AN INVESTIGATION INTO THE PERFORMANCE OF TWO CORROSION INHIBITORS AS CONCRETE STRUCTURE PROTECTION PRODUCTS.

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OPSOMMING

'n Studie waartydens die prestasie van twee korrosie afwerende produkte (Surtreat TPS 2 en TPS 4) as beton herstel- en beskermingsprodukte ondersoek word. 'n Aantal betonblokke was gegiet en nabehandel vir 28 dae. Van die blokke is behandel met TPS 2 of TPS 4 soos voorgeskryf deur die verskaffer terwyl sekere blokke nie behandel was nie. Die blokke wat behandel is, se oppervlaktes was voor die behandeling eers goed skoon gemaak. Die twee herstelprodukte is geevalueer deur die volgende toetse te doen:

- korrosietoetse (halfsel lesings)
- druktoetse
- aftrektoetse
- waterpermeabiliteitstoetse
- chloriedtoetse
- chemiese weerstand teen sure

Resultate van hierdie toetse is vergelyk en 'n gevolgtrekking ten opsigte van die prestasie van elk van die produkte is gemaak.

SUMMARY

A study through which the performance of two corrosion inhibitors (Surtreat TPS 2 and TPS 4) as concrete repair and protection products is investigated. A number of concrete blocks were cast and cured for 28 days. Some of the blocks were treated with TPS 2 or TPS 4 as prescribed by the manufacturer and some of the blocks were not treated. The surfaces of the blocks that were treated had been cleaned thoroughly prior to the treatment. The two repair materials were evaluated by doing the following tests:

- corrosion tests (half-cell measurements)
- compressive tests
- pull-off tests
- water permeability tests
- chloride tests
- chemical resistance to acids

Results of these tests were compared and a conclusion was made regarding the performance of each of the products.

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PROBLEM STATEMENT

It is to the credit of concrete that the infrastructure of the world is in place. Most of the structures around us are composed of concrete and we rely on it to be in good condition to make our lives easier and more productive. But like everything else, concrete isn't indestructible and deteriorates with time requiring maintenance and repair to prolong its useful life.

The cost of protecting and restoring concrete structures worldwide is a large and growing problem. Most problems that occur with concrete are related to a breakdown of the chemical and physical properties of the concrete.

One of the most common problems with reinforced concrete is corrosion of the embedded reinforcing steel. This corrosion is an oxidation process requiring the presence of air and moisture and it is promoted by chlorides and an acid environment.

Freshly poured low water-cement ratio concrete provides an excellent protection for the imbedded reinforcement due to the high alkali environment. Subjected to the physical and chemical environment, over time, concrete will eventually deteriorate. Thus, concrete becomes increasingly permeable and susceptible to intrusion of contaminants and moisture. As the pH of concrete falls, electrochemical activity increases. The process perpetuates itself as oxidized reinforcing steel expands forcing concrete to crack and delaminate thus encouraging air and water penetration.

The purpose of this study is to investigate the performance of two commercial products (Surtreat TPS 2 and TPS 4) as concrete repair and protection products. Throughout this report, reference to these two products will be made as follows:

Surtreat TPS 2 \rightarrow Product A Surtreat TPS 4 \rightarrow Product B

CHAPTER 1 CONCRETE

1. General

Concrete is made by mixing cement, sand, stone and water in predetermined ratios. This mixture sets and hardens to become a stone-like material. Concrete and steel are the most widely used construction materials with the use of the composite material, concrete reinforced with steel, becoming one of the most popular methods for civil construction. The main reason for using reinforcing steel in concrete is that concrete gains most of its flexural and tensile strength from the imbedded reinforcing steel.

It is to the credit of concrete that the infrastructure of the world is in place. Most of the structures around us are composed of concrete yet it is barely noticed unless there is something wrong. We rely on it to be in good condition to make our lives easier and more productive. But like everything else, concrete isn't indestructible and it deteriorates requiring maintenance and repair to prolong its useful life.

2. The history of cement and concrete

Cementitious materials have been used for many thousands of years. The first historical record of aggregate bound with cement being used from an archaeological site in Yugoslavia which is thought to be over 5000 years old. The cementitious materials used at this site were transported over 100 km down a river, which indicates that this act was premeditated ³⁾.

A little later, the Egyptians used a mortar made from calcined impure gypsum. The Greeks and Romans used calcined limestone with, later, addition of lime, sand and crushed stone or brick. Volcanic ash from the volcano Pozzuoli was also added to some cement. This addition of volcanic ash, which contained silica and aluminium elements gave the cement some pozzolanic properties ³⁾.

3. Cement

Cement is defined as a binder, glue or adhesive. Cement in hardened concrete and mortar forms a matrix which binds aggregate particles to form a strong, rigid composite ²).

Cementitious materials for building and construction consist, with few exceptions, of portland cement on its own or blended with a cement extender. Such materials are supplied in powder form and, if mixed with water, will set and develop strength ².

3.1 Portland cement

The most commonly used cement in building and construction is Portland cement.

Because it is relatively cheap and setting and hardening take place at normal temperature

and pressure, portland cement is used as a basis of cementitious materials and concrete

made with portland cement can be made to be strong and durable.

3.1.1 Manufacturing and composition of portland cement

The main raw materials that are used in the manufacturing of Portland cement are chalk or limestone and clay or shale. Lime is produced by heating calcium carbonate. Silica, alumina and ferric oxide are obtained from clay or shale ².

Firstly calcium carbonate is converted to calcium oxide in the kiln at temperatures between 800°C and 1000°C. The materials then flow to a hotter part of the kiln where, at temperatures between 1400 to 1450°C, the blend of lime, silica, alumina and ferric oxide is converted to cement clinker ².

Cement clinker consists of four main compounds: tricalcium silicate, dicalcium silicate, tricalcium aluminate and tetracalcium aluminoferrite. Gypsum is added to the clinker at the milling stage to retard the rate of hydration of the cement ²). Tricalcium silicate is the compound that distinguishes portland cement from other cements made with lime and silica ²).

3.1.2 Hydration of portland cement ²⁾

The reaction of cement and water is called hydration and it is exothermic.

In this section, cementing reactions are discussed in simplified terms. The following abbreviations are used:

> C = CaO, calcium oxide S = SiO₂, silica A = Al₂O₃, alumina F = Fe₂O₃, ferric oxide H = H₂O, water

Therefore

 C_3S = tricalcium silicate C_2S = dicalcium silicate C_3A = tricalcium aluminate C_4AF = tetracalcium aluminoferrite CH = $Ca(OH)_2$, calcium hydroxide

The hydration of portland cement is described by the following reactions:

$2C_3S + 6H \rightarrow C_3S_2H_3 + 3CH$	(1)
$2C_2S + 4H \rightarrow C_3S_2H_3 + CH \dots$	(2)
$C_3A + CH + 12H \rightarrow C_4AH_{13}$	(3)
$C_4AF + 4CH + 22H \rightarrow C_4AH_{13} + C_4FH_{13} \dots \dots$	(4)

CH for reactions (3) and (4) is provided by reactions (1) and (2). Reaction (3) has intermediate stages involving sulphate from the gypsum that are not shown. Reactions (1) to (4) are all exothermic.

Reaction products have the following characteristics: S_2H_3 , Calcium silicate hydrate, is in the form of very fine needles and plates, and contributes most of the strength of the hardened cement paste. CH, calcium hydroxide, is in the form of relatively large crystals which do not contribute to the strength of the hardened cement paste. C_4AH_{13} and C_4FH_{13} do not contribute significantly to the strength of the hardened.

3.1.3 Setting and hardening

The main compounds in portland cement are calcium silicates. When portland cement is mixed with water in concrete, the calcium silicates react with the water to produce:

- Gel consisting of calcium silicate hydrate
- Lime

Concrete receives its strength from the gel in the hardened cement paste. Lime gives the hardened cement paste its alkalinity. The alkaline environment prevents corrosion of the reinforcing steel ¹⁾. The eventual density and strength of the gel structure depends on the ratio of water to cement (W/C) in the mixture. The lower the W/C the stronger the gel structure ¹⁾.

If cement and water are mixed to make a sample of cement paste, little appears to happen for some hours. The mixture then starts to set and harden. Cement paste in concrete goes through the same stages. The hardened concrete gains strength, rapidly at first but more slowly as time goes on ¹⁾.

The cement will continue to hydrate only while water is available. That is why concrete should be cured. The long-term strength of well cured concrete depends on the type of cement and the ratio of water to cement ¹⁾.

A batch of cement may exhibit a sudden stiffening within a few minutes of adding the mixing water. This condition may be due either to false set, or to flash set.

False set is characterized by a negligible evolution of heat by the cement paste. When the stiffened concrete is re-mixed without additional water, it regains its plasticity and may then be handled and placed in the normal manner. False set is caused by overheating during grinding of the clinker ²⁾.

With flash set the cement paste heats up excessively. Reworking does not restore the original workability. Flash set is caused by including too little gypsum in the cement ¹⁾.

4. Aggregates

Aggregates are used in concrete in order to make the concrete dimensionally more stable, e.g. lower shrinkage. Aggregates are also used in order to provide bulk and therefore make the mix cheaper. Aggregates are devided into two categories according to size: sand or fine aggregate, and stone or coarse aggregate. Sand refers to particles that will pass through a sieve with 4,75 mm square openings. Stone refers to particles too big to pass through such a sieve. About three-quarters of the volume of concrete are occupied by aggregates. Therefore the properties of the aggregates have a big effect on the properties of the concrete $^{1,2)}$.

Aggregates in South Africa are obtained from solid rock, which is crushed or has been broken down by natural processes. Other sources of aggregates are waste products such as slag and crushed building rubble; synthetic compounds such as polystyrene; and heat-treated minerals such as perlite and vermiculite. The latter two types are used for low-density concrete ².

The grading and particle shape of aggregate is very important. If concrete is made with the wrong shape aggregate, bleeding can occur. Water can become trapped under the aggregate particles causing voids and the concrete will need more water to keep its workability. If the grading of aggregates is wrong, the voids in the concrete aren't properly filled and this will lead to dimensional instability ³⁾.

The strength of aggregates is not important, but with high strength concrete of about 70MPa and higher, the aggregate strength becomes very important.

The bond between cement paste and aggregate is an important factor in the strength of concrete. Bond is due, in part, to the interlocking of the hydrated cement paste and the aggregate due to the roughness of the surface of the latter. Better bond is usually obtained with a rougher surface such as that of crushed particles, due to mechanical interlocking ³.

5. Mixing water ¹⁾

Mixing water makes the fresh concrete workable and it reacts with cement to form strength-giving compounds.

The criterion for water to be used for making concrete is that it should be drinkable. Water taken from municipal sources can be accepted as suitable. Other waters may contain sufficient impurities to affect the quality of the concrete.

If the suitability of the water is in doubt, it may be used for concrete if mortar cubes made with the suspect water set normally and have a 28-day strength of at least 90% of the strength of similar cubes made with water of known purity.

Sea water may be used in unreinforced concrete where the salt content is not important: where efflorescence or mottling does not matter and aggregates are not liable to be attacked by alkalis present in sea water.

6. Admixtures

Admixtures are materials other than hydraulic cement, water, aggregates and supplementary cementing materials, that are used as ingredients of concrete or mortar and are added to the batch immediately before or during mixing. Admixtures are used to improve or modify one or more of the properties of concrete ^{2,3)}.

The properties of fresh concrete can be modified in order to:

- Increase slump, without increasing water content
- Reduce water content, without changing slump
- Adjust setting time
- Reduce segregation

- Improve pumpability
- Reduce bleeding ²⁾

The properties of hardened concrete can be modified in order to:

- Accelerate the rate of strength development at early ages
- Increase strength, without increasing cement content
- Improve durability and reduce permeability ²⁾

Admixtures are commonly classified in terms of their function:

Air-entrainer: By using an air entrainer, small amounts of air bubbles may be entrained in concrete to reduce bleeding and improve workability of the fresh concrete and enhance durability of hardened concrete exposed to cycles of freezing and thawing. Entrained air is different from entrapped air resulting from incomplete compaction of the fresh concrete during placement. Entrained air reduces strength and density of the hardened concrete. Mix proportions should be revised accordingly if necessary ^{1,2)}.

Plasticizers or **water reducers:** Plasticizers and water reducers are water-soluble, organic materials which increase the slump of concrete without increasing the water content of the concrete. Alternatively they reduce the water content without changing the slump. The cement content may be reduced for the same strength $^{1,3)}$.

Superplasticizers: Superplasticizers act in a similar way as plasticizers and water reducers but are more efficient in dispersion of the cement grains, so very high workabilities can be achieved. Superplasticizer is an important ingredient of high-strength concrete. By using superplasticizers and South African aggregates the water can be reduced by 15 to 25% and will result in a much higher strength ^{2,3)}.

Retarders: Most retarders are based on sugar. Retarders form a film around each cement particle to slow down the initial hydration process which will result in delaying of the setting and hardening of the concrete. This may be necessary when a truck mixer is delayed on its way to site or ambient temperatures are higher than normal. By selectively retarding some of the concrete, cold joints in extensive placements may be prevented ^{1,3}.

Accelerators: Accelerators are chemicals which increase the rate of the hydration reaction, thus accelerating the setting and early strength development. Accelerators are mainly used when high early strengths are required, for example in repair and marine work $^{1,3)}$.

The overall effect of the admixture on the fresh and hardened concrete must be assessed by preliminary tests including trial concrete mixes. The stage of the mixing cycle at which the admixture is added, is very important. The manufacturer's recommended dosage and instructions must be followed strictly. Over- or under-dosage may lead to serious problems such as uncontrolled retardation, plastic-shrinkage cracking, settlement cracking and low strength ¹.

7. Properties of fresh concrete

Concrete is in the fresh state from the time it is mixed until it sets. The concrete is handled, transported, placed and compacted during this time. Concrete is in the fresh state for only a few hours, compared with a service life that may be several decades. The properties of fresh concrete influence the properties of the hardened concrete and are therefore very important $^{1)}$.

7.1 Consistence and workability

The measure of the stiffness/sloppiness or fluidity of the mix is known as the consistence of the mix. The consistence of a mix is generally measured with the slump test ¹).

The workability of a mix is the ease with which concrete is handled, transported, placed, compacted and finished without separation or segregation of the individual materials¹).

It is not possible to measure workability, but the slump test, together with an assessment of cohesiveness and plasticity, gives an indication.

Workability, at a given consistence, is influenced by the following:

- Stone size: The smaller the stone the better the workability.
- Fines content of sand: The cohesiveness of the concrete increases with increasing fines content.
- Cement content: The cohesiveness also increases with increasing cement content.
- Stone content: The concrete tends to be harsh and difficult to compact and finish if the stone content is too high. If the stone content is too low, the mix contains excess mortar and becomes dimensionally unstable and expensive because of the high cement content ¹.

7.2 Bleeding

Cement and aggregates have densities about three times that of water. Some of the mixing water rises to the surface of the concrete as the solid materials settle. In fresh concrete they tend to settle and displace mixing water which migrates upward and may collect on the top surface of the concrete. Bleeding will continue until the cement paste has stiffened sufficiently to prevent further settlement $^{1,2)}$.

Settlement and bleeding have beneficial and harmful effects on concrete:

Beneficial:

- Bleeding reduces the water/cement ratio by removing water from the concrete and improves potential strength and impermeability.
- A film of bleed water on the surface of concrete will result in the reduction of the evaporation of water from the concrete and so reduces plastic shrinkage¹.

Harmful:

- When bleed water gets trapped under reinforcing steel and stone it creates weak internal surfaces and increases the permeability of the hardened concrete.
- Where settlement is restrained, e.g. by horizontal reinforcement or by steps in the formwork surface, the concrete may crack.
- Bleeding results in a weakened top surface because of the increased water/cement ratio at the top surface ¹⁾.

7.3 Plastic shrinkage ¹⁾

If water is removed from compacted concrete before it sets, the volume of the concrete is reduced by the amount of water removed. This volume reduction is called plastic shrinkage. Water may be removed from the plastic concrete by evaporation or by being absorbed by dry surfaces such as soil or old concrete.

Plastic shrinkage is not harmful in itself, but the concrete may crack where shrinkage is restrained, e.g. by formwork.

Plastic shrinkage can be avoided by preventing the loss of water from the fresh concrete, e.g. by pre-wetting soil before placing concrete on it and by covering with plastic sheeting.

8. Properties of hardened concrete

Concrete structures must have the following properties to be safe and serviceable:

- They must be strong enough to carry their loads.
- Distortion from loading or environmental conditions must be acceptably small.
- They must be durable.
- They must be capable of holding water if necessary ¹).

The performance of concrete structures depends on the properties of the hardened concrete from which they are made.

8.1 Strength

The strength of hardened concrete is very important to structural engineers. It is also used as an index of other concrete properties and of concrete quality ²). Most of the time the strength of concrete is determined in compression.

Compressive strength is used as a criterion of concrete quality and is measured by making cubes and loading them to failure. The cubes are made of concrete sampled from the concrete being placed in the structure, and cured in water at a standard temperature. Three water-saturated cubes must be tested at each age $^{1)}$.

The compressive strength of concrete in the structure may also be measured by testing cores removed from the structure. Cores are crushed after they have been sawn to the correct length and their ends capped or ground flat.²⁾.

The factors that influence the strength of concrete is the following:

- Water-cement ratio and cement type: The lower the water-cement ratio, the stronger is the concrete.
- Aggregates: Aggregates play only a significant role in high strength concrete of about 60 MPa and stronger.
- Compaction: If compaction is incomplete, there is still air left in the concrete and the strength is reduced by about 6% for every 1% of air.
- Age of concrete: Strength increases rapidly once concrete has set but the rate of strength gain reduces with time.
- Curing: Strength of concrete develops only while sufficient water is present for hydration to take place.

- Temperature: The rate of strength gain is retarded by low temperatures and accelerated by high temperatures ¹).

8.2 Shrinkage and cracking

Concrete will shrink when it dries out. It may shrink as much as 1 mm in 2,5 m without cracking occurring, if the shrinkage is completely unrestrained. A similar but smaller expansion will occur when dry concrete becomes wet. All concrete cracks to some extent on drying. Fortunately, most of the cracks are too small to be seen by eye and do not affect durability ³⁾.

Properly distributed reinforcement in a structure helps to spread the stresses evenly and minimizes the occurrence of large cracks. With richer mixes, greater shrinkage and cracking can occur. Wetter more workable mixes may produce more small invisible cracks but are less likely to produce large unsightly cracks ³⁾.

8.3 Durability

Stronger concretes will be more durable and the engineer may rely on his or the industries' experience to assess the quality he needs for the job, rather than devise special testing techniques ³⁾.

For greater durability, specific cements, aggregates and admixtures may be preferred. To provide additional safeguards, a minimum cement content and/or a maximum water/cement ratio may be specified ³⁾.

8.4 Elastic stiffness

Concrete behaves elastically when loaded. While under load, it distorts to some extent but when the load is removed, it recovers its original dimensions. The degree to which concrete distorts as a result of a given stress, is important to the structural engineer and is dependent on the elastic stiffness of the concrete. Elastic stiffness is defined as stress per unit strain ¹).

CHAPTER 2

CORROSION OF STEEL IN CONCRETE

1. Introduction

Reinforced concrete is formed by placing steel bars in the concrete form. The strength of the steel bars, when bonded to the concrete, significantly increases the strength of a structure. Reinforcing steel corrosion, one of the most common problems with concrete, is an oxidation process requiring the presence of air and moisture. It is promoted by anions, like chloride, which can be carried in by sea spray, and an acid environment. Corrosion is inhibited by an alkaline environment such as cations and barrier coatings.

Freshly poured low water-cement ratio concrete provides an excellent protection for the imbedded reinforcing steel due to the high alkali environment. As time passes, under the influence of salts and atmospheric acids, cement bonds in concrete begin to deteriorate. Thus, concrete becomes increasingly permeable and susceptible to intrusion of contaminants and moisture. As the pH of concrete falls, electrochemical activity increases. The process perpetuates itself as oxidized reinforcing steel expands forcing concrete to crack and delaminate thus encouraging air and water penetration.

2. Causes and mechanisms of corrosion and corrosion damage in concrete

2.1 Carbonation

Carbonation is the process by which carbon dioxide gas in the atmosphere reacts with the alkaline hydroxides in the concrete. Carbon dioxide dissolves in water to form weak carbonic acid, which reacts with calcium hydroxide to form calcium carbonate $(CaCO_3)^{12}$.

There is a lot more calcium hydroxide in the concrete pores than can be dissolved in the pore water. This helps maintain the pH at its usual level of around 12 or 13 as the carbonation reaction occurs. Eventually all the locally available calcium hydroxide reacts. The removal of hydroxyl ions from the cement paste pore solution results in reduced alkalinity, which results in carbonation of the reinforcing steel ¹².

Carbonation damage occurs most rapidly when there is little concrete cover over the reinforcing steel. If the density of the concrete is low, carbonation can occur even when the concrete cover depth to the reinforcing steel is high. It may also happen when alkaline reserves in the pores are low. These problems occur when there is a low cement content, high water cement ratio and poor curing of the concrete ⁴.

The carbonation rate is a function of cover thickness, so good cover is essential to resist carbonation. Good reserves of alkali are needed to resist carbonation because the process is one of neutralizing the alkalinity of the concrete. The concrete must be well compacted to resist carbonation because the diffusion process is made easier if the concrete has an open pore structure. Well-cured concrete has small pores and lower connectivity of pores so the CO_2 has a harder job moving through the concrete ⁴.

Carbonation is easy to detect and measure. A pH indicator, usually a solution of phenolphthalein in dilute alcohol, will detect the change in pH across a freshly exposed concrete face. This test is cheap and easy to use. Dust and water must be prevented of contaminating the surface to be measured ⁴⁾.

2.2 Chloride attack

2.2.1 Sources of chlorides ⁴⁾

Chlorides can come from several sources. They can be cast into the concrete or they can diffuse in from the outside. Chlorides cast into concrete can be due to:

- the deliberate addition of chloride set accelerators
- use of sea water in the mix.
- contaminated aggregates (usually sea dredged aggregates which were unwashed or inadequately washed).

Chlorides can diffuse into concrete as a result of:

- sea salt spray and direct sea water wetting.
- deicing salts.
- use of chemicals (structures used for salt storage, brine tanks, aquariums).

The main problem in most places is the diffusion of chlorides into concrete either due to marine salt spray or use of deicing salts. A low level of chloride cast in can lead to rapid onset of corrosion if further chlorides become available from the environment.

This often happens in marine conditions where seawater contaminates the original concrete mix and then diffuses into the hardened concrete.

2.2.2 Chloride transport through concrete

The chloride penetration rate is approximated to the laws of diffusion.

The dry concrete rapidly absorbs saltwater. Then there is some capillary movement of the salt-laden water through the pores followed by true diffusion. There are opposing mechanisms that slow the chlorides down. These include chemical reaction to form chloroaluminates and adsorption on to the pore surfaces 4,13 .

Another problem with trying to predict the chloride penetration rate is defining the initial concentration, as chloride diffusion produces a concentration gradient, not a front $^{4)}$.

2.2.3 Chloride attack mechanism

The passive layer is attacked by chloride ions but there is no overall drop in pH. When there is sufficient concentration of chlorides at the reinforcing steel surface, the chlorides act as catalysts to corrosion. They are not consumed in the process but help to break down the passive layer of oxide on the steel and allow the corrosion process to proceed quickly. Chloride attack is hard to eliminate $^{4,13)}$.

2.3 Corrosion damage

Corrosion is a concern because of wastage of metal leading to structural damage such as a collapse, perforation of containers and pipes and so forth. The problems with the corrosion of the reinforcing steel in concrete are due to the growth of the oxide. The rust product is much larger than the original steel and will result in tensile stresses in the surrounding concrete that will lead to cracking and spalling of the concrete cover 4,12 .

The most common problem caused by corrosion is spalling of concrete cover. A man was killed in New York City by a slab of concrete which spalled of a bridge substructure due to deicing salts⁴⁾.

The volume of oxide and where it is formed are the important factors regarding the corrosion of steel in concrete. A dense oxide formed at high temperatures such as in a power station boiler usually has twice the volume of the steel consumed. The major problem is that the pore water is static because there is no transport mechanism to move the oxide away from the steel surface. All the oxide is deposited at the

metal/oxide interface. Another problem is that the oxide has a very low density and a very high porosity and therefore takes up a much larger volume than the original steel $\frac{4,13}{2}$.

Corners tend to crack first on corroding reinforced concrete structures. This is because the oxygen, moisture, chlorides and carbon dioxide have two faces as paths to the steel. Delaminations occur as corrosion proceeds on neighbouring reinforcing steel bars and the cracks join up $^{4,13)}$.

3. Condition evaluation

3.1 Initial survey

The initial survey is done to determine the likely cause of the deterioration and to provide the information from which a detailed survey can be planned. An initial survey is based on a close visual inspection of elements that are accessible. In areas of obvious damage, limited testing such as half-cell potential readings and carbonation depth measurements can be done ¹². It is useful to note any problems likely to be encountered with access to critical locations during the more detailed survey. The initial survey is very important as the impressions gained will set the tone of the later stages of the survey ¹³.

3.2 Detailed survey

Once the initial survey has been completed, a program for the detailed survey would be prepared, by using the information gained from the initial survey. The purpose of a detailed survey is to determine the extent and severity of deterioration as accurately as possible. Such a survey generally requires between 10% and 20% of the elements that are at risk are selected for testing. It is essential to know the extent and the cause of the damage. The first question that must be attended to is whether the observed deterioration is a local problem or one that occurs widely around the structure. Quantities for repair tenders will probably be based on the results of this survey, so a full survey of all affected elements may be required. Deterioration of concrete will vary from member to member. A full visual and hammer survey may be required, with detailed measurements of half cell potentials, chloride contents, carbonation depth, cover, etc. at a few locations. The weather conditions are also recorded as these can affect some readings ^{4,12,13}.

3.3 Visual inspection

A visual inspection of the exposed concrete is the first step in any investigation. The purpose of the visual survey is to locate and define areas of deterioration. If concrete is spalling off then that can be used as a measure of extent of damage. Weighing the concrete that spalls off over set periods can be used as a direct measure of the deterioration rate $^{4,6)}$.

The main equipment is the human eye and brain, aided with a notebook and a camera. The date, time and weather conditions must be recorded when doing the survey. Visual observations such as water or salt run down and damp areas must be recorded. The Strategic Highway Research Program has produced an expert system which guides the less experienced engineer or technician through the different type of defects seen on concrete ⁴⁾.

3.4 Delamination

The corrosion product formed takes up a larger volume than the steel consumed. Tensile stresses are generated around the reinforcing steel bars. A layer of corroding reinforcing steel bars will often cause a planar fracture at reinforcing steel bar depth, before the concrete spalls. This can be detected at the surface by various means from hitting the surface with a hammer and listening for a hollow sound to sophisticated techniques using radar, infrared, sonic and ultrasonic equipment $^{4,6)}$.

The aim is to measure the amount of cracking between the reinforcing steel bars before it becomes apparent at the surface. The horizontal cracks are detected by a hollow sound when the surface is hit with a hammer. It can be detected from the effect on its physical properties associated either with the presence of a layer of air in the concrete or the phase change from concrete to air to concrete, when subjected to radiation or ultrasound $^{4,12)}$.

The hammer survey is quicker, cheaper and more accurate than the other alternatives such as radar, ultrasonics or infrared thermography. The hammer survey is done at the same time as the visual survey. Hollow sounding areas are delaminated and are marked directly on to the surface of the structure with a marker and recorded on the visual survey pro forma.

Infrared cameras can be used to detect the temperature difference between solid and delaminated concrete. This is best done when the concrete is warming up or cooling down as the delaminated concrete heats and cools faster $^{4,6)}$.

Radar measures changes in the dielectric constants associated with the concrete/air phase change. The radar also senses the dielectric changes at the steel-concrete interface, the presence of water and chlorides. The interpretation of radar images is therefore a difficult process.

The major use of radar and infrared has been for bridge deck surveys with vehicle mounted systems $^{4,12)}$.

3.5 Cover

Concrete cover protects the reinforcing steel against the effects of carbonation and corrosion. The cover needs to be of an adequate thickness and composed of sound concrete to provide such protection. The depths of concrete cover to the reinforcement are measured at the surface of the concrete ¹². The depth of reinforcing steel bars is sometimes difficult to disentangle from the bar size because a large bar at a great depth can give the same reading as a small bar near the surface. The depth of the reinforcing steel can be estimated by covermeter readings to about + or -5 mm^{-14} . A covermeter survey is also carried out when corrosion is observed because low cover will increase the corrosion rate by allowing chlorides and carbonation more rapid access to the steel and also allowing more rapid access of moisture and oxygen. A cover survey will help explain why the structure is corroding and show which areas are most susceptible to corrosion due to low cover ⁴.

3.6 Half cell potential measurements

Reinforcing steel that is in its ideal non-corroding state is covered with a very thin layer of oxide that is continuously being maintained and repaired by the alkaline materials which surround it. Corrosion causes electrical potentials to be generated and the half-cell provides a method of detecting and categorizing these electrical potentials. The half-cell consists of an electrode of a metal contained in an electrolyte consisting of a saturated solution of one of its own salts, such as copper in copper sulphate and silver in silver chloride. Electric connections have to be made with the reinforcing steel and with concrete surrounding it to make electrode potential measurements. If it is connected to another metal in a solution of its own ions there will be a potential difference between the two half-cells. If the potential measured is small (0 to -200 mV against a silver/silver chloride half-cell), the steel is passive. If the potential moves towards -350 mV, the passive layer is failing and increasing amounts of steel are dissolving. At readings more negative than -350 mV, the steel is corroding actively.

A disadvantage of potential measurements is that very negative potentials can be found where there is no oxygen to form a passive layer and without oxygen corrosion is not possible $^{4,13,14)}$.

It is recommended to use the silver/silver chloride half-cell rather than the copper/copper sulphate half-cell. Copper/copper sulphate cells are also used but are not recommended because of the maintenance needs, the risk of contamination of the cell, the difficulty of use in all orientations and the leakage of copper sulphate ⁴.

3.7 Carbonation depth measurement

Depth of carbonation is measured by exposing fresh concrete and spraying on an indicator solution that changes colour at a certain pH. It is essential to carry out the test on a freshly exposed surface, because carbonation can take place quite quickly. This can be done by breaking away a fresh surface, or by coring and splitting or cutting the core in the laboratory. Phenolphthalein is the most commonly used indicator and it is colourless at a pH of less than 10 and purple at higher values. The phenolphthalein is applied by spraying it on a freshly broken face that is approximately perpendicular to the surface of the member. The depth to the purple coloration is measured and the average depth is recorded if the carbonated layer is of fairly uniform thickness. If the carbonated layer is not of uniform thickness, the average depth and maximum depth, or the limits of the range of carbonation depths are recorded ¹³.

An alternative method to estimate the carbonation depth is by drilling holes into the concrete in small increments and spraying the hole with phenolphthalein after each increment. The bottom of the hole is coloured purple after spraying when the uncarbonated layer is reached. The problem with this method is that drilling tends to break up and expose the alkaline unhydrated elements of the cement and gives a false result ^{13,14}.

3.8 Chloride determination

Chloride contents are measured from dust samples removed from the concrete using rotary drilling. The chloride content is determined by acid extraction of the powdered concrete, followed by a chemical determination of the chloride contents. The concrete samples are treated with acid to dissolve the cement and then titrated to find the concentration ¹².

Simple analytical devices are available for use on site and give a good indication of chloride levels, but they are not as accurate as standard laboratory analyses ¹⁴⁾. Chlorides in the field can be measured with Quantab strips or specific ion electrodes. The specific ion electrodes method is very accurate, but it is expensive and requires training to use effectively ⁴⁾.

3.9 Resistivity measurement

Corrosion of reinforcing steel is an electrochemical process which is dependant on the movement of electrically charged ions through the pore liquid in the concrete. The movement of ions causes concrete to be electrically conductive. Conductivity or resistivity is a measure of how easily corrosion current can flow as a result of the potential differences caused by corrosion conditions¹⁴.

The electrical resistivity is an indication of the amount of moisture in the pores, and the size of the pore system. Resistivity is also related to the concrete quality, i.e. cement content, water-cement ratio, curing and additives used. Chlorides are accused of reducing concrete resistivity, because they encourage the concrete to retain water ⁴.

Resistivity is usually measured by the four-probe system. An electric current is passed between outer probes and the potential difference generated between the inner probes gives a measurement of resistivity. An alternative approach measures the resistivity of the cover concrete by a two electrode method using the reinforcing network as one electrode and a surface probe as the other $^{4,14)}$.

3.10 Corrosion rate measurement

The measurement techniques can be physical or electrochemical. The weight-loss method is a physical method. Because this method is destructive and time-consuming, it is not suitable for frequent monitoring in reinforced concrete. Another physical method is the resistance probe method. This method involves embedding a metal probe in the concrete and then inferring the rate of metal loss from the resulting increase in electrical resistance 12.

The linear polarization method is an electrochemical method. Linear polarization utilizes reference and auxiliary electrodes and a variable low voltage direct current (DC) power supply. The potential for corrosion is measured first. A small current is passed from the auxiliary electrode to the reinforcement and the corresponding change in potential is measured ¹².

The corrosion current is related to the change in potential by the equation:

Corrosion rate = B/R_p

Where B is a constant and R_p is the polarization resistance(in ohms):

 $R_p = (change in potential)/(applied current)$

The change in potential must be kept to less than 20 mV or so for the equation to be valid and remain linear. Corrosion rate measurement is slow compared with half cell potential measurement. This is because the concrete reacts slowly to the electric field and changes must be reasonably slow to ensure that the electro-chemistry in the concrete is changing linearly and without capacitance effects ⁴.

A disadvantage of this method is that the readings can be misleading when the corrosion rates are localized and another disadvantage is the difficulty in accurately determining the area of steel being polarized ¹²⁾. Because the technique is slower than taking half cell measurements, it is important to take measurements at the most significant locations on the structure ⁴⁾.

3.11 Survey and assessment methodology

Following the investigation stage, the results should be processed and assessed to provide information on the risk and extent of corrosion. The interpretation of results must comprise the data from all the test methods ¹².

When carrying out a survey, it is important to define what information is needed and how that information can be collected accurately but economically. If access is a problem, it may be important to collect available information during a single access period rather than go through the expense or difficulty of providing repeat access. The type and location of measurements must be planned. Their should be allowed for flexibility as the information changes during the survey. If potentials are high in one area that may be the best place for coring and drilling ⁴.

It is important to know what information is wanted when planning a survey. While executing the survey it is important to interpret the data as it is collected to ensure that the most useful measurements are taken and that new information is used to draw the correct conclusions, not just the expected ones. The survey report should draw conclusions and make recommendations ⁴.

3.12 Monitoring

The ladder macrocell system is used where long term monitoring is required and where conditions are aggressive. The advantage of long-term monitoring is that the progression of condition changes can be monitored. The growth of anodic areas, using half cells, changes in corrosion rates using linear polarization or macrocell approaches, and the changes in concrete resistivity with time are more helpful in predicting long-term durability than the 'snapshot' approach that a survey entails⁴).

Where access is difficult on new structures, the installation of monitoring systems is recommended. The installation of monitoring systems is also recommended for structures with very long lifetimes.



Figure 3.1: Reinforcing steel corrosion

CHAPTER 3

A CONCRETE REPAIR SYSTEM

Steps in a Concrete Repair System⁷⁾

- 1. Determine the causes of damage
- 2. Evaluate the extent of damage
- 3. Evaluate the need to repair
- 4. Select the repair method
- 5. Prepare the old concrete for repair
- 6. Apply the repair method
- 7. Cure the repair properly

1. Determine the causes of damage⁷⁾

The first step of repairing deteriorated concrete is to determine the cause of the damage. If the cause of the damage to concrete is not determined and eliminated, or if an incorrect determination is made, the repaired concrete will also be damaged. Larger and more expensive replacement repairs will then be required ⁷⁾.

Remediation must be addressed, or the repair method and materials must be made resistant to predictable future damage if the cause of damage is of a continuing nature ⁷.

There is a difference between causes of damage and symptoms of damage. In the event of freezing and thawing deterioration to modern concrete, the cause of the damage may lie with the use of low quality aggregate in the concrete mix. The resultant scaling and cracking is a symptom of low durability concrete ⁷.

2. Evaluate the extent of damage⁷⁾

The purpose of this step is to determine how much concrete has been damaged and if this damage will affect the serviceability of the structure. Prediction of the rate at which damage is occurring is included in this step.

The extent of damage is determined by sounding the damaged and surrounding undamaged concrete with a hammer. This method will provide the needed information on the concrete damage when combined with a close visual inspection. If high strength concrete is given hammer blows, the concrete resounds with a ring noise and the hammer rebounds smartly. If low strength concrete is given hammer blows, it resounds with a dull noise and little rebound of the hammer ⁷⁾.

The extent of damage can also be determined by nondestructive testing methods such as the Schmidt Rebound Hammer. The Schmidt Rebound Hammer is a simple and quick method for testing concrete in place ⁶⁾.

It is a good idea to increase the calculated quantity estimates by 15 to 25 percent, because the actual area and volume of deteriorated concrete often exceeds the original estimate ⁷.

3. Evaluate the need to repair⁷⁾

Not all damaged concrete requires immediate repair. If the damage affects the safety or safe operation of the structure, then repair is required. Repair is also required if the deterioration is progressing at a rate, such that future serviceability of the structure will be reduced. With early detection, it may be possible to arrest the rate of deterioration using maintenance procedures⁷⁾.

The most optimum time must be selected to perform needed concrete repair. Many irrigation structures cannot be removed from service during the water delivery season. The costs of the repairs may be exceeded by the expense or loss of income involved with the inopportune release of reservoir water in order to lower water surface elevations to accomplish repairs. It might be better to postpone or even cancel performance of the repairs if such costs exceed the expected benefits from repairs ⁷⁾.

4. Select the repair method⁷)

The selection of proper repair methods and materials becomes easier, once the above three steps of the repair process have been carried out. These steps define the types of conditions the repair must resist, the available repair construction time period, and when repairs must be accomplished. This information, combined with data on the volume and area of concrete to be repaired, will determine which repair material should be used ⁷.

Probably more than one type of material will satisfy the design criteria for repair of a specific structure. In this case, other factors such as available labor skills and equipment, cost and ease of application should be considered in selection of the repair material ⁶⁾.

5. Prepare the old concrete for repair

Most repair projects involve removal of deteriorated concrete. Preparation of the old concrete for application of the repair material is very important in the accomplishment of durable repairs. The care with which deteriorated concrete is removed and with which a concrete surface is prepared will often determine whether a repair project will be successful ⁶. The repair material must be able to bond to sound concrete.

Concrete removal:

All damaged or deteriorated concrete must be removed from the repair area to provide sound concrete for the repair material to bond to. Sometimes it is difficult to determine when all the deteriorated concrete has been removed. The best recommendation is to continue to remove concrete until aggregate particles are being broken rather than being removed from the cement matrix ⁶. When concrete is removed with impact tools such as jackhammers, there is the potential for microfractures in the surface of the concrete left in place. The replacement material will suffer a bond failure if this damaged layer is not removed. Following impact removal, all exposed surfaces must be prepared with dry or wet sandblasting or hydroblasting to remove any damaged surface material ⁶.

The best concrete removal technique is high-pressure hydroblasting or hydrodemolition, because these techniques remove the damaged concrete and they do not leave microfractured surfaces on the old concrete ⁷⁾.

Shot blasting or wet or dry sandblasting is used to remove shallow surface deterioration. "Shot blasting equipment is highly efficient and includes some type of

vacuum pickup of the resulting dust and debris. The use of such equipment is more environmentally acceptable than dry sand blasting"⁷⁾.

Reinforcing steel preparation:

All weak, damaged, and easily removable concrete should be chipped away. If more than one-half of the perimeter of the steel bar has been exposed during removal of deteriorated concrete, then concrete removal should continue to give a clear space behind the reinforcing steel of 6 mm plus the dimension of the maximum size aggregate. If less than one-half of the perimeter of a steel bar is exposed after concrete removal, the bar should be inspected and cleaned without further concrete removal. If inspection indicates that a bar or bars must be replaced, concrete must be removed to give the clear space indicated above $^{6)}$.

Once deteriorated concrete has been removed, reinforcing steel should be inspected. If rusting has reduced the cross-sectional area of the steel bar by more than 20%, the affected steel bars should be removed and replaced $^{14)}$.

The easiest method of replacing reinforcement is to cut out the damaged area and splice in replacement bars. A conventional lap splice is preferred ⁶⁾.

It is essential to remove all rust and foreign matter with a steel brush or by highpressure water or sand blasting. For cleaning the steel, dry sandblasting is better than wet sandblasting or water-jet blasting, because the latter two methods provide the water and oxygen necessary to begin the corrosion process again ⁶⁾.

After preparation, the repair area must be maintained in a clean condition and protected from damage until the repair materials can be placed and cured ⁷).

6. Apply the repair method

There are 15 different standard concrete repair methods or materials. Each of these materials has uniquely different requirements for successful application ⁷.

7. Cure the repair properly

The final step of the repair process is curing. Proper curing represents a sound investment in long-term insurance. If curing was inadequate, it might be necessary to remove and replace the repairs. If it is necessary to remove and replace the repairs, the costs of the original repair are completely lost. The replacement repair will be even more expensive than the original repair, because the replacement repairs will be larger and must include the costs of removal of the failed repair material ⁷⁾.

CHAPTER 4

CORROSION INHIBITORS

1. Introduction

Corrosion of reinforcing steel is the most common form of deterioration of concrete structures. It affects reinforced concrete which is exposed to the effects of carbonation and/or to significant concentrations of chloride salts. "Over the past decade, the concrete repair industry has developed novel techniques that are claimed to restore the protective character of cover concrete by introducing corrosion inhibitors into the carbonated and chloride-contaminated material" ¹⁰. This approach can reduce costs and inconvenience to users of affected structures, because it requires only physically unsound or heavily contaminated concrete to be removed and replaced ¹⁰.

2. Definition

"A corrosion inhibitor is a chemical substance that decreases the corrosion rate when present in the corrosion system at suitable concentration, without significantly changing the concentration of any other corrosion agent"⁸⁾.

Coatings, pore blockers and other materials that act on the water, oxygen and chloride concentrations, are not included in this definition. Corrosion inhibitors are either mixed into fresh concrete or travel through the hardened concrete to react on the reinforcing steel surface to slow down the rate of corrosion⁸.

3. Subdividing inhibitors:

3.1 By their action

Corrosion of reinforcing steel occurs by the formation of anodes and cathodes. Corrosion inhibitors can therefore be divided in three classes:

- anodic inhibitors
- cathodic inhibitors
- mixed inhibitors

An **anodic inhibitor** suppresses the anodic reaction. The most commonly used materials for anodic inhibitors are calcium and sodium nitrite. Other materials that can also be used, are sodium benzoate and sodium chromates ¹⁵.

A **cathodic inhibitor** suppresses the cathodic reaction. Cathodic inhibitors increase the circuit resistance and restrict the diffusion of reducible species to the cathode, by slowing the cathodic reaction or precipitating on cathodic sites ¹⁵.

Mixed inhibitors contain molecules in which electron density distribution causes the inhibitor to be attracted to both anodic and cathodic sites ¹⁵.

3.2 By their chemistry and function

- inorganic inhibitors nitrites, phosphates and other inorganic chemicals
- organic inhibitors amines and other organic chemicals
- vapour phase or volatile inhibitors a subgroup of the organic inhibitors that have a high vapour pressure

Calcium nitrate is the active material in **inorganic corrosion inhibitors** and it is added during batching. Calcium nitrate inhibits the corrosion process by enhancing the formation of the passivating layer on the surface of the reinforcing steel bar. The nitrate ions compete with any chloride ions present to react with the free iron ions. If there are more nitrate ions than chloride ions present at the steel surface, the nitrate ions will react with the iron to reinforce the passive layer on the steel. If there are less nitrate ions than chloride ions present at the steel surface, the chloride ions will react with the iron to begin the corrosion process ¹⁶.

The **organic corrosion inhibitor** is added during batching. The material forms a protective barrier on the reinforcing steel which prevents reactions between the iron and chloride ions. It also reduces the permeability of the concrete to slow the rate of water- and chloride penetration¹⁶.

Vapour phase corrosion inhibitors are volatile compounds with amino alcohols as the main volatile component. They will diffuse as a vapour through the concrete pores to the steel surface ¹⁷⁾.

Amino alcohols are ambiodic, forming a film on the steel surface, blocking both anodic and cathodic reactions. They can be applied as a coating on the surface of the concrete. These materials will move rapidly through the air voids in the concrete, through pores and microcracks to reach the steel and protect it ⁸⁾. They have an

advantage because of their ability to diffuse as a vapour. They also have a disadvantage in that they can diffuse out of the concrete unless trapped in place ¹⁷.

A migrating inhibitor with no pretensions of volatility is monofluorophosphate. which relies on capillary action and the normal transport mechanisms to migrate down to the steel through the concrete $^{8)}$.

CHAPTER 5

COMMERCIAL PRODUCTS TESTED

1. General

Surtreat Corporation in the USA has developed and uses in commercial practice two chemical formulations. The two products, Product A and Product B are both corrosion inhibitors which can be applied by spraying or painting on the surface with a brush or a roller at a rate of $1,2 \text{ m}^2/1$. Product A and Product B, which when applied to the surface of a reinforced concrete structure in a corrosion active condition, penetrates the concrete and forms a corrosion inhibiting surface on the rebar.

Product A also changes the chemical condition of the surrounding concrete to a corrosion passive state ¹⁸.

Product A is a water soluble formulation of chemicals which penetrates the concrete surface reacting with cement components and solidifies inside the concrete microstructure becoming a permanent part of the structure. It reacts with iron oxide on the surface of reinforcing steel and converts rust into a strong chemically inert. It also forms a protective film on the reinforcing steel bar surface.

The supplier claims that Product A inhibits corrosion by:

- Complexing water-soluble chlorides
- Inhibiting penetration of chlorides
- Raising the pH
- Restricting access of water and air to the reinforcing steel bar

Product B is a water-soluble chemical that migrates into the gell pore to react with the free calcium. It also fills the voids in the concrete.

The supplier claims that Product B has the following results:

- increases surface adhesion
- increases compressive strength
- reduce porosity

According to the manufacturer, their corrosion inhibitors have been successfully used since 1989 on numerous concrete restoration projects including bridges, hazardous material storage facilities, parking garages, sea walls, ocean front facilities and other structures exposed to hostile environments¹⁸.

"In 1989, a parking garage in Colombus, Ohio was exhibiting symptoms of rebar corrosion in the form of concrete slabs falling from the ceiling and raising from the floors. The structure was given applications of an earlier version Product A. The symptoms of corrosion stopped and 10 years later have not returned. The garage, which was slated for closure by the city building inspector, is still in operation" ⁽¹⁸⁾.

2. Results of tests previously done ¹⁹⁾

The Korean Construction Technology Research Institute has done testing on Product A previously. They obtained the following results:

Table 5.1: Results obtained by Korean	Construction	Technology	Research
Institute on the testing of Product A			

Tests done	Performance results
Compressive Strength	
New	3% Increase
Deteriorated	37% Increase
Flexural Strength	
New	13% Increase
Deteriorated	78% Increase
Freeze-Thaw Durability by Dynamic Modulus	37% Increase
Water Permeability	
New	29% Reduction
Deteriorated	70% Reduction
Resistance to Chloride Penetration	
0-15 mm	32% Reduction
15-30 mm	33% Reduction
Reduction in Water Soluble Chlorides	
0-15 mm	38% Reduction
15-30 mm	33% Reduction
Chemical Resistance (Reaction with Hydrochloric Acid)	Reduced from vigorous to almost none

CAPO Pullout Strength at 2 inches	46% Increase
Rebar Corrosion Inhibition Based on Half- Cell Potential Change	
9.5 cm	
min 90 days max 15 days	-200 mV (passive corrosion) -550 mV (active corrosion)

The percent change on new concrete is small in comparison to deteriorated concrete because the new concrete is very strong.

3. Treatment process

Structure inspection

The structure is inspected to determine the damage and the cause of the damage. An initial survey is done to determine the likely cause of the deterioration and to provide the information from which a detailed survey can be planned. An initial survey is based on a close visual inspection of elements that are accessible. In areas of obvious damage, limited testing such as half-cell potential readings and carbonation depth measurements can be done to determine if corrosion is taking place.

Once the initial survey has been completed, a program for the detailed survey would be prepared, by using the information gained from the initial survey. The purpose of a detailed survey is to determine the extent and severity of deterioration as accurately as possible. Such a survey requires between 10% and 20% of the elements that are at risk are selected for testing. The first question that must be attended to is whether the observed deterioration is a local problem or one that occurs widely around the structure. Quantities for repair tenders will probably be based on the results of this survey, so a full survey of all affected elements may be required. A full visual and hammer survey may be required, with detailed measurements of half-cell potentials, chloride contents, carbonation depth, cover, etc. at a few locations. The weather conditions are also recorded as these can affect some readings.

Surface preparation

Severely deteriorated concrete is removed. The surface is cleaned thoroughly with a steel brush or by sandblasting to remove oil, dirt, coatings and sealants.

Application of products

Two successive applications of the product must be made on the hardened concrete about twenty minutes apart at a rate of $1.2 \text{ m}^2/\text{l}$ by using a brush or a roller or by spraying it on.

CHAPTER 6

EXPERIMENTAL WORK

1. Concrete sample preparation

Concrete test samples were prepared using the following mix design:

- Water/cement ratio of 0.59

-	Cement (CEM II 32,5)	$= 390 \text{ kg/m}^3$
-	Water	$= 232 \text{ l/m}^3$
-	River Sand	$= 926 \text{ kg/m}^3$
-	Crusher Stone(13 mm)	$= 858 \text{ kg/m}^3$

This mix delivered a 28 day compressive strength of 29.5 MPa. The samples were given a 28-day water curing period at 25 $^{\circ}$ C.

2. Inhibition of reinforcing steel corrosion as measured by half-cell potential

Sample preparation and treatment

Three 100x100x300 mm concrete beams with reinforcing steel bars embedded at depths of 20 mm(top) and 50 mm(bottom) from the surface were cast and cured for 28 days. After the curing period the beams were taken out of the water and left to dry in the air. One day after the beams had been taken out of the water, beam no.3 was given two applications of Product A twenty minutes apart. The applications were made by spraying it onto the surface at a rate of $1,2 \text{ m}^2/1$ with a little spray-can. The beam was left for another two days before it was submerged together with the other two beams in a 10% sodium chloride solution. Three weeks after the beams had been taken out of the sodium chloride solution, beam no.1 was treated with Product B and beam no.2 was treated with Product A according to the same procedure as mentioned above. All the beams had been cleaned thoroughly with a steel brush to remove all dirt and contaminants on the surface, before they were treated.

Test procedure and results

Half-cell potentials were measured using the silver-silver chloride electrode method between reinforcing steel bars at 20 mm(top) and 50 mm(bottom) and the concrete surface. The measurements were made over a 75-day period every 2 to 3 weeks. Table 6.1 reports the time period half-cell measurements and the half-cell potential change from day 1 to day 75 is shown on the chart in figure 6.1. The day that the beams were taken out of the curing tank, is referred to as day one for the purpose of this test.

Table 6.1: Half-cell measurements

Potential mV			
Beam no.1	Beam no.2	Beam no.3	

Time (days)	Тор	Bottom	Тор	Bottom	Тор	Bottom
1	-149	-118	-124	-103	-102	-146
15	-329	-337	-352	-400	-300	-327
36	-266	-290	-296	-308	-224	-243
43	-248	-271	-282	-290	-202	-219
57	-256	-247	-276	-263	-155	-211
75	-188	-137	-215	-197	-59	-159



Figure 6.1: Half-cell potential change over time

Half-cell readings less negative than -200 mV show a 90% probability that there is no reinforcing steel corrosion. Half-cell readings between -200 mV and -350 mV show an increasing probability of corrosion and readings more negative than -350 mV indicate a 90% probability of corrosion.

Conclusion

The data presented in table 6.1 and on figure 6.1 show that beam no.1 and beam no.3 moved out of the corrosion phase, because their half-cell potentials were less negative than -200 mV after 75 days. Beam no.2 with its half-cell potential a little more negative than -200 mV was busy moving out of the corrosion phase after 75 days. Unfortunately there was no control specimen to use as baseline, but based on the limited results it can be said that both Product A and Product B inhibited corrosion for the reinforcing steel bars at depths of 20 mm and 50 mm.

For future work it is recommended to use a control specimen as baseline and to carry out testing for longer periods than 75 days to see if the half-cell potentials keep on getting less negative. An ideal test period would be a few years.



Figure 6.2: The silver-silver chloride half-cell testing instrument

3. Effect on concrete compressive strength

Sample preparation and treatment

Twelve 150x150x150 concrete cubes were cast and cured for 28 days in water at 25 °C. After the curing period, the cubes were taken out of the water and were left to dry in the air for two days. The cubes were thoroughly cleaned with a steel brush to remove all dirt and contaminants. Four sets of two cubes each were given two applications of Product B twenty minutes apart. The applications were made by spraying it on the surface at a rate of $1,2 \text{ m}^2/1$. There was a control specimen for each set. The applications were given when the concrete was 30 days old.

Test procedure and results

Compressive tests were done according to SABS method 863:1994.

Tests were done on four different dates to study the effect of Product B on the compressive strength of the concrete as time goes on. Results that were recorded were the compressive force required to cause failure. The data was converted to stress using the compression force and the cube area. The average stress was calculated and represented on a graph.

The tests gave the following results.

	Compressive strength (MPa)			
Age of concrete (days)	Control	Product B		Product B (average)
28	29.5	-	-	-
35	32.5	30.5	31	31
47	34.5	35	35	35
67	37.5	40	39.5	40
89	37.5	40	40	40

Table 6.2: Results of compressive strength testing



Figure 6.3: Compressive strength over time

Conclusion

Unfortunately due to time constraints there were not enough cubes cast and tested and therefore there was not enough data to make a clear conclusion. Based on the limited data in table 6.2 and figure 6.3 it appears that the compressive strength of the concrete increased by 6% after 67 days due to the treatment with product B. Because the values are so close, it is necessary to calculate the standard deviation to determine if the difference is significant. But it was not possible to calculate a standard deviation because there was not enough data. Thus the 6% difference may be due to the treatment with Product B or it may be due to other reasons.

For future work it is recommended that compressive strength testing must be carried out by using at least three control cubes and at least three treated cubes for each test so that the standard deviation can be calculated.

It is also recommended that the same tests be done on old and deteriorated concrete with and without treatment.

4. Effect on concrete pull-off strength

Sample preparation and treatment

Three 150x150x750 concrete beams were cast and cured for 28 days in water at 25 °C. The beams were taken out of the curing tank and were left to dry. The beams were thoroughly cleaned with a steel brush. The first beam was given two applications of Product A on one of its surfaces by spraying it on with a spray-can at a rate of $1,2 \text{ m}^2/1$. The two applications were made twenty minutes apart. The second beam was treated with Product B according to the same procedure as mentioned above and the third beam was used as the control specimen.

Test procedure and results

Three weeks after the beams had been treated, pull-off tests were done according to BS 1881 part 207:1992. Cores of 42 mm diameter were drilled about 80 mm deep. Metal discs were glued to the surfaces of the cores. Four pull-off tests were done on each beam with the Dyna Pull-off Tester. Results that were recorded were the tensile strength required to cause failure and the position where the core has broken.

The pull-off data was converted to stress using the tensile force and the core area. Take the first test on the control beam for example:

Stress = Force/Area Area = $(\Pi(42)^2)/4 = 1385 \text{ mm}^2$ = 3000 N/1385 mm² = 2.17 Mpa

The average stresses and standard deviations were calculated and these were represented on a graph. The tests gave the following results.

Control		Product A			Product B			
kN	MPa	Failure	kN	MPa	Failure	kN	MPa	Failure
3	2.17	Bottom	3.9	2.82	Bottom	3.4	2.45	Bottom
3.6	2.6	Bottom	4.6	3.32	Surface	4	2.89	Bottom
3	2.17	Bottom	3.9	2.82	Bottom	4	2.89	Bottom
3.9	2.82	bottom	5.5	3.97	Surface	4.9	3.54	Surface

Table 6.3: Results of pull-off strength testing

Ave. stress (Mpa)	2.44	3.23	2.95
St. deviation (Mpa)	0.32	0.55	0.45



Figure 6.4: Results of pull-off strength tests

Conclusion

The depth of penetration of the material into the concrete is not known. All the cores on the control beam failed at the bottom. Some of the cores on the treated beams failed at the surface and some failed at the bottom. The cores on the treated beams that failed on the surface, generally required higher tensile forces to fail than the other cores. The reason for the failures taking place on the surface rather than at the bottom may be that the materials penetrated the concrete deeper than the depth of the cores and thus made the cores stronger at the bottom. Based on the table and the graph, the pull-off strength of the concrete increased by 31% and 20% due to the treatment of Product A and Product B respectively. These results are not very clear, because the standard deviations are somewhat high. It is recommended that further pull-off testing be done in the future with the core depths only 50 mm instead of 80 mm to make a clear conclusion.



Figure 6.5: The Dyna pull-off tester

5. Resistance to chloride penetration

Sample preparation and treatment

Four 150x150x150 mm concrete cubes were cast and cured for 28 days in water at 25° C. After the curing period the cubes were left to dry for four days. Then the cubes were cleaned thoroughly with a steel brush. The first cube was given two applications of Product A twenty minutes apart. The applications were made by spraying it onto the surface at a rate of $1,2 \text{ m}^2/\text{l}$ with a little spray-can. The second cube was treated with Product B according to the above-mentioned procedure. The third cube was treated with both products. It was first treated with Product A according to the above-mentioned procedure. The cube was left for a day and was then treated with Product B according to the above-mentioned procedure. The last cube was used as a control specimen. Five days after the cubes had been treated, they were submerged in a 10% sodium chloride solution for 5 days.

Test procedure and results

The cubes were sampled three weeks after they had been taken out of the sodium chloride solution. Before a cube was sampled its surface had been thoroughly cleaned with a grindstone to remove all chlorides from the top of the surface. Holes of 8 mm in diameter were drilled 25 mm deep and the dust was sampled with special equipment shown on the photo in figure 6.6. Between each sampling, all the equipment had to be cleaned thoroughly with distilled water to ensure that chlorides of other samples won't contaminate the samples. Five gram of each sample was weighed on a very accurate scale in a small clean measuring-jug. Each measuring-jug was filled up to 100 ml with distilled water. The measuringjugs were left to stand over night. The following morning the measuring-jugs with the samples in were stirred for about an hour to let the chlorides dissolve in the distilled water. The solutions were then filtered into clean measuring cylinders. The measuring cylinders were filled with distilled water very accurately up to 100 mm. The solutions were analyzed for chloride content according to EPA Test Method 300.1. The chloride test results are shown in table 6.4.

Table 6.4: Results of chloride tests

	Control	Product A	Product B	Product A + B
Mass of sample (g)	5.0679	5.0316	5.0085	5.0122
Chloride content (mg/l)	62.910	29.505	31.008	21.571
Chloride content (%)	0.124	0.059	0.062	0.043

The chloride content was obtained in milligram per liter. It was converted to percentage chloride as follows:

Take the control sample for example.

62.910 mg/l = 6.2910 mg/100 ml = 6.2910 mg/5.0679 g sample

Cl% (w/w) = $(6.2910 \times 10^{-3} \text{ g})/(5.0679) \times 100 = 0.124 \% \text{Cl}$



Figure 6.6: Taking samples for chloride tests



Figure 6.7: Results of chloride tests

Conclusion

When studying table 6.4 and figure 6.7, it can be seen that there was a 52% and a 50% decrease in chloride content of the cubes that were treated with Product A and Product B respectively. Thus both materials offer about the same resistance to chloride penetration. There was a 65% decrease in chloride content of the cube that was treated with both Product A and Product B. The cube that was treated with both materials had the best resistance to chloride penetration. The best way to resist chloride penetration is to treat the concrete first with Product A and then with Product B.

6. Resistance to water penetration

Sample preparation and treatment

Six 150x150 mm concrete cubes were cast and cured for 28 days in water at 25 °C. After the curing period, the cubes were taken out of the water and were left to dry in the air for four days. The cubes were thoroughly cleaned with a steel brush to remove all dirt from the surfaces. Two cubes were treated with Product A and two cubes were treated with Product B according to the same procedure as

mentioned earlier in the chapter. The last two cubes were used as control specimens. The second cube that was treated with Product A was cracked and couldn't be used for testing.

Test procedure and results

Four weeks after the cubes had been treated, water permeability tests were done at 0.5 bar of pressure using the Autoclam permeability system. The pressure is applied by a piston of 15 mm in diameter. Water permeability is reported every minute for 15 minutes in terms of mm (travelling distance of the piston). The data of each test were put into a computer program and an index with units m^3/\sqrt{min} was calculated by the program for each cube. The volume of flow for the data between the 5th and 15th minutes is calculated by multiplying the travel of the piston with the area of the cylinder. These values are plotted on the Y-axis and the square root of the corresponding time in minutes on the X-axis. This will result in a straight line graph. The slope of this straight line is the water permeability index with units m^3/\sqrt{min} .

	Traveling distance of the piston (mm)					
Time (min)	Cont	rol	Produ	Product A		
0	0	0	0	0	0	
1	0.778	1.374	0.080	0	0	
2	1.410	2.399	0.389	0.160	0	
3	1.960	3.290	0.602	0.270	0	
4	2.433	3.910	0.778	0.389	0	
5	2.884	4.438	0.904	0.480	0	
6	3.285	4.920	1.024	0.552	0.146	
7	3.656	5.366	1.117	0.625	0.267	
8	4.009	5.771	1.194	0.699	0.404	
9	4.541	6.159	1.267	0.765	0.807	
10	4.657	6.515	1.334	0.823	0.965	
11	4.954	6.860	1.399	0.876	1.059	
12	5.251	7.190	1.447	0.928	1.534	
13	5.527	7.502	1.493	0.983	2.027	
14	5.799	7.811	1.539	1.041	2.102	
15	6.058	8.106	1.590	1.087	2.173	
Index (m ³ / \sqrt{min})	3.51 E ⁻⁷	3.95 E ⁻⁷	7.24 E ⁻⁸	6.47 E ⁻⁸	2.59E ⁻⁷	
Ave Index	3.73 E ⁻⁷		0.686	2.59E ⁻⁷		

Table 6.5: Results of permeability tests



Figure 6.8: Water permeability index

Conclusion

Table 6.5 and the graph in figure 6.8 show that the average permeability index of the control concrete cubes is more than five times higher than the average permeability index of the cubes that were treated with Product B. Thus there was an 82% reduction in water permeability of the concrete due to the treatment with Product B. Thus Product B has a high resistance to water penetration.

Unluckily one of the cubes that was treated with Product A, had a big crack in it and it gave much different results than the other cube. Based on the limited data of only the one cube that wasn't cracked, it can be seen in the table and the graph that there was a reduction of 30% in permeability of the concrete due to the treatment with Product A. This conclusion is not clear and it is recommended that more water permeability tests be done on Product A. At least three cubes per set must be tested to get more accurate values.

7. Chemical resistance to acid

Sample preparation and treatment

Nine 100x100x100 mm concrete cubes were cast and cured for 28 days in water.

After the curing period, the cubes were taken out of the water and were left to dry. The cubes were divided into three sets. In each set the first cube was treated with Product A, the second cube was treated with Product B and the third cube was used as a control specimen. The cubes were cleaned and treated as mentioned earlier in the chapter.

Test procedure and results

Two weeks after the cubes had been treated, they were exposed to acid. The first set of cubes was exposed to a 32% concentration of hydrochloric acid, the second set was exposed to sulphuric acid and the third set was exposed to a 60% concentration of nitric acid. The cubes were exposed to the acid simply by wetting the surface with a few drops of the acid.

The degrees of reaction were observed and photos were taken. The reactions can be seen on the photo.



Figure 6.9: Reactions between hydrochloric acid and concrete

Conclusion

The hydrochloric acid immediately reacted violently with the control specimen, but it reacted very little with the treated cubes. The sulphuric acid and the nitric acid had little or no reaction with any of the cubes. On the photo can be seen that the untreated cube gave a violent reaction when hydrochloric acid was placed on its surface. The surface was eaten away. When hydrochloric acid was placed on the Product A and Product B treated cubes, there was little reaction. Thus the treated cubes were more resistant to chemical attack by hydrochloric acid.

CHAPTER 7

CONCLUSIONS AND RECOMMENDATIONS

1. General remarks

Through this study, the performances of two corrosion inhibitors were investigated and compared to untreated concrete. All the conclusions derived in this investigation are based on analysis of laboratory test results, accounting for random experimental errors.

2. Summary of study

Corrosion inhibition by the two products

Based on the results obtained, it can be said that both Product A and Product B inhibited corrosion for the reinforcing steel bars at depths of 20 mm and 50 mm at the end of the investigation period, but unfortunately there was no control specimen to use as a baseline.

Effect of the products on the compressive strength

Unfortunately due to time constraints there were not enough cubes cast and tested and therefore there was not enough data to make a clear conclusion. Based on the limited data, it appears that the compressive strength of the concrete increased by 6% after 67 days due to the treatment with product B. Because the values are so close, it is necessary to calculate the standard deviation to determine if the difference is significant. But it was not possible to calculate a standard deviation because there was not enough data. Thus the 6% increase may be due to the treatment with Product B or it may be due to other reasons.

Effect of the products on the pull-off strength

The depth of penetration of the material into the concrete is not known. All the cores on the control beam failed at the bottom. Some of the cores on the treated beams failed at the surface and some failed at the bottom. It was interesting to note that the cores on the treated beams that have failed on the surface, generally required higher tensile forces to fail than the other cores. The reason for the failures taking place on the surface rather than at the bottom may be that the materials penetrated the concrete deeper than the depth of the cores and consequently made the cores stronger at the bottom. Based on limited data, the average pull-off strengths of the treated beams were higher than the average pull-off strength of the untreated beams. A clear conclusion cannot be made, because the standard deviations are somewhat high and the penetration depths of the materials are unknown. It is recommended that further pull-off testing be done in the future with the core depths only 50 mm instead of 80 mm to make a clear conclusion.

Resistance to chloride penetration

There was a 52% and a 50% decrease in chloride content of the cubes that were treated with Product A and Product B respectively.

There was a 65% decrease in chloride content of the cube that was treated with both Product A and Product B.

Both Product A and Product B offer about the same resistance (50%) to chloride penetration. The cube that was treated with both materials had the best resistance to chloride penetration. The best way to resist chloride penetration, is probably to treat the concrete first with Product A and then with Product B.

Resistance to water penetration

The average permeability index of the control concrete cubes was more than five times higher than the average permeability index of the cubes that were treated with Product B. Thus there was an 82% reduction in water permeability of the concrete due to the treatment with Product B.

Unluckily one of the cubes that was treated with Product A, had a big crack in it and it gave much different results than the other cube. Based on the limited data of only the one cube that wasn't cracked, it can be seen that there was a reduction of 30% in permeability of the concrete due to the treatment with Product A. It is recommended to carry out further tests on Product A treated cubes by testing at least three treated cubes and at least three control cubes.

The main conclusion that can be made is that Product B treated cubes offer high resistance to water penetration.

Chemical resistance to acid

The hydrochloric acid immediately reacted violently with the control specimen, but it reacted very little with the treated cubes. The sulphuric acid and the nitric acid had little or no reaction with any of the cubes. On the photo in figure 6.9 can be seen that the untreated cube gave a violent reaction when hydrochloric acid was placed on its surface. The surface was eaten away. When hydrochloric acid was placed on the Product A and Product B treated cubes, there was little reaction. Thus the treated cubes were more resistant to chemical attack by hydrochloric acid.

3. Future work

For future work it is recommended to carry out half-cell potential testing for longer periods than 75 days to see what the half-cell potential curve does over a long period. A control specimen must be used as a base line.

It is recommended that the same compressive strength tests be done on deteriorated concrete with and without treatment of Product B. According to previous tests in Korea, the treatment of deteriorated concrete with Product B increased the compressive strength significantly.

A recommendation is to carry out further permeability tests on concrete treated with Product A. At least three treated and three untreated samples have to be tested to obtain more accurate answers. Another recommendation is to carry out permeability tests on deteriorated concrete to determine the effect of the products on the permeability of deteriorated concrete.

For future work it is also recommended that Products A and B be tested and compared to other corrosion inhibitors.

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