ACIDIC CORROSION OF HYDRATED CEMENT BASED MATERIALS

PART 2. - KINETICS OF THE PHENOMENON AND MATHEMATICAL MODELS

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FACTORS INFLUENCING THE KINETICS OF THE PHENOMENON

The rate of the total process of deterioration of acid attack may be more or less influenced, i.e. accelerated or inhibited, by a number of factors. All of these factors can be classified into three groups as follows:

- Factors related to acid or acidic solution including strength of acid, solubility of its calcium salt (aluminum salt in the case of HAC), concentration of acid or *pH* value of the acidic solution, diffusivity of acid and its calcium salt, and mobility of the acidic solution.
- Factors related to cement or cement based material including type of cement i.e. chemical composition and mineralogy of hydrated phases and their thermodynamic stability limits in acidic media, stability and thickness of the corroded layer, permeability of the material, cement content of the material, curing time and conditions, neutralizing capacity of the material, and influence of aggregate.
- Other factors including temperature, and capillary suction forces acting under the condition of alternative cycles of exposure and drying.

Factors related to acid or acidic solution

Strength of acid and solubility of its calcium salt

One of the rate controlling factors is acid strength. Strong acids fully ionizing in water appear to have the same strength (i.e. leveling effect of water). The strength of weak acids can be expressed in terms of their equilibrium constants describing the extent of ionization reaction. For the general mono-proton weak acid HA:

$$HA(aq) + H_2O(l) \Leftrightarrow H_3O^+\ (aq) + A^-(aq)$$
$$K_a = [H_3O^+][A^-]/[HA]$$

where K_a (i.e. equilibrium constant) is known as the acid dissociation or ionization constant.

The severity of the acid attack, in addition to dissociation ability of the acid, is significantly dependent on the solubility of the calcium salt formed . When a highly soluble calcium salt is formed e.g. calcium chloride and calcium nitrate, it is removed by leaching into the acidic solution, and the other corrosion products generally remain and form a sparingly soluble layer of corrosion products with increased porosity and relatively weak diffusion resistance [25, 26, 33, 34, 35, 36, ...]. The porosity of the corroded layer is extremely high. Bajza *et al* [27, 29, 30, 31] reported a porosity of nearly 80% for completely corroded hardened cement paste specimens with a water/cement ratio of 0.4 in 3 vol.% solutions of acetic and formic acids. On the other hand, there are acids e.g. sulfuric, phosphoric and oxalic acids which give rise to the formation of less soluble or almost insoluble calcium salts which remain in the corroded layer and increase its resistance to diffusion [33, 34, 35, ...]. In such a case, the process of deterioration is inhibited or almost stopped due to the protective effect of the corroded layer. It means that under the influence of a stable corroded layer the corrosion rate of a strong acid can be lower than that of a weak one. As it confirmed by Pavlík [33] nitric and hydrochloric acids are the most aggressive ones due to both their dissociation ability and high solubility of their calcium salts whereas sulfuric acid is less aggressive than acetic acid due to significantly lower solubility of calcium sulfate i.e. 2.4 g kg^{-1} compared to that of calcium acetate i.e. 374 g kg^{-1}. However as it is mentioned previously for the case of attack by sulfuric acid some authors [38, 41, 48, 49, 50] reported that extensive formation of gypsum not only does not provide any protective effect but also tends to cause expansion and high internal stresses which ultimately lead to spalling and exposure of the fresh surfaces.

In a series of papers [26, 33, 34, 35], Pavlík studied the rate of corrosion of hardened cement paste made from OPC with *w/c* = 0.4 in solutions of different inorganic and organic acids including nitric, hydrochloric, sulfuric, acetic, and formic acids. The results

[33] confirmed that the primary factor controlling the rate of corrosion is the solubility of the calcium salt of the acid and not the acid strength. The results also showed that the aggressive effect of acids forming easily soluble calcium salts depends to a large extent on their acidic strength.

In an another experimental work [63] on durability of HAC in 12 different types of acidic media, similar results were obtained. Therefore it can be said that the acid strength is a secondary factor in the process of acidic corrosion.

Concentration of acid or pH value

The results reported in the literature [33, 46, 63, 65] indicate that intensity of aggression increases with an increase in acid concentration, except some anomalous behavior observed in the case of sulfuric acid. Hendrik and Orbison [53] investigated the effect of sulfuric acid concentration on concrete specimens. Concrete cylinders of nearly 21 to 62 MPa strengths made from ASTM type I PC, a blend of calcareous and noncalcareous coarse aggregate, silica sand, and chemical admixtures were exposed to simulated solutions of acidic rain with *pH* values of 2, 3, 4, and 5. The solutions were prepared by adding concentrated sulfuric and nitric acids to distilled water in a two-to-one ratio respectively and weight loss was used as the criterion for the extent of deterioration in a 90 days period of immersion. The $pH = 3$ solution produced a greater degree of deterioration than $pH = 2$ solution in all except the 62 MPa specimens.

The resistance of the corroded layer to diffusion depends also on the concentration of the acidic solution. An increase in the concentration may result in a variation in the composition of the corroded layer due to increased decalcification or dissolution of corrosion products e.g. aluminium and ferric hydroxides.

Since measurement of *pH* value is more easier than that of the concentration, it is very often to use *pH* value for determining the acceptable limits of acidity without any considerable corrosive effect. However it is to be considered that every acid has its own acceptable limits due to its acidic strength. Strong acids like nitric or hydrochloric acids have lower values for *pH* limits than weak acids like acetic or lactic acids [33, 44, 63]. This is due to the fact that to achieve a given *pH* value, a much higher concentration of a weak acid is needed than that of a strong acid.

Diffusivity of acid and its calcium salt

It is well known that different acids have different diffusivities in the pore structure of the cement matrix. Formation of the core layer [26, 38] in the case of attack by acetic, nitric, hydrochloric, and ethanoic acids and the conclusion confirmed by many authors [38, 40, 52, 53] that in the case of attack by sulfuric acid chemical changes are restricted to the regions close to the surface, are due to the existence of such differences. Diffusivity of soluble calcium salt also plays an important role, because the reaction between acid and cement hydrates is probably extremely rapid compared to diffusion process of calcium salt.

However it must be considered that diffusion process is dependent not only on the activity gradient between the pore and the external solutions, but also on the microstructure of the cement matrix. As it is confirmed by the experimental results, a reduction in w/c ratio which leads to a finer pore size distribution, reduces diffusivity of acid and its calcium salt and thus slows down the process of degradation.

Mobility of the acidic solution

It is worth noting that in practice failures of concrete due to attack by acidic groundwater have only been reported when there is a constant flow of groundwater [15]. Such a condition exposes the concrete to a continuous flow of fresh acidic solution. On the other hand it is to be noted that attrition due to high velocities of the flowing groundwater may disturb the stability of the corroded layer.

According to Grube and Rechenberg [36], in freely flowing groundwater the flow rate has a greater influence than the acid concentration. Presenting practical results on depth of dissolved concrete after 20 years exposure to different concentrations of dissolved carbon dioxide and at different external conditions of exposure, they reported that in a compact soil with a permeability coefficient of $K<10^{-4}$ cm s^{-1} and a very slowly moving or stagnant groundwater the chemical attack is negligible whereas in a more permeable soil with a freely flowing groundwater the loss of mass increases significantly depending on the velocity of the flow.

In fact in a stagnant acidic solution, with the progress of the corrosion reaction the acid present in a layer of solution adjacent to the surface of the cement matrix will be consumed resulting in an increase in the concentration of dissolved components. The adjacent layer of the solution therefore approaches chemical equilibrium and this influences the course of corrosion.

Factors related to cement or cement based material

Type of cement

Cement is composed of at least four major phases which possess different chemical identities, and therefore different chemical resistances. Concretes made with cements of high C_3S content which show a higher 28-days compressive strength need a higher *w/c* ratio and hydrate faster. With a higher *w/c* ratio, the pore size distribution contains larger and probably more interlinked pores [67]. On the other hand hydration of such a cement will result in a higher content of calcium hydroxide which is more vulnerable to attack by acid and is believed to be the initial point of attack in OPC based materials. Therefore such a larger and interlinked pore structure along with a higher content of $Ca(OH)_2$, is more easily permeated and attacked by aggressive solutions [67, 68]. In addition to these major phases, there are some minor constituents which also influence the cement properties. Partial replacement of cement by pozzolanic admixtures or addition of either pozzolanic or chemical admixtures, also can significantly affect the strength and durability of cement based materials. In general, the type of cement and the content of pozzolanic or chemical admixtures are among the more important factors responsible for the strength and durability of cement based materials. Many authors [21, 22, 23, 28, 39, 40, 41, 42, 45, 56, 57, 69, ...] claimed that in the process of acid attack, the extent of deterioration in a given period of time varies among different cement based specimens due to differences in their mix composition i.e. cement type or admixtures used.

Contrary to the authors who reported the potential of pozzolanic admixtures in enhancing the acid resistance of cement based materials, a number of authors [15, 20, 27, 31, 34, 43, 51, 68, ...] claimed that the use of pozzolan blended cement had no or a very less positive effect. In fact the reported data in the literature are contradictory on whether cements containing pozzolanic materials are effective in improving the acid resistance. However it is to be considered that when dealing with the effect of pozzolanic admixtures on durability of cement based materials, in addition to the type, the amount, and the fineness of pozzolanic admixture, the type of cement, and especially the curing time and conditions are among responsible factors which must also be considered.

In comparison to the OPC and its usual derivatives, there are a number of special and new cements or cementitious binders possessing considerably much higher acid resistance. The extensive use of high alumina cement for construction of sewer pipes and pipe linings has proved that well designed and made HAC-mortars and concretes withstand not only aggression from sulfate bearing environments, but also biogenic sulfuric acid attack from sewerage [71]. The good performance of HAC-concretes compared to that of OPC-based systems can be attributed not only to the absence of calcium hydroxide and the presence of more stable calcium aluminate hydrates, but also to the formation of aluminum hydroxide in the course of acidic corrosion which encapsulates and protects the hydrates [18, 72, 73]. Traditional applications of HAC have been reported for acidic environments of *pH* down to about 4. However recent studies have shown that based on the solubility of $Al(OH)_3$, the usefulness of HAC in such environments can be extended to *pH* levels well below the traditional limits [63, 72]. In a series of laboratory investigations by Schmidt *et al* [18, 19], using a new type of testing equipment and based on the results of weight loss it was concluded that the resistance of mortars made with HAC to attack by biogenous sulfuric acid is up to ten times higher than that of mortars made with OPC. Exposure of hardened HAC-paste to acidic solutions of low concentration (*pH* values higher than 3.5) usually results in an increase in weight [63, 66] due to precipitation of complex calcium aluminates such as calcium monocarboaluminate and calcium monosulfoaluminate.

Pore reduced gypsum free Portland cement (PRGFPC) is a new cement developed in Czech Republic [7, 8, 9]. It is a very low porosity hydraulic binder based on finely ground PC clinker with addition of an anion-active surface active agent and an inorganic salt for regulating setting process [7]. Although chemical composition of PRGFPC is not very different than that of OPC, the properties of which are different. Rapid strength development and higher final strength, along with a better corrosion resistance to aggressive media (salts, low and high *pH*) are among the superior properties of PRGFPC [7]. The resistance of both OPC and PRGFPC mortars to sulfuric acid were compared by Škvára [9]. Mortars of approximately identical workability were prepared and after 24 hrs of hydration were placed in 5 vol.% solution of sulfuric acid. The results showed that the corrosion rate was much lower for mortar specimens of PRGFPC. The author attributed the superior properties of PRGFPC to different mineralogy and microstructure of its hydration products [7]. The absence of crystalline formations together with the high density and high degree of dispersion of all hydration products and considerably lower porosity are among the mineralogical and microstructural characteristics of hardened pastes of PRGFPC [7].

In the past decades, the use of alkali-activated cementitious materials has significantly been increased not only due to their potential in reducing CO_2 emission from manufacture of PC, but also due to their long-term engineering properties. Alkali activation process which was originally limited to slag cements, recently has been extended for several industrial by-products and wastes. Recent investigations [10, 11, 12, 13, 14, 75, 76,...] on some of these materials suggest that alkali activation results in the formation of an aluminosilicate phase.

Aluminosilicate hydrates can be formed by mixing some alkaline activator with a wide variety of silicate and/or aluminum rich minerals such as ; clay, ground rock, ash, and slag [10, 11, 12, 13, 14, 75]. The effect of alkali activators such as NaOH, Na_2CO_3 or Na_2SiO_3 on hydraulically active substances is based on disintegration of Si-O-Si bonds, yielding hydrates of alkali-calcium aluminosilicates similar to zeolites, apart from C-S-H phase hydrates, gehlenite hydrate and hydrogarnates [12]. The nature of these binders and their engineering properties have been discussed in a number of papers [10, 11, 12, 13, 14, 75, 76, 77, ...]. Malek, and Roy [75] attributed the higher compressive strength and durability of aluminosilicate structures to the fact that they exist in three dimensional network which encompass the entire structure through chemical bonding. Such a structure is harder and more durable than hydrated PC in which the strength is mostly mechanical through foiled sheets of calcium silicate hydrate. Škvára and Bohuněk [12] achieved compressive strengths of 120 to 170 MPa by activating mixtures of ash-slag. Rostami, and Silverstrim [13, 14], developed an alkali-activated material, called as Chemically Activated Fly Ash (CAFA), by activating

Class F fly ashes. They tested CAFA concrete [13, 14] for durability properties. The resistance of CAFA concrete to chemical attack by acids such as sulfuric, nitric, hydrochloric, and organic acids is claimed to be far better than that of PC concrete [13]. According to Silverstrim *et al* [14] CAFA specimen exposed to 70 vol.% nitric acid for 3 months retained its dense microstructure.

Stability of the corroded layer

Another important factor which significantly influences the rate of deterioration is stability of the corroded layer. It is to be considered that stability of the corroded layer may be significantly influenced either by its low content of SiO_2 and/or by the presence of external mechanical effects i.e. attrition caused by high flow rates of the aggressive fluid. In general there are two extreme possibilities. The corroded layer may be stable due to its high content of SiO_2 and/or to the absence of any external mechanical effects. Such a condition can be seen in the case of concrete exposed to acidic groundwaters with limited rates of flow [36]. The developed corroded layer is called a protective layer because of its action as a barrier to the transport of acid molecules and/or ions to the corrosion front and also removal of dissolved constituents from the material. In the presence of a stable protective layer the course of corrosion, i.e. corrosion depth or weight loss, with time follows a parabolic function [25, 29, 30, 33, 35, 36].

The other extreme possibility for the corroded layer is the case where it is removed continuously without any considerable growth. Such a possibility can happen in the cases where concrete is exposed to the aggressive acidic solutions of very high velocities or turbulent flows [36]. In such an external conditions it is to be expected that the parabolic function turns to a linear one. There are also some cases in which the corroded layer is removed regularly e.g. acidic corrosion of concrete by feed acids in animal houses [21, 22, 23] or by flowing acidic waters of medium velocities [36]. Grube and Rechenberg [36] investigating the influence of external mechanical effects on the kinetics of the acidic corrosion of the concrete, showed that a disturbance of the protective layer, even if it occurs at relatively long intervals, can have a much more damaging effect than an increase in the concentration of the aggressive acid. Therefore when dealing with the kinetics of the acidic corrosion of the concrete under practical conditions, in addition to the type and concentration of the attacking acid and the composition of the concrete, the stability of the corroded layer must also be considered.

Permeability of the material

Laboratory studies and field experiences have shown that durability of cement based materials in aggressive chemical environments is closely related to their permeabilities. Mehta [78] claimed that the rate determining step in the process of degradation is the ingress of the chemical into the concrete, and thus permeability reduction is likely to be the key factor in imparting increased durability.

Now let us consider the influence of permeability on the kinetics of degradation due to acid attack. According to Moskvin *et al* [79] permeability of the uncorroded part of hardened cement paste does not play any role in the process of acidic corrosion. Pavlík and Unčík [34] claimed that since the H^+ ions can not simply diffuse via the pore fluid in the uncorroded part of the hardened cement paste, it is the diffusion resistance of the corroded part that determines the rate of diffusion of H^+ ions into the reaction zone of the cement matrix composite. Israel *et al* [38] who investigated the resistance of pore reduced (PR) and OP cements in sulfuric, hydrochloric, and ethanoic acids with concentrations of 0.2, 0.27, and 0.05 mole/liter respectively, claimed specific interaction with regard to interconnected porosity. After 1 year immersion, attack by hydrochloric and ethanoic acids both resulted in the formation of portlandite free zone (the core-layer reported by Pavlík [26]), and cracks parallel to the surface in OPC and PRC paste specimens respectively. BSE micrograph of cracks proceeded through the core of PRC paste specimens showed altered paste similar to the corrosion products, i.e. silicon rich gels and hence they concluded that attack by hydrochloric and ethanoic acids predominantly proceeds via penetration into the interconnected pores and fissures. They claimed that the reduced porosity of PRC compared to OPC reduces the susceptibility to attack by such a mechanism. In the case of attack by sulfuric acid, both PRC and OPC paste specimens were damaged to almost the same extent due to a different mechanism of degradation. The extensive gypsum precipitation on the cement surfaces occurring with sulfuric acid attack results in mechanical stresses which finally lead to spalling, i.e. loss of material and exposure of fresh surfaces. Since such a mechanism predominantly happens on the external surfaces, the dense microstructure of PRC has no benefit to this kind of attack. Therefore when dealing with the influence of permeability on the kinetics of degradation due to acid attack, in addition to the microstructural characteristics of the cement matrix, the type of acid also must be considered.

Cement content of the material

In the process of acidic corrosion, generally the amount of acid consumed for corrosion of a unit volume of a given specimen is proportional to its cement content. Pavlík [35] investigated the influence of *w/c* ratio, i.e. cement content, on the corrosion process of hardened cement paste by acetic and nitric acids. He reported that the rate of corrosion decreases with an increase in the cement content per unit volume of hardened cement paste. The author stated that there are two main causes accounting for this fact. The increased neutralization capacity of the matrix and the increase in diffusion resistance of the corroded layer.

For the case of attack by sulfuric acid, however it is to be considered that an adverse influence have been reported. Hendrik and Orbison [53] arrived at the conclusion that concrete containing a higher cement content is more vulnerable to deterioration by sulfuric acid attack. Later Fattuhi and Hughes [46, 65, 69] studied the influence of a number of parameters including cement content on the process of sulfuric acid attack. They also concluded that the generally recommended practice of using a relatively high cement content for concrete subjected to sulfate attack will produce a negative effect when concrete is subjected to sulfuric acid solution of 1 vol.% or higher concentration. The authors attributed such an adverse effect to the formation of gypsum layer which were thicker and more difficult to brush from the surfaces of specimens with higher *w/c* ratios or lower cement contents. They further stated that sulfuric acid attacks the calcium hydroxide which has a higher content in cement pastes with lower *w/c* ratios or higher cement contents. In our opinion however, in addition to the above reasons an increased *w/c* ratio which result in a higher total porosity probably to some extent may work like an air-entraining agent in partially relieving internal disintegrating stresses due to precipitation of gypsum crystals in the regions close to the surface.

Curing time and conditions

As it is previously mentioned a number of laboratory tests [15, 20, 27, 31, 43,...] resulted in the conclusion that the use of pozzolanic admixtures had no or a very less positive effect in improving the resistance of cement based materials to acid attack. However it seems that in some cases such a conclusion may be due to insufficient curing time and/or improper curing conditions. It is to be noted that contrary to PC with a hardening process nearly complete after 28 days, blended cements are usually characterized by a prolonged later hardening process.

Fattuhi and Hughes [46] investigated the effect of curing time. They immersed a number of 7, 14, and 28-days water cured paste and concrete specimens made from OPC in a channel containing continuously flowing solution of 2 vol.% sulfuric acid up to a maximum period of 50 days. The results of weight loss for cement pastes ($w/c = 0.417$) showed that when the curing time increased from 7 to 28 days, the weight loss after an exposure period of 48 days was reduced to 75%. The effect of age was slightly more significant for cement paste than for concrete cubes.

Ravindrarajah and Mercer [42] compared the effects of air and water curing conditions on the resistance of 560 days old high strength concretes made from Portland BFSC and OPC with and without partial replacement by silica fume to 5 and 15 vol.% sulfuric acid solutions. Comparison of the relative weight loss between air-cured and water-cured specimens after 84 days of acid attack indicated that air-cured concrete had better resistance to sulfuric acid than water-cured concrete particularly at high concentration of acid. The results also showed that concrete mixes with silica fume were less sensitive to the curing condition than those without silica fume.

Neutralizing capacity of the material

One more factor to be taken into consideration in the process of acidic corrosion of cement based materials is the capacity of the material to neutralize the acidic solution. This factor is very important when the material is to be exposed to a limited volume of acidic solution. In fact limited amount of acids can be neutralized by the material before any degradation occurs. It is previously mentioned that in acidic groundwaters practically concrete degradation have only been reported when there is a constant flow of acidic water [15]. Such a flow in addition to the possibility of washing away any reaction products causes a continuous replenishment of acid which can eliminate the neutralizing effect of concrete.

The capacity of a cement based material to neutralize an acidic solution depends not only upon its cement content, but also upon the chemical and mineralogical characteristics of the cement it is made with. In an experimental work on the effects of 1 vol.% hydrochloric acid on mortar specimens made with OPC, PC without C_3A and a BFSC, Ceukelaire [28] compared the neutralizing capacity of the mortar specimens during a limited period. It took about 7 days for *pH* to reach the neutral value when mortars of OPC and PC without C_3A were immersed. For the case of mortar made with BFSC, the *pH* value rose more slowly and the neutral value was reached after 14 days. The author stated that the lower neutralizing capacity of BFSC mortar is due to its lower alkali content and to its lower capacity to produce calcium hydroxide.

Based on a different reference (unpublished work), George [73] reported the comparative neutralization capacity of high alumina and PC systems. He claimed that a given level of attack requires nearly 70 vol.% more acid in the case of HAC than for a PC based material and this in practice would translate into a much longer service life.

Influence of aggregate

Pavlík and Unčík [34] investigated the influence of aggregate shape and size on the acid resistance of cement matrix composites. A number of cement mortar specimens prepared with laboratory glass balls of equal size and with graded silica sand of different fineness after a 28-days period of water curing, were subjected to attack by 0.2 mol l^{-1} solutions of nitric and acetic acids. The rate of corrosion of mortar specimens was lower than that of paste specimens and the incorporation of smaller, angular and evenly dispersed sand particles was more effective than that of glass balls.

Pavlík related the difference between the corrosion rates of cement paste and mortar specimens to the positive effects of sand particles in reducing the size and the number of cracks in a unit volume of the corroded layer and reducing the amount of shrinkage in this layer. He further mentioned the positive effect of sand particles to increase the diffusion pathway of the acid in the corroded layer due to a tortuosity effect which in turn results in a lower rate of acid transport and consequently a lower rate of corrosion.

In addition to the shape and particle size, aggregate type also plays an important role particularly when the amount of attacking acid is limited. Bayoux *et al* [63] measured weight losses of HAC-mortars made with siliceous and calcareous aggregates and immersed in a sulfuric acid solution with a $pH = 1$. The authors reported that calcium carbonate aggregates were better than silica, because they neutralize the acidic solution which in turn results in a lower extent of decomposition of cement paste. They call these reactive aggregates sacrificial because the acid is more quickly neutralized and reaches a pH less harmful to the interstitial cement paste. Belie *et al* [22] also reported similar results for the influence of the gravel and limestone aggregates on the acid resistance of HAC-concrete exposed to limited amount of feed acids.

Other factors

Temperature

Mehta [39] evaluated the effect of temperature on the acid resistance of a number of concrete specimens to solutions of 1 vol.% HCl, 1 vol.% H_2SO_4, 1 vol.% lactic acid, and 5% acetic acid. He reported that data from immersion tests at 45 °C were not significantly different from those at 20 °C. However Bayoux *et al* [63] investigating the effect of temperature on the corrosion rate of HAC-mortars immersed in 0.1N solutions of acetic, lactic and sulfuric acids concluded that the temperature effect is sensible only when the solubility of calcium salt of acid is low. The authors reported that an increase of temperature from 20 to 40 °C does not modify significantly the rates of attack by acetic and lactic acids whereas the rate of attack by sulfuric acid is increased by about 25%.

Herold [80] investigated the effect of temperature on dissolution behavior of hardened OPC paste specimens in solutions of hydrochloric acid at different pH values. He claimed that the plot of measured dissolution rates versus $1/T$ leads to a straight line and hence the equation of Arrhenius is valid. He further calculated the effective activation energy of dissolution reaction for a number of H_3O^+ concentrations at a given temperature range.

Capillary suction forces

The process of acidic corrosion of cement based materials can be accelerated by capillary suction forces when the material is under the action of alternative wetting and drying cycles. During wetting period acid enters the material due to capillary action, permeation and diffusion and when the material undergoes drying period, microcracking due to drying shrinkage results in a higher permeability [38, 40]. The effect of capillary suction forces in accelerating the rate of concrete deterioration due to acid attack was confirmed by Attigobe and Rizkalla [40] and Sersale *et al* [20].

MATHEMATICAL MODELS

Whenever a cement based material is to be exposed to acidic environments, it is necessary to assess the extent of corrosion over long periods of time to have an estimation of the material service life. A number of mathematical models have been developed for such a purpose. These models are of two groups ; empirical equations based on regression analysis of experimental results and theoretical equations based on theoretical analysis of the corrosion process.

Empirical equations

Most of the empirical equations published so far express the extent of corrosion (i.e. corrosion depth) of hardened cement pastes as a function of two factors ; the concentration of the acidic solution and the time of exposure.

For the corrosion of hardened PC pastes with a *w/c* ratio of 0.4 in 0.5- 5 vol.% solutions of formic acid during 1-1460 days of exposure time, Bajza [30] presented the following equation:

$$d(\mathrm{mm}) = 0.174C^{0.579}\, t^{0.583}$$

where C = acid concentration (vol.%), t = exposure time (days)

Pavlík [33] investigating the corrosion of hardened OPC paste with a *w/c* ratio of 0.4 by solutions of acetic and nitric acids with concentrations ranging from 0.025 to 0.5 mol l^{-1} presented the following equations:

for corrosion by acetic acid: $d\ (\mathrm{mm}) = 1.232C^{0.525}t^{0.52}$
for corrosion by nitric acid: $d\ (\mathrm{mm}) = 4.11C^{0.7}t^{0.56}$

in which C = acid concentration (mol l^{-1})
t = exposure time (days)

Herold [80] presented an equation for dissolution of hardened OPC pastes with *w/c* = 0.5 in solutions of hydrochloric acid at different pH values:

$$m = kC^{0.4074}t^{0.5572}$$

where m = dissolved amount of CaO (g m^{-2}), C = acid concentration (mol l^{-1}), t = exposure time (min), $K = a$ constant depending on pH value

Theoretical equations

By means of models based on Fick's laws of diffusion a number of equations were developed for calculating the extent of corrosion. Grube and Rechenberg [36] developed a model to describe concrete deterioration due to carbonic acid attack:

$$d = [2D(A_l/A_{ges})(C_s-C_l)t/m_l]^{0.5}$$

in which d = thickness of destroyed concrete layer (cm), D = diffusion coefficient of $Ca(HCO_3)_2$ in the protective gel layer ($cm^2\ s^{-1}$), m_l = mass of soluble matter (CaO) per cm^3 of concrete (g), C_s = $Ca(HCO_3)_2$ concentration in the solution surrounding intact concrete ($g\ cm^{-3}$), C_l = = $Ca(HCO_3)_2$ concentration in solution unaffected by the concrete ($g\ cm^{-3}$), A_l/A_{ges} = ratio of soluble matter area to total area, V_l/V_{ges} = ratio of the volume of soluble constituents (volume of hardened cement paste if insoluble aggregate is used) to total volume (A_l/A_{ges} = = V_l/V_{ges})

CONCLUSIONS AND REMARKS

Ordinary Portland cement and its usual derivatives which are highly alkaline are more or less vulnerable to attack by acidic solutions.

Mechanism of the acidic corrosion of hydrated Portland cement consists of subsequent dissolution of portlandite and hydration products and formation of the corresponding calcium salt of the attacking acid as well as hydrogels of silicium, aluminium and ferric oxides.

In the process of acidic corrosion of hydrated cement based materials, acid strength is not the primary factor. The severity of the attack is dependent mostly upon the solubility of the calcium salt of acid and stability of the corroded layer.

In general there are two basic modes of deterioration in the process of acid attack. In one the calcium salt of acid is soluble and is leached away into the attacking solution. This leads to loss of material, higher porosity and loss of strength. Such a mechanism not only commences on the external surfaces but also acts internally via interconnected porosity of the cement. Deterioration of the external surfaces and internal microstructure of the cement matrix respectively leads to the formation of a highly porous and cracked corroded layer which does not provide any protective effect and a portlandite free zone, i.e. the so called core-layer, in the uncorroded part. Hydrochloric, nitric and acetic acids resemble such a mode of attack. In the other deterioration mode the calcium salt of acid which is less soluble or almost insoluble remains in the corroded layer. In such a case the process of deterioration which predominantly happens on the external surfaces is inhibited or almost stopped due to the protective effect of the corroded layer. However it is to be considered that extensive deposition of insoluble salts may result in expansion and high internal disintegrating stresses leading to cracking and spalling of the corroded layer. Attack by sulfuric, phosphoric and oxalic acids are examples of such a mode of deterioration.

In addition to the strength of acid, solubility of its calcium salt and stability of the corroded layer, there are some another factors which more or less influence the kinetics of the total process of deterioration. These factors include; concentration of acid, diffusivity of acid and its calcium salt, mobility of the acidic solution, chemical composition and mineralogy of hydrated phases and their thermodynamic stability limits in acidic media, permeability of the cement matrix, cement content and neutralizing capacity of the material, curing time and conditions, aggregate type and size, temperature and capillary suction forces acting under the condition of alternative exposure and drying cycles.

Experimental results show that high alumina cement, pore-reduced gypsum-free Portland cement and in particular alkali-activated materials (aluminosilicate hydrates) exhibit comparatively higher acid resistance than ordinary Portland cement.

Here the authors would like to point out that the lack of appropriate standard and rapid test methods for assessing the performance of cements in acidic media together with the complexity of the phenomenon due to a relatively high number of rate influencing factors, make it difficult to correlate the results of the few studies available in the literature. In addition it is to be considered that still there exist many fundamental unanswered questions and technical items which need to be considered in future research activities. Some of these questions include:

1. What is the best failure criterion in the process of acidic corrosion of hydrated inorganic binders?
2. What are the critical parameters needed for predicting the rate and time of failure of concrete exposed to acidic medium?
3. Is it valid to use cement paste as a relative representative model for concrete?
4. What is the relative influence of microstructure (porosity) on the extent of corrosion compared to chemical and mineralogical aspects?
5. What are the effects of concentration of acid (*pH* value) on the extent and mechanism of the acidic corrosion?
6. How much the improvements in pore structure can be effective in reducing the rate of internal attack?
7. In the case of attack by sulfuric acid, what are the consequences of gypsum formations (inhibiting or accelerating)? Does ettringite formation has any important role in the process of deterioration?
8. What is the mechanism of acidic corrosion of new alkali activated materials (e.g. alkali-activated fly ash-blast furnace slag [12])? What is the reason for their relatively higher acid resistance and how much is the potential for increasing their acid resistance?

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