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Cement and Concrete Research 34 (2004) 7–11

CEMENT AND CONCRETE RESEARCH

Alkali–aggregate reaction in concrete containing high-alkali cement and granite aggregate

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Received 6 November 2002; accepted 12 May 2003

Abstract

The paper discusses results of the research into the influence of high-alkali Portland cement on granite aggregate. The deformation of the concrete structure occurred after 18 months. The research was carried out by means of a scanning electron microscope equipped with a high-energy dispersive X-ray analyzer that allowed observation of unpolished sections of concrete bars exhibiting the cracking pattern typical of the alkali–silica reaction. Both the microscopic observation and the X-ray elemental analysis confirm the presence of alkali–silica gel and secondary ettringite in the cracks.

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Keywords: Alkali–aggregate reaction; Granite; Expansion; Ettringite formation; SEM

1. Introduction

The establishment of alkali influence on concrete durability has been, for many years, one of the most important problems to which the professional technical press all over the world and regular series of international conferences dealing with the alkali–silica reaction have devoted a lot of attention. Concrete failure is due to certain unfavorable phenomena observed during the reaction between alkali and aggregate. Yet the application of aggregate reacting with alkali and high-alkali cement is necessary.

The purpose of this paper is to assess the impact that the increased amount of alkali in cement has on the structure formation of concrete with broken granite aggregate. The research work covers such areas as linear expansion and deterioration of concrete bars caused by the alkali–silica reaction as well as the structure and phase composition of concrete.

2. Experimental procedure

The chemical compositions of cement and granite are given in Table 1. Table 2, on the other hand, shows the mineral composition of granite. Industrial cement containing 1.26% Na_2O_{eq} and broken granite were used to prepare bars ($25 \times 25 \times 250$ mm) according to the standards given in Ref. [1]. The bars were stored in a sealed container at a temperature of 38 °C and relative humidity of >85%. Their elongation was first measured after 48 h. Successive measurements were taken after 14, 28, 60, 90 days, and then every 90 days. Mortar bars with surface cracks attributed to the alkali–aggregate reaction were cut into test pieces and observed using an SEM equipped with a high-energy dispersive X-ray analyzer. Similar testing methods were applied in the research discussed in Refs. [2,3]. Then the specimens were thinly coated with gold. The X-ray semiquantitative technique enabled determination of the elemental composition of the examined material. 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 and a micrograph. A special computer program (SEM-Quant) was applied to eliminate the coincidence of peaks of gold with those of other elements denoted in the specimen, especially sulfur, in the semiquantitative analysis.

3. Results

During the period of 18 months, the bars showed little linear expansion, just below 0.1%, which allowed us to

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doi:10.1016/S0008-8846(03)00189-3

Table 1
Chemical composition (%) of the cement and granite aggregate

Component	LOI[a]	Insoluble in HCl	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Na_2O_{eq}
Cement	1.29	0.31	20.64	5.05	2.62	63.83	1.88	2.48	0.14	1.71	1.26
Granite	0.4	–	73.85	12.78	2.53	2.45	0.21	0.14	2.77	1.85	–

[a] Loss on ignition.

classify the aggregate as nonreactive. Significant expansion was observed after 21 months, and after 30 months it reached 0.6%. At the same time, cracks typical for alkali–silica reaction appeared on the surface of the bars. Fig. 1 shows a concrete bar after the development of the alkali–silica reaction. The results of linear changes are presented in Fig. 2. The bar fractures were analyzed with a scanning electron microscope, and well-crystallized ettringite (Fig. 3a and b) was found in the cracks. A lot of carbonation products were observed on the outer edges of the specimens in the white efflorescence region (Fig. 4a and b). The X-ray elemental analysis in the micro-region indicates the presence of ettringite and small amounts of silica and alkali, which proves the presence of alkali–silica gel (Fig. 5a and b).

4. Discussion

The typical formation of ASR gel was observed in unpolished sections of samples cut from mortar bars exhibiting the pattern normally attributed to the alkali–silica gel reaction. As a rule, granite makes a good aggregate. However, Sibbick and Page [4] and also Deloye [5] associate concrete failure with granite aggregate whose reactive component is cryptocrystalline or stressed quartz. The process of aggregate decay is slow and depends on the degree of structure disturbance of the siliceous phases as well as on the thermal–humidity conditions. The greatest expansion was noticed at a relative humidity of approx. 85% and room temperature [6]. The effect of temperature on the expansive behavior of concrete was studied in detail. It is generally assumed that the degree and range of the alkali–aggregate reaction, as well as the resulting expansion, increase at higher temperatures, as reflected in the standard expansion test carried out at 38 °C [1].

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. After a certain period, coarse-crystallized secondary ettringite appeared in the cracks along with alkali–silica gel (Fig. 5).

Pettifer and Nixon [7] described the occurrence of large amounts of ettringite in concrete—the evidence of the alkali–silica reaction—in a sulfate 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 concrete because there were no external sulfates either from the surroundings or the aggregate. This suggests that ettringite crystallization is regulated by other factors. The coexistence 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 sulfate ions during the alkali–silica reaction, as described by Salomon et al. [8]. It is generally assumed that in case of lack of the sulfate ions the primary ettringite reacts and produces monosulphoaluminate. Carbonation of monosulphoaluminate leads to the formation of secondary ettringite. The quantitative X-ray analysis and the thermal analysis (DTA) [9] both confirm that there is no difference in the amount of ettringite in the samples before and after the test. The formation of coarse-crystallized secondary ettringite is probably facilitated by the increased permeability resulting from numerous micro-cracks, so indirectly by the alkali–silica reaction.

The symptoms of the alkali–aggregate reaction were observed in concrete constructions after 15 or 30 years [10]. The early stages of the reaction development were identified by means of the microscopy technique, which involved observing small amounts of gel with high content of alkali. The surface of younger concrete samples was covered with transparent hygroscopic gel, while on older (i.e. 20-year-old) samples the gel was usually white non-hygroscopic and carbonated with creamy consistency. In the case of 25-year-old or older concrete samples, the gel was often accompanied, to a smaller or larger extent, by ettringite needles. The formation of ettringite in the micro-cracks

Table 2
Mineral composition (%) of the granite

Component	Quartz	Potassium feldspar	Plagioclase	Biotite	Chlorite	Ferric oxide and others
Contents	38.0	15.4	39.7	5.8	0.6	0.4

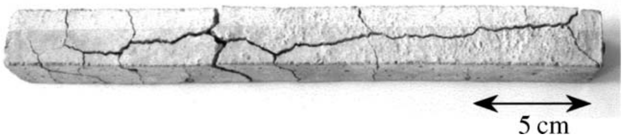

Fig. 1. Concrete bar after alkali–aggregate reaction.

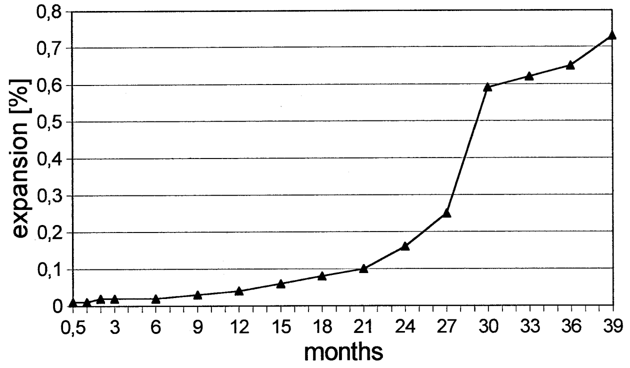

Fig. 2. Linear expansion of concrete bars stored in sealed container at 38 °C and >85% humidity.

of samples subjected to the accelerated expansion tests was connected with an increase in humidity and temperature. Continuous concrete expansion—an effect of the alkali–aggregate reaction—may also be a consequence of the ettringite growth in a warm and damp environment. Kawamura et al. [11] describes the testing of mortars prepared from cement with different C_3A contents immersed in NaCl solution. Ettringite crystals appear inside cracks that result from the ASR expansion (after 14 to 56 days). The coexistence of ettringite and ASR gel was proved using the EDX analysis. The amount of secondary ettringite was not determined, so it is not clear whether its formation has any effect on the expansion of mortars with reactive aggregate immersed in NaCl solution. Basically, the occurrence of ettringite in cracks and voids is interpreted as a result of the displacement of pore solution (containing sulfates ions)

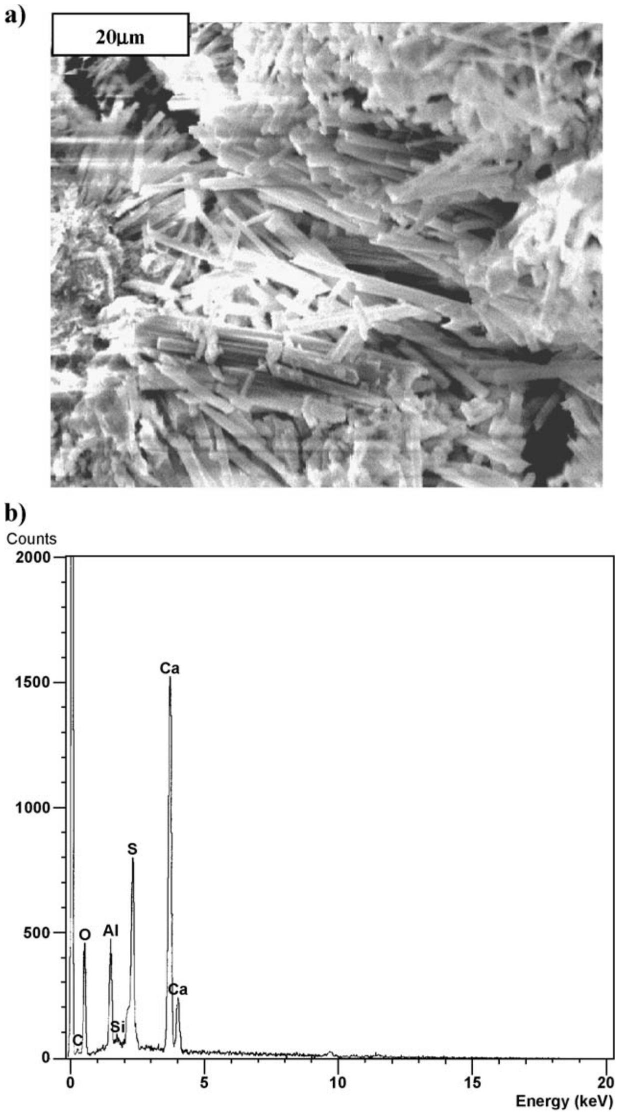

Fig. 3. (a) SEM photograph of microcrystal of the ettringite filling the crack. (b) The X-ray elemental analysis of ettringite.

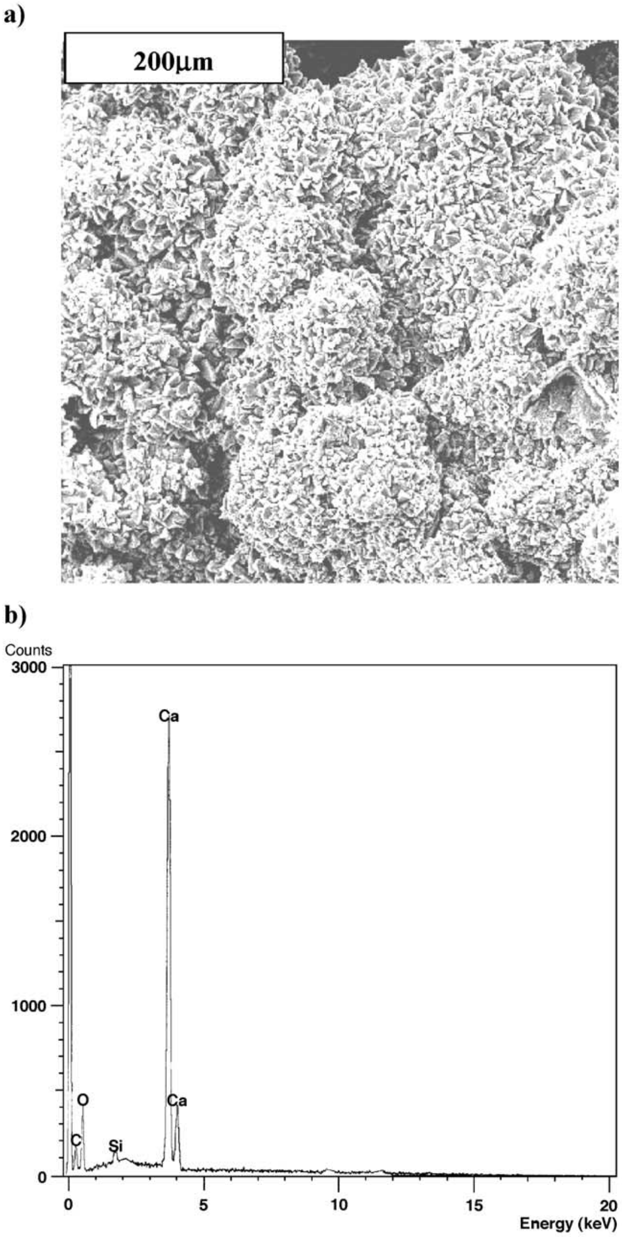

Fig. 4. (a) SEM phptograph of micro-region rich in carbonation products. (b) The X-ray elemental analysis of calcium carbonate.

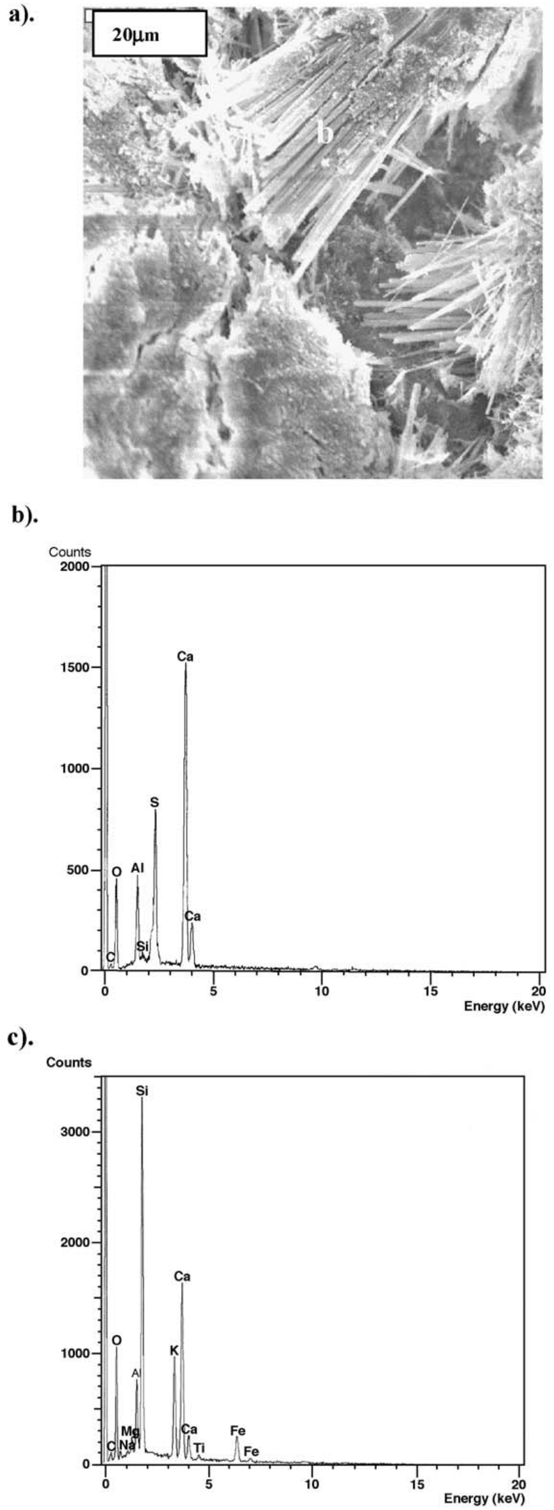

Fig. 5. (a) SEM photograph of the alkali–silica gel next to ettringite filling the crack. (b) The X-ray elemental analysis showing ettringite. (c) The X-ray elemental analysis showing alkali–silica gel.

in the direction of the hydrated alkali–silica gel. The ettringite nucleation takes place in the gel phase region that ensures a favorable growth environment. The expansion is usually attributed to the colloidal ettringite effect [12]. According to Pettifer and Nixon [7], coarse-crystallized ettringite always occurs in the case of large expansion. Jones and Poole [6] suggest that the pressure generated by the growth of ettringite crystals can have a considerable effect on the expansion. Hence, secondary ettringite formation in the voids and micro-cracks filled with gel can give rise to the destruction of concrete structure.

5. Conclusions

- The alkali–aggregate reaction causes deterioration of structures containing granite aggregate. However, it is not certain whether the products identified in the concrete specimens and which are associated with alkali–aggregate reaction are the ones that caused the initial expansion.
- The mortar bars containing granite aggregate and 1.26% Na_2O_{eq} cement stored in sealed containers at a temperature of 38 °C and >85% relative humidity displayed a linear expansion of 0.1% after 21 months. Further deformation (reaching 0.6% after 30 months) was connected with the deterioration of the concrete structure.
- The concrete structure was examined using a scanning electron microscope equipped with the X-ray elemental analysis in the micro-region. The observations of the bars proved the presence of alkali–silica gel and coarse-crystallized ettringite in the micro-cracks as well as clusters of carbonation products in the superficial layer.

References

[1] PN-91/B-06714/34, Mineral aggregates, Testing, Deformation of alkali reactivity, 1991, in Poland.

[2] S.L. Marusin, Sample treatment to distinguish alkali–silica gel from delayed ettringite formations in concrete, Mag. Concr. Res. 46 (168) (1994) 163–166.

[3] O.R. Batic, C.A. Milanesi, P.J. Maiza, S.A. Marfil, Secondary ettringite formation in concrete subjected to different curing conditions, Cem. Concr. Res. 30 (2000) 1407–1412.

[4] R.G. Sibbick, C.L. Page, Susceptibility of various UK aggregates to alkali–aggregate reaction, Proc. 9th Int. Conf. AAR Concr., London, 1992, pp. 980–987.

[5] F.X. Deloye, Bull. Liais. Lab. Points Chaussee 164 (1989) 41.

[6] T.N. Jones, A.B. Poole, Alkali–silica reaction in several UK concerts: The effect of temperature and humidity on expansion and the significance of ettringite development, Proc. 7th Int. Conf. AAR Concr., Ottawa, 1986, pp. 446–450.

[7] K. Pettifer, P.J. Nixon, Alkali metal sulphate—A factor common to both alkali–aggregate reaction and sulphate attack on concrete, Cem. Concr. Res. 10 (2) (1980) 173–181.

[8] M. Salomon, J. Caude, L. Hasni, Diagnosis of concrete structures affected by alkali–aggregate reaction, Proc. 9th Int. Conf. AAR Concr., London, 1992, pp. 902–932.

[9] I. Odler, S. Abdul-Maula, Possibilities of quantitative determination of

the Aft-ettringite and Afm-monosulfate phases in hydrated cement pastes, Cem. Concr. Res. 14 (1) (1984) 133–141.

[10] W.J. French, A review of some reactive aggregates from the United Kingdom with reference to the mechanism of reaction and deterioration, Proc. 7th Int. Conf. AAR Concr., Ottawa, 1986, pp. 226–230.

[11] M. Kawamura, N. Arano, K. Katafuta, ASR gel composition, secondary ettringite formation and expansion of mortars immersed in NaCl solution, Proc. 11th Int. Conf. AAR Concr., 2000, pp. 199–208.

[12] P.K. Mehta, Mechanism of sulfate attack on Portland cement concrete—another look, Cem. Concr. Res. 13 (3) (1983) 401–406.