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MAINTENANCE AND REPAIR OF CONCRETE STRUCTURES

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Preface

In 1987 and 1988 a series of articles was published in the Dutch journal "Cement" about maintenance and repair of concrete structures. The series was written to promote the transfer of know-how concerning maintenance and repair of concrete structures.

Use has been made of know-how developed in the Netherlands. The Centre for Civil Engineering Research, Codes and Specifications, CUR, is performing an extensive research program regarding repair and protection techniques for concrete.

After reading the report it will be clear that successful maintenance and repair of concrete requires a thorough knowledge of degradation mechanisms, the compatibility of the concrete with the materials, and durability. Many uncharted areas remain. However the world-wide ongoing scientific efforts will rapidly increase the expertise in the near future.

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Prof. dr. J. Bijen has edited these articles to compile the present report.

April 1989

Maintenance and repair of concrete structures

1 Introduction

For many decades concrete structures were regarded as almost eternal. Concrete was a maintenance-free material. The useful life-time of buildings was thought not to be determined by concrete but by other factors. This image has changed dramatically in the last decade. The multibillion dollar damage of bridge decks in North America due to corrosion caused by de-icing salts, the fact that more than 90% of concrete structures in the Arabian Gulf Area are suffering from chloride initiated corrosion, the degradation of sewer-pipes due to sulfuric acid attack and the occurrence of deterioration caused by alkali-silica reactions in many countries are the most outstanding examples of the tarnished image of concrete.

In the Netherlands, just as in many other countries, there is also damage to concrete structures. In 1981 an inventory was made of the extent of damage of concrete exposed to the outdoor environment. This inventory related to houses which were built during the period from 1950 to 1980 (1). The total damage was assessed at about Dfl 400 million. Another example is the 5 km long Zeeland bridge in the Delta Area for which preventive measures were necessary to avoid damage in the near future.

As is always the case, where problems arise people initiate developments to solve them. In the case of concrete, this has triggered off developments on measures to prevent corrosion, on corrective actions when the performance of structures is affected (repair techniques), on techniques to detect corrosion and to monitor the performance of structures. In the Netherlands an extensive development program is being performed by the Centre for Civil Engineering Research, Codes and Specifications, CUR. This program comprises, inter alia, practice trials on various repair techniques on balcony slabs. In this document on the maintenance and repair of concrete structures, use is made of the preliminary results of this program as well as of various other CUR reports issued in the past. The report is mainly based on a series of 12 articles published in the Dutch journal "Cement" in the years 1987 and 1988. The authors contributing to these series of articles are mentioned in the preface.

The following subjects will be discussed:

- maintenance strategy;
- degradation mechanisms (briefly)
 - chemical reactions in concrete
 - practical cases of chemical degradation
 - frost-thaw (salt) damage
 - corrosion of reinforcement;
- repair mortars;
- surface protection;
- repair of chloride initiated corrosion damage by "traditional" methods;
- cathodic protection of reinforcement steel in concrete;

- repair of damage due to reinforcement corrosion initiated by carbonation.

The authors and the editor hope that this document will contribute to the effective maintenance and repair of concrete structures.

2 Maintenance strategy

In this chapter definitions will be given and the purpose and strategy of maintenance and repair will be highlighted. The most important degradation factors with respect to the performance of structures related to degradation mechanisms and consequences are inventorized.

2.1 Definitions

Durability: this is the capability of a building, assembly, component, product or structure to maintain its serviceability over at least a specified period of time.

Maintenance: maintenance refers to all activities aimed at maintaining/restoring a specified performance of building materials, building elements or structures. Such activities comprise not only execution of activities but also preparations and design. Maintenance activities could be divided into: inspective, preventive, and corrective maintenance.

Corrective maintenance: concerns repair activities to restore the functioning of the artefact.

Preventive maintenance: regards the activities which increase the performance of the artefact at the moment when its performance is still not unduly affected.

Inspective maintenance: involves activities performed to assess the present performance of the structure. It could be regarded as part of preventive maintenance.

Damage: in the case of damage, the performance of an artefact is affected, the occurrence of which was not predicted in the service life design of the artefact. Fig. 1

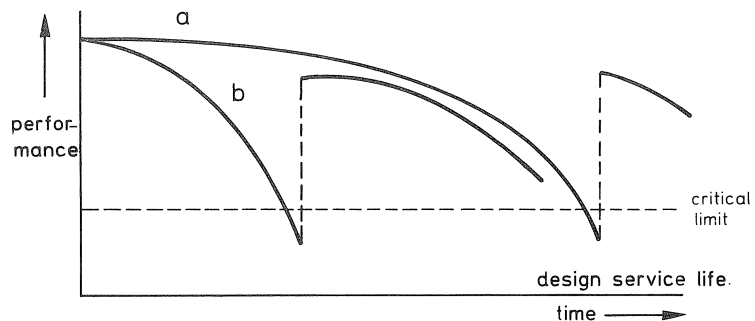


Fig. 1. Performance of concrete structure in time.

- no damage: corrective maintenance after exceeding design service life
- damage: corrective maintenance before reaching design service life

illustrates this. Curve A presents the predicted performance in time. Curve B is the actual performance versus time function. The maintenance required to keep the performance above the critical level was not predicted, with the result that damage has occurred.

For concrete structures the word “damage” is often used, because mostly the failure of concrete is neither predicted nor expected. Maintenance for many other products is mostly not related to damage, e.g. when we replace the tyres of our car, we don’t experience this occurrence as an instance of damage.

2.2 Maintenance strategies

For concrete structures two extreme situations could be distinguished regarding maintenance strategy:

- a. No maintenance planning, but waiting until a critical performance limit has obviously been reached. The passing of such a limit could be deduced from marks on the structure, like cracks, falling pieces of concrete etc.
- b. A maintenance planning as part of the building management, which includes a procedure for inspective maintenance which enables one continuously to monitor the state of performance.

In practice, most situations are close to (a).

Purposes of maintenance of concrete structures could be several. For instance:

- Minimizing of maintenance costs at a chosen level of performance.
- Maintenance in such a way that corrective maintenance is not required.
- To repair everything as cheaply as possible.
- Only a limited amount of money is available. The maintenance procedure is adjusted to this amount.
- Maintenance must be done in such a way that there is no loss of prestige.

From an economic point of view the target with respect to costs must be to minimize the total sum of investment and maintenance costs over the service life of the structure. The formula below gives an example of the various factors that are involved in such a strategy (2).

$$E\{C_{\text{cap}}\} = S + \sum_{j=1}^n \frac{V_j}{(1+r)^j} + \sum_{j=1}^n \frac{P\{F_j\}D_j}{(1+r)^j}$$

in which

- $E\{C_{\text{cap}}\}$ = expected value of the capitalized costs C_{cap}
- S = investment costs
- V_j = maintenance and management costs for the year j
- $P\{F_j\}$ = probability of failure in year j

- D_j = costs for corrective maintenance due to failure in year j
- r' = real interest (nominal interest adjusted for inflation)
- n = the number of years the structure has to function without defects

This formula can also be used in a situation where there was no maintenance strategy in the past, but where at a certain moment corrective maintenance was found to be necessary. S could be regarded then as the costs for corrective maintenance.

2.3 Problems with respect to maintenance strategy

In the above formula there are a number of parameters which have to be quantified. Preventive maintenance costs and building management costs are in general relatively easy to inventory. For concrete these involve the costs of inspection, preceded by a first extensive assessment of the performance of the structure. In general, the probability of failure of a structure could be assessed fairly reliably on the basis of these results. For instance for carbonation we could monitor the rate of penetration. The concrete cover can be measured while the corrosion propagation after corrosion initiation could be estimated fairly accurately. With these features it will be possible to calculate the probability of failure, although in a rough way only. Carbonation rate, concrete cover, and corrosion propagation rate are stochastic parameters. That means: they could be predicted with a certain accuracy. For example, the probability that corrosion of reinforcement will occur and the probability that concrete will crack due to this corrosion could be calculated by means of these stochastic parameters. In general the probability function of such an occurrence will be as shown in Fig. 2 (2).

An example of the assessment of the performance of a structure by means of inspective maintenance and of preventive measures taken on the basis of the results of this inspection could be found in the Dutch Zeeland bridge. The preventive actions were based on results of measurements of chloride penetration and an assessment of the quality of concrete especially with respect to its permeability.

However, it is not always possible for the probability of failure to be determined with an acceptable reliability. This would be the case, say, when we have to deal with chloride ions mixed into the concrete, for instance when chloride containing accelerators are

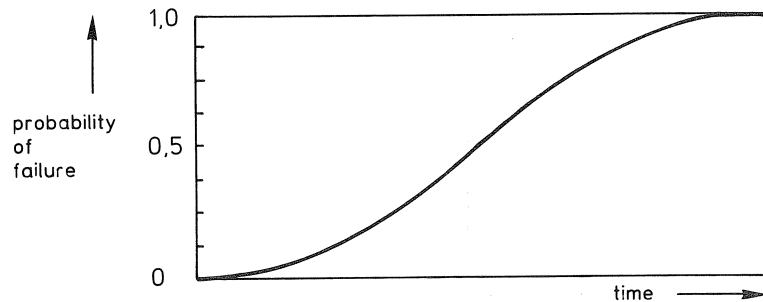


Fig. 2. Probability of failure in time (2).

used. Often in these cases a large variance in chloride concentration could be observed, which makes an accurate assessment of the corrosion propagation difficult.

2.4 Durability of the repair

One of the costs most difficult to estimate are the maintenance costs after preventive or corrective measures have been taken. This has to do with the lack of know-how about the durability of the repair itself.

A striking illustration of this difficulty could be found in reference 3 where the results of a field study in the Netherlands are described. Although the projects investigated were submitted by the repair companies themselves, most of the protective measures, like coatings etc., were found to show defects, especially failing adhesion.

2.5 Comparison of alternatives

Despite the problems discussed with respect to optimization of maintenance costs, useful estimates could still be made in a number of cases.

In reference 2 a probabilistic calculation method for a number of these cases is presented. Table 1 shows the results of these calculations. For a (new) balcony of a multi-story residential building four design alternatives are considered.

1. Cover 15 mm, no coating
2. Cover 30 mm, no coating
3. Cover 15 mm, with coating, maintenance of coating every 20 years
4. Cover 15 mm, with coating, maintenance every 10 years

Table 1. Estimate of capitalized costs in Dutch guilders for balcony slab (2)

| cost item | alternatives | | | |
|---|---------------------------|---------------------------|-------------------------------------|-------------------------------------|
| | 1 | 2 | 3 | 4 |
| | $d - 15$ mm no coating | $d - 30$ mm no coating | $d - 15$ mm coating $T - 20y$ | $d - 15$ mm coating $T - 10y$ |
| S (slab) | 1000 | 1060 | 1000 | 1000 |
| S (coating) | - | - | 500 | 500 |
| $\Sigma V_j / (1 + r)^j$ | - | - | 860 | 1250 |
| $\Sigma P\{F_j\} \cdot D_j / (1 + r)^j$ | 860 | 0 | 260 | 40 |
| $E\{C_{cap}\}$ | 1860 | 1230 | 2620 | 2790 |

The table clearly shows that the alternative with the highest cover is by far the cheapest. Further, it has to be noted that the required maintenance periods of coating systems are debatable, so that the alternatives 3 and 4 can hardly be estimated reliably. Fig. 3 (2) gives an example of the performance of such a coating system. The performance is adjusted where preventive measures are applied with a regular frequency.

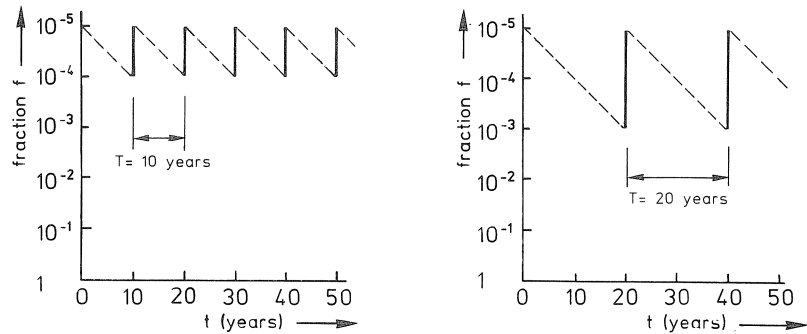


Fig. 3. Fraction of coating degraded as a function of time for 10-year and 20-year maintenance periods respectively (2).

With the increase in our knowledge about the performance of preventive and corrective maintenance measures it will be possible in future to calculate the costs of maintenance more reliably than nowadays.

2.6 Degradation mechanisms

The gap between the actual state of performance of a structure and the target of a maintenance program to restore or to maintain the performance at a specified level has to be bridged by maintenance measures.

The first step to achieve the target is to identify the degradation mechanisms affecting the performance of the structure. Only when we know the degradation mechanisms we can develop adequately a maintenance system and quantify costs.

Degradation factors, degradation mechanisms, and their consequences on the performance of the structure, are shown in Table 2 for a number of environments in the Netherlands.

In the Netherlands some of the degradation factors which are well known occurrences in other countries are not present (for instance, alkali-aggregate reaction) or are less prominent, such as the problems of concrete durability in hot countries.

2.7 Preventive and corrective measures

An inventory of degradation factors and mechanisms shows that new buildings could be designed effectively with respect to service life and durability. With the present level of know-how it must be possible to design more than 95% of the concrete structures to serve their full service life without corrective measures.

For some environments it will be necessary to undertake protective measures to preserve the concrete structure. These measures could be taken during the erection of the building, but for economic reasons it could be decided to take such measures later on. When, on the basis of a thorough design, it could be expected that a concrete structure will not require preventive or corrective measures during its service life,

Table 2. Major threats to the durability of concrete in the Netherlands

| structures | part | threat | | mechanism | effect | severity |
|---------------------------------------|--|---|--|---|---|----------|
| | | external | internal | | | |
| housing + utility building | exterior surfaces | carbonation | insufficient cover + porous concrete | depassivation of reinforcement | corrosion of reinforcement/ cracks in concrete | 1 |
| | balcony slabs | frost/thaw (salts) | no air bubbles insufficient density | expansion | scaling above aggregate grains | 3 |
| marine structures | quays, piles, etc. | chloride penetration | (sometimes) insufficient cover + sometimes no blast furnace cement | depassivation of reinforcement | pit corrosion reinforcement/ cracks in concrete | 1 |
| | quays, piles, etc. | salt in seawater | porous concrete | deterioration of cement paste Ca(OH)_2 + CSH gel | surface deterioration/ leach out cement paste | 2 |
| road structures | bridge decks and fly-overs | chloride penetration frost/thaw salts | (sometimes) insufficient cover and/or porous concrete | depassivation of reinforcement | pit corrosion reinforcement/ cracks in concrete | 1 |
| | bridge decks and fly-overs | frost/thaw salts | no air bubbles insufficient density | expansion | scaling over total surface | 2 |
| sewer structures | sewer pipes/ sewage sanitary plants | H_2S gas from waste water | | dissolving of cement paste by sulfuric acid | surface deterioration by mm's per year | 1 |
| foundations at the soil-air interface | electricity poles, lamp post (e.g. in Belgium) | sulfate (SO_4^{2-}) from ground-water, concrete itself | non-sulfate resistant cement/ porous concrete | expansion by ettringite/ thaumasite formation | cracks in concrete | 1/2 |
| | green-house foundation | $\text{NO}_3^-/\text{SO}_4^{2-}$ $\text{NH}_4^+/\text{Mg}^{2+}$ | non-sulfate resistant cement/ porous concrete | deterioration cement paste = ettringite expansion | loss cohesion cement paste + cracks | 1 |

Table 2. *Continued*

| structures | part | threat | | mechanism | effect | severity |
|-----------------------|-------------------------|--|--|---|--------------------------------|----------|
| | | external | internal | | | |
| manure storage | cellars + silos | H ₂ S gas | non-sulfate resistant cement/porous concrete | deterioration cement paste by sulfuric acid + ettringite expansion | storage deterioration + cracks | 2 |
| potable water storage | pure water cellars etc. | soft water + carbon dioxide aggressive water | porous concrete portland cement | deterioration/ dissolving of cement paste by water and carbon dioxide | surface deterioration | 3 |

* severity 1 = very strong
 2 = strong
 3 = less strong

inspective maintenance will be necessary. During execution of the works it will hardly be possible to avoid incidental defects in the structure. For instance, local areas with too little cover, and concrete with somewhat lower quality etc. Remembering the experience of the past there is no justification for the attitude that "it will be all right". The preparation of a thorough inspective maintenance program should therefore be part of the task of the consultant/structural engineer.

When corrective measures are required during the service life of a building the predictability with respect to the service lifetime of the effects of these measures is mostly much less than for new buildings. By way of illustration, Fig. 4 shows a photograph of the Shindagah Tunnel in Dubai which was recently repaired. Corrosion of the reinforcement was not only the result of penetration of salt water, but also because during the construction of the tunnel, chloride contaminated fine aggregate as well as porous coarse aggregates and permeable cement paste were used.

The severity of the corrosion differed from location to location. Some parts of the structure could not be repaired fully because of structural considerations. There is no guarantee that after repair there will be no occasional problems in the tunnel.

3 Chemical degradation mechanisms

In general three types of chemical reactions leading to degradation of concrete can be distinguished. These are:

- a. the degradation of cement paste by acids;
- b. degradation by formation of expansive salts;
- c. degradation by reaction with cations.

Sometimes two or three of these degradation mechanisms are present simultaneously.

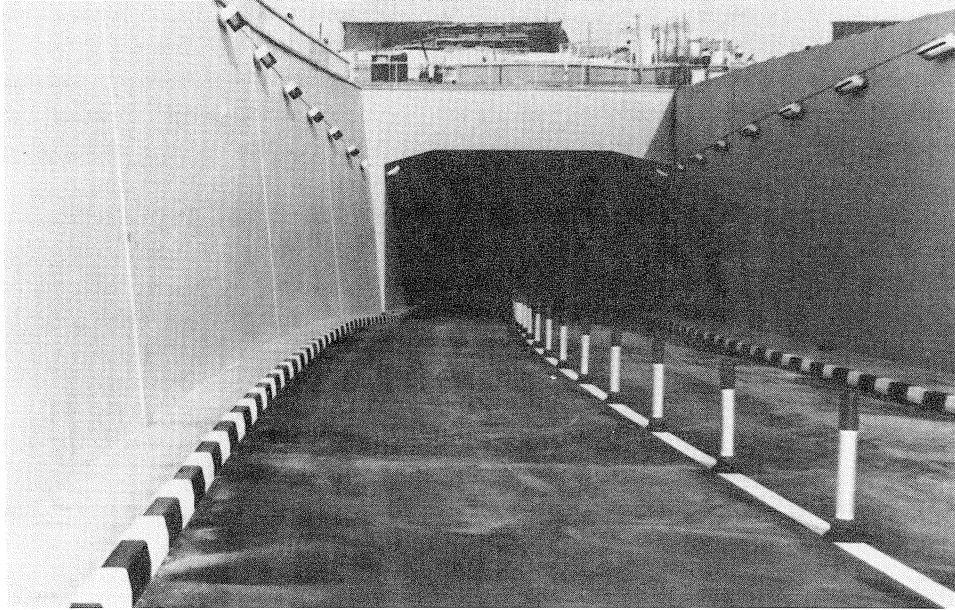


Fig. 4. Repair of Al-Shindagah Tunnel in Dubai.

3.1 Acids

Liquid acids

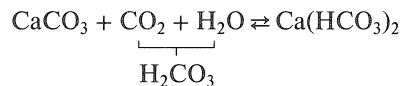
A cement paste is mainly a composition of lime and silica. Because silica is a very weak acid and lime a strong base, even weak acids like carbon dioxide could convert these cement pastes, in this case to calcium carbonate and silica. In principle the rate of deterioration is determined by the pH of the acid. The Dutch standard NEN 5996 “Determination of the aggressiveness of water, soils and gases” gives the criteria for aggressiveness as shown in Table 3. The most aggressive acids are the strong mineral acids like sulfuric acid, hydrochloric acid and nitric acid. Even if these acids are strongly diluted they still fall in the class “very strongly aggressive”. A weak mineral acid is hydrogen sulfide. This could be present in waste waters, especially in sewer systems, but also in manure. This acid is too weak to attack concrete severely. However, in the

Table 3. Classes of aggressiveness according to the Dutch standard NEN 5996

| aggressiveness | pH | aggressive | sulfate | ammonium | magnesium |
|----------------|---------|-----------------|-------------------------------|------------------------------|------------------|
| | | CO ₂ | SO ₄ ²⁻ | NH ₄ ⁺ | Mg ²⁺ |
| | | mg/l | mg/l | mg/l | mg/l |
| weak | 6.5-5.5 | 15- 30 | 200- 600 | 15- 30 | 100- 300 |
| moderate | 5.5-4.5 | 30- 60 | 600-3000 | 30- 60 | 300-1500 |
| strong | 4.5-4.0 | 60-100 | 3000-6000 | 60-100 | 1500-3000 |
| very strong | < 4.0 | > 100 | > 6000 | > 100 | > 3000 |

case of closed systems like sewer systems, it could condense on concrete surfaces above the waste water and then be oxidized biogenically to form sulfuric acid. It is well known that this bacterial conversion to sulfuric acid could degrade concrete sewer systems severely. Typically the degradation process involves an initiation period, in which the concrete is neutralized and bacteria populations are built up, followed by a propagation phase.

A special case of acid attack is the exposure to low hardness carbon dioxide aggressive water. This water is able to convert calcium carbonate to a soluble calcium bicarbonate. The Dutch standard NEN 5996 specifies the criteria for carbon dioxide aggressive water as shown in Table 3. The reaction of aggressive carbon dioxide containing water is as follows:



The determination of the aggressiveness of carbon dioxide containing water is described in the German standard DIN 4030.

German test results indicate that the lower limit for strong aggressiveness must be increased to 100 mg CO₂/l instead of 60 mg/l (4).

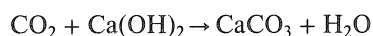
In general organic acids are less strong than mineral acids. Nevertheless acids like acetic acid and lactic acid can degrade concrete seriously, which is due to the lime-complexing ability of these acids. Also the attack of concrete by the strong acidic extracts of corn has attracted much attention during the past years.

The general pattern of this acid degradation of concrete is that it slowly dissolves the cement paste starting from the surface. Mostly the aggregates degrade less quickly than the cement paste. After some time they are no longer embedded in the cement paste. Sometimes also the aggregate itself is degraded. This happens for instance when limestone or dolomite aggregates are used. The latter could mean that the degradation initially looks more severe, but when degradation proceeds the opposite could occur, because the lime or dolomite provides an extra alkaline buffer able to neutralize the acid.

Carbonation

A special type of an acid reaction is the reaction due to the penetration of carbon dioxide gas into empty pores of concrete. When the carbon dioxide reaches the water frontier in the pores it will partly dissolve in the water. Subsequently it reacts in the water at the water/air surface with free lime and later on also with calcium silicate hydrate and other calcium compounds.

The reaction formula for the reaction of carbon dioxide with free lime is as follows:



In this reaction one mol or 34 ml calcium hydroxide is converted to 37 ml calcium

carbonate and 18 ml water. Thus the volume increases by about 60%. Most of it is water, but the solid content is also increased by 9% in volume. The water formed has to evaporate before carbonation can proceed. The increase in volume of the solids means that porosity diminishes and, for Portland cement, permeability decreases as well. Because of the low permeability of concrete, the consumption of carbon dioxide and the release of water during the reaction, degradation generally occurs slowly. If the attack by carbon dioxide continues, the calcium silicate hydrate could also be converted over the long term, which could have an adverse effect on the concrete properties.

However the main danger of carbonation is the neutralization of the concrete. The pH decreases from more than 13 to about 9. When the neutralization zone reaches the reinforcement corrosion will be triggered off. Prediction of the moment of this triggering off and the time when the corrosion propagation process will pass a critical level is very important for maintenance programming.

The penetration of the carbonation frontier takes place at the water/air surface and proceeds simultaneously with the drying out of the concrete.

In an indoor climate with relatively constant humidity and temperature, concrete mostly dries out quickly. The carbonation frontier moves in line with the moisture frontier. Both proceed in accordance with the second diffusion law of Fick. Therefore carbonation depth at a certain moment is proportional to the square root of the exposure time. For concrete which is exposed to outdoor weather conditions, drying periods will be followed by periods in which the concrete will absorb or adsorb water. When the pores are (re)filled with water carbonation will stop until the concrete has dried out again to the existing carbonation frontier. When the frontier moves deeper into the concrete, the length of the standstill period of the carbonation frontier will increase. The carbonation frontier movement can no longer be predicted by the square root of time formula. In the end, the frontier will come to a complete standstill. The carbonation frontier will coincide with the largest drying-out depth. The moisture content of concrete is schematically shown in Fig. 5 (5). If the effects of the moisture movement are taken into consideration the position of the carbonation frontier could be calculated using the formula:

$$X_{ct} = A\sqrt{t_1} + A\sqrt{t_2 - (X_{c1}/B)^2} + A\sqrt{t_3 - (X_{c2}/B)^2} + A\sqrt{t_4 - (X_{c3}/B)^2} \dots A\sqrt{t_n - (X_{cn-1}/B)^2}$$

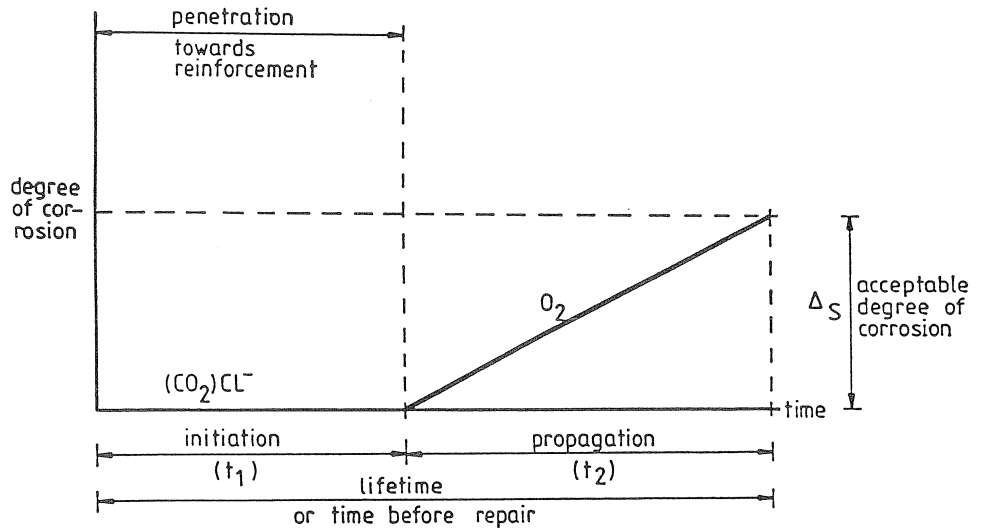
$(X_c/B)^2$ = time required for moisture border to reach carbonation border after wetting

t = time of drying period

The most extreme situation for concrete will occur when it is continuously wet. In that case there will be no carbonation at all. Examples of these kinds of exposure are underwater structures and above the waste water level in sewer systems.

SO₂ and NO_x gases

Not only carbon dioxide gas can penetrate concrete pores but obviously also other



SCHEMATIC DRAWING OF THE CORROSION PROCESS OF STEEL IN CONCRETE

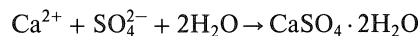
Fig. 5. Moisture content of concrete as a function of distance to surface (4).

aggressive gases, like sulfur dioxide and nitrogen oxide. These gases can also react in principle at the water/air surface. However, they are more aggressive when oxidized to sulfuric acid and nitric acid. Not only sulfuric acid attacks concrete, but the sulfate ions involved will too. It is shown that the quantities of these gases are too low to present a serious threat to concrete (6). Except, possibly, in very polluted industrial environments.

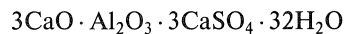
3.2 Expansive salts

Sulfate attack

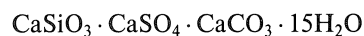
Sulfates are present in many natural waters, like groundwaters etc. but are also present, sometimes in high concentrations, in industrial waste waters. When the sulfate ions penetrate the pore systems by absorption of sulfate containing water or by diffusion, they can react with the free lime present in the concrete and form gypsum via the reaction:



Subsequently this gypsum reacts with calcium aluminate hydrates to form ettringite:



The formation of this double salt in ordinary hardened concrete is expansive. When the expansion forces exceed the tensile forces of the concrete cracking can occur. Another expansive sulphate double salt is thaumasite for which the formula is:



For the formation of this salt not only sulfate is necessary but also calcium carbonate. Calcium carbonate is not always present in concrete, but it could be present if the carbonation front proceeds or if limestone aggregates are used. Thaumasite formation is especially expansive at low temperatures. Damage which could be due to thaumasite formation is therefore mostly found in the early springtime. The recognition of thaumasite as a deteriorating salt is only of recent date. In the formation of thaumasite ettringite occurs as an intermediate salt.

The Dutch standard NEN 5996 specifies the classes of aggressiveness for sulfate-containing waters as given in Table 3.

Internal sulfate degradation

Mostly the sulfates which cause the formation of expansive double salts penetrate from the exterior. However, recently it has been discovered that under certain conditions sulfates could also be supplied by the cement paste itself. Cement always contains some percentages of calcium sulfate, acting as a setting time regulator. Normally this calcium sulfate reacts with calcium aluminate and water to form ettringite which later on is converted into monosulfate.

This process is not expansive. In hardened concrete we do not normally find large quantities of ettringite and no free calcium sulfate. In the pore water, too, hardly any sulfate is present. However, in Portland cement concrete, which has been steam cured at temperatures above 60°C, expansive ettringite formation appears to be possible in later years when the concrete is exposed to a very humid environment. The ettringite appears to precipitate especially at the interface of aggregate and cement paste and in micro-cracks. The latter are likely to be present due to the heat treatment, when concrete is cooled down too quickly.

The higher the temperature during accelerated curing, the greater the probability of this ettringite formation. This type of degradation does not appear to occur to a deteriorating extent in portland blast furnace slag cement. The cause of this reaction is still being discussed (7,8).

3.3 *Degradation by cations*

Sodium and potassium

Some aggregates contain reactive forms of silicium dioxide. Compounds of this kind can react with alkaline pore water (potassium and sodium) resulting in the formation of alkaline silicates. These are gel-like materials which can absorb large quantities of water. The absorption is due to osmotic effects in which the cement paste reacts like a semi-permeable membrane. Pressures could be built up high enough to cause the concrete to crack. There are no damage cases known in Holland of concrete produced with ordinary aggregates in which the damage has been exclusively due to alkali-aggregate reaction. However, in a few damage cases the alkali-aggregate reaction was suspected.

Ammonium

The ammonium ion (NH_4^+) is rather innocent in itself. However, the cation is always found in combination with an anion and this anion usually reacts with cement hydrates. As the calcium salts are formed the ammonium is released as gaseous ammonia. The release of ammonia shifts the reaction to the right, as shown for instance in the reaction with ammonium nitrate:



Both water soluble calcium nitrate and ammonia can leave the concrete easily. With respect to ammonia the Dutch standard NEN 5996 specifies the classes of aggressiveness as shown in Table 3. Although the table suggests that ammonium salts are aggressive even in small concentrations, some ammonium salts are less dangerous, e.g. ammonium carbonate, -oxalates, -fluorides. Indeed, though these attack the cement paste, the reaction products are insoluble and non-expansive and therefore these salts are less aggressive than salts like ammonium nitrate and ammonium sulfate. The latter salt provides calcium sulfate in reaction with cement paste. Subsequently this sulfate could lead to ettringite formation.

Magnesium

Magnesium salts react first with calcium hydroxide, forming low soluble magnesium hydroxide. However, magnesium is also able to react with calcium silicate hydrate gel as shown in the reaction:



In this reaction non-cementing reaction products such as brucite are formed. Of course, if the magnesium salt is magnesium sulfate, an extra degradation factor due to sulphate deterioration could occur. The Dutch standard NEN 5996 specifies the classes of aggressiveness as given in Table 3.

4 Cases of chemical degradation

In this chapter some damage cases due to chemical degradation factors will be discussed. These are examples taken from the author's own practical experience and will not cover all degradation factors. They will be discussed in the sequence of the types of degradation mechanisms discussed in the previous chapter, starting with cases in which acid attack was dominant.

4.1 *Sewage water structures*

Mechanism

A kind of deterioration which must be regarded as most severe is the degradation of

sewage water structures by sulfuric acids. This type of degradation is also called biogenic sulfuric acid attack.

In sewage waters various sulfur compounds are present in both inorganic and organic forms. The most important inorganic sulfur compounds are sulfates and sulfites. Sulfates are found above all in domestic waste waters.

In industrial sewage waters sulfites could also be present. Organic sulfur compounds are found in proteins, amino acids, etc. These organic sulfur compounds could be present in domestic waste water as well as in waste water of the food industries. Sulfate reducing bacilli, desulfovibrio-desulfuricans and others reduce sulfates to sulfide. Also organic sulfur compounds are reduced to sulfides or mercaptans.

These bacilli could be found in:

- the waste water;
- the mud layer on the bottom of the sewage structure;
- the slime layer on the wall below the sewage water level.

The slime layer in particular is biogenically active. This layer could be divided into various zones as shown in Fig. 6 (9). In the case where the oxygen content of the sewage water is greater than 1 mg/l, three layers could be distinguished. The outer layer in contact with the water is aerobic. The middle and inner layers are anaerobic. In the middle layer reduction of sulfur compounds could take place. These sulfur compounds diffuse from the waste water into the slime layer. When reduced the sulfide diffuses backwards into the waste water but becomes oxidized again in the aerobic slime layer.

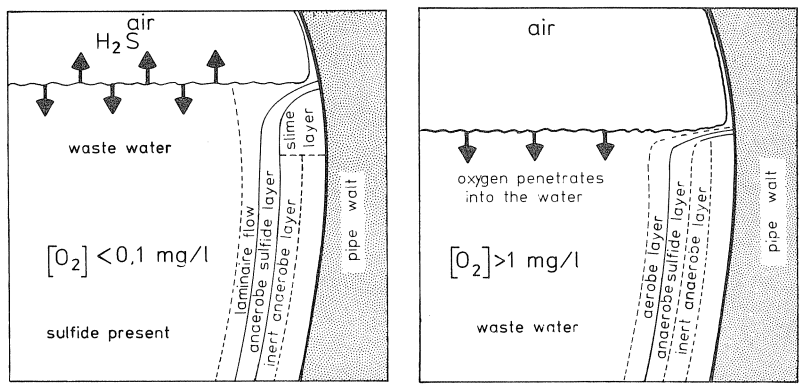


Fig. 6. Slime layer in (9).
 a. anaerobic sewage water
 b. aerobic sewage water

Therefore there will be no net reaction. However, if the waste water itself is anaerobic, i.e. if the oxygen concentration is lower than 0.1 mg/l, the aerobic slime layer will not be present so that the backward diffusion sulfide will enter the waste water. Here it could form hydrogen sulfide which can escape as a gas. The rate of escape is especially high in areas of turbulence.

Domestic waste water in general contains 50 to 100 mg sulfate per liter. From the sulfate 15 to 30 mg hydrogen sulfide per liter could be formed. Proteins and amino acids can contribute another 5 mg hydrogen sulfide per liter. So, the total content of hydrogen sulfide can amount to 20–35 mg/liter of waste water. Above the water level a humid atmosphere will be present especially in the case of closed structures. Concrete walls and ceilings will be continuously wet. The hydrogen sulfide gas will dissolve in this moisture. When other sources of nourishment are present, such as ammonia and carbon dioxide, aerobic bacilli can initiate the oxidation of sulfide. These aerobic bacilli are present because the environment above the water level is mostly relatively oxygen-rich. Various species of bacilli are able to convert sulfide. As a consequence of this conversion the environment of the concrete surface will become more acid. When the acidity of the environment increases some populations of bacilli will die, but other bacilli species will find favourable growth conditions. The most acidic bacillus thio-oxidans (also called bacillus concretivorus) can exist at pH levels of as low as 1. This acidity has indeed been measured in practice. The aggressiveness of sulfuric acid will depend on its concentration. In general, concrete is not resistant to an acid environment with a pH lower than 4. Thus it is certainly not resistant to a pH of 1 as measured for closed sewage systems. The degradation which has been observed is therefore mainly due to the dissolving of the cement paste by a strong acid.

Rate of deterioration

At high hydrogen sulfide concentrations the rate of degradation appears to depend mainly on the lime content of concrete. Pomeroy (10) defines the rate of deterioration of concrete by sulfuric acid as follows:

$$C = \frac{11.5k \cdot \phi_{sw}}{A}$$

in which:

- C = corrosion rate in mm/year
- k = factor taking into account the possible losses during reaction
- ϕ_{sw} = sulfide flux to the surface of the sewer system in g/m² hour
- A = the quantity of acid required to neutralize a certain amount of concrete in comparison with a quantity of acid neutralized by the same mass of calcium carbonate

For a strongly aggressive hydrogen sulfide environment the ordinary concrete durability parameters such as the water/cement ratio no longer appear to be valid. However, at lower levels of aggressiveness, the well-known parameters appear to be dominant again. The transition from weakly to strongly aggressive hydrogen sulfide environments is not very clear. Therefore it is rather difficult to take the measures most appropriate to safeguard the design of service life.

Preventive measures

In volume terms the aggregate is the most important constituent of concrete. According to the above formula less acid will be available for the attack on the cement paste if this aggregate is able to neutralize sulfuric acid too.

In sewage systems with high hydrogen sulfide loading the use of limestone or dolomite aggregates is therefore a measure that could be considered to decrease the rate of deterioration.

At higher hydrogen sulfide levels ordinary concrete in closed sewage structures has to be protected. One of these protective measures could be to increase the cover. At an average degradation rate of 3 mm/year an extra cover of 60 mm will be required to warrant 20 years service without the main structure being affected. In large parts of the Netherlands the soil has a low load-bearing capacity. Therefore an increase in the dead-weight of concrete pipes is not regarded favourably. However, there are many alternative protective measures. These are discussed in Chapters 8 and 9.

4.2 Manure silos (11)

In the past few years thousands of manure silos have been built in the Netherlands and another sixteen thousand will be erected in the next ten years. The silos are being built because of severe restrictions on the use of manure.

There is a ban on manure-spreading on the fields during the winter period because percolation by rain water and leach-out of the manure could pollute the soil, especially with nitrates. Because the manure also contributes to "acid rain" due to evaporation of ammonia, the silos have to be closed so that the ammonia cannot escape into the atmosphere.

Contents of constituents aggressive to concrete in liquid manure are given in Table 4 (11).

Table 4. Contents of aggressive constituents in liquid manure (mg/l) (11)

| | cattle | poultry | pig |
|-----------------|-----------|-----------|------------|
| Mg | 810-1570 | 1260-2380 | 640- 2000 |
| Cl | 1810-4180 | 80-3220 | 640- 3360 |
| N | 3800-7600 | 5950-1575 | 4320-11520 |
| SO ₃ | 2000-3000 | 2000-4000 | 1000- 2000 |

The constituents of the manure itself are not especially aggressive, but like in the sewage systems, here again hydrogen sulfide could be formed by sulfate reducing bacilli. An investigation into existing manure silos has shown that for low concrete quality a similar degradation can occur as in sewage systems. In general, however, this degradation is less severe because the hydrogen sulfide mainly escapes when the manure is periodically stirred. Table 5 (11) shows the conclusions from the field investigation with respect to concrete deterioration in manure silos. The deterioration occurs above the

Table 5. Conclusions field investigation concrete manure silos (11)

| | no degradation | degraded |
|--|----------------|-----------|
| compressive strength (N/mm ² , MPa) | 50-80 | 12-23 |
| porosity (% v/v) | 11.3-15.2 | 15.1-22.3 |
| water penetration DIN 1048 (mm) | 7-25 | 50-75 |

manure level, below the level no significant damage was observed. According to the Dutch Concrete Standard NEN 5950 concrete exposed to this kind of very aggressive environments has to be protected by a coating. However the reliability of coatings as a durable protection of concrete against degradation by sulfuric acid is doubtful. Not only because of the reasons discussed in chapter 8 (defects, formation of gypsum), but also because in manure silos damage of the coating system is virtually unavoidable because of operations occurring in the silos like filling, mixing, emptying, etc. Therefore in the Netherlands the use of an additional sacrificial cover is recommended. On the basis of the results available it is expected that the specified sacrificial cover of 10 mm will be sufficient to warrant the design service life of 20 years for the silos.

4.3 Foundations of high voltage poles

Some concrete foundations of high voltage poles in the Netherlands were found to be damaged, especially at the edges of the foundations above the ground level. The concrete was found to be cracked, spalled and sometimes completely degraded. At the cracks white salt deposits could be observed.

Analysis has shown excessive ettringite in the concrete and calcium carbonate on the outside. The concrete contains a large number of micro-cracks. All the foundations degraded were of rather poor quality concrete.

The environment of the affected concrete foundations appears to be fairly aggressive mainly due to the use of liquid manure which, as discussed in the previous paragraph, can contain rather high quantities of salts.

A possible cause of the damage could be suction of water containing sulfates originating from the liquid manure. The salt-containing water is transported through the capillary pores to the ground level where the water evaporates and the salts remain as shown in Fig. 7. Because of the accumulation of sulfates ettringite could be formed. However in some cases there were also signs that simultaneous degradation of the cement paste could occur by ion-exchanging cations with the calcium silicate hydrate gel. Further in some cases alkali-silica reaction of the aggregates was also suspected.

It was remarkable that the coating applied on the foundation did not prevent this degradation. This coating was not impermeable and was not in general resistant to salts precipitating beneath the surface of the coating. Blistering was observed. Which degrading mechanism dominates was not fully clear.

It was advised that a similar problem could be prevented in future by applying very dense concrete with a very low water penetration rate determined according to the

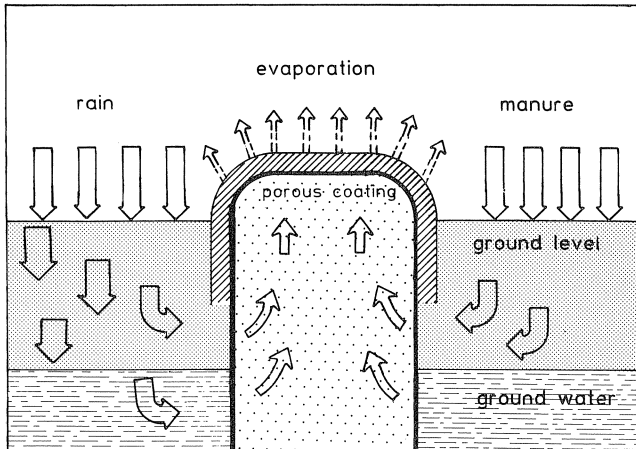


Fig. 7. Degradation mechanism foundation high voltage poles.

German Standard DIN 1048 and manufactured from portland blast furnace slag cement with a high slag content (> 65%). This kind of concrete is chemically resistant according to the German standard DIN 1045.

4.4 Foundations of greenhouses (12)

Agriculture is one of the main exporting sectors of the Dutch economy. Large areas of land are covered by greenhouses or hothouses. The foundations of the greenhouses are mostly made of concrete. They consist of small precast concrete piles which are embedded in in-situ poured concrete as shown in figure 8 (12). In the hothouses a

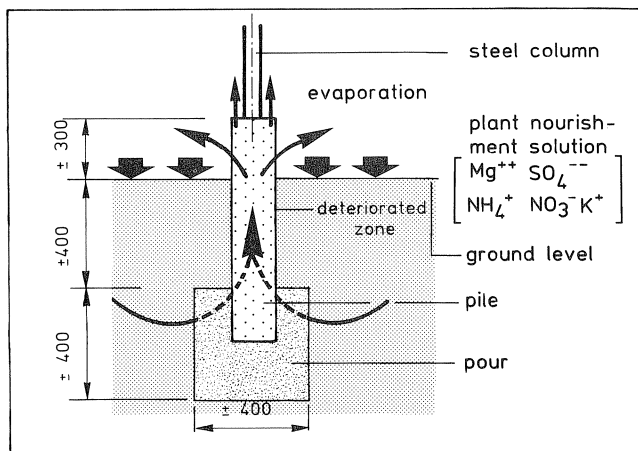


Fig. 8. Foundation of greenhouses, showing transport of salt (12).

temperature of 20 to 25 °C is maintained. Continuously or at regular intervals nourishment solutions are sprayed on the soil. These nourishment solutions have a composition as shown in Table 6. They contain a lot of nitrate, sometimes sulfate, always some ammonium, calcium, and also magnesium. These nourishment solutions penetrate the soil, are absorbed by the concrete and transported through the pore system down to the ground level where the water evaporates and the salts remain. Severe deterioration has been observed at ground level. Sometimes expansion was obvious. Always the concrete appeared to have lost its integrity, often without signs of expansion. Fig. 9 shows a deteriorated pile.

Table 6. Composition plant nourishment solutions (12)

| ions | minimum (mmol/l) | maximum (mmol/l) |
|--------------------|------------------|------------------|
| NO_3^- | 7.5 | 12.25 |
| SO_4^{2-} | 0.75 | 2.5 |
| NH_4^+ | 0 | 1.25 |
| K^+ | 4.0 | 7.25 |
| Mg^{2+} | 0.5 | 1.5 |

A reaction of ammonium salts and magnesium salts with the calcium silicate hydrate gel of the cement paste could take place. But ettringite formation has also been observed. Above the ground level an accumulation of the most mobile ions could be observed, below the ground level the less mobile ions were concentrated.



Fig. 9. Deteriorated greenhouse foundation pile (12).

Sometimes expansion due to ettringite formation was present; in other cases ettringite could be detected but no expansion was observed.

In the last case it was considered likely that cement paste degradation occurred first, while ettringite formation took place later on. The formation of ettringite occurred when there was enough space to release the expansive ettringite forces. The results of the research into hothouse concrete foundations has been used for the formulation of Recommendation Number 8 of CUR “Durability of concrete foundations in greenhouses” (13). The most important requirements in this Recommendation are that a portland blast furnace slag cement has to be applied with a high slag content and that the water penetration must not be higher than 30 mm according to the German standard DIN 1048.

4.5 Prestressed lamp posts

About six/seven years ago in Belgium a prestressed concrete lamp post fell down spontaneously on a motorway. Fig. 10 shows schematically the degradation mechanism. Salt-laden water had been continuously transported to the inner hollow space in the lamp post which acted as a kind of chimney. The water evaporated and the salt remained. Thaumaside as well as ettringite have been observed in the post. Thaumaside formation was possible because in the post limestone was applied as a coarse aggregate. As a consequence of the expansion and subsequent cracking due to this double salt formation the prestressed cables corroded and finally the post fell down.

The groundwater was not especially aggressive. But the precast poles had been subjected to accelerated hardening by steam-curing at rather high temperatures. The most likely damage was caused by the internal sulfate attack as described in the previous chapter.

Fig. 11 shows a photograph of the deteriorated post.

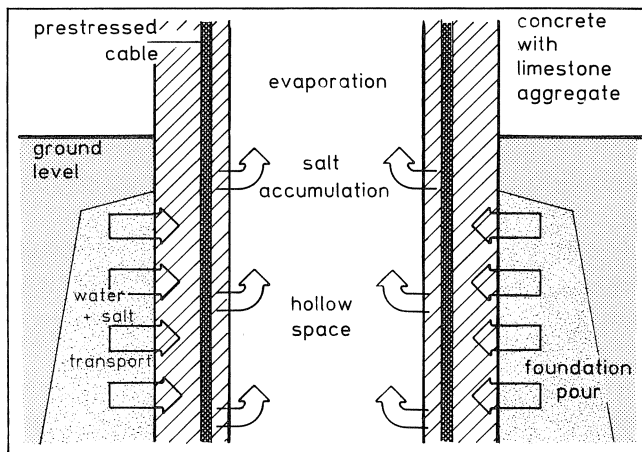


Fig. 10. Cross section of the foundation of hollow prestressed lamp post and transport of salts.



Fig. 11. Photograph of deteriorated lamp post.

5 Frost-thaw (salt) damage

An important degradation factor for concrete structures is frost-thaw (salt) damage. Although the combination of frost, thaw and de-icing salt is far more important than pure frost thaw damage, the latter mechanism will be discussed first, because understanding of this mechanism will be helpful in understanding the more complex mechanism of frost-thaw and salt damage.

5.1 *Frost-thaw*

When water freezes it expands about 9% by volume. If there is no space for the freezing water the concrete will fail. During freezing the expanding ice will push away the not-yet-frozen water.

The water is pushed into finer capillaries where the freezing temperature is lower than in the wider pores. The flow of water through these fine capillaries will be resisted by the pores in a form of hydraulic pressure. This pressure can exceed the tensile strength of the concrete.

Another cause of frost damage is that the water freezes firstly in the larger pores. The smaller the pores in the concrete, the lower the water freezing temperature. In gel pores, for example, the water can freeze at temperatures as low as -80°C . When the water freezes in the larger pores, the water vapour in the smaller pores will diffuse to the

frozen water in the larger pores because the vapour pressure of ice is always lower than the vapour pressure of water as is shown in Table 7. The water vapour will condense on the ice and freeze. This causes the ice in the pores to grow. This phenomenon is well known from frost sensitive soils where the frost heave can be much larger than can be explained by the expansion of the water in the frozen soil alone. This must be related to transport of water from the lower soil layers to the layers where freezing occurs. This is called the ice-lens mechanism.

The growth of ice inside large pores needs not stem solely from vapour diffusion, it could also be the result of transport of water.

Table 7. Vapour pressure above water and ice (mm Hg)

| % | water | ice |
|-----|-------|-------|
| -15 | 1.436 | 1.241 |
| -10 | 2.149 | 1.950 |
| -5 | 3.163 | 3.013 |
| 0 | 4.579 | 4.579 |
| +4 | 6.101 | - |

Thermodynamically it has been established that ice in the large pores will continue to grow by sucking water from the fine pores until the pressure on the walls of the pore caused by the ice is large enough to make iceformation in the finer pores possible too. This is illustrated in Fig. 12. However, after some time it is not likely that continuous water-filled pores will be present. In that case water vapour transport will be more important.

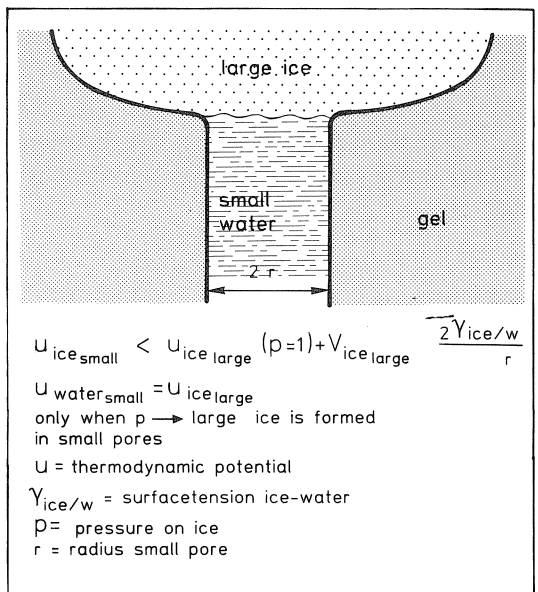


Fig. 12. Growth of ice inside large pores caused by water supplied from small pores.

Thus in general large pores will be filled in time with ice. When the temperature increases again after the freezing period, the ice crystals will show normal linear expansion. The linear expansion coefficient of ice is about 5 times as large as that of cement paste. This means that forces will develop in the filled-up pores. It can be calculated that the tension forces which may be introduced could be as high as $0.36 \Delta T \text{ N/mm}^2$ (MPa). This means that at a temperature difference of 15°K the tensile strength of the cement paste could be exceeded (14).

5.2 De-icing salts

There are a number of reasons why the combined action of frost-thaw loading and the use of de-icing salts has a more severe effect on concrete than frost-thaw alone. De-icing salts are applied on surfaces which are covered with snow or ice. This means that part of the pore water in the top layer will be frozen. The principle of de-icing is based on the fact that the freezing point of a salt solution is lower than that of pure water, e.g. a solution of calcium chloride of 20 g/l freezes only at a temperature of -50°C . In practice the de-icing salt mostly used is sodium chloride. In Fig. 13 the phase diagram is schematically given. The eutectic point, i.e. the minimum equilibrium temperature between ice and liquid, is about -23°C . The solid phase in that case is a mixture of ice and salt. A mixture of ice and sodium chloride will try to find its thermodynamic equilibrium. That means that the ice will melt and the salt will dissolve in the melt water. For both melting of the ice as well as dissolving of the salt heat is required, most of it being needed for the melting of the ice. This heat is extracted from the melting mixture and from the substrate (concrete). As a consequence the temperature of the total system decreases. How much the decrease in temperature will be and how fast it happens will depend on various circumstances. Under the most unfavourable conditions the temperature decrease could be 10°C within a minute. The concrete surface is faced with a sudden temperature drop. As a consequence the water will freeze quickly, unless the pore system is so fine that the water will not freeze even with the application of salts. When quick freezing occurs the hydraulic forces on the pore walls will be high.

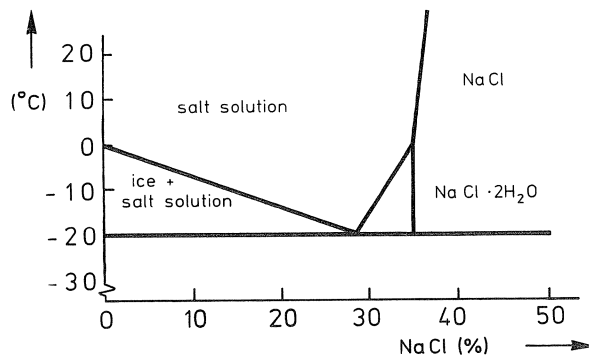


Fig. 13. Phase diagram of sodium chloride solution.

The salt penetrates the pores and because salt solutions have a higher viscosity the hydraulic pressure at ice formation will be higher than without salts.

As the temperature decreases the ice in the concrete will contract more than the concrete. Open spaces will be formed which will induce suction forces.

Consequently the salty solution at the surface will be sucked into the concrete with the effect that the water content will increase and fill up the pores further. The total effect will be that the effects already described for the single frost-thaw loading will be aggravated in the case of salt application.

Another aspect of the penetration of salt in concrete is that it will reduce the freezing temperature of the water in the pores of concrete. There will be a freezing temperature gradient from the surface to the core of the concrete. A situation could occur as shown in Fig. 14. The freezing temperature could be reached at the surface and more towards the core while an intermediate layer will not freeze, because the temperature there is still higher than the freezing temperature. This means that there is no way out for the expanding water from this intermediate layer when it starts freezing. This can cause blistering which is often observed in cases of concrete degrading by frost-thaw salt action.

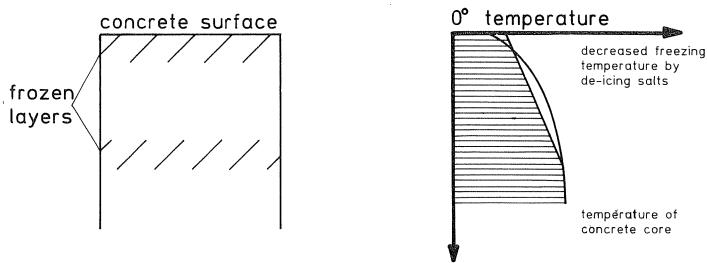


Fig. 14. Frozen layer with intermediate unfrozen layer leading to blistering.

Recently Binbin showed that chemical attack by chloride salts is probably more deleterious than had previously assumed (15). He proved that at freezing temperatures expansive calcium oxychlorides, $m\text{CaO} \cdot x\text{CaCl}_2 \cdot n\text{H}_2\text{O}$, are formed which could be destructive to concrete. The deleterious effect of these crystal formations increases when the temperature decreases.

6 Corrosion of reinforcement

In this chapter the mechanism of the corrosion of reinforcement will be briefly discussed. Corrosion of reinforcement is certainly the main cause of concrete damage in practice. Specific corrosion mechanisms affecting prestressed steel, such as hydrogen embrittlement and stress corrosion, will not be taken into consideration.

6.1 Protection by concrete

Thermodynamically rust (iron oxide) is a more stable compound than iron. The metal iron does not occur in nature. Nevertheless iron does not normally corrode in concrete. The protection of steel reinforcement by concrete can be explained by two factors:

1. The oxygen available in the concrete reacts in the strong alkaline environment of the concrete to form a very thin but also very dense impermeable layer of iron oxide which protects the steel against corrosion. The steel becomes passivated.
2. The concrete cover, provided it is dense, intact and sufficiently thick, forms a barrier against the penetration of exterior degradation agents, especially carbon dioxide and chloride ions, which could destroy the passivation.

The passivation can be lost if the alkalinity of concrete decreases due to carbonation. Another important degradation mechanism with respect to passivation is the presence of chloride ions. Normally chloride ions are not present in concrete in concentrations high enough to break through the passivation. However, chloride can penetrate from the outside, e.g. in marine structures or when de-icing salts are applied, and can cause corrosion when the concrete is permeable and/or cover thickness is low. According to the Hausmann criterion passivation will be disrupted when the chloride/hydroxyl ratio of the pore water at the steel surface is higher than 0.6. Lower values for concrete are also advocated in the literature. Mostly the critical chloride concentration is expressed as a percentage of the cement mass. However, it has to be realized that the actual chloride concentration in the pore water is dependent on many factors, such as the amount of chlorides bound physically or chemically to the cement paste, the water/cement ratio, etc. Carbonation can release bound chloride ions and increase the chloride content in the pore water in front of the carbonation frontier.

6.2 Polarization

The understanding of corrosion processes and how to influence them could be greatly improved by studying the so-called polarization curves of the various partial reactions in an electro-chemical system. Fig. 15 (E-I) shows a potentiostatic polarization curve for iron and oxygen. At the free potential of iron (E_{Fe}^0) the corrosion current is zero. When iron and oxygen are in contact with each other, however, a so-called mixed or corrosion potential will occur. This means that the potential of both elements will be similar if ohmic drops over the electrolyte (concrete) are not taken into consideration. The increased potential of the iron increases the corrosion current of iron by a factor of about 100. This phenomenon occurs in neutral or low-alkaline (water) solutions. However in concrete, where iron is in contact with high-alkaline pore water, another effect occurs. It is illustrated in Fig. 15. In contact with oxygen above a certain potential the corrosion current decreases strongly. This is due to the formation of a thin but very dense iron oxide layer which prevents iron-ions from diffusing through this layer so that the corrosion process is stopped almost completely; the so-called polarization of the anode.

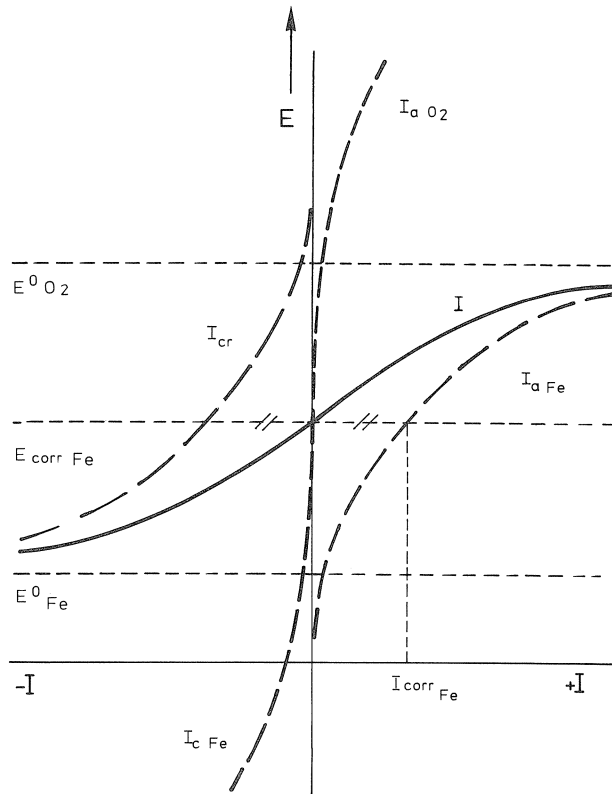


Fig. 15. Polarization curves for:
 - iron: partial current $I_{a Fe}$ and $I_{c Fe}$
 - oxygen: partial current $I_{c O_2}$ and $I_{a O_2}$
 - mixed iron-oxygen sum curve I

The polarization curves depend not only on the specific elements involved but also on their concentrations. Fig. 16 shows the polarization curve (E -log I) for the oxygen reduction, which is the reaction occurring at the cathode. The inclination of the curve increases when the oxygen concentration (pressure) decreases. When enough oxygen is available the combination as shown in the upper curve of Fig. 17 occurs. At the mixed potential the corrosion current is only low. When the oxygen concentration diminishes an unstable situation can occur, as is shown for the other two curves in Fig. 17. As a result the corrosion current could be higher for low than for high oxygen contents in the event of passivation. In general, however, the corrosion current will stay small. For wet concrete, e.g. under water, the supply of oxygen to the reinforcement is very low so that the corrosion current is negligible.

The corrosion current density is further determined by the mobility of ions, which have to maintain the corrosion circuit through the electrolyte. The latter consists of the (water) solution in the pore system. If the pores are empty, the corrosion rate will be low because the ohmic resistance will be too high.

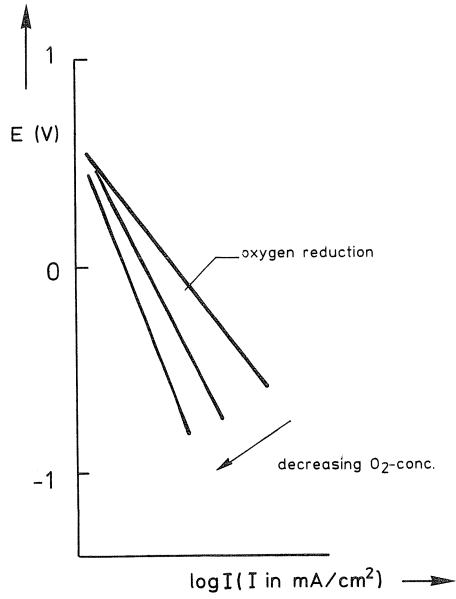


Fig. 16. E -log I diagram for reduction of oxygen.

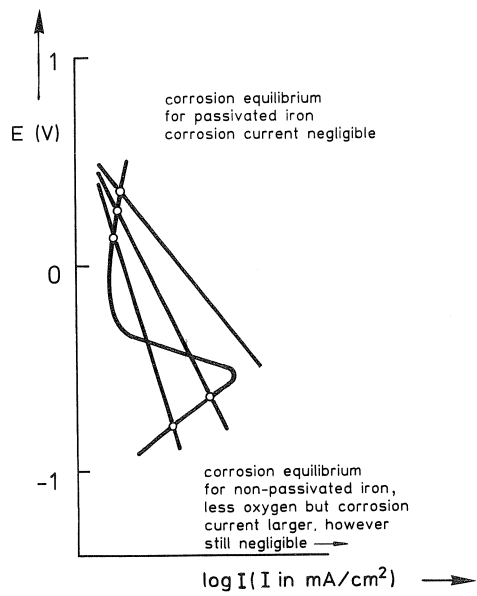


Fig. 17. E -log I diagram for reduction of oxygen and iron oxidation.

The resistance could also be high for very dense pore structures with small pores and high tortuosity. This is known from good quality concrete made with portland blast furnace slag cement or portland cement mixed with silica fume.

In the event of carbonation the passivation disappears. Homogeneous corrosion may occur.

When the chloride concentration in concrete exceeds a critical level the passivation will only be locally disrupted, except where the chloride concentration is extremely high. In the areas surrounding these local defects the passivation will still exist. In that case we have rather irregular polarization curves. Because the passivated areas act as cathodes and the relatively small, depassivated areas as anodes, the cathode/anode surface ratio is large. As a result, current density at the anodes is relatively high. This causes what is termed pit-corrosion, which could be considered as a special case of macrocell corrosion.

The positive anodes attract chloride ions from the environment. Moreover the anodic reactions release hydrogen ions. Consequently in the pit a very corrosive environment will grow, as shown in Fig. 18. This environment differs greatly from the adjacent cathodic areas.

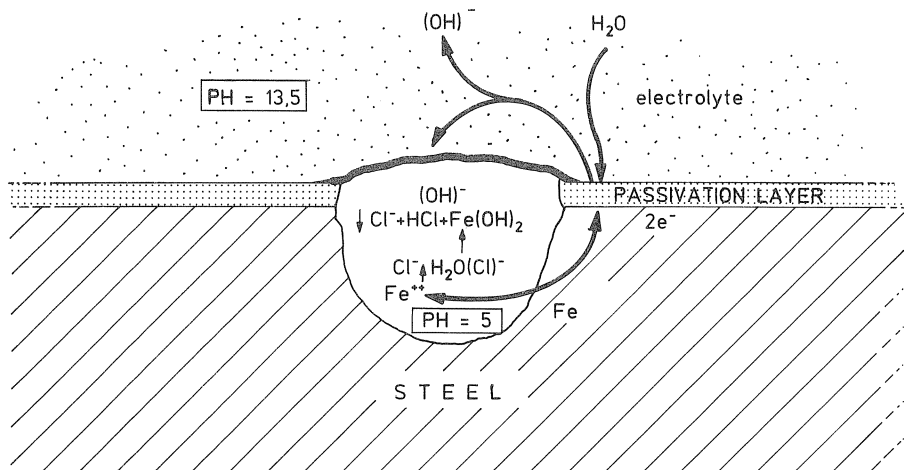


Fig. 18. Aggressive environment in chloride corrosion pit.

6.3 Pourbaix diagrams

Other tools for understanding corrosion of reinforcement are the so-called Pourbaix diagrams. In the Pourbaix diagrams the potential of a specific system is given as a function of pH for the various reactions that could occur. The constituents involved are assumed to have constant concentrations, with the exception of the hydroxyl ion concentration. Fig. 19 gives an example of a Pourbaix diagram for steel in concrete. Curve A shows the potential for aerated concrete while curve B gives the situation for non-aerated concrete. Beyond a pH of 8 the iron appears to be passive.

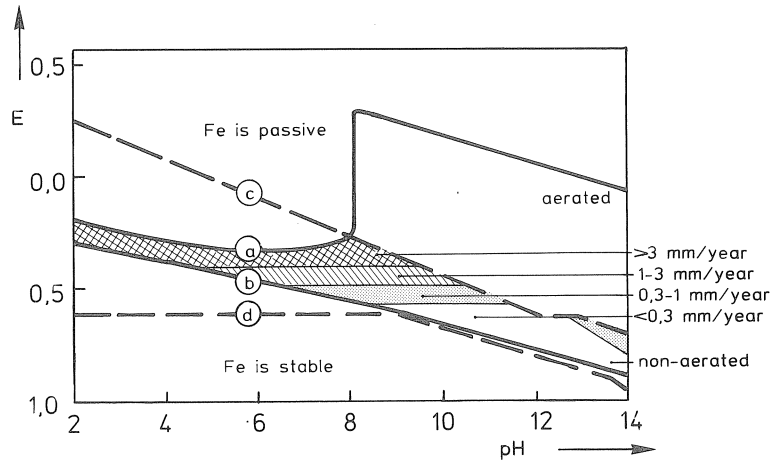


Fig. 19. Pourbaix diagram for iron in contact with aerated and non-aerated water
 a. aerated
 b. non-aerated
 c. passivating potential
 d. iron stability border line

When chloride is present the curves change as shown in Fig. 20. The passivation area decreases when chloride concentration increases. Moreover passivation makes the material unstable. When an active corrosion pit has been formed the pit is no longer in the passivated zone and will move further away from the passivated zone because of the decrease in pH in the pit.

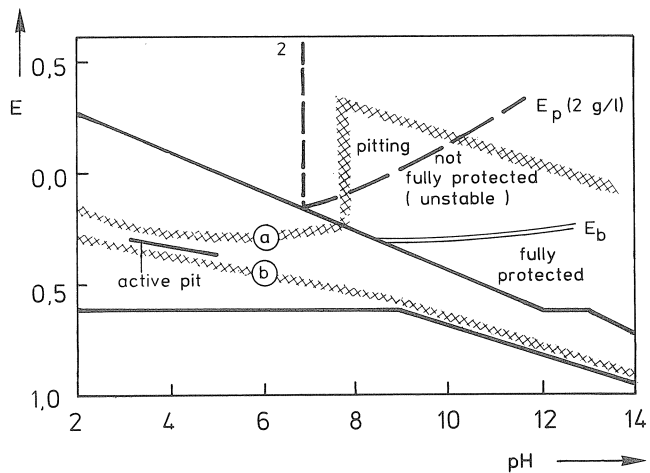


Fig. 20. Pourbaix diagram as in Fig. 19 but with chloride concentration of 2 g/l.

7 Repair mortars

As part of most repair techniques, damaged areas of concrete are removed and replaced by substitutes. In this chapter various substitutes will be discussed. These regard the following mortars:

- traditional cement/sand mortars;
- concrete casting;
- shotcrete;
- polymer modified cement mortars;
- polymer mortars.

The various advantages and disadvantages of these mortars will be discussed and related to the type and size of the corrective maintenance required.

7.1 Functions

Repair mortars have various functions. These are:

- They can restore the alkaline environment, so that the environment is repassivated. This restoration could to a certain extent involve the carbonated substrate (concrete) due to diffusion of alkaline matter (re-alkalization). This will be discussed in Chapter 12.
- Alternatively they can provide passive protection because they do not allow oxygen to get at the reinforcements and prevent water from making contact with the reinforcement, so that corrosion is prevented. The latter will not always be achieved by a dense mortar alone, but requires the application of a coating or primer to the reinforcement, as is discussed for example in Chapter 10.
- They can provide a durable barrier to the (renewed) ingress of aggressive components from outside. For example, they prevent renewed carbonation during the remaining service life of the structure. This could be achieved by the repair mortar alone, or in combination with other repair measures (as part) of the repair techniques chosen, e.g. surface protection.

7.2 Traditional cement mortars

For small size repairs unmodified cement mortars are often applied. However, it has been proved that these mortars have rather poor behavior. There is mostly a lack of adhesion to the substrate and, as a result of drying shrinkage, the repair mortar can easily shrink away from the substrate. Improvement could be achieved by applying a primer to the substrate. This could be a cement slurry which could be modified, e.g. by polymer dispersion, but a moisture compatible epoxy adhesive primer could also be applied.

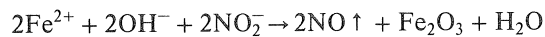
When the mortar is applied to repair frost-thaw damage, the mortar has to be frost resistant. This could be achieved by air entrainment.

7.3 Casting with concrete

Casting of concrete for repair work is applied when larger areas are involved. For durability reasons a concrete with a low water/cement ratio has to be used. However, for casting a flowable mix is required. This demands a high range water reducer to make the concrete easily flowable. Because the repair mostly concerns confined areas, the maximum aggregate size has to be reduced in comparison with ordinary concrete.

7.4 Corrosion inhibitors

In cement/sand mortars or concrete the use of corrosion inhibitors can be considered. The most commonly used in the world is calcium nitrite which prevents of the passivation layer being disrupted by chloride due to the reaction:



One precondition is that sufficient nitrite must be present. If the chloride content is very high the nitrite concentration could be too low, so that pit corrosion may occur after all. In this case the presence of nitrite could even be deleterious because areas of pit corrosion will then be adjacent to areas where passivation still exists, which promotes macrocell corrosion. However, this inhibitor obviously has some advantages: it can easily be mixed in concrete or cement mortar, it prevents corrosion in the case of contaminated old concrete which is not replaced (levelling out can sometimes cause renewed corrosion, see Fig. 21), and it is a rather cheap method. Some doubts about the durability of the effects of this agent hamper full exposure to the market.

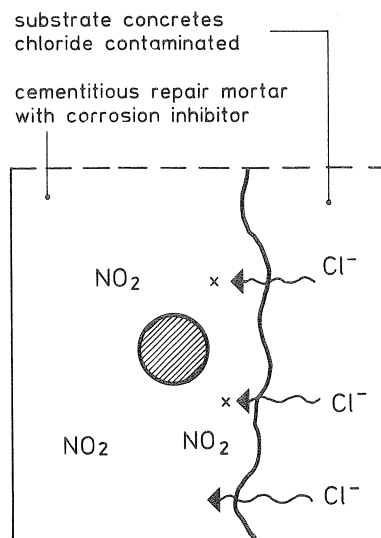


Fig. 21. Penetration of chloride ions from contaminated substrate concrete into cementitious repair mortar with added corrosion inhibitor.

7.5 Polymer modified cement mortars

To improve the rather poor performance of cement/sand patching mortars and at the same time maintain their positive effects, especially the (re)passivating capacity and the fact that cement mortars have properties such as Young's modulus, linear expansion coefficient, etc. which are similar to the substrate concrete, more and more polymer modified mortars are used.

These polymers consist of elastomeric polymers or thermoplastic polymers, like polyvinylidene chloride, polyvinyl propionate, styrene butadiene, styrene acrylates, polyvinyl versatate, etc. Also thermosetting resins are used, mainly water emulsified epoxy resins. When applied with a percentage of lower than 5% by mass of cement these mortars are called polymer modified mortars. When the polymer content is higher they are called polymer cement concrete (PCC). In the case of epoxies the name epoxy cement concrete (ECC) is used. The polymers have to meet various requirements. These include:

- They must be alkaline resistant. Some of the polymers used in the early days like polyvinyl acetate were not alkaline resistant, which caused early failure in some cases. Polyvinylidene chloride mortars are known to release chloride ions which have induced corrosion of reinforcement in some projects in the US. The polymers halogen content (exclusive fluoride) must therefore be low.
- The polymers must have a water reducing effect, so that the mortars with polymer will have a lower water/cement ratio than those without.
- The polymers must have a minimum film temperature lower than the temperature during application. In Western Europe this means that the film temperature must not be higher than 10 °C.
- The polymers must not introduce large quantities of air. If so a defoaming agent has to be applied.

In the literature large variations in properties of polymer cement concrete and polymer modified concrete have been found depending on the polymer type, the polymer content, water/cement ratio, etc. Table 8 illustrates this for properties found in a German investigation (16).

Table 8. Variation in properties of thirty repair mortars (16)

| | | |
|---------------------------------|----------|--------------------------|
| compressive strength | 14 -69 | N/mm ² (MPa) |
| bending strength | 6 -14 | N/mm ² (MPa) |
| Young's modulus | 8 -25 | kN/mm ² (GPa) |
| drying shrinkage | 0.3- 2.0 | mm/m |
| adhesion strength | 1.3- 3.6 | N/mm ² (MPa) |
| coefficient of linear expansion | 10 -17 | 10 ⁻⁶ /K |

The polymer increases the strain capacity of the mortars. For dry conditions the tensile strength is increased up to polymer contents of about 10% by mass of cement. Beyond that level it decreases again. When wet, the tensile strength is hardly increased. The Young's modulus of polymer modified concrete decreases with increasing polymer

contents. The adhesion to substrates could be greatly increased by applying appropriate polymers. Adhesion strength equal to the tensile strength of the substrate concrete is achievable. In general the performance of these polymer modified mortars is much better than that of traditional mortars. Mainly because of better adhesion, less drying shrinkage stresses and higher strain capacity. Moreover the polymers make the mortars less sensitive to the quality of curing.

7.6 Shotcrete

The use of shotcrete (gunitite or sprayed concrete) is a very popular method for filling up areas where concrete has to be replaced. It does not require moulds as are needed for casting of concrete. Moreover, because of the presence of a cement-rich layer at the substrate interface, good adhesion can be achieved.

Further it can be made dense and less permeable. It can serve as an effective barrier against (renewed) carbonation due to its low permeability as well as its high cement content. However the quality depends very much on the craftsmanship of the guniter and the specific conditions of the projects. This can sometimes lead to poor results. In the Netherlands investigations have been conducted into the use of silica-fume in sprayed concrete (17). This has shown substantial improvements. The rebound was drastically reduced to a few percentage points, while adhesion strength was found to be improved. The strength of the shotcrete increased and it was noted that permeability had decreased. Nowadays it is used more and more for remedial works with sprayed concrete. Also the use of polymer modified sprayed concrete is advocated in the Netherlands. The polymer dispersion is applied through the spray nozzle. The advantages, in additions to reduced rebound, are the same as those discussed in the previous paragraph. Sprayed concrete is not only used to fill up areas where concrete needs to be replaced, it is also used to increase the cover as a barrier to carbonation or to aid re-alkalization of the carbonated substrate. It could also be used to level out existing chloride gradients in the substrate concrete, as shown in Fig. 22 (18).

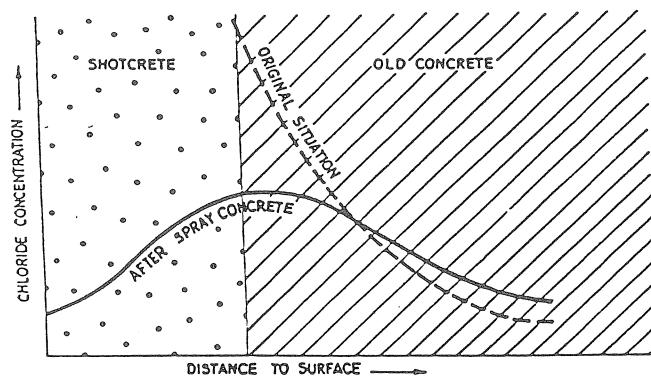


Fig. 22. Chloride concentration expressed as a function of distance from the surface before and some time after applying sprayed concrete.

7.7 *Polymer mortars*

For hand-patching the use of polymer-bound mortars or polymer concrete (PC) has become increasingly popular in the last decade, although in the past few years polymer modified cement mortars are also making a lot of headway.

Epoxy resins, acrylics or polyurethanes are mostly used as binder for these mortars. Polyester resins are not used any more because of their high hardening shrinkage, their moisture sensitivity as well as their proneness to saponification when applied on concrete.

For this type of mortars adhesive primers are always applied. These often contain anti-corrosive agents when the reinforcement has to be treated, although it is not sure that the use of these agents is necessary.

The patching operation is rather critical because the polymer mortar has to be applied to the polymer primer when wet.

In a field study in the Netherlands most of the polymer mortars investigated showed debonding (3). This was due to insufficient preparation of the substrate. But other contributory factors may have been differences in temperature-expansion and exceeding of the glass-rubber transition temperature of the epoxy, could have contributed. This will be discussed in Chapter 8.

8 **Protective surface treatments**

A survey of concrete surface protection treatments will be given in this and the next chapter. In this chapter general principles of surface protection will be discussed. The questions why and how will be answered and general requirements of the surface protective agents will be addressed. In the next chapter the various agents commercially available will be considered.

8.1 *Types*

The following types of surface protection can be distinguished; see Fig. 23 (19-21):

- impregnation/hydrophobation;
- impregnation/partially filling up of pores;
- impregnation/fully filling up of pores (sealing);
- surface layers.

When concrete is made water-repellent by impregnation/hydrophobing, the walls of the concrete pores are lined with a hydrophobic agent. In general impregnation occurs by suction of the agent into the concrete. This process is sometimes aided by previous drying. Hydrophobing does not significantly influence transport of water vapour, but could reduce water absorption strongly.

In the cases impregnation and filling up of pores, the concrete surface is penetrated by an agent which fills up the pores. The impregnation can be performed by making use of the absorptive capacity of concrete which can be promoted by drying the surface

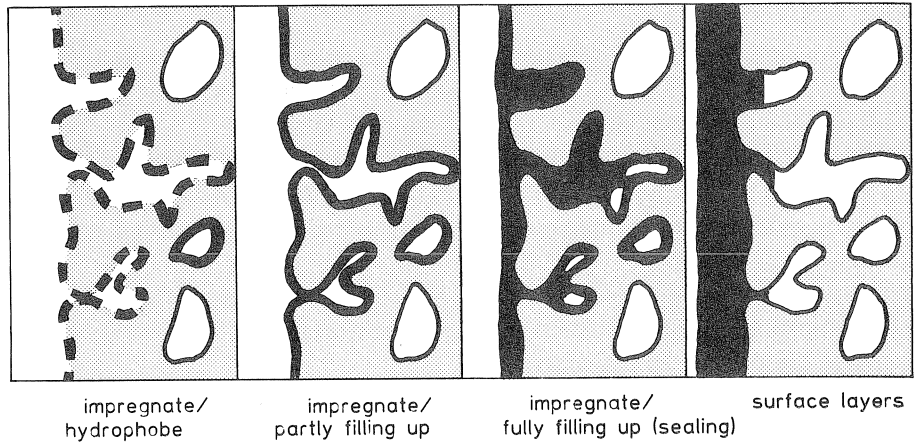


Fig. 23. Types of surface protection (19-21).

and/ or evacuating the air. A distinction can be made between agents which fill up the pores under reaction with constituents of concrete and in agents which do not react with concrete.

Where the pores of the surface layer of concrete become totally filled up by impregnation, the process is called sealing.

A further method of surface protection is protection by applying a surface layer. Various types of surface layers can be distinguished.

These are:

- thin coatings: layers less than 100 μm thickness;
- thick coatings: layers with 100 to 500 μm thickness;
- plasters both with an organic and with an inorganic basis, with a thickness of 500 μm to 5 mm. At lower thicknesses these plasters are also called high built coatings;
- prefabricated polymer membranes which do not adhere to the concrete
- rubber linings;
- sheets of plastics or other materials, for instance stainless steel;
- tiles.

In Table 9 a survey of the various methods of surface protection is given. The last four surface protection methods mentioned above will not be taken into account.

8.2 Why protection?

There are a number of reasons for protecting concrete. These include:

- To prevent (further) penetration of chloride ions, for example in the splash zone of sea or marine structures or in the case of concrete loaded with de-icing salts.

- To avoid progress of carbonation in non-repaired concrete parts or renewed carbonation in cement based repair mortars.
- To decrease corrosion propagation.

Sometimes in repair work the continuation of reinforcement corrosion could not be excluded from all parts of the structure. This means that renewed initiation of corrosion might be possible. In those cases decrease of corrosion propagation by means of

Table 9. Survey of various methods of surface protection

| treatment | effect | substrate conditions |
|---|---|--|
| impregnate/ hydrophobe | water-repelling/water vapour permeable; not resistant to chemical loading | fine pores |
| impregnate/ fill up pores | decrease water absorption and increase water and water vapour resistance; not resistant to chemical loading | fine pores |
| thin coatings | water and water vapour tight; sensitive to mechanical loading; restricted chemical and thermal resistance | smooth surface, free from large pores and cracks* |
| thick coatings | water and water vapour tight; more resistant than thin coatings | smooth surface, fine cracks allowed |
| inorganic plasters | fairly water tight, water vapour permeable; non chemical resistant (excluding special types) | free of large macropores (air bubbles, honeycombs) non moving fine cracks allowed* |
| organic plasters/ high built coatings | water and water vapour tight; resistant to chemical loading, less resistant to mechanical loading | free of macropores, non moving fine cracks allowed* |
| film membranes | water and water vapour tight; resistant to chemical loading; less resistant to mechanical loading | smooth surface, cracks to 3 mm width allowed |
| rubber lining | water and water vapour tight, resistant to chemical, temperature and mechanical loading | smooth |
| lining with thermoplasts, sheeting or pipes | water and water vapour tight, resistant to chemical, temperature and mechanical loading | smooth |
| tiling | resistance, depending on kind of tiles, adhesive and joint filler | smooth |

* crack bridging ability can be increased by fibre reinforcement

surface treatments could be considered. The protection can decrease the moisture content so that the ohmic resistance of concrete could be increased or oxygen flow could be cut off.

- Prevention of de-icing salt damage, e.g. in road structures.
- To prevent degradation of concrete just above the ground level as a consequence of capillary suction of water and transport of water through the pore system to the ground level where the water evaporates and the salts remain, Fig. 24.

Pressure as a consequence of crystallization from supersaturated solutions and hydration of salts can degrade the concrete surface. This phenomenon, called salt-weathering, is often observed in concrete in arid marine coastal areas, for instance along the Arabian Gulf. A similar damage mechanism was found on the surface of concrete in the splash zone of marine structures.

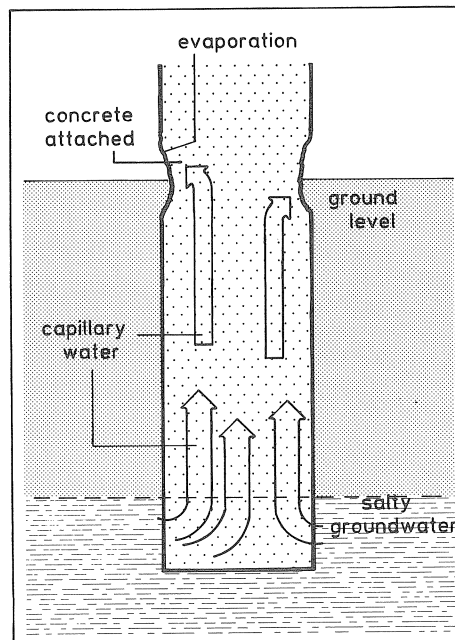


Fig. 24. Suction of groundwater and evaporation at ground level with deposition of salts.

- To decrease (further) sulfate expansion of concrete in contact with ground water (external) but also of concrete with Portland cement that has been steam cured at high temperature (internal) as discussed in Chapter 3.
- To decrease (further) degradation by sulfuric acid in waste water structures (sewer pipes, closed manure silos, etc.).
- Esthetical considerations. These will not be taken into consideration.

8.3 *How to protect?*

Now that we have established why we want to protect, the next question is how we are going to protect. In general two principles can be distinguished. These are:

1. To keep the material dry. Without water no degradation can occur. In practice this means that absorption of water has to be avoided. This principle could be applied to restrict the absorption of chloride containing water in the splash zone of marine structures, to decrease the corrosion propagation of carbonated concrete, to prevent de-icing salt damage, to avoid surface damage due to salt precipitation and to reduce internal sulfate deterioration.
2. To avoid contact between concrete and aggressive agents. This principle could be applied to carbonation, external sulfate attack and sulfuric acid attack.

With respect to the first principle – keeping the concrete dry – all protective possibilities mentioned before could be applied: impregnating, hydrophobing, filling up of pores and the protective layer on the surface.

With respect to the second principle – preventing contact between concrete and aggressive agent – hydrophobing is not the best choice. The other protection methods are more appropriate.

The above only discusses in what way degradation factors could be combatted. Further specifications will be required to make sure that the various protection methods will combat the degradation factors sufficiently and will do so over the design (remaining) service life.

8.4 *Durability of protection*

An important aspect with respect to protective measures is their durability. The durability could be affected by external factors. These factors could cause degradation of the protection agent. They include u.v. light, oxidation, etc. One factor that seems to be of special importance is the interaction with the substrate: the “old” concrete and the “new” repair mortars that have been applied.

When the protective treatment renders the surface very dense, as in the cases of sealings or impermeable coatings, a high moisture content could be built up under the protective layer which could make the concrete vulnerable to frost attack. This appears to occur especially on surfaces with frequent cycling of frost-thaw (36). Another aspect is that, when the surface of the protective agent contains water-soluble constituents, osmotic effects could occur, resulting in blistering. To avoid those problems Kunzel (19–21) has proposed the following limit values:

$$\begin{aligned}W &\leq 0.5 \text{ kg}/(\text{m}^2 \cdot \text{h}^{1/2}) \\S_d &\leq 2 \text{ m} \\S_d \cdot W &\leq 0.1 \text{ kg}/(\text{m} \cdot \text{h}^{1/2})\end{aligned}$$

in which:

W = water absorption coefficient

S_d = water vapour diffusion resistance

To put it in popular terms: The protection must not allow water absorption but must permit water vapour to leave the concrete.

Fig. 25 shows that a large number of protective materials can meet these requirements (19-21).

Obviously when these criteria are considered, hydrophobing is a better protective measure than sealing or a dense coating.

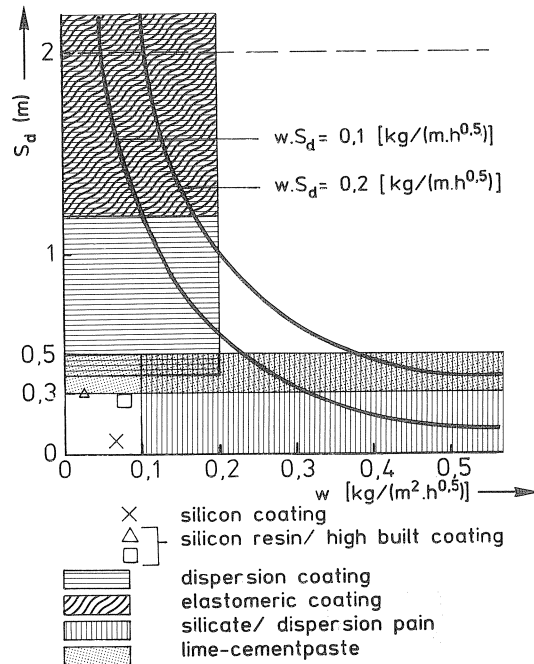


Fig. 25. Kunzel relation between water absorption coefficient (W) and water vapour diffusion resistance (S_d) and positions of various protective agents (19-21).

Problems with sealings or impermeable coatings could be avoided if the concrete is dried before it is protected. However, this is not usually a very practical solution. The danger of frost-thaw damage caused by freezing of condensed water underneath an impermeable layer could be decreased by applying a thick coating or plaster instead of a thin coating. Then the rate of condensation and the probability of freezing will decrease, as Fig. 26 illustrates (22).

Another aspect of durability is the debonding of a surface protection. In general, even when the surface of concrete is well prepared the interface between the surface layer and the concrete will still be most vulnerable. Often when the substrate is not prepared well the concrete itself is the weak link in the system. With respect to the latter the conclusions of a field study in the Netherlands on the performance of repair work are illustrative (3).

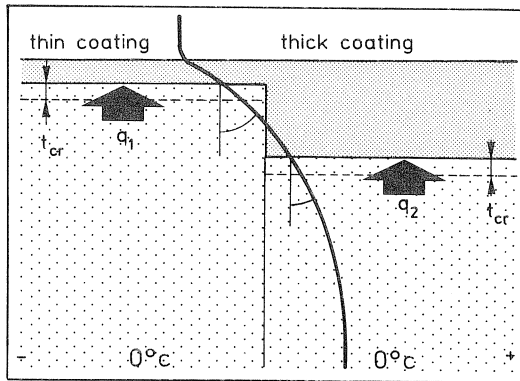


Fig. 26. Temperature gradient and moisture transport for a thin coating and a thick coating (22).

Stresses leading to debonding are often temperature related.

The basic formula with respect to the linear expansion stresses is as follows:

$$\sigma = E \cdot \alpha \cdot \Delta T$$

in which:

σ = stress

E = Young's modulus

α = coefficient of linear thermal expansion

ΔT = average temperature difference between surface layer and substrate

The difference ΔT between the average temperature of the surface protecting layer and the concrete depends on the thickness. When thin coatings are applied ΔT is of the magnitude of some degrees Kelvin. For plasters thicker than 10 mm this can amount to some ten degrees or more. Fig. 27 shows temperature gradients taken from reference 23. However at very thick layers ΔT will decrease again.

For a thin coating the shear stresses at the interface resulting from differences in the expansion coefficient and stiffness are small. However, in general with thin coatings the temperature gradient over the interface will be large. This means that not only shear stresses could occur but also debonding forces normal to the interface.

Often the strength of the substrate is determined by the strength of the system. With a shear strength of a coating on concrete of 4 N/mm² it could be calculated that for a ΔT of 10 degrees Kelvin $E \cdot \alpha > 0,2 \text{ N/mm}^2 \cdot \text{K}$ has to be avoided since it would bring a risk of shear failure (24). This emphasizes the importance of a good preparation of the substrate. Table 10 illustrates how $E \cdot \alpha$ could be influenced for an epoxy coating/mortar (25).

It also appears from Dutch research that the failure of epoxy based repair mortars and protective layers could be due to the fact that epoxies mostly have a glass-rubber transition temperature (T_g) lower than the temperature of the mortars in practice (3).

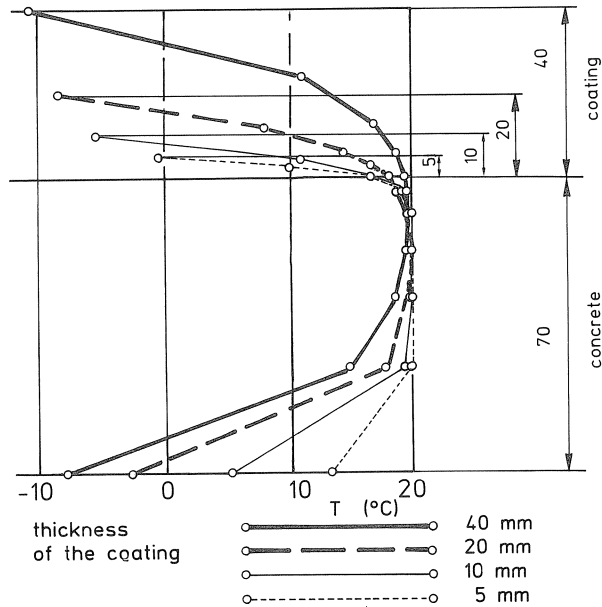


Fig. 27. Temperature gradient over the symmetry axis of a testing sample at various thicknesses of a coating with decrease of the exterior temperature from 20°C to -10°C at the moment when the difference between surface temperature of coating and concrete is at a maximum (23).

Moreover, this T_g appears to depend on the temperature during hardening of the epoxy. When the temperature during application is lower the epoxy does not appear to polymerize fully which results in a low T_g .

The consequence is that at temperatures above T_g the mortars could deform plastically. When they are subsequently cooled down suddenly, for instance by rain, the deformation becomes more or less frozen in. This induces stresses. This phenomenon will be repeated as time passes so that fatigue failure could occur after a certain period. Therefore a protective polymer material in a West European climate must have a T_g of at least 50 degrees Celsius.

Table 10. Influence of filler concentration on temperature expansion of epoxy mortar (25)

| percentage of filler (resin: filler) % m/m resin | pure resin 100 | 1:3 25 | 1:9 10 | 1:15 6.25 | concrete B35 |
|---|----------------------|-----------|-----------|--------------|-----------------|
| modulus of elasticity E (GPa) | 2900 | 9700 | 25000 | 33500 | 35000 |
| coefficient of linear expansion α_T ($10^{-6}/K$) | 69 | 29 | 19 | 15 | 11 |
| $E \cdot \alpha_T$ (MPa/K) | 0.21 | 0.28 | 0.48 | 0.50 | 0.39 |

Problems with surface protecting agents for concrete repair can also occur when cracks in the substrate have to be bridged. When cracks are formed in the substrate most surface layers are not able to bridge those cracks. However, systems do exist which can bridge cracks. They include fiber reinforced coatings, especially flexible polyurethanes. An important condition for every protecting agent that has to be applied on concrete is that it must be resistant to the high alkaline environment of concrete. A well known binder used in the past which was not alkaline resistant was polyvinyl acetate.

The adhesion of most surface layers in concrete is not the result of chemical bonding but of van der Waals' forces and mechanical interlocking via the pores of concrete. In a humid environment such systems will sometimes prefer water at the surface above the protective material. Often the adhesion strength will therefore be lower under humid conditions than when dry.

Sometimes one requirement imposed on protective layers is that the surface layer must be able to "breathe" to prevent the build-up of pressure under the layer due to water or water vapour. When protective layers, coatings etc., are applied on water retaining structures like tunnels, a water pressure could be applied on the coating by hydraulic forces through the pores. At 10 m below the water surface the maximum tensile force on the interface of concrete and surface layer will be about 0.1 N/mm^2 . Water vapour pressure will never be higher than 0.1 N/mm^2 under normal practical conditions. This is the pressure of boiling water.

For an epoxy coating a normal requirement is 1 to 1.5 N/mm^2 adhesion strength. At stresses of 0.1 N/mm^2 most coatings will behave with almost perfect elasticity so that failure due to these pressures is very unlikely.

Of course when coatings are applied which show plastic deformation, such as coatings on basis of bitumen or chlorinated rubber, blistering could occur.

8.5 *Specific requirements*

With respect to carbonation it is recommended to use protective layers with a CO_2 diffusion resistance $S_{d\text{CO}_2}$ of at least 50 m. In a draft German recommendation (35) a resistance of at least 100 m is required. Obviously if this criterion is related to the Kunzel criteria previously discussed, this resistance must preferably not be much larger. Some surface protecting materials are claimed not only to have their own resistance against carbon dioxide but also to decrease carbonation because they increase the moisture content of concrete.

With respect to the protection of concrete against a sulfuric acid environment, e.g. in sewage systems or manure silos, the concrete must be totally protected by impermeable membranes. Thin or thick coating systems have proved in practice not to be reliable although the coatings in themselves mostly have very good resistance to sulfuric acid. Small defects in the coating could introduce blistering. This mechanism is illustrated in Fig. 28.

Systems which can provide durable protection are:

- Polymer mortars which are absolutely water vapour and gas impermeable. The

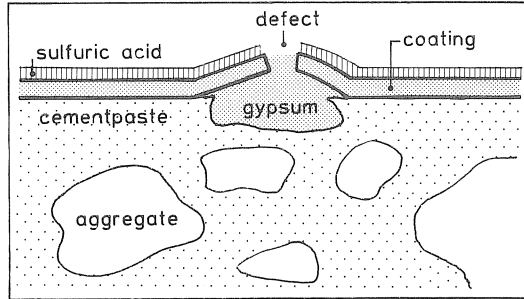


Fig. 28. Blistering of coating on concrete due to attack of sulfuric acid through defects.

mortars must have a thickness of at least some millimeters and must be provided with a very dense top coat. Problems at joints can still occur.

- Rendering of the concrete with sheets or pipes of a durable material such as for instance polyvinylchloride or polypropylene sheets.

In case where not all carbonated or chloride contaminated concrete can be removed in the area of reinforcement it might prove necessary to apply a protection which will diminish corrosion propagation. One of the principles for achieving this is to cut off oxygen ingress. However this must be a very dense layer without defects. Fig. 29 shows that the oxygen diffusion resistance must be in the magnitude of 4.000 m to depress the corrosion rate sufficiently (18). Moreover all exposed concrete must be covered to prevent oxygen ingress. When it is possible to meet this requirement the specific coating will probably not meet the Kunzel criteria. The conclusion is that the application

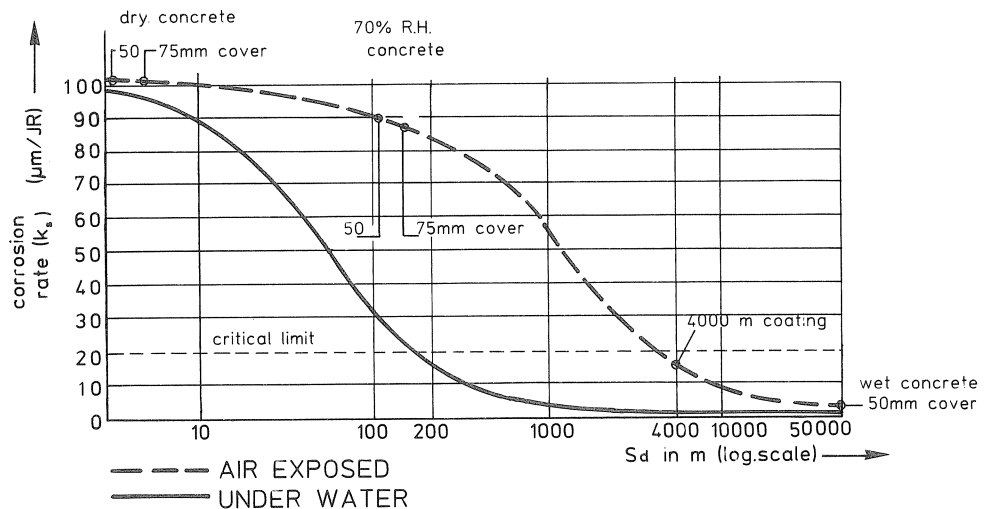


Fig. 29. Corrosion rate k_s ($\mu\text{m}/\text{yr}$) as a function of the oxygen diffusion resistance S_d (m) for concrete under water, air-exposed and with and without coating respectively (18).

of this principle will only make sense in some specific cases. It must be noted that one consequence of applying of a very dense protecting layer, like a coating etc., could be an increase in the moisture content directly under the coating. This may substantially increase the oxygen diffusion resistance of the concrete. Furthermore, moisture fluctuations at the reinforcement will decrease, thus reducing the corrosion ability of the environment.

9 Surface protection: agents

In the previous chapter the questions of why and how to protect as well as the durability aspects were discussed and translated into specific requirements. In this chapter the various agents used for protection of concrete surfaces will be considered.

9.1 Impregnating/hydrophobing

The hydrophobic agents mostly applied are those consisting of organosilicium compounds. The right choice of organosilicium compounds will give concrete very good hydrophobic properties and its water repellence will be retained for about a period of at least 10 years. In general the data available do not cover more than 10 years so that further prediction about the service lifetime of this agent is difficult. The following compounds are distinguished:

- Siliconates with a molecular weight $M = 100-200$;
- Silicon resins, $M > 2000$;
- Alkylalkoxy silanes (silanes), $M = 100-200$;
- Oligomeric alkylalkoxy siloxanes (siloxanes), $M = 400-600$;
- Polymeric alkylalkoxy siloxanes (similar to resins), $M > 1000$.

These agents can form chemical bondings with concrete, as is shown in diagram form in Fig. 30 (19-21). The non-polar groups provide the water-repellent properties. Consequently the contact angle between water and the surface of the concrete will be larger than 90 degrees (Fig. 31). Instead of the original capillary suction a water repellent behaviour will exist.

Hydrophobic impregnation is used not only as an isolated measure but also as part of complete protective systems, for instance, combined with coatings. The advantage of

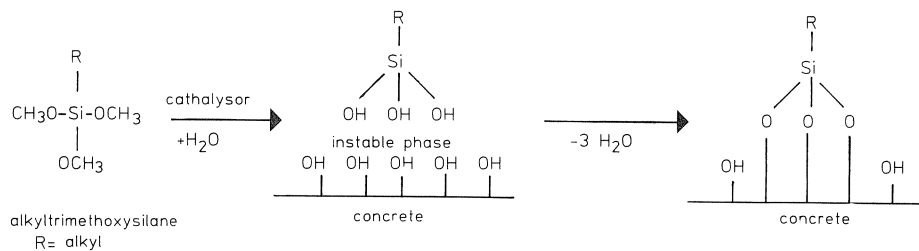


Fig. 30. Bonding of silanes with concrete (19-21).

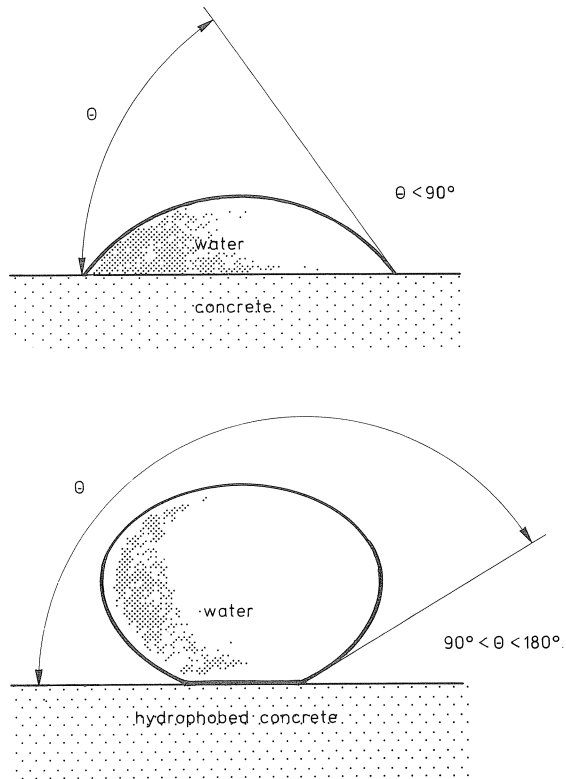


Fig. 31. Increase in contact angle by making concrete water-repellent.

such a system is that when the coating shows defects, water and aggressive agents will not enter the concrete easily through these defects, thus preventing the coating from being attacked from the back.

Siliconates

Siliconates are water soluble or alcohol soluble products (often with about 40% solids). When applied on concrete they react with carbon dioxide according to the reaction given in Fig. 32.

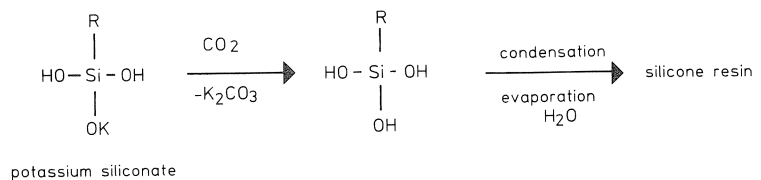


Fig. 32. Reaction of silicate with concrete.

The R-group in the reaction formula is ethyl or propyl. To be effective siliconates need carbon dioxide from the air. The K_2CO_3 released during the reaction with carbon dioxide may blemish the concrete. However, this blemishing will be temporarily, because it will be washed away by rain.

Siliconates are hardly used for concrete surface protection.

Silicon resins

The second generation of water repellent impregnants for concrete or other stone-like building materials are the silicon resins. These resins are dissolved in an aliphatic-soluble agent (typically containing about 5% solids). This agent does not have the disadvantage of K_2CO_3 formation. The resin reacts and is able to bond (cross-link) with the pore walls in places.

A disadvantage is that this resin can only be applied effectively on dry materials with relatively coarse pores. Further it should be noted that these silicon resins could easily lead to sticky surfaces.

They are not very suitable for application on concrete, mainly because the pores in this material are too fine.

Silanes

Alkylalkoxy silanes have been commercially available for about 15 years now. Mostly they are dissolved in aliphatic or aromatic solvents. The silane content is relatively high, e.g. 40%. To enable the reaction with polysiloxanes, moisture and a catalyst are required. Concrete catalyzes the polymerization itself. The reaction mechanism is shown in Fig. 30.

Advantages of silanes in comparison with the previous hydrophobic agents are:

- The better and deeper impregnation, as a consequence of the low-viscosity solvent, when compared with siliconates, and the small molecules when related to silicon resins.
- The high percentage of active material, which is about 40% compared with 5 to 10% for the silicon resins.

A disadvantage of the silanes is that the material itself is volatile and could evaporate together with the solvent, which makes the results of the impregnation very much dependent on the weather.

Oligomeric alkylalkoxy siloxanes

To overcome the problem of evaporation of silanes slightly polymerized silanes have been developed. These are known as oligomeric alkylalkoxy siloxanes, or siloxanes for short. The advantages of the silanes are maintained while the agents are less volatile. Siloxanes are available as solutions in aliphatic agents or in alcohols. Their active material content ranges between 5 and 10%. The reaction is given in Fig. 33.

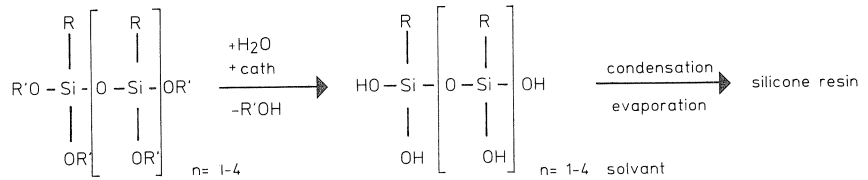


Fig. 33. Reaction of siloxane with concrete.

Polymeric alkylalkoxy siloxanes

When silanes or siloxanes are polymerized further, long chain molecules are developed. These polymer chains look very much like the silicon resins, but are very sticky if no catalyst is applied.

These types are hardly used for concrete.

9.2 Impregnation/filling up pores

There are various impregnating agents available to fill up pores. Because the degradation of concrete often happens through the pores, this filling-up could make the concrete less vulnerable.

Reaction with concrete constituents

Some agents are used not only for filling-up pores but also to react with the constituents of concrete, mostly lime. Well known in this context are the fluates which react with lime, as are shown in the reaction mechanisms of Fig. 34. Another type in this class is waterglass (potassium or sodium silicate solution in water) for which the reaction mechanism is shown in Fig. 35. Because of the relatively high viscosity of water and the fact that concrete usually contains water, impregnation with waterglass could be rather difficult. Moreover, after the reaction a substantial quantity of alkali carbonate remains which is rather more soluble. For instance 1 kg of pure potassium silicate can yield 0.8 kg of potassium carbonate.

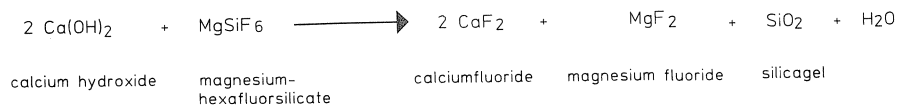


Fig. 34. Reaction of fluate in concrete.

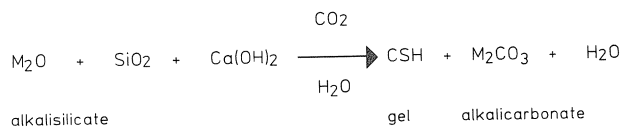


Fig. 35. Reaction of waterglass in concrete.

Many combinations of waterglass and polymers have been put on the market, specifically waterglass with polymer dispersions (silicate/dispersion).

The polymer content is in the range of a few percentage points. Sometimes water repellent agents are also added, for instance silanes.

These combinations are recommended by some suppliers for preventing carbonation. However, no definite conclusions about the effectiveness of compounds of this kind can be drawn from the available literature.

Other agents which might be considered to react with the constituents of concrete are the siliciumester compounds. They react with free water.

The reaction mechanism is shown in Fig. 36. Mostly ethyl silicium esters are used. These react with water to form silica gel and alcohol. In general the reaction is slow. Per kg of silicium ester (70%) solids, about 0.3 kg of silicate is formed. The silicium ester is diluted with alcohol or ketones. The diluting agents evaporate. To fill up the pores effectively the treatment has to be repeated at least 4 times. Advantages in comparison with other impregnating agents are that the agent is able to react with the moisture in the concrete. It is also able to penetrate the concrete easily because of its low viscosity. Experience with application of this agent on concrete is limited.

None of these agents will fill up the pores fully.

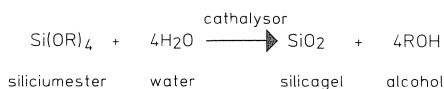


Fig. 36. Reaction of silicium esters in concrete.

Impregnating with polymers and prepolymers

The monomer methacrylic-acid-methyl ester easily penetrates dry concrete. Once it has penetrated, it could be polymerized to form polymethylmethacrylate (PMMA). In Germany this method is used to restore/preserve statues. The procedure for this preservation is as follows:

- drying;
- evacuating;
- impregnating under pressure;
- heating up for hardening.

This method might show good results, but is restricted in its application because the size of the objects is governed by maximum limits. For concrete structures which cannot be evacuated and impregnated under pressure results are in general rather poor. The reasons are that the impregnation does not fully fill up the pores and that the required drying can cause micro-cracks in the concrete.

Another organic compound which could be applied for impregnation is a one-component polyurethane. This involves a prepolymer which polymerizes further by reacting with the moisture from the air or from the concrete. The concrete must be relatively dry during application to prevent excessive foaming.

9.3 Protective surface layers

Coatings

Coatings in general comprise the following constituents:

- the binder;
- fillers (sometimes);
- pigments;
- additives;
- dispersing agent;
- solvents/dilutants.

Binding is achieved through polyaddition or polymerization reactions between the binding components (resins) or by drying as a result of evaporation of the solvents and dispersing agents.

The most important resins are:

- *Epoxy resins* (EP): Mostly, epoxy resins provide good adhesion to concrete. Epoxy resins show minor polymerization shrinkage, are resistant to light chemical attack and can be formulated in such a way that they hardly show discoloration (yellowing).
- *Two component polyurethanes* (PUR): These adhere well to dry concrete surfaces, are almost shrinkage-free and are resistant to light chemical attack. However, they are not very resistant in high alkaline environments and must therefore not be applied to surfaces which will be wet continuously unless an alkaline resistant primer is used. PUR resins sometimes show discoloration (yellowing).
- *Tar epoxy and tar PUR resins*: These have some advantages such as higher flexibility in comparison with EP and better alkaline resistance compared with PUR. A disadvantage is that they do not have such a good resistance to u.v. light, oxidation and temperature.
- *Polymethylmethacrylate* (PMMA): PMMA resins show very good adherence to concrete substrates. However, they shrink quite a lot during polymerization of the polymer. Other features are their high mechanical strength and a good resistance to light chemical attack.

Drying types of bonding agents are:

- *Acrylics*: in solution as well as in dispersion. Acrylics have generally a good adherence to concrete and good resistance to alkalis, oxidation and weathering.

Further drying type agents are:

Chlorinated rubber, cyclo rubber, vinylchloride copolymers, vinylfluoride copolymers, silicon resins and polymeric alkylalkoxy siloxanes.

The latter are applied not only for coatings but also for impregnation, as discussed previously.

Combinations of drying binders are also on the market, such as acrylics combined with polyvinyl(tetra)fluoride.

In the previous chapter specific requirements for coatings are given. Though a number of coating systems will indeed meet these requirements, many of the binders mentioned above do not meet the Kunzel requirements. However, they could be

adjusted through the addition of fillers, pigments etc. When the so-called critical filler or pigment volume concentration is exceeded the permeability of coatings strongly increases (see Fig. 37).

Further it must be emphasized that the generic names of binders such as acrylics, etc. are not a sufficient basis for deciding on whether or not a coating is appropriate for a certain application. An acrylic in solution is something different than in dispersion and is also different from an acrylic polymerized in situ. The generic name does not convey very much about whether or not the binder is a copolymer, a homopolymer, not does it say anything about the molecular weight, etc.

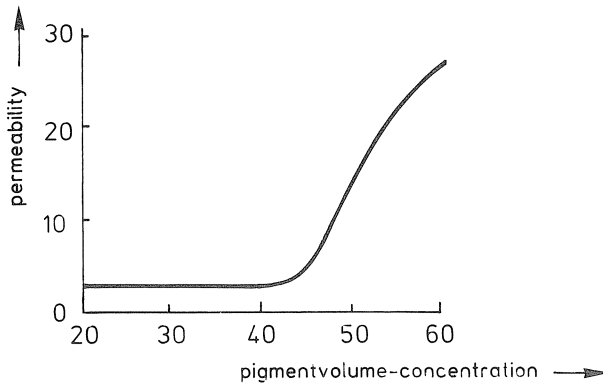


Fig. 37. Influence of pigment volume concentration on permeability.

Mortars

Plaster mortars could be applied as a protection for concrete. Mortars have already been discussed in Chapter 7 and will not be considered further here.

Some special types of mortars will be discussed briefly. One such type of mortar is for instance a polymer modified alumina cement mortar. Alumina cement was used for a long time for construction work, although it was later abandoned after problems relating to the conversion of the alumina cement hydrates, which makes the material more porous and less strong. However when applied with a very low water/cement ratio it could be safely used if the conversion is taken into account. When modified with polymers the material appears to have a rather good chemical resistance to light chemical attack and could serve as an alternative for some other protection systems. (Light) chemical resistant and acid resistant cementitious mortars based on additions of silica fume and additives have been on the market for a few years now. Sometimes modified by polymers. Tradenames are for instance Corrocem® and Densit®.

A special type of binder developed in the Netherlands is a material called Polysil®. It consists of powdercoal fly-ash and a special waterglass and may also contain silica fume. It has good resistance to acids, as shown in Fig. 38.

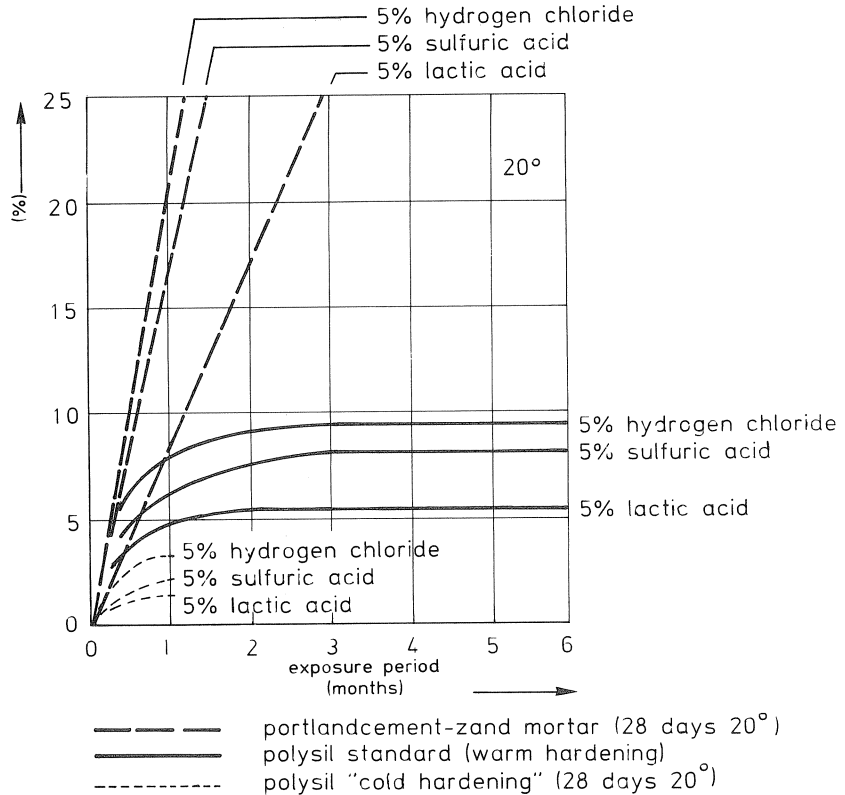


Fig. 38. Weight loss of portland cement and Polysil® mortars submerged in various acids.

9.4 The choice

The kind of concrete protection that is chosen will depend on the degradation mechanism, the quality of the concrete to be protected and the specific environment. In addition, not only the macro-environment but also the micro-environment of the material itself has to be considered. The choice could be based on experience with the system over a long period. However for many materials this feed-back does not exist because the history is only very short. In that case an understanding of the specific degradation mechanism and of the way the protective material will react are of major importance. Another factor which will influence the choice of a protective agent is its toxicity. Many impregnants and coating systems could be toxic to man when inhaled, which means that safety precautions have to be observed when they are applied in restricted areas. Research into human and environment friendly agents is one of the main fields of development in the coating industry. The results will change the future market substantially.

In Tables 11 to 13 qualitative judgements of some protection systems are given. These relate to systems aimed at preventing carbonation or chloride penetration respectively.

Table 11. Carbonatation-preventing surface protections methods meeting so-called Kunzel criteria.

| system | application | | | durability | | |
|------------------------------|----------------|---------------------|--------|------------|--------------------|-------------------------------------|
| | humid concrete | ease of application | health | u.v. | mechanical loading | |
| surface layer | | | | | | |
| <i>coating (dispersion)</i> | | | | | | |
| acrylate | + | + | + | + | + | |
| styrene acrylate | + | + | + | +/o | o | |
| versatate | + | + | + | o | o | |
| propionate | + | + | + | o | o | |
| acrylate + teflon | + | + | + | + | o | |
| <i>plaster</i> | | | | | | |
| shotcrete | + | o | + | + | + | |
| impregnate/filling up | | | | | | |
| waterglass + dispersion | o | + | + | + | o | + = good o = moderate - = bad |

Table 12. Water-containing chloride absorption preventing protection methods, meeting so-called Kunzel criteria.

| system | application | | | durability | | |
|--------------------------------|----------------|---------------------|--------|------------|--------------------|-------------------------------------|
| | humid concrete | ease of application | health | u.v. | mechanical loading | |
| surface layer | | | | | | |
| <i>dispersions</i> | | | | | | |
| acrylate + teflon | + | + | + | + | o | |
| <i>plaster</i> | | | | | | |
| shotcrete | + | o | + | + | + | |
| impregnate/hydrophobing | | | | | | |
| silane | + | + | - | o | + | + = good o = moderate - = bad |
| siloxane | o | + | o | o | + | |

Table 13. Protection methods which reduce absorption of water containing chloride, but do not meet the Kunzel criteria (list not complete)

| system | application | | | durability | | |
|----------------------|----------------|---------------------|--------|------------|--------------------|--------------|
| | humid concrete | ease of application | health | u.v. | mechanical loading | |
| surface layer | | | | | | |
| epoxy resin | o/- | o | o | o | o/+ | |
| coal tar-epoxy | o/- | o | o | - | o | + = good |
| chlorinated rubber | o | + | o | - | o | o = moderate |
| polyurethane | - | o | o | o | o/+ | - = bad |

10 Repair of degradation caused by chloride initiated corrosion

Corrosion of steel reinforcement initiated by chloride ions is a main causative factor of degradation in concrete structures throughout the world, notably in marine environments and in structures exposed to de-icing salts such as bridges, parking garages, etc. Chloride damage may also be caused by chloride being used as an accelerator for concrete hardening or it may be due to the use of salt contaminated aggregates. The latter frequently happened in the past in arid coastal areas.

The degradation factors and mechanisms of this chloride initiated corrosion are discussed in Chapter 6. The present chapter contains a discussion of methods used to repair concrete structures damaged by chloride initiated corrosion.

The repair method is understood to include the total package of corrective measures taken to reinstate the concrete structure in such a way that it will meet the specified requirements for its remaining service life.

Structures affected by chlorides are increasingly repaired by applying cathodic protection. Cathodic protection will be discussed in the next chapter. The present chapter will be restricted to methods in which corrosion is stopped by removing its cause – chloride – or by reducing the corrosion propagation rate.

Before discussing the repair methods we will briefly consider the various circumstances which could exist for chloride contaminated concrete and the consequences that these circumstances have for the repair method to be chosen.

10.1 *Types of chloride contamination*

Corrosion damage could be caused by mixing concrete with chlorides (primary) or by penetration of chlorides from the exterior (secondary). When chloride is mixed with the concrete the structure will as a rule be totally contaminated. In such cases removal of old concrete is often impossible because of structural considerations or is not feasible economically in comparison with replacement. Moreover concrete with mixed-in chlorides is mostly characterized by strong inhomogeneity. Adjacent to areas with strong contamination there could be locations which are hardly affected at all. Due to this phenomenon large cathode/anode surface ratios could exist, resulting in corrosion pits with strong current densities.

When chlorides penetrate from the exterior we often find a concentration gradient as shown in Fig. 39. In those locations where chloride loading of a structure is highest we usually find the most severe corrosion.

An exception is concrete under water which, as discussed in Chapter 6, does not corrode significantly because of a lack of oxygen.

Examples of structures with chloride penetrating from the exterior are the splash-zone in marine structures and under viaducts.

Another aspect relating to the repair of chloride damage is the quality of the concrete and concrete cover above the reinforcement. The chloride concentration causing corrosion damage could be substantially larger for a good quality of concrete cover than for a

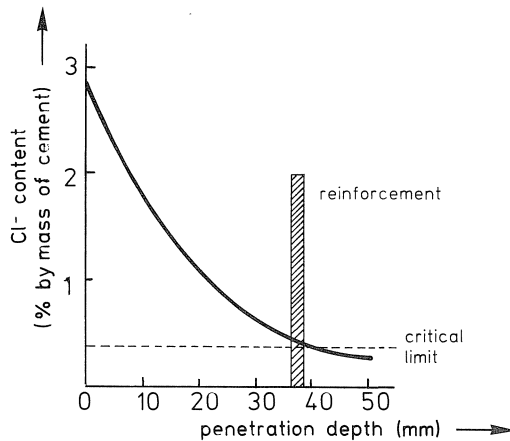


Fig. 39. Chloride concentration profile.

low quality concrete and low cover. In the Federal Republic of Germany preliminary regulations on the repair of concrete mention limiting values for the chloride concentrations. For a good quality concrete a limiting value is stated of 0.6 to 0.8% m/m by mass of cement. Where the concrete cover is of low quality, this is 0.3 to 0.4%. This means that repair specifications should not state that all concrete with chloride concentrations higher than 0.3 to 0.4% by mass of cement must be removed, except where the quality of the concrete is low. Obviously the critical corrosion concentration is exceeded when pit corrosion is present. This phenomenon could be taken as a yardstick in cases of doubt.

The discussion of the critical corrosion concentration of chloride ions is not new. In the sixties in the Netherlands, for instance concentrations of 0.9% m/m of chloride on mass of cement with a good quality of concrete were regarded as acceptable when the chlorides were added dissolved in the mixing water. The above is not a plea in favour of increasing the present critical corrosion chloride concentrations which are mostly in the range of 0.2 to 0.4% m/m. However, in the case of repairs it makes sense to distinguish between limiting values which depend on the quality of the concrete of the structure.

10.2 Removal of chloride

One of the first measures that comes in mind in the case of chloride contaminated concrete is to remove the chloride. Although various methods are claimed to be effective, such as chloride extraction by electrophoresis, the only proven method is to remove the contaminated concrete. This is mostly only a realistic option when chloride is present locally such as in the case of gradients due to penetration from outside. When contaminated concrete is removed the structural safety of the structure during

and after repair has to be safeguarded. If mechanical loads in the repair area are not released, the total load that could be borne by the structure will decrease.

After removal of the concrete the reinforcement has to be cleaned to remove corrosion products and chlorides from the steel reinforcement. A brightness grade Sa of $2\frac{1}{2}$ (Swedish brightness grades) is required. However in practice it is difficult to remove all corrosion pits. If the steel is grit blasted or wire brushed the core of the pits will not always be removed.

If the cleaned reinforcement is then covered with a repair mortar the possibility exists that the reinforcement will continue to corrode (26). Cleaning by high pressure water jetting appears to give better results. Nevertheless it is probably illusory to expect this to achieve pit removal over the whole structure.

Another requirement could be that the repair mortar must fully envelop the reinforcement. In general this is difficult to realize.

A further problem is that in areas where the structure is not repaired, the possibility of chloride pits being present or developing in future cannot always be totally excluded. Then the repair areas could start to act as cathodes which could cause a high current density at the pits in the non-repaired areas, see Fig. 40. The latter, of course, occurs only when there is electrolytic conductance and sufficient oxygen supply. The presence of oxygen at the reinforcement in the repaired area is mostly caused both by the mortar and by cracks, especially along the interface of repair mortar and substrate.

10.3 *Insulation of steel reinforcement*

One method used to “extinguish” chloride pits is to treat the cleaned steel surface with a solution containing an inhibitor (an anodic inhibitor). To ensure efficient penetration

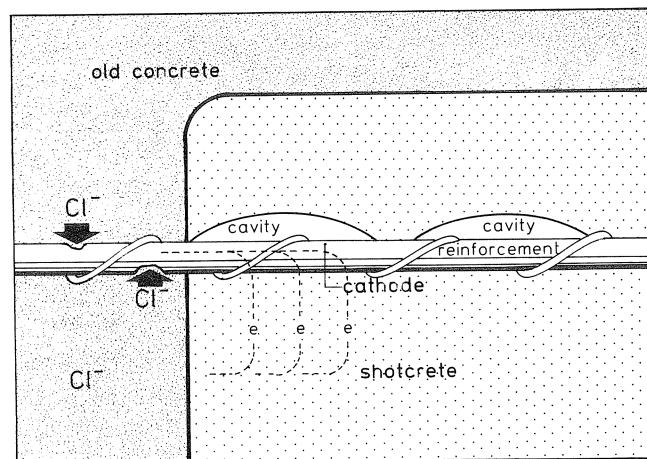


Fig. 40. Macrocell formation due to introduction of (re)passivated area in further chloride-contaminated concrete.

of the inhibiting solution the pits should be dried. This means that the steel has to be dried before being treated with the inhibiting solution. This can be done for instance with a flame beam. However, high temperatures could damage the adjacent concrete. This aspect is under investigation at the moment by CUR in the Netherlands. In principle treating the cleaned reinforcement with a mixture of an anodic and a cathodic inhibitor can prevent both the cathodic behaviour of steel as well as the anodic. However, the effectiveness of this method has not been confirmed so far. Another method of treating the steel reinforcement is to insulate it electrically. In the event of corrosion a closed electrical circuit is necessary. The current must be transferred by the electrolytic solution in the pores of concrete, as shown in Fig. 41. Once the cleaned reinforcement has been coated, any active pits which have not been cleaned up could be electrolytically insulated.

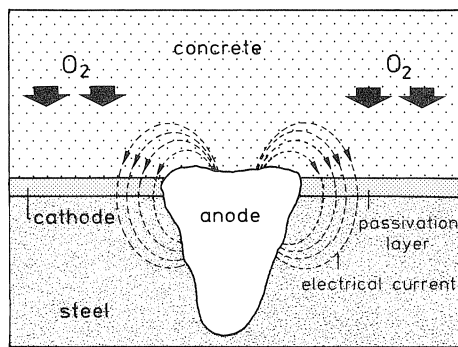


Fig. 41. Current in the area of a chloride pit.

This also prevents a possible cathodic behaviour of the reinforcement in repaired areas. A further advantage of a coating on the reinforcement is that any chlorides remaining in the old concrete adjacent to or underneath repaired areas will cause no renewed damage to the reinforcement if chloride concentrations still present in the substrate diffuse into the clean repair mortar.

The products most used at the moment are solvent-free or solvent-poor epoxy coatings. These have to be applied in several layers to minimize the risk of defects as far as possible. The top layer could be sprinkled with dried fine aggregates such as sand in order to improve the adhesion between coating and repair mortar. Fig. 42 shows a photograph of the coating operation of steel reinforcement during the repair of the Al Shindagha Tunnel in Dubai. Other coatings that can be applied are:

- Epoxy resins with zinc extender.

The zinc has to protect the steel cathodically also in areas adjacent to areas where the coating had been applied. With respect to the adhesion of this coating on steel and concrete there are still some unanswered questions, while the long term effect has not effectively been established.



Fig. 42. Photograph of the coating operation of steel reinforcement during the repair of the Al-Shindagah Tunnel in Dubai.

- Polymer modified cement coatings or polymer cement concrete coatings.
The advantage of these types of coatings are that they provide an alkaline environment at the reinforcement. The performance of this kind of protection was proved during the construction of the Saudia Arabian Bahrain Causeway (now called the King-Fahd Causeway) in which the reinforcement bars protruding from the precast bridge deck were protected and showed no signs of corrosion after one year above the water of the Arabian Gulf. Concrete poured later on between the precast bridge deck segments did show good adhesion to these coatings.

Although the target is to apply coatings of this kind to the reinforcement as perfectly as possible, it is illusory to think that this kind of coating can be optimally applied during repair work. The circumstances during repair work are rather difficult.

However, despite its imperfections such coating will have a positive effect with respect to corrosion of reinforcement initiated by chloride ions.

10.4 *Concrete as insulator*

Another method sometimes advocated for stopping corrosion is to insulate the reinforcement electrically by drying the concrete. Dry concrete is a good electrical insulator. If there is no water in the pores the electrical circuit will be cut off.

That is the reason why concrete does not corrode indoors, although after some time it

could be carbonated beyond the reinforcement. The question is how to realize such dry concrete. When coating systems are applied to the surface, water will be kept out but water already present in concrete will be prevented from leaving it. Therefore, if the concrete is wet it needs to be dried before applying such a coating. Moreover, unless the concrete is completely blocked off from the air, there will be an “equilibrium” moisture content. If the concrete is contaminated with chloride this moisture content will be higher than without chloride because of the hygroscopic character of chloride salts. This moisture content might be high enough to enable the corrosion process to continue.

Complete drying of chloride contaminated concrete and keeping it dry is therefore a difficult task.

A measure more easy to carry out in practice is to insulate the repair area electrically from the substrate concrete by applying an insulating adhesive at the interfaces. This measure is in line with the direct insulation of the reinforcement as discussed above. When cement based mortars are applied, this can be done for instance by using an epoxy primer, which could be sanded to improve adhesion, or by using a water compatible epoxy in which the mortar could be applied “wet in wet”. For polymer based repair mortars a primer consisting of the neat binder is generally applied. Polymer mortars and, to a lesser extent, polymer modified cement mortars have a high electrical resistance themselves. With respect to the effectiveness of this electrical insulation of repaired areas, no experimental results are available as far as is known.

10.5 *Cutting off oxygen flux*

Where it is not possible to remove all chloride contaminated areas, attempts can be made to cut off the oxygen flux (oxygen diffusion polarization).

For instance by applying a coating to the surface. In Chapter 8 it was shown that the oxygen diffusion resistance of coated concrete must be in the magnitude of some thousand meters to provide sufficient protection. The concrete surface in contact with air must be covered fully. In general this will be difficult to realize. A positive effect of such a coating will be that it will reduce the water moisture movements in concrete around the reinforcement, which will decrease corrosiveness. If an oxygen impermeable coating is chosen for a specific repair project it must be the last step in a repair process. It must be taken into account that generally this kind of coating would not meet the “Kunzel” criteria discussed in Chapter 8.

10.6 *Repair methods*

For repair structures suffering from chloride initiated steel-reinforcement corrosion there are many repair options. The choice of a specific package of remedial measures will depend on many factors. However, in general, the procedure will be as shown in Fig. 43. Note: this procedure is not applicable to repairs made using cathodic protection.

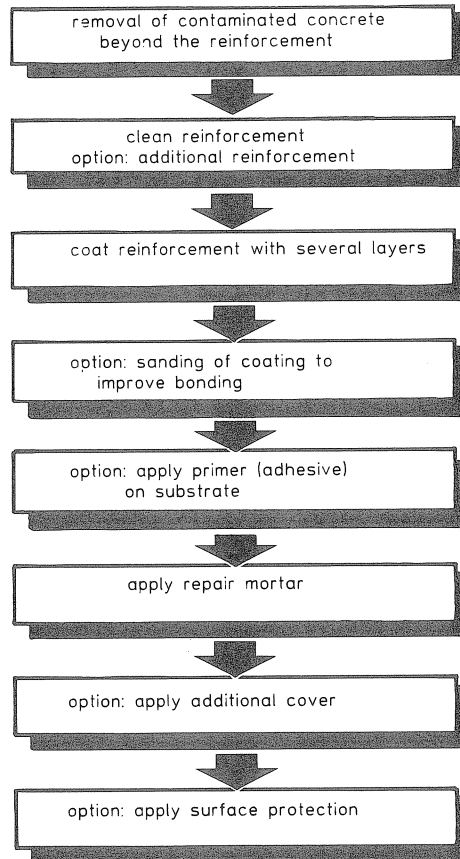


Fig. 43. Flow sheet showing “traditional” repair procedure for chloride initiated corrosion.

The first step in the repair process will be to remove chloride contaminated concrete to at least 10 mm behind the reinforcement and 20 mm adjacent to the reinforcement; see Fig. 44. For large diameter rebars the 10 mm must be increased to 15 or 20 mm. It must be noted that sometimes repair work starts with the filling up of cracks by injection or in some other way. This subject is not within the scope of this chapter and will not be considered. However, injection repair of cracks caused by corrosion of reinforcement makes no sense as a single remedial action!

The concrete must be removed in such a way that adjacent to the corroded areas at least 100 mm of non corroding reinforcement is revealed. The reinforcement will be cleaned by grit blasting, etc. to a brightness grade $Sa\ 2\frac{1}{2}$. New or additional reinforcement is applied when required for structural reasons.

This reinforcement must overlap the existing reinforcement or, if possible, must be welded to it.

The reinforcement is dried and subsequently coated or treated in another way.

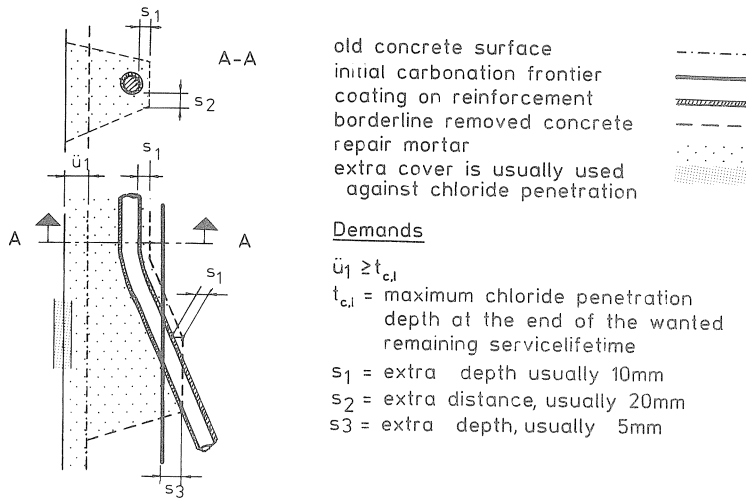


Fig. 44. Corrective measures (repair) for chloride contaminated reinforced concrete where chlorides can penetrate over the whole surface.

Coatings have to be applied in at least two layers. The last one must be sanded to provide enough adhesion for the repair mortar.

Not only the reinforcement must be cleaned but also the substrate. Mostly this is done in one single operation.

Before applying the repair mortar a primer is often applied to improve the adhesion of repair mortars to the substrate or to insulate the mortar electrically. Subsequently the repair mortar (cement based, polymer-modified cement based, or polymer based) is applied. For details about repair mortars see Chapter 7.

When the damage involves only local chloride contamination and there are no reasons to expect further chloride to penetrate from the exterior the repair could be regarded as complete. However, if new chloride can penetrate the concrete after the repair a chloride resisting surface protection must be applied. The reader is referred to Chapters 8 and 9.

It is impossible to rule out the risks of areas with “corrosive” chloride concentrations being left over after the repair, this might be a reason to decide to provide an additional concrete cover layer. The advantage of an extra cover is that it not only protects concrete against further penetration from the exterior but also provides capacity for levelling out the existing chloride concentration corroding gradient as discussed in Chapter 7. This extra cover could be finished off with a chloride repelling surface treatment. Fig. 44 shows this situation. The figure is taken from reference 35 but with the addition of a protective coating on the reinforcement.

For structures where chloride contaminated concrete could not be removed in more than incidental locations, one possibility might be to cut off the oxygen flux by applying an oxygen impermeable coating.

11 Cathodic protection of steel in concrete

Cathodic protection (CP) is a well established anti corrosion method for protecting steel exposed to aggressive liquids (e.g. seawater) and soils. In the last decade cathodic protection of steel-reinforced concrete structures has also become popular. As shown in the previous chapter damage cases due to steel reinforcement corrosion initiated by chlorides are rather difficult to repair by “traditional” methods. Sometimes it is impossible to exclude further corrosion of some parts of the structure, e.g. when complete removal of contaminated concrete is not possible for structural reasons. Moreover cleaning of all corrosion pits is difficult to achieve.

Cathodic protection seems to provide a more reliable way to stop the corrosion process. In the United States the Federal Highway Administration (FHWA) has come to the conclusion: “The only rehabilitation technique that has proven to stop corrosion in salt contaminated bridge-decks regardless of the chloride content of concrete is cathodic protection” (27).

In the Netherlands a project is being performed under the responsibility of the Centre for Civil Engineering Research, Codes and Specifications, CUR, and executed by INTRON, institute for material and environmental research. The finance is provided by a number of major repair companies and the Ministry of Economic affairs. The principles of the research project are described in reference 29.

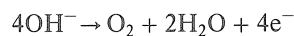
11.1 Principles of cathodic protection

The principle of cathodic protection is that the potential of the steel reinforcement is artificially decreased. This diminishes the current density and consequently the corrosion rate of the anodic reaction.

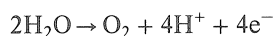
When the potential is decreased from the mixed-potential (corrosion potential) to the free potential of iron (E_{Fe}^0) there will be no net conversion of iron in ferro-ions any more; see Fig. 15. The corrosion process is brought to standstill. The steel is cathodically protected. In practice a low corrosion rate of the steel can be tolerated so that complete cathodic protection is not required. Adequate protection could be achieved at a slightly less negative potential than E_{Fe}^0 .

An anode system is fixed on the surface of the concrete and the steel is artificially made into a cathode by means of current from a DC source. The current flows through the concrete from the anode to the cathode. The most important electrochemical reactions occurring are given in Fig. 45. At the anode the following reactions will occur:

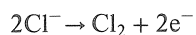
In an alkaline environment



In a neutral environment



If chloride is present the following reaction could also occur:



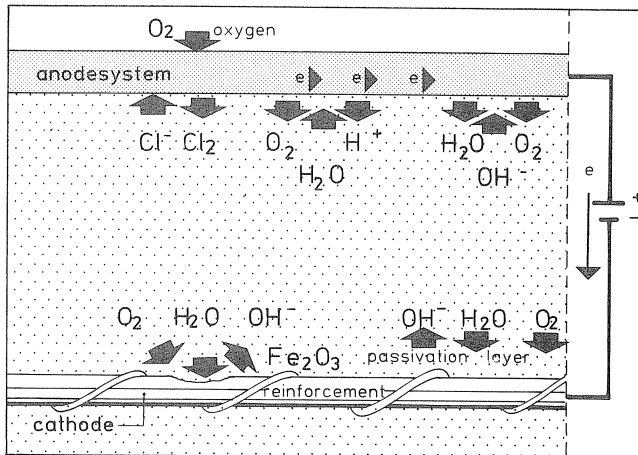


Fig. 45. Electrochemical reactions in reinforced concrete with CP systems.

Negative ions like OH^- and Cl^- will migrate to the anode system, while the positive ions (Na^+ , K^+ , Ca^{2+}) will move in the opposite direction. This means that in the case of chloride contamination of concrete the chloride concentration at the steel-reinforcement will decrease and, as chloride is removed from the steel-reinforcement, the alkalinity will increase.

11.2 Protection criteria

Various cathodic protection criteria for steel-reinforced concrete are advocated. The following criteria are known:

1. Potential or current density related to the commencement of the cathodic Tafel plot in the E-log i curve (Tafel plot is an expression used in the corrosion technology for the linear part of the E-log i curve).
2. Potential -850 mV with respect to the reference electrode Cu/CuSO₄ (copper/copper sulfate electrode = CSE). This potential must be adjusted to allow for the ohmic voltage drop over the concrete cover. The latter can be measured by using what is named the instant off potential. This is the potential measured directly after switching off the cathodic current density, thus eliminating the ohmic voltage contribution.
3. Potentials -770 mV relative to CSE (instant-off).
4. 100 mV depolarization after 4 hours. The change in potential at the steel electrolyte interface in the period after switching off the cathodic protection (instant off potential) until 4 hours depolarization must be a minimum of 100 mV. This is the criterion stipulated by NACE (National Association of Corrosion Engineers) (28).
5. Potential shift of 300 mV of cathodic protection in comparison with the initial or steady potential, again adjusted to allow for the ohmic potential contribution.

None of the above criteria have been generally accepted.

A frequently used criterion is the draft recommendation of NACE, which prescribes 100 mV depolarization after 4 hours. Sometimes, however, the steel is adequately protected but needs more than 4 hours time for depolarization to meet the 100 mV criterion.

Overprotection must be avoided. Not because of the higher costs due to high currents which are mostly smaller than a 100 W per thousand m² of concrete surface, but because it results in high current densities, with consequent danger for the durability of the system.

11.3 *Components*

Cathodic protection systems with impressed potential comprise the following components:

- a DC source;
- an anode system;
- a conductive electrolyte: concrete. The moisture content has a dominant influence on conductivity;
- a cathodic system: the steel reinforcement, which must be an electrical continuity;
- electrical connecting cables which must be mechanically and chemically durable;
- control and monitoring devices (reference electrode, data compilers, control units, etc.).

11.4 *Anodes*

The anodic system serves to supply the protecting current homogeneously. It has to meet the following requirements:

- it must be able to resist mechanical, physical and chemical influences of the environment;
- the lifetime must be longer than that of the covering layer, with a minimum of at least 20 years;
- the anode surface must be large enough to ensure that the current density is sufficiently low to prevent failure of the system because of degradation of the anode or its interface layer in the surrounding concrete;
- it must be economically feasible.

Anode systems which can be distinguished are:

- conductive overlay: a layer acting as anode covering the entire concrete surface.
- distributed anodes: discrete anodes are spread evenly over the concrete surface. Only a part of the concrete surface is covered with active anode material.
- sacrificial metal layer. A covering metal layer acting as a sacrificial anode.

Some of the available systems will be discussed below.

Conductive overlays

An anode which covers the entire surface of the concrete. It mostly consists of a com-

combination of primary and secondary anodes. The primary anode consists of an inert metal. The secondary anode is an overlay consisting of a mortar, asphalt, or paint which is made conductive by adding carbon particles.

Examples of systems of this type are:

1. Silicon iron anodes in combination with an overlay of conductive asphalt. This is the oldest system or cathodic protection of concrete. The asphalt is made conductive by applying coke-breeze as a filler. The primary anodes are discs of $\varnothing 300$ mm, thickness 10 mm or squares of 150×230 mm², on which conductive asphaltic overlay is applied as a secondary anode. The system is shown in Fig. 46 (30). In use on bridge decks in the United States, since 1973, the system can only be applied on top of horizontal surfaces.
2. Platinized wires. Other variants of the covering anode are the use of platinized niobium copper wires applied as primary anodes and laid on the concrete surface. Perpendicular to these wires, carbon fibers are applied as secondary anodes. The mesh of anode wires and fibres is covered with a conductive asphalt or conductive cement mortar. The application is restricted to horizontal surfaces.

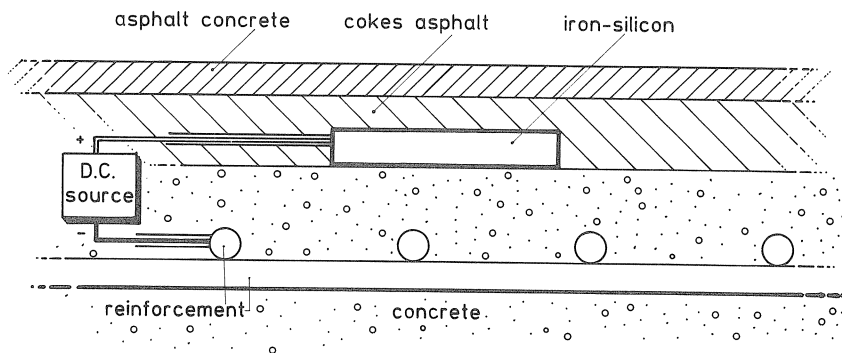


Fig. 46. Cathodic protection of bridge deck. The iron silicon anodes have been embedded in a layer of conductive coke breeze asphalt (30).

3. Conducting paint systems. Platinized wires are used as primary anodes on the concrete surface. They are fixed to the surface and protected by pieces of glass fiber-mats over which a conductive paint is applied as a secondary anode as shown in Fig. 47. The paint is a dense coating made conductive by using graphite as a filler. For esthetic reasons the black paint is often covered with a paint in the desired colour. This type of anode is appropriate for both ceilings and vertical and horizontal surfaces, but not for surfaces which are exposed to wear and tear. The durability of this paint system is estimated to be 5 to 10 years. After that period the concrete must be cleaned and coated with a new paint system. Experiences with these paint systems as described by Schell and Manning (31) are not favourable. After the first winter two out of three paint systems investigated by these authors failed. Ad-

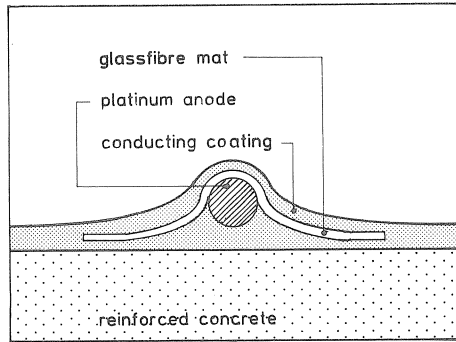


Fig. 47. Principle of covering anode system with conductive paint.

vantages of the paint systems are the relative ease of application, the ease of repair of possible defects, and the favourable ratio of anode to concrete surface (1 to 1). Because of the latter factor the acid deterioration of the concrete below the paint (see paragraph 11.5) will proceed relatively slowly due to the low current density at the anode. However, a minor degradation at the interface can severely damage the effectiveness of the system.

In addition a combination of a dense paint system with a water rich concrete layer underneath it will be sensitive to de-icing salt. General requirements as discussed in Chapter 8 are also applicable here.

Distributed anodes

There are a number of systems available:

1. Slotted anode system. In this system (Fig. 48) platinized niobium copper wires are

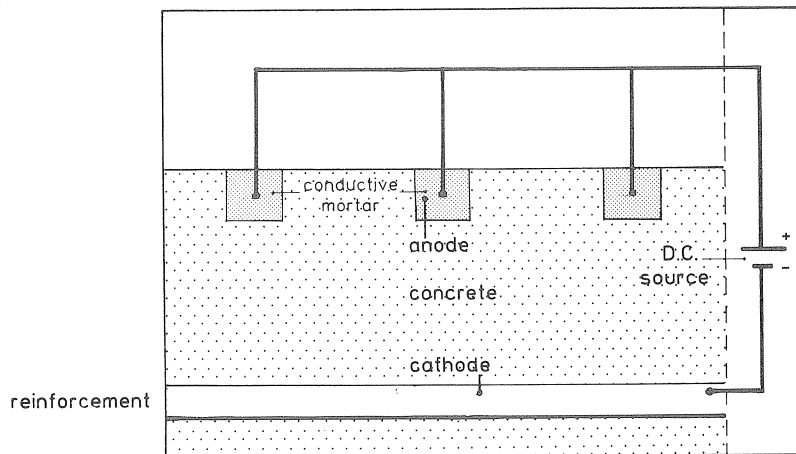


Fig. 48. Slot system with local anodes embedded in conductive filling mortar.

used as primary anodes. These are embedded in slots which are cut into the concrete and subsequently filled up with a conductive mortar. Graphite filled cement mortars were originally used but later on graphite filled polymer mortars for filling up these slots have also been used. No overlay is applied.

2. Carbon fibers as secondary anodes. A variant on the previously discussed slot system is to use carbon fibers as secondary anodes. These are fixed perpendicular to the platinized wires. These slots are also filled up with conductive mortar. The secondary anodes are applied to obtain a more homogeneous current density and to reduce costs of primary anodes. In this slot system the typical anode/concrete surface ratios are in the range of 1 to 7. These are relatively unfavourable ratios with respect to the formation of acids, etc. at the anode surface. Other phenomena which could lead to reduced adhesion between the conductive filling mortar and the surrounding concrete are temperature stresses and frost-thaw loading.
3. Graphite filled polymer cable with a copper core. The cables are fixed to the concrete by means of plastic fixings and the system is covered with sprayed concrete or a cast concrete overlay. This system could be applied both to horizontal substrates and to vertical surfaces. It is applied on bridge decks, parking garages, beams, columns, etc. The service lifetime of the system will depend on the current density applied, but is estimated to be in excess of 25 years. The anode/concrete surface ratio is about 1 to 4. In other words, it is more favourable than the slotted system but less favourable than the paint system. For a cable diameter of about 8 mm, an overlay thickness of about 40 mm is required.
4. Anodes of metal mesh. This system is based on a metal mesh in combination with mortar overlay. The mesh consists of titanium as a substrate for activated, special metal oxides. The system has been developed by producers of anode material for the electrochemical industry, e.g. chlorine production.
The system is regarded as very durable. It is claimed that the development of chlorine will be low, in comparison with other systems, because the special metal oxides have a very low overvoltage for the development of oxygen, so that oxygen will be formed instead of chlorine. Damage of the metal oxide layer is claimed not to have negative consequences because the titanium then exposed is strongly passivated. The anode/concrete surface ratio is relatively small and ranges from 1 to 4 to 1 to 10. As for the graphite filled polymer cable the system is covered by fairly large amounts of concrete – about 30 mm thick – so that the possibility of total failure due to acid formation etc. will be low.
5. Strip anodes. Another variant of the local anode systems is formed by strip anodes. The strips consist of a platinized copper wire as primary anode embedded in a conductive mortar (secondary anode). The strip is connected to the concrete and covered with cast or sprayed concrete. The strips have a width of about 50 mm, a thickness of 10 mm and a length of 300 mm.
6. Tiles of titanium oxide. An anode system consisting of tiles of titanium oxide to the concrete without a mortar overlay is being investigated in the U.K. The anode surface is very small with respect to the concrete surface.

Sacrificial anodes

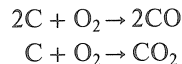
Another type of anode is the flame sprayed zinc anode. A zinc layer of about 200 μm is sprayed on the concrete and connected electrically with the reinforcement. This is what is known as a sacrificial anode which does not need an external potential source. The service life of this system appears to be limited.

11.5 Durability

To be durable all parts of a cathodic protection system must perform well through the lifetime. In a number of pioneering projects some defects have appeared. Those include: corroding of connecting cables on primary anodes, damage of the electrical control unit, the erosion of conducting asphalt layers and debonding of a sprayed concrete cover. Not all of them are typical of cathodic protection systems. However, attention needs to be paid to a number of phenomena which occur in concrete provided with an activated cathodic protection system.

Anode consumption

One of the possible degradation mechanisms concerns the anode. At the anode various reactions occur as described previously in this chapter. With respect to the use of graphite for anode cables, conductive mortars etc., the following reactions can occur:



This means that the anode will slowly lose its thickness. Anodic polarization curves for carbon containing anodes and titanium mesh anodes in chloride contaminated concrete have been investigated. Fig. 49 shows some results taken from reference 32. The carbon containing anode starts to generate carbon monoxide, carbon dioxide and oxygen at relatively low anode potentials. Up to 0.1 A/m^2 the polarization for the carbon containing anode starts to increase steeply. 0.1 A/m^2 current density is the maximum anodic value recommended by NACE. The titanium mesh anode appears to behave considerably better in this respect.

Acid production at the anode

Another durability aspect of cathodic protection is the production of acid at the anode. As a consequence of the reactions described previously in this chapter the alkalinity at the interface of anode and concrete will decrease, thus increasing the acidity. The anode materials might have very good resistance to acid. However, the surrounding cement mortar will not be resistant to acid formation. It is likely that a thin layer of concrete will be degraded. At the present it is not known how serious this effect is. The quantity of acid produced in time is proportional to the current density. For instance if we assume a current density of 0.01 A/m^2 at the anode, and equal reinforcement and

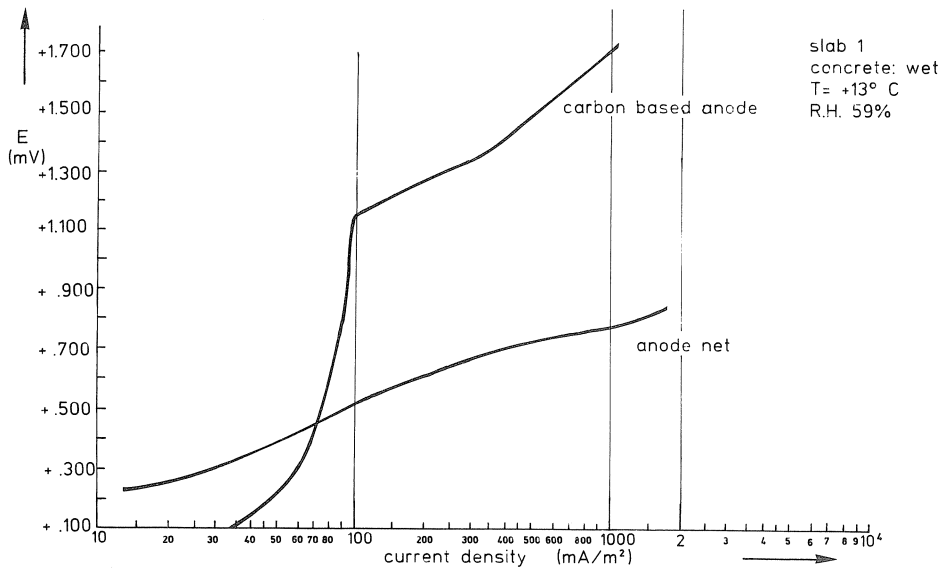


Fig. 49. Anodic polarization curves for titanium net anode and carbon based anode in chloride contaminated concrete (32).

concrete surfaces an acid production of 3 g H^+ (per year/per m^2) will occur. This quantity must be neutralized by 51 g OH^- . If this OH^- is totally supplied by the free lime from the concrete this will mean a degradation of 0.3 to 0.4 mm concrete per year for portland cement sprayed concrete with a cement, aggregate ratio of 1 : 5. However the actual rate of deterioration will be restricted by the supply of hydroxyl ions from the underlying concrete.

The latter contribution will decrease as the contribution of other ions like chloride in the electric transport increases.

In reference 31 results are described of experiments with an anode current density of 0.1 A/m^2 . The researcher found a pH decrease from 13 to about 8 after 7 months. However, this decrease occurs only in the first millimeter. Only when the current density was 10 to 20 times higher than the NACE criterion was a pH decrease of about 4 measured. The concrete investigated contained 2% m/m of chloride on cement. When the chloride content was 6% m/m a higher pH decrease was observed.

Therefore high anode/concrete surface ratios are favourable for both anode consumption as well as acid formation.

Over-protection

For various reasons over-protection has to be avoided. Over-protection means that a greater negative potential is applied than required. Over-protection means higher current densities, which means:

- restriction of the service lifetime of the anode system
- faster degradation of the concrete

- possible debonding between steel reinforcement and concrete because of the accumulation of alkalis at the interface.

Hydrogen embrittlement

Prestressed or post-tensioned cables or bars are vulnerable to embrittlement when hydrogen is generated at the steel surface. It has been found that as long as the potential is more positive than -1100 mV in comparison to CSE there is hardly any danger of hydrogen embrittlement.

11.6 Repair procedure with CP

Fig. 50 shows a possible procedure for repair work where CP is applied (18). Some of the steps are different from traditional repair methods as discussed in Chapter 10. In the CP system the reinforcement has to be continuously electrically connected to avoid stray currents. Due to stray current a particular rebar not connected to the CP system could corrode even more quickly than without CP.

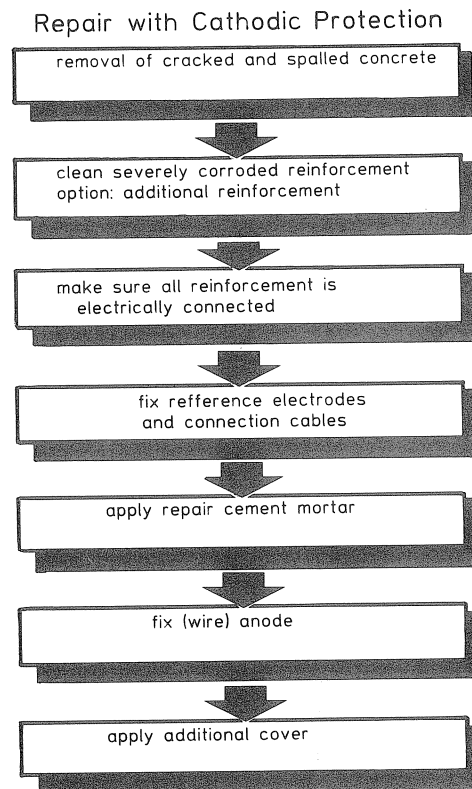


Fig. 50. Flow sheet repair procedure with CP in cases of chloride initiated corrosion (18)

Another important principle is to remember that the electrical circuit must in no way be intersected by non-conductive materials during the repair.

This could happen for instance where polymer based repair mortars or injection agents are used.

When a cathodic protection system is applied, an elaborate investigation of the structure has to be made first. This regards: the position of the reinforcement, the presence of electrical continuity, chloride contents, the presence of previous repair actions, the measuring of any decrease of rebar thickness due to corrosion, and the potential of the steel.

The installation of the cathodic protection involves the following: removal of cracked and spalled concrete and filling up these areas with an electrically conductive mortar, which could be a normal concrete mortar. If the reinforcement is corroded too far, the structural engineer involved has to investigate whether or not new reinforcement is required. If so, new reinforcement should be placed before filling up the removed concrete with repair mortar. The repaired concrete surface will be grit-blasted and cleaned to provide a good substrate for a conducting paint layer, overlay or whatever agent is chosen. Subsequently the anode material is applied, cables connected etc. and the overlay/paint is then applied.

After completion the cathodic protection system is applied and checked periodically as to its effectiveness. When required, adjustments are made to the applied input voltage and current.

12 Repair of degradation caused by carbonation initiated corrosion

Corrosion of reinforcement due to carbonation of concrete is one of the main degradation factors in the Netherlands. From a Dutch field investigation into damage of concrete exposed to the environment and used in houses built in the 1950–1980 period (1) it appeared to be by far the most frequently occurring damage factor. The main causes are lack of cover thickness and permeable concrete.

In general the repair of structures affected by carbonation is much less complicated than for chloride-initiated corrosion. This is mainly due to the fact that corrosion appearance is homogeneous and pitting does not occur. But also the ability to re-alkalize carbonated concrete is helpful to a certain extent.

The principles of repair are based on reinstating passivation or reducing the corrosion propagation rate by increasing the electrolytic resistance by making the concrete drier. In this chapter various repair alternatives will be discussed. Many details are similar to those discussed in the previous chapter to which reference will be made. Use is made of draft German recommendations for concrete repair and protection (35).

12.1 Carbonated but not severely corroded

Often damage is observed locally but closer examination reveals carbonation has reached the reinforcement more than in incidental locations, even though corrosion

has still not reached the critical level; see Fig. 51 (33).

The following questions could be raised:

- is it sufficient to stop further corrosion?;
- does re-alkalization and repassivation occur due to diffusing of hydroxyl ions from the substrate concrete into the carbonated area? (backward diffusion);
- can re-alkalization be achieved by applying a cementitious surface protection? (forward diffusion);
- can re-alkalization be accelerated and improved?;
- can corrosion effectively be stopped by making the concrete drier e.g. increasing the electrolytic resistance?;
- is cathodic protection possible?

If these questions are answered partially in the affirmative, the removal of concrete can be substantially reduced.

We have seen in Chapter 8 that the progress of carbonation can be stopped effectively when a surface protection with a carbon dioxide resistance S_{dCO_2} of 50 m is applied. However, that is something different from stopping the corrosion. The latter will only happen when passivation is reinstated or when the ohmic resistance of the concrete is increased sufficiently.

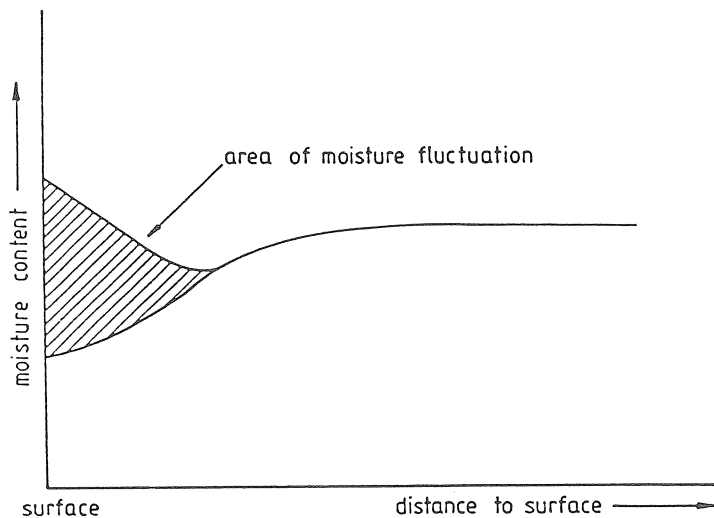


Fig. 51. Schematic drawing of the corrosion process of steel in concrete (33).

12.2 Re-alkalization

It has been observed in a number of investigations that when carbonation is stopped by applying a protective surface layer, hydroxyl ions start migrating from the non-carbonated substrate to the carbonated area, as illustrated in Fig. 52:

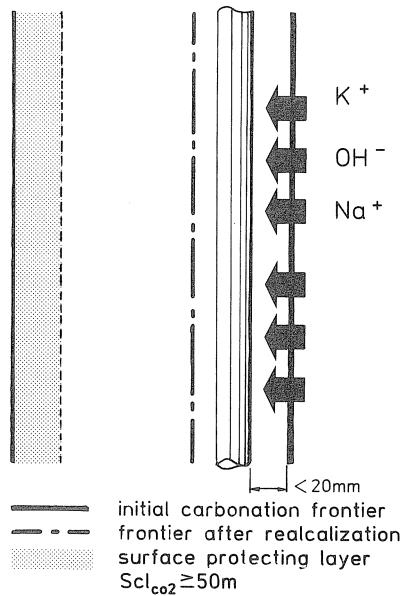


Fig. 52. Migrating alkaline ions from non-carbonated to carbonated portland cement concrete when distance from reinforcement to carbonation frontier is less than 20 mm without serious corrosion.

The carbonation-blocking surface treatment not only hinders carbonation but also dampens moisture fluctuations, thus assisting the re-alkalization process. It is likely that effective re-alkalization and repassivation can occur when the reinforcement is no further away from the non-carbonated portland cement concrete than 20 mm. In that case and provided that corrosion is only minor, it may suffice to apply a surface protection with a S_{dCO_2} of at least 50 m, and to remove and replace cracked areas only on a level with the reinforcement, see Fig. 53 (35).

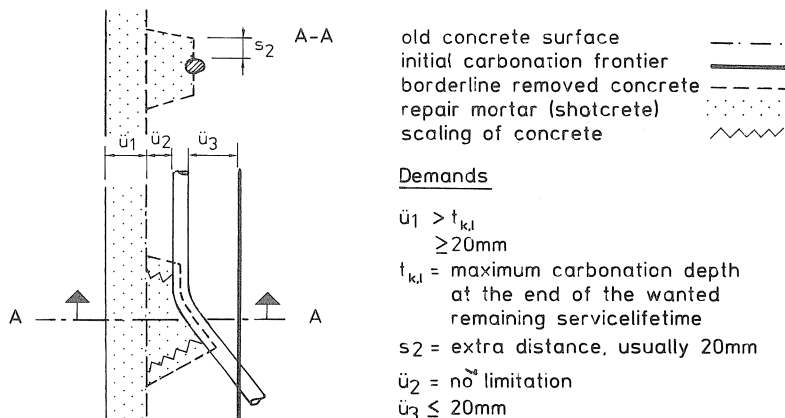


Fig. 53. Repair of locally cracked portland cement concrete due to carbonation corrosion when carbonation frontier is less than 20 mm behind reinforcement (35).

For cements with a less alkaline buffer such as portland blast furnace slag cement the re-alkalizing ability appears to be lower. Research is being carried out in the Netherlands, where portland blast furnace slag cement is the cement most applied, to assess the re-alkalizing ability of this cement.

If the carbonation frontier is more than 20 mm behind the reinforcement in the case of portland cement concrete and in the case of portland blast furnace slag cement concrete has reached the reinforcement, the concrete cover must be removed down to the reinforcement and replaced by a dense cementitious mortar of concrete (shotcrete, polymer modified, etc.). This repair mortar must have a sufficiently high CO₂ resistance to avoid renewed depassivation during the remaining service life; if the cover thickness does not meet this requirement an additional cover has to be applied or a CO₂-resistant coating on the reinforcement. In the latter case removal of concrete around the reinforcement is required, see Fig. 54. Removal of concrete around the reinforcement is also required when excessive corrosion has occurred at the back of the reinforcement.

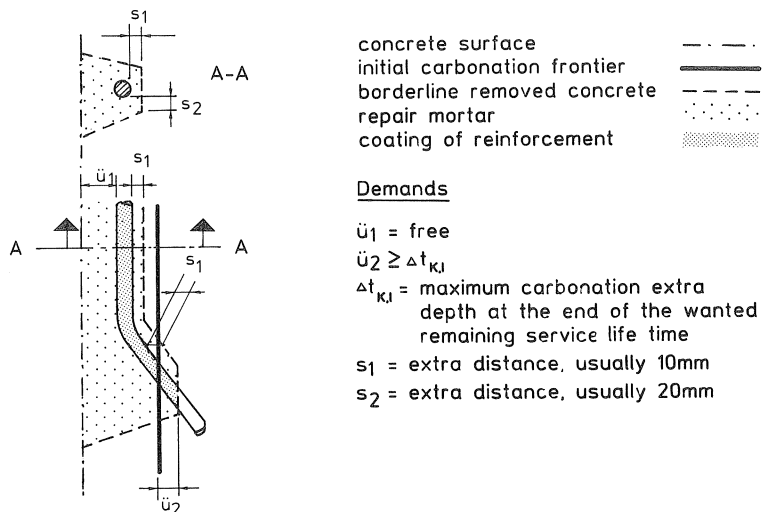


Fig. 54. Repair of carbonated concrete with coating of reinforcement (35).

In principle re-alkalization also can occur when an additional concrete cover is applied, e.g. by shotcreting (forward realkalization).

Alkaline ions can migrate from this cover into the carbonated substrate concrete, as shown in Fig. 55. Insufficient data are available to assess the effectiveness of this method.

12.3 Forced re-alkalization

Various attempts have been made to develop methods for forced re-alkalization. In some countries a method developed in Norway (34) is applied. In this method a strongly alkaline paste (soda, cellulose fibers, gel, etc.) is applied on the surface. An anode mesh

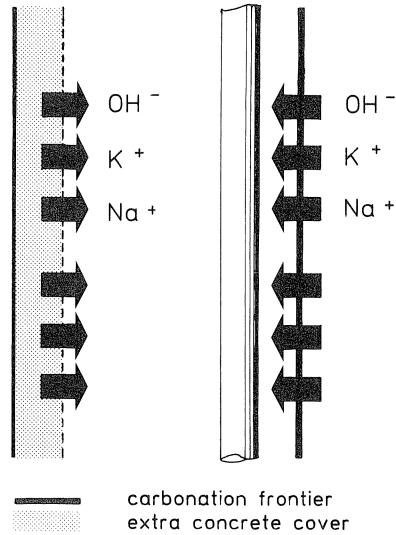
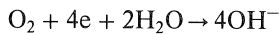


Fig. 55. Re-alkalization from both non-carbonated substrate concrete (backward) as well as additional concrete cover (forward).

is embedded in the paste, see Fig. 56. The anode is electrically connected to the reinforcement via a DC source. A relatively high CP voltage is applied, e.g. 10 V. According to the inventors the alkaline solution is drawn into the concrete due to electrolytic osmotic forces. When the pH is raised high enough at the cathode, hydroxyl ions form through the reaction



This reaction should reinforce the alkalization process. The presence of electro-osmosis is not proven but re-alkalization through hydroxyl formation is.

Not enough data are available to assess the effectiveness of this method or its possible disadvantages.

Because the alkaline buffer that is built up will be relatively small it is likely that the method will have to be completed with a CO_2 -resisting surface treatment.

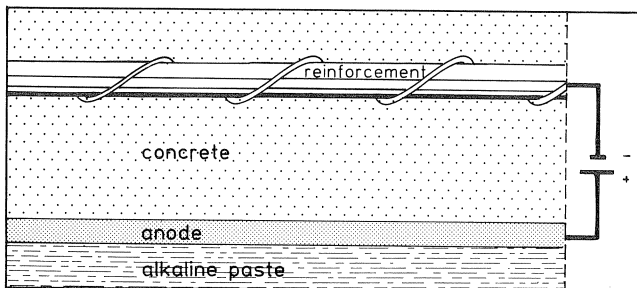


Fig. 56. Forced re-alkalization according to reference 34.

12.4 *Increased ohmic resistance electrolyte*

When concrete has a moisture content corresponding to the equilibrium state of 20°C and 65 to 70% R.H. its electrical conductivity will be too low to maintain the corrosion process. Results of German investigations indicate that for West European climatological conditions this could mean that it will be sufficient to apply water-repelling agents. The method has to be completed by applying a carbonation resisting surface protection. Feedback from practice regarding the effectiveness and durability of this method is not available.

12.5 *Cathodic protection*

Cathodic protection as discussed in chapter 11 for chloride initiated corrosion could also be applied for carbonated concrete, although this has so far not been done on a large scale. Probably due to the relatively high costs when compared with other repair methods.

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