Acid attack on hardened cement paste by acids forming low soluble calcium salts

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Abstract. Solutions of acids have very aggressive effect on the cement matrix in concrete. Aggressiveness of the solutions increases with concentration of an acid but also depends on the acid type. The corrosion effect of solutions of various types of acids and their mixtures on hardened cement pastes is described in the paper. The results confirmed, that the rate of corrosion of hardened cement paste in solutions of strong acids (HCl, HNO₃) was faster than in solutions of weak acids. However, the rate of corrosion of hardened cement paste was lower in solutions of acids that produce low soluble calcium salts, because calcium salts filled the pores in the layer of corrosion products and thus increased its diffusion resistance.

1. Introduction

Solutions of acids represent a specific and very aggressive environment for buildings and constructions based on cement composites. Acid solutions attack hardened cement matrix. Carbonaceous aggregate is likewise a subject of acid attack. The occurrence of acid solutions in the natural environment is relatively rare and acidity of the environment is usually relatively low. Waters with increased natural acidity include peat waters that contain humic acids and acids produced by the plants root system. Atmospheric acid precipitation with pH values in the range of 3 to 4 also may occur. Solutions of various acids with increased concentrations may occur mainly in agriculture, industry or in waste waters. A special case is an acid attack in the sewage pipes and sewage systems that is caused by sulfuric acid originated from biochemical oxidation of hydrogen sulfide by the action of aerobic sulfur bacteria of the genus Thiobacillus.

There exist various types of acids. By their composition we distinguish between inorganic and organic acids. By their strength acids can be divided into “strong” and “weak” acids. “Strong acids” are very highly, or totally ionized in the water solutions into hydrogen cations H⁺ and corresponding anions (e.g., HCl, HNO₃, H₂SO₄). “Weak acids” are only partially ionized and establish equilibrium between the unionized molecules and ions in the solution (e.g. organic acids and carbonic acids). Acids also can be classified by solubility of their calcium salts in water (Tab. 1), because this property strongly affects the rate of an acid attack on concrete.

Specimens made of hardened cement paste (HCP) or cement mortar are often used to study the corrosion resistance of a cementitious material. All compounds of cement hydration are unstable in an acidic environment. Acids react with both, hydrated and unhydrated compounds in HCP and decompose them. The end products of the chemical reactions between the acid solution (H⁺ ions) and the cement hydration products are the calcium salts of the acid and a decalcified residue of the cement.
hydration products [1-7] (Fig. 1). If the calcium salts of the acid are well soluble in water, the ions of Ca\(^{2+}\) gradually diffuse from the reaction zone into the aggressive solution (Fig. 2). Other, less soluble or insoluble decalcified corrosion products remain on the surface of the sample where they form a porous layer of decalcified residue [3, 8-15]. The layer of corrosion products in this case consists of amorphous hydrated oxides - SiO\(_2\)\(_{aq}\), Al\(_2\)O\(_3\)\(_{aq}\), and Fe\(_2\)O\(_3\)\(_{aq}\). At a sufficiently low pH values, the hydrogels Al\(_2\)O\(_3\)\(_{aq}\) and Fe\(_2\)O\(_3\)\(_{aq}\) also gradually dissolve. The porosity of the corrosion product layer in this case is up to 80% for the paste with w/c = 0.4 [6, 8, 9].

| Acid type                              | Solubility of Ca-salts (g /100 g of water) |
|----------------------------------------|---------------------------------------------|
| HCl, HNO\(_3\), HCOOH, CH\(_3\)COOH    | High solubility                             |
| Citric, tartaric or sulfuric acid      | Middle solubility                           |
| Oxalic or hydrofluoric                 | Low solubility                              |

The aggressive effect of various acids depends on many factors, predominantly on type and concentration of an acid and also on water-to-cement ratio (and neutralization capacity) of HCP. Diffusion of aggressive substance across the layer of corrosion products to the reaction zone is the slowest stadium of the corrosion process and it is a factor that determines the corrosion rate. It is affected by the depth and diffusion resistance of the corrosion layer. Thickness of the layer of corrosion products progressively increases in time and follows a \(\sqrt{t}\) function. There are two types of mathematical relationships that express progress of acid corrosion as a function of time. The first are derived theoretically from the diffusion models (Fick I. and II. law). Rombén [1], for example presented a mathematical model in the form:

\[
x = \sqrt{2kDct}
\]

where \(x\) is the thickness of the diffusion layer, \(D\) is diffusion coefficient the acid in the corrosion layer, \(k\) is a non-specified constant, and \(c\) is the concentration of acid and \(t\) is duration of acid attack. Other corrosion models were published by numerous authors, e.g. [16-19]. Modification of some simpler models can also be written in a form [9]:

\[
x = \frac{2Dct}{\beta_c}
\]

where \(\beta_c\) is a total neutralising capacity of hardened cement paste. Neutralisation capacity corresponds to the amount of acid (mol) required to completely decompose a volume of HCP (m\(^3\)) and transform it
into a soluble or insoluble corrosion products (mol/m$^3$). Neutralisation capacity of HCP increases with decreasing value of water-to-cement ratio of the paste.

Other (empirical) relationships were derived from evaluation of experimental results by the method of the least squares. These empirical relationships were presented usually in the form (3) or (4)

$$x = k_1 \cdot t^n$$ (3)

$$x = k_2 \cdot c^m \cdot t^n$$ (4)

where again, $x$ is depth of corrosion, $c$ is concentration of acid (in mol/l), $t$ is time of corrosion, and $k_1$, $k_2$, $m$ and $n$ are constants derived from experimental results; values of $m, n$ are near to 0.5.

2. Experimental

2.1. Materials and methods

a) Portland cement CEM I 42.5. Chemical composition of cement was as follows: CaO 63.43 %, MgO 1.37 %, SiO$_2$ 19.10 %, Fe$_2$O$_3$ 2.13 %, Al$_2$O$_3$ 5.87 %, SO$_3$ 1.85 %, insoluble residue 2.13 % and ignition loss 2.22 %.

b) Pure acids: (a) Hydrochloric acid (38%); (b) Acetic acid (96%), (c) Formic acid (98%), (d) Sulfuric acid (98%), Benzoic acid (crystalline, solubility about 0.29 g/100g of water at 20 °C).

Two types of test specimens were prepared from cement pastes with water/cement ratio (w/c) of 0.4:

a) Glass tubes that were opened on only one side were filled with the cement paste and then cured initially in water for 28 days. The tube samples were then immersed in diluted aggressive solutions of different acids (Fig. 3). The acid solutions were kept at nearly constant concentration during the test. Weight of samples and depth of corrosion were determined at predetermined time.

b) Test samples of cubical and cylindrical shape. The cubes with side of 20 mm and/or cylinders with diameter and height of 30 mm were prepared in steel molds and after demolding were initially cured in water for 60 days. Thereafter they were immersed in aggressive solutions of acids. In both experiments the concentration of aggressive solutions was kept constant by changing the solution during the experiment. Compressive strength of samples was determined after predetermine time periods.

![Figure 3: Method of testing the corrosion rate of HCPs in glass tubes immersed in acid solutions, where: $L$ and $d$ is the thickness of a corrosion products layer, shrinkage of the corrosion products layer and corrosion depth, respectively.](image)

Analytical techniques: Mineralogical composition of the pastes was studied by powder X-ray diffraction using Bruker D2 PHASER diffractometer (results are mentioned but not presented here). Scanning electron microscope (SEM) Vega 3, Tescan was used for observing samples morphologies. The SEM was equipped with x-act SDD Oxford Instruments detector for EDX/EDS microanalysis.

2.2. Results and discussion

2.2.1. Acid attack by strong and weak acids

Effect of solutions of different acids with equal concentration on the development of depth of corrosion ($d$) of hardened cement paste (HCP) is presented in Fig. 4. Concentrations of acids were kept constant by changing aggressive solutions. The highest rate of corroded layer development was
obtained in hydrochloric and nitric acids that represented strong acids giving a highly soluble calcium salts. Effect of weak acids (formic and acetic acid) was lower. Increase in depth of corrosion of HCP was the slowest in the sulfuric acid solution. The reason was a relatively low solubility of calcium sulfate dihydrate that formed in the reaction and accumulated in the corrosion products layer, making the layer less porous and permeable.

Effect of solutions of hydrochloric acid with different concentrations on depth of corrosion (d) of HCP with w/c = 0.4 is presented in Figure 5. By applying the method of least squares on the experimental results the relation between depth of corrosion and two variable parameters, concentration (c) and time (t) was found (equation (5)).

\[ d = 2.19 c^{0.69} t^{0.63} \]  

\( (5) \)

**Figure 4.** Increase in depth of corrosion in HCPs (w/c = 0.4) in glass tubes in the aggressive solutions of different acids with constant concentration (c = 0.1 mol.dm\(^{-3}\)).

**Figure 5.** Corrosion of HCP with w/c = 0.4 in solutions of HCl with various concentration (mol.dm\(^{-3}\)).

2.2.2. Acid attack by a solution of hydrochloric and sulfuric acids and their mixtures

Aggressive effect of solutions of HCl, H\(_2\)SO\(_4\) and equimolar solutions of a mixture of both acids was studied using cubic samples of HCP and also samples in glass tubes. Calcium salt of hydrochloric acid is well soluble, calcium salt of sulfuric acid is much less soluble. Solubility of CaCl\(_2\).6H\(_2\)O is 279.3 g/100g of water and CaSO\(_4\).2H\(_2\)O is 0.22 g/100g of water at 0°C.

The layer of corrosion products on the surface of HCP increased faster in the solution of HCl than in the solution of H\(_2\)SO\(_4\). Compressive strength decrease of cube samples was also faster in the solution of HCl (Fig. 6). The rate of corrosion in the solution of a mixture of both acids was intermediate. Visual appearance of test specimens is in Fig. 7. Corrosion layer formed on the surface of HCP in the solution of HCl was mostly composed from the decalcified SiO\(_2\).aq gel. It was weak and porous. When it dried it shrunk and cracked, its color was lighter and it could be easily peeled off.

**Figure 6.** Compressive strength of HCP’s specimens subjected to attack of hydrochloric acid, sulfuric acid and mixed solution of both. Concentration of H\(^+\) ions in each solution was equal ([H\(^+\)] = 0.25 mol/l).
In the case of the H$_2$SO$_4$ attack, the layer of corrosion products was less porous and was composed from the mixture of low soluble gypsum (CaSO$_4$.2H$_2$O) and SiO$_2$.aq gel (Figs. 7 - 9). After drying the layer was relatively hard and solid. The layer of corrosion products was less porous and generated greater diffusion resistance for the penetrating sulfuric acid. The corrosion rate, therefore, was slower (Figs. 4, 6 and 10). The results are in agreement with those of other authors [20].

In the case of an acid attack of a solution composed of mix of HCl and H$_2$SO$_4$ the calcium sulfate precipitated not only inside the corrosion layer but also in the close vicinity of the sample in the form of a porous wad of irregular shape (Fig. 7). The reason was higher concentration of H$^+$ ions originating from both acids and resulting Ca$^{2+}$ ions than sulfate anions in the solution ([Ca$^{2+}$] > [SO$_4^{2-}$]).

**Figure 7.** Visual appearance of HCP samples with w/c = 0.4 after curing for 25 days in water (top left) and after their exposure in the aggressive solution of hydrochloric acid, sulfuric acid and a mixture of both acids, with molar proportion of HCl : H$_2$SO$_4$ = 1 : 1. All the acid solutions had equal concentration (c(H$^+$) = 0.25 mol/l).

**Figure 8.** Cut section of a HCP cube sample attacked by the sulfuric acid solution with SEM images of areas near the reaction zone and gypsum crystals in the layer of corrosion products.

Figures 10 (a, b) show corrosion of HCP pastes (tubes) subjected to an attack by solutions of hydrochloric and sulfuric acids and their mixes. Figure 10 (a) shows that thickness of the layer of corrosion products increased more rapidly in the solution of HCl than the solution of H$_2$SO$_4$. In the cases of an attack of aggressive solutions containing a mixture of HCl and H$_2$SO$_4$ the corrosion rate was lower than in the HCl alone despite the fact that the solutions had nearly equal concentration of H$^+$ ions. The rate of corrosion decreased with the increasing ratio of sulfuric to hydrochloric acid. The corrosion rate in solutions of H$_2$SO$_4$ slightly increased with increasing concentration of sulfuric acid.
Figure 9. SEM image of areas near reaction zone in the sample attacked by the sulfuric acid solution (Fig. 8) and EDX distribution maps for Ca, S, Si, Al and Fe. Products of cement hydration were decomposed. Ions of Al, Fe and partly Ca were leached out from the corrosion layer. S and Ca are present in the layer in the form of a low soluble gypsum.

Figures 10 (a, b). Corrosion of hardened cement pastes in solution of HCl, H$_2$SO$_4$ and mixtures of both acids. Concentrations of solutions in mol/dm$^3$ is in parentheses. Symbol (H$^+$) refers to the solutions with equal concentration of H$^+$ ions ([H$^+$] = 0.25 mol/dm$^3$). The results correspond to tests performed on samples in glass tubes.
Weight of the samples stored in the HCl solution gradually decreased due to dissolution of Ca\(^{2+}\) ions from the corrosion layer. However, the weight of the samples in the solution of H\(_2\)SO\(_4\) increased or did not change (Fig. 10 b). The changes confirm accumulation of gypsum in the corrosion product layer, corresponding to Figs. 7-9. In the samples immersed in a mixture of hydrochloric acid and sulfuric acid, gypsum precipitated in the layer of corrosion products and also around the surface of the sample as was described previously. The low soluble gypsum precipitate in the corrosion layer and spreading around the sample slowed the diffusion of the aggressive component to the reaction zone.

2.2.3. Acid attack by solutions of acetic and benzoic acids
Corrosion effect of solutions of two weak acids, acetic and benzoic acids was studied using cylindrical samples of HCP (Fig. 11 a, b). The acids differ in size of their molecules and solubility of their Ca-salts (the solubility of calcium acetate hydrate at 0 °C is about 43.6 g/100 g water; the solubility of calcium benzoate trihydrate is about 4.5 g /100 g water). Concentration of both acids was about 0.025 mol/l (saturated solution in the case of benzoic acid).

![Figure 11](image1.png)

**Figure 11.** (a) Appearance of samples of HCPs after storage for 120 days in the solution of acetic (left) and benzoic acid (right). (b) A cross-sectional area of the cores of samples in the solution of benzoic (left, B) and acetic acid (right, A) with a visible "core" layer on the edges.

![Figure 12](image2.png)

**Figure 12** (a-c). Corrosion of HCP samples immersed in acetic and benzoic acid solutions (c = 0.025 mol/l): (a) Depth of corrosion, (b) Mass loss, and (c) Compressive strength changes.
Corrosion layer that formed on the surface of samples in the solution of acetic acid was porous. It shrank and cracked after drying (Fig. 11 a, b). The layer of corrosion products that formed in benzoic acid was relatively compact and it could not be separated from the “core” of samples. A thin "core" layer also was formed under the layer of corrosion products during the action of both acids (Fig. 11 b).

Corrosion of HCP samples in the acid solutions proceeded at different rates (Figs 12 a-c). The thickness of a layer of corrosion products increased much more rapidly in the solution of acetic acid (Fig. 12 a). It was difficult to determine thickness of the corroded layer in corroded sample from benzoic acid as there was no defined interface boundary between the layer of corrosion products and uncorroded core. The weight of samples immersed in the benzoic acid solution decreased more slowly than in acetic acid solution (Fig. 12 b). The compressive strength of HCP samples immersed in the benzoic acid was reduced by about 24% over the 120 days and then began to increase slightly (Fig. 12 c). This was probably the result of two conflicting effects. The first was slight increase of the compressive strength of the core, the second was a very slow decrease of a cross-section area of uncorroded core. The rate of both effect changes differently in time.

3. Conclusions
Solutions have a significant corrosion effect on cement based materials. Aggressiveness of the solutions increases with concentration of acids but also depends on the acid type. The results presented confirmed, that the rate of corrosion of hardened cement paste in solutions of strong acids (HCl, HNO₃) was faster than in solutions of weak acids (acetic and formic acid). However, the rate of corrosion of hardened cement paste was much slower in solutions of acids that produce low soluble calcium salts (sulfuric and benzoic acid), because calcium salts fill the pores in the layer of corrosion products and thus increase its diffusion resistance. Formation of low soluble salts can affect corrosion rate also in the cases of attack by mixture of different acids with high and low Ca-salts solubility.

Acknowledgment
This article was supported by the Slovak Research and Development Agency under the contract No. APVV-15-0681 and by the Science Grant Agency - project VEGA No. 1/050/17.

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