# ELECTRON PROBE MICROANALYSES OF
## REACTION ZONES AT CEMENT/OPAL INTERFACES

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ABSTRACT

Small rectangular prisms of Beltane Opal embedded in ordinary portland cement, and cements containing 2% and 6% of NaCl were prepared in the laboratory and stored at 40°C for 7 and 28 day periods. Microscopic examination and electron probe microanalyses of reaction zones developed near the interface show that the reaction zone develops within the opal and is a composite of two or three optically distinct regions. The width of the zone increases with time and varies with the alkali content of the cement, the cement containing 2% NaCl giving the widest reaction zones. The variation of sodium and potassium as well as certain other elements across the reaction zone changes with time, but their variation is also partly dependent on the levels of sodium chloride present in the cement.

## Introduction

Since the work of Stanton[1] in 1940 a considerable volume of research work has been published concerning the nature and effects of alkali-silica reaction in concretes, and case studies have been reported from many parts of the world. As researches have progressed the mechanism of the reaction has become better understood, and the suggestion of pessimism proportions for maximum expansive reaction made by Mielenz et al[2] and recently clarified and elaborated by Ozol[3] has become an important consideration in present researches. Detailed investigations of the reaction zone between the aggregate and cement paste such as those carried out by Thaulow and Knudsen[4] have provided further information on the details of the reaction processes but have in their turn raised further problems which require explanation.

In reports of some case-study investigations it is clear that alkali-silica reactivity combines with other factors such as sulphate or chloride contamination of the aggregates to produce the deleterious effects observed[5] 7b These observations raise the possibility that the alkali-silica reaction may be modified by interaction with other reactions and processes taking place in the concrete at the same time. Alkali-silica reactivity has been reported in a number of case studies from Mediterranean and Middle Eastern countries[5,6,7] and a further example from Das Island in the Arabian Gulf is currently under investigation. The wide temperature and humidity fluctuations in these countries appears to accelerate the deleterious processes; and aggregates contaminated by chlorides or sulphates which are not uncommon in this region present a problem for the construction engineer.

In order to begin to investigate some of these problems in the laboratory a series of samples were prepared using a reactive low cristobolite opal set in cements to which sodium chloride had been added. After a storage period the progress of the alkali-silica reaction was monitored using an electron probe microanalyser.

## Experimental Procedures

The specimens used in this study were prepared from 10mm by 7mm rectangular tablets of Beltane Opal which were 2mm thick. These tablets were embedded in a cement paste with a water/cement ratio of 0.4. After a curing period of 24 hours at 20°C the small specimen blocks were stored over water in pairs in sealed containers at 40°C. Specimens 1 and 2 were

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stored together and prepared using ordinary portland cement with total alkalies 0.54%. Specimens 3 and 4 stored together had 2% by weight analar sodium chloride added to the cement at time of manufacture. Specimens 5 and 6 were similar to 3 and 4 but with a 6% addition of sodium chloride. The analyses of the cement, and a partial analysis of the opal used are given in Table 1.

TABLE 1

Analyses of cement and opal used in this study

|  | Portland Cement | Beltane Opal |
|---|---|---|
| $SiO_2$ | 20.2 | – |
| $Al_2O_3$ | 7.2 | 0.33 |
| $Fe_2O_3$ | 2.2. | – |
| $Mn_2O_3$ | 0.04 | – |
| $P_2O_5$ | 0.16 | – |
| $TiO_2$ | 0.33 | – |
| $CaO$ | 64.1 | 0.12 |
| $MgO$ | 1.3 | – |
| $SO_3$ | 2.7 | – |
| $K_2O$ | 0.41 | 0.12 |
| $Na_2O$ | 0.13 | 0.10 |
| L.O.I. | 0.8 | – |
| I.R. | 0.33 | – |

Specimens 1, 3 and 5 were removed from storage after 7 days, dessicated, impregnated with araldite and prepared as petrographic thin sections suitable for electron probe microanalysis. Specimens 2, 4 and 6 were similarly treated after a storage period of 28 days. A summary of the specimen numbering scheme is given in Table 2 below.

TABLE 2

Test specimen numbering scheme

| Type of cement used | | 7 days storage | 28 days storage |
|---|---|---|---|
| O.P.C. | w/c 0.4 | Specimen 1 | Specimen 2 |
| O.P.C. + 2% NaCl | w/c 0.4 | Specimen 3 | Specimen 4 |
| O.P.C. + 6% NaCl | w/c 0.4 | Specimen 5 | Specimen 6 |

The prepared petrographic thin sections were examined and suitable portions of reaction zone selected for electron probe microanalysis. The microanalyses were carried out using the non dispersive electron probe in the Department of Mineralogy, Cambridge. This instrument is linked to a small computer which allows spectrum stripping and correction procedure programmes to be applied to the X-ray results. The instrument provides complete analyses of 5 to 10 micron diameter areas which can be selected optically. Numerous spot analyses were made along approximately linear traverses from the cement paste through the reaction zone and into the opal.

## Results

Petrographic examination of the specimens clearly shows that the reaction zones lie entirely within the opal and appear to have developed after the cement had set. The reaction rims themselves were seen to consist of several zones. The cloudy irregular zone extending inwards for 2mm noted by Thaulow and Knudsen[4] was only clearly seen in specimen 1. However, a consistent feature of all the specimens was the development of a dark irregular zone at the inner part of the rim as seen under transmitted light. As a result of the high storage temperatures gels developed within the reaction rim tended to escape along cracks so that the specimens stored for 28 days had patchy developments of reaction product and void areas in the reaction rim areas nearest to the cement. Some of these features may be seen in the photomicrographs in Figure 1. These photomicrographs show typical areas of reaction rim and were taken in plane polarized transmitted light. The most obvious feature of the rims developed in the 6 specimens is their width variation. As expected the rims increase in size with time, and in all cases they approximately double in width under the storage conditions noted above during the 21 day interval selected in this study. It is interesting to note the comparison of the 150 micron rim developed after 8 months storage at room temperature reported by Thaulow[4] using a cement with 2.02 alkalies, and the 100 micron rim developed after 7 days at $40^{\circ}$C with a 0.54 alkali cement in specimen 1. A second feature of importance is that the specimens containing 2% of added sodium chloride exhibit wider reaction rims than those containing 6% sodium chloride.
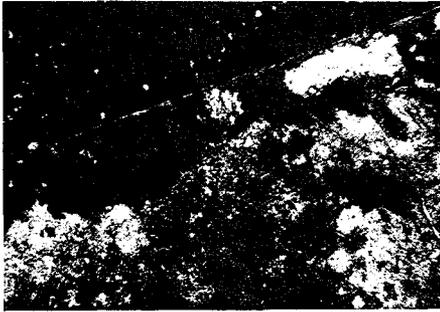
The petrographic sections were coated with carbon and between 10 and 17 individual analyses were made on each sample along a traverse perp-
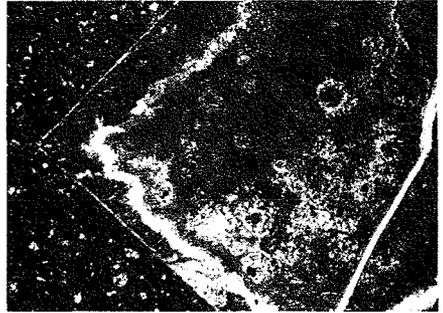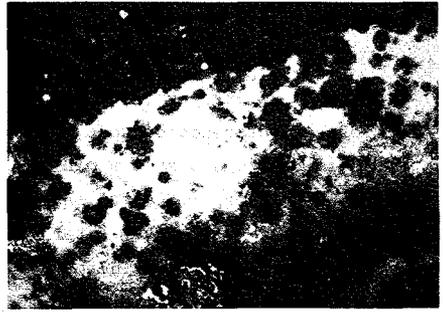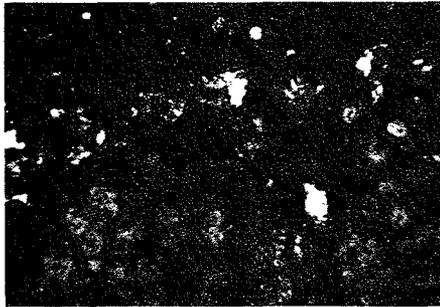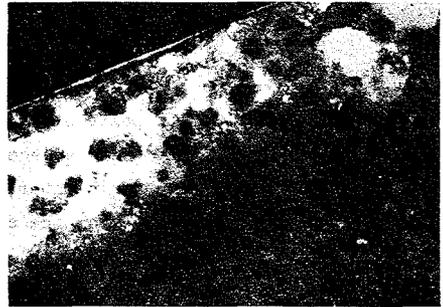
Specimen 1

Specimen 2

Specimen 3

Specimen 4

Specimen 5

Specimen 6

Fig.1
Photomicrographs of the 6 specimens used for electron probe microanalysis
The width of the field of view is 2.0mm

endicular to the interface from the cement through the reaction zone and into the unaltered opal. Of these analyses 7 were selected from each specimen and are recorded in Tables 3, 4 and 5. The additional analyses confirm that the analyses shown here are typical of the particular area in the specimen from which they come. The porous zones and void areas in the wider reaction rims were avoided so that analyses from the central part of these rims reflect the composition of the solid reaction product materials in those areas. The analyses tabulated show typical compositions of small areas in the specimens as indicated in the key to analyses. The particular spots chosen for the individual analyses appeared to be homogeneous in transmitted and reflected light but clearly must represent the composition of only the few mineral grains at the focus of the electron beam. As is to be expected the greatest variation between closely spaced analyses was observed in the cement paste areas.

The analytical results given in Tables 3, 4 and 5 have a number of features of interest, silica typically shows a gradual increase from the front of the reaction zone to the back and into unaltered opal, though specimens 2 and 3 show a minimum in the central region of the rims. These minima are also reflected in lower totals for these particular analyses and may indicate higher water contents. With the exception of specimens 1, 5 and 6 no iron was detected as having migrated into the rims and in even these specimens it was only present in the outermost rim zones. Magnesium similarly does not easily enter the reaction zone, the outermost part of the very narrow zone in specimen 1 being the only exception.

TABLES 3, 4 and 5

Electron Probe Spot Microanalyses across cement/opal reaction zones

Key to Analyses

1. Cement paste at a distance of more than 1mm from the opal

2  Cement paste adjacent (within 0.01mm) to the reaction rim

F  Reaction rim material close to the cement interface

C  Material from the central zone of the reaction rim

B  Material from the inmost part of the visible reaction rim

3  Material adjacent to but just beyond the visible reaction rim

4  Material from the central part of the opal prism

*  Total Iron as $Fe_2O_3$

**  Water and $CO_2$ are not determined by this method

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TABLE 3

Specimen 1        Width of Reaction Rim 0.10 mm

| % Oxide | Cement | | Reaction Rim | | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 13.84 | 17.07 | 29.99 | 74.10 | 76.18 | 94.22 | 94.99 |
| $Al_2O_3$ | 1.77 | 2.77 | 3.55 | 0.68 | 0.33 | 0.00 | 0.22 |
| $Fe_2O_3$* | 0.60 | 0.45 | 0.97 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.31 | 0.66 | 1.01 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 57.79 | 51.77 | 47.04 | 4.44 | 0.63 | 0.25 | 0.14 |
| $Na_2O$ | 0.00 | 0.00 | 0.00 | 1.69 | 0.80 | 0.00 | 0.00 |
| $K_2O$ | 0.00 | 0.00 | 0.00 | 3.55 | 0.81 | 0.42 | 0.00 |
| S | 0.74 | 2.15 | 2.73 | 0.51 | 0.28 | 0.19 | 0.00 |
| Cl | 0.00 | 0.00 | 0.00 | 0.09 | 0.00 | 0.00 | 0.00 |
| Total** | 75.05 | 74.87 | 78.29 | 85.06 | 79.03 | 95.08 | 95.35 |

Specimen 2        Width of Reaction Rim 0.25 mm

| % Oxide | Cement | | Reaction Rim | | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 19.37 | 17.68 | 70.62 | 64.56 | 89.37 | 97.10 | 94.35 |
| $Al_2O_3$ | 2.74 | 9.61 | 0.71 | 0.00 | 0.83 | 0.38 | 0.23 |
| $Fe_2O_3$* | 0.66 | 3.58 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.76 | 1.07 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 51.58 | 41.62 | 0.34 | 0.11 | 0.14 | 0.00 | 0.00 |
| $Na_2O$ | 0.00 | 0.00 | 0.52 | 0.42 | 0.49 | 0.00 | 0.00 |
| $K_2O$ | 0.00 | 0.14 | 0.18 | 0.60 | 0.45 | 0.40 | 0.28 |
| S | 1.02 | 1.87 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cl | 0.00 | 0.36 | 0.14 | 0.15 | 0.00 | 0.00 | 0.00 |
| Total** | 76.13 | 75.93 | 72.51 | 65.84 | 91.28 | 97.88 | 94.86 |

TABLE 4

Specimen  3          Width of Reaction Rim 0.60 mm

| %<br>Oxide | Cement | | Reaction | Rim | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 21.21 | 19.03 | 51.24 | 49.62 | 78.18 | 92.61 | 96.38 |
| $Al_2O_3$ | 3.39 | 2.97 | 0.30 | 0.21 | 0.40 | 0.30 | 0.00 |
| $Fe_2O_3$* | 0.94 | 0.55 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.75 | 0.36 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 46.56 | 47.10 | 3.01 | 0.39 | 0.35 | 0.20 | 0.20 |
| $Na_2O$ | 0.00 | 0.00 | 2.52 | 1.80 | 1.78 | 1.27 | 0.00 |
| $K_2O$ | 0.00 | 0.23 | 1.32 | 0.38 | 0.94 | 0.46 | 0.00 |
| S | 3.18 | 3.14 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cl | 1.27 | 0.85 | 0.19 | 0.17 | 0.00 | 0.09 | 0.00 |
| Total** | 77.30 | 74.23 | 58.58 | 52.57 | 81.65 | 94.93 | 96.58 |

Specimen  4          Width of Reaction Rim 1.60 mm

| %<br>Oxide | Cement | | Reaction | Rim | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 23.02 | 22.99 | 70.38 | 73.33 | 88.18 | 96.27 | 95.24 |
| $Al_2O_3$ | 2.66 | 4.99 | 0.23 | 0.00 | 0.00 | 0.40 | 0.49 |
| $Fe_2O_3$* | 0.41 | 0.66 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.28 | 0.68 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 42.61 | 43.78 | 5.65 | 0.14 | 0.11 | 0.00 | 0.00 |
| $Na_2O$ | 0.00 | 0.46 | 3.52 | 1.72 | 1.75 | 0.92 | 0.38 |
| $K_2O$ | 0.09 | 0.00 | 2.30 | 0.93 | 0.82 | 0.36 | 0.16 |
| S | 3.40 | 4.34 | 0.18 | 0.34 | 0.00 | 0.00 | 0.00 |
| Cl | 0.71 | 1.27 | 0.12 | 0.10 | 0.00 | 0.00 | 0.00 |
| Total** | 73.18 | 79.17 | 82.38 | 76.56 | 90.86 | 97.95 | 96.26 |

TABLE 5

Specimen 5          Width of Reaction Rim 0.55 mm

| % Oxide | Cement | | Reaction Rim | | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 10.06 | 15.92 | 8.93 | 55.75 | 72.48 | 90.91 | 91.99 |
| $Al_2O_3$ | 2.20 | 5.15 | 1.31 | 0.44 | 1.37 | 0.23 | 0.29 |
| $Fe_2O_3$* | 0.35 | 0.46 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.49 | 0.48 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 57.76 | 39.44 | 54.06 | 0.37 | 0.27 | 0.20 | 0.15 |
| $Na_2O$ | 0.46 | 1.24 | 0.63 | 7.96 | 3.01 | 1.46 | 1.09 |
| $K_2O$ | 0.00 | 0.32 | 0.10 | 0.68 | 0.92 | 0.33 | 0.13 |
| S | 2.08 | 3.61 | 1.37 | 0.23 | 0.00 | 0.00 | 0.00 |
| Cl | 1.52 | 2.68 | 1.28 | 0.17 | 0.12 | 0.25 | 0.36 |
| Total** | 74.92 | 69.30 | 67.86 | 65.60 | 78.17 | 93.38 | 94.01 |

Specimen 6          Width of Reaction Rim 0.90 mm

| % Oxide | Cement | | Reaction Rim | | | Opal | |
|---|---|---|---|---|---|---|---|
| | 1 | 2 | F | C | B | 3 | 4 |
| $SiO_2$ | 9.67 | 13.38 | 27.14 | 75.90 | 89.34 | 95.97 | 93.56 |
| $Al_2O_3$ | 11.56 | 7.69 | 2.11 | 0.21 | 0.66 | 0.00 | 0.23 |
| $Fe_2O_3$* | 3.05 | 2.76 | 0.18 | 0.00 | 0.00 | 0.00 | 0.00 |
| MgO | 0.66 | 1.11 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| CaO | 41.65 | 43.91 | 45.77 | 1.22 | 0.37 | 0.22 | 0.33 |
| $Na_2O$ | 0.00 | 0.00 | 1.85 | 3.32 | 1.19 | 0.55 | 0.65 |
| $K_2O$ | 0.00 | 0.14 | 0.47 | 1.25 | 0.22 | 0.15 | 0.11 |
| S | 3.37 | 4.09 | 1.01 | 0.00 | 0.22 | 0.00 | 0.00 |
| Cl | 3.84 | 3.04 | 1.73 | 0.12 | 0.00 | 0.17 | 0.14 |
| Total** | 73.80 | 76.12 | 80.26 | 82.02 | 92.00 | 97.06 | 95.02 |

Calcium however does appear to be present in concentrations above that in the opal in all reaction rims and the pattern is consistent for all specimens. In the very outermost zone of the reaction rim CaO is present in amounts comparable with the adjacent cement paste, but within a few microns of the interface the concentration drops to a few percent and in the back part of the rim zone the concentration levels are only a little higher than the trace amounts found in the opal. Although the detection limit for sodium is about 0.1% (as $Na_2O$) it is interesting to note that only sample 5 has sodium present in the cement at a distance from the interface. Several specimens contained areas with $K_2O$ present in trace amounts within the cement paste, though there is also some evidence to suggest that $Na_2O$ and more especially $K_2O$ tend to become concentrated in the cement pastes adjacent to the interface and this effect is best shown by specimen 5 in these results.

The concentration of both sodium and potassium in the reaction zones is very obvious from the tables. The variations across and beyond these reaction zones are illustrated in Figure 2. These diagrams show how the alkalies are distributed within the reaction zones and how the concentration levels change with time. Specimens 1 and 2 clearly show a dissipation of the alkalies as the reaction rim widens, while specimens 3 and 4 show a build up of both sodium and potassium in the rim over the 28 day period. Specimens 3 and 4 with 2% added sodium chloride contrast with 5 and 6 (6% added NaCl) in that these last two specimens show that sodium increases to very high concentrations in the rim at first but reduces with time. However, the potassium in 5 and 6 does not reflect the change in concentration shown by the sodium in the way that it does in 3 and 4.

## Discussion

If the addition of sodium chloride is regarded only as a straightforward addition of sodium ions to the cement, then these experiments would appear to indicate that the pessimism for alkalies in this cement with the opal used and the storage conditions of these experiments would lie between 0.5 and 3.7% total alkalies as oxides. However, the addition of sodium chloride causes complex changes in the formation of the cement minerals. As an example X-ray diffraction results show that the development of calcium hydroxide is modified by the addition of salt. Although under the conditions used in this work calcium hydroxide formation is
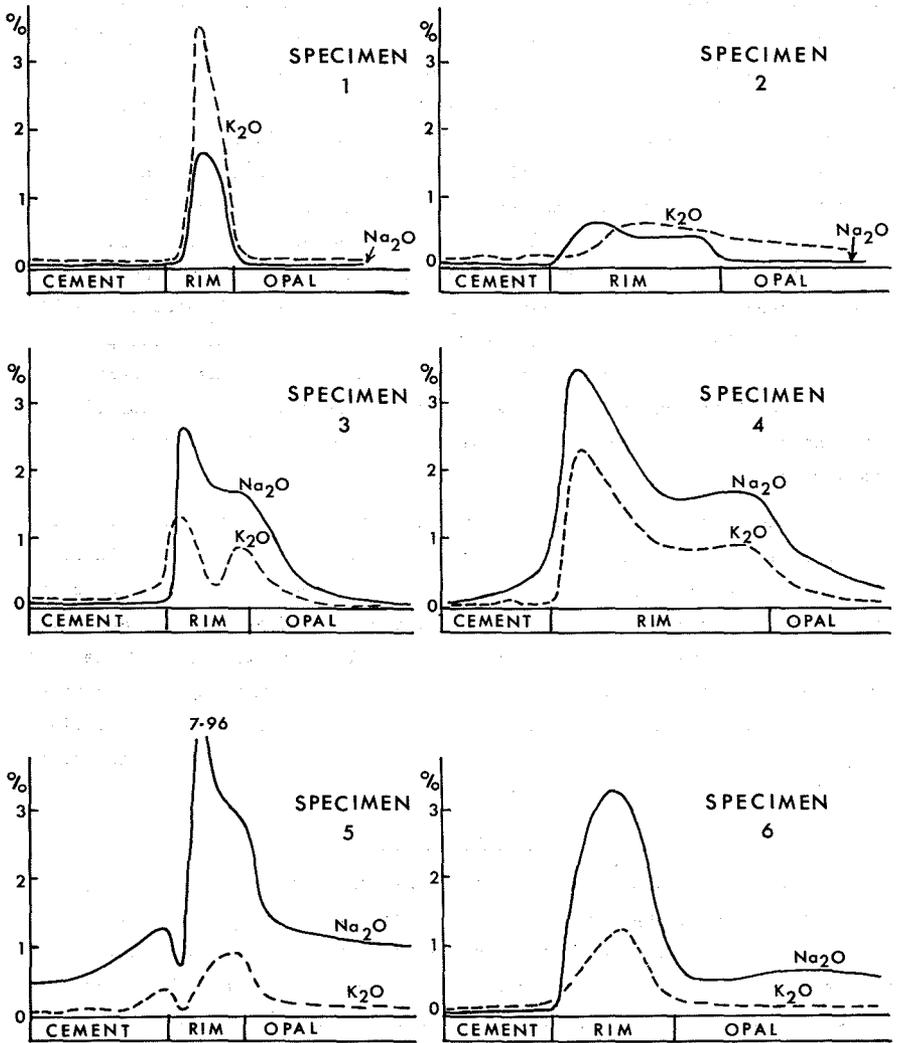
Fig. 2

Alkali variation across reaction zones

virtually complete after 7 days storage for the normal cement, calcium hydroxide is still developing at 28 days in the cements containing sodium chloride and this retardation is most marked in the specimens containing 6% additional sodium chloride. The addition also introduces chlorine to the cement, this is at first taken up in forming $C_3A(CaCl_2)H_{10}$ and similar minerals but chlorine ions are also absorbed onto the hydrates and to a lesser extent on unhydrated phases. Up to about 5% sodium chloride the chlorine can be accounted for in this way but at higher concentrations free sodium and chlorine ions may be present in pore solutions and halite may be detected in the dry cement paste. The presence of these ions will also affect the concentration of other ions notably calcium in the pore solutions and since the alkali-silica reaction progresses as a result of alkali ions being carried to the silica at the reaction site in solution any change in ionic concentrations will be reflected the progress of this reaction.

The results show that maximum local concentrations of sodium ions occur close to the reaction site within the opal reaction zones in these specimens, and as a result of these local high concentrations some calcium ions must be removed from solution[8]. The analyses of specimens 5 and 6 in particular show very high concentrations of calcium at the edge of the reaction zone and this insoluble calcium phase may form a physical barrier to the further movement of alkalies towards the reaction site thus providing an explanation for the reduced reactivity of specimens containing high alkali concentrations of this type.

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