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Effects of seawater on AAR expansion of concrete

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ABSTRACT

Recently, AAR was identified in submerged piles of some bridges in tidal waters. Microstructural examination detected chloroaluminate salts in some cracks. To clarify whether seawater had influenced the deterioration an experimental program was planned to examine the effects of sodium chloride on AAR under various curing conditions.

Concrete prisms containing either of highly-reactive, slowly-reactive or nonreactive aggregate, and either low or high alkali contents, were stored in saltwater (representing seawater) or at 100% RH, at temperatures of 38, 60 and 80 °C, for expansion measurement over 600 days, after which the temperature for those stored in saltwater was lowered to 23 °C, to check its effect on further expansion, which could be attributed to precipitation of ettringite and/or Ca-chloroaluminate.

The results indicate that the type of aggregate and concrete alkali content had the greatest effect on AAR expansion. Exposure to saltwater did not have any significant effect on the AAR expansion.

1. Introduction

It is known that alkali–aggregate reaction (AAR) can cause serious cracking and deterioration of concrete structures, particularly those in moist environments. The requirements for AAR to occur in the concrete are the presence of sufficient amounts of reactive components, alkali and moisture, and the mechanisms of the reaction are well established. AAR has been identified in many locations worldwide to have caused damage to structures exposed to a variety of environmental conditions, including de-icing salts and marine conditions. The latter are more aggressive than normal exposure conditions as the concrete is subjected to the effects of a number of salts present in the seawater. The salt content of seawater is broadly about 3.5%, and its composition includes about 19,400 ppm Cl, 10,800 ppm Na, 1290 ppm Mg, 900 ppm S, 410 ppm Ca, and 390 ppm K, among numerous other elements of far less abundances.

Extensive research in the past few decades has established the mechanisms of seawater attack on cement paste and concrete, and shown that seawater certainly causes deterioration of cement paste as a result of reaction with susceptible components of the paste, and formation of new reaction products such as gypsum, ettringite, brucite, calcium-chloroaluminate phases (Friedel's salt) and magnesium silicate hydrate (e.g. Kalousek and Benton [1]; Regourd [2,3]; Sayward [4]).

Seawater can probably adversely affect the behaviour of concrete containing reactive aggregates and enhance the deterioration. It has, in fact, been implicated in the mechanisms of AAR. For instance, the Danish accelerated AAR test, as used by Chatterji et al. [5] for testing a flint aggregate, involves storage of concrete or mortar specimens in saturated NaCl solution at 50 °C. Swamy and Al-Asali [6] showed that storage of concrete prisms (cement content of 520 kg/m^3), containing fused silica or opal as aggregate, in a 4% NaCl solution resulted in a higher expansion compared to storage in water. The latter authors [5,6] did not report the composition of the cements used. It should be noted that storage in water [6] leads to leaching of alkali and reduced expansion compared to storage at 100% RH.

Addition of NaCl to mortar or concrete mixes, at the time of casting, Nixon et al. [7], had the same effect as using Portland cements with higher native alkali contents. This effect was stated to arise from the reaction of the added NaCl and the C_3A component of cement, which released OH ions into the pore solution of concrete, thereby exacerbating AAR expansion of their flint-bearing specimens. The cement used had 11.7% C_3A, which is far greater than that in modern cements (~5%), and would generate correspondingly more OH in the concrete pore solution, as a result of this reaction.

Storage of specimens in seawater or NaCl solutions has been shown [8–11] to enhance AAR expansion, partly due to increased alkalinity arising from reaction with the aluminates, but the authors concerned did not fully explain why extra expansion took place. Kawamura et al. [12] also observed that mortar specimens expanded more in NaCl than NaOH solution, and attributed this to the formation of AAR gel with low alkali content. They found ettringite in AAR-induced microcracks, but could not state whether the presence of ettringite contributed to the expansion. However, work by the present author [13] showed that unless elevated alkali levels were present, the presence of the saturated

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NaCl solution per se did not induce AAR expansion in concrete prisms. Duchesne and Bérubé [14] also arrived at the same conclusion. This may have arisen from the slowly-reactive nature of the Australian aggregates used, compared to the Danish aggregates. The interaction of NaCl with the C_3A phases (calcium aluminates) of cement generates Friedel's salt, and results in the dissolution of portlandite and formation of extra alkali hydroxide in the concrete pore solution, which is the reason for the enhanced expansion.

Based on mineralogical investigations of some cementitious systems, hydrated under accelerated testing conditions, Shayan [15] suggested that there may be a different reason for the extra expansion observed by some authors, in the presence of NaCl solution, which would be analogous to the mechanism of expansion caused by delayed ettringite formation. The process was suggested to involve paste expansion due to formation of Friedel's salt, and also filling of AAR-induced microcracks, similar to the case of DEF.

Inspection and scrutiny of some published AAR expansion results for a reactive aggregate, presented in [11], strengthened the belief that such a mechanism may be operative. It was suggested [15] that the formation of calcium chloroaluminate phases in AAR-induced microcracks in the concrete prisms studied in [11] could have exacerbated the expansion. Shayan and Morris [16] found field evidence for this mechanism in the examination of deteriorated, precast, prestressed concrete bridge piles, in which compact layers of chloroaluminate were found in AAR-induced microcracks, in the same morphological form as that of expansive ettringite in heat-cured concrete. However, there is no proof that this caused deleterious expansion.

If Friedel's salt formation in the paste, or its precipitation into AAR-induced microcracks, can cause additional concrete expansion, then the type of aggregate, the alkali and aluminate contents, precasting temperature and exposure to seawater would all contribute to the expansion and deterioration of elements subjected to seawater. Consequently, precautions, in addition to the usual steps taken to avoid AAR damage, may be necessary for elements immersed in seawater. This could also have implications for the testing environment of mortar bars or concrete prisms, and the prediction of performance of concrete elements submerged in seawater.

Recent observation of significant deterioration of some precast, prestressed, AAR-affected bridge piles in marine conditions [16] has highlighted the need to investigate the possible influence of seawater on AAR expansion and cracking.

This paper presents the results of testing aggregates of varying reactivity under standard AAR test conditions, in comparison to those obtained at different alkali levels, varying temperatures, and under saltwater exposure, and discusses the influence of seawater on the expansion of AAR-susceptible elements in tidal waters.

2. Experimental work

2.1. Materials

2.1.1. Coarse aggregates

Three coarse aggregates were used in this work, viz., a nonreactive basaltic aggregate from near Melbourne, Victoria Australia; a slowly-reactive deformed granitic (gneissic) aggregate from Western Australia; and a highly-reactive rhyodacite aggregate from New South Wales, Australia. The basaltic aggregate has features of a dolerite and has been used extensively in both field concrete and laboratory tests, and is a well known nonreactive aggregate. The slowly-reactive gneissic granite originates from deformed granitic masses, in which dykes of intrusive rocks and fault zones are evident. The rock contains moderate amounts of strained quartz and microcrystalline quartz, and has cause AAR-induced damage to some concrete bridges. The rhyodacite is a silica-rich aggregate and contains considerable amounts of microcrystalline silica. It causes rapid expansion in laboratory AAR tests, using both accelerated mortar bar test (AMBT) and concrete prism test (CPT).

2.1.2. Sand

A nonreactive concrete sand (EXL) was used in the manufacture of concrete prisms, in combination with the coarse aggregates. Table 1 presents the expansion results for these aggregates, when tested by the RTA T363 AMBT method.

2.1.3. Cement

Blue Circle GP cement with Na_2O equivalent of 0.5% was used as the binder. Two cement alkali levels were used in the manufacture of concrete prisms, being the original alkali content (0.5%) and elevated alkali (1.4%) as Na_2O equiv; the additional alkali being added in the mixing water at the time of casting the specimens. The cement contained 5.5% C_3A and 10.2% C_4AF.

2.2. Procedures

Concrete prisms, measuring 75 × 75 × 285 mm, were used to evaluate the effects of seawater on AAR expansion of concrete under different exposure conditions. The concrete comprised a cement content of 420 kg/m^3 and a W/C ratio of 0.45 (RTA T364 concrete prism test (CPT), or ASTM C1293). After casting the specimens and demoulding at 24 h, they were stored under different conditions. Table 2 shows details of the aggregate types used, the alkali content, curing temperature and storage conditions of the various specimens. The total number of concrete mixtures was 6, each comprising 12 concrete prisms; a set of four prisms being kept at each temperature of 38, 60 and 80 °C.

The storage conditions for concrete prisms were either at 100% RH or in a saltwater comprising 5% NaCl + 0.72% $MgSO_4$. The 5% saltwater was slightly more concentrated than seawater (3.5% salt) to ensure adequate supply of the salt to the specimens. The $MgSO_4$ content was the same as 0.06 M, the average Mg concentration in seawater. The terms seawater and saltwater have been used synonymously in this paper. Note that for each aggregate, specimens containing different alkali contents were stored in different containers of saltwater.

The storage temperatures employed corresponded to test conditions of 38 °C (RTA T364 and ASTM C1293 condition), 60 °C (Rilem Concrete Prism Test condition) and 80 °C (steam curing condition, also AMBT storage temperature). The expansion criteria for these tests are, respectively, 0.03% at one year (note: ASTM C1293 limit is 0.04%); 0.03% at 4 months; but there is no agreed limit for concrete prisms tested at 80 °C. The expansion values are expressed as linear expansion.

For the normal CPT (RTA T364) a set of two prisms were stored under 100% RH at 38 °C, and two in the saltwater at 38 °C. For the CPT at 60 °C, the specimens were stored in sealable boxes either at 100% RH (i.e. the Rilem CPT) or containing the seawater. The boxes were then placed in a sealed constant temperature bath kept at 60 °C. The specimens for the 80 °C test were treated similarly to those at 60 °C, but the sealed boxes were placed in an oven kept at 80 °C rather than in a bath. Each expansion measurement was the average of the expansion values for two prisms.

Examination of results at about 290 days showed that the expansion values had dropped after 200 days for a number of specimens especially those held in the 80 °C storage conditions, which appeared to be a systematic trend. It was thought that either poor sealing of the relevant containers and loss of moisture, or some chemical changes occurring at

Table 1
List of aggregates used and their AMBT expansion values.

Aggregate reactivity	Rock type	Expansion (%)[a] (RTA T363 AMBT)
Nonreactive (Nr)	Basalt	0.01
Slowly reactive (Lr)	Gneissic granite	0.118
Highly reactive (Hr)	Rhyodacite	0.45
Nonreactive sand	EXL sand	0.120

[a] AMBT 21-day expansion limit: for coarse aggregate = 0.10%; for sand = 0.15%.

Table 2
Experimental parameters used in the test program.

Exposure condition	Aggregate type	Cement alkali (%)	Storage temperature (°C)	No. of combinations
100% RH	Nonreactive	0.50, 1.40	38, 60, 80	6
	Slowly reactive	0.50, 1.40	38, 60, 80	6
	Highly reactive	0.50, 1.40	38, 60, 80	6
Saltwater[a]	Nonreactive	0.50, 1.40	38, 60, 80	6
(5% NaCl +	Slowly reactive	0.50, 1.40	38, 60, 80	6
0.72% $MgSO_4$)	Highly reactive	0.50, 1.40	38, 60, 80	6

[a] For each aggregate, specimens containing different alkali contents were stored in different containers of saltwater.

high temperature, could have caused this drop. Consequently, containers with saltwater were moved, into the 23 °C constant temperature room at exposure age of 293 days. These specimens remained in this condition since then to the end of measurement period.

Specimens that were subjected to humid air exposure remained in their conditions. The containers with specimens at 80 °C air exposure were moved into the water tank with the lid sealed at 290 days. This tank has ensured a more humid condition than that when the oven was used. Expansion was measured after some 100 days to check whether the drop in expansion has recovered. In addition, at the end of one year the other specimens which had been stored in seawater at 38 °C and 60 °C were transferred to a constant temperature room at 23 °C, and measurements continued under this condition for a long period. This was to check whether a drop in temperature would lead to additional expansion which could be attributed to precipitation of ettringite and/or chloroaluminate in the microcracks. Note that all the specimens, regardless of storage temperature, were equilibrated at 23 °C for 24 h prior to expansion measurement.

3. Results and discussion

The compressive strength results for the six concrete mixtures are presented in Table 3. The strength of mixes containing the additional alkali was lower than the corresponding mixes without the added alkali, which is expected.

The expansion of concrete specimens up to around 600 days is summarised in Figs. 1–3 for the nonreactive, slowly-reactive and highly-reactive aggregate types, respectively. Examples of mass changes measured at the time of expansion measurements are given in Fig. 4. Expansion limits for the tests are indicated by horizontal dashed lines in the expansion graphs. The linear expansion values were recorded using a digital gauge readable to 0.001%. Specimen masses were recorded using a digital balance readable to 0.001 g. Data for each aggregate type are discussed in the following sections.

3.1. Nonreactive aggregate

Fig. 1 shows that the concrete prisms containing the nonreactive aggregate did not expand deleteriously under any condition. Therefore, storage conditions and alkali levels per se would not cause any AAR-related deterioration, in the absence of a reactive aggregate. However, it appears that storage in seawater at both 60 °C and 80 °C may have a minor effect on the cement paste, as the recorded expansion values were slightly higher under these conditions. This could be due to factors such as the larger size of the hydrated sodium ions, incorporated in the C–S–H under these storage conditions, formation of chloroaluminates in the cement paste. Ftikos and Parissakis [17] found that Portland cement paste became more porous as a result of exposure to chloride solution, due to leaching of calcium to form $CaCl_2$ (presumably in the process of Ca-chloroaluminate formation). This level of expansion is not deleterious. Note that at 300 days, specimens in 100% RH environment were not measured, so as not to disturb the environment and continuously maintain the humidity.

Table 3
Concrete strength results.

Mix no.	Aggregate type and alkali content	ID	Casting date	28-day compressive strength (MPa)
1	Nr-0.5% alkali	C06/1320	14/02/2006	48.2
2	Nr-1.4% alkali	C06/1321	14/02/2006	38.8
3	Lr-0.5% alkali	C06/1322	16/02/2006	55.1
4	Lr-1.4% alkali	C06/1323	16/02/2006	32.3
5	Hr-0.5% alkali	C06/1324	22/02/2006	51.6
6	Hr-1.4% alkali	C06/1325	22/02/2006	37.0

3.2. Slowly-reactive aggregate

The concrete prisms containing the slowly-reactive aggregate did not expand deleteriously at low alkali content, under any of the storage condition (Fig. 2). However, as stated for the data in Fig. 1, it seems that, storage at high temperature in seawater may lead to minor expansion of the paste, due to factors stated above. This implies that, for the slowly-reactive aggregate, seawater would not cause AAR expansion, if the original amount of alkali in the concrete is inadequate.

The results for specimens containing low alkali appear to show a systematic error, as all the expansion values show a drop after 190 days of exposure. This was thought to have arisen from loss of moisture, but it also happened for specimens stored in solution. In fact, moving the container which originally had the specimens at 80 °C in saltwater to the 23 °C condition room only partially recovered the drop in expansion. It was found that a faulty thread in the specimen holder anvil in the comparator had caused this problem,

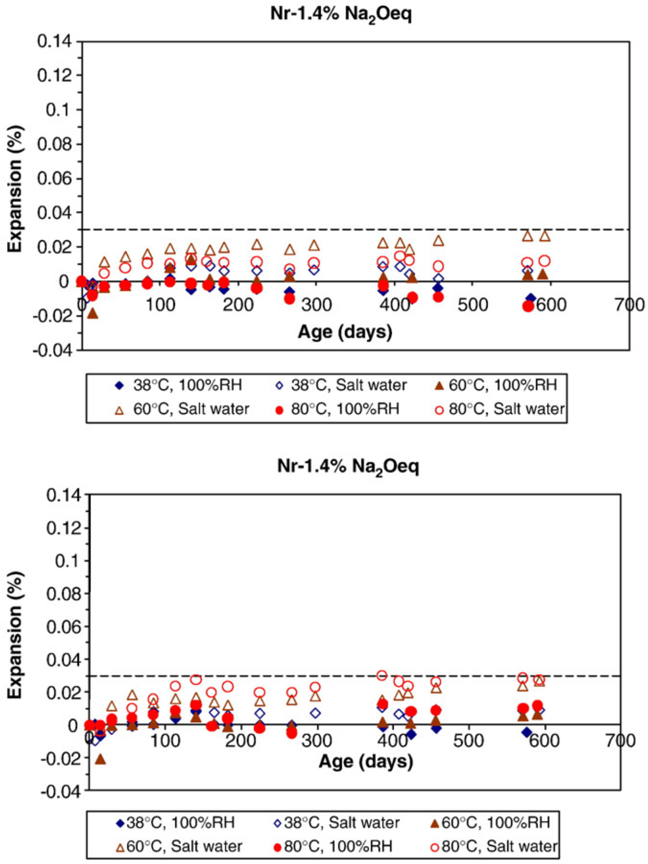

Fig. 1. Expansion of concrete prisms made with the nonreactive aggregate, at different alkali contents and under different conditions. Note expansion limits of 0.03% (RTA T364) and 0.04% (ASTM C1293) at 1 year for 38 °C CPT, and 0.03% at 3–4 months for 60 °C CPT.

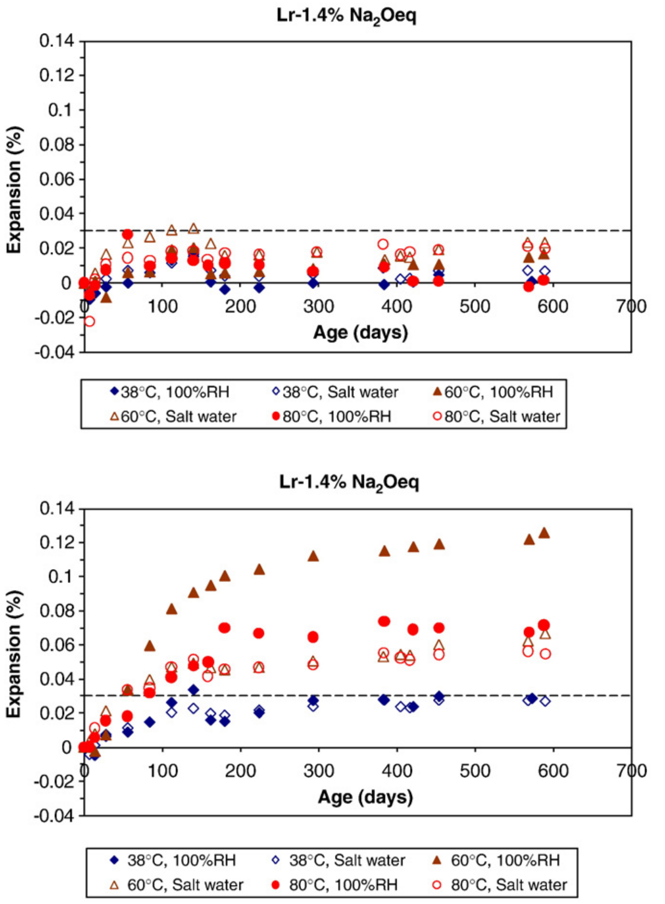

Fig. 2. Expansion of concrete prisms made with the slowly-reactive aggregate, at different alkali contents and under different conditions. Note expansion limits of 0.03% (RTA T364) and 0.04% (ASTM C1293) at 1 year for 38 °C CPT, and 0.03% at 3–4 months for 60 °C CPT.

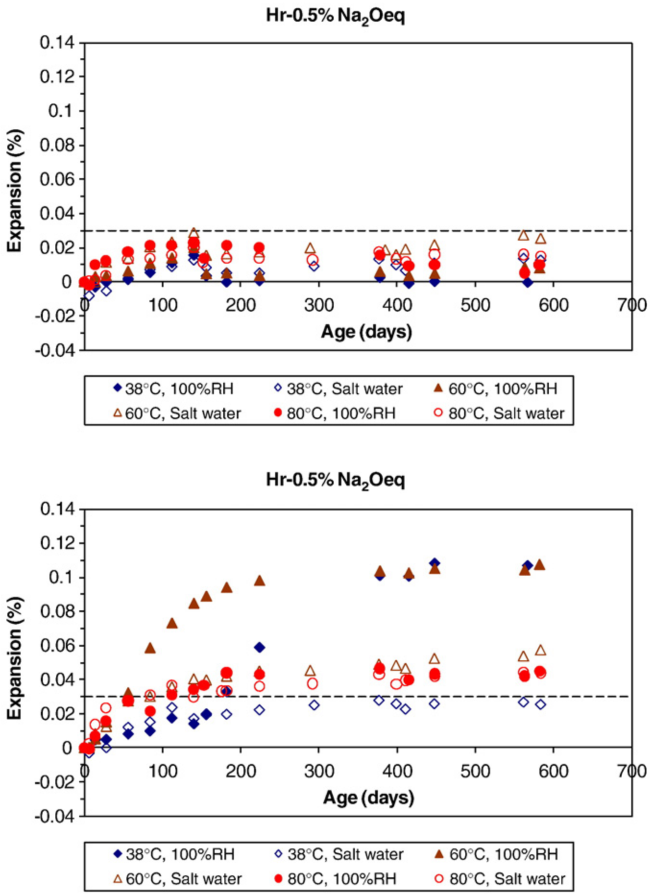

Fig. 3. Expansion of concrete prisms made with the reactive aggregate, at different alkali contents and under different conditions. Note expansion limits of 0.03% (RTA T364) and 0.04% (ASTM C1293) at 1 year for 38 °C CPT, and 0.03% at 3–4 months for 60 °C CPT.

which was fixed after this observation was made. Nevertheless, the conclusion highlighted above remains valid.

Specimens containing the slowly-reactive aggregate and high alkali content showed significant expansion at the higher temperatures. Despite the high alkali content, expansion at 38 °C was low in both 100% RH and in seawater, due to the nature of the aggregate. This type of aggregate may need to be monitored for expansion for two years before CPT can become conclusive. This is an example of the type of aggregate for which the CPT test at 38 °C is not conclusive, and the Rilem CPT at 60 °C is a better option. Experience at ARRB shows that the Rilem CPT (100% RH, 60 °C) is most suitable for slowly-reactive aggregates containing microcrystalline/strained quartz, for which neither the Australian CPT (RTA T364), nor the ASTM C1293 CPT gives satisfactory results in one year, whereas the Rilem test produces conclusive results in 3–4 months.

The 60 °C at 100% RH storage condition gave the highest expansion, followed by 80 °C at 100% RH. It must be pointed out that the 60 °C at 100% RH test was carried out in a reasonably sealed box, stored in a large sealed water bath (where no moisture loss was possible), whereas the 80 °C at 100% RH test was in a similar box stored in an oven where, it appears, moisture loss could not be prevented. Fig. 4 shows graphs of mass change during the course of the testing period for the test conditions at 60 °C and 80 °C both in seawater and at 100% RH. The latter condition resulted in considerable moisture loss from the box at 80 °C, which had an adverse effect on the expansion.

The steel container for specimens at 80 °C at 100% RH was moved from the 80 °C oven to a water tank kept at 80 °C at the age of 290 days, and left undisturbed for three months, which considerably reduced the moisture loss compared to the earlier age (Fig. 4). The specimen mass was checked and expansion measured after this period. The mass had almost recovered at 390 days, and the expansion also recovered, as shown for the measurement at 390 days.

Nevertheless, the 80 °C expansion was lower than the 60 °C, which may be related to chemical destabilisation of some hydration products, such as ettringite, at 80 °C. Results presented earlier [15] provided XRD evidence that ettringite does not form in cement paste hydrated and maintained at 80 °C. It is known that ettringite can eventually form in such specimens, a prolonged period after they are returned to ambient temperature, causing delayed ettringite formation (DEF).

There was little difference in the expansion of specimens stored in seawater between the 60 °C and 80 °C temperatures. It appears that in both cases, the leaching of alkali was probably the main factor in failing to achieve the full expansion potential, compared to 60 °C at 100% RH conditions.

Ehtesham Hussein and Rasheeduzzafar [18] reported that the concentration of hydroxyl ions in the pore solution of their specimens was significantly reduced at 70 °C, compared to 20 °C, and that in the presences of chloride, the concentration of Cl in the pore solution increased correspondingly. In the context of the present experiments, this would lead to leaching of hydroxyl ions and reduction in alkalinity.

Storage in seawater at 60 °C and 80 °C resulted in lower expansion at both temperatures than the corresponding expansion at 100% RH and the same temperatures, which indicates that seawater did not promote AAR. On the contrary, the saltwater storage condition most likely resulted in the leaching of alkali hydroxide from the high-alkali specimens, and consequently reduced the AAR expansion. These

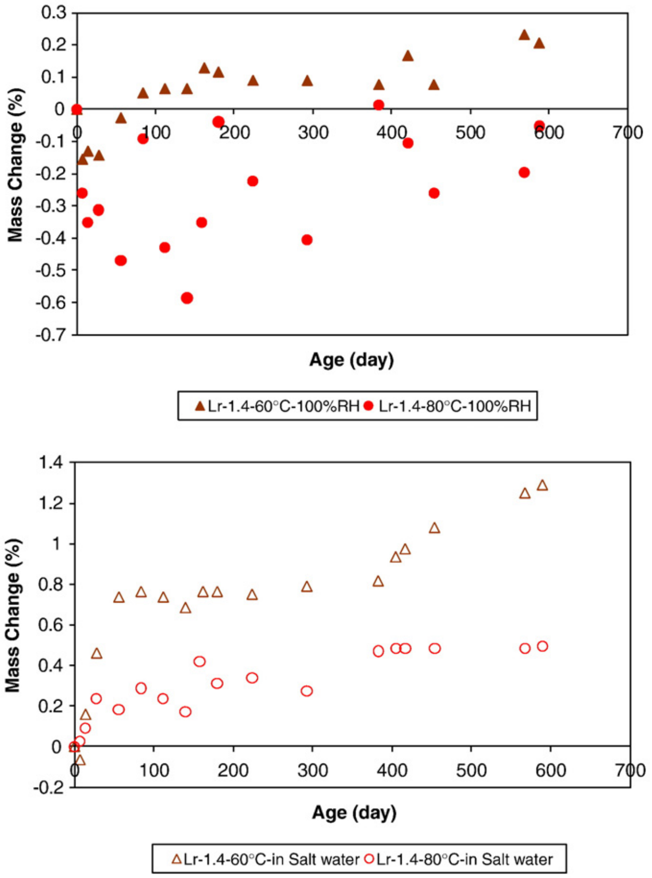

Fig. 4. Mass changes of concrete prisms, made with Lr aggregate at 1.4% alkali content, during the test period either at 100% RH (top) or in saltwater (bottom).

results agree with previous results [13] obtained on some Australian aggregates subjected to the Danish test (saturated NaCl solution at 50 °C). It is important to note that the 60 °C at 100% RH was the best condition for revealing the expansion potential of this aggregate. This is, in fact the conditions used for the Rilem Concrete Prism Test (60 °C). Shayan et al. [19] tested 50 Australian aggregates by the Rilem CPT method, and showed that it was faster and more reliable than the normal CPT (38 °C) for slowly-reactive aggregates.

3.3. Highly-reactive aggregate

Fig. 3 shows the results obtained on the highly-reactive aggregate. At low alkali content, they parallel the results for the slowly-reactive aggregate. Note that at 300 days, specimens in 100% RH environment were not measured so as not to disturb them and keep the humidity continuously until one year of age. For the high alkali content, the concrete specimens in 100% RH, 38 °C and 100% RH, 60 °C reached the same final expansion of about 0.10%, which indicated high reactivity. However, deleterious expansion was reached in a much shorter time at 60 °C than at 38 °C.

The specimens at 80 °C at 100% RH, expanded only half the amount reached at 38 °C or 60 °C, which could be due to the destabilisation of ettringite at 80 °C and probably other chemical changes. Results of Shayan [15], supported by XRD analysis, clearly showed this effect for both ettringite and chloroaluminate salts. It has also been shown by Ogawa and Roy [20] that the presence of chloride reduced the expansive effect of ettringite formation due to substitution of Cl in the ettringite structure, and formation of less expansive minerals.

The results obtained here contradict those of Kawamura et al. [21] who reported that expansion of mortar bars made with calcined flint aggregate (highly-reactive) increased after storage in IM NaCl solution at 38 °C, when the alkali content of the mortar was high. They attributed the additional expansion partly to the increase in hydroxyl ion concentration and partly to enhanced ettringite formation in the presence of NaCl solution. The present results also contradict those of Swamy and Al-Asali [6] who used opal and fused silica as aggregate and storage conditions of 4% NaCl solution at 40 °C. The difference in the behaviour of specimens used in these studies and those used in the present study may be related to the very different natures of the aggregates used in the two studies. It is also possible that the cements used by the latter authors [6,21] were very high in C_3A, similar to that used by Nixon et al. [7], and their reaction with saltwater generated sufficient OH ions to promote AAR in their specimens. Therefore, the nature of the aggregate and the cement type in the concrete could have a significant effect on its interaction with saltwater.

In another study Kawamura and Takeuchi [22] found that only when hydroxyl ion concentration in the pore solution was high, could NaCl or seawater accelerate alkali silica reaction at 20 °C. They stated that the reaction proceeded differently at 38 °C in IM NaCl solution, i.e., by an increase in the hydroxyl concentration in the presence of chloride ions. The present work shows that the level of alkali hydroxide in the specimen was the determining factor with respect to AAR expansion, and that the presence of saltwater did not play a role, because in our low alkali specimens additional hydroxyl ions were not produced, at least to the extent that could cause deleterious expansion.

All the specimens kept in seawater expanded much less than their counterparts at 100% RH, which is attributed to the leaching of alkali from the specimens. Therefore, storage in seawater did not contribute to the expansion of the concrete prisms made with reactive aggregate. It should be noted that the leaching of alkali from the relatively small concrete prisms, could reflect the condition of the outer layer of piles in seawater, but may not be translatable to the interior of large piles submerged in seawater.

Although the RTA T363 accelerated mortar bar test results, obtained previously for the coarse aggregates, were much higher for the reactive aggregate (0.45%) compared to the slowly-reactive aggregate (0.118%), the results of CPT at 60 °C at 100% RH were similar (∼0.10%) for both aggregates, indicating that the 60 °C at 100% RH test is most suitable for detecting the slowly-reactive aggregates.

Overall, it has been shown that storage of concrete prisms in the saltwater at elevated temperatures, even though they contained reactive aggregates, did not exacerbate the AAR problem. On the contrary, this probably caused leaching of alkali from the prisms and reduced the expansion.

For all the specimens stored in saltwater, which were transferred to 23 °C in their containers at the age of about 300 days, no further expansion was subsequently noted during the storage period, up to the age of about 450 days (Figs. 1–3). Therefore, lowering the storage temperature to 23 °C had little effect on expansion, i.e., it did not cause precipitation of ettringite and/or chloroaluminate, or if it did, then they could not cause additional expansion.

4. Conclusions

The results obtained in this study indicate that the types of aggregate and alkali content of concrete have the greatest effect on AAR expansion. The CPT 60 test method, involving storage of concrete prisms at 60 °C at 100% RH appeared to cause the largest expansion. Storage of specimens in saltwater caused reduced expansion, probably due to leaching of alkali from the specimens.

Unlike some results reported in the published literature, exposure to saltwater (seawater) at low or elevated temperatures did not have a significant effect on the AAR expansion. This difference may be attributed to the differences in the nature of aggregates used as well as the C_3A contents of cements employed by the other authors. It is recommended that these factors be further studied.

Lowering the storage temperature from 60 °C and 80 °C to 23 °C, and prolonged storage (300 days) at 23 °C, did not induce further expansion, which indicated that precipitation of ettringite and/or Ca-chloroaluminate either did not occur, or if it did, then it had no significant effect on the expansion.

It appears that the deterioration of the prestressed piles in seawater, previously reported by Shayan and Morris [16], was mainly due to AAR and DEF, and that the exposure to seawater does not appear to have had a significant role in the AAR-related deterioration of the affected piles.

5. Disclaimer

The opinions expressed in this paper are those of the authors, and do not necessarily reflect the policies or practices of their supporting organisations.

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