



Degradation processes of reinforced concretes by combined sulfate–phosphate attack



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ABSTRACT

A novel form of alteration due to the interaction between hydrated cement phases and sulfate and phosphate-based pollutants is described, through the characterization of concrete samples from an industrial reinforced concrete building. Decalcification of the cement matrices was observed, with secondary sulfate and phosphate-based mineral formation, according to a marked mineralogical and textural zoning. Five alteration layers may be detected: the two outermost layers are characterized by the presence of gypsum–brushite solid solution phases associated with anhydrous calcium sulfates and phosphates, respectively, while a progressive increase in apatite and ammonium magnesium phosphates is observable in the three innermost layers, associated with specific apatite precursors (brushite, octacalcium phosphate and amorphous calcium phosphate, respectively). The heterogeneous microstructural development of secondary phases is related to the chemical, pH and thermal gradients in the attacked cementitious systems, caused by different sources of pollutants and the exposure to the sun's radiation.

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1. Introduction

1.1. Scientific background

The alteration of concrete structural elements due to the action of external chemical degrading agents is one of the main causes for the reduction of the service life in modern constructions [1]. These dynamics are particularly aggressive in environments characterized by heavy soil and atmospheric pollution, leading to a progressive decalcification of the cementitious matrix and oxidation of the rebars [2,3]. Among the various forms of concrete chemical degradation, the external sulfate attack has been widely studied over the last two decades. Several theories on the actual contribution of this alteration dynamic on the physical and mechanical decay of concrete structures have been formulated [4–6]. Furthermore, the leaching and decalcification processes due to the exposure of concrete to acidic solutions have been extensively investigated in several scientific studies [7–10]. Such chemical alteration dynamics are extremely detrimental to the durability of cement-based materials, leading to the dissolution of cement hydration

products – mainly portlandite and C–S–H – and consequent loss of concrete strength.

Yet, there are few literature references on phosphate attack in cementitious materials, despite the interactions between phosphate ions and calcium-saturated systems that are widely demonstrated [11–13]. Some authors refer to limited decalcification on hydrated cement pastes under the action of phosphoric acid [14]. Moreover, an experimental and modeling study on concrete samples in contact with phosphate-rich solutions has been carried out to assess potential phosphate ion–concrete interactions [15]. The results of this integrated study showed that, while the formation of apatite on the expense of portlandite is thermodynamically favored in such systems, this mineral phase is not found experimentally, most likely due to kinetic factors. Nevertheless, the interaction between phosphates and concrete has never been evaluated on systems far from equilibrium characterized by local pH and chemical concentration gradients, corresponding to actual situations in attacked concrete structures materials. Moreover, the interaction between phosphate ions and other chemical species (e.g. sulfates) in case of concrete degradation by several types of chemical pollutants has never been taken into consideration before, as well as the possible evolution of the altered cementitious systems under variable temperature regimes, typical for temperate climates.

As for the influence of pH in the evolution of a hypothetical phosphate-related alteration of concrete, several studies confirmed

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the strong correlation between this parameter and the type of calcium phosphate phase formed [16–18]. The most common and least soluble mineral, hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, commonly abbreviated HAP), is stable under neutral or basic conditions [17]. On the other hand, phases such as brushite ($\text{Ca}(\text{HPO}_4) \cdot 2(\text{H}_2\text{O})$, commonly abbreviated as DCPD) and octacalcium phosphate ($\text{Ca}_8(\text{HPO}_4)_2(\text{PO}_4)_4 \cdot 5(\text{H}_2\text{O})$, commonly abbreviated as OCP) are generally crystallized from more acidic solutions [16,18]. Both brushite and octacalcium phosphate are reported to be precursors of apatite at acidic and neutral pH, respectively [17]. The higher solubility and lower stability of the two phases with respect to apatite cause their progressive transformation into apatite, both by dissolution and re-precipitation processes and by epitaxial growth [17].

Apart from the alteration dynamics related to the sole calcium-phosphate ion interaction in concrete, it is necessary to take into account other mutual interactions between phosphate compounds, concrete constituents and other external chemical species. Regarding this topic, the possible synergic action of phosphate and sulfate-based pollutants toward the alteration of cement-based materials needs to be considered, due to the extensive literature devoted to the study of calcium phosphate and sulfate phases in solid solution [19–22]. Gypsum and brushite both belong to the monoclinic system and have similar structures, despite the fact that they are not isomorphous ($a = 5.182 \text{ \AA}$, $b = 15.180 \text{ \AA}$, $c = 6.239 \text{ \AA}$, $\beta = 116.43^\circ$, sp.gr. $I2/a$ for brushite; $a = 5.670 \text{ \AA}$, $b = 15.201 \text{ \AA}$, $c = 6.533 \text{ \AA}$, $\beta = 118.60^\circ$, sp.gr. $I2/c$ for gypsum [21]). Although they have different sizes (the phosphate group is larger than the sulfate one), the substitution of sulfate and phosphate groups can occur within certain limits [20], and a solid solution between the two phases, which also comprehends the stoichiometric mineral ardealite ($\text{Ca}_2(\text{SO}_4)(\text{HPO}_4) \cdot 4(\text{H}_2\text{O})$, monoclinic system, Cc space group), can form. Furthermore, it has been demonstrated [22] that the relative proportions between the two end members of the solid solution have relevant influences on the dehydration behavior of the resulting compounds, being significantly different from the ones of the pure end members within certain composition intervals. Supposedly, such behavior influences the evolution of the secondary phases in case of alteration of the concrete elements exposed to significant seasonal temperature variations [23], as it happens in temperate climates.

Furthermore, the interaction between phosphate ions, nitrogen-based pollutants and magnesium ions deriving both from concrete cementitious matrix and aggregate fraction, needs to be considered, both due to the extensive scientific literature regarding the detrimental action of ammonium salts on concrete [24–26] and the occurrence of ammonium phosphate phases like struvite under certain chemical-physical conditions. Struvite ($(\text{NH}_4)\text{MgPO}_4 \cdot 6(\text{H}_2\text{O})$) is a hydrated phase consisting of magnesium, ammonium and phosphate in equal molar concentrations. Ammonium can be substituted to a certain extent by alkaline ions, in particular potassium [27]. Struvite precipitation is controlled by pH, degree of supersaturation, temperature and the presence of other ions in solution such as calcium, and can occur when the concentrations of magnesium, ammonium and phosphate ions exceed the solubility product for struvite. Among the various factors, pH is crucial for the formation of this phase, being sparingly soluble in neutral and alkaline, but readily soluble in acid conditions [28].

Finally, the possible interaction between phosphate ions and concrete rebars due to hypothetical phosphate attack of reinforced concrete shall be considered, taking into account the reported occurrence of iron phosphate phases like vivianite ($\text{Fe}_3(\text{PO}_4)_2 \cdot 8(\text{H}_2\text{O})$) and mitridatite ($\text{Ca}_2\text{Fe}_3(\text{PO}_4)_3\text{O}_2 \cdot 3(\text{H}_2\text{O})$) under specific chemical-physical conditions [29].

1.2. Characteristics of the case study and aims of the research

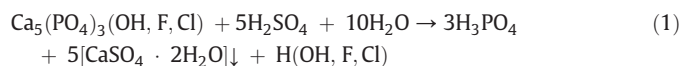
The cementitious materials studied in this work were sampled from one of the dismissed structures of the Ex-Agrimont industrial facility, building C3, built in the 1950s near the coastline of Porto Marghera (Venice area, north-eastern Italy) (Fig. 1).

The Porto Marghera industrial area suffered from heavy pollution during the 20th century, due to uncontrolled emissions from chemical industries and oil refineries [30]. All production plants of the area were responsible for severe forms of atmosphere, water and soil pollution.

As for atmospheric emissions, a detailed monitoring during the years of maximum activity of the area is not available. Yet, an intensive monitoring campaign performed by the Regional Association for Environmental Protection (ARPA) during the years 1998–2004 [31], when most of the factories had already closed, still showed particularly severe atmospheric pollution from gaseous sulfur- and nitrogen-based pollutants, like hydrogen sulfide, sulfur dioxide and trioxide and ammonia.

Furthermore, during the years of maximum activity in the area, unauthorized dumps for the storage of toxic waste were frequently excavated, and by-product slurries and non-depurated process waters were dumped and dispersed with no control. All these activities contributed to the progressive pollution of the groundwater and soils of Porto Marghera with abnormal amounts of chlorinated and aromatic solvents, aromatic hydrocarbons, phenols, ammonia, aromatic amines, sulfates, phosphates, lead, cadmium, zinc, mercury and arsenic. The Ex-Agrimont area was particularly affected by soil and water pollution due to the leakage of process water from the industrial plant, which produced phosphate- and ammonia-based fertilizers by chemical extraction from insoluble minerals from 1927 until its closure in 1997.

The main sources of phosphate minerals are naturally-occurring sedimentary deposits of phosphorites, sedimentary rocks containing significant amounts (about 30%) of cryptocrystalline apatite. After the mining, phosphates are separated from accessory minerals (mainly clay minerals), and the concentrated material is then chemically processed to obtain phosphate-based fertilizers, mainly through what is known as the wet process method [32]. In this process, the phosphate raw materials react with sulfuric acid to produce phosphoric acid. More precisely, the reaction combines calcium from the phosphate with sulfate to form phosphoric acid and calcium sulfate, mainly gypsum (called phosphogypsum), according to the following simplified reaction:



During the reaction, gypsum crystals precipitate and are separated from the acid by filtration and washing. Wet processed phosphoric acid normally contains 26 wt.% to 30 wt.% of P_2O_5 , and depending on the types of fertilizer to be produced, it is usually concentrated from 40 wt.% to 55 wt.% of P_2O_5 through a series of vacuum evaporators, and subsequently, after reaction with ammonia, granulated to produce diammonium phosphate (DAP) and monoammonium phosphate (MAP). Granular triple superphosphate (GTSP), a non-nitrogen fertilizer, is produced by adding phosphoric acid to ground phosphate rock.

The production of fertilizers requires and produces a large volume of process water, a dilute mixture of phosphoric, sulfuric, and fluosilicic acids with very low pH (about 1 to 2) [32]. Furthermore, it contains several other ions found in phosphate rock, as well as ammonia from the solid fertilizer-manufacturing process [32]. In order to reduce its environmental impact, process water commonly undergoes a series of chemical treatments, by sequential additions of calcium hydroxide and acids, to obtain a final solution with a pH of about 6.5 from which all solids and ammonia have been removed [32].

The studied structure (Fig. 1a) is a 20 m tall building, constituted by 22 couples of load-bearing reinforced concrete semi-arches. The structure is enclosed by a reinforced concrete wall up to 2 m high. Above this height the semi-arches are connected by prefabricated non-structural reinforced concrete beams which constituted the backing for the original fiber-cement roofing. A binder classifiable as CEM I-type cement (European Standard EN 197-1) was used for the manufacturing of all concrete elements, employing dosages between 300 and 350 kg/m^3 and with w/c ratios varying from 0.6 to 0.7. No chemical admixtures were added to the fresh mix. The aggregate fraction is characterized by

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