LONG TERM DURABILITY OF GROUTS IN MARINE ENVIRONMENTS

Prepared by Imperial College for the Health and Safety Executive
LONG TERM DURABILITY OF GROUTS IN MARINE ENVIRONMENTS

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SUMMARY

As part of the Health and Safety Executive (HSE) Research Project to investigate the long-term durability of grouts exposed to a marine environment. A programme of work has been carried out on chloride penetration of grout samples and the effects on the cement paste microstructure at the Department of Materials, Imperial College, London. This has been done using a number of techniques including the backscattered electron imaging facility and image processing systems available on the scanning electron microscope.
1. INTRODUCTION

As part of the Health and Safety Executive (HSE) Research Project to investigate the long-term durability of grouts exposed to a marine environment. A programme of work has been carried out on chloride penetration of grout samples and the effects on the cement paste microstructure at the Department of Materials, Imperial College, London. This has been done using a number of techniques including the backscattered electron imaging facility and image processing systems available on the scanning electron microscope. The aims were as follows:

(a) To study a range of grout samples obtained from the HSE-funded exposure tests at Bincleaves, and other appropriate grout samples, using scanning electron microscopy techniques.

(b) To identify the relative amounts of the different phases present, the depth of the chloride penetration and the chemical nature of the surface layer formed during exposure.

(c) To investigate how the compositions of the grouts had varied with time of exposure in sea-water from early ages, and how this was affected by different grout mixes.
2. BACKGROUND

Grouts are very commonly used in offshore platform installations, in such applications as grouted steel connections and grouted sleeves, and to stiffen areas of weakness. More importantly, grouts are used for repairs where damage has occurred from causes such as impact, fatigue and general wear and tear. Grouts find applications in both steel and concrete offshore structures.

There are obvious advantages in using sea-water for the mixing water offshore and this practice is permitted by the HSE for grouted pile-sleeve connections using Portland cement grouts. It is not permitted for mixing high alumina cement (HAC) grouts or for duct grouting in pre-stressed concrete.

Sea-water has a total salinity of about 3.5% and it also contains some dissolved gases and organic matter. Of the total salt content, chloride ion concentration is about 18.85 g/l or 52% of the total ion content, while the concentration of sodium ions is about 12.21 g/l (34%) and sulphate ions about 2.21 g/l (6%). Other ions present are those of magnesium, calcium and potassium. The British Standards (BS 3148:1980) recommended limit of chlorine for mixing water is 500 ppm and this precludes the use of seawater with reinforced concrete.

2.1 THE EFFECTS OF MIXING PORTLAND CEMENT WITH SEA-WATER

Mixing of Portland cement with sea-water accelerates the reactions taking place between the compounds in cement and the sea-water [2]. This causes high early heat of hydration and results in reduced initial setting times and high early strength compared with Portland cement mixed with fresh water. The development of the compressive strength of cement and concrete mixed with sea-water has received some attention in the literature. Some of the reports have suggested a slightly higher early strength but a lower ultimate strength as compared with cement and concretes mixed with fresh water. It has been recommended that sea-water should never be used for mixing HAC. This is because the setting and hardening and the compressive strength are adversely affected as a result of reactions with the chloride ions present in sea-water [1].

Jensen [4] has studied the effect of mixing with sea-water on the microstructure of cement. It has been found that the pattern of early heat evolution was changed when sea-water rather than tap water or distilled water was used as the mixing water. Heat of hydration peaks were accelerated and enhanced, and the reduction in the induction period was attributed to the acceleratory effects of chlorides on alite hydration.

The results were confirmed by data from X-ray analysis which showed that early age hydration was accelerated. It was reported that monochloroaluminate was found as a main X-ray peak after as early as 3 days curing and it was observed consistently up to 365 days. However, this was absent in the specimens mixed with distilled water. Data obtained from DTA showed that Portland cement specimens mixed with sea-water contained increasing amount of calcium hydroxide up to about 60 days but were reduced thereafter and much more so by 365 days. From microscopic studies, it was found that the difference in the microstructure of specimens mixed with sea-water compared with those mixed with distilled water
was less noticeable after the early hydration period. However, there was a marked presence of calcium aluminates hydrates in the microstructure of the cement mixed with sea-water at all times. Apart from the work of Jensen [4] scarcely any other report on this subject was found in the literature.

The mechanism causing reactions to be accelerated when Portland cement is mixed with sea-water is still unclear. However, it is believed to be related to the effects of chlorides present in sea-water and it affects hydration and microstructural development in much the same way as the addition of chlorides used as accelerators, prior to or during the mixing of cement. It has been suggested that the attack of C₃A and C₄AF by chloride ions and the formation of chloroaluminates and chloroferrites in a divided state, may tend to provide extra sites for hydration products to nucleate [5]. It has also been suggested that the accelerated C₃A-gypsum hydration reaction leaves more free chlorides in solution, which would enhance the hydration of alite and belite. Furthermore, an adsorption complex containing chloride ions is said to form on particles, activate the surface and thereby accelerate hydration [5]. However, Jensen [4] has discounted this theory for cement mixed with sea-water. He found from X-ray analysis data that the formation of chloroaluminate and chloroferrite takes place in the period corresponding to peak 4 in the heat evolution curve, well after the hydration of alite and C₃A has been accelerated. Microstructural studies also did not show evidence of C-S-H or CH nucleating on or in close proximity to any AFm hydrates.

2.2 THE EFFECTS OF EXPOSURE TO SEA-WATER

The effect of exposure of hydrated Portland cement, mortar and concrete to sea-water is well documented in the literature. Where the structure is fully immersed, the attack on the material by sea-water is mainly chemical, but where the structure is in the tidal zone the attack is both of a physical and a chemical nature. The alternate wetting and drying, mechanical action of waves, freezing and thawing are physical processes which add to the effects of chemical attack. The microstructure of Portland cement paste fully immersed in sea-water is severely affected by chemical action of aggressive sea salts causing dissolution and leaching, and also crystallisation of salts within pores in the microstructure. The chemical action of sea-water is mainly due to the presence of MgSO₄, MgCl₂ and NaCl, and, to some extent, the presence of small amounts of dissolved CO₂ which is mainly absorbed from the atmosphere and high concentrations of which are localised within decaying vegetation.

The sulphate ions attack aluminate hydrates and to a lesser extent the ferrite hydrates in hardened current paste to form expansive ettringite. This formation of ettringite is inhibited however in sea-water because of its high solubility in chloride rich solution [3]. Magnesium sulphate also attacks the CH and C-S-H phases. It reacts with CH to form secondary gypsum and brucite, and slowly transforms C-S-H into a hydrated calcium magnesium silicate, C-M-S-H, or by direct substitution of Mg for Ca to form hydrated magnesium silicate M-S-H, which has no binding capacity [6].

Magnesium chloride is the more active of the two chlorides (MgCl₂ and NaCl) present in sea-water. The chloride ions released by the dissociation of MgCl₂ react with the aluminates present in cement paste to form monochloroaluminate. However, they tend to be unstable in sulphate rich environments or where there is a significant drop in PH, and readily convert to ettringite [7]. Reactions with CH lead
to the formation of complex salts which are soluble in sea-water. The high solubility of CH in sea-water tends to increase the likelihood of leaching. Hydrated calcium silicate, C-S-H, is also attacked and is transformed into a more porous reticular network which helps to increase permeability and reduce strength [6]. The main reaction of CO$_2$ of any importance is with CH to form CaCO$_3$, typically calcite and aragonite. However, in a Mg-rich environment, aragonite is the stable polymorph of CaCO$_3$.

The surface region of cement, mortar of concrete exposed to sea-water is altered from very early ages of exposure as a result of the formation of layers of impermeable brucite and aragonite. These layers which are known to form from as early as two days after immersion of specimens in sea-water may reach about 200 microns in thickness after two years of exposure. A description of the formation of these layers has been given by Regourd [6] and Conjeaud [7].

### 2.3 DIFFUSION OF CHLORIDE IONS INTO HARDENED CEMENT PASTE

The diffusion of chloride ions into hardened cement paste is influenced by several different factors. It is widely acknowledged that such factors as the water/cement ratio, chemical composition of cement, type and proportions of blending material, and the time of exposure to a chloride environment play significant roles [8-14]. These influence the structure of the material, its porosity and pore size distribution and therefore permeability. However, it has also been found that the rate of chloride diffusion into hardened cement pastes and concrete follows an ionic penetration process and is therefore affected by the type of cation associated with the chloride and the ion exchange capacity of the system [10-14]. The importance of the effects of "surface interaction" [9, 14] and the conditions of curing on diffusion have also been highlighted [9].

Goto and Daimon [13] in a review have described three different methods used in measuring chloride ion diffusivity in hardened cement paste. These are (i) the colorimetric measurement of chloride ions with depth of penetration which is based on precipitation and colour change using an aqueous solution of 1% fluorescent sodium salt and 0.1 N AgNO$_3$ solution; (ii) measurements using fluorescent X-ray spectroscopy, and (iii) diffusion through an HCP plate.

The diffusion coefficients of chloride ions under non-steady state conditions may be calculated from the quantity of chloride ions penetrated at various distances within the specimen:

$$D_d = \frac{-1}{2t} \cdot \frac{dx}{dc} \int_0^c x dc$$

[1]

where $D_d$ (cm$^2$/s) is the diffusion coefficient at the maximum concentration, x is distance (cm) from the boundary, and t is the time in seconds. $dx/dc$ is calculated from the slope of the chloride concentration vs distance plot and $\int_0^c x dc$ is calculated from the area under the curve. This relationship is often described as Fick's Law [8, 9, 12, 14]. In practice the situation is more complicated than this because the diffusion coefficient $D_d$ varies with the concentration of chloride ions.
3. BRIEF DESCRIPTION OF TEST PROGRAMME AT BINCLEAVES

Part of the HSE research project located at the Admiralty Research Establishment (ARE) at Bincleaves is being carried out by Wimpey Laboratories (now SLP Engineering). The aim of this group is to validate the permitted use of chloride in the mixing water in the Executive's guidance on pile/sleeve connections by investigating the effect of chloride on the steel, while at the same time making a direct comparison with sea-water mixed grouts used for repairs in the splash and tidal zones [15]. In 1983, steel tubes 15 cm (6 inches) diameter and 3 m (10 feet) long, were filled with various grout mixes. Some are fully submerged in a test tank at Portland harbour, and the tank is constantly replenished with sea-water which is fully oxygensaturated from the harbour. A second batch of specimens is mounted in the tidal zone of a jetty in the harbour. These specimens are submerged for about 10 hours each day. One specimen is being kept in constant conditions in the laboratory and serves as a control. The specimens were prepared from five different grout mixes. Details of the specimens, mixes and the conditions of exposure are given in Table 1. The parameters under investigation by the Wimpey group are steel wall thickness, bond strength by push-out tests, and compressive strength measurements on cubes.

For the work carried out at Imperial College, core samples, 50 mm diameter by 50 mm length, were obtained from the submerged zone, one from each of the five grout mixes. One core sample was obtained from the tidal zone from one of the more critical mixes. Details of the grout mixes are given in the following section.
4. EXPERIMENTAL PROGRAMME

4.1 MIX PROPORTIONS

To facilitate better understanding of the microstructure of the five year old grout specimens obtained from ARE Bincleaves, new specimens were prepared to study the process of hydration at younger ages up to 90 days. The mix proportions for the freshly prepared specimens are given in Table 2. In addition to the four mixes (a-d) in the Health and Safety Executive programme, control specimens with mixes listed (e-g) were also prepared to facilitate better understanding of the hydration processes. Mix 5 of the Health and Safety Executive programme was excluded on the advice of the sponsors.

4.2 MATERIALS

The class B Oilwell cement and the ordinary Portland cement were supplied by Blue Circle Industries. The high alumina cement was supplied by Lafarge Special Cements, and the naphthalene sulphonate Cormix superplasticiser SPIG, a water-reducing agent, was supplied by Cormix Ltd.

The oxide compositions of the class B oilwell cement and the ordinary Portland cement are given in Table 3, and the phase composition determined by quantitative X-ray analysis and by Bogue in Table 4. The oxide composition of the high alumina cement is given in Table 5 and a typical phase composition [16] is given in Table 6. Particle size gradings of the three cements were carried out using the Malvern laser particle size analyser 3600, and are shown in Fig 1. Fresh water for mixing was obtained direct from the mains and the sea-water with ionic concentration given in Table 7, was obtained through London Zoo from off the East Anglican coast.

4.3 SPECIMEN PREPARATION

Appropriate quantities of tap water or sea-water and cement to make up the water/cement ratio were hand mixed with a spatula in a plastic beaker for about 4 minutes. Where applicable, Cormix SPIG superplasticiser and calcium chloride salt were added in appropriate proportions to the mixing water prior to addition to the cement. The mix was poured into 25 mm diameter x 25 mm length plastic cylindrical moulds and compacted by means of vibration for about 60 seconds to allow trapped air to escape and to homogenise the mix. All specimens were moist cured at room temperature for 24 hours after which they were demoulded and placed in sea-water at about 23°C. The specimens designated OPCT and OBT (Table 2) were not demoulded; the covers were removed and the specimens were placed in lime-saturated distilled water about 23°C. The specimens were removed at 1, 3, 7, 28 and 90 day intervals, each was sawn in half along the transverse axis using a diamond cutting wheel lubricated with sea-water or lime saturated distilled water, as appropriate. Both halves of each specimen were placed in a methanol and solid carbon dioxide mixture to prevent further hydration and then freeze dried. One half of each specimen was resin-impregnated and polished to ¼ μm using diamond paste. A thin layer of carbon was evaporated onto the surface prior to examination in the SEM using a backscattered electron detector. From the other half a small portion was ground in an agate mill for thermogravimetric and differential thermal analysis.
The 50 mm diameter x 50 mm length core samples obtained from Bincleaves were sawn into three equal sections along the longitudinal axis using the diamond cutting wheel lubricated with sea-water. Of these sections, two were freeze dried; one was resin-impregnated, cut polished and prepared for examination in the SEM, and the other was cut into sections at the following distances from the surface exposed to sea-water, 2, 4, 6, 8, 10, 15, 20, 25, 30, 40 and 50 mm. Each of the latter was ground in an agate mill for fluorescent X-ray analysis. From the third part of the core specimen, powder samples were obtained from certain sections by drilling using appropriate size drill bits. The samples were then chemically analysed by the Volhardt titration method as described in BS 1811: Part 6: 1972.

4.4 EXPERIMENTAL TECHNIQUES AND METHODS

4.4.1 Scanning electron microscopy

Microscopic examination of samples were carried out in a JEOL JSM 35CF scanning electron microscope. The SEM is a powerful analytical tool and has been used extensively in the field of cement technology. The two most common methods of obtaining images on the SEM are secondary electron images (sei) and backscattered electron (bse) images. The secondary electron imaging mode can be used to observe individual particles or fracture surfaces, hydrate surface morphology and pore structure.

Bse images can yield information on the distribution of phases and composition of hydrated cement paste. The technique relies on the fact that the intensities of bse are dependent on the average atomic number of the scanned area, and not on minor variations of topography. A clear contrast between the phases in cement specimens can be seen, with the areas of anhydrous cement appearing bright, CH is light grey, other hydrate phases are dark grey and porosity is black.

Further details of the principles on which the techniques are based have been described elsewhere [17, 18].

4.4.2 Image analysis of backscattered electron images

Quantitative analysis of bse images obtained from the SEM was performed using a Kontron SEM-IPS image analyser, interfaced to a Link AN10000 energy dispersive X-ray analyser and to the SEM.

The Kontron image analyser is a very versatile system capable of performing a wide variety of functions, some of which have been described by Patel [18] and Jensen [4], as well as by Dilks and Graham [19]. For the purpose of this study, it was used for measuring the amounts of phases in the cement paste microstructure, namely anhydrous cement grains, calcium hydroxide, other hydration products and porosity >350 nm.

In analysing the specimens exposed to sea-water, successive fields at x400 magnification were taken from the SEM, extending from the surface of exposure to the centre of the sample. By choosing starting positions on the exposed surface, the sample could be divided into successive bands of approximately 240 µm depth. At least six measurements were taken in each measured band at distances from the surface of 240 µm, 480 µm, 720 µm, 960 µm, 1200 µm, 2 mm, 5 mm and 10 mm, on
the laboratory prepared specimens. The measurements in each band were averaged and plotted against the distance from the exposed surface and the time of hydration.

For the core samples from Bincleaves only, the chloride contents in each band were obtained using the Link AN10000 chemical analyser, by taking measurements from at least five points in each band. These were averaged and plotted against the distance from the exposed surface and the time of hydration. The depth of penetration of chloride ions into the laboratory prepared specimens was monitored qualitatively using the Link EDX analyser.

**4.4.3 Fluorescent X-ray analysis**

One of the methods used in determining the total amount of chloride ions in hardened cement paste and concretes is the fluorescent X-ray analysis technique. The distribution of chloride ions obtained using this technique is almost the same as that given by Flick's Law, because the amounts of Cl-ion which have reacted with hydrates is roughly proportional to the concentration of pre solution. In this test, a Link Systems XR500 energy dispersive X-ray fluorescence analyser was used. However, only the 5-year old specimens obtained from Bincleaves were tested using this method.

Slices were cut from the freeze-dried grout samples at distances 2, 4, 6, 8, 10, 15, 20, 25, 30, 40 and 50 mm from the surface exposed to sea-water. They were ground to powder in an agate mill. One gram of the powder was made into a pellet disc backed up in cellulose and placed in the X-ray chamber. A spectrum was collected and a ‘window’ was set around a selected peak and the exposure ended when a set number of counts had been collected in that window. Because the amount of calcium present was similar in all samples (except for the HAC), the window was set around the Ca Ka peak.

**4.4.4 Thermal analysis**

The thermal analysis technique allows the simultaneous measurement of the rate of heat evolution by differential thermal analysis (DTA) and dynamic weight loss by thermogravimetry (TG) as a sample is heated at a controlled rate. In the DTA method, chemical changes occurring in the sample are manifested as heat peaks on a temperature difference diagram. The peaks could be either endothermic or exothermic. In the thermogravimetric technique, rapid weight loss occur at the dehydration temperatures of hydrated phases. A Stanton Report type STA780 was used for the thermal analysis. The samples prepared for studying the hydration of oilwell B cement were ground to a fine powder and 40g from each was heated from 30 to 800°C at a rate of 10°C per minute in an atmosphere of CO₂-free nitrogen.

**4.4.5 Calorimetry**

The process of hydration of cement is a transformation from a high energy state to a lower one, the excess of which is evolved as heat. Observations of the heat of hydration can therefore reveal information about the chemical reactions taking place in the cement during hydration. Conduction calorimetry is a useful method for studying the hydration behaviour of different types of cement and the influence of factors such as temperature and the addition of admixtures are clearly indicated.
The heat evolutions from all the cement mixes were measured in a Wexham Instruments isothermal conduction calorimeter at 20°C, using 10 g samples and appropriate amounts of mixing water and admixtures. They were hand-mixed in polythene bags outside the calorimeter for 3 minutes.

4.4.6 The microstructure of unhydrated cement

Both the Blue Circle ordinary Portland cement and the Oilwell B cement displayed similar microstructural features in the anhydrous state, as can be seen in Figs 2 and 3 respectively. In both cases, it can be seen that the cement grains showed a wide size range. However, the OPC had a larger amount of smaller sized grains, in agreement with the particle size analysis of Fig 1. Some agglomeration of the smaller particles was observed in both cements.

Microstructural features of the anhydrous high alumina cement grains differ significantly from those of the OPC and Oilwell B cement, as the backscattered image of Fig 4 illustrates. The phase distribution in the anhydrous HAC grains is different because it is produced via a crystallisation process from the liquid phase. Fig 4 shows that most of the grains are multiphase, with a significant amount of monocalcium aluminate (CA) which is dark grey in colour and a mixture of other minor phases which are lighter in colour. There are also some single phase grains which are either CA or pleochroite. The particle size distribution of the anhydrous HAC grains does not differ much from that of the Oilwell B cement, again in agreement with the results of Fig 1.
5. RESULTS

5.1 HEAT OF HYDRATION

5.1.1 Oilwell B cement

The rate of heat evolution during the hydration of the neat Oilwell B cement mixed with tap water at a water/cement ratio of 0.34 (OBT), is compared with that of OPC of a similar mix proportion (OPCT) in Fig 5. The heat output curves for both cements are essentially the same, with similar maximum heat peaks occurring about 1 hour apart (Table 8). The reaction of the Oilwell B cement was fractionally delayed due to the slightly longer induction period, and therefore shifted to the right of the OPCT curve in Fig 5. The major heat peaks (2nd heat peaks) in both cements occurred between 2 and 30 hours and can be attributed principally to the alite phase in the cements hydrating to C-S-H and calcium hydroxide.

In the case of the OPCT, there is evidence of a second peak superimposed on the main peak which can be associated with renewed reaction of C₃A to form AFt [20]. There is also some evidence of a second peak in the OBT but this is less well defined due to the low C₃A content of the Oilwell B cement used in this study. C₃A and gypsum contents, composition of the surfaces of the cement grains, grain particle size and the nature of the mixing, all play a role in determining the length of the ‘induction period’. The significance of the interstitial phases (A/F) in the formation of ettringite can be linked indirectly with the length of the induction period. It has been suggested [21] that most of the heat liberated during the formation of ettringite arises before the occurrence of the second heat peak, namely during the period of the first heat peak and of any supplementary peaks prior to the second heat peak. The low ratio of aluminate phase to ferrite phase (A/F) of the Oilwell B cement relative to the OPC (Table 3) may have contributed to the longer induction period of the OBT paste.

5.1.2 Mixing with sea-water

The rate of heat evolution of Oilwell B cement mixed with sea-water (OBS) at a water/cement ratio of 0.34, is shown in Fig 6 in comparison with that mixed with tap water (OBT). The pattern was changed for the sea-water mixed sample (OBS) which showed a faster rate of reaction, a significantly higher peak 2 reached about 1 hour earlier than for the OBT (Table 8) and the formation of a distinct third heat peak at about 10 hours. Figure 6 also shows evidence of a fourth peak between about 30 and 45 hours, although this was broad and weak. The significant increase in peak 2 is an indication that alite hydration was accelerated as a result of mixing with sea-water. The formation of a distinct peak 3, which was less well defined in the OBT paste, suggests the hydration of C₃A in reactions with the chlorides present in sea-water to form trichloroaluminates and ettringite despite the low C₃A content of the cement. The formation of peak 5 can be associated with the formation of monochloroaluminate [6,7] and monosulphate.
5.1.3 Superplasticiser

Examination of the rate of heat evolution curves of Fig 7 show that the addition of a polymeric sulphonate, Cormix SPIG superplasticiser (2% by weight of cement) to the mix resulted in extended induction periods and reduced heat peaks for the Oilwell B cement mixed with tap water (OBTC) and that mixed with sea-water (OBSC). For both the OBTC and OBSC pastes, the effect of the superplasticiser was of similar proportions relative to the OBT and OBS pastes respectively, in terms of the extended induction periods and reduced heat peaks (Table 8). However, it has been observed that retardation refers to a slowing down of setting or thickening, not to a slowing down of all chemical reactivity [21]. By measuring the first heat peak during the hydration of Portland cement containing a calcium lignosulphonate retarder, Bensted [21] had found that the first heat peak was increased in comparison with that of a neat cement slurry. Although the second heat peak was delayed and reduced in comparison with the neat cement mix, there was an overall increased heat evolution. He concluded that the overall chemical reactivity in the presence of the retarder had increased, not decreased. The inability to measure accurately the first heat peak with the system used in this study has made it difficult to test this hypothesis. The mechanism whereby the hydration process is delayed is as yet unknown, but has been found to vary with the type of admixture used [21, 22]. For inorganic salts like those of Pb and Zn, retardation is associated with the precipitation of dense and impenetrable coatings of hydroxide gel around the cement grains [23]. The rate of hydration depends on the permeability and cohesion of these coatings, and it is the nature of the modification of the colloidal gel by the admixture which will determine whether hydration is accelerated or retarded [22]. In the case of organic admixtures, the general conclusion seems to be that the chemistry of precipitation of C-S-H gel is altered by preferential complexation of Ca and/or Si either in solution or by incorporation into the precipitated gel. This leads to less permeable and more adhesive gel coatings forming around the cement grains, and results in a retardation of hydration [22].

5.1.4 Added chloride

The addition of calcium chloride (2% by weight of cement) to the mix had a dramatic effect on the rate of heat evolution of the Oilwell B cement mixed with sea-water and containing the Cormix superplasticiser (OBSC2), as can be seen in Fig 8. The Cormix superplasticiser had delayed slightly the onset of the main reactions, however the induction period was short and was much less than for the comparative OBSC mix which had no added chloride (Table 8). Similar to the other Oilwell B cement paste mixes, the major peak (2nd heat peak) occurred between about 5 and 30 hours, appearing to reach a maximum (extending for about 7 hours) between 9 and 16 hours. The maximum measurable rate of heat evolution of about 16 W/kg is some four times the maximum evolved in the case of the OBSC paste, and more than three times that evolved by the OBS paste (see Table 8). However, the response of the calorimeter sensors appears to have been saturated at these high rates of heat output. There is no distinct third peak, and this had probably overlapped with the 2nd peak, but there seems to be some evidence for a peak between 40 and 50 hours which is broad and weak and is probably due to the reactions of the C₄AF phase. Even after 55 hours, the rate of heat evolution was still quite large at about 2.5 W/kg.
5.1.5 High alumina cements

The rate of heat evolution during the hydration of the neat high alumina cement (HAC) mixed with tap water (0.4 w/c) at 23°C is shown in Fig 8 and the heat output data are given in Table 8. There is a major peak between 4 and 15 hours, due to the hydration of monocalcium aluminate (CA) to form principally CAH$_{10}$, alumina gel and some C$_2$AH$_8$ [24]. The heat output reached saturation at a peak of about 13 W/kg after about 5 hours. The maximum heat evolved, although less than that for the OBSC2 paste, is still very high and is more than four times that obtained for the OPC and Oilwell B cement pastes mixed with tap water. The time of the maximum heat peak obtained in this study coincides with the time of peak temperature rise of between 6 and 7 hours after mixing, observed for high alumina cement studied by means of adiabatic calorimetry [25]. Furthermore, Halse and Pratt [24] in their study of the development of microstructure in high alumina cement on the SEM, had observed that the hardness of the paste increased significantly after 6 hours, as large amounts of hydrates form. This indicates that the reactivity of the CA phase reaches a peak about 6 hours after mixing. In fact Rodger and Double reported that at the time of the rapid temperature rise the paste became too hot to touch and had generated steam [25], putting into perspective the high heat peak of 13 W/kg over the period 5 to 62 hours after mixing as shown in Fig 8.

5.2 THE DEVELOPMENT OF MICROSTRUCTURE DURING THE HYDRATION OF OILWELL B CEMENT

The development of the microstructure during hydration of the Oilwell B cement mixed at a water/cement ratio of 0.34, has been followed by measuring the relative areas, and thus the volumes, of the different distinguishable phases in the microstructure using the image analyser. The changing proportions of the anhydrous cement, calcium hydroxide, C-S-H and other products, as well as porosity >350 nm, are shown in Fig 9 as functions of the time of hydration up to 90 days. The changing proportions of the products of hydration with time, of an OPC paste of similar water/cement ratio are shown in Fig 10. The results of Figs 9 and 10 are similar and follow the expected trends. As the anhydrous cement had reacted with the mixing water and reduced in volume, calcium hydroxide, C-S-H gel and other products had formed increasingly and occupied the water filled spaces. Correspondingly, the coarse porosity >350 nm in the paste had reduced.

Comparison of the results of Figs 9 and 10 for the Oilwell B cement paste and the OPC paste respectively show that after 1 day there was a larger amount of unreacted cement and greater porosity in the former, compared with the latter. In addition, the results show that there was more calcium hydroxide in the OPC paste than in the Oilwell B cement paste at all ages. The TG results of Fig 11 show a broadly similar trend.

5.3 VOLUME PROPORTION OF PHASES IN SPECIMENS EXPOSED TO SEA-WATER (SUBMERGED CONDITIONS)

The relative areas, and thus the volumes, of the different distinguishable phases in the microstructure, observed in a given field at x400 magnification, have been measured using the image analyser. Measurements were obtained at intervals, as described earlier, from the exposed surface to depths of up to 10 mm in the laboratory prepared specimens and 40 mm in the core specimens from Bincleaves. The relative volume proportions of the different phases have been plotted against
distance from the exposed surface, for each age of storage in sea-water. The results are shown for each of the four mixes, HAC, OBTC, OBSC and OBSC2, in Figs 12 to 15 respectively, and are given below for each of the measured phases. Results of measurements of the phase composition of the only specimen obtained from the tidal zone, from the OBSC2 mix, are given in Fig 16. In Figs 12 to 16 the depth scale for the 5 year old specimens is about four times greater than that for all the other ages, owing to the larger size of these specimens.

5.3.1 Porosity

The results of Figs 12 to 15 for the four mixes show a general trend of decreasing degree of porosity in the specimens, with increasing distance away from the surface. Furthermore, the amount of porosity decreased with increasing duration of exposure to sea-water. Irrespective of age, the total porosity decreased rapidly from the region of the surface to about 2 mm depth into the specimen. Beyond this depth there was very little variation in the measured total porosity, which became almost constant. The trend was similar for the OBSC2 specimen from the tidal zone (Fig 16).

In comparing the four laboratory mixes for specimens submerged in seawater, the HAC specimens mixed with fresh water (Fig 12), had a significantly lower degree of porosity than the other mixes. This exhibited the lowest total porosity at all ages, and showed very compact microstructures, even in regions close to the sea-water. The mean relative volume of porosity at depths beyond 1 mm decreased from about 5.3% at 1 day to about 2.5% at 28 days and 0.27% at 90 days, for the laboratory prepared specimens (Figs 12a to 12e).

The OBTC specimens mixed with fresh water (Fig 13), exhibited the largest degree of porosity at all ages and they were also the most adversely affected as regards the degree of porosity at the regions around the surface of exposure. The mean relative volumes of porosity at depths beyond 1 mm for this mix were about 12.5%, 6.4% and 5.2% at 1, 28 and 90 days respectively, for the laboratory prepared specimens (Figs 13a to 13e), and about 3.1% for the 5 year old specimen from Bincleaves (Fig 13f). The porosities of the two Oilwell B cements mixed with sea water, OBSC2 and OBSC, with and without added chloride respectively, were fairly similar at 1 day and also after 5 years of exposure; but the relative volumes of porosity in the period between 28 and 90 days were lower in the OBSC than in the OBSC2. For the laboratory prepared OBSC specimens (Figs 14a to 14e), the means from below 1 mm depth were about 6.75%, 2.7% and 2.5% at 1, 28 and 90 days respectively, and about 2% for the 5 year old specimen (Fig 14f). These compare with about 6.6%, 3.9%, 3.2% and 1.9% at the same ages for the OBSC2 (Figs 15a to 15f).

The porosity in the 5 year old specimens from Bincleaves followed the expected trend of lower relative volumes of porosity with age and with distance from the exposed surface. The exception was the HAC mix for which the porosity was higher than at earlier seen in the SEM, as will be shown later. Exposure to the tidal zone had not caused any significant difference to the degree of porosity of the OBSC2 specimen at depths beyond 1 mm from the surface, compared with the specimen from the submerged zone. The porosities beyond this depth were closely similar for both specimens. The absence of the surface covering of about 1 mm depth from the specimen from the tidal zone has not permitted comparison of this critical region.
5.3.2 Calcium hydroxide

Calcium hydroxide is not present in detectable quantities in hydrated high alumina cement. The results presented are therefore only for the three Oilwell B cement mixes.

The relative volumes of calcium hydroxide present in the three different Oilwell B cement mixes are shown in Figs 13 to 15, for each age of exposure to sea-water. The results show that there is a clear negative correlation between the degree of porosity with depth of the specimens and the amounts of calcium hydroxide formed. As the degree of porosity decreased away from the surface, the amounts of calcium hydroxide present increased to reach a maximum (porosity being a minimum) about 2 mm into the specimen and both had stabilised thereafter. The trend was similar in the tidal zone (Fig 16). For each mix, the variations in the amounts of calcium hydroxide formed in the core region of the specimens (i.e. from about 2 mm away from the surface) with time, were much less compared with the variations observed in the exposure zone (up to 1 mm from exposed surface). In the latter, the amounts of calcium hydroxide had reduced with time and with depth into the specimens. In some cases, particularly for the OBTC specimens, calcium hydroxide was not observed even at depths of up to 500 mm from the exposed surface.

The average relative volume of calcium hydroxide present in the specimens at each age, has been calculated for each mix and plotted against the duration of exposure to sea-water in Fig 17. The results for the laboratory prepared specimens (up to 90 days) show a trend of decreasing amounts of calcium hydroxide with time. The average relative volume of calcium hydroxide was lowest for OBSC2 at all ages, decreasing from about 5.6% at 1 day to about 3.6% at 90 days. The amounts were closely similar for the OBTC and OBSC, with averages of 6.6% and 6.9% respectively at 90 days. The overall averages in the 5 year old specimens (submerged), calculated up to similar depths to the laboratory prepared specimens, were 6.56%, 3.67% for the OBTC, OBSC and OBSC2 mixes respectively. If the surface 1 mm is excluded, comparison of the calcium hydroxide contents with depth for the OBSC2 specimens from the submerged and tidal zones, showed that there is very little difference between the two. The averages over the entire depth (excluding the surface 1 mm) were 5.84% and 5.68% for the specimens from the submerged zone and tidal zones respectively.

5.3.3 Anhydrous cement

The relative volumes of anhydrous cement present in the microstructure are shown in Figs 12 to 15 for each mix and at all ages. The results show that, at each age, the variation of the relative volume of anhydrous cement with distance from the surface was not significant. Similar relative amounts of anhydrous cement were found at all depths, for each mix. The trend was similar for the OBSC2 specimen from the tidal zone (Fig 16). However, the results also show decreasing anhydrous cement contents with duration of exposure for all mixes. This trend is seen more clearly in Fig 18 which is a plot of the mean of relative volumes of anhydrous cement for each age, against the duration of exposure to sea-water. The degrees of reaction of the mixes had differed, with the OBSC2 mix reacting faster than all others throughout the duration of exposure to sea-water (Fig 19). This was closely followed by the OBSC mix, but less rapidly by the OBTC mix. The degree of reaction of the high alumina cement (HAC) mix has not been estimated, firstly because there is no available data about the apparent particle density which is needed in the calculations,
and secondly because of doubt about the accuracy of the method used in measuring the high alumina cement content, as will be discussed later. In general, the relative volumes of anhydrous cement in the microstructure, for all mixes, decreased from about 21-25% at 1 day to 14-21% at 28 days and 14-18% at 90 days.

The proportions of unhydrated cores in the 5 year old specimens were about 10-17%, with the OBTC specimen containing the largest amounts of unhydrated cores and the OBSC2 specimen the least. Again, as with the other phases, there was very little difference between the contents of unhydrated cement of the OBSC2 specimens from the submerged zone and the tidal zone, with averages of 10% and 9% respectively. The difference of about 1% is not significant.

5.4 DEPTH OF CHLORIDE PENETRATION

The total chloride contents in the slices cut from the 5 year old submerged specimens, measured using the fluorescent X-ray method, have been plotted against the depth of penetration from the surface in Fig 20. The results show a trend of diminishing chloride content from the surface region, into the interior of the specimens. The total chloride content was highest in the first 20 mm of the HAC specimens, varying from about 2.3% at the surface to 0.7% at a depth of 50 mm.

The OBTC specimen had the lowest concentration of chloride ions varying from about 0.2% at the surface to zero from about 25 mm depth. Chloride contents in the sea-water mixed specimens, OBSC and OBSC2, were higher and decreased slowly with depth. The OBSC2 specimen with the higher chloride levels, varied between 1.4% near the surface and 1.1% at 50 mm depth, while variations in the OBSC specimen were between 0.6% in the surface region and about 0.3% at the 50 mm depth. In all cases, except possibly the HAC specimen, the maximum chloride level was not at the surface. Rather, the chloride ions accumulated within a region of about 4-6 mm from the surface, where they reached a maximum, after which the chloride levels decreased. This is confirmed by the data obtained from EDX analysis. The results obtained using the EDXA followed a similar trend to those obtained with the XRF, however the chloride contents as measured by the EDXA were generally higher, in some cases by about 30%. Several factors are known to affect the accuracy of the EDX method when it is used in the analysis of cement paste microstructure, but these will not be discussed here. The data obtained using the XRF method are believed to reflect more closely the chloride levels in the specimens. The results were within 5% of those obtained from samples taken at random depths from the different specimens and chemically analysed using Volhardt’s titration method.

Comparison of the chloride levels with depth in the OBSC2 specimens from the submerged zone and the tidal zone in Fig 2.1, show that there is no significant difference between the two curves. The absence of data from the 1 mm depth in the specimen from the tidal zone is not considered as significant since it has been shown that the maximum chloride level is reached at depths of up to 4-6 mm from the surface.
5.5 THE NATURE OF THE SURFACE LAYERS AND THE DEVELOPMENT OF MICROSTRUCTURE AFTER EXPOSURE TO SEA-WATER

5.5.1 Laboratory specimens

(a) Surface layers

Visual inspection showed that a thin skin had formed on the surface of the laboratory prepared specimens after 1 day of exposure to seawater. This appeared as a mist on the surface of the HAC specimen, but was clearly evident as a thin surface skin on the Oilwell B cement specimens, particularly those mixed with sea-water and on the OSBC2 specimen (containing 2% added CaCl₂). The surface formations became thicker and firmer on the specimens with age, although it still appeared as a thick mist on the HAC specimen, even after 7 days. However, a well-formed skin was evident by 28 days. Backscattered electron images of the surface layers are shown in Fig 22, (a) on the OBSC specimen at 3 days, (b) on the OBTC specimen at 7 days, (c) on the OBSC2 specimen at 7 days, and (d) on the HAC specimen at 90 days. Chemical analysis of this surface using the EDXA indicated that for the Oilwell B cement specimens, this layer is predominantly brucite \( \text{Mg(OH)}_2 \) but also contains aragonite \( \text{CaCO}_3 \). The thickness of the brucite layer around the surface of a specimen at any age is variable, but it increased with the duration of exposure to sea-water from between 40-70 mm at 3 days to about 160-200 mm at 90 days. EDX analysis of the surface skin on the HAC specimen at 90 days indicated that in addition to brucite and aragonite, there was a notable presence of Al ions, which may indicate the presence of a mixed magnesium-aluminium hydroxide. The thickness of the layer on the HAC specimen 90 days varied between 20 and 30 mm. There were signs of distress on the surface of the OBTC and OBSC2 specimens from about 3 days and longitudinal cracks could be seen forming along the length of the specimens starting from the top and bottom edges. The cracking increased with the duration of exposure and was widespread in the surface region as can be seen in Figs 22b and 22c. However, the cracks had not spread beyond a depth of 1 mm.

(b) Microstructure of HAC

Hydration of the HAC specimen was rapid and, 24 hours after exposure to sea-water, the microstructure was denser than in any of the Oilwell B cement specimens. Even in the region near the surface, where the Oilwell B cement specimens had a high degree of porosity, in the HAC specimen porosity was much lower. The backscattered electron image of Fig 23a shows the microstructure of the surface region of HAC specimen 24 hours after exposure to sea-water. A dense alumina gel had formed to fill up virtually the entire space previously occupied by water. However, there is a network of fine cracks which had formed, probably as a result of drying shrinkage. Hydration rims, some of which are thick, can be seen forming around most of the anhydrous high alumina cement grains, but there were also a number of hollow-shell or Hadley grains. A closer look at some of the multi-phase grains shows that dissolution of CA may be taking place from the surface of the grains. Near the centre of the micrograph, some of the anhydrous material seems to have hydrated almost completely, leaving relicts of multiphased grains. The differing contrasts of the dense gel structure are an indication of the presence of the different crystalline hydrates formed. As the sea-water attack progressed with age, the smooth gel structure of the HAC specimen seen at 1 day
(Fig 23a) became disturbed as chloroaluminates formed; more cracks could be seen and the microstructure seemed to have become slightly porous (Fig 24a). By 90 days (Fig 24b) most of the smaller high alumina cement grains had completely reacted and only relicts of the multiphased grains could be seen. At this age a porous band 60-70 mm thick could be seen just below the surface as shown in Fig 22d. This porous band resembles the interior of the Bincleaves HAC specimen exposed to sea-water for 5 years (Fig 26a), and is probably due to conversion to the cubic $C_3A_{H_6}$ Monochloroaluminate can be seen in the band due to continued hydration with sea-water.

(c) Microstructure of Oilwell B cement

The backscattered electron images of Fig 23b-d show the microstructure of the surface regions of the Oilwell B cement specimens after 1 day in sea-water. There is a high degree of porosity in all cases, although this was slightly less in the interior of the specimens (from about 1 mm depth). Reaction rims of C-S-H could be found around almost all the cement particles, with the formation of a large number of Hadley grains. Large amounts of CH can be found in the OBTC specimen (Fig 23b), but less in the OBSC specimen (Fig 23c) and very little in the OBSC2 specimen (Fig 23d). It seems that a significant amount of CH had been leached out in the surface region of the specimens which were mixed with sea-water, in particular the OBSC2 specimen mixed with added chloride (Fig 23d). This specimen had a high degree of porosity and a network of open pre structure which indicates that other soluble products of the reactions with sea-water have also been leached out of the surface region. Nevertheless, the microstructure in the interior in all cases was denser with more regions of CH and C-S-H.

The microstructure in the interior of the Oilwell B cement specimens became denser with age, and was similar for all the specimens. The decreasing water space had been filled by CH nucleating around and between cement grains and by more C-S-H. After 28 days the microstructure was more closely packed and rims of C-S-H 10-15 mm across could be seen around the remaining large anhydrous cement grains. By 90 days a marked densification had taken place (Fig 25), most of the pore spaces visible at younger ages had largely vanished and only a few discontinuous pore spaces could be observed. However, the porosity at the surface region had increased, and large transverse cracks had formed parallel to the surface, particularly in the OBSC2 specimens (Fig 25d). In this zone, significant amounts of leaching had occurred and no trace of CH could be seen.

5.5.2 Five year old specimens from Bincleaves

(a) Surface layers

Unlike the laboratory specimens, whose history was well-known, little evidence of coherent surface layers could be found on the specimens from Bincleaves. A brucite layer was observed only on the OBTC specimen that had been immersed in sea-water for five years. Marine growth was found on the exposed surface of the grouts and this had been cleaned off to enable the coring to be carried out. It is possible that this cleaning operation had removed the surface layers from the other remaining specimens or, alternatively, that the marine growth itself had been responsible for its absence. The surface regions of the Bincleaves specimens were
not as porous as might have been expected, probably because of the protection of the surface by the marine growth.

(b) **HAC specimen**

The 5 year old HAC specimen contained some 10% porosity >350 nm compared with only 0.27% for the 90 day old laboratory specimen, with more porosity in the interior than around the surface as shown in Fig 12f. There was a lot of cracking in the interior, where many of the anhydrous grains had hydrated completely and the remains of the bigger polymineralic grains could be seen (Fig 26a) in the porous matrix. The control specimen of HAC, which was moist cured for 28 days and then stored in air for 5 years (Fig 26b), showed an even higher degree of porosity, with very limited contact between individual particles. This control specimen, provided by Wimpey Laboratories, was in the form of a cylinder 6” in diameter and dark brown in colour, from which a small sample was cut. A noticeable difference between the specimen stored in sea-water, Fig 26a, and that in air, Fig 26b, is the presence of a lamellar phase resembling monochloroaluminate around the remaining anhydrous grains. This appears to have formed as a result of continuing hydration in the sea-water, reducing the volume fraction of coarse porosity from about 20% in Fig 26b to 10% in Fig 26a. These porosities are very much greater than the 0.27% found in the laboratory specimen immersed for 90 days, in Fig 24b.

(c) **Oilwell B cement specimens**

The microstructure of the 5 year old Oilwell B cement specimens was dense with only a few pockets of discontinuous pore spaces (Fig 27). Thick rims of C-S-H could be seen around cores of hydrating cement grains, of which quite a few still remain. The microstructure of the OBTC and OBSC specimens was denser than that of OBSC2. Similar hydration products were present in all the specimens. Large regions of the interior were occupied by CH, C-S-H and other products. In some cases the remains of polymineralic grains could be seen.

For the pastes mixed with tap-water, OBTC, Figs 13e and 13f showed a significant reduction in the porosity between 90 days and 5 years. This reduction is clearly visible on comparing Fig 25a with Fig 27a. A similar but smaller reduction in porosity was found for the sea-water mixed specimens OBSC in Figs 14e and 14f and this is confirmed in the micrographs of Fig 25b and Fig 27b. With the addition of 2% CaCl₂, OBSC2 shows the lowest porosity of all the laboratory specimens after 90 days, both in Fig 25c and in Fig 15e.
6. DISCUSSION

6.1 THE DEVELOPMENT OF MICROSTRUCTURE IN OILWELL B CEMENT AND OPC AT W/C = 0.34 AND 23°C

At a w/c ratio of 0.34, the microstructure of the hardened cement paste became relatively dense, even at early ages. By 90 days, the porosity >350 nm was less than 5% in all the mixes, although the importance of prolonged curing is apparent from Figs 9 and 10. For Oilwell B mixed with tap water (Fig 9), this porosity drops by a factor of eight with curing extended from 1 day to 90 days, whereas for OPC the decrease is less than a factor of four. This reflects the increased C3S content of the Oilwell B cement compared with OPC. The effect of mixing with sea-water is to accelerate the hydration in agreement with earlier work and the increase in peak 4 in the calorimeter output suggests very strongly the formation of chloroaluminates phases. Their presence is not easily detected in the micrographs of Oilwell B at low magnification although they can be seen in OPC mixed with sea-water after 1 day where their identity was confirmed by X-ray diffraction and by X-ray microanalysis [4]. The lower C3A content of the Oilwell cement would be expected to give rise to the formation of less chloroaluminate than with OPC, in agreement with Conjeaud [7]. However her mortar made with cement D, which contained no C3A at all by Bogue calculation, still produced significant quantities of calcium chloroaluminates presumably from the C4AF.

The degrees of hydration found for the laboratory specimens of Oilwell B cement (Fig 19), at ages of up to 90 days are relatively low because of the low w/c ratio of 0.34. OBTC, mixed with tap-water has the lowest degree of hydration at 62% after 90 days and this increases only slightly after 5 years. Sea-water mixing, especially with added chloride, leads to a significantly higher degree of hydration and after 5 years this increased to 80% for specimens of OBSC2. While the degree of hydration increases, the relative volume of calcium hydroxide appears to decrease with time of immersion (Fig 17). Only the 5 year old specimen of OBTC appears to reverse this trend. OBSC2 has the lowest amount of calcium hydroxide at all ages, suggesting that leaching may have been more significant in this material. Unlike other workers, Conjeaud [7] found that no leaching of CaO occurred from her mortars for up to 3 years and she attributed the consumption of calcium hydroxide, which she found for some cements, to a partial decomposition of stoichiometric ettringite leading to an ettringite containing up to 50% SiO₂ and some chlorine.

6.2 The development of microstructure in HAC

At a w/c ratio of 0.4, the microstructure of the laboratory specimens of HAC was denser than that of the Oilwell B specimens at all ages. The contrast between the dense laboratory specimens and the more porous 5 year old specimens from Bincleaves and from Wimpey (Fig 26a and b) was due to the conversion of the hexagonal CAH₁₀ and C₂AH₈ hydration products to the cubic C₃AH₆. Complete conversion, which leads to an increase in porosity of about 20% was confirmed in the control specimen stored in air at Wimpey Laboratories, using differential thermal analysis. The brown colour of this specimen and the level of porosity >350 nm can be explained by the conversion and it would appear from Fig 26a that the grout specimen cast at Wimpey Laboratories and subsequently immersed for 5 years at Bincleaves was fully converted also before immersion. The result of the immersion has been to continue the hydration of the remaining larger particles of anhydrous HAC, filling part of the porosity left by the conversion with at 23°C by Halse and
Pratt [24] using X-ray diffraction techniques. Midgley [26] states that HAC concrete exposed to sea-water will convert very slowly by up to 15% in 34 years whereas Neville [16] suggests that ‘for the more porous concretes of practical mix proportions, the periods are much shorter as full conversion has been observed after some 20 years at 20°C or thereabouts’. The rate of conversion increases rapidly with temperature and for HAC pastes Midgley [27] found 50% conversion after less than one day at 60°C. An upper limit to the temperature of the Bincleaves grout specimens can be estimated using the figures quoted by Neville [16] for the heat of hydration of HAC of 77-93 cal/gm at one day. The Bincleaves specimens were made with neat HAC at w/c=0.4, cast in 6” diameter steel tubes, 10 ft long and with a wall thickness of 0.75”. If we assume that all of the heat generated by the exothermic reaction is used to warm up the HAC paste and the steel mould adiabatically, the upper limit of temperature is 134°C above room temperature, i.e. about 154°C. This is in keeping with the observation by Rodger and Double [25] of steam being generated under adiabatic conditions 6-7 hours after mixing HAC in a test tube. Such a temperature is sufficient to ensure complete conversion to C₃AH₆ within 24 hours.

This finding of complete conversion in HAC grout cast in a 6” diameter steel tube is at first slightly surprising and somewhat unexpected. Further specimens have been cast in a variety of small diameter metal and plastic tubes and an increase in temperature up to 130°C was measured. Two points of interest emerge. The temperature rise occurs after 6-7 hours and so would only be observed if the grouts were cast very early in a normal 8 hour working day; for the specimens cast at Wimpey Laboratories it has not been possible to establish when they were cast. Secondly we have assumed no loss of heat either axially or radially beyond the outer wall of the steel tube. The tubes were sufficiently long for there to be no loss axially except close to the ends. Radial loss from the walls of the cylinder will take place but the hydration products of both HAC and OPC are not good thermal conductors. Littlejohn and Hughes [28] have measured temperatures of 105°C only 2 cm in from the surface of pipe-line support bags filled with OPC grout immersed in water at 6°C. The heat output of OPC is about half that of HAC in the first 24 hours.

6.3 THE FORMATION OF SURFACE LAYERS IN SEA-WATER

The chemistry and the properties of the surface layers of brucite and aragonite have been considered in some detail by Conjeaud [7] and more recently by Buenfeld and Newman [29]. Using artificial sea-water in the laboratory, Conjeaud found that the growth of the surface layers prevented the penetration of Cl and SO₃ ions into cement mortars after 1-3 months immersion. Buenfeld and Newman have shown the effect that the surface layers have on the permeability of mortars, by studying the initial surface absorption, chloride ion diffusion and electrical resistively of specimens before and after immersion. They noted that natural sea-water, as in the Bincleaves experiments, contains traces of dissolved polar organic substances which may be adsorbed onto the surface of cement and concrete, blocking nucleation sites and thereby inhibiting precipitation. Furthermore they noted that the surface layers of specimens taken from sea-water may dissolve if stored in tap-water and the aragonite might invert to calcite. These factors could well have played some part in the failure to find surface layers on the specimens from Bincleaves, apart from the layer of brucite on OBTC.
6.4 CHLORIDE PENETRATION

The depth of the chloride penetration in the specimens exposed at Bincleaves depends very much upon the composition of the specimen. Table 9 summarises the results shown in Fig 20 and compares the chloride content of the fresh pastes with that after 5 years immersion in water.

The sea-water at Bincleaves and the sea-water used for mixing is assumed to have the same ionic concentration as that from the East Coast. In the case of chloride ions this amounts to 1.9%, so that the OBSC specimens, at a w/c ratio of 0.34, contained 0.64% of chloride by weight of cement after mixing. OBSC2 with 2% of CaCl$_2$.2H$_2$O added to the mixing water contained 0.97% of chloride after mixing while the HAC and OBTC specimens were free from chloride. The HAC specimens, which contain the greatest amount of porosity above 350 nm, have the greatest concentration of chloride ions near the surface and show a concentration gradient falling to a near uniform level of 0.72% chloride at a distance of 50 mm from the surface. The three specimens of Oilwell B cement show a maximum concentration of chloride a few millimetres below the surface, like a number of the mortar specimens of Conjeaud [7], some of the concrete specimens described by Leeming and Sharp [30] and all of the paste specimens of Cabrera and Plowman [31] in which sulphate was the diffusing species. Conjeaud explained this maximum, which persisted in some of her specimens even after two years, in terms of a redistribution of the chloride already within the specimen after the surface had been effectively sealed from the sea-water, after 3 months, by the protective layers of brucite and aragonite. This explanation could well apply to our specimens and to those described by Lemming and Sharp.

Much larger peak concentration of sulphate ions of up to 30% and SO$_3$ were found by Cabrera and Plowman [31] in cement specimens immersed in sodium sulphate solution. Sharp peaks were found at a depth of 0.4-0.7 mm after 28 days, with the peak moving gradually deeper into the paste as exposure continued. X-ray and SEM studies associated the peak with bands of ettringite and gypsum which formed and filled cracks beneath the surface of the paste. The inward diffusion of the ions was accompanied by the chemical reaction of SO$_3$ with calcium hydroxide and the associated expansion produced cracks which filled with the products of further reaction. This raised the local concentration of bound SO3 in the paste to the very high levels they observed. This seems a possible explanation of the peaks found in the Bincleaves specimens immersed for five years, bearing in mind the observation of monochloroaluminate from the surface to a depth of 5 mm. The concentration gradient for OBSC2, from the maximum at 5 mm to 50 mm in Fig 20 shows a continuous steady fall towards the original chloride content after mixing, estimated at 0.97%. At 50 mm the concentration is 1.1% for the submerged specimen compared with 0/91% for the specimen from the tidal zone (Fig 21). For the OBSC specimen a more complicated picture emerges, with the maximum concentration of 0.63% some 3 mm in from the surface, already equal to the theoretical concentration just after mixing, and the concentration falling to 0.28% with increasing depth. It is difficult to explain this in terms of the growth of a protective surface layer or a zone of monochloroaluminate beneath the surface. The OBTC specimen, with a similar porosity to the sea-water mixed specimens but which had a surface layer of brucite, showed the lowest chloride content of all with a penetration depth of only some 20 mm after 5 years exposure. The levels of chloride in the Oilwell B cement grout specimens are lower than those found by Conjeaud in her mortar specimens. This may be due to the low w/c ratio used in the Bincleaves specimens. It is difficult to
compare because Conjeaud mixed her mortars at undefined w/c ratios chosen to give an ASTM flow of 110 ± 5% for all her specimens.

The chloride level in the first 25 mm of OBSC, and to the greatest depth of coring of 50 mm in OBSC2, is well above the maximum level of 0.4% by weight of cement permitted in BS8110 for all grades of reinforced concrete. In view of the overall length of the grouted connection between pile and sleeve this is unlikely to have serious engineering consequences unless shrinkage of the grout allows seepage of sea-water to much greater distances along the grout-steel interface. For the HAC specimen with what looks like a plateau level of 0.72% at 50 mm the situation is more complicated. With little or no calcium hydroxide present the HAC grouts are unable to passivate the steel so that any level of chloride is potentially dangerous. The key factor is the extent to which the Bincleaves grout specimens are representative of grouted pile-sleeve connections, in particular of their porosity and degree of conversion. If we assume a 3” gap filled with HAC grout between a pile of wall thickness 2” and a sleeve of wall thickness 1\(\frac{1}{2}”\), the upper limit to the temperature rise is 106°C for adiabatic heating from the exothermic reaction. With a starting temperature of 5°C in the North Sea, the upper limit becomes 111°C, which is significantly lower than the 154°C estimated for the Bincleaves specimens. It seems possible nevertheless that grouted pile-sleeve connections made with HAC are largely converted to the cubic phase C\(\alpha\)AH\(_6\) within 24 hours after grouting and that further densification and increase of strength will depend upon the penetration of sea water through the porosity to permit renewed hydration of the coarser particles of HAC.
7. CONCLUSION

From this study of several different grout samples, some of which had been exposed to seawater for periods of up to 5 years, the changes in microstructure taking place with time have been determined. The development of phases, the quantitative changes in the phases formed and the degrees of reaction with time on exposure to sea-water have been ascertained. The phase compositions and the state of the microstructure of the specimens after about 5 years of exposure to sea-water in the submerged zone have been established. Furthermore, the chloride contents in these specimens have been measured, and found to be higher near the surface in the HAC specimen than in the Oilwell B cement specimens. In the latter, the chloride contents reflected the amounts of added chloride in the mix water; chloride ingress into the Oilwell B cement specimens was very small. The low w/c ratio in the mixes had ensured generally low degrees of porosity in the specimens. At these low levels of about 2% porosity >350 nm, chloride ingress into the specimen depended both on the amount of porosity and on its degree of connectivity.

There was no difference either in the chloride level or in the microstructure of the Oilwell B cement specimens, mixed with sea-water and 2% added chloride (OBSC2), between that placed in the ridal zones and that in the submerged zone.

The chloride levels in the first 25 mm of several of the specimens exceeded 0.4% by weight of cement, permitted in the BS8110 Code for all grades of reinforced concrete. The engineering consequences of this are discussed and it is concluded that underwater the effects are likely to be small.

While the formation of brucite and aragonite layers were observed and were prominent features of the surfaces of the laboratory prepared specimens, this was not the case in the 5 year old specimens obtained from Bincleaves. However, vegetatational growths were clearly apparent to the eye in the latter. Several factors have been identified which may have led to the loss of these latter in the 5 year old specimens.

High levels of porosity of up to 10% were found in the HAC samples which had been exposed for five years. This was consistent with almost complete conversion of the hexagonal \( \text{CAH}_{10} \) and \( \text{C}_2\text{AH}_8 \) hydration products to the cubic \( \text{C}_3\text{AH}_6 \), followed by further hydration during the immersion in seawater. It is thought that the conversion occurred due to the heat generated during the curing process.

It has been shown that HAC grouts cast in 6" diameter sections inside 0.75" thick steel are able to become fully converted within 24 hours to the stable cubic phase, with increased porosity and reduced strength. Whether this can happen with thick wall steel containers, like those around the annulus of a full-scale pile-sleeve connection, is not known and attempts should be made both to measure and to model this situation.

Overall the microstructure of the grout samples examined after exposure to seawater for several years confirmed both the results from laboratory tests in this programme and other published work.
8. ACKNOWLEDGEMENTS

We are grateful to the Health and Safety Executive (formerly the Department of Energy) for financial support for this programme, to Blue Circle Industries, Lafarge Special Cements, London Zoo and Cormix for supplying materials and to Wimpey Laboratories for help with access to the specimens at Bincleaves and in their own laboratories.

This project was planned as part of the Managed Programme on Grouts and Grouting for Construction and Repair of Offshore Structures, published by HMSO as OTH 88 289. The project was carried out and completed independently of the Managed Programme.

We are grateful to Dr John Sharp now of the Health and Safety Executive, London, Chairman of the Steering Committee of the Managed Programme, for his continued interest and help with this project.
9. REFERENCES


### TABLE 1

**SPECIMEN NUMBER, CONDITIONS OF EXPOSURE AND GROUT MIX DETAILS OF TEST PROGRAMME AT ARE BINCLEAVES**

<table>
<thead>
<tr>
<th>Specimen number/Condition of exposure</th>
<th>Grout mix details</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Monitor</td>
<td>Mix 1</td>
</tr>
<tr>
<td>2. Submerged</td>
<td>100 pbw high alumina cement</td>
</tr>
<tr>
<td>3. Submerged</td>
<td>40 pbw fresh water</td>
</tr>
<tr>
<td>4. Submerged</td>
<td>Mix 2</td>
</tr>
<tr>
<td>5. Submerged</td>
<td>100 pbw Oilwell B cement</td>
</tr>
<tr>
<td></td>
<td>34 pbw fresh water</td>
</tr>
<tr>
<td></td>
<td>2 pbw Cormix SPIG</td>
</tr>
<tr>
<td>6. Submerged</td>
<td>Mix 3</td>
</tr>
<tr>
<td>7. Submerged</td>
<td>100 pbw Oilwell B cement</td>
</tr>
<tr>
<td>8. Tidal zone</td>
<td>34 pbw fresh water</td>
</tr>
<tr>
<td>9. Tidal zone</td>
<td>2 pbw Cormix SPIG</td>
</tr>
<tr>
<td>10. Submerged</td>
<td>Mix 4</td>
</tr>
<tr>
<td>11. Tidal zone</td>
<td>100 pbw Oilwell B cement</td>
</tr>
<tr>
<td>12. Tidal zone</td>
<td>34 pbw fresh water</td>
</tr>
<tr>
<td></td>
<td>2 pbw Cormix SPIG</td>
</tr>
<tr>
<td></td>
<td>2 pbw added chloride</td>
</tr>
<tr>
<td>13. Submerged</td>
<td>Mix 5</td>
</tr>
<tr>
<td>14. Tidal zone</td>
<td>100 pbw Oilwell B cement</td>
</tr>
<tr>
<td>15. Tidal zone</td>
<td>34 pbw sea-water</td>
</tr>
<tr>
<td></td>
<td>2 pbw Cormix SPIG</td>
</tr>
<tr>
<td></td>
<td>4 pbw added chloride</td>
</tr>
</tbody>
</table>

### TABLE 2

**MIX PROPORTIONS**

<table>
<thead>
<tr>
<th>Mix</th>
<th>Mix proportion</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>High alumina cement + 40% fresh water</td>
<td>HAC</td>
</tr>
<tr>
<td>b</td>
<td>Oilwell B cement +34% fresh water + 2% Cormix SPIG</td>
<td>OBTC</td>
</tr>
<tr>
<td>c</td>
<td>Oilwell B cement +34% sea-water + 2% Cormix SPIG</td>
<td>OBSC</td>
</tr>
<tr>
<td>d</td>
<td>Oilwell B cement +34% sea-water + 2% Cormix SPIG +2% CaCl₂</td>
<td>OBSC2</td>
</tr>
<tr>
<td>e</td>
<td>Oilwell B cement +34% fresh water</td>
<td>OBT</td>
</tr>
<tr>
<td>f</td>
<td>Oilwell B cement +34% sea-water</td>
<td>OBS</td>
</tr>
<tr>
<td>g</td>
<td>Blue Circle OPC +34% fresh water</td>
<td>OPCT</td>
</tr>
</tbody>
</table>
### TABLE 3
**OXIDE COMPOSITIONS (%) OF OPC AND OILWELL BE CEMENT**

<table>
<thead>
<tr>
<th>Oxide</th>
<th>OPC Per cent content</th>
<th>Oilwell B Per cent content</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>65.0</td>
<td>64.91</td>
</tr>
<tr>
<td></td>
<td>19.9</td>
<td>21.46</td>
</tr>
<tr>
<td>Al₂O₃SiO₂</td>
<td>5.2</td>
<td>3.86</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.3</td>
<td>5.07</td>
</tr>
<tr>
<td>MgO</td>
<td>1.2</td>
<td>0.81</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.6</td>
<td>2.25</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.60</td>
<td>0.4</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.18</td>
<td>0.1</td>
</tr>
<tr>
<td>LOI</td>
<td>1.3</td>
<td>0.96</td>
</tr>
<tr>
<td>IR</td>
<td>0.17</td>
<td>0.17</td>
</tr>
</tbody>
</table>

Equivalent alkalis as Na₂O: 0.36

Free CaO: 1.0

A/F: 1.6

S/A+F: 2.3

### TABLE 4
**PHASE COMPOSITIONS BY BOGUE AND QXRA**

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Bogue</th>
<th>QXRA</th>
<th>Bogue</th>
<th>QXRA</th>
</tr>
</thead>
<tbody>
<tr>
<td>C3S</td>
<td>62.3</td>
<td>70</td>
<td>61.5</td>
<td>55</td>
</tr>
<tr>
<td>C2S</td>
<td>10</td>
<td>10</td>
<td>15.2</td>
<td>24.5</td>
</tr>
<tr>
<td>C3A</td>
<td>8.2</td>
<td>6.0</td>
<td>1.67</td>
<td>0.5</td>
</tr>
<tr>
<td>C4AF</td>
<td>10</td>
<td>9.5</td>
<td>15.4</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Anhydrite: 5.6

Hemi-hydriate: 1

QXRA: 0.5
### TABLE 5
OXIDE COMPOSITION OF HIGH ALUMINA CEMENT (HAC)

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO (combined)</td>
<td>38.5</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>39.0</td>
</tr>
<tr>
<td>SiO₂</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>12.0</td>
</tr>
<tr>
<td>FeO</td>
<td>4.0</td>
</tr>
<tr>
<td>MgO</td>
<td>0.6</td>
</tr>
</tbody>
</table>

### TABLE 6
TYPICAL PHASE COMPOSITION OF HIGH ALUMINA CEMENT

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>60</td>
</tr>
<tr>
<td>C2AS</td>
<td>5-20</td>
</tr>
<tr>
<td>Pleochroite (C3A2F)</td>
<td>5-15</td>
</tr>
<tr>
<td>C12A7</td>
<td></td>
</tr>
<tr>
<td>Ferrite phase</td>
<td>5-30</td>
</tr>
<tr>
<td>FeO</td>
<td></td>
</tr>
<tr>
<td>C2S</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 7
IONIC CONCENTRATION OF SEA-WATER

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Concentration (g/l)</th>
<th>Content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chloride</td>
<td>18.85</td>
<td>51.9</td>
</tr>
<tr>
<td>Sodium</td>
<td>12.21</td>
<td>33.6</td>
</tr>
<tr>
<td>Sulphate</td>
<td>2.21</td>
<td>6.1</td>
</tr>
<tr>
<td>Magnesium</td>
<td>1.98</td>
<td>3.5</td>
</tr>
<tr>
<td>Calcium</td>
<td>1.26</td>
<td>2.7</td>
</tr>
<tr>
<td>Magnesium</td>
<td>0.65</td>
<td>1.8</td>
</tr>
<tr>
<td>Bicarbonate</td>
<td>0.15</td>
<td>0.4</td>
</tr>
</tbody>
</table>
### TABLE 8
HEAT OUTPUT AT 20°C

<table>
<thead>
<tr>
<th>Mix</th>
<th>Peak 2</th>
<th>Peak 3</th>
<th>Peak 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPCT</td>
<td>3.37 w/kg</td>
<td>3.60 w/kg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>7.5 hrs</td>
<td>8.5 hrs</td>
<td></td>
</tr>
<tr>
<td>OBT</td>
<td>-</td>
<td>3.67 w/kg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.4 hrs</td>
<td></td>
</tr>
<tr>
<td>OBTC</td>
<td>3.10 w/kg</td>
<td>1.81/kg</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>18 hrs</td>
<td>27.7 hrs</td>
<td></td>
</tr>
<tr>
<td>OBS</td>
<td>4.67 w/kg</td>
<td>3.69 w/kg</td>
<td>0.4-0.8 w/kg</td>
</tr>
<tr>
<td></td>
<td>8.5 hrs</td>
<td>10 hrs</td>
<td>25-45 hrs</td>
</tr>
<tr>
<td>OBSC</td>
<td>4.10 w/kg</td>
<td>-</td>
<td>0.4-0.8 w/kg</td>
</tr>
<tr>
<td></td>
<td>16 hrs</td>
<td></td>
<td>39-60 hrs</td>
</tr>
<tr>
<td>OBSC2</td>
<td>16.2 w/kg</td>
<td>-</td>
<td>2.4-3.2 w/kg</td>
</tr>
<tr>
<td></td>
<td>7-14 hrs</td>
<td></td>
<td>38-60 hrs</td>
</tr>
<tr>
<td>HAC</td>
<td>12.9 w/kg</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>5.3-7.0 hrs</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 9
CHLORIDE CONTENTS OF BINCLEAVES SPECIMENS AS % OF CEMENT

<table>
<thead>
<tr>
<th>Specimen</th>
<th>After mixing %</th>
<th>After 5 years 50mm deep</th>
<th>Maximum</th>
<th>Porosity &gt;350 nm %</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAC</td>
<td>0.0</td>
<td>0.72</td>
<td>2.0-2.4</td>
<td>6.7-10</td>
</tr>
<tr>
<td>OBSC2</td>
<td>0.97</td>
<td>1.11</td>
<td>1.39</td>
<td>2.0</td>
</tr>
<tr>
<td>OBSC</td>
<td>0.64</td>
<td>0.28</td>
<td>0.63</td>
<td>2.0</td>
</tr>
<tr>
<td>OBTC</td>
<td>0.0</td>
<td>0.0</td>
<td>0.22</td>
<td>2.5</td>
</tr>
</tbody>
</table>
FIGURE 1
PARTICLE SIZE DISTRIBUTIONS OF CEMENTS

Percent by weight below

Log particle size

0 OPC
+ OILWELL B CEMENT
X HAC
FIGURE 2
BEI OF ORDINARY PORTLAND CEMENT POWDER IN RESIN (X260)

FIGURE 3
BEI OF OILWELL B CEMENT POWDER IN RESIN (X260)

FIGURE 4
BEI OF HIGH ALUMINA CEMENT POWDER IN RESIN (X400)
FIGURE 5
HEAT OUTPUT CURVES FOR OBT AND OPCM MIXES (0.34 W/C)
FIGURE 6
HEAT OUTPUT CURVES FOR OBT AND OBS MIXES
FIGURE 7
HEAT OUTPUT CURVES FOR OBT, OBS, OBSC
AND OBTC MIXES
FIGURE 8
HEAT OUTPUT CURVES FOR HAC AND OBSC2 MIXES
FIGURE 9: Development of phases in Oilwell B cement ($w/c = 0.34$)
FIGURE 10: Development of phases in OPC (w/c = 0.34)
FIGURE 11: Calcium hydroxide content from TG (g/g of cement)
FIGURE 12: Relative volume contents of HAC specimens

(a) 1 day
- Porosity
- Anhydrous
- Others

(b) 3 days
- Porosity
- Anhydrous
- Others

(c) 7 days
- Porosity
- Anhydrous
- Others
FIGURE 12 (continued)

(d) 28 days

(e) 90 days

(f) 5 years

Relative volume (%)

Distance from exposed surface (mm)

Porosity
Anhydrous
Others

Relative volume (%)

distance from exposed surface (mm)

Relative volume (%)

distance from exposed surface (mm)
FIGURE 13: Relative volume contents of OSIC specimens

(a) 1day

(b) 3days

(c) 7days

Legend:
- □ porosity
- × anhydrous
- ■ CH
- + others

Relative volume (%) vs. distance from exposed surface (mm)
FIGURE 14: Relative volume contents of OBSC specimens

(a) 1 day

(b) 3 day

(c) 7 days
FIGURE 14 (continued)

(d) 28 days

(e) 90 days

(f) 5 years

Relative volume (%) vs. distance from exposed surface (mm)

- Porosity
- Anhydrous
- CH
- Others
FIGURE 15: Relative volume contents of OBSC2 specimens

(a) 1 day

(b) 3 days

(c) 7 days
FIGURE 15 (continued)

(d) 28days

(e) 90 days

(f) 5yars

Relative volume (%) vs. distance from exposed surface (mm)

Symbols:
- Porosity
- Anhydrous
- OH
- Others
- porosity
- anhydrous
- OH
- OTHERS
FIGURE 16: OBS2 - 5 years in tidal zone

FIGURE 17: Average CH content at each age
FIGURE 18: Average of anhydrous cement contents
FIGURE 19: Degrees of reaction
FIGURE 20: Total chloride contents

FIGURE 21: Chloride contents from OBSC2 specimens
FIGURE 22 BEI OF SURFACE LAYER OF BRUCITE
FIGURE 23 BEI OF SURFACE ZONE AFTER 24 HOURS IN SEA-WATER
FIGURE 24 BEI OF INTERIOR OF HAC LABORATORY SPECIMENS
FIGURE 25 BEI OF SPECIMENS AFTER 90 DAYS IN SEAWATER
FIGURE 26a) BEI OF INTERIOR OF HAC SPECIMENS FROM BINCLEAVES, AFTER 5 YEARS EXPOSURE IN SEA-WATER (x400)

FIGURE 26b) HAC CONTROL SPECIMEN, CURED FOR 28 DAYS AND LEFT IN AIR FOR 5 YEARS (x400)
FIGURE 27 BEI OF INTERIOR OF SPECIMENS FROM BINCLEAVES, AFTER 5 YEARS EXPOSURE TO SEA-WATER