Effects

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on

Alkali-Aggregate Reaction

EFFECTS OF SODIUM CHLORIDE ON THE ALKALI-SILICA REACTION IN HARDENED CONCRETES.

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Previous work has shown that an external source of NaCl accentuates alkali-silica reaction (ASR) expansion in high-alkali concretes containing a number of UK aggregates. In low-alkali concretes the ASR expansion caused by NaCl was even greater than that developed by the high-alkali materials and for concretes exposed to salt solutions, it was proposed that an 'initial alkali pessimum' existed for each type of reactive aggregate. Further expansion tests on concretes made from the same aggregates at lower alkali contents have been carried out, exposing them to salt solution of various concentrations at temperatures of 38°C and 20°C. Two cements of differing C_3A content were used to establish whether the reaction of NaCl with hydration products of C_3A is involved in exacerbating the ASR expansion. The observations suggest that ASR expansion develops which is due at least in part to alkali derived from such a reaction but that considerable expansion can still develop in low-C_3A cement concretes. Comparison is made with the behaviour exhibited by concrete cores taken from a structure that contained one of the reactive aggregates.
Keywords: Sodium chloride, Low-alkali content concretes, Aggregate types, C_3A content of cement, Initial alkali pessimum.

Introduction

There is conflicting evidence regarding the effects of NaCl on alkali-silica reaction (ASR) in concrete structures exposed to treatment with deicing salt. Whilst additions of salt to concrete materials are known to increase the risk of deleterious expansion (Nixon et al. 1988), some researchers have found no such effects when NaCl is introduced from the surrounding environment into a hardened concrete containing a natural reactive aggregate (Hobbs.1995). Observations of field structures, however, suggest that, in some cases at least, the ingress of NaCl into concretes that would otherwise be considered only marginally reactive has contributed to deleterious expansion (Petersen. 1983, Sibbick & West. 1992). Furthermore, Chatterji (1979, 1986) has presented numerous examples of ASR expansion being accentuated by NaCl from external sources and has emphasised the role of $Ca(OH)_2$ in relation to these effects.

The work of Nixon et al. (1988) suggested that the principal effect of NaCl on ASR was due to reaction of chloride with C_3A hydration products, resulting in enhancement of the pore solution hydroxyl ion concentration. This assumption was challenged by the evidence of Kawamura and Igarashi (1990) that increased ASR expansion could be induced not only by NaCl but also by $CaCl_2$ under some conditions. Since $CaCl_2$ tends to reduce the pore solution hydroxyl ion concentration, it was suggested that chloride ions might exert a catalytic effect on ASR.

In previous work at Aston University (Sibbick. 1993) it was observed that the effects of NaCl ingress on ASR development in hardened concrete made from certain UK aggregates are strongly dependent on the initial alkali content of the concrete concerned, the tendency of the salt to promote enhanced expansion being more noticeable in relatively low-alkali concretes than in high-alkali concretes. The aims of the work to be described in the present contribution were to seek confirmation of this effect, particularly for concretes with initial alkali contents at or below the present UK recommended limit

of 3 kg/m^3 equivalent sodium oxide (Na$_2$O$_e$), and to examine further the role of cement C$_3$A content.

Experimental method

The concretes investigated were all of constant mix proportions, with a water-cement ratio of 0.5, an aggregate-cement ratio of 4.6 and cement content of 400 kg/m^3. The aggregate consisted of a mixture of 2 parts coarse aggregate to 1 part fine aggregate, the nature of the coarse aggregate being varied as indicated in Table 1, and the fine aggregate always being unreactive limestone.

Table 1 Approximate alkali thresholds to produce significant expansion with the various aggregates and the alkali levels of the concretes used.

Aggregate name (Ref.)	Alkali threshold for significant ASR	Total alkali contents of concrete mixes.
1. Chloritised siltstone(DR)	3.5	1.89/2.38, 2.5, 3.0, 3.5, 4.0
2. Silicified limestone(HL)	3.5	1.89/2.38, 2.5, 3.0, 3.5, 4.0
3. Greywacke (MD)	4.5	1.89/2.38, 2.5, 3.0, 3.5, 4.0
4. Trent Valley gravel (RP)	6.0	3.0, 4.0, 5.0, 6.0, 7.0
5. Strained granite (AG)	4.5	1.89/2.38, 2.5, 3.0, 3.5, 4.0

All figures are expressed in kg/m^3 Na$_2$O$_e$. The 1.89/2.38 kg/m^3 mixes were dependent on which cement was used. The Trent Valley gravel consisted of chert and quartzite both of which show ASR reactivity. A full petrographic description of the aggregates is given by Sibbick and Page (1992).

Two UK cements were used in this work, an ordinary portland cement (OPC) and a sulphate-resisting portland cement (SRPC). Table 2 shows a chemical analysis of the cements in terms of oxides and the constituent minerals. These cements were used because of their widely differing C$_3$A contents and their low-alkali contents, which meant a large range of concrete alkali contents could be obtained by additions of NaOH to the mixing water as shown in Table 1.

Table 2 Chemical analysis of cements.

Ordinary Portland Cement, ref.H

CaO	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	SO$_3$	MgO	Na$_2$O	K$_2$O	Na$_2$Oe	Ignition Loss
64.96	20.26	5.72	2.31	3.22	1.10	0.20	0.60	0.59	1.28

C$_3$S = 51.94 %   C$_2$S = 18.26 %   C$_3$A = 11.05 %   C$_4$AF = 6.97 %

Sulphate-resisting Portland Cement, ref.M

63.99	20.60	3.93	5.31	2.06	0.74	0.21	0.40	0.47	1.41

C$_3$S = 64.49 %   C$_2$S = 9.47 %   C$_3$A = 1.27 %   C$_4$AF = 16.01 %

Calculated by method described in Lea (1970).

The research was carried out using expansion test prisms produced in accordance with the relevant standard (British Standards Institution. 1990). Prisms of dimensions, 75 X 75 X 250 mm, were cast and cured under a plastic sheet in a constant temperature room ($20^{\circ}C\pm 2$). After 24 hours the specimens were demoulded, cleaned, and numbered. Gauge markers were stuck to their surfaces at a separation of 200 mm and the prisms were left to cure for a further 27 days above water and under a plastic sheet at room temperature. After 28 days the prisms were measured before being immersed in either 2M or 7M NaCl solution or distilled water. The two saline environments were intended to simulate the field conditions experienced in different locations by typical concrete structures exposed to deicing salt (Wood. 1992). The prisms were stored in temperature-controlled rooms at either 20 or $38^{\circ}C \pm 2$. The $38^{\circ}C$ samples were removed and allowed to cool to room temperature for 24 hours before being measured every month. As an additional comparison method, expansion results were also obtained for concrete cores taken from a structure containing the silicified limestone aggregate that was known to have experienced some degree of ASR. The material was obtained from a prestressed bridge beam that had been steam cured and was 20 years old at the time of coring. These concrete cores were placed in the same laboratory test environments as the concrete prisms.

Results

The results of the $38^{\circ}C$ expansion tests for three of the aggregates (DR,HL, and RP) are shown in Figures 1 to 12. (Note: The expansion results obtained for the slower reacting aggregates [MD and AG] exhibited similar features to those discussed here but have not been presented to save space). By examining the graphs, the time at which each concrete first expanded and significantly expanded can be established. In Figures 1, 5 and 9, results for the high C_3A concretes immersed in 2M NaCl show that early expansions relate directly to the alkali content, with no expansion being developed by the low-alkali mixes for 2 to 3 months. However, at later ages the rates of expansion for the high-alkali concretes remain constant or even reduce, whilst those of the lower-alkali concretes increase significantly. For the high-C_3A concretes immersed in 7M NaCl solution, Figures 2, 6 and 10 show that the rates of increase are lower and relate less to the alkali content. A slightly quicker start to expansion was observed in the higher-alkali concretes. The same behaviour is observed for the low-C_3A cement concretes in both salt solutions, though the rates of expansion are reduced, see Figures 3,4,7,8,11&12. As in previous work (Sibbick. 1993) there is evidence that an initial alkali pessimum, i.e. an alkali content at which maximum expansion arises on exposure to salt solutions, exists for each aggregate. For the siltstone, (Figure 1) this occurs at about 3.5 kg/m^3 Na$_2$Oe. It was noticed that most of the prisms being tested, especially those containing the slow reacting greywacke and strained granite were still expanding after 16 months and therefore considerable potential for expansion remained in those concretes.

From these data, it is apparent that the high-C_3A concretes exhibit greater expansion than are observed for the equivalent alkali content low-C_3A concretes. When the high and low-C_3A concretes were immersed in the 2M NaCl solution, the expansions developed by these concretes were related to the alkali content of the initial concrete, whereas in the 7M NaCl the expansions developed were related less to the initial alkali content, being more or less equivalent for all the concretes containing the DR and HL aggregates. All the concretes developed expansions that would be considered to

represent significant ASR, this being taken as >0.05% after 12 months (ASTM. 1990)[1]. The difference between the amount of expansion developed by the high and low-C_3A concretes reduces at higher alkali contents until an alkali level is reached at which the cement type has no significant effect on the expansion developed.

Table 3 Expansion results of concretes with no additions of NaOH, when immersed in NaCl solutions at 38°C after 16 months (measured in % strain).

Sample name	High C_3A cement (H).		Low C_3A cement (M).	
	2N NaCl	7N NaCl	2N NaCl	7N NaCl
Chloritised siltstone	0.603	0.389	0.216	0.208
Silicified limestone	0.233	0.244	0.120	0.103
Greywacke	0.171	0.131	0.101	0.075
Trent Valley gravel*	0.121	0.068	0.025	0.050
Strained granite	0.174	0.156	0.089	0.097

* - 3 kg/m^3 Na$_2$Oe mixes used.

An important observation should be made concerning the expansions developed by those concretes in which no NaOH additions were made. These concretes which were immersed in the salt solutions all show significant levels of expansion, see Table 3 which increase with time of immersion in the salt solution. Because the Trent Valley gravel has an alkali threshold of around 6 kg/m^3 Na$_2$Oe the range of alkali content used was different from those for the other aggregates. Interestingly even with these Trent Valley aggregate concretes, immersion in the salt solution accentuates the expansion at alkali levels well below the threshold, both the high- and low-C_3A concretes developing significant expansions down to 4 kg/m^3 Na$_2$Oe within 1 year. With these concretes the amount of expansion generally increases with the alkali content. However, the high-C_3A concretes in both salt solutions also exhibit an initial alkali pessimum at 6 kg/m^3 Na$_2$Oe.

During testing it was observed that all the concrete prisms were covered in gel. It was noted that this gel differed in appearance, depending on which salt solution the prism was immersed in. The gels from specimens immersed in the 2M NaCl were firm, compact blobs associated with specific microcracks or surface voids, whereas the gels from specimens immersed in the 7M NaCl were less well defined, appearing as a uniform surface coating. ASR gels from the concretes immersed in distilled water were similar to those immersed in the 2M NaCl.

Figures 13 to 15 show the expansion data plotted against time for the silicified limestone aggregate concretes immersed in the salt solutions and distilled water, and these are compared with the equivalent data obtained for concrete cores taken from a structure containing this aggregate. The results show that even this older structural concrete will develop similar accentuated expansions when placed in the saline test environments. Figure 15 shows a comparison of the expansion data for the concrete prisms and the concrete cores when immersed in distilled water at 38°C. This shows that the expansion available from the alkalies within the structural concrete is far greater than that of the 4 kg/m^3 Na$_2$Oe laboratory-prepared concrete. This is due to either the

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[1] The concrete made with Trent Valley gravel and low C_3A cement at 3 kg/m^3 Na$_2$Oe had not reached this level of expansion in the 2M NaCl solution after 16 months.

use of a more reactive siliceous limestone as aggregate, a higher percentage of reactive aggregate in the concrete, or a higher internal alkali content, derived from either a higher cement content, a higher alkali cement or de-icing salts. The $20^{\circ}C$ expansion results are incomplete, but many specimens are showing some significant expansion at all the alkali levels tested. At this stage no relationships can be drawn between these results or comparison made with the $38^{\circ}C$ results.

Alkali-silica reaction expansion in saline environments

Figure 16 demonstrates the difference in expansion developed by the high and low-C_3A siltstone-aggregate concretes in the 2M NaCl solution. As the differences are positive for all the low-alkali concretes ($Na_2Oe \leq 3.5$ kg/m^3), it appears that the reaction between C_3A and NaCl has a significant role under these conditions. However, this effect is not observed for the concretes with 4 kg/m^3 Na_2Oe and it seems that the enhanced expansion caused by NaCl in higher-alkali concretes must be attributable to some other process or processes. Essentially similar behaviour to that exemplified in Fig. 16 was reproduced for specimens exposed to 7M NaCl and by concretes made from the other types of aggregate studied, although the levels of expansion were lower than those recorded for the siltstone. The mechanisms of these various effects are being studied in continuing investigations, which will be reported elsewhere.

Conclusions

1. The immersion in salt solution of concretes made from several reactive UK aggregates increased ASR expansion for all the alkali levels and aggregate types studied. For some aggregates, significant levels of expansion were even developed by concretes with alkali contents well below the present UK recommended concrete alkali limit of 3 kg/m^3 Na_2Oe.

2. The effect of the cement C_3A content on the degree of expansion developed was most pronounced at low-alkali levels. At alkali levels on or above the present UK recommended limit, however, the difference in expansion developed by the high and low-C_3A concrete was negligible.

3. Increasing the NaCl solution concentration from 2M to 7M reduced the levels of expansion developed by the concretes and also reduced the effects of the initial alkali content of a concrete on the level of expansion developed.

4. An initial alkali pessimum was observed for a number of aggregates at alkali levels equivalent to the particular aggregate's alkali threshold level in distilled water. This effect was confined, however, to the high-C_3A concretes.

5. The behaviour of concrete cores from a 20-year old structure suggested that late age expansion may still develop if such materials are exposed to de-icing salt.

Acknowledgements

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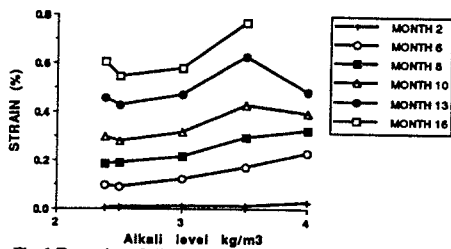
Fig. 1 Expansion of siltstone aggregate concrete containing the high C3A cement at varied alkali contents immersed in 2M NaCl.
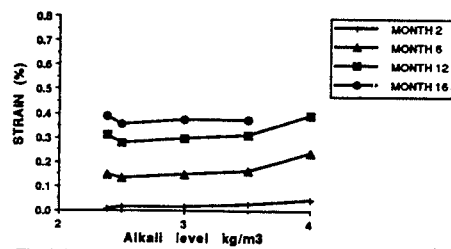

Fig. 2 Expansion of siltstone aggregate concrete containing the high C3A cement at varied alkali contents immersed in 7M NaCl.
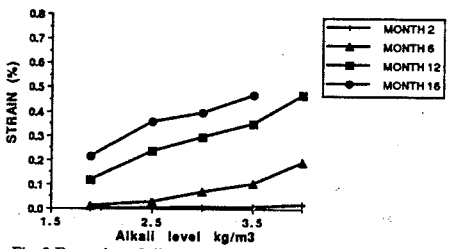

Fig. 3 Expansion of siltstone aggregate concrete containing the low C3A cement at varied alkali contents immersed in 2M NaCl.
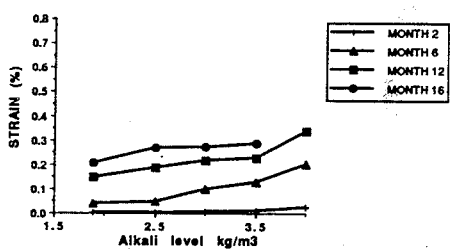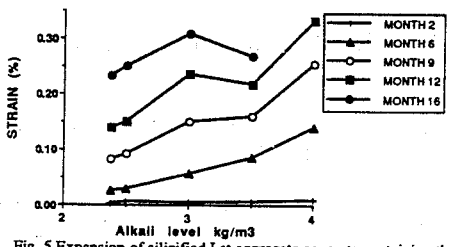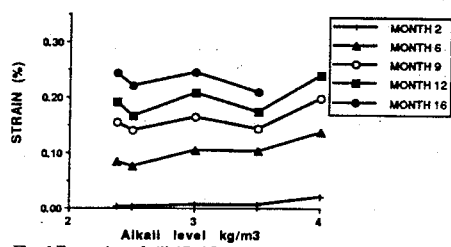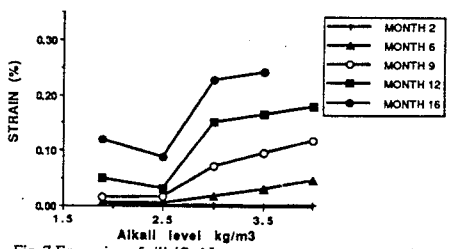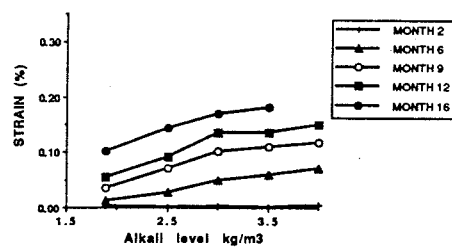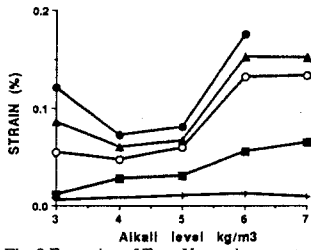

Fig. 4 Expansion of siltstone aggregate concrete containing the low C3A cement at varied alkali contents immersed in 7M NaCl.

Fig. 5 Expansion of silicified Lst aggregate concrete containing the high C3A cement at varied alkali contents immersed in 2M NaCl.

Fig. 6 Expansion of silicified Lst aggregate concrete containing the high C3A cement at varied alkali contents immersed in 7M NaCl.

Fig. 7 Expansion of silicified Lst aggregate concrete containing the low C3A cement at varied alkali contents immersed in 2M NaCl.

Fig. 8 Expansion of silicified Lst aggregate concrete containing the low C3A cement at varied alkali contents immersed in 7M NaCl.

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Fig. 9 Expansion of Trent V gravel aggregate concrete containing the high C3A cement at varied alkali contents immersed in 2M NaCl.
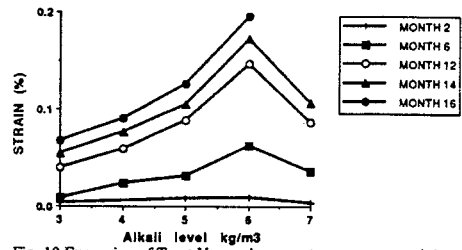
Fig. 10 Expansion of Trent V gravel aggregate concrete containing the high C3A cement at varied alkali contents immersed in 7M NaCl.
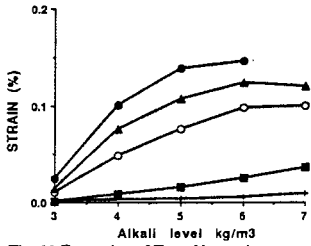
Fig. 11 Expansion of Trent V gravel aggregate concrete containing the low C3A cement at varied alkali contents immersed in 2M NaCl.
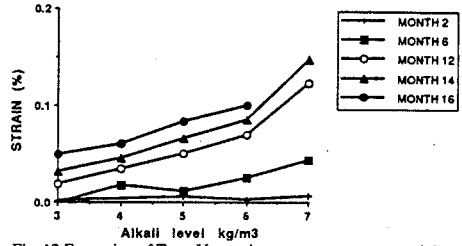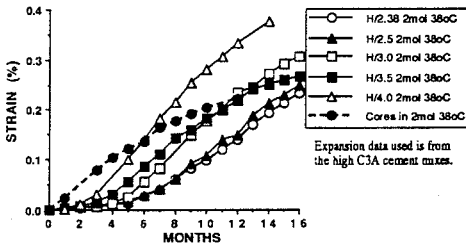
Fig. 12 Expansion of Trent V gravel aggregate concrete containing the low C3A cement at varied alkali contents immersed in 7M NaCl.

Fig. 13 Expansion of silicified Lst aggregate concrete at varied alkali contents immersed in 2M NaCl compared with equivalent structural concrete cores.
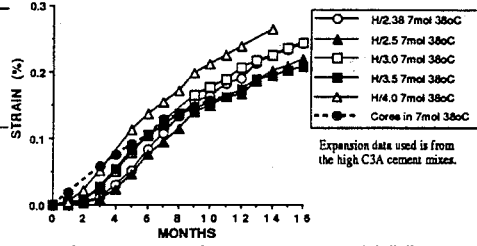
Fig. 14 Expansion of silicified Lst aggregate concrete at varied alkali contents immersed in 7M NaCl compared with equivalent structural concrete cores.
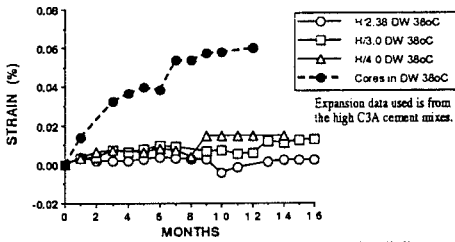
Fig. 15 Expansion of silicified Lst aggregate concretes of varied alkali contents immersed in distilled water compared with equivalent structural concrete cores.
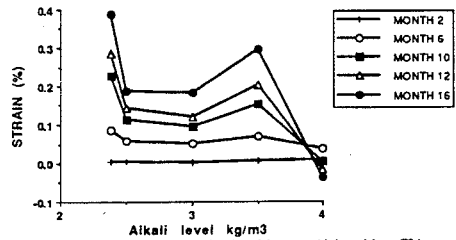
Fig. 16 Difference in expansion developed between high and low C3A cement siltstone concretes with varied alkali contents when immersed in 2M NaCl.

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