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Internal deterioration of concrete by the oxidation of pyrrhotitic aggregates

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Abstract

This paper presents research results on the causes of a severe concrete deterioration, which occurred in many building foundations approximately 2 years after construction. Concrete samples were investigated with X-ray diffraction (XRD) analysis, a scanning electron microscope (SEM) and a petrographic examination performed with a stereomicroscope. It was found that the early cracking of concrete stemmed from the oxidation of the pyrrhotite found in the anorthosite aggregates used to produce the concrete. The oxidation process led to the precipitation of iron hydroxides having a higher volume than the original pyrrhotite does. The presence of micas (biotite) close to the pyrrhotite seemed to promote and accelerate the oxidation process.

Keywords: Concrete; Ettringite; Petrography; SEM; X-ray diffraction; Gypsum; Pyrite; Pyrrhotite

1. Introduction

The weathering and deterioration of rocks are natural processes affecting a large variety of rocks. Most rock types are subjected to the transformation of some of their original minerals into new phases. For instance, a common mineral, such as biotite, is progressively transformed into chlorite. In the natural environment, these alteration processes are very slow and must be considered at the geological scale. However, the incorporation of rock as aggregate into concrete may lead to a drastic acceleration of the rock deterioration. Concrete represents a very aggressive environment compared with the natural conditions to which the rock had been exposed—the concrete pore solution is mainly composed of alkali ions and hydroxide ions, and the pH is generally higher than 13.0.

A harmful reaction affecting rocks is the oxidation of pyrite FeS_2 and pyrrhotite $Fe_{1-x}S$, which are common minerals, disseminated in various rock types. These minerals are unstable in the presence of water. Their oxidation leads to series of chemical reactions and to the formation of products of larger volume than the initial volume of materials. At first, there is oxidation of the iron sulphides in the presence of water and oxygen, followed by the formation of iron hydroxide and sulphuric acid:

$$FeS_2 + 15/4\ O_2 + 5/2\ H_2O \rightarrow FeOOH + 2\ H_2SO_4 \qquad (1)$$

pyrite goethite + sulphuric acid

When the pyrite is disseminated in carbonate rocks, sulfuric acid could react with calcite $CaCO_3$ to form expansive gypsum $CaSO_4.2H_2O$:

$$H_2SO_4 + CaCO_3 + 2H_2O \rightarrow CaSO_4.2H_2O + CO_2 \qquad (2)$$

sulphuric acid + calcite + water → gypsum + CO_2

This reaction is at the origin of several problems in Eastern Canada, where clayey sedimentary bedrock [1,2] or rockfill made up of clayey sedimentary aggregates [3] have caused a large range of damage to building foundations and concrete slabs.

If reaction (1) occurs in a hardened concrete, the sulphuric acid reacts with the portlandite $Ca(OH)_2$, which

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is one of the hydration products of Portland cement, and gypsum is formed according to the following reaction:

$$\mathrm{Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4.2H_2O} \tag{3}$$

portlandite + sulfuric acid → gypsum

The gypsum then reacts with aluminates in the Portland cement (anhydrous or hydrated), which leads to the formation of potentially expansive secondary ettringite $\mathrm{CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O}$:

$$\mathrm{3CaO.Al_2O_3 + 3\ CaSO_4.2H_2O + 26\ H_2O \rightarrow 3\ CaO.Al_2O_3.3CaSO_4.32H_2O} \tag{4}$$

tricalcium aluminate + gypsum + water → ettringite

This secondary ettringite must be differentiated from the primary ettringite normally formed in the first days of cement hydration by the gypsum and the aluminate phase of the cement (the tricalcium aluminate). Thereafter, the primary ettringite turns into monosulfoaluminate ($\mathrm{3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O}$), which is a more stable form of sulfoaluminate, and finally, into hydrogarnet ($\mathrm{C_4AH_{13}}$). The remaining sulfate ions are trapped in the structure of the C-S-H gel. Secondary ettringite can be expansive; if the germination degree is higher than the crystalline growth degree, the product formed will be more or less crystallized, having a molar volume three to eight times larger than that of the initial solid [4]. If there is sufficient space for the ettringite to crystallize, needle-shaped crystals will be formed.

The pyrite oxidation reaction is greatly exothermic, producing about 1410 kJ of heat by mole of oxidized pyrite, which contributes to locally increase the temperature and, therefore, accelerate the oxidation reactions of pyrite [5].

In concrete, the main factor increasing the oxidation degree of pyrite, found either in framboidal or massive form, is a high pH, related to the amount of OH -ions in the pore solution. In concrete, both forms of pyrite have the same behavior in a high-pH solution; the higher the alkalinity of the solution, the faster the reaction [6].

The porosity and the pore connectivity of the aggregate and concrete also represent important parameters regarding aggregates weathering, as well as concrete deterioration. Certain aggregates are more subject to weathering and deterioration, owing to their petrographic nature. For instance, schist and shale rocks have a laminar structure, which increases the permeability and porosity of the rock. Moreover, shale rocks contain a certain amount of clay minerals that absorb water and oxygen. Carbonate rocks are generally compact, but a significant proportion of aggregate particles (up to 30%) can be cracked before their incorporation into concrete, due to tectonics or to quarrying operations, such as drilling, blasting and crushing [7]. The pyrite disseminated in the aggregate particle would then be more accessible for water and oxygen and may react faster.

2. Scope of work

Most cases of concrete deterioration associated with the expansive action of the pyritic rocks published to date deal with the cracking and uprising of concrete buildings lying on swelling rock foundation or on a swelling rockfill. These cases represent concrete deterioration stemming from an “external” cause. This paper is one among very few others [4,8–11] dealing with concrete deterioration stemming from an “internal” cause. Indeed, the expansion of the pyrrhotite present in the aggregates used for concrete production was found to be responsible for the early cracking of the concrete. Concrete samples (cores of 100×200 mm) were taken from the foundations and the porch of several houses exhibiting severe deterioration signs and were investigated. According to the information collected, the concrete was cast in the summer of 1998. The compressive strength of concrete at 28 days was 25 MPa for the foundation walls and 30 MPa for the porch. The first cracks in the concrete appeared in 2000, i.e., two years after construction, and have been continuously growing and extending since then. The study presented here on the determination of the potential causes of the cracking was carried out between September and October 2001.

3. Experimental work and methods

A characterization of cement paste and a complementary qualitative characterization of aggregate samples taken from concrete cores were performed with X-ray diffraction (XRD) analysis. XRD analysis enables the identification of the crystalline phase. Every crystalline species will give a characteristic diffraction spectrum with a set of diffraction peaks, whose position and intensity correspond to a specific crystalline structure. Prior to the X-ray analysis, samples were manually ground to a fineness lower than 45 μm, set down and compacted on the rough surface of a glass blade to be randomly disorientated.

A Rigaku, D/MAX model, B series was used to perform the XRD analysis. The X-rays are produced in a vacuum with a Coolidge tube that consists of a cathode and an anode made of copper.

The samples prepared from the cores were also observed under a scanning electron microscope (SEM). For the SEM analysis, fresh broken surfaces of massive samples were used. To increase the conductivity of the surface, a thin layer of gold and palladium of 100–200 Å in thickness was applied on the surface of samples. The elementary analysis of crystals detected on the surface was conducted with the energy dispersive X-ray spectrometer (EDXS).

The SEM used for this study is a Jeol JSM840A, coupled with an X-energy analysis system (Link System AN-10085).

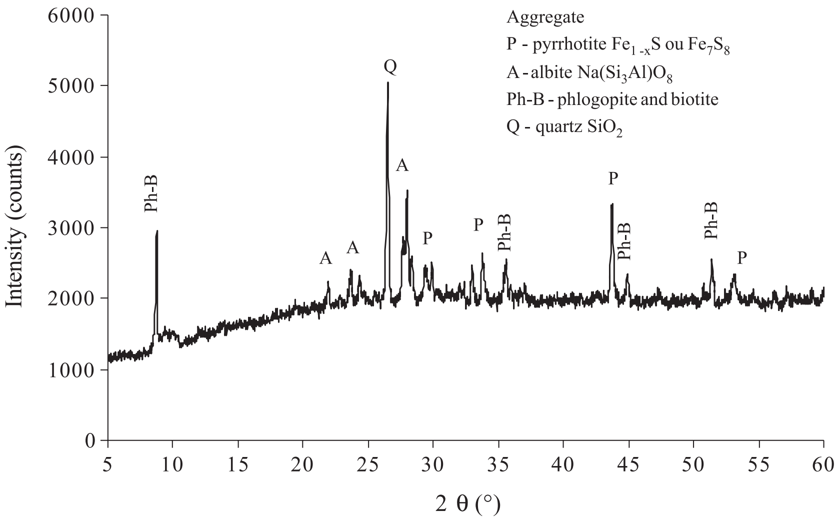


Fig. 1. XRD spectrum of aggregate.

Polished sections were prepared from the cores. The petrographic examination was conducted at a magnification of 16× using a stereomicroscope. A few thin sections were also prepared and observed with a petrographic microscope.

4. Results

4.1. Characterization of aggregate and cement paste by XRD

The XRD analysis of aggregate used to produce the concrete showed that the rock is composed of the following minerals (Fig. 1):

- albite $Na(Si_3Al)O_8$
- pyrrhotite ($Fe_{1-x}S$ or Fe_7S_8)
- biotite $KMg_3(Si_3Al)O_{10}(OH)_2$.

The analysis of the samples of cement paste taken from the concrete cores (Fig. 2) revealed the presence of the following minerals:

- ettringite $Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$
- portlandite $Ca(OH)_2$
- calcite $CaCO_3$
- quartz SiO_2
- melanterite $FeSO_4\cdot 7H_2O$
- albite $Na(Si_3Al)O_8$.

The C-S-H gel, the major hydration product of Portland cement, is represented by a halo of approximately 28–30°2θ due to its amorphous nature. The cement paste was sieved after grinding, which removed the majority of the sand feldspar particles from the cement paste so that only the peaks of albite were detected.

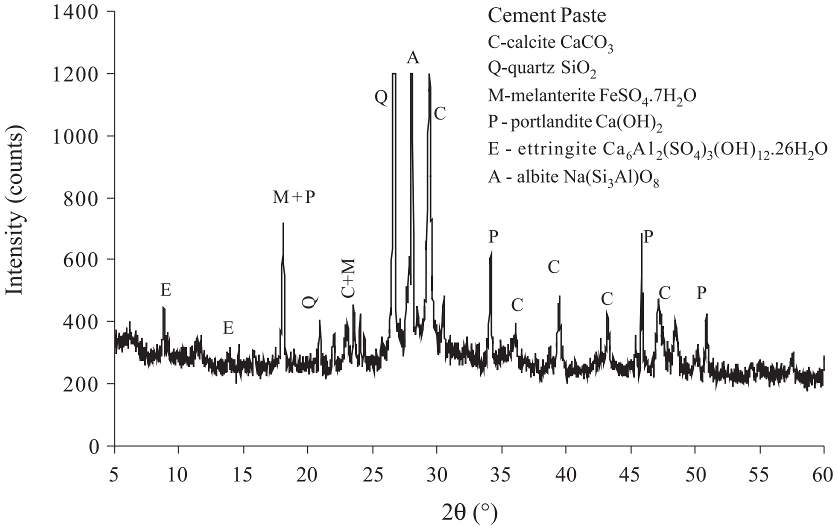


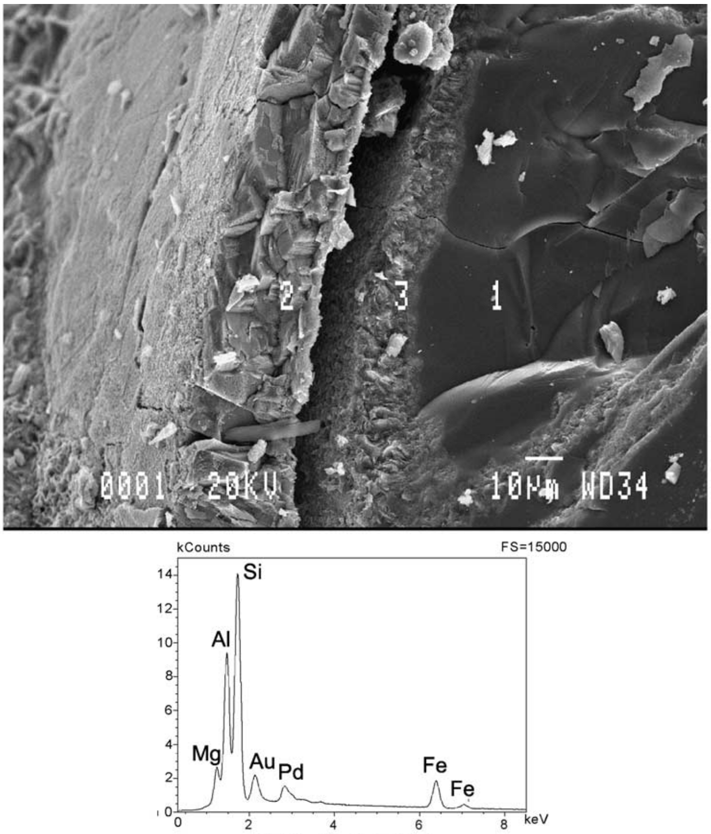
Fig. 2. XRD spectrum of cement paste.

4.2. SEM and EDXS analyses

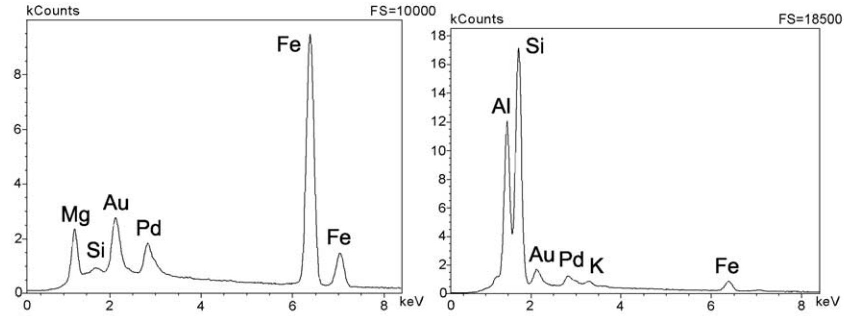
At first view, the aggregates seemed to be relatively heterogeneous and composed of different phases. Some aggregate phases were extensively cracked, while some phases did not show any cracking. Some cracks ran through the aggregates particles and extended into the cement paste, which is a typical sign of expansive aggregate.

Large deposits of crystalline material were observed around several aggregate particles (Fig. 3). Elementary analysis of these deposits revealed that they were essentially composed of iron (Fe). It must be pointed out that our EDXS spectrometer does not enable analysis of oxygen and hydrogen. The globular shape of these crystals (typical of goethite) was also present on other aggregate particles (Fig. 4). In some aggregates, the presence of pyrrhotite was noticed, as confirmed in the XRD (Fig. 5).

At a microscopic scale, the cement paste is very porous in some locations (Fig. 6). In all samples, an important amount of ettringite is observed (Fig. 7). This ettringite is generally found very close to the weathered aggregates. Only a small amount of ettringite was found in the cement paste near sound aggregates. The ettringite frequently filled up the air voids in the cement paste (Figs. 8 and 9).



Analysis at point 1



Analysis at point 2

Analysis at point 3

Fig. 3. Iron deposit around aggregate.

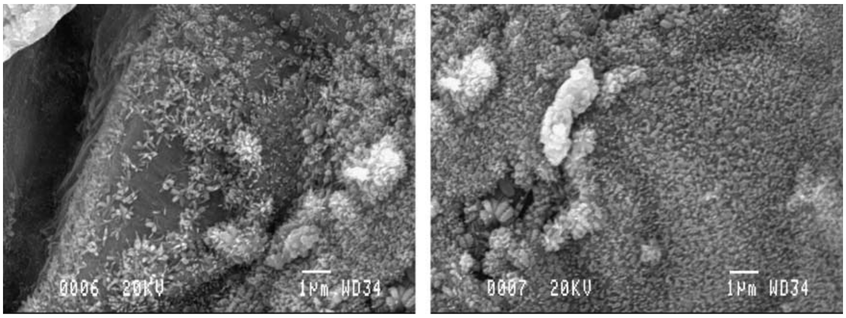
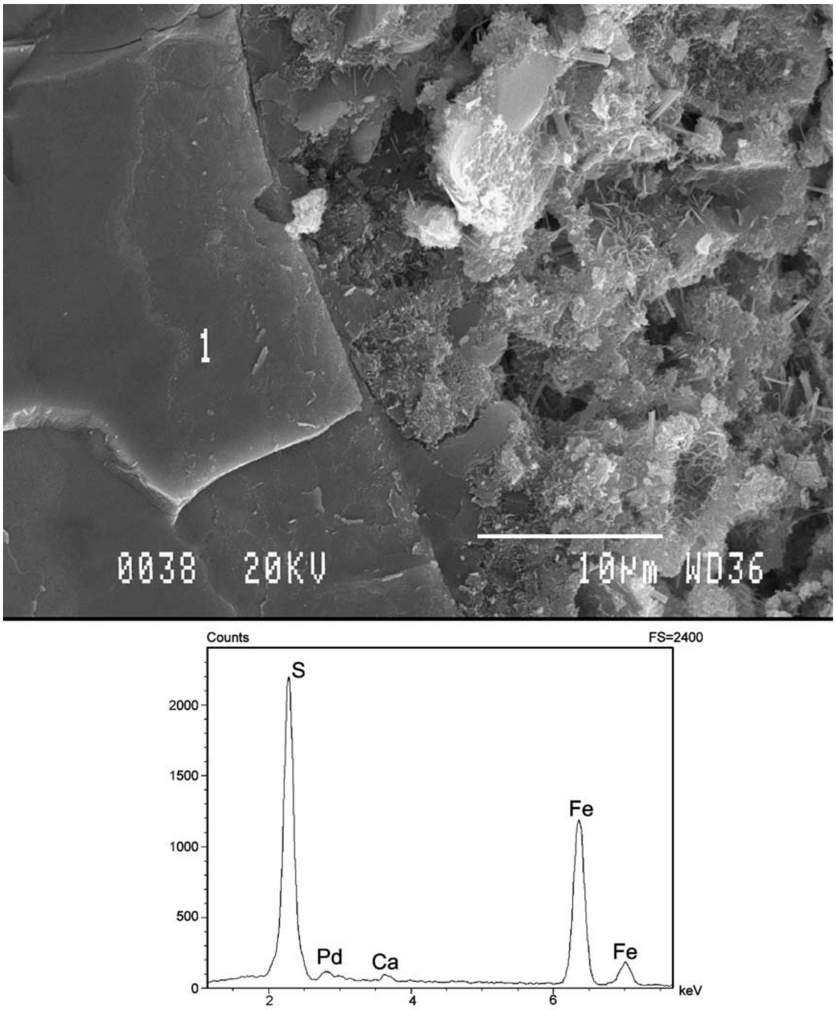


Fig. 4. Crystals (probably goethite) deposited on aggregate surface.

4.3. Petrographic examination on polished sections

The coarse aggregate consists in a gray anorthosite, mainly made of feldspars, with traces of micas and sulphides. The aggregate was crushed before incorporation into concrete. The particle size varies between 5 and 25 mm. The cement paste is very pale, nearly white and it crumbles under the pressure of hands in the poor-quality samples.

The concrete cores exhibit various degrees of damage. In the most severe cases, several cracks are observed in the aggregate particles and cement paste (Fig. 10). Crack



Analysis at point 1

Fig. 5. Sulphide particle.

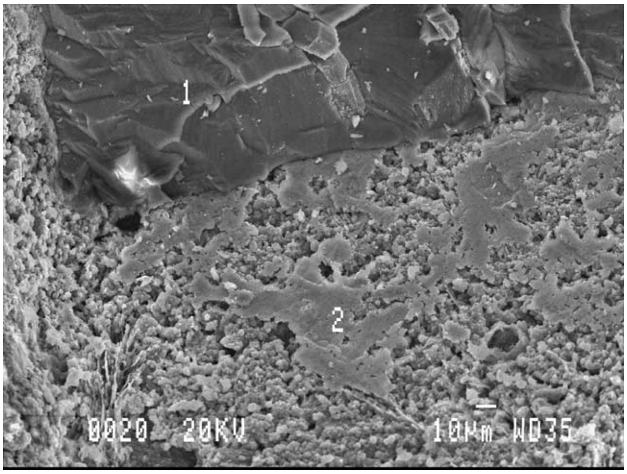


Fig. 6. Porous cement paste (1—aggregate, 2—cement paste).

openings in the cement paste reach up to 2 mm. Cracks in the cement paste skirt around aggregate particles, but in some heavily weathered cases, crack runs through the aggregate particles.

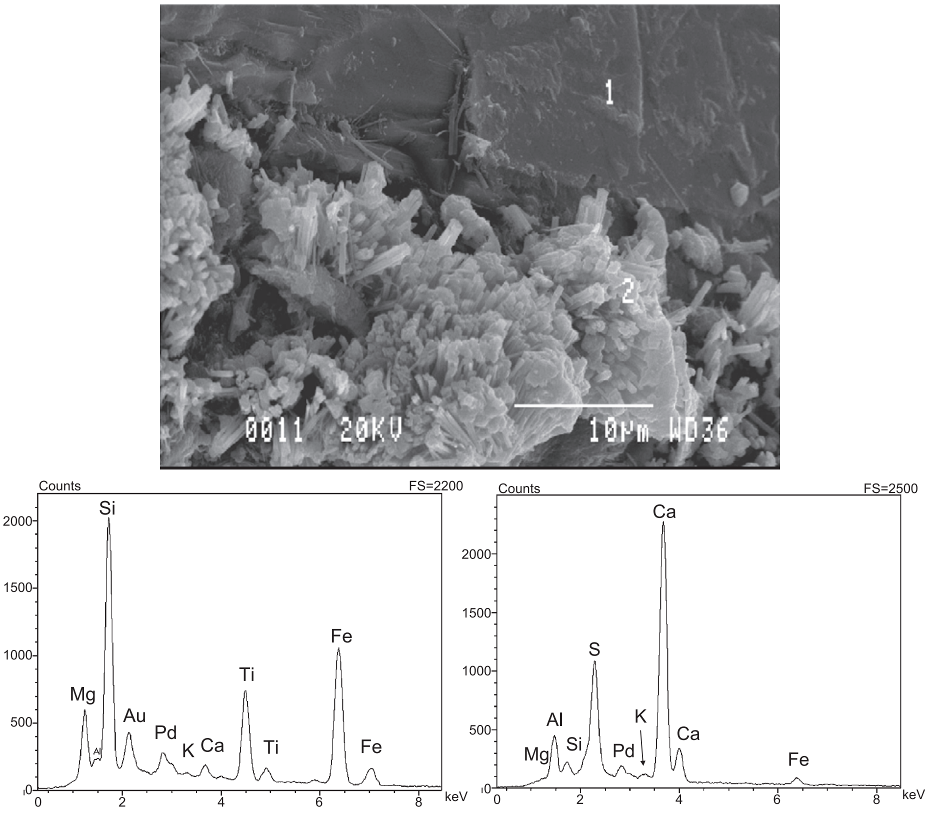
In sound aggregates, pyrrhotite shows a typical glittering aspect. On the other hand, pyrrhotite exhibits a rusty aspect in cracked aggregates, and sometimes, the crystals seem to be completely dissolved. Most of the time, weathered micas are observed within these reacted zones. Moreover, the porosity of the cement paste is higher in the vicinity of weathered aggregates.

4.4. Petrographic examination on thin section

The aggregates were found in various deterioration states, which correlates with the degree of damage of the surrounding concrete. In locations where concrete appears to be in good condition, feldspars and bitotite minerals do not exhibit any weathering symptoms (Fig. 11). However, in severely deteriorated zones, feldspars and biotite are barely visible and extensively cracked (Fig. 11).

5. Discussion

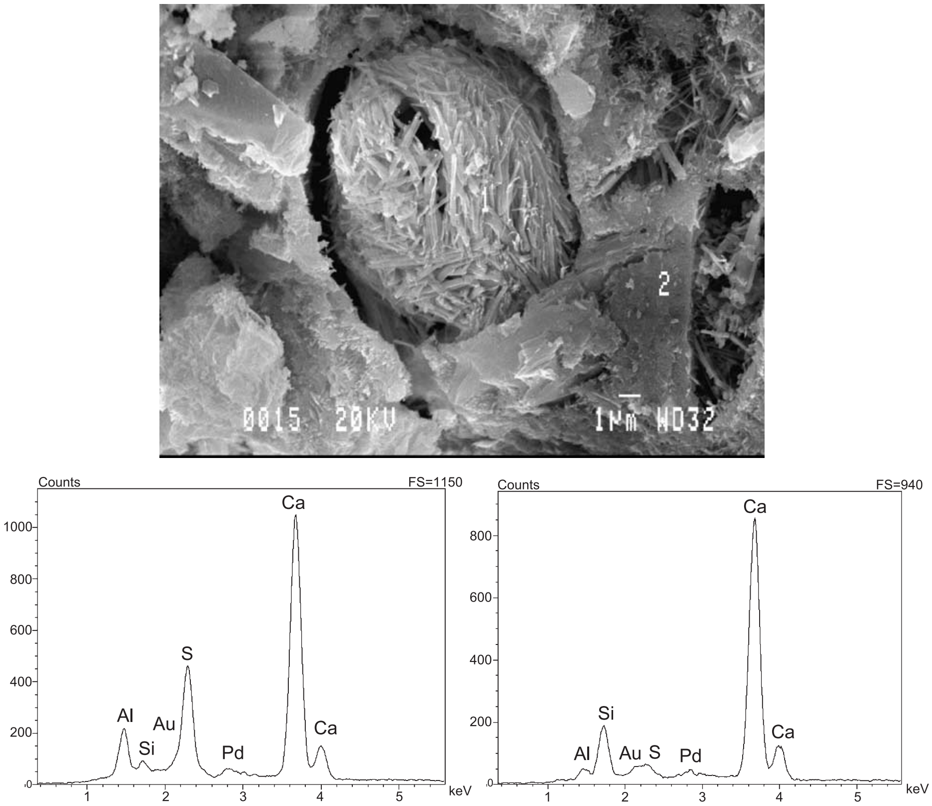
The analysis of this concrete showed an early and advanced stage of deterioration of both the aggregates and the cement paste. The XRD and SEM analyses of the aggregates indicated the presence of pyrrhotite $Fe_{1-x}S$, especially in the sound aggregates, whereas it was oxidized in the cracked aggregates. The oxidation would have led to the formation of iron hydroxide–goethite (typical globular shape), causing the expansion and



Analysis at point 1 - aggregate particle

Analysis at point 2 - ettringite

Fig. 7. Many ettringite crystals formed in cement paste near aggregate particle.



Analysis at point 1 - ettringite

Analysis at point 2 – cement paste

Fig. 8. Ettringite-filled air voids.

cracking of aggregates, as observed with the optical and electronic microscopes. Along with the formation of goethite, sulphuric acid H_2SO^4 was formed. This acid attacked the cement paste and, in the presence of portlandite, would have formed ettringite. The cement paste in the vicinity of the reacted zone was more porous, friable and seemed to have been dissolved. Indeed ettringite was abundant in the investigated samples, especially close to the damaged aggregates and in the

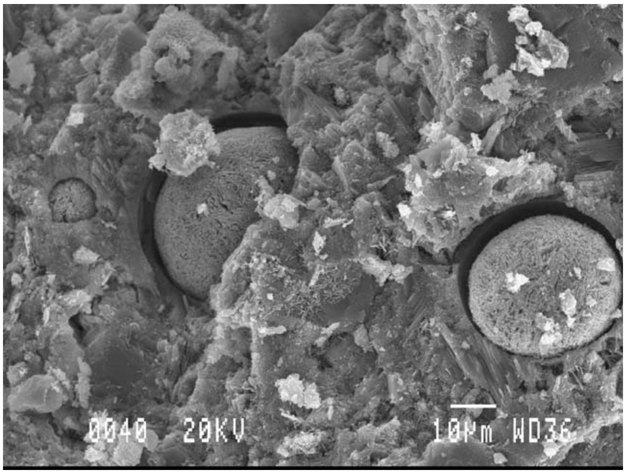


Fig. 9. Cement paste rich in ettringite.

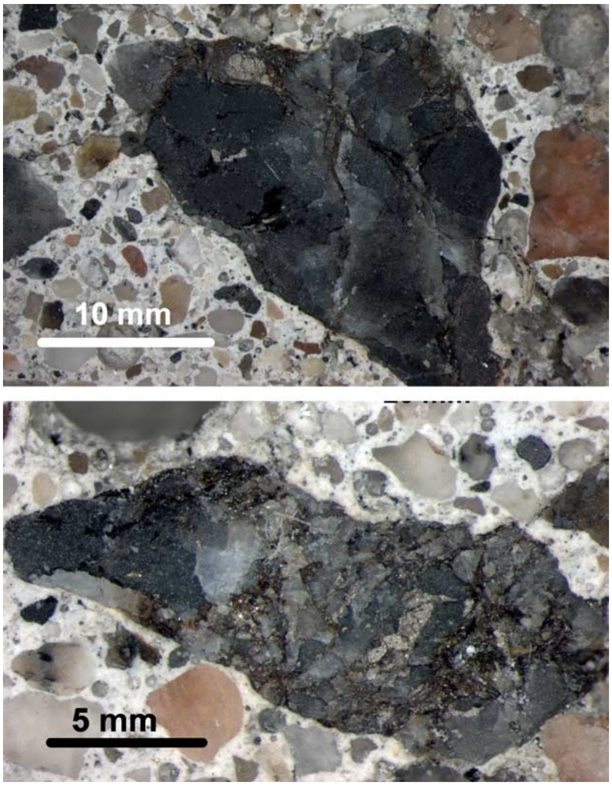


Fig. 10. Heavily damaged aggregates and cracked cement paste.

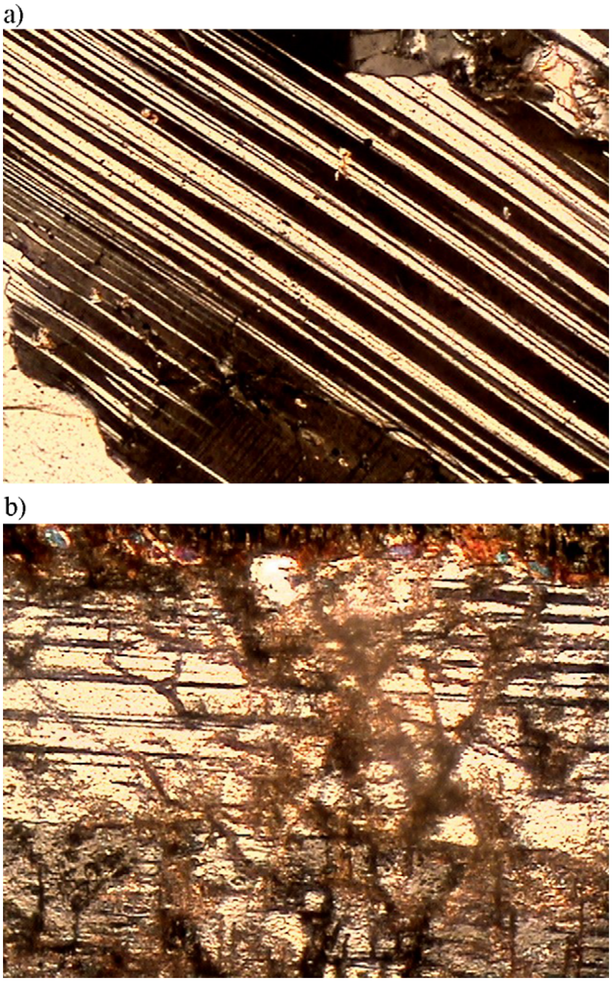


Fig. 11. Feldspar in thin section. (a) Feldspars in sound aggregates. (b) Weathered feldspars in cracked aggregates.

air voids. The ettringite crystallized in a needle shape, which is considered its nonexpansive form, is usually produced where there is available space [12]. In this case, the free space was found in the air voids and in the cracks previously caused by the oxidation of the sulphides in the aggregates, at the same time providing the sulphate ions necessary for ettringite formation.

Some sound sulphide minerals were found, probably embedded deeply into rock aggregate and consequently protected from contact with water and oxygen, while others close to the aggregate surface were in contact with water and oxygen required for their oxidation.

The presence of micas in the aggregate seemed to have accelerated and enhanced the deterioration process; the most severely damaged zones are observed where biotite flakes are in contact with pyrrhotite. This may be related to two factors:

(1) Micas are friable and are composed of laminar structures, which constitute a natural path for oxygen and water to reach reactive pyrrhotite.
(2) Micas might have reacted previously with alkalis dissolved in the concrete pore solution to form expansive products. Such deleterious reaction has been reported by Prince et al. [13].

Classic alkali–aggregate reaction as the cause of distress must be discarded because of the following:

(1) Anorthosite is not considered as an “alkali-reactive” rock.
(2) No silica gel was observed in the sample.

It is obvious that an external water gain and the presence of oxygen are required for the chemical process to occur. The volume of water in concrete is not sufficient to initiate and sustain the pyrrhotite oxidation process. Because the investigated concrete has a high W/C ratio, concrete permeability is important, and weather precipitations contribute the external water and oxygen necessary for the development of the chemical reaction.

6. Summary and conclusion

The cause of the internal deterioration of concrete cores has been investigated. It was shown that the presence of chemically unstable iron sulphides (pyrrhotite) in aggregates would have caused the early cracking of concrete.

The oxidation of the iron sulphides provokes a series of chemical reactions leading to the precipitation of iron hydroxides and ettringite. These secondary products have a larger volume than the initial products do. Their formation initiates microcracks in aggregates particles, which exposes a larger amount of iron sulphides to water and oxygen, etc. Reactions end with the formation of needle-shaped ettringite, which is only, in our opinion, a secondary expansion.

The most deteriorated zones were observed where pyrrhotite was found along with micas. Micas have probably contributed to accelerating and enhancing the deterioration process by absorbing water and oxygen.

Precautions should be taken with aggregates containing minerals such as pyrrhotite or pyrite combined with micas before incorporation into concrete. Historical performance of the aggregate in concrete is considered to be a good criterion for assessing its durability.

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