

**THE EFFECT OF DIFFERENT OUTDOOR EXPOSURE CONDITIONS
ON THE EXPANSION DUE TO ALKALI SILICA-REACTION**

G Davies and R E Oberholster

Building Materials Technology Programme
Division of Building Technology
CSIR, P O Box 395, Pretoria, South Africa.

1. INTRODUCTION

Three 300-mm concrete cubes made with a highly alkali-reactive aggregate and a high-alkali cement were exposed under the following conditions:

- 1) normal atmospheric conditions in Pretoria, South Africa
- 2) in a fine-mist spray enclosure for 24 hours on Monday, Wednesday and Friday of each week using tap water spray. The other four days the cubes were exposed as in (1) above.
- 3) in a fine-mist spray enclosure for 24 hours on Monday, Wednesday and Friday of each week using a 3 % NaCl solution (Facility for accelerated marine climate exposure testing (FAMCET)). The other four days the cubes were exposed as in (1) above.

2. MATERIALS AND METHODS

The physical and chemical properties of the cement and aggregates used in the study are presented in Table 1. The alkali content of the cement was raised to 1.10 % Na₂O equivalent by the addition of Na(OH) and K(OH) to the mix water, in the same ratio as the total alkalis. Details of the concrete from which the cubes were made are presented in Table 2.

The cubes have an edge length of 300 mm. A 19-mm, graded run-of-quarry Malmesbury metasediment coarse aggregate was used. A non-reactive coarse quartz sand was used as fine aggregate. The mix ratio was 1: 2: 3.29: 0.48 (cement: sand: aggregate: water). The slump of the mix was 30 mm and compaction was by poker vibrator. Two sets of extensometer targets at 200-mm centres were fixed to each of the five exposed faces of the cubes. The expansion of the cubes was monitored at approximately 3-monthly intervals.

Exactly 2493 days after the casting of the specimens, a 50-mm diameter core, 150 mm in length, was removed from the centre of one face of each of the three cubes. Each core was divided into five specimens 30-mm in length, which were halved, with one half used for the determination of the carbon, and total and water-soluble alkali and chloride contents, while the other half was used for the X-ray diffraction analysis and the SEM investigation. The methods used are presented in the Appendix.

3. RESULTS

3.1 Expansion

A plot of expansion versus time for the three cubes is presented in Figure 1. From this it can be seen that during the induction phase of the reaction the three cubes behaved very similarly and all reached the 0.05 % expansion point after approximately 500 days. After 500 days the cube subjected to the NaCl solution spray started expanding at a much faster rate than the other two samples and, to date, has expanded approximately 70 % more than the

TABLE 1 : Chemical and physical properties of the materials used in the concrete cubes

Property	Cement	Aggregate
SiO ₂	20.2	61.2
Al ₂ O ₃	5.66	18.1
TiO ₂	0.23	nd
Fe ₂ O ₃	3.77	7.75
MgO	1.40	3.53
CaO	63.20	0.86
SO ₃	2.60	nd
Na ₂ O	0.16	1.84
K ₂ O	0.98	5.03
P ₂ O ₅	0.16	nd
Mn ₂ O ₃	0.20	nd
LOI	1.38	2.20
Total	98.81	100.51
Na ₂ O equiv.		
Total	0.82	—
Active	0.80	—
Water Soluble	0.66	—
Relative Density	3.15	—
Specific surface, cm ² /g	3280	—

Table 2 : Details of the concrete

Cement Na ₂ O eq., %			Concrete			
Total	Active	Water Soluble	Cement content kg/m ³	Na ₂ O eq., kg/m ³		
				Total	Active	Water Soluble
1.10	1.08	0.94	350	3.85	3.78	3.29

*The alkali content of the cement was increased by the addition of alkali hydroxide in the ratio of the total K₂O to the Na₂O originally in the cement

other two cubes (0.827 %). The cubes exposed to tap water spray and to the normal ambient conditions expanded almost identically, and to date have expanded 0.499 and 0.487 %. The shape of the expansion curve is very similar to that obtained for the ASTM C227 tests, with a long induction phase, followed by rapid expansion, followed by a plateau. Although it is too early to be certain, the cubes appear to have reached the plateau phase in the expansion cycle.

3.2 XRD Analysis

The cement paste was concentrated by the gentle crushing and sieving of the mortar of the concrete specimens. Each concentrated sample was then ground to pass a 0.053 mm sieve and analysed by XRD. The phases found are presented in Table 3.

The XRD data cannot be used to evaluate the depth of carbonation because of the presence of calcite in the

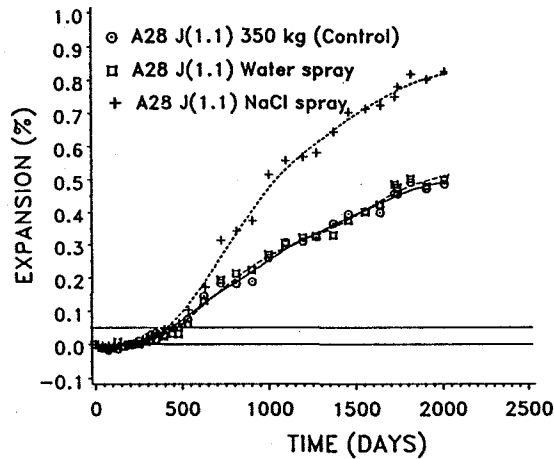


FIGURE 1: Graph showing the effect of exposure conditions on the dimensional change of concrete cubes made with the same alkali-reactive aggregate and high-alkali cement.

coarse aggregate; the mortar was not separated from the coarse aggregate as well as in the samples used for the chemical analysis which were first heated to 550 °C to destroy the gels in the cement paste. The calcium monochloroaluminate phase was only detected in the sample subjected to the NaCl solution spray, as expected, and then only to a depth of 90 mm. Ettringite was present in all samples in approximately equal concentrations.

TABLE 3: Summary of XRD data for phases found in the cement matrix of the concrete.

Sample	Depth (mm)	Phases			
		Ettringite	Calcium hydroxide	Calcite	Calcium monochloroaluminate
Control	0 - 30	x	xx	xxx	—
	30 - 60	x	xxx	xx	—
	60 - 90	x	xxx	x	—
	90 - 120	x	xxx	x	—
	120 - 150	x	xxx	x	—
Tap Water	0 - 30	x	xx	xxx	—
	30 - 60	x	xxx	x	—
	60 - 90	x	xxx	xx	—
NaCl Solution	0 - 30	x	xx	xxx	x
	30 - 60	x	xx	xxx	x
	60 - 90	x	xx	xxx	x
	90 - 120	x	xxx	xx	—
	120 - 150	x	xxx	x	—

TABLE 4. Chemical analysis based on the cement

Sample and depth (mm)	Water-soluble			Total			
	Cl	Na ₂ O	K ₂ O	Cl	Na ₂ O	K ₂ O	C
Control							
0 - 30	0.03	0.02	0.18	0.09	0.12	0.81	5.28
30 - 60	0.03	0.02	0.06	0.09	0.06	0.30	2.82
60 - 90	0.03	0.02	0.12	0.09	0.09	0.57	2.01
90 - 120	0.00	0.03	0.21	0.09	0.18	0.90	0.54
120 - 150	0.00	0.06	0.27	0.06	0.18	1.23	0.60
Tap water							
0 - 30	0.03	0.03	0.15	0.15	0.15	0.51	2.04
30 - 60	0.03	0.02	0.06	0.12	0.09	0.39	0.54
60 - 90	0.00	0.03	0.18	0.09	0.24	0.75	0.48
90 - 120	0.03	0.03	0.18	0.09	0.18	0.87	0.51
120 - 150	0.00	0.03	0.21	0.09	0.18	1.08	0.87
NaCl solution							
0 - 30	1.77	0.51	0.12	3.99	0.99	0.36	2.46
30 - 60	1.11	0.42	0.33	2.58	0.81	0.84	0.60
60 - 90	0.39	0.12	0.30	1.14	0.42	0.96	0.42
90 - 120	0.03	0.03	0.24	0.15	0.21	0.93	0.54
120 - 150	0.00	0.03	0.24	0.09	0.18	1.05	0.57

TABLE 5. The average alkali content of the different cubes at the time of casting and approximately 7 years after exposure

Cube	Na ₂ O equivalent, kg/m ³					
	At time of casting			After 7 years' exposure		
	Water-soluble	Available	Total	Water-soluble	Available	Total
Control	3.29	3.78	3.85	0.49	—	2.14
Tap-Water	3.29	3.78	3.85	0.46	—	2.25
NaCl Solution	3.29	3.78	3.85	1.28	—	3.72

3.3 Chemical Analyses

The chemical analyses give a good indication of the Cl penetration into the cube subjected to NaCl solution spray. As expected, the control cube and that subjected to tap water had a very low Cl content throughout. Corrosion of steel in concrete can be initiated by small concentrations of soluble chloride (0.6 to 0.95 kg/m³) [1]. For this particular concrete mix the value of 0.6 kg/m³ translates to a value of 0.17% Cl, based on the cement content. The fall-off in soluble chloride, based on the cement content, in the sample subjected to NaCl solution spray is evident from Table 1. The value falls off quite rapidly from a value of 1.77% in the first 30 mm, to below 0.03% after 90 mm, into the cube. Between 60 and 90 mm the value is 0.39%, which is more than double the concentration that reportedly can be tolerated in concrete with reinforced steel.

The total, available and water-soluble alkali content of the concrete, based on the analysis of the cement, at the time of casting and after 2493 days is presented in Table 5. The amount of water-soluble alkali in the concrete was originally 3.29 kg/m³ Na₂O equivalent (all present in the cement), which decreased to 0.49, 0.46 and 1.28 kg/m³ Na₂O equivalent (based on the cement) after 7 years for the control cube, the cube subjected to tap water spray and the cube subjected to NaCl solution spray. Even the acid-soluble alkali is now less than the available alkali content originally (3.78 kg/m³ Na₂O equivalent), namely 2.14, 2.25 and 3.72 kg/m³ Na₂O equivalent respectively. There are a number of possible reasons for the observations: 1) there could have been considerable alkali leaching with time, or (2) the alkali in the mortar could have combined in a phase that is not water- or acid-soluble, or (3) the

alkalis could have diffused with time into the crack surfaces and around the periphery of the alkali-reactive coarse aggregate fragments, and a considerable amount of alkali may now be tied up in the reaction product phases present at these sites. The second option is thought to be unlikely while the third is the most probable. It is also possible that some of the alkalis were leached from the concrete during the drilling of the samples, although the amount of alkali removed in this way is thought to be small, given the high water-soluble chloride and sodium contents determined for the sample subjected to NaCl solution spray. Assuming that there was only a small amount of leaching and assuming that the alkali not accounted for in the analysis of the cement paste is present on crack surfaces and around the periphery of the coarse aggregate, this means that the water-soluble alkali has more or less been redistributed throughout all the phases of the concrete as a whole. There is no clearly discernible variation of either the water-soluble or total alkali with depth into the cubes with the exception of Na₂O (both water-soluble and total) in the cube subjected to NaCl solution spray, which as expected decrease towards the centre of the cube.

The carbonation rate, as determined by the C content of the concrete, is obvious from Table 4. It is clear that although the first 30 mm of the concrete is carbonated in all the samples, it is only in the control sample that the carbonation penetrates deeply; up to 90 mm.

The SEM investigation has revealed the normal variation in morphology of the asr reaction products, namely blade- and needle-like reaction product and the more ubiquitous gel and rosette phases. Although a sample from each depth interval was examined under the SEM and the different reaction products analysed by X-ray microanalysis, no particular trend was evident in either the type of reaction product or the chemistry of the individual phases.

4. DISCUSSION

There is evidence that addition of NaCl at the mixing stage increases the OH⁻ ion concentration of pore fluids [2], thereby exacerbating the alkali-silica reaction. There is less convincing evidence as to what happens to hardened concrete which is subjected to NaCl bearing solutions. Chatterji and co-workers [3], from experiments on cured mortar specimens containing both reactive and non-reactive aggregate which were immersed in saturated NaCl solutions at 50 °C, have suggested that the NaCl reacts with Ca(OH)₂ in the cement paste to form Na⁺ and OH⁻ ions, which then attack the reactive aggregate in the samples, causing expansion. They furthermore suggested that the degree of expansion is determined by the difference between the influx of Na⁺, Ca²⁺, OH⁻ and H₂O into the reactive grain and the diffusion of Si⁴⁺ ions out of the grain. If the rate of influx is higher than the rate of diffusion, expansion occurs. The role of NaCl is to increase the rate of influx while diffusion out of the grain is determined by the presence or absence of Ca(OH)₂. In a later paper, Chatterji et al (1987) [4] tested mortar prisms made with reactive sand in different solutions (concentration 3N) of Na and K salts. The amount of expansion varied for the different salts with NO₂ solutions, giving the highest absolute expansion followed by Cl⁻, NO₃⁻, OH⁻ and PO₄³⁻ respectively. The reason for the above could not be explained. The results, however, indicate that the anion also plays a role in the expansion mechanism and the possibility therefore exists that the reaction of the anions with 3CaO.Al₂O₃ hydrate forms salts of the general formula 3CaO.Al₂O₃.CaX₂.12H₂O which, because of their high molar volumes could cause expansion unrelated to the alkali-silica reaction.

5. CONCLUSIONS

The following conclusions can be drawn from the results presented.

1. The action of NaCl solution spray increases the expansion of concrete by up to 70 % after about 7 years. This is probably because NaCl exacerbates the alkali-silica reaction by releasing additional Na⁺ and OH⁻ by reacting with Ca(OH)₂ and C₃A in the cement matrix, but also possibly by the formation of an expansive monochloroaluminate hydrate.
2. Although the concrete was badly cracked, the penetration of both Cl and Na ions was no longer noticeable after a depth of 90 mm. The Cl concentration in the outer 90 mm of the sample is more than double the maximum which reportedly can be tolerated by reinforced steel.
3. The expansion measured for the sample exposed to normal environmental conditions and that subjected to tap water spray, were very similar, which indicates that the sample exposed to normal atmospheric conditions in Pretoria does not dry out sufficiently to retard the reaction, even during the dry winters. This suggests there

is apparently sufficient water in the concrete itself to sustain the reaction all year round.

REFERENCES

- [1] Berke, N.S., Pfeifer, D.W. and Weil, T.G., Protection against Chloride-induced Corrosion, Concrete International, 45, December 1988.
- [2] Nixon, P.J., Page, C.L., Canham, I. and Bollinghaus, R., Influence of Sodium Chloride on Alkali-Silica Reaction, Advances in Cement Research, 1, 2, 99, 1988.
- [3] Chatterji, S., Jensen, A.D., Thaulow, N. and Cristensen, P., Studies of Alkali-Silica Reaction. Part 3. Mechanism by which NaCl and Ca(OH)₂ affect the Reaction, Cement and Concrete Research, 16, 246, 1986.
- [4] Chatterji, S., Thaulow, N. and Jensen, A.D., Studies of Alkali-Silica Reaction. Part 4. Effect of Different Alkali Salt Solutions on Expansion, Cement and Concrete Research, 17, 777, 1987.

APPENDIX

Chemical analysis

The concrete samples were first heated in a furnace at 550 °C for one hour. The coarse aggregate fragments were picked out by hand after slight grinding in a pestle and mortar. The finer fraction of the coarse aggregate was then removed by sieving the sample through a 2-mm sieve. The rest of the sample (now consisting of only the mortar) was ground until the whole sample passed through a 300-µm sieve. The following methods were used:

Water-soluble alkalis	ASTM C114
Total alkalis	ASTM C114
Total and water-soluble chlorides	SABS 831
Carbon	Determined on a Leco CS-125 instrument

XRD Analysis

A representative aliquot of the mortar approximately 10 g in mass was obtained by gently crushing the sample with a rubber pestle and sieving through a 0.053-mm sieve. A representative sample of approximately 3 g was loaded into a round aluminium holder by the back-loading technique and run from 3° to 65° 2-theta on a Philips PW1700 X-ray diffractometer using Cu-K-alpha radiation.

SEM Techniques

Samples are first examined carefully to ascertain whether they had visible reaction products. The selected specimen was then gold-coated using a Polaron E5200 Autocoating Unit. This apparatus uses a voltage of 2.5 kV and a current of 20 mA in the presence of an ionised argon gas atmosphere to deposit a layer of gold (100-200 Å) on the sample, in order to prevent charging of the sample during the examination with the electron beam. The Scanning Electron Microscope (SEM) used was a Jeol 733 JXA. The samples were examined in the range 10-20 kV, using a final aperture of 130 micrometres and a sample current on brass of approximately 5 x 10⁻¹⁰ amperes.