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Corrosion Protection of Reinforcement by Hydrophobic Treatment of Concrete

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ABSTRACT

Penetration of de-icing salts into concrete bridge decks may cause corrosion of reinforcement, even with an asphalt overlay. Hydrophobic treatment of concrete was studied in the laboratory as additional protection. It was shown that hydrophobic treatment strongly reduces chloride ingress, both during semi-permanent contact and in wetting/drying situations. The protection remains effective for at least five years under full exposure to outside conditions. Carbonation of concrete is not significantly accelerated. Hydrophobic treatment does not stop corrosion if initiation by chlorides has already taken place 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. It has become standard for all new concrete bridge decks in The Netherlands.

1. Introduction

Exposure to de-icing salts of concrete bridge decks is a potential cause of damage because chloride ions may promote corrosion of steel reinforcement. Bare concrete bridge decks under de-icing salt load may show severe corrosion damage, 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 membrane between concrete and asphalt. In The Netherlands, this is not the usual practice: the asphalt is applied directly on the concrete. In the 1990s, 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 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 of those bridges. Hydrophobic treatment of the concrete with silicone compounds seemed promising. Such treatment makes concrete water repellent, so theoretically water and dissolved chlorides would no longer be absorbed. It was expected that corrosion initiation would be prevented or at least postponed. Hydrophobic treatment is relatively cheap (5 to 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. First, a test procedure and criteria were

drawn up. Several commercial products were tested [1,2]. Some products complied with the requirements, others failed. Only products specifically developed for use on concrete appeared suitable; products for brick masonry did not comply with 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. Application of hydrophobic treatment with an approved product has become standard practice on all new bridge decks.

2. Theoretical Background

When water comes into contact with a 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 (hydrophilic 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 hydrophobic: forces of attraction exerted on the liquid are greatly reduced and the contact angle is >90°. A drop takes the form of a sphere, while capillary rise is negative, so the level of liquid in the pore is lower than the surrounding liquid. Both cases are shown in Fig. 1.
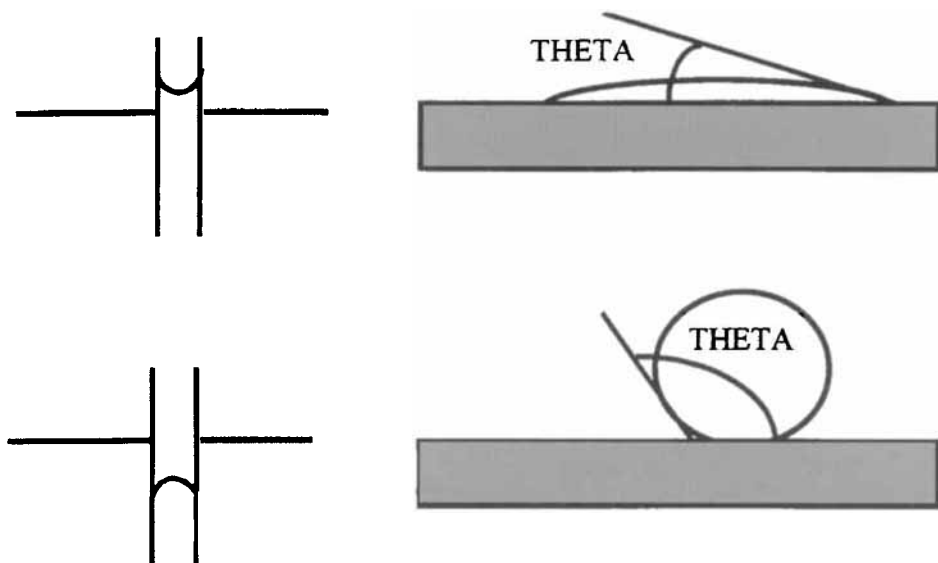

Fig. 1 *Interaction between wter and either non-hydrophobic (top) or hydrophobic (bottom) concrete surface.*

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 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. Objectives of Research

Hydrophobic treatment is expected to reduce the penetration of water and dissolved ions (chloride). However, the water-repellent pores may not resist water under pressure; imperfections in the treated layer will allow some liquid absorption; the hydrophobic effect may be lost gradually due to ultra-violet light and alkaline attack of the hydrophobic molecules. 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.

Research was carried out into various types of performance and durability of the water-repellent effect. The work reported here includes:

- absorption of salt water during semi-permanent contact ;

- absorption of salt water during intermittent contact;

- water absorption as a function of exposure time to outside conditions;

- effect on corrosion of bars in chloride-contaminated concrete; and

- 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 amount of slag,). For the experiments, two standard concrete compositions were designed, one with OPC (CEM I) and one with BFSC (CEM III/B LH HS, *ca.* 70% slag). Both mixes contain 340 kgm^{-3} cement, have a w/c 0.50 and river sand and gravel with maximum grain size 32 mm [1,2]. The compressive cube strength of these mixes at 28 days is about 43 MPa.

From these two 'standard' mixes, slabs of 0.5×0.5 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 h with plastic foil. Then the slabs were cured for 48 h in a fog room. Specimens were sawn of 100×100 mm^2 (finished or bottom) surface with a depth of about 75 mm. 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 specimens twice in the liquid for 5 s with 10 min intervals. After application, specimens were stored for (at least) four weeks in air of 20°C and 65% RH before testing.

5. Materials: Hydrophobic Agents

Commercial hydrophobic products for concrete consist of silanes and/or siloxanes. Silanes contain 100% active substance or they are dissolved in alcohol or hydrocarbons (with 10–40% active substance). Siloxanes are dissolved in alcohol or hydrocarbon solvents (*ca.* 10–20% active substance). Silanes and mixtures of silanes and siloxanes are also available as water-borne systems (with 10–20% active substance). For environmental reasons, in the Netherlands the product is not allowed to contain any volatile organic solvents. 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); and

- 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. Salt Water Absorption during Prolonged Exposure

In previous work, absorption of pure water was tested up to 24 h only. Water absorption was reduced by a factor of five to ten [1,2]. 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 for longer periods. Standard specimens (controls and those treated with hydrophobic agents B (100% silane) and E (20% silane dispersed in water)) were brought in permanent contact with pure water or 10% NaCl (by mass) solution for 28 days. At any time during these 28 days, salt water absorption was much lower for hydrophobised concrete than for untreated concrete, roughly
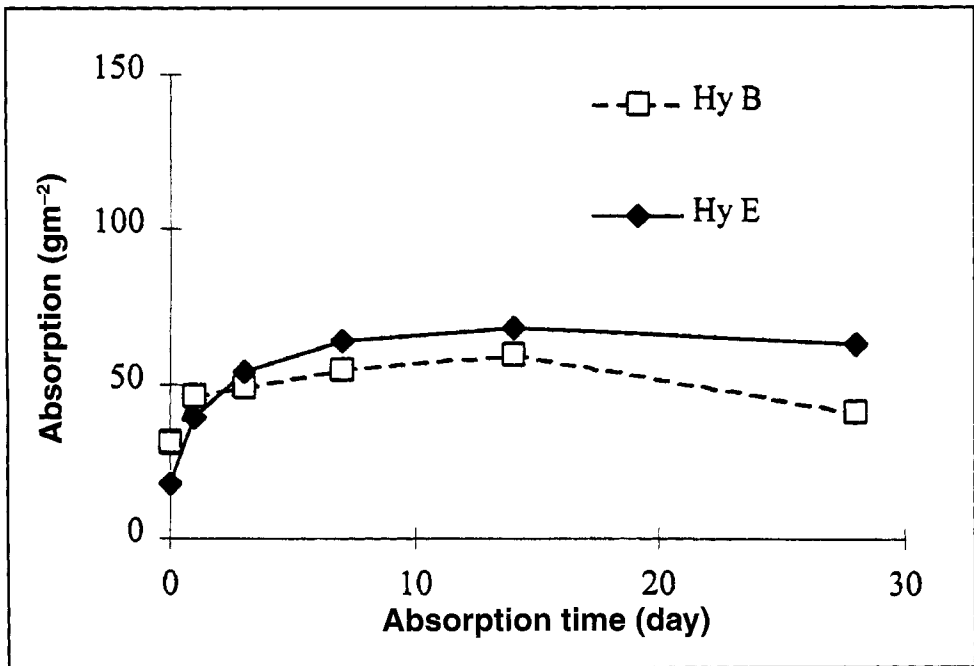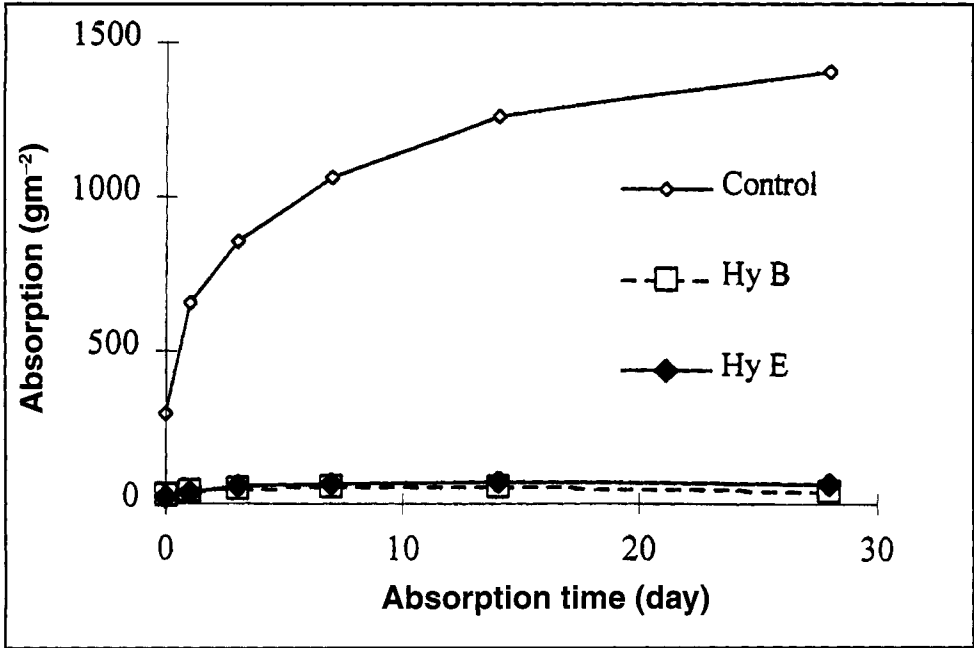
Fig. 2 *Salt water absorption of OPC concrete (top): same with tenfold vertical magnification showing hydrophobised specimens only (bottom).*

by a factor of ten (Fig. 2); similarly 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 high chloride concentrations.

7. 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 wetting and drying cycles with a salt solution, simulating de-icing salt application. The specimens (only finished surfaces) were made with OPC and BFSC (standard composition). They were treated with product B or product E according to the standard application procedure. Per cycle, the treated surfaces were allowed to absorb a 10% NaCl (by mass) solution for 24 h 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 (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; in non-treated OPC concrete this was 2.8%; in BFSC non-treated concrete 2.4%, as shown in Figs 3 and 4. 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 (pure) water absorption. The chloride content of the outermost layer is reduced by at least a factor of 3. It may be concluded that hydrophobic treatment of concrete, made with either Portland
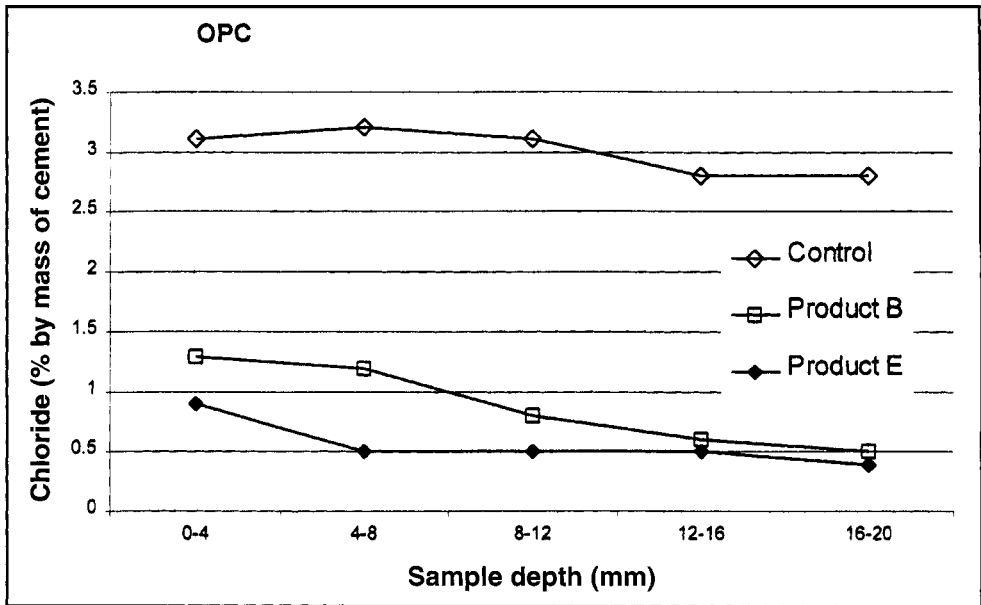

Fig. 3 Chloride penetration in control and hydrophobic Portland cement concrete after 12 months weekly de-icing salt cycles.
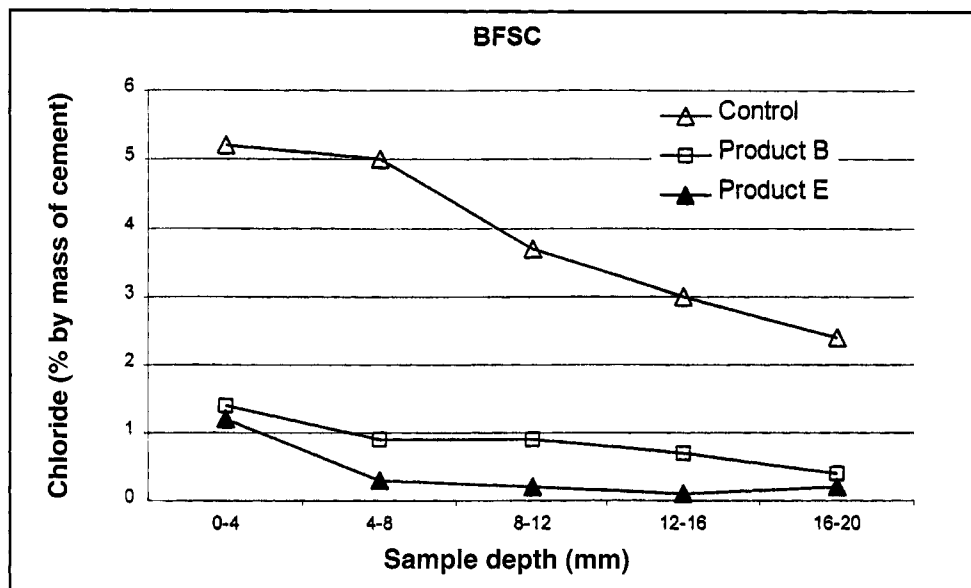
Fig. 4 Chloride penetration in control and hydrophobic blast furnace slag cement concrete after 12 months weekly de-icing salt.

cement or blast furnace slag cement, strongly slows down the penetration of chloride under salt application drying cycles.

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 surface. They were exposed horizontally for a total of 62 months with the treated sides upward, on the roof of a building with free access of wind and rain. 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 h, 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 Fig. 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 h against the square root of time. Three different trends can be seen: (i) the WAC of OPC controls show a strong reduction, (ii) the WAC of BFSC controls showed only a small reduction, and (iii) 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
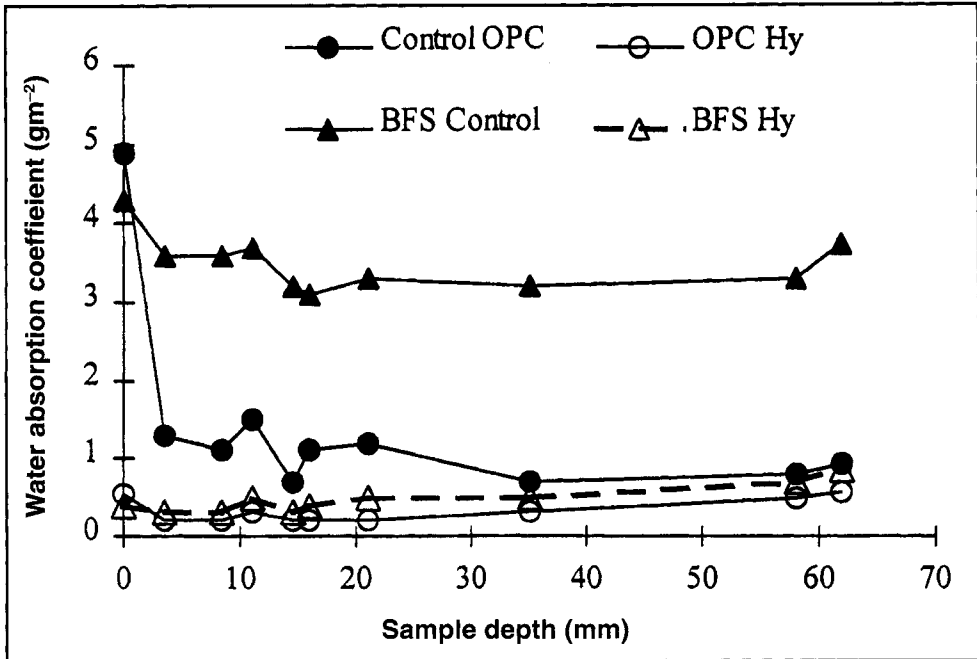
Fig. 5 *Water absorption coefficient (24 h) after exposure outside.*

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 h the water had penetrated gradually but deeply into the OPC sample, corresponding to a rather homogeneous capillary structure (see Fig. 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, i.e. in the absence of UV-radiation, the durability of the hydrophobic effect is expected to be at least the same or better.
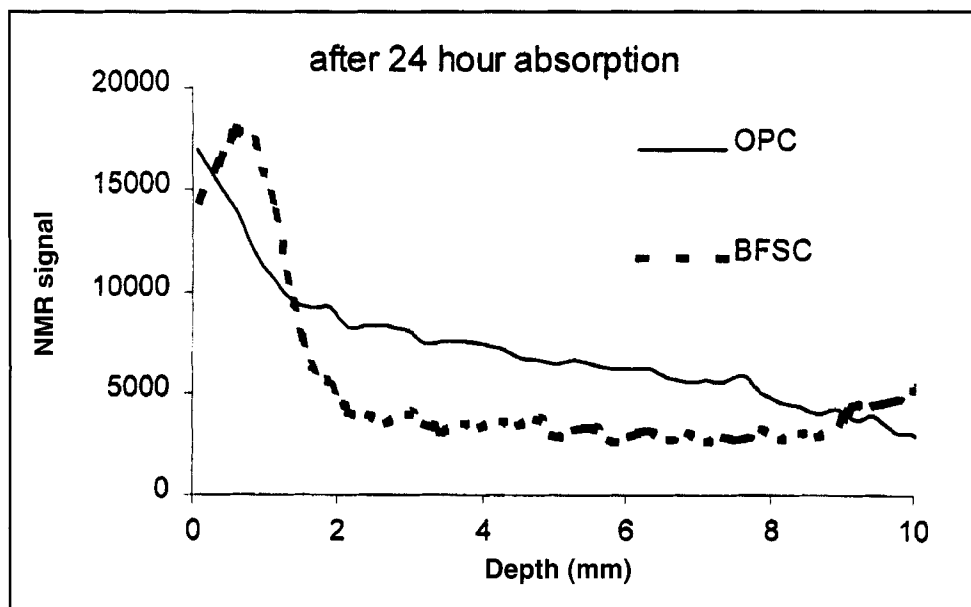
Fig. 6 *Moisture profiles obtained by Nuclear Magnetic Resonance (NMR) in non-hydrophobised samples of OPC and BFSC after absorption of water for 24 h.*

9. Effect on Chloride-Induced Corrosion

To study the corrosion rate of bars in chloride-contaminated concrete, twelve macrocell specimens were made of standard OPC and BFSC concrete. They were beams of $300 \times 150 \times 150\ mm^3$ with two reinforcing bars (12 mm × 200 mm length) at 25 mm depth from the upper surface (intended anodes) and two bars at 110 mm depth (intended cathodes) (see Fig. 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
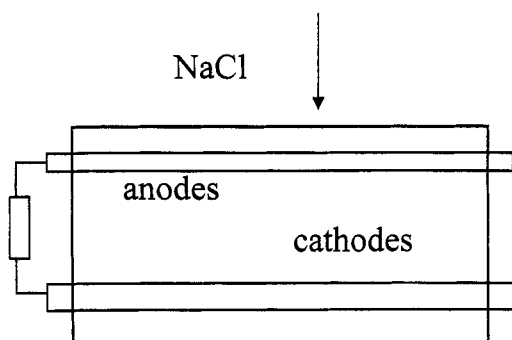

Fig. 7 *Macrocell specimen.*

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 Am^{-2}, 59 weeks after the 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 as follows:

- outside for about a year;

- in air of 20°C and 80% RH for half a year;

- for a short time in a fog room; and

- outside for another half year.

The total exposure after hydrophobic treatment lasted four years. Corrosion rates were determined as macrocell currents between top and bottom bars and as linear polarisation resistance of top bars using current confinement (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.

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 μAcm^{-2}. Macrocell currents and linear polarisation results corresponded well. Steel potentials were quite negative (–250 to –400 mV vs Ag/AgCl). In BFSC specimens, the chloride content was lower (0.4% to 1.1%) and low corrosion rates were observed (below 0.2 μAcm^{-2}); potentials were much less negative (–100 to –200 mV vs Ag/AgCl). 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 (Fig. 8). During exposure in the fog room, the corrosion rate increased, indicating that hydrophobic treatment did not prevent moisture from entering the concrete 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 500 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 16 μm loss of steel diameter, fine cracking took place. From 80 μm 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, this does not stop the corrosion if the concrete is exposed to regular wetting.
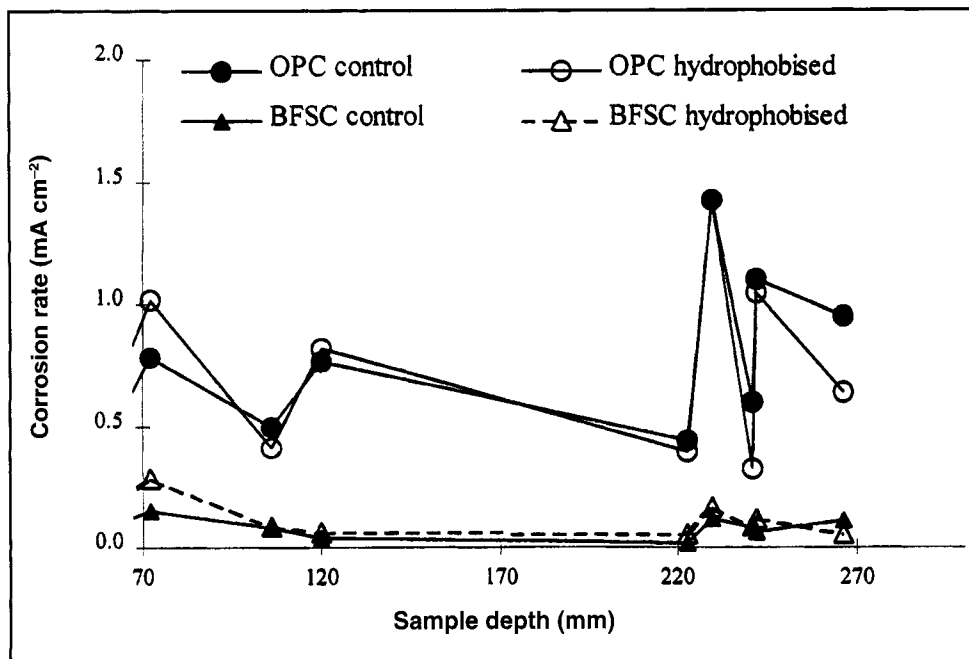
Fig. 8 *Corrosion rates in chloride-contaminated OPC and BFSC concrete, control (untreated) and hydrophobised (in week 70 after casting).*

10. Carbonation

There is some concern that drying out due to hydrophobic treatment causes deeper carbonation and may promote corrosion of reinforcement. It could be argued, 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 1–2 mm; in OPC hydrophobised 1–3 mm. In BFSC controls, carbonation depths were 1–7 mm, in BFSC hydrophobised 1–5 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.

11. Conclusions

Hydrophobic treatment of concrete is an effective, low cost preventative measure against corrosion. It has become the standard practice in The Netherlands for all new bridge decks built for the Ministry of Transport. The beneficial effect is mainly a strong reduction of chloride ingress, both in semi-permanent contact and in wetting/

drying situations. The protective effect remains intact for many years. Carbonation of concrete is not significantly accelerated. Hydrophobic treatment does not stop corrosion that has already been initiated by chloride penetration before the treatment.

12. Acknowledgements

References

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