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Modelling acid attack on concrete: Part I. The essential mechanisms

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Abstract

At present, a computer model is being developed to predict the corrosion of concrete construction components subjected to acidic solutions with pH values ranging between 4.0 and 6.5, i.e. exposure classes XA3 down to XA1 according to DIN EN 206-1. The concrete may contain Portland cement based binders with dissolvable or acid resistant aggregate. Calcium aluminate cement is also considered. The concrete degradation is characterised by a corroded layer of high porosity whose thickness is determined by the combination of dissolution, precipitation and transport processes which depend on cement chemical composition, binder reactivity, aggregate reactivity, grading curve as well as concrete composition. It is also intended to include the effect of abrasion. The model components will be described in detail in forthcoming publications.

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1. Introduction

When unprotected concrete surfaces of sewer pipes, waste water treatment plants, cooling towers and other industrial constructions are attacked by acidic solutions degradation of the concrete microstructure occurs which seriously limits the service life of the construction components. In the standard DIN EN 206-1 the severity of acid attack is divided into three exposure classes, Table 1.

In the case of acids with pH values in the range XA3 or lower, protective coatings, rather than mix design optimisation, are in general necessary to prevent rapid deterioration.

In the course of acid attack protons enter the concrete and dissolve solid hydration products in the binder and, depending on its mineralogical composition, the aggregate. Hydroxyl ions contained in the hydration products are, in effect, neutralised by the protons. Calcium, iron, aluminium as well as sulphate ions enter the pore solution and diffuse toward the concrete surface, Fig. 1. A highly porous corroded layer develops consisting essentially of hydrated silicates [1–3]. The growth rate of the layer is determined by (a) the diffusion of the acid through the corroded layer to the reaction front and (b) the reaction rate of the acid with the undamaged concrete.

This paper is the first of a series of publications accompanying the development of a computer model to describe the corrosion of concrete made with Portland or Portland blastfurnace cement at pH values between 4.0 and 6.5. Concrete made with calcium aluminate cement will also be considered. The simulation of the corrosion process requires detailed knowledge, not only of the chemical reactions between the acid, the solid hydration products and the aggregate, but also of the transport of ions in the pore system of the corroded layer. Since the model should ultimately be applicable to a wide range of concrete compositions used in practice and the different types of acidic environments encountered, a modelling approach based on integral material properties rather than basic thermodynamics has been chosen.

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Table 1
Exposure classes for chemical attack according to DIN EN 206-1

Property	XA1	XA2	XA3
pH	5.5–6.5	4.5–5.5	4.0–4.5
Severity	Weak	Medium	Strong

This paper deals with the various mechanisms which should be considered when modelling the corrosion process.

2. Corrosion of the cement paste matrix

Experiments have shown that the corrosion resistance of concrete depends on the type and chemical composition of the cement as well as the pH of the attacking acid [4]. The rate of corrosion is determined by the concentration of the acid and the type and quantity of the hydration products taking part in the reaction. The dissolution of ferrite or aluminate hydrates and the corresponding loss of Fe^{3+} and Al^{3+} is slower and occurs at lower pH values than the release of Ca^{2+} from C–S–H and calcium hydroxide [4,5].

Obviously, the pH of the pore solution in the corroded layer will increase from the value of the attacking acid at the concrete surface to the pH of the pore solution inside the intact concrete, approximately pH 13. The corroded layer comprises zones of varying composition and structure determined by the different pH-stabilities of the hydration products and the solubility of the dissolved ions with respect to pH, see Ref. [2]. As the pH value decreases, calcium hydroxide (12.6), ettringite (10.7), C–S–H (≈10.5) and finally calcium aluminate and ferrite hydrates decompose successively until a silica gel residue is obtained at pH values below roughly 2 (the values in parentheses referring to pH stability). At pH values between 4.0 and 6.5 a small amount of calcium remains with residual phases containing iron and aluminium [4].

At pH values below 6.5 the neutralisation reaction may, as far as stoichiometry is concerned, be thought of as a reaction between the acid and $Ca(OH)_2$, i.e. the consumption of two protons in the pore solution by the hydroxyl ions transfers one calcium ion from the solid phases to the pore solution. Fig. 2 shows schematically the neutralisation reaction at an arbitrary point in concrete.

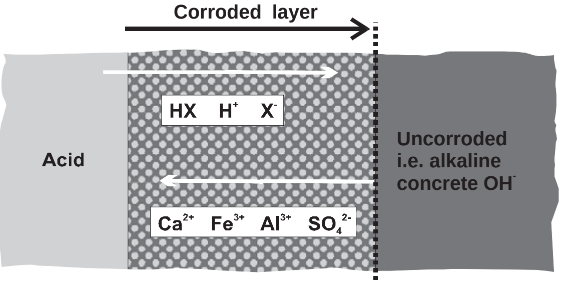

Fig. 1. Corroded layer due to attack by acid HX.

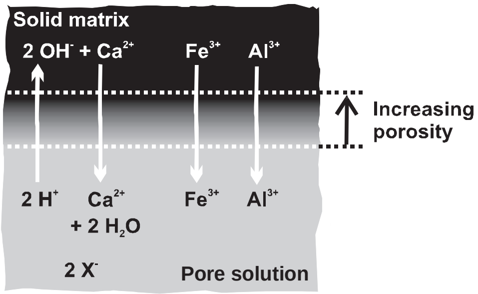

Fig. 2. Neutralisation reaction in a small volume at an arbitrary point in concrete. Dissolution of the solid matrix increases the volume of pore solution and thus porosity. Ca^{2+}, Fe^{3+} and Al^{3+} enter the pore solution.

The rate of neutralisation depends on the proton concentration of the pore solution c_H and the content of potentially soluble solid hydration products. If the reaction kinetics are of the second order the change in calcium concentration of the pore solution can be described by:

$$\frac{\partial c_{Ca}}{\partial t} = k_{Ca} c_H s_{Ca} \tag{1}$$

Here s_{Ca} is the amount of potentially soluble calcium in concrete with respect to pore solution volume and k_{Ca} the rate constant. This equation does not include the effects of physical microstructure and transport. The quantities c_H and s_{Ca} vary over the thickness of the corroded layer and are non-stationary. For finely divided pore systems it may be assumed that the potentially soluble calcium is, at all stages of corrosion, accessible to the acid. Thus s_{Ca} is essentially the neutralisation capacity as determined by the quantities of calcium as hydroxide in Portlandite, calcium silicate hydrates and, to a lesser extent, in hydrated aluminate, ferrite and sulphate phases in the hydrated binder. Unreacted clinker phases will also contribute to neutralisation capacity. It may, at the pH values in question, be assumed that the neutralisation reaction is not significantly affected by the phase type, see Ref. [2]. Thus the initial neutralisation capacity of the binder is given by its total calcium content which may be calculated from the CaO content of the cement and the cement content of the binder. These considerations may also be applied to calcium aluminate cements as well as Portland and Portland blastfurnace cement.

The corrosion process also results in extreme coarsening of the pore size distribution and a large increase in porosity, Fig. 3.

Porosity increases as calcium is removed from the solid matrix thus boosting the transport of ions in the corroded layer, see Fig. 2. The porosity increase can be related to the increase in calcium concentration c_{Ca} of the pore solution by a coefficient κ_{Ca}.

$$\frac{\partial P}{\partial t} = \kappa_{Ca} P \frac{\partial c_{Ca}}{\partial t} \tag{2}$$

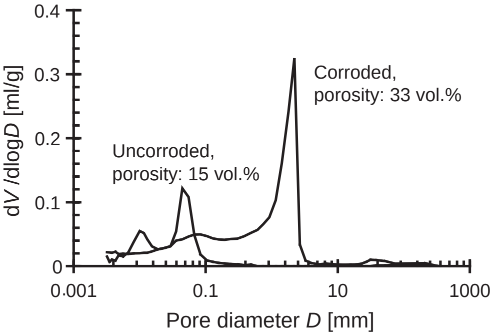

Fig. 3. Mercury intrusion pore size distributions for Portland cement mortar (cement: 449 kg/m^3, w/c: 0.6) made with acid resistant quartz sand (maximum grain size: 0.5 mm) before and after 16 d corrosion in an acetic acid buffer solution at pH 4.5.

From a chemical point of view, κ_{Ca} is simply the pore volume created by the dissolution of calcium hydroxide contained in the hydration products.

During the neutralisation reaction, the dissolution of Ca^{2+} is accompanied by the release of Fe^{3+} and Al^{3+} into the pore solution from ferrite and aluminate hydrates and residual clinker phases. These phases are less vulnerable to acid attack and, as already pointed out, dissolve more slowly. Since, in Portland cement based binders their content is well below that of calcium their contribution to the porosity of the corroded layer will be smaller.

3. Transport phenomena

When dry concrete is exposed to an acidic solution the acid species rapidly enter the pore structure convectively by capillary suction. In particular, alternating wet and dry conditions can drastically increase the acid uptake of the concrete and thus the rate of corrosion. However, in many industrial environments concrete surfaces are, to quote DIN 4030-1, exposed to large amounts of stationary or slowly moving liquids whose corrosive power is not reduced by their reaction with concrete. In view of this, our model focuses on acid attack on water-saturated concrete where acid ingress occurs by diffusion.

The composition of the pore solution at any point within the corroded layer (i.e. the local value) depends on the diffusion flux of the various participating species i as determined by the local values of concentration gradient in the pore solution and effective diffusion coefficients D_i^{eff}.

$$J_i = -D_i^{\mathrm{eff}} \frac{\partial c_i}{\partial x} \tag{3}$$

The effective diffusion coefficient is a bulk concrete property related to ion transport in the pore system as a whole. Values can be found for mortar or hardened binder specimens typically 3 mm in thickness using conventional diffusion cells [6]. For thicker concrete specimens values can be obtained with the help of electrical fields in accelerated migration tests, see Ref. [7].

The effect of pore structure on the specific diffusion coefficients of ions in bulk water (Nernst–Einstein values) can be written in terms of the water filled pore volume within which diffusion occurs and the lengthening of the diffusion path by tortuosity τ, i.e.

$$D_i^{\mathrm{eff}} = D_i^0 \frac{P}{\tau} \tag{4}$$

Since diffusion coefficient measurements are often restricted to certain ions (e.g. chlorides or iodides in migration tests) and specific diffusion coefficients are available for a large number of ions, Eq. (4) may used to find effective diffusion coefficients which would otherwise be unknown. It is assumed that the diffusivities of the ions in bulk water and in corroded concrete correlate.

During corrosion, the dissolution of the solid phases leads to a large increase in porosity affecting diffusion. Investigations at the Centre for Building Materials [8] show that effective diffusion coefficients of corroded mortar are more than an order of magnitude larger than the values for the uncorroded material. Furthermore, the penetration of protons into the undamaged alkaline pore system is strongly limited by the rapid neutralisation reaction. It is therefore expected that the pore system of the uncorroded concrete has only a secondary effect on the rate of corrosion of the undamaged material. At first sight this suggests that conventional concrete design methods aimed at lowering capillary porosity or increasing strength have little effect on corrosion resistance. However, the porosity and mechanical integrity of the corroded layer, which govern the acid diffusion towards the uncorroded material, also depend on concrete composition. Thus the capillary porosity associated with the w/c ratio of the particular concrete will contribute to the porosity of the corroded layer. Increasing the neutralisation capacity of the concrete by using more cement in the mix, ultimately results in a more porous corroded layer promoting acid diffusion. In Ref. [9] an optimum in calcium hydroxide content is foreseen for the leaching resistance of Portland cement paste where calcium hydroxide dissolution enhances diffusion. On the other hand, low cement contents reduce neutralisation capacity and can affect the loss of corroded material (pop-outs), especially during abrasion.

The effect of silica fume and fly ash on corrosion resistance is essentially due to their residual volume in the corroded layer and the contribution of their hydration products to neutralisation capacity. Thus in most cases silica fume does not significantly improve the corrosion resistance of concrete [3,4]. However, improvements in acid resistance with silica fume and fly ash have been achieved by concrete designed to maximise particle packing, e.g. Ref. [10].

3.1. Diffusion potential and chemical activity

The different diffusivities of the ions in the pore solution lead to charge separation and an electric diffusion potential ψ whose local values may be found from the electrical charge density ρ distribution according to the Poisson equation, see Ref. [11].

$$\frac{\partial^2\psi(x)}{\partial x^2} = -\rho(x)/\varepsilon \qquad (5)$$

Here ε is the dielectric constant of the medium. The flux of ions due to the diffusion potential is

$$J_i^{\psi} = -D_i^{\mathrm{eff}} c_i \frac{z_i F}{RT}\frac{\partial\psi}{\partial x} \qquad (6)$$

where F is the Faraday constant, R the universal gas constant, z_i the valence of the particular species and T temperature.

Since pore solutions are concentrated electrolytes, ionic activities rather than concentrations are required for the calculation of diffusion flux as well as dissolution, precipitation and dissociation processes. However, if effective diffusion coefficients of the corroded layer can be experimentally determined under conditions near the real pore solution their values include the effects of activity and charge separation. Thus rigorous calculation of activity coefficients for a particular solution composition may not be necessary.

4. The acid

In order to simulate the corrosion process, the chemical composition of the particular attacking medium must be taken into account. The strength of attack depends on the ability of the acid to dissociate and the solubility of its calcium salt [12]. Thus although acetic acid dissociates far less readily than mineral acids its strong attack is attributed to the high solubility of calcium acetate. When concrete is attacked by sulphuric acid, gypsum precipitates in the corroded layer reducing the acid ingress [2]. However, in this case expansion and disintegration of the surface concrete will eventually take place.

Acids attacking concrete may be divided into strong highly dissociated mineral acids and weak poorly dissociated organic acids and their buffer solutions. The pH of the acid is determined by the equilibrium between the dissociated protons and acid anions with the non-dissociated acid molecules as defined by the dissociation constant of the acid K_d.

$$K_\mathrm{d} = \frac{c_\mathrm{H} c_\mathrm{X}}{c_\mathrm{HX}} \qquad (7)$$

The different diffusivities of the acid species within the pore system and the consumption of protons continually disturb this equilibrium. It is therefore necessary to be able to calculate new solution equilibria in the corroded layer in the course of corrosion.

As opposed to strong mineral acids, weak organic acids lead to buffering effects which can affect the rate of corrosion. Buffer solutions can be—despite a relatively high pH—very aggressive. This is because a large quantity of undissociated acid molecules is able to enter the corroded layer and be available at the reaction front for the replacement of protons consumed in the neutralisation reaction. In the case of non-buffered acids, proton replacement is governed by diffusion through the corroded layer.

5. Acid resistant aggregate

If concrete is made with acid resistant aggregate such as quartz only the cement paste matrix is vulnerable to acid attack. The rate of corrosion will be affected by the presence of aggregate particles embedded in the paste matrix and will therefore be different for mortar or concrete compared with the pure hardened binder. Thus Pavlík and Unèík [3] observed a systematic decrease in corroded layer thickness with the sand content of mortar exposed to 0.2 mol/l nitric acid.

A precise description of corrosion should be based on the combined effects of aggregate and binder on transport and neutralisation capacity.

The diffusion path of ions through the corroded layer is governed by the continual changes in direction caused by the aggregate particles [12]. The degree of tortuosity due to aggregate particles depends on the amount of aggregate and its grading curve for the particular mix. Although larger quantities of well-packed acid resistant aggregate increase tortuosity, the neutralisation capacity of the concrete as a whole is lower. At Berlin Technical University a concrete (SRB 85/35, *S*äure*r*esistenter *B*eton=acid resistant concrete) with high resistance against acid attack was developed for power station cooling towers [10]. This was achieved by the experimental optimisation of the mix for the densest packing of aggregate and binder particles over their range of particles sizes. This resulted in binder contents below those of conventional high performance concrete. Slabs subjected for 6 months to sulphuric acid (approximately pH 2) showed virtually no signs of corrosion.

Considering that acid attack takes place at the surface of concrete components, the higher binder content and spatial distribution of aggregate particles of the near-surface concrete may also affect the rate of corrosion. The variation of binder content with depth is also known to affect chloride binding and consequently ingress into concrete [13].

6. Soluble aggregate

If concrete is made with reactive carbonaceous aggregate such as limestone or dolomite other factors besides those discussed for acid resistant aggregate must be considered.

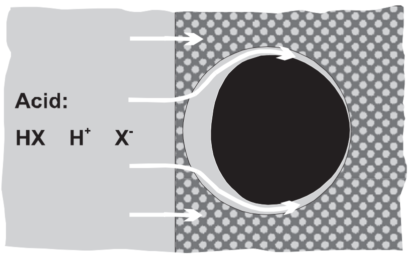

Fig. 4. Partially corroded aggregate particle with a water-filled surface layer embedded in the corroded layer.

As opposed to quartz aggregate, the neutralisation capacity of concrete made with limestone aggregate will, in general, increase with the volume fraction of calcite. This is because calcite contains much more dissolvable carbonate than the binder. However, the potential neutralisation capacity of the aggregate is not available at all times because the reaction between the acid and aggregate with low porosity takes place at the aggregate surface adjacent to the pore solution. In general, the dissolution is controlled by surface reactions and the transport of the dissolved reactants and products through a solvent boundary layer, see Ref. [14]. For calcite and dolomite at pH values above approximately 4.0 the surface reactions dominate. The surface area normalised dissolution rate is given by

$$r = k_a c_H^n \tag{8}$$

where c_H is the proton concentration adjacent to the mineral surface and k_a the rate constant. The exponent n is the order of the reaction. Thus aggregate dissolution is determined by the reactivity of the aggregate, the severity of attack and the size of the particles. Smaller aggregate particles will tend to dissolve first and be replaced by water-filled holes [15] whereas larger particles will diminish in size and, on average, acquire a water-filled surface layer.

Depending on their size, coarser aggregate particles may be in different stages of corrosion over their width, i.e. the thickness of the water-filled layer will be thicker at the side facing towards the oncoming acid and thinner at the opposite side, Fig. 4. Moreover, the diffusion of acid through the water-filled layer can act as a means of transporting acid to greater depths, accelerating corrosion. In laboratory tests we have observed that aggregate corrosion enhances the detachment of surface aggregate particles and worsens the mechanical integrity of the corroded layer.

Since the water-filled space left behind by dissolved aggregate material will enhance diffusion, a coefficient κ_a is required for the different types of soluble aggregate describing the volume created by the dissolution of $CaCO_3$ or other carbonaceous materials. The diffusion flux will also be affected by the change in diffusion path around the dissolved aggregate particles. On complete dissolution tortuosity is removed.

The above effects will be modified by the particle size distribution of the near-surface concrete.

The neutralisation capacity provided by the aggregate appears to be a quantity which can be optimised with respect to diffusion and dissolution processes. According to experiments with nitric acid at pH 0.7 [15] aggregate which dissolves at a slower rate than the paste matrix (travertine) can result in concrete corrosion rates which are slower than those with acid resistant quartz.

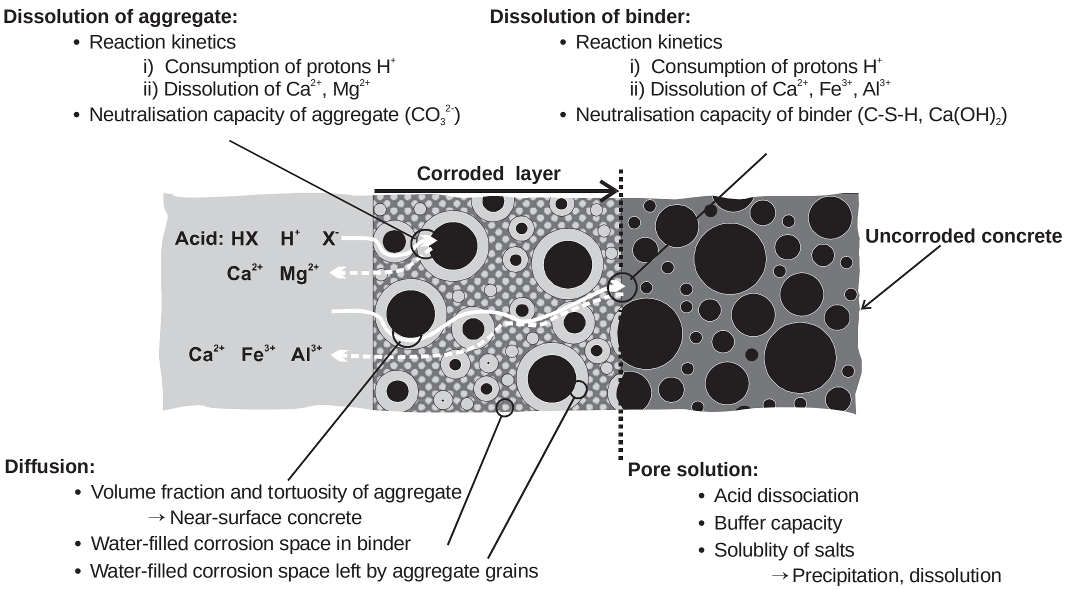

Fig. 5. Summary of processes affecting the corrosion resistance of concrete.

7. Precipitation processes

Changes in the porosity of the corroded layer due to precipitation of calcium salts, ferric or aluminium hydroxides and their various derivates formed with acid anions are possible. This can reduce the diffusion flux as exemplified by gypsum precipitation during sulphuric acid attack. Pavlík [2] attributed a brown zone, formed adjacent to the undamaged material during exposure of hardened Portland cement paste to nitric or acetic acid, to the diffusion of Fe^{3+} ions and the subsequent precipitation of ferric hydroxide at pH values above 2. Our tests have shown that iron and aluminium compounds within the corroded layer dissolve slowly at for example pH 4.5 and are subsequently removed by diffusion into the external acid [4]. In view of the relatively low content of iron and aluminium in Portland cement based binders the volume of precipitate will probably be relatively small.

8. Abrasion

Abrasion enhances aggregate particle pop-outs and leads to the removal of material from the surface of the corroded layer, the amount depending on the severity of abrasion and the strength of the layer. Continuous complete removal would mean that the rate of corrosion is determined by the kinetics of the neutralisation reaction. This would result in extremely high rates of corrosion which are not observed in most application environments. Abrasion effects are difficult to model, but could be simulated by assuming an upper limit on corrosion layer thickness adjacent to the undamaged concrete which is valid at all times.

9. Conclusions

The optimisation of concrete composition to maximise acid resistance is not necessarily achieved by the application of strength criteria, e.g. high cement content, low w/c ratio. In Germany acid resistant concrete has been designed successfully with quartz aggregate by maximising particle packing which resulted in low binder contents [10]. In the case of normal concretes a certain degree of aggregate reactivity may even be advantageous [15].

The corrosion rate of concrete is a complex process governed by the combination of dissolution, precipitation and transport processes as determined by cement chemical composition (especially calcium content), paste matrix reactivity, aggregate reactivity, grading curve and concrete composition. The corrosion rate may also be affected by the spatial packing of aggregate particles and variation of binder content over the near-surface concrete layer. The abrasion of the corroded layer and the pop-out phenomenon will modify the effect of these processes and thus the rate of corrosion. The main mechanisms are summarised in Fig. 5.

Currently, a computer model is being developed which is aimed at the prediction of the corrosion of concrete construction components of known composition attacked by acidic solutions with pH values ranging between 4.0 and 6.5, i.e. exposure classes XA3, XA2 and XA1 according to DIN EN 206-1. The concrete may contain Portland or Portland blastfurnace cement with dissolvable or acid resistant aggregate. Calcium aluminate cement will also be considered. The effect of the processes in Fig. 5 will be included in the model. The degree of corrosion is defined by the thickness and porosity of the corroded layer and, if abrasion effects occur, the thickness of removed material. The model will be described in detail in forthcoming publications.

Acknowledgements

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