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Laboratory short-term evaluation of ASR
A contribution

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Abstract

Accelerated tests were performed at 80°C to evaluate alkali–silica reactions (ASRs) in mortars made with alkali-enriched cement. Sodium salts (NaCl, Na_2SO_4, and $NaHCO_3$) and sodium hydroxide were used in the mortars, and the microstructural alterations induced in the mortars by the alkaline compounds were investigated as their effect on mechanical properties. Data so far collected indicate that, at this temperature, the expansion of mortars without reactive aggregate is limited and, at least at the investigated alkali concentration, negligible compared to the expansion of mortars containing artificial reactive aggregates. Results show, however, that the extent of expansion can be influenced by the type of salt used to increase the alkali concentration. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Alkali–silica reactions; Accelerated tests; Durability; Microstructure

1. Introduction

Despite the large number of articles dealing with alkali–silica reactions (ASRs), the information concerning the mechanism of reaction and the factors affecting it are still scanty. Recently [1], some doubt has been expressed even about the methodologies applied to ASR simulations carried out in many laboratories. Indeed the absence of a common, well-established standardization of tests reflects these uncertainties. Almost all the test methods are based on measuring the expansion of the mortars or concrete specimens affected by the ASR. Experimental procedures usually vary in two parameters: (i) amount and origin of alkali present in the materials and (ii) the curing conditions. As concerns the first point, either a set of different cements containing high amount of alkali [2,3], a procedure also suggested by ASTM C 227, is used to obtain a required alkali concentration, or using the same cement, alkali concentration is increased by adding salts or hydroxides [4–6]. In the first case only low values of alkali concentrations can be obtained and different cement compositions will unavoidably lead to slightly different hydration products or reaction. In the second case, the addition of alkaline compounds can alter the hydration reaction of the cement. It is important to establish whether this alteration can induce different dimensional changes in the investigated samples, i.e. give rise to expansion reactions that would superimpose on the ASR. As to the second point, the need for short-term results leads to the increase of the experimental temperature: environmental conditions of 38°C, 80°C [7], 110°C, 127°C [8], and 150°C [9] have been proposed.

The aim of the present paper is to try to establish how reliable accelerated ASR tests can be when using alkali-enriched cements. We examined the effect of four sodium compounds: hydroxide and chloride, which have already been used, and also bicarbonate and sulfate. The addition will unavoidably lead to different hydration reactions or possibly side-reactions and also to different mechanical properties and microstructures (the decrease of compressive strength when using NaOH has already been underlined [10]).

2. Experimental

2.1. Aggregates

(i) Siliceous sand according to the Italian Standard (UNI-EN 196/1) as nonreactive aggregate, and (ii) Pyrex cullets,

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according to ASTM C441 as reactive aggregates with a grading conforming to the given Italian Standard.

2.2. Cement

Portland Cement (Type I) 52.5, with an oxide composition as reported in Table 1:

2.3. Alkali content

NaOH, Na_2SO_4, NaCl, and $NaHCO_3$ were used to increase to a weight content of 2.4% expressed as Na_2O. They were added directly to the mixing deionized water. Hereafter, mortars containing sodium hydroxide will be referred to as Hydroxide; the same labeling will be used for the other salts. Mortars mixed without any salt additions, i.e. just containing the alkalis deriving from the cement, will be referred to as Water.

2.4. Mortars

They were mixed with a binder/aggregate ratio of 3 at a water/cement ratio of 0.5. Two sets of mortars were thus obtained, differing only in the type of aggregate used: the one mixed with the standard, nonreacting sand will be taken as a reference as concerns dimensional stability, microstructure, and mechanical properties in the absence of ASR. Samples containing nonreactive sand will be labeled as UR, while those containing reactive aggregate will be labeled as RE. Mixing procedures followed closely the Italian Standard (UNI-EN 196/1). Mortars showed different workabilities and setting times on account of the different salts present: in particular, bicarbonate and hydroxide accelerated the cement set.

2.5. Curing procedures

Prisms 4 × 4 × 16 cm were cast and cured for 24 h at 25°C and 100% RH in PVC closed boxes. They were subsequently stored in sealed steel containers at 80°C and 100% RH. This temperature was chosen to shorten all tests but also to decompose ettringite formed during the first curing period and impede its further formation [11]. Some of the samples were periodically cooled to room temperature and their length measured till 60 days after casting: the cooling process lasted for 80 min.

2.6. Experimental procedures

Mortars porosity was evaluated by mercury intrusion by means of an Erba 2000 porosimeter. SEM (Philips 501) and EDAX analysis were carried out to evaluate differences in microstructures and compositions of the mortars.

Table 1
Cement composition oxide wt.%

SiO_2	Al_2O_3	CaO	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	LOI
20.31	3.75	62.17	2.40	3.26	0.27	0.38	3.75	4.4

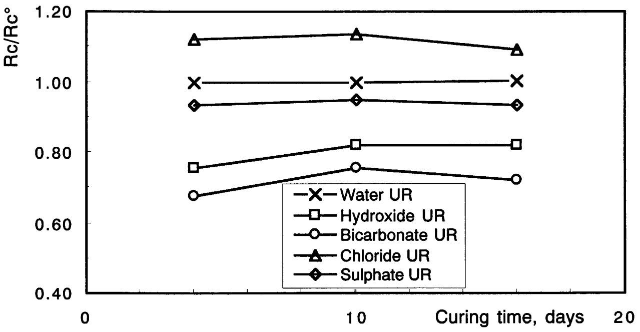

Fig. 1. Ratio of compressive strength (Rc/Rc°) of sodium-enriched mortars containing unreactive aggregate, compared to the plain one, as a function of curing time.

3. Results and discussion

Fig. 1 shows the ratio of compressive strength of modified mortars, containing the unreactive aggregate and the various chemicals, and the compressive strength of the plain mortars, as a function of curing time till 16 days: Rc is the compressive strength of the modified mortars, while Rc° is the compressive strength of the reference. Sodium hydroxide and sodium bicarbonate decrease the compressive strength while sodium chloride, accelerating cement hydration, provides higher mechanical properties. Sulfate slightly decreases compressive strength. The ratio does not change as curing proceeds.

Figs. 2 and 3 show porosity data at different curing times (4 and 10 days) for mortars containing unreactive aggregates.

The addition of bicarbonate leads to higher porosity, particularly at short curing time, while sodium chloride, acting as an accelerating additive, leads to more compact structures, even at short curing times: these results are consistent with mechanical data. The distribution and

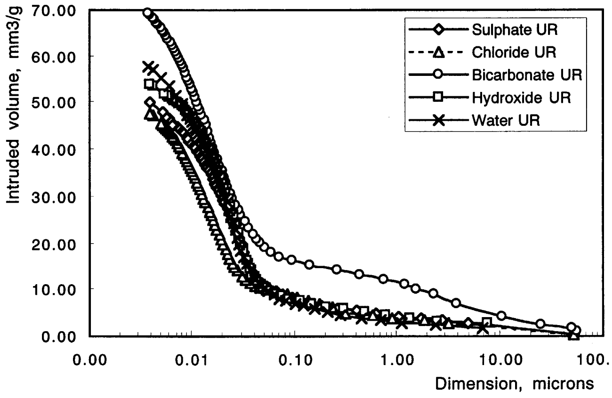

Fig. 2. Porosity measurements at 4 days of curing for different mortars containing unreactive aggregate.

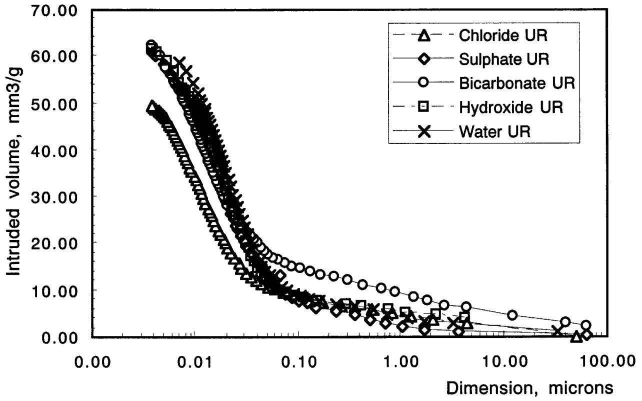

Fig. 3. Porosity measurements at 10 days of curing for different mortars containing unreactive aggregate.

amount of pores are, however, similar for the standard mortar and those containing hydroxide and sulfate.

Fig. 4 shows the dimensional changes as a function of time, for the same mortars. During the first days of curing all samples undergo a slight expansion and afterwards a reduction in their length approaching a constant value, which is indeed very similar for all the investigated salts. Mortars kept at 80°C and measured only after 60 days showed comparable values of expansion.

Fig. 5 reports the expansion till 60 days of curing of mortars containing the reactive aggregates. The reference mortars (Water) undergo a very slight expansion, while those alkali-enriched quickly expand during the first 10 days of curing period, reaching an almost steady value afterwards. Conventional SEM observation on mortars fracture surfaces allowed to verify the presence of ASR products, which are shown in Fig. 6 on the upper right corner. EDAX analysis of the ASR products (Fig. 7a) and of the cementitious matrix (Fig. 7b) after this curing period are reported: the extremely low intensity of the sodium peak in the cement paste allow to conclude that the expansion can possibly be stopped by the alkali depletion in the cement paste. It should be underlined that after 3 days, i.e. during the first measurement, mortars have already undergone about 80–90% of the total expansion. The chloride salt induces the highest expansion, indeed almost double than that obtained for the bicarbonate: hydroxide and sulfate have a rather similar, intermediate effect.

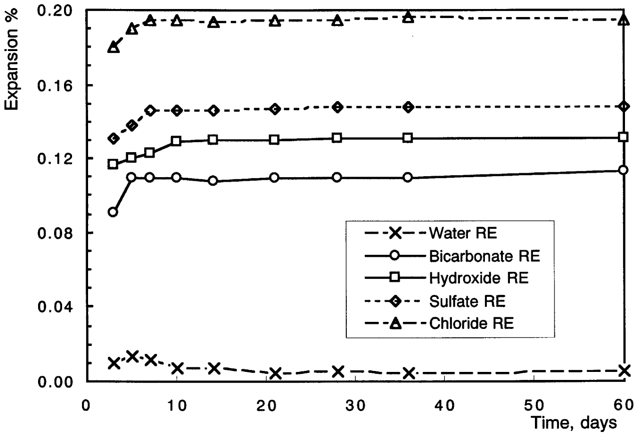

Fig. 5. Dimensional changes as function of time for mortars containing reactive aggregates.

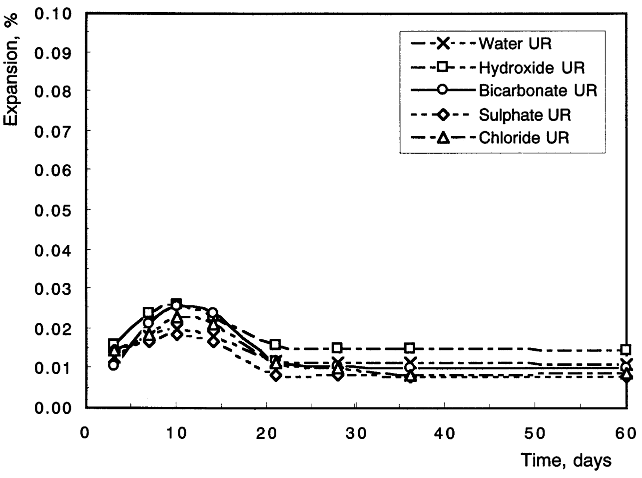

Fig. 4. Dimensional changes as function of time for mortars containing unreactive aggregates.

Fig. 6. ASR products in a sodium chloride modified mortars (16 days of curing).

ASRs proceed quickly under the experimental test conditions used: the expansion of mortars containing the reactive aggregate is remarkably higher than that of those containing the nonreactive aggregate (Fig. 4 vs. Fig. 5). These observations should allow us to conclude that tests carried out under these experimental conditions provide reliable results: it should, however, be underlined that different salts produce a rather different extent of expansion in mortars containing the reactive aggregate. Particularly, sodium chloride, and to a smaller extent, also sodium sulfate, induces the highest levels of expan-

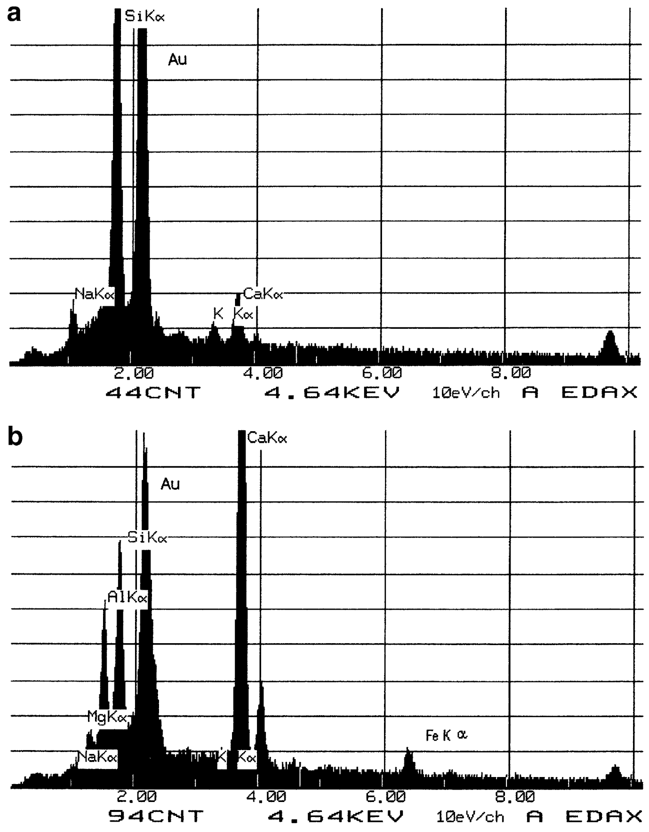

Fig. 7. EDAX spectra of (a) ASR products and (b) of cement paste in Fig. 6 (gold metallization).

sion. As to what concerns the sulfate evidence has been found by other authors [12] that a synergistic effect of delayed ettringite formation in microcracks produced by ASR can enhance the expansion of mortars affected by ASR: observation were made at longer curing times. In the present experimental conditions, ettringite can form only during the cooling process, which lasts for a definite and short period of time. Mortars containing the nonreactive aggregate (Fig. 4), as already noticed, are not affected by this mechanism. The deleterious effect of chloride ions on ASR has already been reported in the literature [12–14]. It is known that the reaction of chloride ions with C_3A can lead to the formation of the Friedel's salt and to the contemporary release of oxidryl ions. In our conditions, this reaction can, again, take place only during the cooling process. Moreover, the reduced porosity of these mortars enhances the tendency to expansion and it should also be underlined that increased mechanical properties do not lead, in this case, to an increased resistance to ASR. The effect is opposite in bicarbonate-modified mortars where increased porosity, which can partially accommodate ASR products, leads to lower values of expansion despite the low mechanical properties of the composites.

4. Conclusions

- At 80°C the reaction of alkali-enriched cement pastes with the artificial reacting aggregate is fast enough to provide information after a few days, at least at the concentration investigated here.
- The degree of expansion is, however, dependent on the type of sodium compound used to artificially increase the amount of alkali.
- Microstructral features (i.e. porosity) must be taken into account when evaluating the effect of ASR. High mechanical strengths do not seem to provide higher resistance to the deleterious expansion effects.

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