



Acid attack on hydrated cement – Effect of mineral acids on the degradation process



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ABSTRACT

During acid attack on concrete structural components, a degraded layer develops whose properties as a protective barrier are decisive for durability. ²⁹Si NMR spectroscopy and ²⁷Al NMR spectroscopy were used with XRD to investigate the degraded layer on hardened cement paste exposed to HCl and H₂SO₄. The layer comprises an amorphous silica gel with framework silicates, geminate and single silanol groups in which Si is substituted by Al. Amorphous Al(OH)₃ and Fe(OH)₃ are present. The gel forms by polycondensation and cross-linking of C-A-S-H chains at AlO₄ bridging tetrahedra. In the transition zone between the degraded layer and the undamaged material, portlandite dissolves and Ca is removed from the C-A-S-H phases maintaining their polymer structure at first. With HCl, monosulphate in the transition zone is converted into Friedel's salt and ettringite. With H₂SO₄, gypsum precipitates near the degradation front reducing the thickness of the transition zone and the rate of degradation.

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1. Introduction

Concrete structures in industry and agriculture are frequently exposed to aggressive aqueous media. As well as shortening service life and increasing expenditure for renewal or maintenance, this is ecologically disadvantageous with regard to the conservation of resources and the reduction of CO₂ emissions. Acid attack is extremely diverse. For example, containers for liquid manure, silage, biomass for methane production, deicing agent run-off at airports can be exposed to a variety of organic acids. Cooling towers, sewers, structures for geothermal energy production, concrete pavement and industrial plant can be attacked by inorganic acids, see state-of-the art report by Alexander et al. [1] and [2,3].

During acid attack, dissolution of the hardened binder paste matrix and, if soluble, the aggregate results in the formation of a visible degraded layer, low in mechanical strength and high in porosity, on the concrete surface. Acid attack is often characterized by a light-brown discolouration at the degradation front which is probably due to the precipitation of ferric hydroxide [4]. The rate of degradation is governed primarily by the diffusion of acid species through the degraded layer to the undamaged concrete and is therefore accelerated markedly by the loss of degraded surface material caused by the mechanical action of, for example, cleaning and mixing processes or agitation by fast liquid flow [5]. Thus the residual mechanical strength of the degraded layer and its bonding to the undamaged material are major factors affecting the acid resistance of concrete [6]. Consequently, testing

methods for acid resistance [7,8] often include systematic brushing of the concrete surface to simulate abrasion.

Depending on the pH of the acid and its type, zones of different mineralogical composition form during degradation [4,9,10]. Since the OH⁻ concentration of the pore solution in the undamaged material is many orders of magnitude higher than the proton concentration in the reaction zone of the acid [11], the neutralization of the protons occurs at the degraded layer/undamaged concrete interfacial region. As degradation proceeds, first portlandite dissolves transferring calcium ions to the pore solution. A solution-filled space is produced thus increasing porosity. At the same time porosity can be reduced by the precipitation of the corresponding calcium salt of the acid depending on its solubility, e.g. gypsum (CaSO₄·2H₂O) in the case of sulphuric acid. However, precipitation does not always improve acid resistance because expansive precipitate with a large molar volume can enhance erosion, e.g. calcium citrate as observed by Larreur-Cayol et al. [12].

Once portlandite is depleted, the pH of the pore solution falls below about 12.4 and, along with the dissolution of AFm and Aft, decalcification of the calcium silicate hydrate phases (C-S-H) proceeds causing a substantial decrease in mechanical strength and a further increase in porosity [1]. As a result, the diffusivity of the acid species is typically an order of magnitude higher in the degraded layer compared with the undamaged material [13,14]. The exchange of calcium in C-S-H with acid protons separates water molecules linking the silicate chains [15–17] until ultimately an amorphous silica gel forms. Depending on the pH of the acid, the degraded material also contains residual aluminium (pH > 3 to 4) and iron (pH > 1 to 2), probably in the form of hydroxides and, depending on its solubility, the calcium salt of the acid [4].

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In terms of the pH distribution over depth, the degradation process may be described by two zones which gradually move into the undamaged material as time progresses, see for example [18,19].

- a) A porous degraded layer of low mechanical strength containing silica gel in which the pH of the pore solution is near that of the external acid. The degraded layer is often light in colour.
- b) A transition zone in which the pH of the pore solution increases continuously until levelling off at the value for the undamaged core material. Portlandite dissolution and C-S-H decalcification occur in the transition zone. The transition zone includes the mechanically sound region in which portlandite dissolves and the C-S-H phases are essentially intact, i.e. zone 2 as defined by Bertron et al. [18].

As already pointed out in earlier publications [20,21], the resistance of concrete to acid attack is determined primarily by the properties of the degraded layer rather than the undamaged concrete. Thus measures in concrete design which increase the mechanical resistance of the degraded layer to abrasion and lower its porosity should prolong service life. As observed by Oueslati and Duchesne [22], the replacement of Portland cement by supplementary cementitious materials is beneficial for acid resistance because this lowers the calcium content of the hardened binder paste reducing the porosity of the degraded material. Knowledge of the changes occurring in the hardened binder matrix during acid attack is therefore a key to the production of concrete with improved acid resistance.

This paper focuses on the changes in chemical and phase composition occurring during acid attack on hardened ordinary Portland cement paste which lead to the formation of the degraded layer. Attack by mineral acids forming highly or scarcely soluble calcium salts is represented by experiments with hydrochloric and sulphuric acid, respectively. Samples were stored at controlled pH values of 2, 3 and 4 because the solubility of aluminium in C-A-S-H and $\text{Al}(\text{OH})_3$ and therefore the composition of the degraded layer are expected to depend on pH. Results are presented for investigations with ^{29}Si and ^{27}Al MAS NMR as well as chemical analysis (ICP-OES) and X-ray diffraction.

2. Experimental

2.1. Materials

A cement paste was prepared at a water to cement ratio (w/c) of 0.4 using ordinary Portland cement CEM I 42.5 R, (20.62 wt.% SiO_2 , 61.93 wt.% CaO , 5.23 wt.% Al_2O_3 , 3.49 wt.% Fe_2O_3 , LOI 1.51 wt.%) and deionized water. Immediately after mixing, the paste was poured into cylindrical polyethylene vials 30 mm in diameter which were vibrated and sealed with a cap. After 90 days' storage at 20 °C, the hardened cement paste cylinders were cut into disks 3.00 mm in thickness using a high-precision saw.

The degradation process occurring with hydrochloric and sulphuric acids was studied at constant pH 2, 3 and 4 using an automatic titrator with an automatic sample changer. It was therefore not necessary to renew the acid during storage in order to maintain acid strength. This is also in better agreement with the exposure conditions which often prevail in field practice. For each sample position, three disks were weighed and placed in a special sample holder in a capped beaker with 150 mL acid which was stirred with a magnetic spin bar. The pH of the acid solution at each sample position was measured and readjusted at intervals of 9 min by titrating with 1 M HCl or 0.5 M H_2SO_4 . The volume of acid added was recorded continuously. Between the measurements, the pH electrode was cleaned automatically by rinsing in distilled water. Later the titration interval was extended to 90 min.

After 28 d, the samples were removed from the acid, dried at 40 °C, weighed and prepared for the different investigations. Parallel reference samples, not exposed to acid, were prepared in the same manner and stored in a closed container filled with inert gas until analysis.

2.2. Measurements

All the samples were finely ground in isopropyl alcohol. For the NMR investigations, zirconia rotors (4 and 7 mm for ^{29}Al , and ^{27}Si NMR, respectively) were filled with the dry powder. Spectra were recorded with a Bruker Avance 300 spectrometer (magnetic field strength 7.0455 T) in MAS mode (magic angle spinning) using the single pulse technique and the settings listed in Table 1. The ^{29}Si NMR spectra were deconvoluted using the Bruker WINNMR software. The interpretation of the spectra was carried out according to [23,24] using the Q^n nomenclature. To avoid ambiguities, the Q^n nomenclature will be written with small letters (q^n) in the interpretation of the ^{27}Al NMR spectra.

The samples used for NMR were also used for qualitative XRD investigations and chemical analysis with ICP-OES. The diffraction data were collected using an XRD 3003 TT instrument of GE Sensing & Inspection Technologies with θ - θ configuration and Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Intensities were recorded over scattering angles between 5° and 70° at steps of 0.02°, with each step measured for 6 s. A number of additional samples were mixed with 10 wt.% ZnO as an internal standard for quantitative analysis using the Rietveld refinement. For the chemical analysis of the solid material, samples were fused at 1000 °C for 15 min with three times their mass of lithium metaborate. The loss on ignition was documented and the annealed melt pellets digested in 1 M nitric acid. The solutions were then diluted up to 100 mL with ultrapure water. The corresponding storage solutions were additionally acidified with nitric acid to avoid matrix effects in the analysis and diluted to 1 l with water. Quantitative chemical analysis of the solutions was performed using inductively coupled plasma optical emission spectroscopy (ICP-OES) in a HORIBA Jobin Yvon Ultima 2 ICP-OES.

3. Results and discussion

3.1. Degradation in the autotitrator

The appearance of the sample disks after 28 d in hydrochloric acid depended on pH (Fig. 1). At pH 4 they were visually similar to the reference samples, whereas at pH 3 brownish areas were evident on the surface. The samples stored at pH 2 were much lighter in colour and possessed a low mechanical strength. Breaking the samples revealed a layered structure over the thickness of the disks.

After 28 d in sulphuric acid at pH 4 (Fig. 2), the surface of the disks also exhibited brownish areas of discolouration. At pH 3, a well-defined white layer (verified as gypsum by XRD) had formed in the surface region. At pH 2 the gypsum layer was thicker and the brownish region no longer visible on the surface, but was adjacent to the non-degraded core.

The titration data in Fig. 3, left, show that the rate of acid consumption is, on the whole, much slower for H_2SO_4 compared with HCl. After 21 d at pH 2 in HCl, acid addition was no longer necessary, indicating that the maximum degree of degradation had been reached. In contrast, at pH 3 and 4 and even at pH 2 for H_2SO_4 the degradation process had not terminated after 28 d.

Table 1
Settings used for NMR experiments.

Type	Resonance frequency [MHz]	Rotation speed [kHz]	Repetition time [s]	No. of scans	Shifts relative to
^{27}Al	78.21	14	0.5	2000	$[\text{Al}(\text{H}_2\text{O})_6]^{3+}$
^{29}Si	59.63	5	5.0	15,000	$\text{Si}(\text{CH}_3)_4$

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