

Characterization cement pastes degraded in laboratory solutions and physicochemical parameters employed for modeling the process

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Abstract

Previously degradation studies carried out, over a number of different mortars by the research team, have shown that observed degradation does not exclusively depend on the solution equilibrium pH, nor the aggressive anions relative solubility. In our tests no reason was found that could allow us to explain, why some solubility anions with a lower pH are less aggressive than others. The aim of this paper is to study cement pastes behavior in aggressive environments. As observed in previous research, this cement pastes behaviors are not easily explained only taking into account only usual parameters, pH, solubility etc. Consequently the paper is about studying if solution physicochemical characteristics are more important in certain environments than specific pH values. The paper tries to obtain a degradation model, which starting from solution physicochemical parameters allows us to interpret the different behaviors shown by different composition cements. To that end, the rates of degradation of the solid phases were computed for each considered environment.

Three cement have been studied: CEM I 42.5R/SR, CEM II/A-V 42.5R and CEM IV/B-(P-V) 32.5 N. The pastes have been exposed to five environments: sodium acetate/acetic acid 0.35 M, sodium sulfate solution 0.17 M, a solution representing natural water, saturated calcium hydroxide solution and laboratory environment. The attack mechanism was meant to be unidirectional, in order to achieve so; all sides of cylinders were sealed except from the attacked surface. The cylinders were taking out of the exposition environments after 2, 4, 7, 14, 30, 58 and 90 days. Both aggressive solution variations in solid phases and in different depths have been characterized. To each age and depth the calcium, magnesium and iron contents have been analyzed. Hydrated phases evolution studied, using thermal analysis, and crystalline compound changes, using X ray diffraction have been also analyzed. Sodium sulphate and water solutions stabilize an outer pH near to 8 in short time, however the stability of the most pH dependent phases is not the same. Although having similar pH and existing the possibility of forming a plaster layer near to the calcium leaching surface, this stability is greater than other sulphate solutions. Stability variations of solids formed by inverse diffusion, determine the rate of degradation.

Originality

The majority of studies establish aggressive levels considering the aggressive environment pH and the relative solubility of calcium salts formed by anions present in the aggressive solution. This paper tries to explain the different found, taking as parameter physicochemical characteristics of the solution. Also, this paper intends to determine the relative stability of the different compounds present in hydrated cement. Moreover, it intends to determine the “double layer protection” formation process which was proposed, by certain studies, to take place in pH organic acid originated environments which in principle cannot be justified by the formed salts solubility. The aim of the paper is to obtain a numeric model which starting from the composition data of the used cements and the environment characteristics could predict the material deterioration, considering the different aggressive ion reactivity.

Chief contributions

As expected the Ca^{2+} ion was the most sensitive to the leaching effects. This phenomenon can be observed both in the leaching ion analysis results and in the corresponding solid phase analysis. Other ions such as magnesium and sulfate also present leaching profiles, however, in lower concentrations. Calcium and magnesium results indicate that during study time, a leaching profile is produced within both the acetic acid-acetate and sodium sulphate environments. This profile is present in a much higher degree in the acetic acid-acetate environment as expected, arriving to concentrations of 3 g/L of Ca^{2+} and 0.065 g/L of Mg^{2+} approximately. Among the studied cements, we can observe that the type II cement present the worst behaviour related to leaching of Ca^{2+} and Mg^{2+} . This phenomenon appears to be clearer in the acid environment and being less evident in the sodium sulfate environment. With regard to leaching of Ca^{2+} and Mg^{2+} , the cements CEM IV/B-(P-V) 32.5N and CEM I 42.5R/SR present similar behaviours in environments where leaching is observed. A slight improvement is detected in the case of the cement type 42.5R/SR referring to leaching Mg^{2+} content in relation with other cements when submerged in the most acid solution.

Keywords: paste, microstructure, degradation, leaching, thermal analysis.

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Introduction

The various existing standards relating to the aggressiveness classification of the different environments, establish the pH as one of the key variable. However it does not explain itself all observed effects. The aggressive behavior may be classified in a simple way according simultaneously to two parameters, those being the pH and the present anions. Media with a pH higher than 7 are considered low aggressive whereas media with a pH lower than 7 may be considered of important aggressiveness. There is only one exception to this general rule and it is referred to the high level of ammonia content media. In this case the medium pH after the first minutes of being in contact with the cement material establishes its pH level around of 8, presenting however high aggressiveness.

The numerous studies carried out in the leachability field have justified the existence of these two facts, by the formation of a “double layer” of carbonates in the case of pH higher than 7 and in the case of the ammonia by the increase of calcium salts solubility when the medium present an important ionic power. This fact may take place in solutions with a high content of ammonia by the high solubility of its salts.

Basically, the degradation process is determined by the portlandite solution, so the variation of this must ultimately determine the extension of the process. The data existent in the bibliography (Cardé, *et al.*, 1996) allow obtaining the concentrations of Ca^{2+} in equilibrium. In deionized water, for portlandite and CSH gel, these concentrations have the values of $20 \cdot 10^{-3}$ mol/L and $2 \cdot 10^{-3}$ mol/L, respectively. When the used medium is an aqueous solution of ammonia nitrate 6 M (Heukamp, 2003) the value of this same equilibrium concentration, in of 2.7 mol/L for the portlandite and of 0.5 mol/L to the CSH gel. This variation of concentration of equilibrium Ca^{2+} is which gives justification to the acceleration of the decalcification process. Considering this information the apparent Kps of calcium hydroxide in deionized water has a value of $3,2 \cdot 10^{-5}$. For the case of 6 M ammonia solution the apparent Kps of solubility would have a value of $8 \cdot 10^{-4}$, 25 times higher. These results may point that this equilibrium, is ultimately, the one who defines the aggressiveness. This is equivalent to say that the ionic strength and the pH are what determine the medium aggressiveness. However, if we only regard to the degradation mechanism, the medium pH has influence in the decalcification process because, basically, it is an acid/base reaction. But in order that the process progress reaches an adequate speed the electro neutrality must be maintained. Given this, in spite of the quick diffusion of the H^+ and OH^- , the process will be controlled by the calcium diffusion (Kamali *et al.*, 2008; Segura, I *et al.*, 2008). The objective of this research is establishing the importance of the different stages in the process and the influence of the different parameters of those stages.

Materials and methods

The study was carried out with paste samples of cement CEM I 42.5R/SR (reference cement) and CEM II/A-V 32.5R. The range of fly ash content is specified in UNE-EN 197-1:2000, and is in the range of 6-20%. The chemical composition is shown in Table 1.

Table 1. Mineralogical composition of the cements

Cements	Ca O	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	K ₂ O	SO ₃	P ₂ O ₅	Ign.loss
CEM I SR 42.5R	62.39	18.50	3.60	2.94	0.98	0.81	0.89	3.02	0.44	2.19
CEM II/A-V 32.5R	53.33	20.64	6.84	4.37	1.90	0.73	1.05	2.71	0.38	2.93

The cement paste samples were prisms of 10x10x60 mm² according to UNE-EN 196-3. The water/cement ratio was of 0.4. The specimens were removed from the molds after 24 hours and cured in climatic chamber for 28 days for cement type CEM I and 90 days for cements type CEM II, in order to ensure hydration reactions from the fly ashes. The climatic conditions were 96 ± 2% HR and 20 ± 2° C. There were made 4 batches (84 specimens) for the cement CEM II and 3 batches for the reference cement. Aggressive media are solutions: acetic acid/sodium acetate with a pH 4.8 and a concentration of 0.35 M; sodium sulfate with a pH 8.3 and a concentration of 0.21 M; natural water with a pH 8. The pH of the different media was measured daily during the first week of the trial and weekly from the second week. There were two control media: one was a saturated solution of calcium hydroxide and the other the laboratory environment. The specimens were covered on all sides with an epoxy resin Sikagard 62. The end of the specimens was cut in order to remove the resin from it. After this the specimens were immersed in a saturated calcium hydroxide solution, which allows the surface saturation of the specimens before reaching the stage of degradation. This will limit the phenomena of capillary suction, reducing the process to a phenomenon of diffusion/reaction. A stirring solution device was designed and manufactured in order maintain solution homogeneity (Figure 1).



Figure 1. Continuous agitation system

A system for N₂ gas bubbling was also provided, in order to prevent the dissolution of CO₂ and thus the carbonation of the samples and solutions. In this system, 9 specimens of each type of cement were immersed in each degradation media. The times of exposure to aggressive media have been 2, 30 and 92 days. At each exposure time were extracted 6 specimens for CEM I and 9 for CEM II. Then the specimens are cut into sections approximately 2 mm thick, perpendicular to the longitudinal axis of the specimen. 8 cuts were carried out in every sample obtaining 8 layers per sample. The cut was made with a precision cutter petrographic Struers, Model Secotom-10, with diamond of 0.4 mm thick. After removing the resin, samples were pulverized in an agate

mill Retsch RM 200 Automatic. Then the powder was sieved with a screen size of 0.16 mm. The ion Ca²⁺, Mg²⁺ and Fe³⁺ determination was carried out through an Ionic Chromatograph professional series mark Metrohm model 882 Compact IC, with an automatic sample processor model 858 equipped with ultra-filtration. The coupled columns are: anionic column Metrosep A Supp 5 250 and a cationic Metrodep C-3 250 column. In the layers 1, 2, 3, and 8 the ions were determined for both cements and in aggressive and reference media.

The thermal analyses were carried out within a Simultaneous Thermal Analyser Labsys Evo 1600 of Setaram, equipped with a precision balance of ±0.01%. The employed detector was a TG/ATD CAÑA that includes a platinum-rhodium transducer capable of operating in conditions of up to 1600°C. The employed crucibles were alumina (α-Al₂O₃). As reference for data acquisition of ATD it was employed alumina from the own reference crucible. The dynamic heating ramp applied to the samples varied from 25°C to 1200 °C. The heating speed was of 10°C/min. The test atmosphere was N₂, with an approximate flow of 80 ml/min.

Results

Figures 2 and 3 show the percentage of Ca²⁺ and Fe³⁺ related to cement weight of the different analysed wafers in the samples subject to a solution of sodium acetate/acetic acid. Figure 4 show the percentage of Ca²⁺ and Fe³⁺ related to cement weight at different depths of the samples exposed to sodium sulphate. In Figure 2 it is observed that for both cements and after two days of exposure there is already a slight loss of Ca²⁺. The behavior of both cements is almost the same. After 30 days of exposure, the Ca²⁺ is more significant being established at a depth of around 4.5 mm. This degradation

depth matches with the experiments after 2 days of exposure. The loss of Ca^{2+} concentration after 90 days of exposure ceases at a depth of around 10.5 mm. In Figure 3 there is no substantial Fe^{3+} content variation after 2 days of exposure, however, after 30 days, the Fe^{3+} variations relating the reference simple contents are considerable. These percentages are increases of 4.5 and 5.5 in the CEM II and the CEM I respectively. The behaviour of both cements is similar, being the Fe^{3+} content stabilised at a depth around 4 mm. At last, after 90 days of exposure the decrease of Fe^{3+} content starts at a depth of around of 10.5 mm. In figures 4 it is observed that in the calcium sulphate medium for any depth and any exposure time, there is not degradation of cement matrix due to ion Ca^{2+} loss. The values of the calcium concentration remain constant.

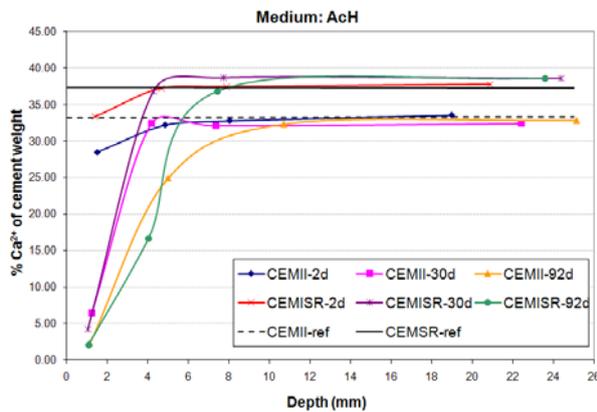


Figure 2. % Ca^{2+} cement weight at different depth in acetic acid/sodium acetate solution

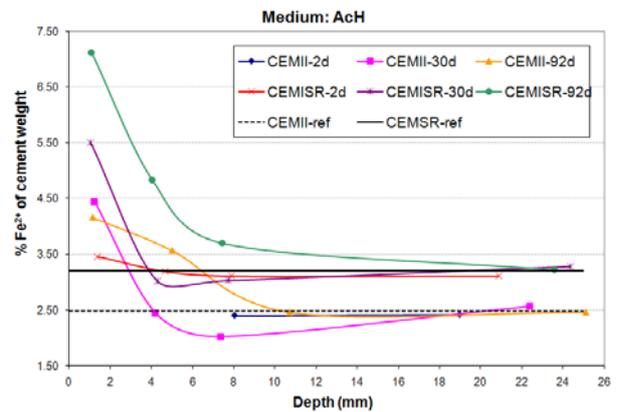


Figure 3. % Fe^{3+} cement weight at different depth in acetic acid/sodium acetate solution

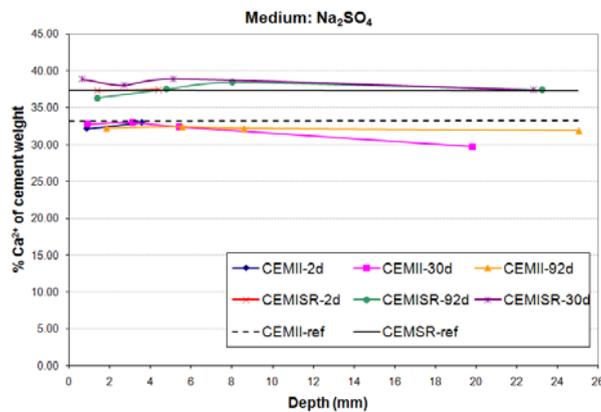


Figure 4. % Ca^{2+} cement weight at different depth in Na_2SO_4 solution

Figure 5 present the results made for our research group about of Ca^{2+} leached of samples of mortar made with cement CEM IV/B-V 32.5N exposed to three solutions with pHs 4.5, 6 and 8 [5]. Figure 6 show the result of Ca^{2+} leached obtained in the present work. In figure 5 it is observed that calcium ion leaching correspond to the pH 4.5 medium followed of the pH 8 and pH 6. In this last case, we found values almost constant since the first days of the test. In the figure 6 it is noticed a much more different behavior. The Ca^{2+} concentration is much higher in acetic acid solution. Between sodium sulfate solution and natural water the differences between the ion Ca^{2+} leached is higher in the CEM II cement being more evident when the pH decreases.

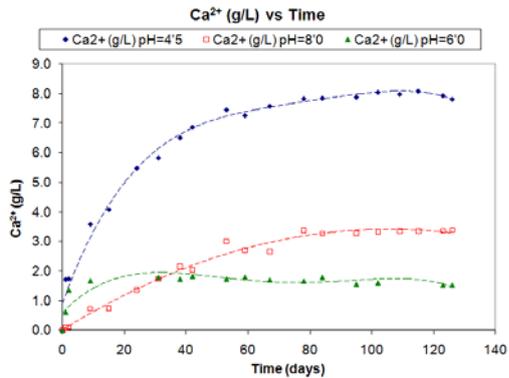


Figure 5. Ca^{2+} leached of samples of mortar made with cement CEM IV/B-V 32.5N ($a/c=0.5$)

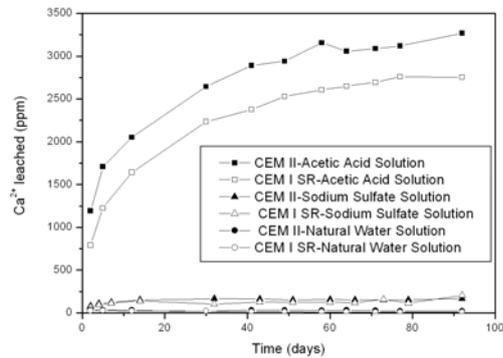


Figure 6. Ca^{2+} leached in the different solutions for cement paste samples during the time of exposition

Figures 7 and 8 show the DTA of CEM I exposed at calcium hydroxide solution and CEM II exposed at sodium sulfate solution during 30 days. Figures 9 and 10 shows the DTA of both cements exposed at acetic acid solution during the same time.

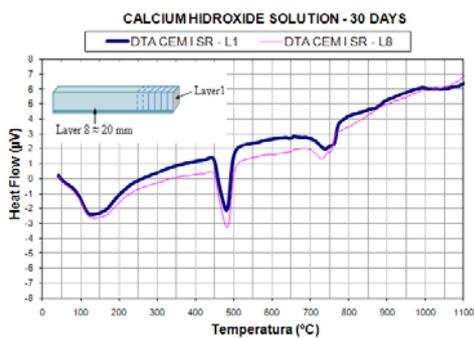


Figure 7. DTA of CEM I exposed to calcium hydroxide solution during 30 days

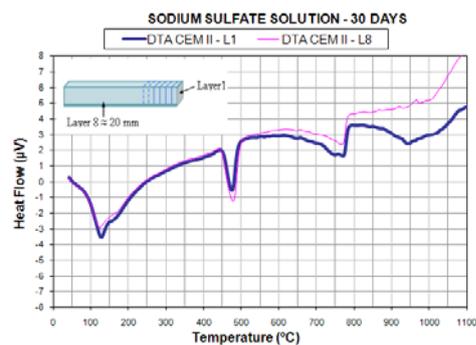


Figure 8. DTA of CEM II exposed to sodium sulfate solution during 30 days

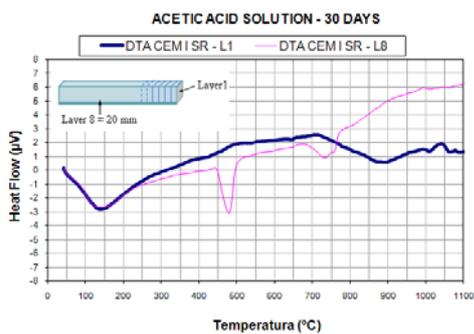


Figure 9. DTA of CEM I exposed to acetic acid solution during 30 days

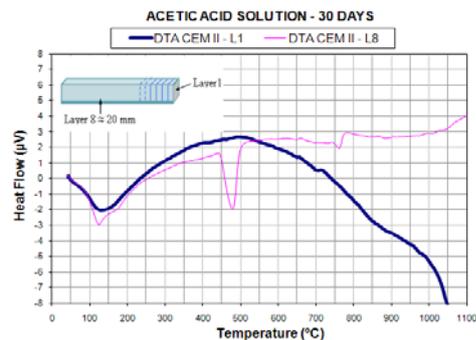


Figure 10. DTA of CEM II exposed to acetic acid solution during 30 days

In figure 7 and 8 it is shown that the portlandite and bonding water contents do not vary throughout the length of the sample. In the CEM II, the percentages of water bonding are slightly higher than those of the CEM I, at expenses of the portlandite percentages. This slight variation may be due to the pozzolanic reaction that takes place within the CEM II. After 30 days of exposure to

acetic acid solution in both cements (figures 11 and 12) is observed the total portlandite disappearance in the superficial layers. Also it is observed a decrease of the carbonate content in the same layers, compatible with the dissolution of these compounds in acid media. The resulted obtained from the calculation of the bonding water, indicate that the tendency of a slightly lower content in the CEMI regarding CEM II. The bonding water band keeps its qualitative shape although a slight decrease in the layer 1 regarding the layer 8. This decrease is more evident in the CEM II.

Discussion

The leaching analysis (Fig. 6) shows that two of the media (natural water and calcium sulphate) do not present almost calcium leaching. The calcium concentration is stabilized after few days and it is maintained on this value. In both cement generated leached by the sodium sulphate are bigger than natural water. This behavior is similar to the one shown by the mortar leached whose aggressive medium had been prepared with a buffer solution of pH 6 (Antón, 2008). In all of them there is a small stage of little extension and there is no diffusion phase. Usually this behavior has been attributed to the formation of a carbonate calcium layer (Gerad, 2002) due to the carbonization of the aggressive medium. In our experimental design it is being compared solutions of significantly different pH (between 6-9). In addition the solutions used for paste samples have been maintained with a nitrogen flow. For the mortar samples the aggressive solutions have been kept on the air, so the carbonate concentration in the solution should not be the same. In spite of all this variations of the external medium analog results are produced. This fact seems to indicate that the precipitation of carbonates is determined by the conditions of the aqueous phase, oversaturated of calcium ions in the diffusion process towards the exterior (Le Bellego, 2003), and that has almost no relevance the carbonate content of the aggressive medium.

The increase of calcium concentration present in the sulphate solutions may be caused by the increase on the solution ionic strength generated by the contribution of the sulphate ion to it. This hypothesis is reinforced comparing the apparent solubility constant value in the both leached solutions, considering them supposedly in equilibrium. The mentioned constants would have a relation of 23.97. The average values of calcium, much lower than the saturation values calculated, allow us to state that in this media the equilibrium is not reached during the studied period. The concentration values of the leaching in the ammoniac media and in pH values lower than 5 (Fig 5 and 6) show clearly the existence of two stages in the degradation process: the initial degradation stage with a kinetic of first order with respect to time and the calcium diffusion stage that according to the second Fick's law depend on square root of t. In order to determine the level of accomplishment of this hypothesis in the tested samples in the different media it has been obtained the coefficient diffusion for all the studied mortars in the two solutions of different pH. In all solution it has been favored the formation of a buffer solution that allows to keep, as far as possible, the pH constancy and the not formation of calcium insoluble precipitates. In order to calculate the diffusion coefficient ANSI standard has been used, according to which and considering the limits of the effective diffusion coefficient application, it may be calculated according to the following equation [1]

$$D_{ef} = \pi \left(\frac{a_n/A_0}{(\Delta t)_n} \right)^2 \left(\frac{V}{S} \right)^2 T \quad (1)$$

Where: a_n is leached element mass of the sample during the leaching interval (mg), A_0 is total element mass in the simple at the beginning of the test (mg), $(\Delta t)_n$ is leaching duration interval (s), D_{ef} is effective diffusion coefficient (cm^2/s), V is sample volume (cm^3), S is sample geometric surface area and T is average leached time (s). The obtained results show an initial linear stage, whose speed coefficient is function of t, and for the same type of cement its slope is in direct relation with the pH. The second leaching stage corresponds to the diffusion stage. The diffusion coefficients obtained with the paste CEM II in the solutions with pH 4.5 is of $17 \times 10^{-11} \text{ cm}^2/\text{s}$ and of $2 \times 10^{-11} \text{ cm}^2/\text{s}$ for the solution of pH 8.5. The leaching analysis in pH 4.5 for the studied cements shows the existence of a higher

slope in the solution stage for the cement with higher calcium content. However the ratio between slopes and calcium initial content remains constant in both mentioned cases. That is to say that the solution stage depends on pH and initial portlandite content (Beddoe et al., 2005). The diffusion stage depends only on the sample characteristics. The calcium and iron content analyses in the solid phases for different ages studied (fig 2 and 3) show the calcium medium degradation, pointed out simultaneously by the calcium content reduction or by the increase of iron content. This increase is not an absolute increase in the concentration of Fe^{3+} ion, but a relative increase due to loss of material. That is, it is due to loss of density of the sample. Both may be used to determine the degradation level. The thermal analysis results allow following both the evolution of the portlandite content and the water bonding. The more significant data for our study it is shown by the constant carbonate content at the different studied depths. Considering the observed effects in the iron caused by the degradation, it may be evaluated to the different ages the carbonate variation at different depths.

Conclusions

1. The media with a comprised pH between 6 and 9 do not present aggressiveness regardless of the solubility level of the existing anions. The only media that present aggressiveness to the pH are concentrated solutions of the salt, that are determined by the high variation of the ionic strength of the medium.
2. The absence of leaching is determined by the carbonate layer formation. This precipitation is produced regardless of the carbonate content of the outer solution.
3. The leaching process in the media where no protection layer is formed presents a fast initial dissolution stage and followed by slower diffusion stage. The dissolution stage presents a first order kinetic and its speed is dependent of the pH. The reaction between the amount of calcium leaching and the initial calcium content in the sample during this stage is maintained constant in the studied cements.
4. The calcium content reduction and the growth of iron content in the samples allow determining indistinctively the degradation depth.

References

- Antón Fuentes, R. (2008) Caracterización mecánica y microestructural de morteros de cemento en ambiente agropecuario, Memoria para la obtención del Diploma de Estudios Avanzados, Escuela de Ingenieros de Caminos, Canales y Puertos, Universidad Politécnica de Madrid.
- Beddoe, R. E. y Dörner, H. W.; (2005) "Modelling acid attack on concrete: Part I. The essential mechanisms". *Cement and Concrete Research*, 35, 2333-2339.
- Cardé, C., Francois, R. y Torrenti, J.; (1996) "Leaching of both calcium hydroxide and CSH from cement paste: modelling the mechanical behaviour". *Cement and Concrete Research*, 26 (8), 1257-1268.
- Gerad, B.(2002) Simplified modelling of calcium leaching of concrete in various environments. *Materials and Structures*. Vol 35, 2002,pp 632-640,35 632.
- Heukamp, F. H. (2003) Chemomechanics of Calcium Leaching of Cement-Based Materials at Different Scales: The Role of CH-Dissolution and CSH Degradation on Strength and Durability Performance of Materials and Structures. Tesis doctoral. Massachusetts Institute of Technology. Massachusetts.
- Kamali, S., Moranville, M. y Leclercq, S.; (2008) "Material and environmental parameter effects on the leaching of cement pastes: Experiments and modelling". *Cement and Concrete Research*, 38, 575-585.
- Le Bellego, C; Pijaudier-Cabot, G; Gérard, B; Dubé, J.-F. y Molez, L.; (2003) "Coupled mechanical and chemical damage in calcium leached cementitious structures". *Journal of Engineering Mechanics*, 129 (3), 333-341.
- Segura, I., Moragues, A., Macphée, D. E., Anaya, J. J. y Hernández, M. G.; (2008) "Estudio del proceso de descalcificación en morteros degradados en NH_4NO_3 ". *Materiales de Construcción*, (aceptado, en prensa)