Sodium Chloride and Alkali-Aggregate Reaction

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ABSTRACT

Sodium chloride is a common contaminant of sands and gravels, especially those dredged from the sea. The possibility that it may enhance the alkalinity of concrete and hence may exacerbate alkali aggregate reactions is therefore a matter of importance. This paper describes the results of experiments in which the effect of sodium chloride and synthetic sea water added at the mixing stage on both the composition of the pore solution in cement pastes and the expansion of mortars and concretes containing reactive aggregates has been explored.

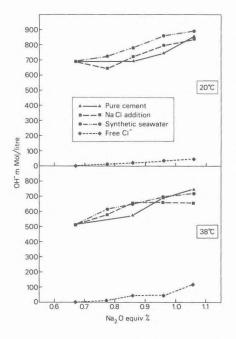
It was found that both sodium chloride and synthetic sea water elevated the hydroxyl ion concentration of the cement pastes to a level similar to that produced by a Portland cement with an equivalent alkali level. Similarly the sodium chloride and synthetic sea water had an effect on the expansion of mortars and concretes which was in line with the effect produced by an equivalent amount of alkali in the cement.

INTRODUCTION

Sodium chloride is a common contaminant of sands and gravels, especially those dredged from the sea. It is also extensively used as a deicing salt on roads. The possibility that it may enhance the alkalinity of concrete and hence may exacerbate alkali aggregate reactions is therefore a matter of importance. This paper describes the results of experiments in which the effect of sodium chloride and synthetic sea water added at the mixing stage on both the composition of the pore solution in cement pastes and the expansion of mortars and concretes containing reactive aggregates has been explored.

PORE SOLUTION COMPOSITION

The composition of the pore solution expressed from three series of pastes was determined. Each series consisted of cement paste specimens with 0.47 water/cement ratio which were cured in sealed containers for increasing periods from 28 to 50^4 days. For each series two sets of specimens were made, one set cured at 20° C, the other at 38° C. The first series was made with four Portland cements (A, B, C, D) with alkali contents of 0.67, 0.86, 0.94 and 1.06% sodium oxide equivalent respectively. The second series consisted of specimens made using cement A as base but with additions of sodium chloride, via the mixing water, such that the total calculated sodium oxide equivalent was the same as the cements in the first series together with an additional mix with 0.775% Na₂O equivalent. In the third series synthetic sea water powder (BDH to meet DEF 1053, BS 3900) was used and again additions were made to cement A in order to produce alkali levels equivalent to the Portland cements A to D plus the additional mix.



were pressed as previously described by Page and Vennesland (1983). The expressed fluid was collected in a plastic syringe and analysed for OH-, Na+, and Cl-. At each age the proportions of evaporable and non-evaporable water in the specimens were estimated by heating to constant weight at (The effect of the addition 105°C. of sodium chloride and synthetic sea water on the hydroxyl ion concentration of pastes stored for 84 days is shown in Figure 1 compared with the effect of an equivalent rise in the alkali level of the Portland cement). The free chloride ion produced by the sodium chloride addition is also shown.

After demoulding the specimens

Figure 1 Effect of chloride additions on hydroxyl ion concentrations 84 days storage. w/c = 0.47

EXPANSION OF MORTAR PRISMS

The length change of mortar prisms $(275 \times 25 \times 25 \text{ mm})$ made with the same series of cements and additions of sodium chloride or synthetic sea water was monitored. The reactive aggregate was Beltane opal, a porous opaline rock from the Beltane quarry, California. It was used in the 150 to 300 micron fraction in a proportion of 12 g per 100g cement, which is a proportion close to that found to give the maximum expansion at this level of alkali. The remaining aggregate was a crushed Carboniferous limestone. The water/cement was 0.47 and the aggregate/cement was 2.75.

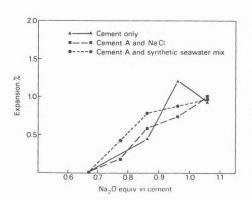


Fig. 2 Expansion at 1 year of mortar prisms made with Beltane opal. Storage temperature 38°C

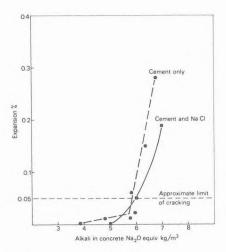
The prisms were stored in a water saturated atmosphere either at 20 or 38° C. The expansions at 1 year of mortars stored at 38° C are shown in Figure 2.

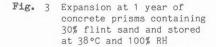
EXPANSION OF CONCRETE PRISMS

Tests have also been carried out in which the length change of concrete prisms containing a reactive flint sand have been monitored. This sand contains about 40% flint concentrated in the 1.18 to 5 mm fractions. It was used as 30% of the whole aggregate, with carboniferous limestone coarse aggregate so the flint content of the whole aggregate was about 12%. Examination of concrete from structures in the UK affected by alkali aggregate reaction and containing similar aggregate combinations together with laboratory studies (Nixon and Bollinghaus, 1983) have shown this to be a reactive

proportion. However, to demonstrate alkali reactivity under laboratory conditions with UK aggregates even those of a type known to have been used in concrete structures affected by alkali aggregate reaction it has been found necessary to subject the aggregates to highly alkaline conditions. The threshold of reactivity for this particular aggregate in laboratory tests has been found to be about 5.6 kg of sodium oxide equivalent per cubic metre of concrete.

In these tests the concrete was made with 400 kg/m³ of the high alkali cement C such that the alkali level in the concrete was 3.84 kg Na_20 equivalent/m³. The water/cement ratio was 0.45. A series of mixes was made with the concrete in which sodium chloride was added in the mixing water to give calculated Na₂0 equivalent levels of 5, 6 and 7 kg/m³.





The prisms were stored at 100% RH and 38°C after demoulding at 1 day and length change on duplicate prisms was monitored up to 1 year. The mean results of the expansion measurements are compared in Figure 3 with those in which the enhanced alkalinity was obtained by increasing the cement content.

DISCUSSION

The analyses of the expressed pore solutions show that the hydroxyl ion concentration in solution rose in line with the alkali content of the Portland cement, albeit rather erratically in some cases. Some of this erratic behaviour may reflect differences in the proportions of the total alkali present as the readily soluble sulphate compared with that in solid

solution in the cement minerals. The hydroxyl ion concentrations in the pastes to which sodium chloride or synthetic sea water was added, also increased in line with the calculated alkali level in the paste and in a roughly equivalent manner to the series of control Portland cements.

The synthetic sea water mix consistently produced more hydroxyl ions than the sodium chloride or the equivalent cement. This is understandable as in addition to sodium chloride sea water contains small amounts of potassium and sulphate ions which will also contribute to the hydroxyl ion concentration. The free chloride ion concentration increases in the pastes with higher levels of chloride addition. This increase is more noticeable at 38° C than 20° C. It suggests that the complexing ability of the aluminate phases in this cement (which has a C₃A content of 11.7%) is being exhausted. This is also shown by the tailing-off in the rate of increase of hydroxyl ion concentration at the higher alkali levels at 38° C. The sharp increase in free chloride ion corresponds to an addition of 0.3% chloride ion by weight of cement. This suggests that in concrete likely to be subjected to elevated temperatures for long periods the current BS 8110 limit of 0.4% chloride ion by weight of cement in reinforced concrete may be a little high.

The good correlation between the behaviour of cement pastes containing added chloride and the control series of different Portland cements was also found in the experiments with mortar bars containing beltane opal.

The concrete prisms containing flint sand and added sodium chloride started to show deleterious expansions at very similar levels of alkali to prisms in which the alkalinity was produced by the cement only. At higher alkali levels the expansions of the chloride-containing prisms were lower. This is to be expected, as to produce an alkali level in the concrete of 6 kg/m³ the addition level of chloride ion was 0.62% by weight of cement and to produce 7 kg/m³ the chloride added was 0.90%. At these levels there would be appreciable free chloride and hence lower hydroxyl ions levels.

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Overall then there is clear evidence that addition of sodium chloride or synthetic sea water to a cement paste, mortar or concrete at the mixing stage can result in both an elevation of the hydroxyl ion concentration in the pore solution and an exacerbation of the alkali aggregate reaction. In the UK this is being taken into account in the recommendations for minimizing the risk of damage from alkali silica reaction (The Concrete Society 1986). One of the principal recommended ways of minimizing the risk of damage from alkali silica reaction is by limiting the total alkali level originating from the cement in each cubic metre of concrete mix to no more than 3 kg of sodium oxide equivalent. However, where alkalis are contributed to the concrete from sources other than the cement it is recommended that the limit is reduced by an appropriate amount. If the source of alkali is sea salt contamination of aggregates the equivalent alkali should be calculated from:-

 $E = \frac{0.76}{100} \times (CF \times MF + CC \times MC)$

- where E = alkali contribution made to the concrete by the salt $(kg/m^3 \text{ of } Na_2O \text{ equivalent})$
- CF & CC = chloride ion content of the fine and coarse aggregates respectively as a percentage by mass of dry aggregate measured according to BS 812.
- MF & MC = fine and coarse aggregate content of the concrete (kg/m^3) .

The factor of 0.76 has been derived empirically from the chemical analyses of typical samples of sea water.

CONCLUSIONS

Introduction of sodium chloride or synthetic sea water to a cement paste, mortar or concrete at the mixing stage results in an elevation of the hydroxyl ion concentration of the pore solution to a level similar to that produced by a Portland cement with an equivalent alkali level. This in turn can increase the likelihood and severity of damage from alkali aggregate reaction, if the mortar or concrete contains a reactive aggregate, to an extent in line with the effect produced by an equivalent amount of alkali in the cement. If the alkali content of the concrete is being controlled in order to avoid damage from alkali aggregate or other source of sodium chloride should be taken into account.

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