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INFLUENCE OF THE SURFACE TREATMENT WITH OXALIC ACID ON THE BEHAVIOUR OF A PORTLAND CEMENT TO ACID CORROSION

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Cunoaşterea factorilor de mediu şi caracterizarea agresivităţii acestora sunt condiţii esenţiale pentru proiectarea corespuzătoare, din punct de vedere economic şi al siguranţei în exploatare, a cimenturilor şi betoanelor performante, durabile.

Lucrarea prezintă efectele tratamentului de suprafaţă cu acid oxalic, al stratului format la suprafaţa pastei de ciment Portland corodată în soluţii de acid clorhidric, acid azotic, acid formic şi acid acetic. Pentru caracterizarea durabilităţii cimentului tratat, s-au determinat rezistenţele mecanice ale mortarelor de ciment ladiferite intervale de timp.

From the economical and safety in exploitation points of view, the knowledge of the environment factors and the characterization of their aggressiveness are essential conditions for an appropriate design of durable cements and concretes.

The paper presents the effects of the surface treatment with oxalic acid of the top layer of the cement samples corroded in solutions of hydrochloric, nitric , formic and acetic acids. There were also determined the mechanical strengths at different time intervals in order to characterize the cement durability.

Keywords: Portland cement, acid corrosion, surface treatment, oxalic acid

1. Introduction

Usually, acid corrosion takes place at a pH value less than 6.5 and it is determined by the acids present in natural, industrial or residual waters, or even gaseous substances in the presence of humidity [1-5].

The most common acids which lead to corrosion are: hydrochloric, nitric, sulfuric, sulfurous, hydrofluoric, formic, acetic, lactic and humic acid, and sulfur hydride.

The acids react with all the constituents of the cement stone leading to: calcium salts of the corresponding acids; silicic acid gel, aluminum and iron

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hydroxide, in the case of complete corrosion, or aluminum and iron salts, in the case of very acidic solutions [1, 6].

The corrosive action of the acids depends mainly on their acidic strength and on the solubility of the calcium salts thus formed. In the case of hardly soluble salts, they can form a protective layer on the surface of the cement stone, which slows down or stops the attack in depth of the corrosive agents.

The oxalic acid forms calcium oxalate with a solubility, at 18°C, of only 0.007 g/L. Previous studies [7] proved that keeping samples of cement pastes and mortars in 0.5 mole/L oxalic acid solution leads in the first days to a thin layer of calcium oxalate which does not grow in the following 180 days. Compressive strength of the mortar samples allowed the classification of oxalic acid as a harmless substance for Portland cement.

The purpose of the surface treatment is to obtain a more compact and waterproof layer on the concrete upper layer. This layer is obtained from the interaction of the concrete mass with oxalic acid, and its thickness depends on the depth at which this oxalic acid can penetrate [8].

2. Experimental

Materials

a) Cement. Portland industrial cement has been used for the tests. The chemical and physico-mechanical characterization of this cement is shown in Table 1.

Table 1

Characteristics of the cement used for testing

Characteristic	M.U.	Value	Characteristic	M.U.	Value
Loss of ignition	%	3.05	Standard consistence	%	28.6
SiO_2	%	19.88	Initial setting time	min	150
Al_2O_3	%	5.54	Final setting time	h-min	3-30
Fe_2O_3	%	3.26	Soundness	mm	1.5
CaO	%	61.33	Blaine specific surface area	cm^2/g	3641
MgO	%	1.58	Flexural strength at 28 days	MPa	8.51
SO_3	%	2.75			
Insoluble residue in $HCl\text{-}Na_2CO_3$	%	0.87	Compressive strength at 28 days	MPa	45.7

b) Sand. The mortar samples were prepared with polygranular sand purchased from Société Nouvelle du Litoral – France, that has a SiO_2 content of

95.19% and a grain size distribution that meets the requirements of the SR EN 196-1 standard [9].

c) Solution of oxalic acid. The surface treatment of the cement pastes and mortars has been done with a 0.5 mole/L oxalic acid aqueous solution.

d) Solutions of corrosive acids. The corrosive environments used were solutions of hydrochloric, nitric, formic and acetic acids of 0.1 mole/L concentration. They were prepared from 37% hydrochloric acid, 65% nitric acid, 85% formic acid, glacial acetic acid and distilled water.

Experimental procedures

Mortar specimens, of 40 x 40 x 160 mm, were prepared using a cement: polygranular sand ratio of 1:3 and a water:cement ratio of 0.5. The specimens were kept in the mold for 24 h at 100% relative humidity, then demoulded and finally cured in water up to 28 days.

Three types of treatment were applied on the thus obtained samples, which lead to:

- Reference mortar specimens, which were cured in water for additional 28, 90 and 180 days;
- Treated mortar specimens, which were immersed for 28 days in 0.5 mole/L oxalic acid solution and then cured in corrosive acid solutions for additional 28, 90 and 180 days;
- Untreated mortar specimens, which were cured in corrosive acid solutions for additional 28, 90 and 180 days.

Cement pastes were also prepared using the water for normal consistence. The samples were cured for 24 h in humid air, then in water up to 28 days.

Similarly, three types of treatment were applied on the thus obtained samples, which lead to:

- Reference paste specimens, which were cured in water for additional 28, 90 and 180 days;
- Treated mortar specimens, which were immersed for 28 days in 0.5 mole/L oxalic acid solution and then cured in corrosive acid solutions for additional 28, 90 and 180 days;
- Untreated mortar specimens, which were cured in corrosive acid solutions for additional 28, 90 and 180 days.

Mechanical strength tests were performed for the mortar specimens, while the cement paste specimens were submitted to X-ray diffraction analyses in order to determine their composition.

The codes of the samples used in this study are:

- ***OC, ON, OF, OA*** – treated specimens corroded in hydrochloric acid, nitric acid, formic acid and acetic acid solutions, respectively, for 28, 90 and 180 days;

- ***C, N, F, A*** – untreated specimens corroded in the corresponding acid solutions for 28, 90 and 180 days.

3. Results and discussions

3.1 X-ray diffraction analyses

There were carried-out X-ray diffraction analyses of the specimen pastes corroded in acid, with and without oxalic acid treatment, at the 180 days term. In Figures 1-4, are presented the results obtained for the samples cured in different acid solutions.

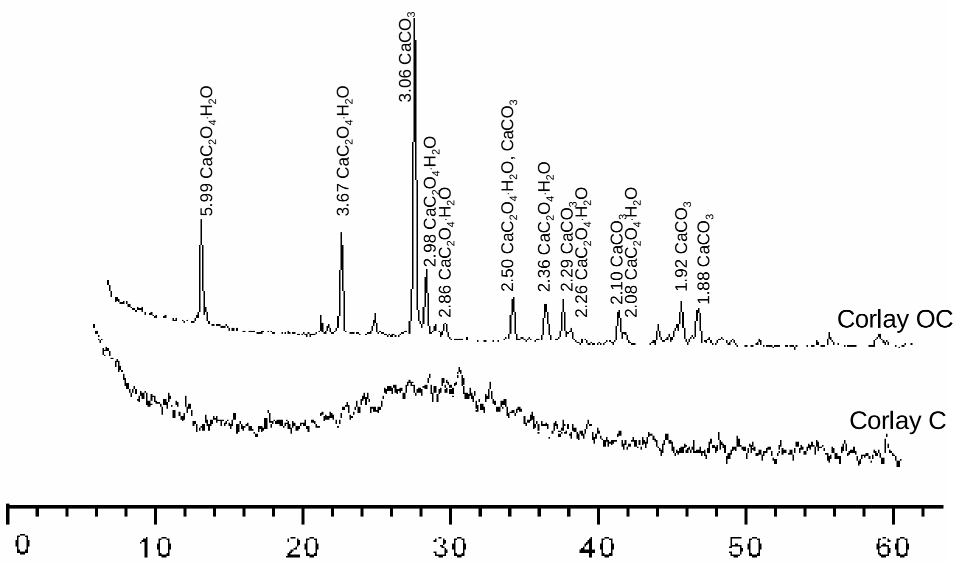

Fig. 1 – X-ray diffraction patterns of the samples corroded for 180 days in hydrochloric acid, with (Corlay OC) and without (Corlay C) oxalic acid treatment

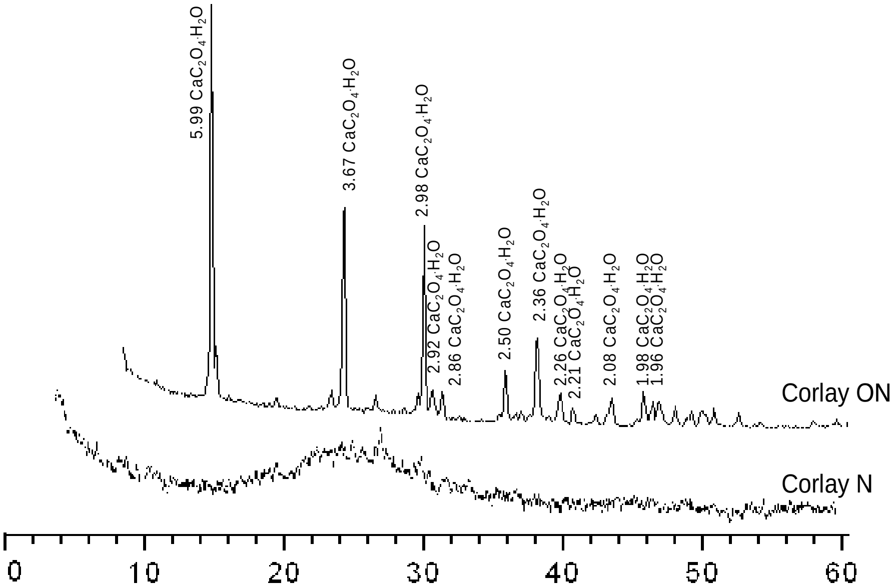

Fig. 2 – X-ray diffraction patterns of the specimens corroded for 180 days in nitric acid, with (Corlay ON) and without (Corlay N) oxalic acid treatment

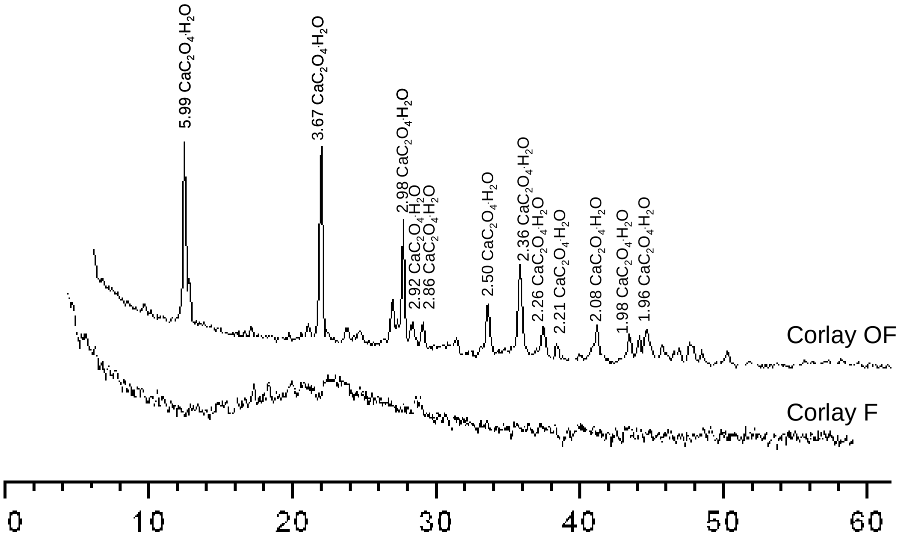

Fig. 3 – X-ray diffraction patterns of the specimens corroded for 180 days in formic acid, with (Corlay OF) and without (Corlay F) oxalic acid treatment

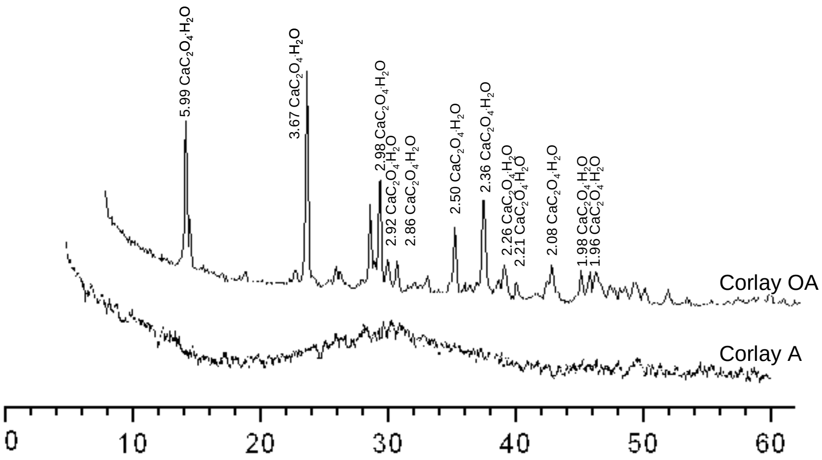

Fig. 4 – X-ray diffraction patterns of the specimens corroded for 180 days in acetic acid, with (Corlay OA) and without (Corlay A) oxalic acid treatment

It can be noticed a different composition of the corrosion products for the specimen layers obtained with and without oxalic acid treatment. The diagrams of the corroded layers formed at the surface of the samples untreated with oxalic acid show the presence of compounds in amorphous state, for all the types of corrosive acids used. For the samples treated with oxalic acid, there are noticed peaks characteristic to the monohydrated calcium oxalate at 5.99Å, 3.67Å, 2.98Å, 2.86Å, 2.50Å, 2.36Å, 2.26Å and 2.08Å; in the case of the hydrochloric acid there are also peaks characteristic to the calcium carbonate at 3.06Å, 2.50Å, 2.29Å, 2.10Å, 1.92Å and 1.88Å.

3.2 Mechanical strength

Compressive strength was assessed on the mortar specimens corroded in acids, with and without oxalic acid treatment. Figure 5 shows the evolution of the compressive strength for the samples corroded in acids, with and without oxalic acid treatment, with respect to the compressive strength of the reference samples. The relative compressive strength was computed as the ratio between the strength of the corroded and reference specimens.

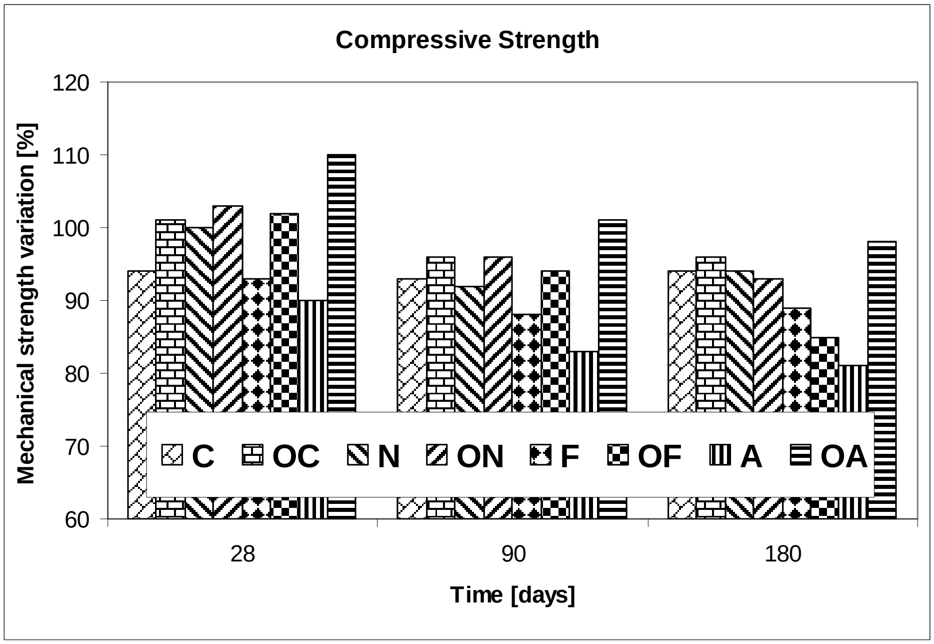

Fig. 5 – Variation of the relative compressive strength for the samples treated and untreated with oxalic acid

The protective effect of oxalic acid can be noticed up to 28 days for the samples cured in hydrochloric, nitric and formic acids.

After 90 days the protective effect of the oxalic acid is still observed in the case of the acetic acid. For the other acids the corrosion becomes obvious, even if the compressive strength of the samples treated with oxalic acid are bigger than those of the samples without surface treatment.

For the 180 days-term, the protective effect of the oxalic acid may be observed only in the case of the samples corroded with acetic acid. In the case of the samples exposed to nitric and formic acids, the decreases in the mechanical strength are even bigger for the treated samples than for the untreated samples.

4. Conclusions

The analysis of the information obtained from the tests carried-out on the cement mortars and pastes led to some conclusions concerning the effect of the acid corrosion on the samples treated or not with oxalic acid.

Obvious differences in composition of the corroded layers between the treated and untreated samples with oxalic acid have been observed. The X-ray diffraction patterns showed the amorphous composition of the corrosion products in the specific layers formed at the surface of the paste samples untreated with oxalic acid and the significant presence of the monohydrated calcium oxalate in the samples treated with oxalic acid, even after 180 days of corrosion in acid solutions.

From the point of view of the durability, the evolution of the mechanical strength pointed out that the oxalic acid surface treatment has no long-term protective effect against the corrosion with hydrochloric, nitric, formic or acetic acids. The delaying effect of this treatment is observed only until the 28 days-term for the hydrochloric, nitric and formic acids and until the 180 days-term for the acetic acid.

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