School of Civil & Environmental Engineering
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Postgraduate Lecture: Physical and Chemical Deterioration Processes

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1. PHYSICAL FORMS OF DETERIORATION

1.1 Abrasion

In this context, abrasion refers to the wearing of the surface of concrete caused by repeated rubbing or frictional actions. This problem mainly manifests itself in pavements or industrial floors carrying wheel or pedestrian traffic.

In itself, hardened cement paste has a low resistance to abrasion. Hence, the abrasion resistance of concrete is largely determined by the hardness and quality of the aggregates used. This is not to imply that the w/c ratio of the concrete is unimportant in determining its abrasion resistance. It has been shown that concrete abrasion resistance decreases linearly with increasing w/c ratio. It is possible that this derives from:

- the marginal improvement in the resistance of the cement paste; and
- the improved aggregate/cement paste bond strength.

1.2 Erosion

Erosion refers to wearing of the concrete surface by the abrasive action of fluids and suspended solids as well as by wind-borne sand particles. Erosion is therefore a special case of abrasion as discussed above.

1.3 Cavitation

Cavitation can be a serious problem because of the high pressures which occur at the surface of the concrete. Cavitation occurs when a high velocity flow of fluid is subject to a sudden change in direction or velocity. This results in a zone of severe subatmospheric pressure forming immediately downstream of the obstruction or abrupt change, allowing pockets of vapour to form. As these vapour

pockets leave the low pressure zone, they collapse by implosion, resulting in a high, localised impact pressure on the surface. These pressures are known to indent very hard metals and can cause fairly rapid deterioration of good quality concrete.

1.4 Freezing

Problems caused by freezing of concrete are seldom encountered in Southern Africa because of the relatively mild climate in this region. However, there are some applications, such as cold rooms or cold liquid storage facilities, in which concrete is exposed to very low temperatures and could be damaged by the freezing of water in the pore structure.

Damage by freezing derives from the fact that water undergoes a 9% volume increase when it turns to ice. Hence, damage occurs when the water in the pore structure expands upon freezing and there is not enough empty space in the pore structure to accommodate this expansion. Tensile stresses are then set up and microcracking of the cement paste occurs. In freeze-thaw deterioration, the cracks are propagated by the cyclic freezing and thawing actions.

2. FORMS OF CHEMICAL DETERIORATION

2.1 Soft Water Attack

The aggressive nature of soft water

Soft waters are aggressive to concrete primarily because of their "ion hungry" nature. These waters occur naturally in springs emanating from igneous rock formations in mountainous areas or in lowland streams or rivers which have not passed through calcareous strata. Soft waters are therefore characterised by their low dissolved ion content. When concrete is placed in contact with this water, the calcium hydroxide ($Ca(OH)_2$) in the hardened cement paste is leached out as the water tries to establish an ion balance. Under these conditions the rate of $Ca(OH)_2$ removal is determined by the concentration gradient, ie. the difference in concentrations of calcium compounds between the concrete and water phases.

The hardness of water, as it is applied to concrete corrosion, is determined by the temporary hardness which is a measure of the concentration of the bicarbonate ion (HCO_3). This is different from the concept of total hardness which measures the concentration of calcium and magnesium cations.
The aggressiveness of soft water as measured by the rate at which $Ca(OH)_2$ is leached from the cement paste, is considerably increased if the water contains dissolved carbon dioxide (CO_2). CO_2

dissolves in water to form carbonic acid (H_2CO_3) as follows:

$$H_2O + CO_2 \rightarrow H_2CO_3$$

This CO_2 assists by first converting the $Ca(OH)_2$ to poorly soluble calcium carbonate (carbonation reaction) and then to soluble calcium bicarbonate which is easily removed by the water. These reactions are represented as follows:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (1)$$

$$CaCO_3 + CO_2 + H_2O \rightarrow Ca(HCO_3)_2 \quad (2)$$

Carbon dioxide exists in water mainly in the dissolved form with a small proportion combining to form carbonic acid. The effect of CO_2 in pure water is therefore to reduce the pH (ie. increase the acidity). The solubility of CO_2 in water increases with decrease in temperature and at 18 ^oC, pure water saturated with CO_2 has a pH of around 3,95. In natural soft waters the acidity is usually a function of the CO_2 content but this can be distorted by the presence of organic acids or polluting mineral acids.

It should be noted that a certain amount of dissolved CO_2 is required to stabilize the carbonate - bicarbonate equilibrium in the water (reaction (2) above). This CO_2 is therefore not available for $Ca(OH)_2$ leaching from concrete and it is only the CO_2 in excess of this amount which contributes to corrosion of concrete. This excess CO_2 is termed aggressive CO_2.

Mechanism of concrete deterioration in soft water

The pore water solution in hardened cement is highly alkaline with a pH of around 12,5. In this environment the calcium silicate, aluminate and ferrite hydrates, the main binding components of cement, are stable. However, as $Ca(OH)_2$ is leached by the soft water, the pH of the pore water decreases, causing the hydrates to become unstable and release calcium oxide (CaO) in order to re-establish the alkalinity. In this manner the binding agent in the cement phase is attacked, causing a decrease in strength.

The high pH of the pore water in concrete also maintains the presence of a layer of gamma-ferric oxide on reinforcing steel which passivates the steel and inhibits corrosion. If the leaching action of soft water reduces the pH around the reinforcement, this protective layer is destroyed and the steel is exposed to possible corrosion.

Determination of water aggressiveness

The discussion above shows that the aggressiveness of natural waters, in the absence of organic or inorganic acids, is determined by a combination of the temporary hardness and the concentration of dissolved CO_2. Table 1 shows a classification of the aggressiveness of natural waters presented by Lea[1]

Table 1: Classification of Aggressive Natural Waters - Lea[1]

Type of Water	Temporary hardness parts $CaCO_3$ per 100 000	Aggressive Carbon dioxide parts per 100 000	Aggressiveness of water towards concrete
I	> 3.5	< 1.5	Practically none
II	> 3.5	1.5 - 4.0	Slight
	0.35 - 3.5	< 1.5	Slight
III	> 3.5	4.0 - 9.0	Appreciable
	0.35 - 3.5	1.5 - 4.0	Appreciable
	< 3.5	< 1.5	Appreciable
IV	> 3.5	> 9.0	Great
	0.35 - 3.5	> 4.0	Great
	< 0.35	> 1.5	Great

Basson[2]has proposed a method for determining the general aggressiveness of water to concrete. Part of this method involves the calculation of a Leaching Index based on the following 3 factors:

- the natural pH of the water;
- the calcium carbonate saturated pH of the water; and
- the calcium hardness of the water.

The index value obtained by appropriate calculation, is then related to a degree of aggressiveness of the water. Recommendations are also presented on project specifications to ensure acceptably low rates of deterioration.

Mackintosh[3] using water treatment curves prepared by Lowenthal et al[4], proposes a quantitative assessment of aggressiveness based on a determination of the calcium carbonate dissolution potential of the water. This method determines the amount of $CaCO_3$ which the water would dissolve to achieve saturation given sufficient time and suitable conditions. A high dissolution potential indicates

a high degree of aggressiveness to concrete. Since it provides a quantitative assessment, this appears to be a useful method for characterising the aggressiveness of water. However, there is insufficient experience with the method to make confident statements regarding its applicability to concrete deterioration.

2.2 Alkali Aggregate Reaction

Three types of alkali aggregate reaction have been identified:

- *Alkali-silica reaction:* this is a reaction between the alkalies in the cement and the microcrystalline phases of silica found in many aggregate types. This form of the reaction is discussed in more detail later.
- *Alkali-carbonate reaction:* carbonate aggregates like dolomite and limestone usually produce good quality concrete with premium strength characteristics. However, some forms of dolomitic limestone have been found to produce expansion in concrete resulting in surface map cracking. This reaction is different from alkali-silica reaction because of the absence of reaction products and is therefore not detected visually or with an optical microscope.

  The reaction involves a de-dolomitization of the aggregate which is chemically expressed as:

  $$CaMg(CO_3)_2 + 2MOH \rightarrow Mg(OH)_2 + CaCO_3 + M_2\,CO_3$$

  where M = K or Na.

  The mechanism of expansion due to alkali-carbonate reaction is not clearly understood but it appears to be an interaction of texture, calcite/dolomite ratio and the presence of clay minerals in the aggregate. This lack of understanding means that it is difficult to predict the potential expansion of particular aggregates.

- *Alkali-silicate reaction:* this form of the reaction has been identified fairly recently and has not yet obtained general acceptance as a separate category of alkali aggregate reaction. It manifests itself differently from alkali-silica reaction in that no correlation exists between the magnitude of expansion and the amount of gel formed, has a very slow rate of expansion and occurs in the absence of some of the minerals known to promote the reaction.

Source of alkalis in cement

In the context of AAR, the important alkalis are the sodium and potassium alkalis, which are largely derived from the fuel used in the production of cement. These go to form sodium and potassium hydroxides dissolved in the pore solution after cement hydration. The total amount of K_2O and Na_2O

in cement does not normally exceed 1%, expressed as Na_2O equivalent (Na_2O equivalent = 0.658 x K_2O + Na_2O) and a cement with a 0.6% Na_2O eq. is considered to be a low alkali cement. Note that this assumes that equal concentrations of KOH and NaOH have the same effect in terms of AAR expansion. This approach has been brought into question since it has been found that NaOH causes more expansion than KOH.

Reactive forms of silica

These include the silica minerals:

opal, chalcedony, cryptocrystalline and strained quartz;

rocks with metamorphic quartz:

greywacke, phyllite, schists, vein quartz, sandstone;

glassy to cryptocrystalline rocks:

rhyolites, andesites, artificial glass.

Reactive forms of silica can be present as a constituent in chert, shale, sandstone and limestone.

2.3 Sulphate Attack

The deterioration effect of sulphates on concrete occurs through a fairly complex mechanism which involves a number of secondary processes. The major cause of deterioration is *sulphoaluminate corrosion* which occurs as follows:

$C_4A\hat{S}H_{12}$	+	$2C\hat{S}H_2$	+	16H	→	$C_6A\hat{S}_3H_{32}$
Monosulphoaluminate		Gypsum		Water		Ettringite

where: C = CaO, A = Al_2O_3, $\hat{S}$ = SO_3 and H = H_2O.

This reaction is accompanied by a large increase in solid volume, causing internal stresses which lead to cracking. However, the process is initiated by a reaction between the sulphate ion and $Ca(OH)_2$ as follows:

$$CH + SO_4^{2-}(aq) \rightarrow C\hat{S}H_2 + 2OH^-(aq)$$

This reaction is termed *gypsum corrosion* and is associated with a small increase in volume. However, the effect of expansion due to gypsum corrosion is only significant at relatively high levels of sulphate concentration (>3000 ppm). It should be noted that, in a water environment where leaching action is possible, the gypsum will be removed with the calcium hydroxide because of its higher solubility. This will reduce the extent of subsequent sulphoaluminate corrosion.

The cation accompanying the sulphate ion can affect the aggressiveness of the sulphate. Ammonium and magnesium sulphate are particularly aggressive because these cations also participate in reactions with $Ca(OH)_2$ in the hcp. In the case of magnesium sulphate, the reaction, also accompanied by an increase in volume, proceeds as follows:

$$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2$$

The magnesium hydroxide is precipitated because of its low solubility and the C-S-H decomposes to release $Ca(OH)_2$ so as to re-establish the balance. This is similar to the leaching action of pure water and also leads to the destruction of the binding agents of the hcp. However, the formation of $Mg(OH)_2$ is such that it tends to precipitate in the existing pores without causing disruptive expansions. The reaction is beneficial in that it seals the pores and hinders further penetration of sulphates.

An interesting result of this action is the fact that concretes in sea water suffer less deterioration due to sulphate attack than would be expected purely from an assessment of the sulphate content of the water. Sea water contains a fair amount of magnesium and the protective effect of the $Mg(OH)_2$ contributes to the reduced deterioration. Another reason is that gypsum and ettringite are more soluble in solutions containing chloride ions, causing a reduction in the amount of expansion.

SABS 0100: Part 2 approaches the control of sulphate attack the calculation of the so-called Basson Spalling Index. This index accounts for the effects of ammonium, magnesium and sulphates present in the water in contact with the concrete. Based on the magnitude of the calculated index, the code recommends the concrete quality, cement type and quality and type of surface coating where necessary. For high sulphate concentrations, the code recommends sulphate resisting portland cement, which is a low C_3A cement.

2.4 Carbonation

This is the process whereby atmospheric carbon dioxide (CO_2) enters the pore structure of hardened cement paste and reacts with $Ca(OH)_2$ to form calcium carbonate ($CaCO_3$). This involves the following chemical reaction:

$$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$$

In this process, the pH of the pore water is reduced from ±12,5 to ±8,5 upon complete carbonation. When the carbonation front reaches the reinforcing steel, the low pH causes the gamma-ferric oxide layer to become unstable and the steel is de-passivated. If sufficient oxygen and moisture is available, the steel will start corroding with subsequent loss in the load-bearing capacity of the structure.

Carbonation moves as a "front" into the concrete as shown in Figure 1. This front does not advance beyond a particular point until all the $Ca(OH)_2$ at that point has been converted to $CaCO_3$. Hence, the amount of $Ca(OH)_2$ in the pore structure of the concrete also has an influence on the rate of carbonation.

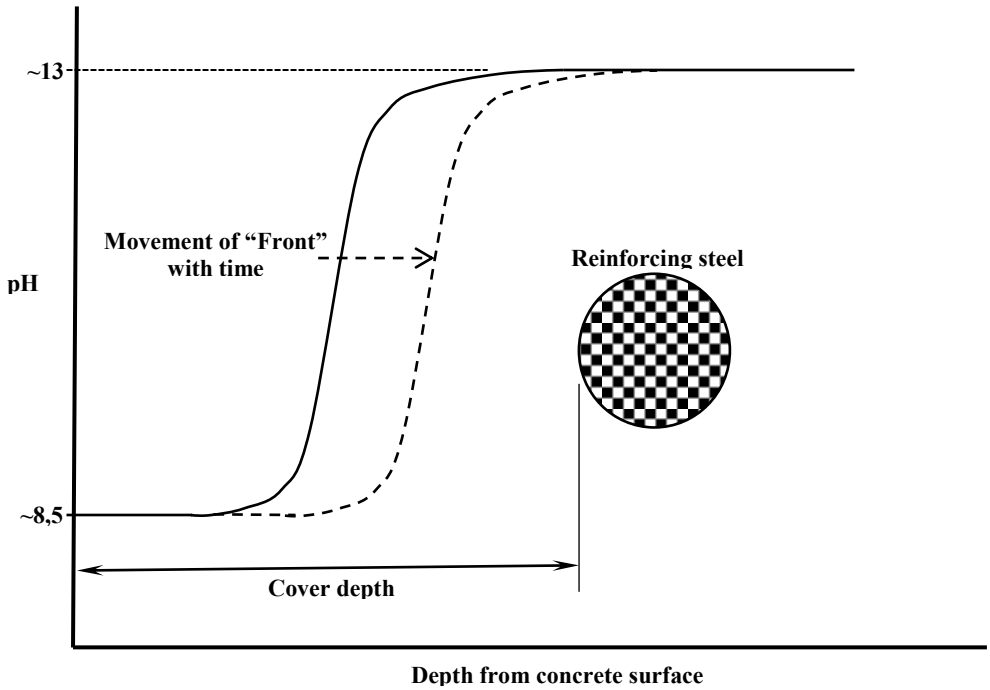

Figure 1: The carbonation "front"

The rate of advance of the carbonation front can be expressed as:

$$x = D\sqrt{t}$$

where:

x = depth of carbonation

t = time of exposure

D = carbonation coefficient

Influence of environmental factors

The rate of carbonation is strongly affected by the moisture content or relative humidity of the concrete pore structure. No carbonation takes place when the pores are completely dry or when they are fully saturated. The rate of carbonation is at a maximum when the relative humidity is at 50%. The rate of carbonation also increases with increasing ambient temperature.

Periods of dryness promote carbonation whereas periods of wetness promote corrosion if de-passivation of the steel has already occurred. The risk of corrosion therefore increases with increasing time of dry periods. Hence, a better quality of concrete cover is required in climates with long dry periods and short wet periods.

Further material decisive parameters:

- cement composition;
- cement content of the concrete;
- compaction;
- curing at early ages;
- surface cracks.

2.5 Chloride ion diffusion

A problem which presents itself at coastal environments is the ingress of chloride ions into the concrete. Chlorides are also introduced into the concrete at the mixing stage, either as contamination of the mix constituents or as a component of an admixture. The presence of free chlorides at the level of the reinforcing steel also causes de-passivation despite the pH being maintained at a high level. The reinforcing steel is then exposed to possible corrosion.

Some of the chloride which enters the concrete is bound by the cement and it is only when a critical concentration of free chlorides is reached that de-passivation takes place. The ability for the cement to bind chlorides varies considerably with the cement type. The addition of GGBS in the binder has been found to be beneficial in this respect because of its high chloride binding ability.

The diffusion of chloride ions into concrete only takes place when there is moisture in the pore structure of the concrete. The higher the moisture content of the concrete, the higher is the rate of diffusion. Alternate wetting and drying cycles create the added problem of salt crystallisation with the associated expansive cracking of the concrete.

The rate of diffusion

The diffusion of ions into porous media is governed by Fick's Law, which can be written as:

$$Q = -D\frac{\partial c}{\partial x}$$

where Q is the mass flow rate, D is the diffusion coefficient and $\partial c/\partial x$ is the concentration gradient.

There are a number of problems in using this equation to predict the rate of ingress of chloides into concrete. The more important of these are:

- the equation applies to fully saturated concrete;
- in the context of chloride ion penetration, concrete is not an "inert porous" material; cement paste interacts chemically with the chloride ions.

This makes the rate of penetration difficult to predict. However, any attempt at prediction must account for the following variables:

- composition of the cement;
- amount of cement;
- composition of the concrete;
- compaction of the concrete;
- curing conditions;
- environmental conditions of exposure.

Synergy between carbonation and chloride penetration

When carbonation takes place in concrete into which chlorides have already penetrated, the two processes interact to accelerate the de-passivation of the reinforcement. The pH lowering effect of carbonation causes some of the chloride bound to the cement to be released. This increases the amount of free chloride ions available for de-passivating the reinforcement.

Influence of the Environment

The following classification of environmental aggressiveness has been proposed by Schiessl and Bakker[1]:

Not aggressive	Indoor conditions: RH < 70%; constantly and totally immersed.

[1] Schiessl, P (Ed.) "Corrosion of steel in concrete" RILEM TC 60-CSC report. Chapman Hall, London. 1988.

Moderately aggressive (without chlorides)	RH always > 70%; infrequent major variations in RH; occasional condensation.
Aggressive (without chlorides)	Frequent major variations in RH; frequent condensation or wetting and drying cycles.
Aggressive (with chlorides)	Marine environments without direct contact to sea water; low chloride attack in combination with infrequent major variations in relative humidity.
Very aggressive	Severe chloride attack; sea water splash zone; frequent wetting and drying.
Extremely aggressive	very severe chloride attack; frequent chloride splash water to horizontal surfaces.