Prevention of reinforcement corrosion by hydrophobic treatment of concrete

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Abstract

Corrosion of reinforcement in concrete bridge decks may occur due to penetration of de-icing salts, even in the presence of an asphalt overlay. This paper reports a laboratory study into additional protection of concrete by hydrophobic treatment. It was found that hydrophobic treatment strongly reduces chloride ingress, both during semi-permanent contact and under wetting/drying exposure. The water repellent effect remains effective for at least five years under full exposure to outside conditions. After five years, carbonation of concrete was found to be similar for non-treated and hydrophobised concrete.
Under wet conditions, hydrophobic treatment does not stop ongoing corrosion that has been initiated by chlorides before the treatment. Methods and criteria for testing hydrophobic products are available. Hydrophobic treatment is an effective, low cost preventative measure against corrosion of reinforcement in chloride contaminated environment. In The Netherlands, it has become standard for all new concrete bridge decks.

Key words: concrete, reinforcement corrosion, hydrophobic treatment, chloride, durability, preventative measures

1 Introduction

The durability of concrete bridge decks exposed to de-icing salts is threatened because damage may occur due to penetration of chloride ions and subsequent corrosion of steel reinforcement. Concrete decks without overlays may show severe corrosion damage under de-icing salt load, as has occurred on a large scale in the United States. In Europe, most decks are provided with a layer of dense asphalt. In many countries, some type of additional protection is applied, like a waterproofing membrane between concrete and asphalt. This is not the usual practice in The

Netherlands: here, the asphalt is applied directly on the concrete. In the early 1990's, the favourable road surface properties of open asphalt (better visibility in wet conditions, lower noise production) led to the decision to use open asphalt on all highways and the bridges in these highways. Because the open asphalt requires a higher amount of de-icing salts and is more permeable to chlorides, the need was felt to introduce some form of additional protection. Hydrophobic treatment of the concrete with silicone compounds seemed promising. Such a treatment makes concrete water repellent, so theoretically the concrete would no longer absorb water and dissolved chlorides. It was expected that corrosion initiation would be prevented or at least postponed. Hydrophobic treatment is relatively cheap (about 10 Euro/m^2), so it seemed an economically attractive way to improve the corrosion protection of bridge decks. A research programme was carried out to investigate the effectiveness and to select suitable hydrophobic products. After a literature survey, a test procedure and criteria were drawn up. The main criteria were: substantial reduction of water absorption, sufficient penetration into standard concrete, resistance to alkaline breakdown. Several commercial products were tested [Vries & Polder 1997, Polder et al. 1996]. Some products complied with the requirements, others failed. Only products specifically intended for use on concrete appeared suitable; products for brick masonry did not comply to the test requirements. The test set-up and the requirements were evaluated, slightly modified and subsequently laid down in a Rijkswaterstaat (Ministry of Transport) Recommendation [Polder et al. 1993]. Application of hydrophobic treatment with an approved product has become standard practice on all new bridge decks in The Netherlands. The surface area of concrete treated on bridge decks is estimated at 100,000 m^2 per year. The amount of literature on hydrophobic treatment of concrete is limited. Other work in this area is mainly confined to the UK [Basheer and co-workers, 1995, 1997, 1998]. Consequently the need was felt to study various aspects of the performance. This paper summarises previous work and reports recent findings.

2 Theoretical background

When water comes into contact with a non-water saturated porous material such as concrete, it is transported rapidly into the pores by capillary action. The rate of absorption depends on the surface tension, the viscosity, and the density of the liquid, on the angle of contact between the liquid and the pore walls and on the radius of the pores. Since the characteristics of the liquid (water) and of the concrete are given constants, the most important factor is the contact angle (theta). In normal concrete, the contact angle is small (<90°) due to the presence of molecular attraction between water and cement paste (hydro**philic** behaviour). Under these conditions, a drop of water will spread on a flat surface, the level inside a capillary pore will rise above the surrounding liquid and the concrete will absorb the water. The opposite may occur when concrete is made hydro**phobic**: forces of attraction between the concrete and the liquid are greatly reduced and the contact angle is >90°. A drop takes the form of a sphere, while the capillary rise is negative, so the level of liquid in the pore is lower than the surrounding liquid. The two cases are shown in Figure 1.

The molecular attraction between water and concrete can be weakened by impregnating the concrete with hydrophobic agents, such as silicones. From the silicone group of substances, silanes and siloxanes are most important for concrete. Silanes are small molecules having one silicon atom; siloxanes are short chains of a few silicon atoms. Their molecules contain (organic) alkoxy groups linked to the silicon atoms, which can react with the silicates in the concrete to form a stable bond. In addition, silanes and siloxanes contain organic alkyl groups which have a fatty and water repellent character. After reaction of the alkoxy-groups, the alkyl groups protrude from the pore surfaces. As a result, water molecules will be repelled, the contact angle is greater than 90° and, ideally, water is no longer absorbed by capillary suction. In reality, capillary absorption is reduced to 10-20% of non-treated concrete. Because the pores are left open, silicone treatment does not block transport of single water (vapour) molecules.

3 Background of research

Hydrophobic treatment of concrete is expected to reduce the penetration of water and dissolved ions (chloride). However, the water-repellent pores may not resist water under pressure; imperfections like (micro)cracks in the treated layer will allow a small amount of liquid absorption; the hydrophobic effect may be lost gradually due to ultra-violet light and alkaline attack of the hydrophobic molecules (breaking off the fatty groups). Hydrophobised concrete exposed to rain will be drier than non-hydrophobised concrete, because the former does not absorb water during rain and loses water in dry periods by evaporation. This might slow down ongoing corrosion. On the other hand, drying out might increase carbonation and potentially promote corrosion. In the UK, hydrophobic treatment of bridge decks is recommended practice, unless chloride ions have already penetrated.

Research was carried out into various aspects of performance and durability of the water-repellent effect. Previous work is summarised [Vries & Polder 1995] here. A set of test methods and requirements was designed and nine commercially available products were tested. The primary objective of the treatment is to minimise water absorption. For a durable effect, the hydrophobic agent should penetrate sufficiently deep to prevent early degradation by Ultraviolet radiation. Water from within the concrete should evaporate freely to avoid damage, for instance due to freezing. The hydrophobic material should withstand the alkalinity of the concrete pore solution. Finally, when the hydrophobised concrete is covered with an asphalt layer, the water repellent effect should not be lost due to temperature increase during asphalting (about 160°C). Considering these issues, the following main requirements for hydrophobic products applied to standard concrete were formulated:

- water absorption less than 20% of control concrete (not hydrophobised);
- penetration depth at least 2 mm;
- water evaporation through hydrophobic concrete > 60% of control;
- water absorption after heating at asphalting temperature < 30% of control;
- water absorption < 20% of control when applied to strongly alkaline Portland cement-sand mortar (alkali resistance).

A similar set of tests and requirements was designed in the UK [Calder & Chowdury 1996]. A range of products was tested and pass/fail criteria were drawn up. Generally, a good agreement exists with the results mentioned above. On-site measurements using portable equipment (Autoclam) confirmed laboratory results in terms of low water absorption for hydrophobised concrete [Basheer et al. 2000]. The absence of chloride penetration was found on a motor way pier after 7 years service. Apparently field conditions, including thermal and load related movement of concrete, do not harm the water repellent effect of hydrophobised concrete.

With a few of the products that complied to all requirements, further investigations were carried out. The work reported here includes:

- chloride ingress after intermittent (wetting/drying) contact with salt solution

- absorption of (salt) water during semi-permanent contact
- water absorption as a function of exposure time to outside conditions
- effect on corrosion of bars in chloride contaminated concrete
- carbonation depth after exposure.

4 Materials: concrete

For bridge decks (exposed to de-icing salts), Dutch standards prescribe a maximum water-to-cement ratio (w/c) of 0.45. The top layers of such decks may have a slightly higher w/c due to bleeding of the fresh concrete mix. It was decided to simulate such top-of-deck concrete with a w/c of 0.50. Traditionally, in our national practice two cement types are used, Portland cement (OPC) and Blast furnace slag cement (BFSC) with a high slag content. For the experiments, two standard concrete compositions were designed, one with OPC (CEM I) and one with BFSC (CEM III/B LH HS, c. 70% slag). Both mixes contain 340 kg/m^3 cement, have a w/c 0.50 and river sand and gravel with maximum grain size 32 mm, fine particle (<0.25 mm) content at least 130 l/m^3 [Polder et al. 1993]. The compressive cube strength of these mixes at 28 days wet curing is about 43 MPa, strength class about B35.

From these two “standard” mixes, slabs of 0.5 x 0.5 m^2 with a thickness of 150 mm were cast and the top surfaces were finished with a steel trowel. The moulds were covered for 24 hours with plastic foil. Then the slabs were cured for 48 hours in a fog room. By horizontal and vertical diamond sawing, specimens were made of 100 x 100 x 75 mm^3 (with one finished or one mould face). They were stored in air of 20°C and 65% RH until (at least) 28 days age before treatment. Hydrophobic agents were applied by dipping mould or trowelled surfaces of specimens twice in the liquid for five seconds with 10 minutes interval. After application, specimens were stored for (at least) four weeks in air of 20°C and 65% RH before testing.

5 Materials: Hydrophobic agents

The commercially available hydrophobic products for concrete consist of silanes and/or siloxanes. Silanes contain 100% active substance or they are dissolved in alcohol or hydrocarbons (with 10 to 40% active substance). Siloxanes are dissolved in alcohol or hydrocarbon solvents (about 10 to 20% active substance). Silanes and mixtures of silanes and siloxanes are also available as water-borne systems (with 10 to 20% active substance). In the Netherlands, the product is not allowed to contain any volatile organic solvents for environmental reasons. Three commercially available hydrophobic products which comply to all test criteria, are used:

- product A, 99% silane (no solvent)
- product B, 100% silane (no solvent)
- product E, 20% silane/siloxane dispersed in water.

In standard concrete, these products penetrate to such depth and amount, that the hydrophobic zone is at least 2 mm and typically up to 5 mm deep.

6 Chloride penetration during simulated de-icing salt exposure

The effect of hydrophobic treatment on the penetration of chloride has been investigated by exposing specimens to cyclical wetting with a salt solution and drying, intended to simulate de-icing salt application in the field. The specimens (only finished/trowelled surfaces) were made with OPC and BFSC (standard composition). They were treated with product B (100% silane) or product E (20% silane dispersed in water) according to the standard application procedure. Per cycle, the test surfaces were allowed to absorb a 10% NaCl (by mass) solution for 24 hours and then allowed to dry in air of 20°C and 50% RH for 6 days. The chloride penetration profiles were determined after 12 months by dry grinding off layers of 4 mm thick and analysing the dust for total (nitric acid soluble) chloride. After 52 weekly cycles the chloride content was between 0.2% and 0.5% by mass of cement at a depth of 16 to 20 mm in hydrophobised concrete (OPC and BFSC); in non-treated OPC concrete this was 2.8%; in BFSC non-treated concrete 2.4%, as shown in Fig. 2 and 3. This means that the hydrophobic treatment (with products B and E) has reduced the chloride penetration by a factor of 5 to 10. This corresponds rather well to the reduction of the water or salt solution absorption. The chloride content in the outermost layer is reduced by at least a factor 3. It may be concluded that hydrophobic treatment of concrete, made with either portland cement or blast furnace slag cement, strongly slows down the penetration of chloride under salt application-drying cycles. The results also show the importance of sufficient concrete cover to the reinforcement. Even with hydrophobic treatment, rebars at less than 20 mm cover depth would have experienced a serious risk of corrosion due to relatively high chloride contents.

7 Salt water absorption during prolonged exposure

In previous work, water absorption was tested for periods up to 24 hours. For concrete treated with suitable hydrophobic products, this short-term water absorption was reduced compared to untreated concrete by a factor five to ten [Vries & Polder 1997]. However, locally on a bridge, water containing de-icing salt may be in contact with the concrete for longer periods. Tests were carried out to determine the influence of hydrophobic treatment on absorption of chloride solution up to four weeks. Standard specimens (controls and treated with hydrophobic agents B and E) were brought in permanent contact with pure water or 10% NaCl (by mass) solution for 28 days. Water and salt solution absorption was tested periodically by weighing. At any time during these 28 days, salt water absorption was much lower for hydrophobised concrete than for untreated concrete, roughly by a factor of ten (Figure 4). This effect was similar for OPC and BFSC concrete. The total amount of liquid absorbed was slightly lower for salt solution than for pure water. It appears that the favourable effect of hydrophobic treatment is maintained during long periods of exposure to water or solutions containing high chloride concentrations.

8 Durability of hydrophobic effect

The durability of the water-repellent effect was studied by exposing treated and control samples to outside climate and repeated testing for water absorption. Specimens made of standard concrete with OPC and BFSC were hydrophobised. Three approved hydrophobic products (codes A, B, E) were applied on the finished/trowelled surface. They were exposed horizontally for a total of 62 months with the treated sides upward, with free access of wind and rain on the roof of a building at Rijswijk, in the Western part of The Netherlands. For each measurement, the specimens were taken inside, stored in 20°C and 65% RH for four weeks and tested for water absorption in 24 hours, after which the exposure was continued. After 5 years exposure, additional testing of one OPC and one BFSC control sample was carried out using polarising and fluorescence microscopy (PFM) and nuclear magnetic resonance (NMR).

In Figure 5 the water absorption coefficient (WAC) of samples is plotted as a function of exposure time. This WAC is the slope of water absorption in 24 hours against the square root of time. Three different trends can be seen:

- the WAC of OPC controls show a strong reduction,
- the WAC of BFSC controls showed only a small reduction,
- the WAC for all hydrophobised specimens was fairly constant at a low level.

Microscopy showed that the control OPC sample was carbonated over a depth of about 3 mm. The microstructure of the carbonated zone had a slightly lower capillary porosity than deeper, uncarbonated parts. The control BFSC sample had carbonated about 7 mm and had become more porous as compared to uncarbonated parts. This is normal for BFSC concrete and is due to the lower calcium hydroxide content of the cement. From NMR testing it was found that in 24 hours the water had penetrated gradually but deeply into the OPC sample, corresponding to a rather homogeneous capillary structure, see Figure 6. In the BFSC sample, the water penetration followed a steep profile. The first few millimetres had absorbed a high amount of water, while the deeper parts were hardly penetrated at all. Qualitatively this steep water penetration profile in the BFSC sample corresponds to the abrupt change in microstructure at the carbonation front. The overall absorption by the OPC control concrete is reduced by the densification due to carbonation. This reduction does not occur significantly in BFSC concrete.

It is clear that the water repellence of concrete treated with each of the three products had not significantly deteriorated during 62 months exposure to outdoor climate. The reduction of the water absorption of untreated OPC concrete is probably caused by further hydration of the cement and densification due to carbonation of the surface layer. For non-treated BFSC concrete, the water absorption of control specimens decreased only slightly. BFSC concrete does not show densification upon carbonation, so the water absorption decreases only due to further hydration of the cement, mainly the slag particles.

The experiments show that under full exposure to climatic weathering conditions, hydrophobised concrete has retained its water repellence for five years and the expectation is that the water-repellent effect will be present for many more years. With a layer of asphalt on top of treated concrete, so in the absence of UV-radiation, the durability of the hydrophobic effect is expected to be at least the same or better.

9 Effect on chloride induced corrosion

Twelve macrocell specimens were made of standard OPC and BFSC concrete in order to study the corrosion rate of bars in chloride contaminated concrete, with and without hydrophobic treatment *applied after corrosion initiation*. The specimens were beams of 300 x 150 x 150 mm^3 with two reinforcing bars (ϕ 12 mm x 200 mm length) at 25 mm depth from the upper surface (intended anodes) and two bars at 110 mm depth (intended cathodes), see Figure 7. Specimens were subjected to cycles of wetting with 10% NaCl solution for one day and 13 days drying for about one year. In order to promote corrosion initiation, the upper bars were polarised anodically with a cathode in the chloride solution on the top surface for one week at 1 A/m^2, 59 weeks after start of exposure. Subsequently, strongly negative steel potentials indicated that corrosion had initiated. Seventy weeks after casting, six specimens were hydrophobised with product E. Cyclical salt application was continued for another year. Subsequently the specimens were exposed:

- outside for about a year;
- in air of 20°C and 80% RH for half a year;
- shortly in a fog room and
- outside for another half year.

The total exposure after hydrophobic treatment lasted four years. Corrosion rates were determined from the macrocell currents between top and bottom bars (flowing through a measuring resistance) and from the linear polarisation resistance of top bars, measured with sensorized current confinement (using a GECOR6). Steel potentials were measured using external reference electrodes. Finally, specimens were destructively analysed. Chloride penetration profiles were determined and steel bars were etched in inhibited acid and visually inspected for number and volume of corrosion pits. Carbonation depths were determined (see below).

In OPC concrete, with about 1% to 1.6% chloride by mass of cement near the bars, a significant corrosion rate was found of the order of 1 $\mu A/cm^2$, equivalent to 12 μm of steel cross section loss per year. This can be considered a significant corrosion rate [COST 509, 1997]. Macrocell currents and linear polarisation results corresponded well. Steel potentials were quite negative (in the range of -250 to –400 mV versus Ag/AgCl), indicating active corrosion. In BFSC specimens, the chloride content was lower (0.4% to 1.1%) and low corrosion rates were observed (below 0.2 μA/cm^2), equivalent to about 2 μm/year steel loss, which is a negligible corrosion rate. Potentials were much less negative (–100 to –200 mV versus Ag/AgCl), indicating passivity [COST 509, 1997]. Apparently the chloride content near the bars (and possibly other cement type related factors) dominates the corrosion rate. Corrosion rates in hydrophobised and untreated OPC concrete were similar (Figure 8). During exposure in the fog room, the corrosion rate increased, indicating that hydrophobic treatment did not prevent moisture from entering the concrete via the vapour phase and accelerating the corrosion process. Three years after hydrophobic treatment, fine corrosion cracks were visible (in OPC specimens). In half a year, they increased in width and number.

Destructive analysis showed that the amount and volume of pits in the anodic bars strongly varied, from 50 to 1000 mm^3 of material loss per bar. The amount of corrosion was related to the appearance of cracking. From 100 mm^3 of corroded material, fine cracks were found on the concrete surface; from 500 mm^3 corrosion, wide cracks occurred. Converted to average loss of cross section, these figures suggest that from an average amount of 16 μm steel diameter loss, fine cracking took place. From 80 μm average material loss, heavy cracking occurred. The observed material loss corresponded roughly with the amount of corrosion calculated from integration of the measured corrosion rates over time.

From these tests, it is clear that in cases where hydrophobic treatment is applied **after** chloride penetration has initiated corrosion, it does not stop the corrosion if the concrete is exposed to regular wetting.

10 Carbonation

There is some concern that the gradual drying out due to hydrophobic treatment causes deeper carbonation, which may promote corrosion of reinforcement. It could be argued, however, that the corrosion rate (for carbonation induced corrosion) would be low in such relatively dry concrete. Carbonation depths were determined in the hydrophobised and non-treated macrocell specimens (see previous section) after 5 years exposure to various conditions, including wetting/drying cycles and outside climate.

Carbonation depths in OPC control specimens were 1 to 2 mm; in OPC hydrophobised 1 to 3 mm. In BFSC controls, carbonation depths were 1 to 7 mm, in BFSC hydrophobised 1 to 5 mm. Obviously, results from each group show a large variation. Carbonation depths of hydrophobised concrete did not significantly differ from untreated concrete. It appears that the cement type has a larger influence than hydrophobic treatment. Both observations may particularly relate to the applied exposure regime, which was relatively wet. Other work has shown no significant effect of hydrophobic treatment on carbonation depths [Basheer et al 2000]. Summarising: hydrophobic treatment does not increase the risk of carbonation induced corrosion under conditions where the treatment was intended for in the first place, de-icing salt exposure (as found on bridge decks).

11 Conclusions

Experiments were carried out to study the effect of hydrophobic treatment of concrete under various exposure conditions. The concrete compositions used for the tests were thought representative for the upper parts of bridge decks. The mixes included Ordinary Portland cement and blast furnace slag cement with a high percentage of slag. It was found that hydrophobic treatment reduces the absorption of water and salt solutions from exposure for hours until four weeks. Furthermore, the penetration of chloride ions is strongly reduced. Under relatively wet exposure, there is no significant effect on carbonation of concrete. Corrosion that has already initiated due to chloride penetration is not stopped by hydrophobic treatment. The water repellent effect remained intact for at least five years exposure of specimens to outdoor conditions.

Hydrophobic treatment of concrete is an effective, low cost preventative measure against corrosion that may be caused by chloride ingress. The beneficial effect is mainly a strong reduction of chloride ingress, both in semi-permanent contact and in wetting/drying situations.

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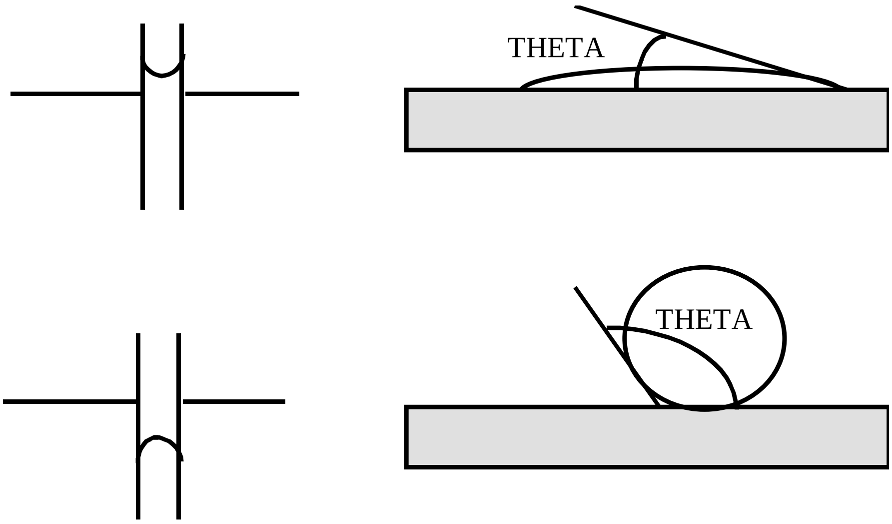

Fig. 1 Interaction between water and either non-hydrophobic (top) or hydrophobic (bottom) capillary (left) or concrete surface (right)

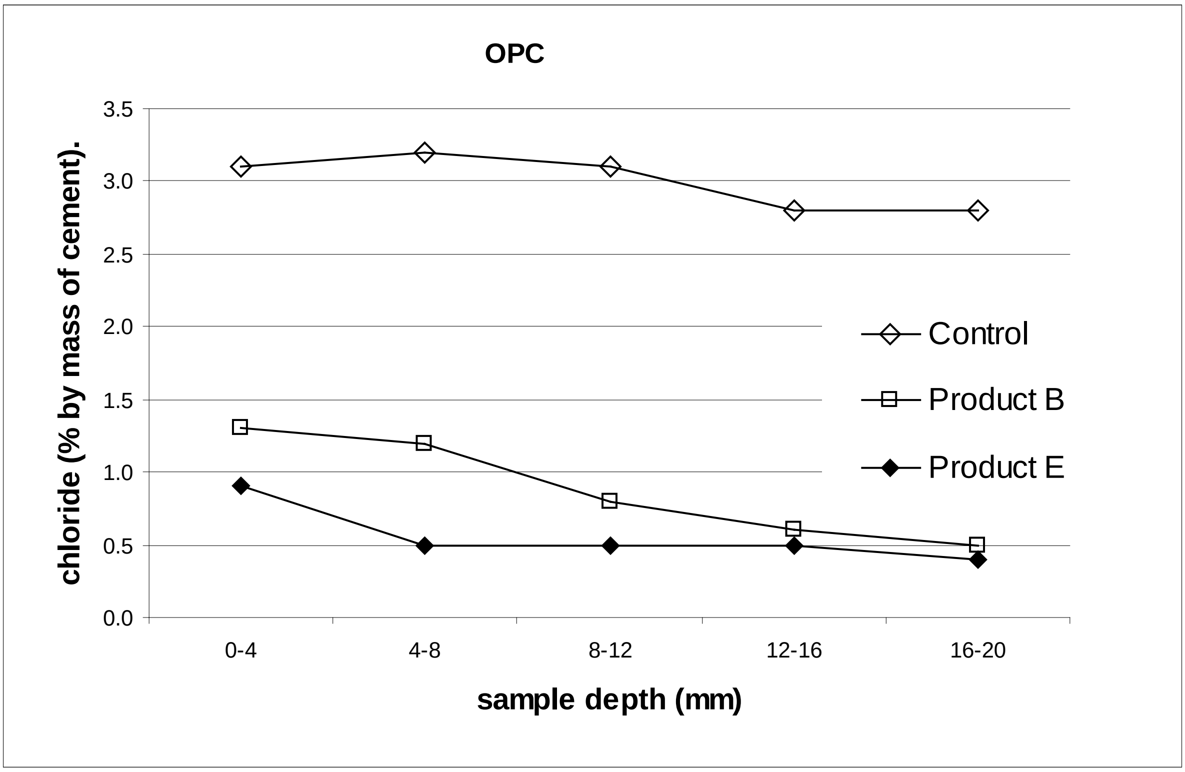

Fig. 2 Chloride penetration in control and hydrophobic Portland cement concrete after 52 weekly de-icing salt cycles; symbols average of six specimens

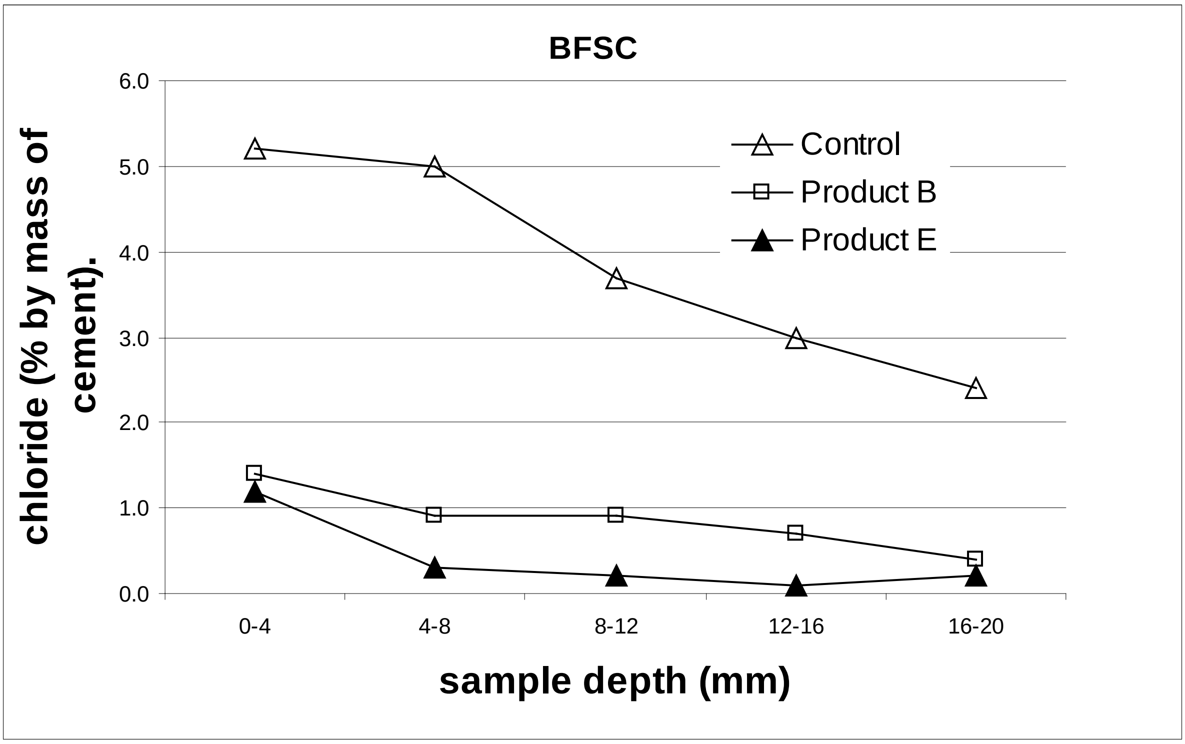

Fig. 3 Chloride penetration in control and hydrophobic blast furnace slag cement concrete after 52 weekly de-icing salt cycles; symbols average of six specimens

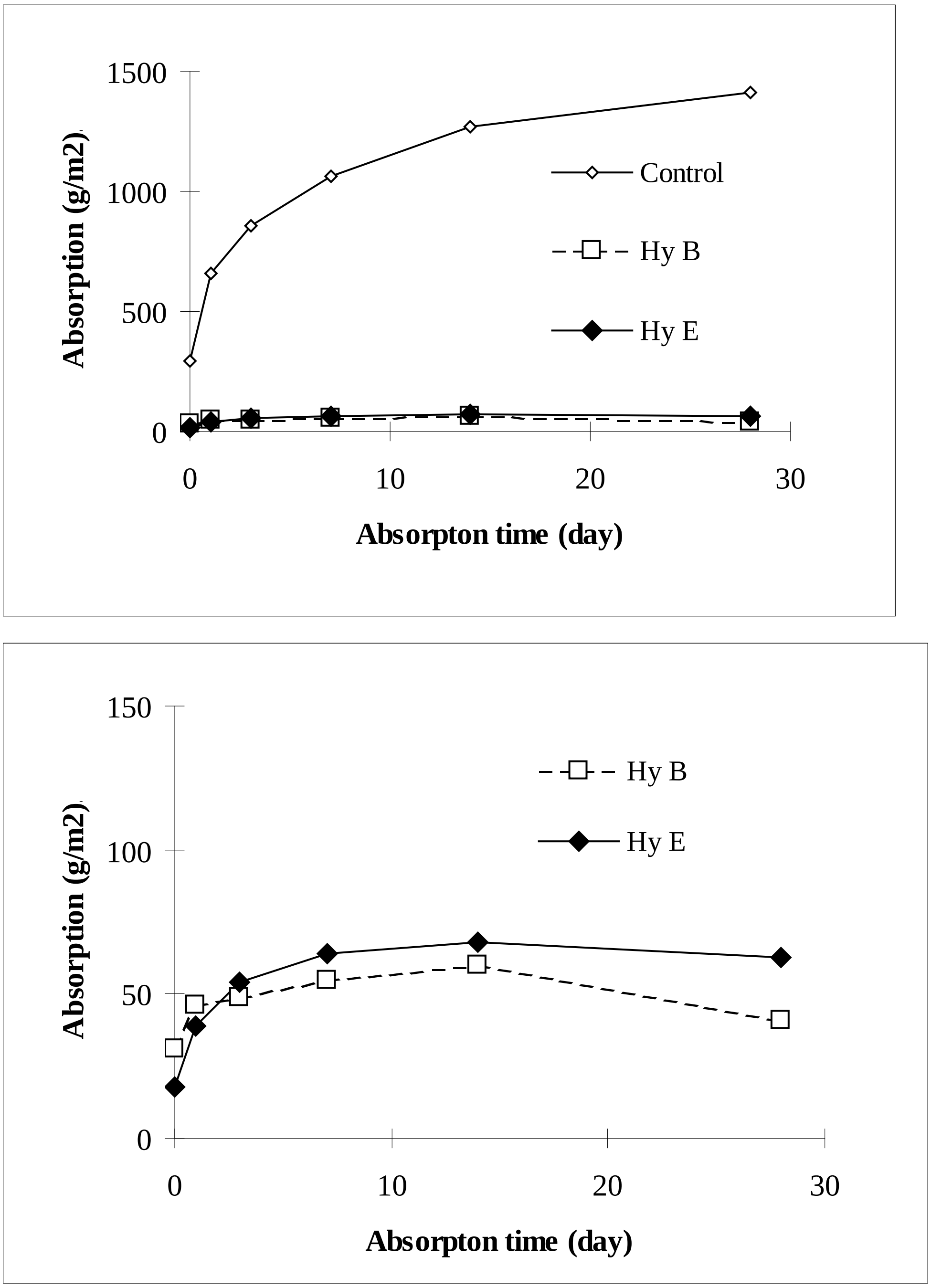

Fig. 4 Salt water absorption of OPC concrete (top), control and treated; same with tenfold vertical magnification showing hydrophobised specimens only (bottom); symbols average of

three specimens

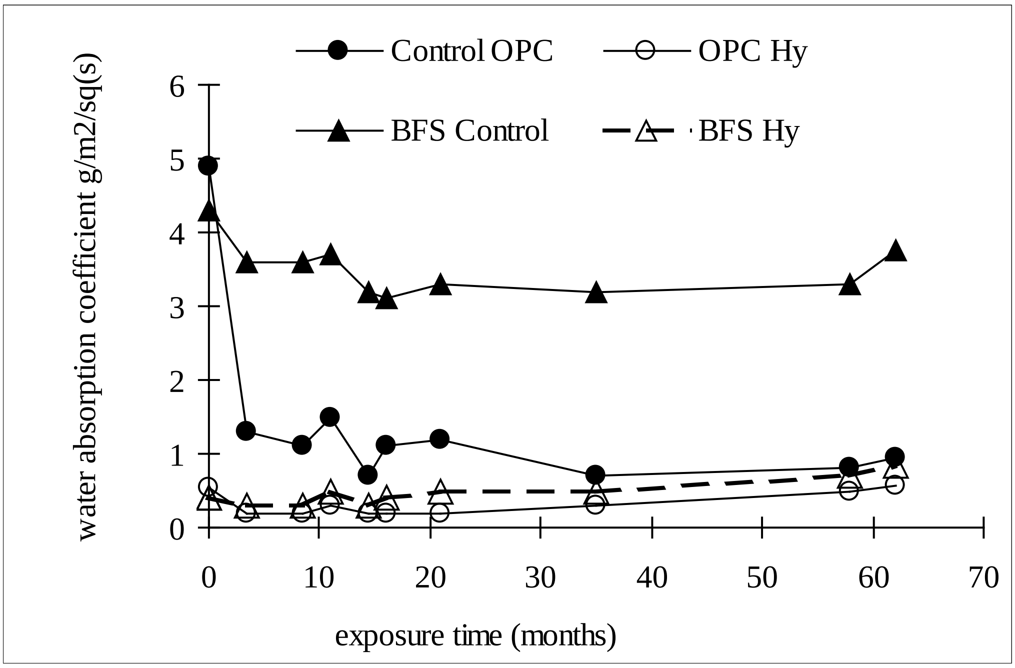

Fig. 5 Water absorption coefficient (24 h) after exposure outside; symbols average of five (0-22 months) or three (>35 months) specimens

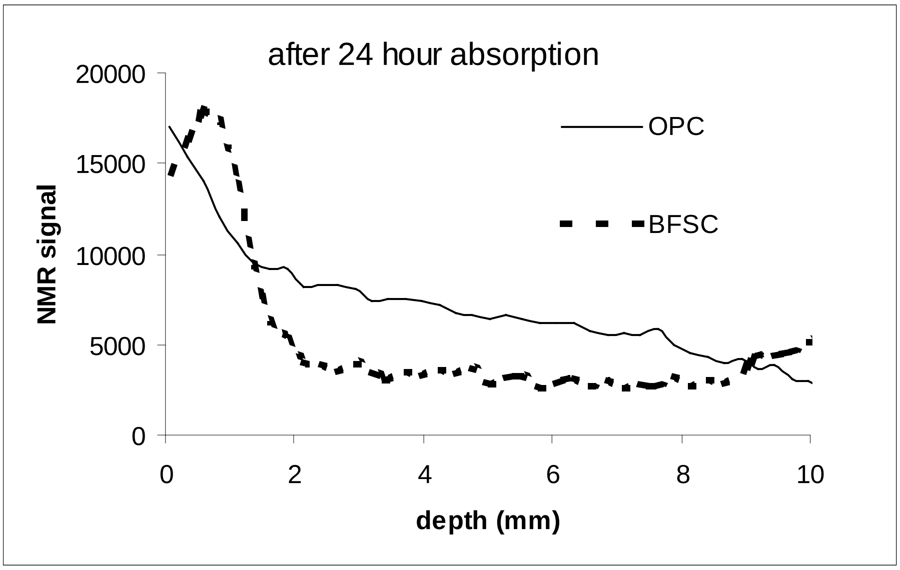

Figure 6 Moisture profiles obtained by Nuclear Magnetic Resonance (NMR) in non-hydrophobised samples of OPC and BFSC after absorption of water for 24 hour; single specimens

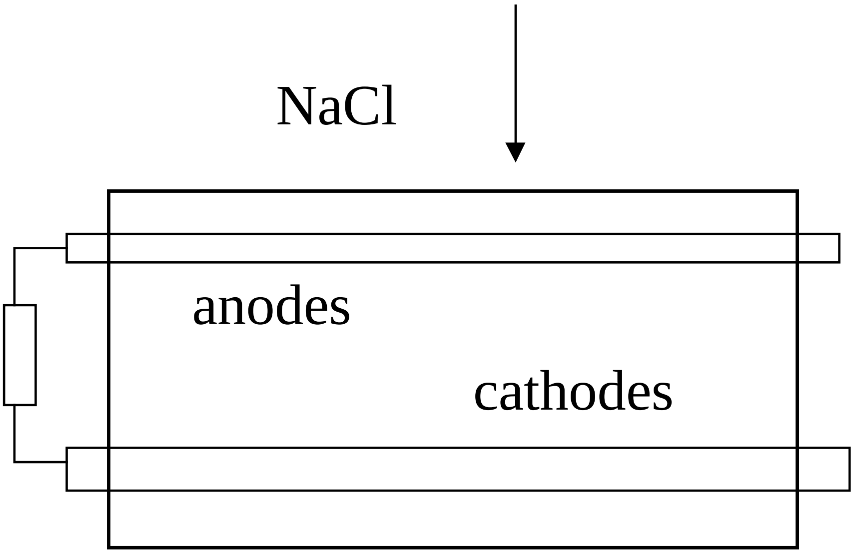

Figure 7 Macrocell specimen

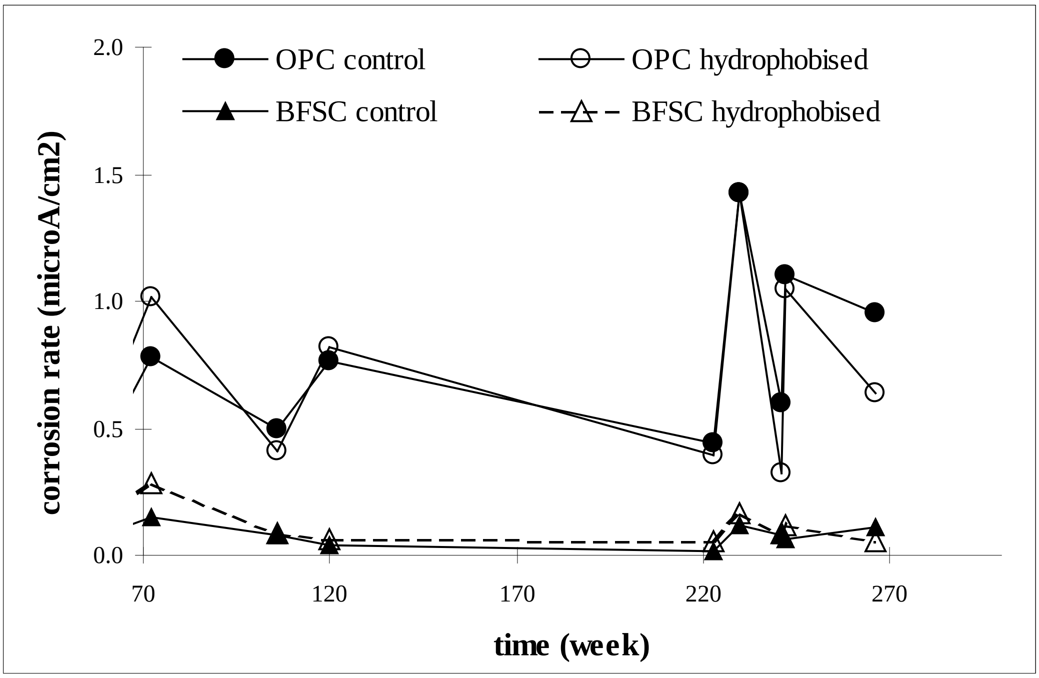

Fig. 8 Corrosion rates in chloride contaminated OPC and BFSC concrete as a function of concrete age for control (untreated) and hydrophobised concrete (applied 70 weeks after casting); symbols average of three (until 120 weeks) or two specimens (after 120 weeks)