersed in water and the container was placed in a water bath at the temperature of  $80 \pm 2^{\circ}$ C for 24 hours. Next, a length measurement of the bars was taken. The bars were then immersed in a normal sodium hydroxide solution in the temperature of  $80 \pm 2^{\circ}$ C and of volume equal to four times the volume of the bars. Expansion measurements were taken every two days, over 14 days, the result after 16 days being the standard end-point.

Following the completion of measurements of linear changes, tested mortar bars with surface cracks attributed to the alkali-aggregate reaction (in the accelerated tests after 16 days and in the standard methods after 30 months) were cut into test pieces and observed using a SEM equipped with a high-energy dispersive Xray analyser (EDX). Then the specimens were thinly coated with carbon. The figures below show each element identified according to the position of its peak. The observed alkali-aggregate reaction products are presented both in the form of an X-ray spectrum (semiquantitative analysis) and a micrograph. Symbols of respective tests series are shown in table 3.

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Table 1	Chemical	composition	of	oranite	and	chald	redonite
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component (%)	cement	granite	chalcedonite
SiO <sub>2</sub>	21.39	73.85	96.24
$Al_2O_3$	5.43	12.78	1.57
$Fe_2O_3$	2.41	2.53	0.56
CaO	62.71	2.45	0.75
MgO	2.10	0.21	0.12
$SO_3$	2.92	0.14	-
$Na_2O$	0.15	2.77	-
$K_2O$	1.55	1.85	-
loss on ignition	1.12	0.4	0.65

Table 2. Chemical and mineral composition of cement clinkers.

component (%)	Clinker 1	Clinker 2
SiO <sub>2</sub>	20.64	23.27
CaO	63.83	66.61
$Al_2O_3$	5.07	4.67
$Fe_2O_3$	2.62	3.45
MgO	1.88	0.91
$SO_3$	2.48	0.12
LOI	1.20	0.35
$Na_2O$	0.14	0.10
$K_2O$	1.71	0.42
$Na_2O_e$	1.26	0.38
$C_3S$	47	51.5
$C_2S$	25	27.8
$C_3A$	10.3	6.6
$C_4AF$	7.3	10.5
$C\overline{S}$	4.96	

Table 3. Symbols used in experiments.

symbols	description	mix alkali content (% (Na <sub>2</sub> O <sub>e</sub> )
M2	Cement 2	0.35
M2+	Cement 2 with K <sub>2</sub> SO <sub>4</sub> added	0.70
M2++	Cement 2 with $K_2SO_4$ added	1.10

## RESULTS

The results of linear changes in bars of mortar with granite and chalcedonite in the standard method are shown in figure 1, and in the accelerated method - in figure 2. Over the first eighteen months, the bars of mortar with granite in the standard method showed negligible elongation - of under 0.1 %, which made it possible for the aggregate to be considered not reactive. In contrast, after 21 months a considerable expansion was noted, which - after 30 months - reached the level of

approx. 0.6 %. At the same time, cracks, typical of alkali-silica reactions, appeared on the bar surface. Expansion of mortar with granite, obtained in the accelerated method after 16 days resembles the expansion level obtained after 24 months in the standard method.

The typical formation of ASR gel was observed in polished sections of samples cut from mortar bars exhibiting the pattern normally attributed to the alkalisilica gel reaction.

Mortar observations after 30 months of standard method testing showed also the occurrence of crystalline ettringite which filled the cracks on the interface between aggregate and cement paste as well as air voids (figure 3). Between the ettringite crystals, there appeared microcracks spreading inside the paste. An EDX microanalysis of the crack-filing material showed that apart from aluminium, sulphur and calcium, there is also silica as well as sodium and potassium, which may mean that there are also sodium potassium calcium silicates.

The mortar with granite after 16 days immediately of testing in the accelerated alkali-aggregate reaction (in 1 N NaOH solution at 80°C) showed a slightly different



Figure 1. Expansion of mortars with Cement 1, granite or chalcedonite aggregate, stored in the chamber of relative humidity exceeding 95 %, at 38°C (Method I), after 30 months.



Figure 2. Expansion of mortars with Cement 1, granite or chalcedonite aggregate, stored in 1 N NaOH at 80°C (Method II).

picture. On the interface between the aggregate and the paste there appear microcracks, filled with alkaline and calcium silicates as well as aluminates. No ettringite was found (figure 4).

Chalcedonite mortar bars after 16 days of the test in an NaOH solution showed less swelling as the formed sodium silicate gel filled pores which are very numerous in the aggregate and thus did not cause swelling. Scanning microscope observation of chalcedonite mortar microsections showed that individual chalcedonite grains had undergone an alkali-silicate reaction, which is suggested by the occurrence of reaction products and visible cracks across grain and-in many cases - across cement paste (figure 5).



Figure 3. a) Micrograph showing formation of alkali-silica reaction products after testing with Method I in the mortar with Cement 1 and granite, after 30 months (SEM, 3500×); b) EDX spectrum in the ettringite area, at location A; c) EDX spectrum in the area of alkali-silicate gel, at location B.

Microstructure of alkali-silica reaction products in conventional standard and accelerated testing



Figure 4. a) Micrograph showing formation of alkali-silica reaction products after testing with Method II in the mortar with Cement 1 and granite, after 16 days (SEM, 200×); b) Magnified area (SEM, 3500×); c) EDX spectrum showing alkali-silica gel, semi-quantitative analysis at location A in (b).

Figure 5. a) Micrograph showing formation of alkali-silica gel after testing with Method II in the mortar with Cement 1 and chalcedonite, after 16 days (SEM,  $500\times$ ); b) Magnified area (SEM,  $5000\times$ ); c) EDX spectrum showing alkali-silica gel, semi-quantitative analysis at location A in (b).

On all bars of mortar with silica sand and opal, after 16 days of testing in 1 N NaOH solution in the temperature of 80°C there appeared cracks which suggested the occurrence of the alkali-silica reaction and bar elongation after 4 days only exceeded 0.1 %, which in this method is considered a dividing line separating nonreactive from reactive aggregates [9]. Figure 6 shows mean results of linear changes in mortar bars. In the experiment conducted, in the accelerated test of alkaline reactivity of the aggregate, the alkali content in cement noticeably affected the course of the alkali-silica reaction. The higher the alkali content in cement, the higher the expansion. Figures 7 and 8 show microstructure of alkali-silica reaction products, formed in mortars tested by means of the accelerated method. Products of the alkali silica reaction appear in the form of cracked gel with composition indicating presence of Na-rich calcium silicates. The gel-like deposits are found within reacted aggregate and also in the air-voids.



Figure 6. Expansion of mortars with Cement 2 of varying the alkali content, silica sand containing 4 % of opal, stored in 1 N NaOH at 80°C (Method II).

#### DISCUSSION

The structure of samples was tested in order to understand the reaction and expansion mechanisms. Numerous micro-cracks and voids present on the surface were filled with products of the alkali-aggregate reaction. In mortar with granite aggregate tested by means of the standard method after a period of 30 months also coarse-crystallised secondary ettringite appeared in the cracks along with alkali-silica gel (figure 3).

Pettifer and Nixon [10] described the occurrence of large amounts of ettringite in concrete - the evidence of the alkali-silica reaction - in a sulphate environment. The Portlandite solution in the pore water frees hydroxyl ions that can generate or intensify the alkali-silica reaction. The phenomenon was not observed in the examined mortar, because there were no external sulphates either from the surroundings or the aggregate. This suggests that ettringite crystallisation is regulated by other factors. The co-existence of secondary ettringite and ASR gel indicates that the alkali-silica reaction reached the advanced phase. Some crystals of secondary ettringite were noticed also when there was no access of external sulphate ions during the alkali-silica reaction, as described by Salomon et al. [11], and Reqourd et al. [12]. It is generally assumed that in case of lack of the sulphate ions the primary ettringite reacts and produce monosulphoaluminate. Carbonation of monosulphoaluminate leads to the formation secondary ettringite. The quantitative X-ray analysis and the thermal analysis (DTA) [13] both confirm that there is no difference in the amount of ettringite in the samples before and after the test. The formation of coarse-crystallised secondary ettringite is probably facilitated by the increased permeability resulting from numerous micro-cracks, so indirectly by the alkali-silica reaction. The formation of ettringite in the micro-cracks of samples subjected to the standard expansion tests was also due to an increase in humidity and temperature (38°C). The coexistence of ettringite and ASR gel was proved using the EDX analysis.

Basically, the occurrence of ettringite in cracks and voids is interpreted as a result of the displacement of pore solution (containing sulphates ions) in the direction of the hydrated alkali-silica gel. The ettringite nucleation takes place in the gel phase region that ensures a favourable growth environment [16]. The expansion is usually attributed to the colloidal ettringite effect [15]. Pettifer and Nixon [10] are of the opinion that coarse-crystallised ettringite always occurs in the case of large expansion. Jones and Poole [16] suggest that the pressure generated by the growth of ettringite crystals can have a considerable effect on the expansion. Hence, the secondary ettringite formation in the voids and micro-cracks filled with gel can cause the destruction of concrete structure.

Figures 4 and 5 show scanning electron micrographs of reaction products observed within the mortar specimens subjected to the accelerated tests. They vary from massive and spongy gel. The composition of these phases was rather similar. As indicated in figure 4, all were Na-rich calcium silicates.

In these areas, an EDX microanalysis showed the presence of alkali-calcium silicates, and inside the cracks - of some aluminates (figure 5). At higher concentration of Na<sup>+</sup>, exceending 0.4 mol/l, due to high concentration of OH- there are formed Al(OH)<sup>-</sup> ions, what facilitates creation of calcium aluminates [17]. There appeared differences in the reaction product composition within the aggregate grain, and considerably greater differences among various grains. This could have been caused by the transfer of the active alkali gel into the solution as well as the short time of the reaction's course.

Microstructure of alkali-silica reaction products in conventional standard and accelerated testing



Figure 7. a) View of the microstructure alkali-silica gel filling air bubble in the mortar (M2++) with Cement 2 containing  $Na_2O_e = 1.1\%$ , after 16 days (SEM, 500×); b) Magnified area (SEM, 7500×); c) EDX spectrum of gel, semi-quantitative analysis at location A in (b).

Figure 8. a) Micrograph showing formation of alkali-silica gel in the mortar M2 (Cement 2 containing  $Na_2O_e = 0.35\%$ ), after 16 days (SEM, 500×); b) Magnified area (SEM, 7500×); c). EDX spectrum of gel at location A in (b).

Considering the large amount of Na<sup>+</sup> available in accelerated test, the morphological and composition features of the reaction products formed in the specimens containing the reactive aggregate are very similar to those found in concrete affected by ASR indicating that the reaction products and probably mechanism are the same but differ in reaction rates. This justifies the use of the accelerated test to predict the reactivity of aggregate in concrete. Davis and Oberholster [18] reported similar findings in relation to the similarity of reaction products in field concrete and specimens subjected to 1 N NaOH at 80°C.

In previous papers, it was demonstrated that in the accelerated test the alkali content in cement does not affect the observed expansion of mortar bars [4,7]. It was assumed that the alkali which take part in the reaction are derived from an NaOH solution, in which the mortar bars are immersed during the test. However, from the tests performed in this study, it follows that the alkali contained in the cement influence the linear changes in mortars with reactive aggregate placed in 1N NaOH at 80°C (see figure 6). The results demonstrate that in the testing of aggregate reactivity by means of the accelerated method the expansion may be different depending on the cement type used [19]. With the alkali content of  $Na_2O_e = 1.10$  %, the expansion of bars of reactive aggregate mortar is two to three times greater than with the content of  $Na_2O_e = 0.35$  % in the cement. These expansion differences may be significant in practice if this is an aggregate-classifying factor (for low reactive aggregate particularly) according to its reactivity and may change the decisions pertaining to the application of aggregate in the constructions. Yet in the case of the very reactive opal, used in the experiment, mortar bar expansion exceeded the limit of 0.2 %, regardless of the alkali content in the cement, which shows that we are dealing with reactive aggregate.

Figures 7 and 8 show scanning electron micrographs of reaction products observed within the mortar specimens subjected to the accelerated tests. The reaction products formed during the accelerated test both in the M2++ mortar (content of  $Na_2O_e = 1.1$  % in the cement) (see figure 7a and b) and in the M2 mortar (content of  $Na_2O_e = 0.35$  % in the cement) (figure 8a and b) are massive gel. The gel showed obvious shrinkage cracks probably as a result of the extraction of water during the preparation. With help of EDS coupled with SEM the gel was found to compose predominantly of SiO<sub>2</sub>, and also contained a considerable amount of sodium. The Na-rich material may by due to NaOH from the storage solution retained within the aggregate [20]. The content of potassium in the reaction products was greater in the M2++ mortar (figure 7c) from cement containing more potassium (see table 3) than in samples from the M2 mortar (figure 8c). The greater content of potassium in gel may be responsible for the increased expansion of mortar in the accelerated test as addition of potassium in the sodium-potassium silicate gel increases its viscosity and swelling properties [21]. The reaction is mainly confined to the external zone coexisting of a porous opal-rich layer. The opal grains often show a resolved internal structure with cracks radiating into the surrounding cement paste.

# CONCLUSION

The conducted tests enable the formulation of the following conclusions:

- expansion of granite mortar bars in the accelerated method achieved the level of expansion obtained after over two years in the standard method as soon as after 16 days;
- in the mortar tested by means of the standard method after 24 months, alongside the products of the alkalisilica reaction which fill the cracks and air voids, there also occurs secondary ettringite;
- in the mortar after the accelerated test (in 1 N NaOH and 80°C) in place of the reactive aggregate or in pores or cracks in the cement paste there appears sodium silica gel as well as calcium aluminates, no ettringite is being observed;
- the alkali content in cement considerably affects the volume of linear changes resulting from the alkali-silica reaction in the accelerated expansion test;
- the accelerated method for the estimation of aggregate reactivity is very helpful, but the note included in the Standard which states that the alkali content in cement used for the test is not significant ought to be verified and specified. The results of the conducted test and literature data [4-7] show that the alkali content (especially potassium) in cement plays an important role in the process of expansion in the accelerated method.

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# MIKROSTRUKTURA PRODUKTŮ REAKCE ALKÁLIÍ A KŘEMENE POMOCÍ STANDARDNÍHO A URYCHLENÉHO TESTOVÁNÍ

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Maltové pruty s granitovým nebo chalcedonitovým agregátem byly testovány standardním postupem založenými na skladování vzorků při  $38 \pm 2^{\circ}$ C a relativní vlhkosti  $\geq 95$  %. Maltové pruty s agregáty granitu nebo chalcedonitu a křemenným pískem obsahujícím opál byly použity pro měření expanze při zrychleném testování, založeném na skladování vzorků v 1 N roztoku NaOH při 80°C. Řádkovací elektronová mikroskopie (SEM) s energiově disperzním rtg detektorem (EDX) prokázala, že vzorky které expandovaly při standardním testu, trvajícím 30 měsíců, obsahovaly křemičitany alkalických kovů a druhotný ettringit. Vzorky které expandovaly při zrychleném šestnáctidenním testu obsahovaly pouze gel alkalického křemičitanu se stejnou morfologií a složením. Reakční produkty po obou testech se zdály stejné, takže odlišné byly jen reakční rychlosti. Výsledky provedených testů ukázaly, že obsah alkálií, zvláště draslíku, v cementu hrají významnou roli při expanzi při zrychleném testu.