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Communication

Effect of drying—rewetting on the alkali concentration of the concrete pore solution

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Abstract

Experience has shown that the pore solution alkalinity of resaturated concrete was lower than expected. Laboratory-concrete specimens were made with reactive aggregates, stored over water at 38 $^{\circ}$ C, and then broken into two pieces. The pore solution of half-specimens was extracted by high-pressure squeezing. The other half-specimens were dried at ambient air and rewetted in humid air to their initial weight. The pore solution was then extracted and compared with the composition results of the first extraction. The results obtained from this investigation confirmed that a certain part of the alkali ions in pore solution that had become fixed by drying are not subsequently extracted after rewetting. The alkali concentration [Na+K] was reduced from 34% to 61% by the drying and rewetting treatments. © 2003 Elsevier Science Ltd. All rights reserved.

Keywords: Drying; Alkalis; Pore solution; Concrete; Extraction

1. Introduction

A suitable method for determining the chemical composition of the concrete pore solution is to directly extract the pore fluid by squeezing a sample in a high-pressure confinement [1,2]. This method has often been used on cement pastes, mortars, and concretes [1-8]. The method usually yields good results but only little amount of liquid can be expressed from aged concrete specimens or partially dry cores, so not enough solution may be recovered for analysis. A procedure for solving this problem consists in bringing the water content back up by rewetting the concrete until mass equilibrium [9]. However, this procedure could lead to erroneous results. Stark et al. [10] wrote that during the drying of concrete in the field, a certain portion of the alkalis dissolved in the concrete pore solution is fixed, thus, making them unavailable for further alkalisilica reaction (ASR) even after resaturating the concrete. On the other hand, other studies indicated that a water

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uptake after partial drying of reactive concrete, in which ASR had stopped, restarts the reaction and the concrete expansion rate becomes similar to specimens kept in humid conditions [11,12].

Other laboratory results showed that partial drying of concrete reduces, rather than increases, the concentration of alkali in the pore solution [13,14]. The authors reported that the alkali fixation would be enhanced by or somehow associated with concrete carbonation. The study suggests, however, that a portion of the fixed alkalis returns to solution after water reequilibration over a long period.

The present work aims at clarifying this issue and tries to bring about valuable hypotheses.

2. Experimental

2.1. Materials

An alkali-reactive concrete batch was prepared incorporating Spratt limestone as coarse reactive aggregate. This rock is a sublithographic, fine-grained limestone extracted from a quarry in the Ottawa area (Ontario, Canada). The water-to-cement ratio of the mixture was 0.55, and the

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Table 1
Pore solution composition before and after the specimen drying

Specimen	Age (week)	Drying period (week)	Rewetting period (week)	Weight change (%)	Composition (mmol/l)			
						Na	K	Na+K
A	4	20	13	4.7	before ^a	187	185	373
					after ^b	102	121	223
					variation, %	-46	-35	-40
В	4	20	13	4.5	before	220	198	418
					after	111	166	277
					variation, %	-50	-16	-34
С	24	20	12	3.2	before	148	125	273
					after	84	88	173
					variation, %	-43	-30	-37
D	24	40	14	3.4	before	148	128	276
					after	87	91	178
					variation, %	-41	-30	-36
E	52	4	10	2.3	before	157	140	297
					after	56	60	116
					variation, %	-64	- 57	-61

^a Means before drying/rewetting period, i.e., the concentration at the age of the specimen.

cement content was 320 kg/m 3 with a normal ASTM Type I high-alkali cement. The alkali content was raised to 1.25% Na $_2$ O $_e$ of the cement mass by adding NaOH pellets to the mixing water. No chemical or mineral admixtures were used [15].

Five concrete prisms $(75 \times 75 \times 300 \text{ mm})$ in size) were cast. The prisms were demolded after 24 h and stored over water in hermetic 25-L plastic pails lined with a damp terry cloth. The pails were kept at 38 °C in a heated room. These conditions correspond to the Canadian CSA A23.2-14A standard (accelerated expansion test for alkali–aggregate reaction in concrete).

2.2. Pore solution extraction

Concrete specimens collected at 4, 24, and 52 weeks were broken into two pieces. The pore solution of one-half of the broken specimens was extracted at 21°C by high-pressure squeezing method. Sodium and potassium concentrations were determined by atomic absorption spectroscopy (Table 1). The second half-specimens were placed at ambient air (21 °C) for drying. The drying periods varied from 4 to 40 weeks. Once the drying period was completed, specimens were placed over water in hermetic pails at 21 °C until they reached their initial weight. The ASR rate is considerably reduced during the drying and rewetting periods at 21 °C.

3. Results and discussion

Table 1 provides the chemical analyses of the pore solution of all tested specimens. A clear decrease in alkali concentration has been measured for specimens subjected to air drying, confirming what was observed by Constantiner and Diamond [14]. The alkali concentration [Na+K] dropped from 34%

(specimen B) to 61% (specimen E). However, the drop in sodium concentration was always higher than the potassium one, which is the opposite of what Constantiner and Diamond found [14]. No significant differences were observed regarding the effect of ageing. Indeed, the alkalinity fall of specimen C (24 weeks, drying period of 20 weeks) was 37% while the falls were 40% and 34% for specimens A and B (4 weeks, same drying period). Long drying periods (20 and 40 weeks) gave about the same proportion of fixed alkalis (specimens A, B, C vs. D). However, a shorter drying period (4 weeks) yielded a higher decrease in alkalinity, which we fail to explain for the time being.

If we consider a normal concrete specimen that is subjected to drying, the alkali concentration of the pore solution increases with the loss of water. As drying proceeds, some alkalis seem to be irreversibly fixed to the surrounding solid phases. When the concrete specimen is rewetted in humid air until mass equilibrium, the portion of alkalis that have precipitated goes back into solution because they remain soluble. Nevertheless, the other portion (absorbed alkalis) would remain fixed on solid surfaces and cannot be extracted under high pressure.

Another phenomenon might be put forward to explain a part of the alkalinity fall after one cycle of drying/rewetting. During drying, larger pores dry faster than smaller pores do. Thus, some air voids develop in larger pores as the water is slowly driven away and pore solution retreats to the interstices of capillary spaces. These voids induce the formation of thin meniscuses at the contact of pore and solid particles, such as aggregates or CSH. These meniscuses may concentrate and entrap alkali ions. When rewetting concrete in humid air, larger pores may be more difficult to fill than small ones because capillary condensation does not take place in them until nearly 100% relative humidity (RH) is attained, whereas smaller pores will undergo capillary condensation at lower RH. Moreover, porosity is probably

^b Means after drying/rewetting period.

saturated faster near the sample surface rather than deeper. The water distribution in porosity is not the same after rewetting by water absorption in humid air, although samples regain their initial weights. The high-pressure extraction method would not be suitable for "removing" the entrapped alkalis.

It must be pointed out that only a small portion of the concrete-free water is extracted during the process, i.e., less than 28% [15]. This could have an impact on the results obtained from our study.

4. Conclusions

Drying and rewetting dry concrete samples before extraction under higher pressure of the pore solution reduce pore solution alkalinity. The alkali content of concrete specimens that have been dried and rewetted was reduced from 34% to 61% compared to specimens kept continuously humid. These results tend to indicate that a significant amount of alkalis is fixed on solid surfaces or entrapped in meniscus of pores during drying and cannot be recovered by extraction in a short period after rewetting. Constantiner and Diamond [14] reported that the fixation would not be fully permanent, but reversible only very slowly and incompletely.

According to the results found here, rewetting dry concrete before pore solution extraction may lead to erroneous conclusions. Indeed, if drying occurred after the concrete was cored from an existing structure, the fixed alkalis that were previously active (i.e., available for ASR in the original undried concrete) will not be analyzed. Thus, it is clearly recommended to wrap concrete cores to be analyzed as soon as they are extracted from concrete elements under investigation.

Further work should be conducted using the hot-water extraction method for determining the alkali content of dried/rewetted concrete.

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