Pergamon

CEMENT AND CONCRETE RESEARCH

Cement and Concrete Research 29 (1999) 2005–2009

Communication

Limitations of Köch-Steinegger test to evaluate the durability of cement pastes in acid medium

A. Macías*, S. Goñi, J. Madrid

Instituto de Ciencias de la Construcción "Eduardo Torroja", c/ Serrano Galvache, s/n, 28033 Madrid, Spain

Received 1 July 1999; accepted 24 September 1999

Abstract

The durability of ordinary Portland cement and ground granulated blast furnace slag pastes in buffered acetic/acetate medium (pH 4.5) was studied by means of the Köch-Steinegger test. Results show that flexural strength measurement is not a good parameter to evaluate the degradation degree of cement paste in acid medium because two effects take place with opposite consequences on flexural strength as a result of acid attack: a densification of the cement paste in the specimen core and a degradation of the outer surface with loss of resistance. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Durability; Acid attack; Pore solution; Granulated blast furnace slag-cement paste

1. Introduction

Cement in not durable in acid medium. The acids completely decompose the hydrated and unhydrated cement paste components. Calcium hydroxide is dissolved and the hydrate silicate and aluminate phases are decomposed, resulting in removal of Ca^{2+}.

Despite the severity of this type of attack, there are few papers aimed at elucidating the processes involved, and there is no standardized method to assess the performance of cements in an acid environment. Both facts make analysis and comparing the few available results difficult, because the parameters used to evaluate the durability differ from one test to another. Thus, some authors measure the thickness of the corrosion layer developed in acid medium [1–5]. Others measure the acid consumption [6] or the pH variations in the surrounding media and evaluate the buffering capacity of the material [7]. Others determine, through scanning electron microscopy or chemical analysis, the decalcification of the material [2,8] and few authors measure the mechanical strengths [2,7].

As a part of a large program to study the behavior of cement matrices in acid media and its influence on metal immobilization in the stabilization/solidification process of toxic wastes [9–13], the authors have tried to evaluate the durability using the Köch-Steinegger test [14]. This test is based on the evaluation of the degradation of the material in a certain medium by its loss of mechanical properties, especially the flexural strength, which is more sensible to the degree of degradation than is the compressive strength. To accelerate the processes and obtain results in a short period of time, the test uses small specimens that are immersed in aggressive solution. The concentration of the aggressive solution must be higher than that of the natural environment. The evaluation of the results is based on comparison of the behavior of similar specimens immersed in the aggressive medium and in distilled water. If the lost of strength is less than 70%, the material is considered durable in the tested medium.

2. Methods

2.1. Materials

The chemical composition of the ordinary Portland cement (OPC) and the ground granulated blast furnace slag (BFS) that were used are shown in Table 1.

2.2. Procedure

Cement pastes with and without addition of 80% BFS (by weight of mixture) were prepared at a water to cement ratio of 0.4. Specimens of 1 × 1 × 6 cm were molded and compacted by vibration. After 1 day at 100% relative humidity (RH) the specimens were demolded, put in insulated bags, and submitted to a curing period of 21 days at 100% RH and 21 ± 2°C. After curing, groups of six samples were

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* Corresponding author. Tel.: +34-3-020-440; fax:+34-3-020-700.

E-mail address: Maria-Angeles.MACIAS@ cec.eu.int;pesqezz@fresno.csic.es (A. Macías)

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PII: S0008-8846(99)00196-9

Table 1
Chemical composition of the cement and ground granulated blast furnace slag used (mass %)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	MgO	Na_2O	K_2O	S^{2-}	IL	IR
OPC	65.32	20.06	5.32	2.92	3.09	1.28	0.20	1.03	–	1.47	0.83
BFS	40.17	37.64	12.54	1.15	–	8.15	0.24	0.64	1.20	1.40	0.11

Abbreviations: IL, ignition loss; IR, insoluble residue.

immersed in an acid buffer solution of 0.87 M AcH/AcNa (pH = 4.5) and in distilled water. In all cases, the samples were stored in sealed bottles and kept at room temperature for different periods of time before making flexural strength measurements. The volume of the liquid was 800 mL per six samples.

3. Results

3.1. Flexural strength measurements

The evolution of the flexural strength (F_s) vs. time is given in Fig. 1 for OPC and OPC + 80% BFS samples. Each value is the average of six measurements and the dashed zone is the standard deviation of the mean value.

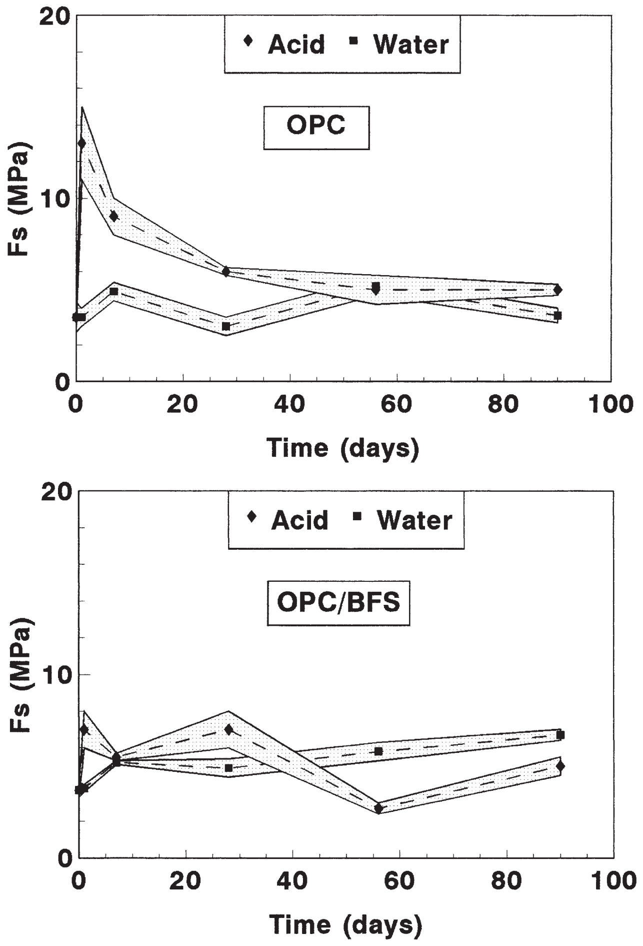

Fig. 1. Evolution of flexural strength vs. time.

At the moment of immersion in the solutions (after 21 days of curing at 100% RH), both paste samples with and without BFS addition have a similar value of flexural strength—about 3.5 MPa. When these samples are immersed in water the values of flexural strength slightly increase after 1 day of immersion and then remain around values of 4 to 5 MPa for plain OPC samples and around 5 to 7 MPa for OPC + 80% BFS samples. In the case of the acid aggressive medium, this initial increase of strength after 1 day of immersion is particularly strong for the plain OPC samples, which reached values of 13 MPa, and in a minor extension for the OPC/BFS ones (F_s = 7 MPa). Afterwards, values started to decrease until reaching about 5 MPa after 56 days. If according to Köch-Steinegger method the values of resistance measured in both media are compared and the corrosion index at the different periods of immersion are calculated (see Fig. 2), both samples of plain OPC and OPC/BFS seem to be resistant to the buffered acid acetic/acetate attack, at least for 56 days. The acid medium even has beneficial effects on durability of plain OPC samples for which corrosion indexes well above 1 are measured until the end of the test. Nevertheless, at periods longer than 56 days, values slightly under 0.7 are registered for OPC/BFS samples, indicating some degradation of the material.

3.2. Corrosion depth measurements

In contrast to what was expected from results of F_s, a degradation of the samples takes place even in the case of OPC samples. Thus, a visual examination of OPC samples show that after only 1 day of immersion in acetic/acetate buffered solution, an external white layer, easily removable with perpendicular cracks, appears [9]. Underneath this layer it is also possible to observe another internal, light grey layer of altered, more amorphous and porous cement. After 7 days, the external layer has a yellowish color attributable to the precipitation of iron products, as other authors have pointed out [4,7], and in the interface between the internal layer and the undamaged core of the sample a white front of ettringite crystals appears, as analyzed and detected by scanning electron microscopy and X-ray techniques. After 28 days, the massive precipitation of crystals in this white front causes the coat to scale off, disclosing another internal degradation coat of altered material.

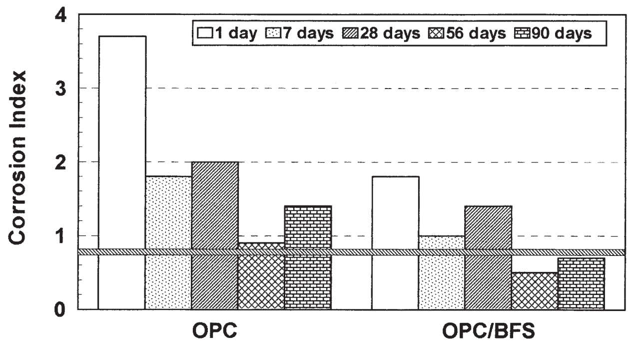

Fig. 2. Corrosion index (F_{sagg}/F_{sw}) for OPC and OPC/BFS samples.

In the case of OPC/BFS samples, it is only possible to see an external degradation layer in the cross section observation. The surface of the sample has an orangish-yellow color and the external corrosion layer is white in its center and then dark grey near the interface with the unaltered core. The white precipitation front seen in plain OPC samples is not present in OPC/BFS samples.

In Fig. 3, the values of the corrosion depth are presented vs. the square root of time. The linear relationship of the corrosion depth with the square root of time confirms the diffusion-controlled mechanism of the acid attack. The relationship found for the external layer is similar to that reported by Pavlík [3] for acetic acid solution of pH = 3.73 ($d = 0.163 \cdot t^{0.525}$). Although the growth of the external layer follows the same law, with time its thickness in OPC/BFS is almost twice that of plain OPC samples.

In agreement with these results and considering that the material in the corroded layer has lost its cohesive properties, the measured flexural strength values have been recalculated for the core dimension of the specimens (Fig. 4). As can be seen, the strength values increase with time, suggesting that the core of the samples is being densified while under acid attack.

The densification of the gel in samples was verified by scanning electron microscopy [9] and corroborated by pore size distribution measurements [10]. In the samples stored in acid medium the CSH gel has a lower pore content, a lower Ca/Si ratio, and a higher content of Na than that of CSH gel formed in OPC and OPC/BFS samples immersed in distilled water. This densification of the gel, which was also reported by other authors in strong chloride solution [15], is related to the decalcification of the gel and probably to the increase of its degree of polymerization in acid medium, leading to higher strength values. As shown in Fig. 5, the increase of flexural strength with time is parallel to the increase of the concentration of calcium measured in the pore solution, which agrees with the progressive decalcification of solid phase.

4. Discussion

The acid attack of cement is a complex mechanism in which several processes are involved, generating different concentration gradients of species from the core of the sample to the surrounding acid medium (see Fig. 6).

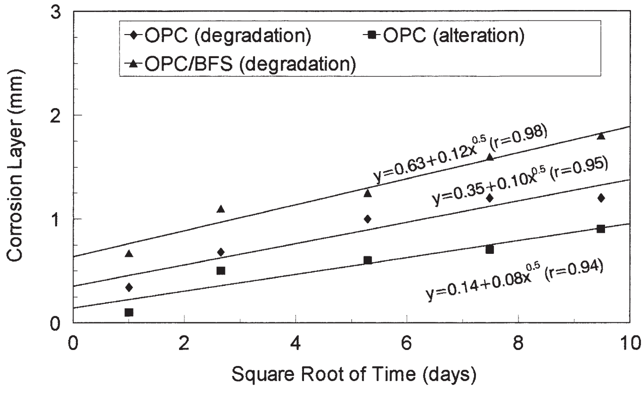

Fig. 3. Depth of corrosion layers vs. square root of time.

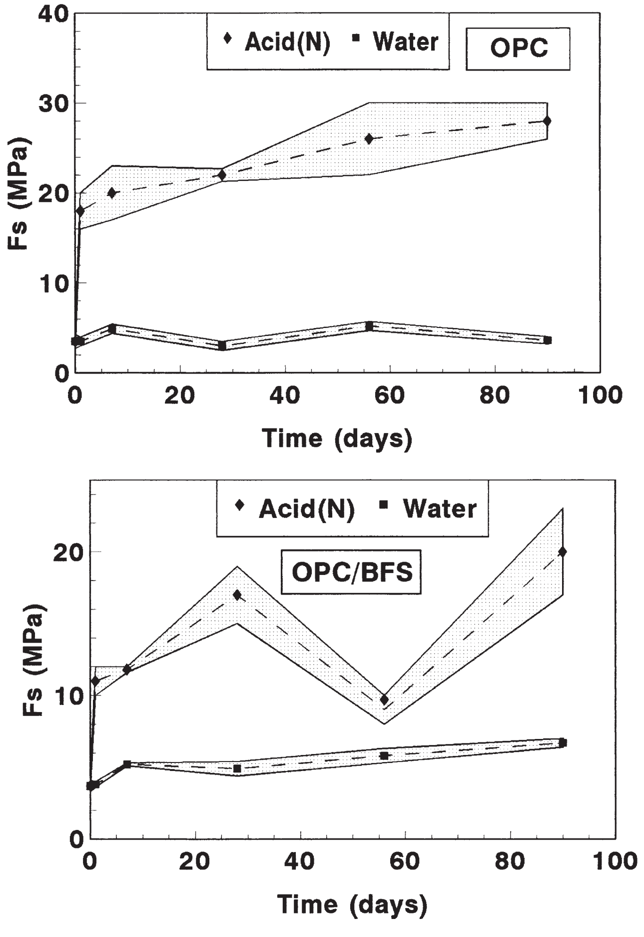

Fig. 4. Evolution of flexural strength calculated for core dimensions vs. time.

- Initial dissolution of calcium hydroxide (CH), leading to an increase of Si/Ca ratio of CSH gel, that becomes denser and polymerizes; consequently flexural strength increases, as porosity and scanning electron microscopy results corroborate.
- After total dissolution of calcium hydroxide, CSH gel is attacked, losing the calcium of its structure, which collapses into a silicate matrix without adherence.
- Due to the pH and concentration of the migrating species and changes in the pore solution of cement paste, processes other than those previously mentioned also take place simultaneously. Thus, the dissolution of other hydrated phases of cement containing calcium could liberate other ions as Fe^{3+} and sulfate. The accumulation of these ions in the inner zone of the degradation layer, caused by their diffusion from the decomposed cement paste into this zone, promotes the precipitation of ferric hydroxide and ettringite. The ferric products are responsible of the yellowish coloration and the precipitation of ettringite can cause disruptive forces and the scaling off of the degradation

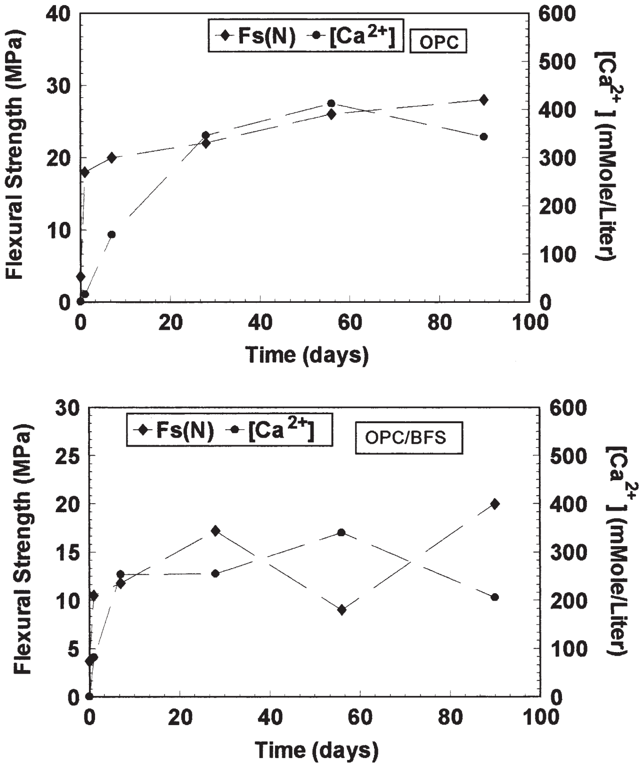

Fig. 5. Values of flexural strength for core dimensions and calcium concentration of pore solution vs. time.

layer. Under hydrochloric acid attack [8], it is also possible that precipitation of $C_3ACaCl_2 \cdot 10H_2O$ also gives rise to disintegrating stresses.

The degree and extension of these processes is a function of the concentration of the acid solution and the buffering capacity of the cement, which is mainly related to its free calcium hydroxide content. In the case of OPC/BFS, there is less CH content and the process mentioned first takes place simultaneously with the second process, making it impossible to distinguish between an external degraded layer and an internal altered layer. In addition, the buffering capacity of OPC/BFS material is lower than that of plain OPC samples, and consequently the acid consumption is lower; also lower is the pH of the acid medium, which is then more aggressive. It should be considered that if the acid medium is not a buffer solution, as the acetic acid/acetate solution used here, the pH decreases rapidly as a consequence of Ca^{2+} and OH^- liberation from cement paste. Nevertheless, the pH of the buffered acid medium increases to values of about 11 for plain OPC samples immersed during 56 days [12], inducing a deceleration of the attack at longer ages. If the acid had been renewed, the specimen would probably have been totally destroyed. For OPC/BFS samples this increase of pH toward basic values does not occur, since the pH value of the acid solution is equal to 5.7 after 56 days [12].

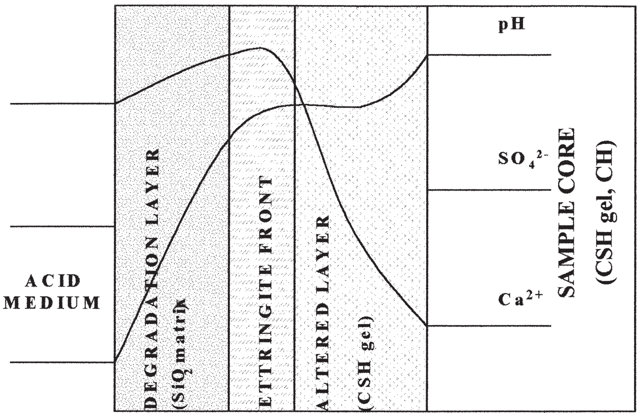

Fig. 6. Schematic view of OPC specimen under acid attack.

Finally, since the calcium dissolution is the main variable that controls the degradation of the cement material, the F_s must be related to it, as well as the growth of the corroded layer at the surface of the material. In Fig. 7 it can be seen that in the present case, this relation can be found: there is a linear relationship between the calcium content of pore solution and F_s, and another between the calcium content and the degradation layer thickness. The parameters of these relationships are quite similar for the two studied materials (OPC and OPC/BFS).

5. Conclusions

Tests based only on flexural strength measurements are inadequate to estimate the cement degradation under acid attack. The remaining calcium content could be a good parameter to evaluate the degree of corrosion. Nevertheless,

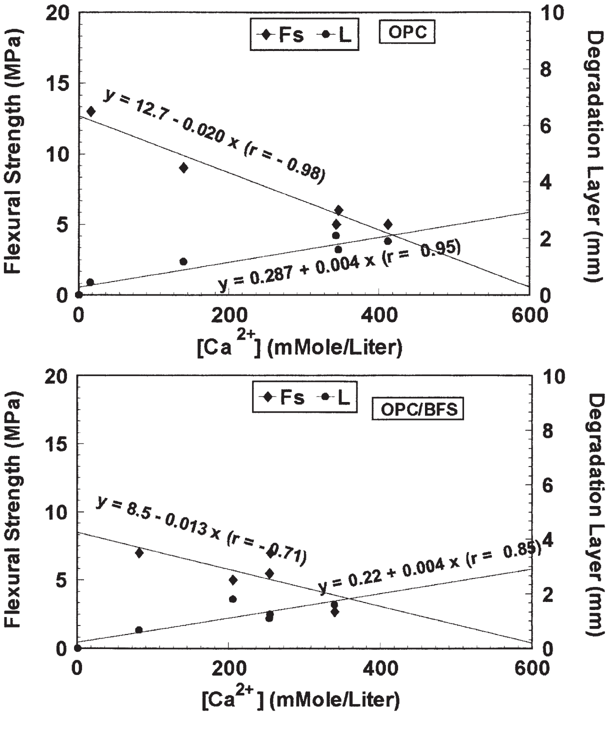

Fig. 7. Flexural strength and degraded layer thickness (degraded + altered for OPC) vs. Ca^{2+} concentration in pore phase.

the total disappearance of calcium hydroxide does not necessarily mean that the material is severely degraded; on the contrary, it could have a matrix of dense CSH gel that leads to high flexural strength and low porosity values. These results have been obtained with small specimens, and cannot be extrapolated to any particular field situation. The difficulty of knowing the limit of calcium content in considering the material as degraded obliges researchers to complement this measure with other tests, such as cross-section examination of the sample to evaluate microstructural evolution.

Acknowledgments

The authors are grateful to CICYT for financial assistance (project AMB93-0022 and AMB96-0451).

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