Assessment of mortar evolution in pig slurry by mechanical and ultrasonic measurements

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A B S T R A C T

This work presents the results obtained in a long-term experiment focused on the study of the evolution of cementitious materials immersed in pig slurry at real conditions. Cement mortars were made with four different cement types and immersed in pig slurry for 48 months. Furthermore, to separate pure hydration process from pig slurry effect, mortar samples were immersed in water for 12 months at laboratory conditions. Compressive strength, X-ray diffraction and ultrasonic measurements were made in all samples. Ultrasonic measurements were made from ultrasonic images obtained from automatic ultrasonic inspections. Use of ultrasonic images has allowed the extraction of information about the state of the studied materials. An empirical relationship between ultrasonic velocity and compressive strength has been obtained and the long-term effect of pig slurry on cementitious materials has been determined.

Keywords:
Ultrasonic velocity
Characterization
Degradation
Fly ash
Mortar
Pig slurry

1. Introduction

Intensive growth in pig industry has resulted in the production of large quantities of pig manure, which is used as compost on farms. Manure storage structures are commonly made of mortar-covered bricks or precast concrete [1]. The degradation of these structures can cause the contamination of soils and underground water [2], constituting an environmental problem.

Pig slurry is the result of dilution of manure with the water used to wash stock farms. Slurry has a variable and chemically complex composition that depends on factors such as the physiology of the animal, feed type, the typology and management of the facility, etc. Therefore, it has a variable composition and a complex mix of mineral and organic compounds. The result is a potentially aggressive environment with an average pH ≈ 7, which is usually considered as non-aggressive. However, research data shows that agrarian facilities in contact with slurry, both mortars and concretes, deteriorate systematically, to the extent that serious losses in resistant capacity occur [3]. Although not clearly proven, degradation of cementitious materials under this environment can be caused by the synergy of chemical and mechanical factors and by the presence of acids and aggressive ions as acetic acid, Cl^-, SO_4^{2-}, Mg^{2+} and NH_4^+ [4].

Building of farming concrete structures is usually done using sulphate-resistant Portland cement, and silica fume and pozzolanic cement [5]. Portland cement with addition of fly ash is frequently used in the building of stock farms in Spain, due to their lower cost when compared to other cements such as OPC. Replacement of cement clinker with fly ash also improves long-term mechanical properties and decreases the hydration rate, the alkali-aggregate reactivity and the permeability of cementitious materials.

Characterization of the degradation process by manure is usually made by destructive testing [6,7], but non-destructive techniques have been little used. Ultrasonic non-destructive techniques are one of the methods frequently used for in situ quality evaluation of concrete structures. Different standards have been designed to improve quality assessment of cementitious materials by means of ultrasonic velocity measurements [8–11]. Nevertheless, for quality assessment of these materials, it is necessary to establish a relation between compressive strength and ultrasonic velocity for each case studied. Due to the obvious advantages of non-destructive testing, numerous authors have proposed relations to determine the compressive strength from the ultrasonic velocity [12–15]. Among others, the most frequently used formula to relate compressive strength (R_c) with ultrasonic velocity (V_i) is:

$$R_c = a \cdot e^{(b\,V_i)} \tag{1}$$

Table 1
Chemical composition of the cements used in this work.

Cement type	Compound (% by weight)									
	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3	Cl	Na_2O	I.L.
CEM I	64.4	19.1	3.9	4.7	1.3	0.7	3.1	–	0.2	2.6
CEM IIA	48.21	35.35	5.67	3.6	1.74	1.35	2.23	0.008	–	1.78
CEM IIB	51.36	24.80	9.19	3.25	2.14	1.41	2.58	0.006	–	1.75
CEM IV	26.05	57.45	7.4	3.5	1.24	1.39	1.26	0.006	–	1.69

where a and b are empirical parameters determined by the least-squares fitting method. Many factors that influence concrete strength (age, porosity, cement and aggregate types, composition, curing and so on) also influence the ultrasonic velocity, though not necessarily in the same way or to the same extent. For example, the presence of aggregates affects the relationship between ultrasonic velocity and compressive strength of concrete. In the same strength scale, concrete with the highest aggregate content will probably have the highest ultrasonic velocity. Therefore, it is necessary to establish a relation for each studied case. Trtnick et al. [16] have obtained a comprehensive record of the relationship between compressive strength and ultrasonic velocity for samples with different cement types and aggregate size and type and water–cement ratio.

2. Materials and experimental methodology

2.1. Materials

This study was carried out in cement mortars prepared using sulphate-resistant Portland cement (CEM I SR 42.5N), and three Portland cements with variable contents of fly ash (CEM II/A-V 42.5R, CEM II/B-M (V-L) 32.5N and CEM IV/B (V) 32.5N). All the cements are commercial cements. Therefore, the exact fly-ash content is confidential. However, the ranges of fly-ash content are specified by Spanish standards [17]: 6–20% for CEM II/A-V 42.5R, 21–35% for CEM II/B-M (V-L) 32.5N and 36–55% for CEM IV/B (V) 32.5N. Cements also had variable additions of limestone filler. The chemical composition of the cements used in this work can be seen in Table 1.

Prismatic bars were made according to Spanish standard [18] with a 0.5 water/binder ratio and a 3/1 sand/binder ratio. The specimens were removed from the casts after 24 h and cured in saturated limewater solutions for 28 days at 22° C. Subsequently the mortar samples were kept for 48 h at 22 ± 2 °C and 50% RH. Some specimens were kept under laboratory conditions to establish a reference condition.

2.2. Field experiment

To study the effect of pig slurry on cement-based materials, mortar samples were immersed in pig slurry up to 60 months (although only results for 48 months are available). To reproduce real conditions for pig manure storage in farms, an experimental pond placed outdoors was used. This pond has a surface of 4 × 8 m and 1 m depth, as described previously [19]. Pig slurry was collected from a nearer storage lagoon, located at a pig farm in Etreros (Segovia, Spain). After 3, 6, 12, 24 and 36 months, three specimens of each cement type were removed from the pond, cleaned, immersed in water for 48 h and subsequently characterized.

The slurry was replaced after each specimen extraction from the pond. Before replacement, the physicochemical characteristics of the pig slurry were analyzed. The minimum, maximum and average values are shown in Table 2. According to the substances content in the slurry, the most important ones are ammonia, sulphurs, chlorides, acetic and propionic acids. Ammonia content in the pig slurry is high enough for the pig slurry to be considered as a chemically medium aggressive environment, according to the Specific Exposure Classes defined by the Spanish Instruction for Structural Concrete [20]. Although the pH of the pig slurry will not lead us to expect an acid attack by this environment, it is potentially aggressive as the pH of the cement pore solution is higher than 12.5.

As the main component of the pig slurry is water, it is necessary to have at our disposal long-term hydration data for the samples under study. Therefore, long-term hydration under water of similar samples was carried out. Mortar specimens were immersed in water for 12 months at laboratory conditions (22° ± 2° C). Three samples of each cement type were taken out from the solution after 3, 6 and 12 months and subsequently characterized.

2.3. Experimental methods

2.3.1. Mechanical characterization

Mechanical characterization was done by compressive strength measurements, carried out in a universal test machine in keeping with the Spanish Standard [18]. Medium values were obtained from the compressive strength measurements.

Table 2
Physicochemical characteristics of pig slurry.

pH	Min. 7.43	Ave. 7.94	Max. 8.20
Conductivity (mS)	5.68	8.92	13.25
Redox potential (mV)	−304.00	−169.38	−71.00
Total solids (mg/l)	4.07	5.87	7.19
Volatile solids (mg/l)	2.04	2.95	3.98
Total nitrogen (%)	0.06	0.12	0.20
Ammonia (%)	0.05	0.09	0.12
Sulphurs (mg/l)	5.36	71.32	105.00
Bicarbonates (mg/l)	3.38	5.68	10.55
Anions			
Sulphurs (mg/l)	0.00	4.51	9.70
Chlorides (mg/l)	61.00	453.04	1388.00
Acids			
Acetic (mg/l)	32.55	153.79	286.70
Propionic (mg/l)	0.00	40.96	124.60
Isovaleric (mg/l)	0.00	2.15	3.50

2.3.2. Microstructural characterization

Microstructural characterization was done to asses the evolution of the hydrated phases of the cement paste, during immersion in pig slurry and limewater. This characterization was made by X-ray diffraction analyses of powdered samples. Samples were taken from the external part of the specimens under study. These samples were crushed and milled in an automatic agate mill. XRD analyses were made in a BrukerD8 Advance Powder Diffractometer scanning from 4° to 60° 2θ with a scan rate of 0.6° 2θ/min.

2.3.3. Ultrasonic characterization

Ultrasonic characterization was done by measuring the ultrasonic velocity of the specimens. The usual way of making those measurements in cementitious materials comprises direct or indirect transmission measures by the contact method and with commercial equipment. In these systems, ultrasonic wave propagation time is determined by the simple threshold-crossing method and generally implies precision in measurements about 0.1 μs. If this method is applied to the specimens under study, the errors made in the measurement of travelling time (approximately 10 μs) are much lower than 1%. However, if the error due to the coupling material (which can be about one wave semi period) is taken into account, the error made at low frequencies (50 kHz) increases and it could reach in the worst case a value of 25%. Besides, at low frequencies, the limited wave path compared to the long wavelength sets up a "guide wave situation" that affects velocity measurements.

To minimize these errors in wave propagation, travelling time measurements were made by immersion (to reduce coupling errors) using high frequencies, digital signal processing and automatic inspection. This inspection technique has several advantages relating to the accuracy and uniformity of the signals, the number and distribution of inspections and time saving, as well as the repetitiveness of the ultrasonic measurements.

The technique employed is called transmission imaging, which forms an image in a perpendicular plane to the acoustic-beam propagation direction. This image shows the behaviour of longitudinal velocity in different zones of mortar samples, allowing observation of the uniformity of samples as well as detection of possible defects provoked during the manufacturing processes or due to the aggressive environments. In this work, the characterization of mortar samples was performed by analyzing ultrasonic images and ultrasonic velocity mean values of each studied specimen. The ultrasonic image is a cross-sectional map made up of relative values of the measured propagation velocity. This kind of ultrasonic images are also called velocity maps.

Mortar specimens were immersed and aligned on the bottom of a water tank with controlled axis, as shown in Fig. 1. Two ultrasonic transducers scanned all the surface of the samples with a spatial resolution horizontally and vertically of 1 mm and 4 mm respectively. This scanning technique allowed obtaining 1600 signals per specimen. The travelling time was measured using a pulser–receiver

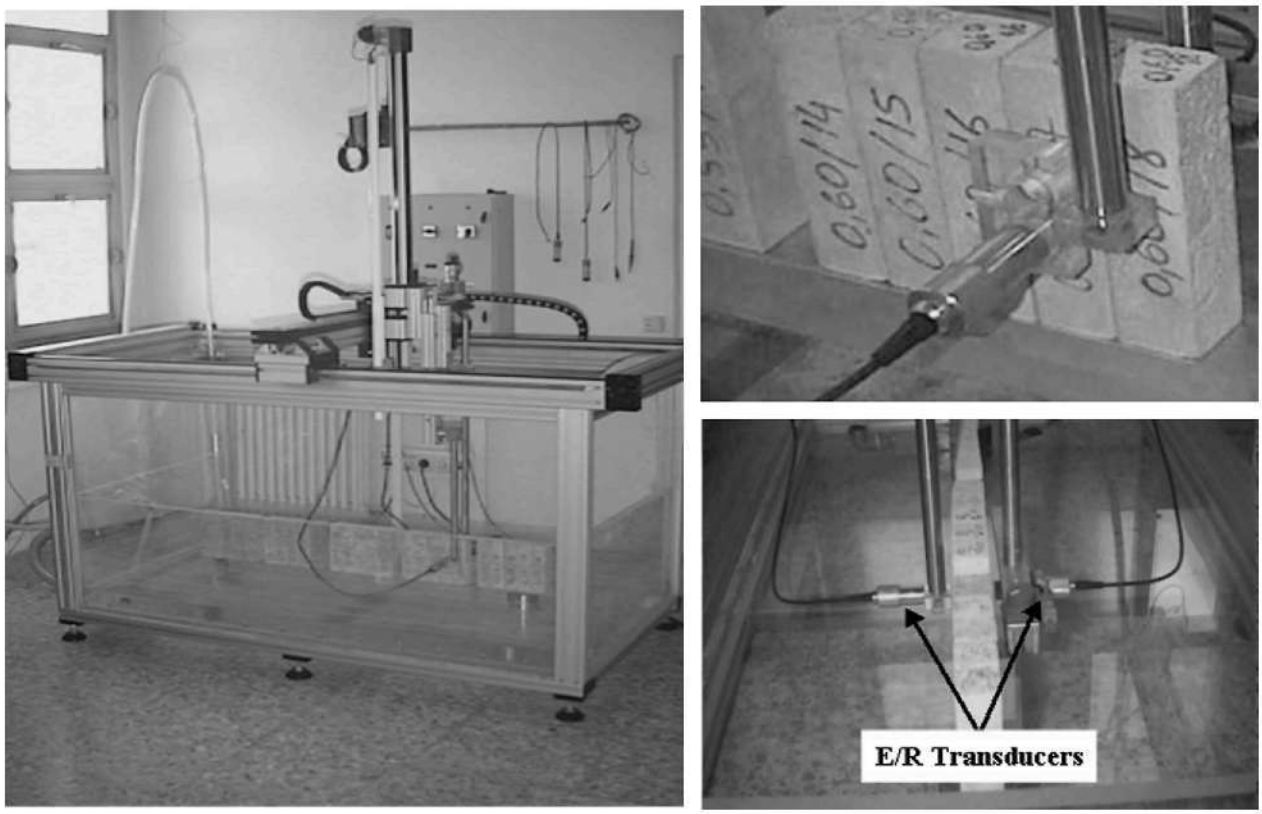

Fig. 1. Experimental setup used for ultrasonic inspections of samples.

(ULTIMO 2000), and ultrasonic signals were acquired, digitized, and processed with a high precision system (SENDAS [21]). Ultrasonic measurements were made by transmission technique, employing broadband transducers with 2 MHz central frequency and 10 mm of aperture (Krautkramer H2K), emitting in longitudinal mode.

The longitudinal ultrasonic velocity of saturated samples was calculated using the following expression:

$$v_L = \frac{X_c}{t_c - t_{water} + x_c / v_{water}} \quad (2)$$

X_c represents the path length of the specimen, t_c is the travelling time of the signal through the specimen, t_{water} is the travelling time in water (with the specimen absent) and v_{water} is the velocity in water at the inspection temperature. A zero crossing algorithm has been used to identify the travelling time of the ultrasonic signal.

The velocity map for each specimen was built with 1600 A-scan signals, obtained by automatic scanning. The map was made only for the central zone of the samples to avoid edge effects, as interferences can be found in these areas. For each sample, approximately 5 mm of each side were removed. Therefore, the velocity map represents a central area of 30 × 160 mm for each specimen. From these velocity maps, ultrasonic velocity mean values of each sample were obtained.

3. Results and discussion

3.1. Evolution of samples immersed in water

Compressive strength of the samples immersed in water can be seen in Table 3. It increases with time in all the samples studied. All samples were cured only for 28 days, so it can be expected that the hydration process has not been fully achieved, especially in those cements containing fly-ash additions [22]. Although cements containing fly ash display lower compressive strength at earlier ages, those cements show greater increases in compressive strength at long-term.

Relative increases in compressive strength at 12 months of immersion are strongly dependent on fly-ash content (CEM I: 15%; CEM IIA: 20%; CEM IIB: 39% and CEM IV: 32%) and can be related with the cement hydration processes. As samples were immersed in water for a long time, hydration reactions can take place continuously. This becomes especially important in cements with fly-ash addition, as the rate of pozzolanic reaction increases with time.

Table 3
Compressive strength of samples immersed in water for 12 months.

Sample	Compressive strength (MPa)			
	Immersion time (months)			
	0	3	6	12
CEM I	66 ± 4	71 ± 2	72 ± 1	76 ± 1
CEM IIA	64 ± 2	72 ± 2	73 ± 1	77 ± 2
CEM IIB	51 ± 1	60 ± 3	64 ± 2	71 ± 2
CEM IV	54 ± 1	61 ± 2	64 ± 2	71 ± 4

These results are in good agreement with those obtained from X-ray diffraction analyses from similar samples. XRD analysis of both reference and water immersed samples identified quartz, portlandite, calcite and ettringite as main crystalline phases. Peaks of higher intensity corresponded in all samples to quartz, due to the sand content of the samples. Evolution of the hydration of the samples was done by following the intensity variation of the portlandite peak placed at $2\theta = 18.05°$. Table 4 shows the intensity evolution with time of the portlandite peak (XRD intensity: ● strong, ○ medium, ◇ weak, — ND). Variations in the intensity of portlandite peak indicate how the pozzolanic reaction progress with immersion time.

Ultrasonic velocity measurements are shown in Table 5. Although ultrasonic velocity shows the same increases as compressive strength does, it can be expected that ultrasonic velocity of the samples made from CEM I was greater than the others, regarding the results of compressive strength. It is known that factors

Table 4
Intensity of portlandite peak (18.05° 2θ) for samples immersed in water.

Sample	Intensity of portlandite peak			
	Immersion time (months)			
	0	3	6	12
CEM I	●	●	●	●
CEM IIA	○	○	◇	◇
CEM IIB	○	○	○	◇
CEM IV	◇	◇	◇	–

Table 5
Ultrasonic velocity of samples immersed in water for 12 months.

Sample	Ultrasonic velocity (m/s)			
	Immersion time (months)			
	0	3	6	12
CEM I	4604 ± 9	4651 ± 8	4685 ± 4	4697 ± 10
CEM IIA	4687 ± 11	4754 ± 4	4783 ± 11	4818 ± 7
CEM IIB	4583 ± 12	4707 ± 13	4753 ± 7	4799 ± 8
CEM IV	4514 ± 14	4628 ± 6	4662 ± 15	4708 ± 6

Table 6
Bulk density of samples immersed in water for 12 months.

Sample	Density (g/cm^3)			
	Immersion time (months)			
	0	3	6	12
CEM I	2.467	2.448	2.463	2.461
CEM IIA	2.445	2.435	2.452	2.444
CEM IIB	2.453	2.431	2.453	2.433
CEM IV	2.455	2.457	2.455	2.460

influencing concrete strength also can influence pulse velocity, though not necessarily in the same way or in the same extent [23] and only when comparing same dosage and cement type.

Bulk density measurements show that mortar samples made from CEM I present higher density than the other samples, as seen in Table 6. Therefore ultrasonic velocity of CEM I samples will be lower, given the inverse relationship between the ultrasonic velocity and density [24].

The next step was obtaining a function capable of describing the results obtained. Several functions can relate concrete hydration or compressive strength with time. Among others, the most frequently used models are the lineal and the parabolic distribution model, developed by Knudsen [25]. Both models differ in terms of hydration kinetics. The lineal model assumes that hydration kinetics for an individual cement particle is a lineal function of time. The parabolic model considers a square root function of time.

Results provided by Bentz [26] and Carino [27] showed that short-term hydration is better described by the lineal model whereas long-term hydration is better described by the parabolic model. Therefore, in this work the parabolic model will be used to describe long-term behaviour of the ultrasonic velocity:

$$A = \frac{A_u \cdot k \cdot \sqrt{t - t_u}}{1 + \sqrt{t - t_u}} \tag{3}$$

where A is any variable that represents hydration variation with time, t is the hydration time, A_u is the saturation value of A, k is a characteristic constant value and t_u is the characteristic time. In this work, ultrasonic velocity variation with time has been modelled in this way:

$$V(t) = \frac{b \cdot \sqrt{t}}{a + \sqrt{t}} + V_0 \tag{4}$$

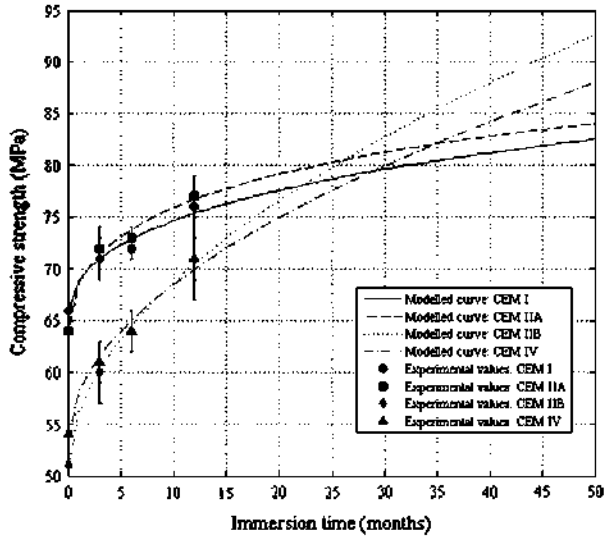

Fig. 2. Compressive strength measurements (dots) and modelled curve (lines) for samples immersed in water.

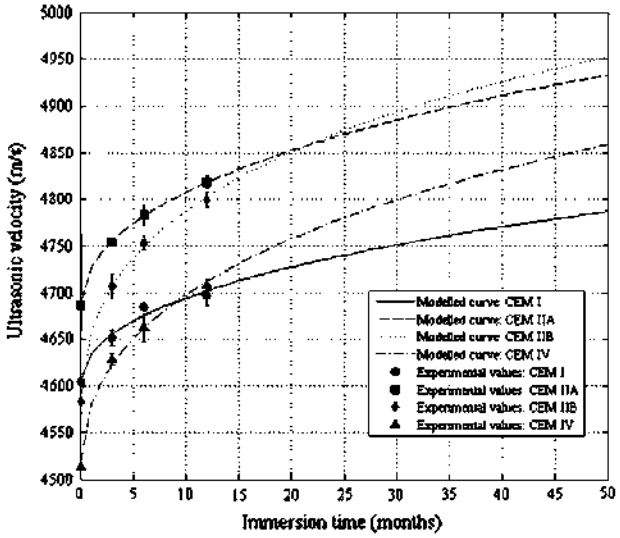

Fig. 3. Ultrasonic velocity measurements (dots) and modelled curve (lines) for samples immersed in water.

where V_0 is the starting ultrasonic velocity and a and b are the fitting parameters of the model.

Compressive strength (S) has been modelled using ultrasonic evolution with time, as follows:

$$S(t) = a \cdot e^{(b \cdot V(t))} \tag{5}$$

Curves for ultrasonic velocity and compressive strength evolution with time were obtained using (Eq. (4)) and (Eq. (5)) respectively. There is a good agreement between experimental results and modelled curves, as can be seen in Figs. 2 and 3.

Samples made from CEM I and CEM II/A cement types show an asymptotic behaviour for long-term compressive strength. Otherwise, samples made from CEM II/B and CEM IV show continuous increase for long-term compressive strength. This behaviour can be explained because of the different fly-ash content of each cement type. It must be taken into account that we have two hydration processes: cement hydration and pozzolanic reaction of fly

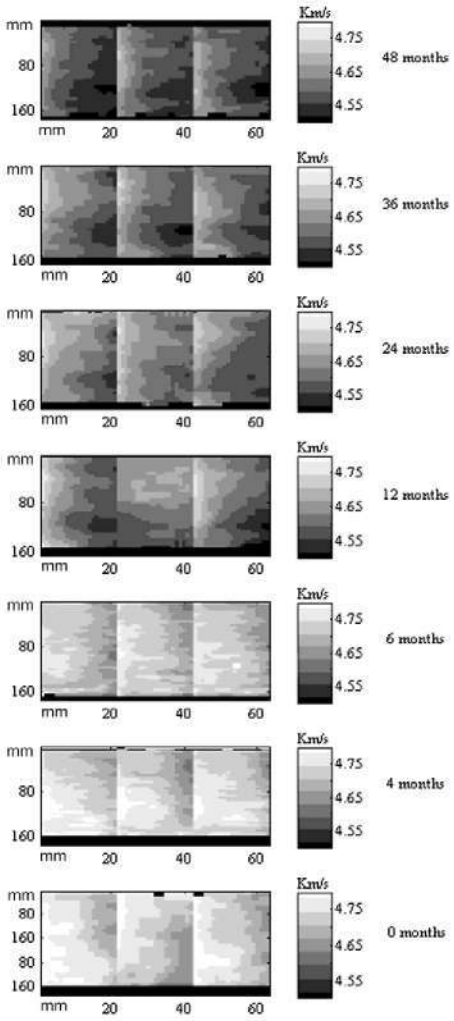

Fig. 4. Velocity maps of reference sample and samples immersed in pig slurry of CEM I mortar.

Table 7
Compressive strength of samples immersed in pig slurry for 48 months.

Sample	Compressive strength (MPa)						
	Immersion time (months)						
	0	3	6	12	24	36	48
CEM I	66 ± 4	70 ± 1	72 ± 0.1	74 ± 2	75 ± 1	72 ± 1	67 ± 2
CEM IIA	64 ± 2	69 ± 1	71 ± 1	76 ± 4	73 ± 1	72 ± 1	72 ± 1
CEM IIB	51 ± 1	57 ± 2	59 ± 3	68 ± 3	72 ± 1	68 ± 2	68 ± 3
CEM IV	54 ± 1	56 ± 1	58 ± 1	66 ± 3	68 ± 2	65 ± 1	67 ± 1

ash. Both processes are related and depend on the fly-ash content. As shown by Wang et al. [28], if enough portlandite is present the hydration of fly ash can continue. This explains why samples made from CEM II/B and CEM IV show higher long-term compressive strengths.

3.2. Evolution of samples immersed in pig slurry

Fig. 4 shows an example of the velocity maps of the reference and pig-slurry immersed samples of CEM I mortar. There is a blue-zone at the bottom part of each image, corresponding to the aluminium stand used during the ultrasonic characterization of the samples. Ultrasonic velocity is represented by a false colour image with a colour range from blue (4200 m/s) to red (5000 m/s). The velocity maps show the non-uniformity of the samples as well as the velocity variation within the same. In all samples, a high-velocity zone in the left part of the images can be seen. This area corresponds to the bottom part of the samples during the manufacturing process and can point out sand segregation phenomena.

Compressive strength of the samples immersed in pig slurry can be seen in Table 7. There is a continuous increase in compressive strength for all samples up to 24 months, after which a slightly decrease is found for all samples. Although other researchers [19,29] indicate deterioration by this kind of environment, results obtained by ultrasonic characterization and X-ray diffraction analyses in this real-time field experiment do not show such evidence of degradation.

Ultrasonic velocity measurements are shown in Table 8. Again, a continuous increase in ultrasonic velocity is seen up to 24 months. After that immersion time, ultrasonic velocity tends to an asymptotic behaviour. These trends are indicative of a hydration process more than of a degradation process. Same conclusions can be drawn from XRD analyses, as shown in Table 9. The main crystalline phases identified in the XRD analyses of samples immersed in pig slurry are the same as in the case of samples immersed in water. No traces of new crystalline phases were found on the diffractograms.

As can be concluded from the intensity variations on the portlandite peak, pozzolanic reaction in the samples immersed in pig slurry is slower when compared with the same samples immersed in water. Similarly, when increasing fly-ash content of the cement, this slowness is greater. When comparing relative increases in compressive strength of samples immersed in water and pig slurry (Fig. 5), a similar trend can be drawn. Thus, the main effect distinguishable upon immersing mortar samples in pig slurry is a decrease in cement hydration and fly-ash pozzolanic reaction rate.

This decrease in cement hydration and fly-ash pozzolanic reaction rate could be due to several factors. Although it shall not be neglected, degradation of mortar samples by effect of pig slurry is ruled out as no evidence can be found on XRD analyses and ultrasonic velocity measurements. Therefore, some kind of physical process must be slowing down the hydration process. Some authors stated that manure degradation creates a semipermeable layer in the surface of hydrated particles that limits ion diffusion [6,7]. Nevertheless, according to mean temperature variations in the area during the field experiment [30] (Fig. 6) it is more plausible that this decrease in hydration and pozzolanic reaction rate is

Table 8
Ultrasonic velocity of samples immersed in pig slurry for 48 months.

Sample	Ultrasonic velocity (m/s)						
	Immersion time (months)						
	0	3	6	12	24	36	48
CEM I	4604 ± 9	4625 ± 5	4643 ± 10	4637 ± 6	4724 ± 17	4726 ± 14	4737 ± 11
CEM IIA	4687 ± 11	4720 ± 14	4751 ± 7	4774 ± 20	4747 ± 11	4795 ± 5	4815 ± 8
CEM IIB	4583 ± 12	4650 ± 5	4678 ± 7	4728 ± 14	4808 ± 12	4809 ± 12	4826 ± 12
CEM IV	4514 ± 14	4588 ± 18	4609 ± 3	4653 ± 13	4806 ± 10	4797 ± 6	4796 ± 6

Table 9
Intensity of portlandite peak (18.05° 2θ) for samples immersed in pig slurry for 48 months.

Sample	Intensity of portlandite peak						
	Reference	3 months	6 months	12 months	24 months	36 months	48 months
CEM I	●	●	●	●	●	●	●
CEM IIA	○	○	○	◇	◇	◇	◇
CEM IIB	○	○	○	○	○	◇	◇
CEM IV	◇	◇	◇	◇	◇	◇	◇

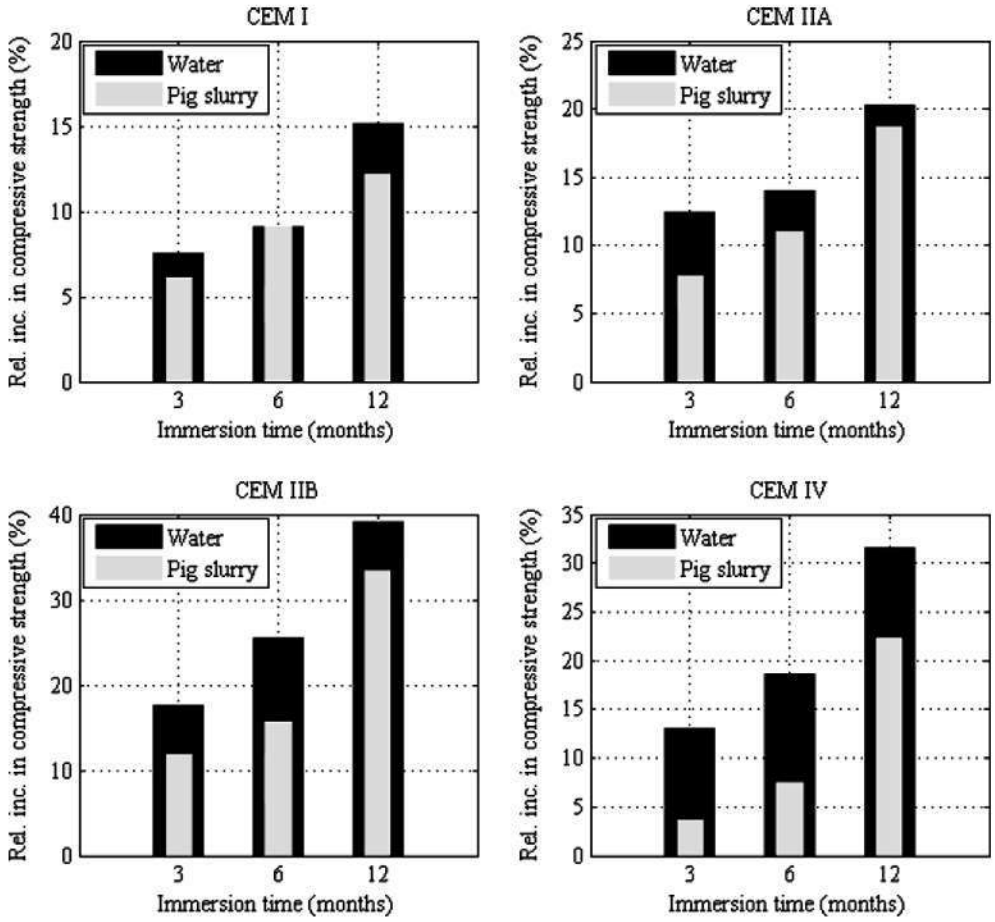

Fig. 5. Relative increases in compressive strength of samples immersed in water and pig slurry.

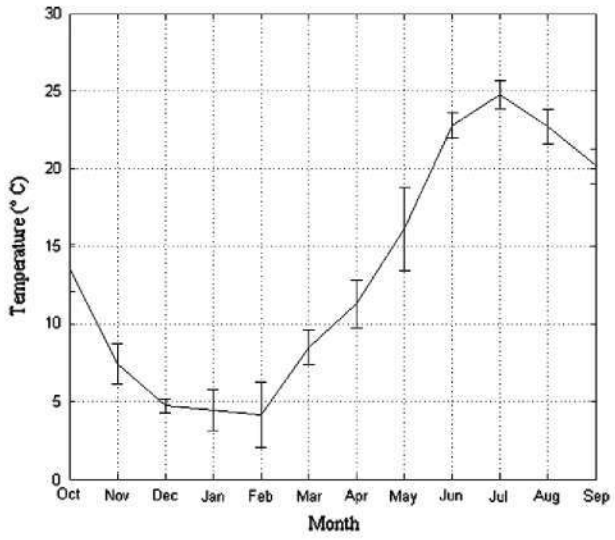

Fig. 6. Mean temperature variations at Segovia during the field experiment.

due to a thermal effect. The effect of temperature in cement hydration reactions [31] it is widely known. Also, the pozzolanic reaction rate depends on external temperature [22,32,33], but the rates of the pozzolanic reaction and of strength development are more sensitive to temperature than are those of hydration and strength development for pure Portland cements [31].

Assuming that the evolution of samples immersed in pig slurry is similar to a hydration process under low temperatures, (Eq. (4)) and (Eq. (5)) were used to model the evolution with time of those samples. Comparison of measured values of compressive strength and ultrasonic velocity and modelled curves can be seen on Figs. 7 and 8 and, respectively.

There is a worse agreement between modelled and measured values for samples immersed in pig slurry. These differences can be due to the questions indicated previously, as hydration and pozzolanic processes may have been modified by temperature variations during field experiment and by physicochemical characteristics of pig slurry. Furthermore, these differences are greater when analyzing compressive strength results, as ultrasonic measurements are more precise than strength measurements.

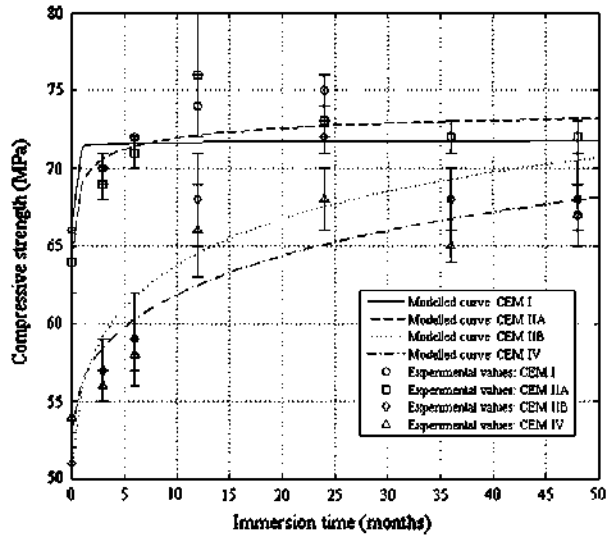

Fig. 7. Compressive strength measurements (dots) and modelled curve (lines) of samples immersed in pig slurry.

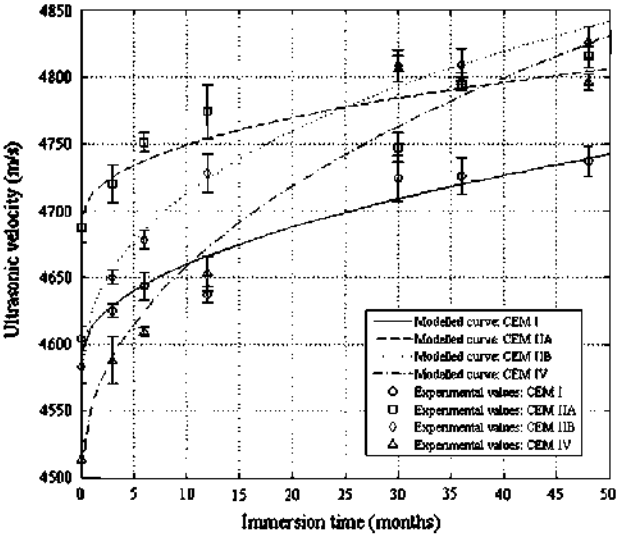

Fig. 8. Ultrasonic velocity measurements (dots) and modelled curve (lines) for samples immersed in pig slurry.

5. Conclusions

It has been observed there is no evidence of mortar degradation by its immersion in pig slurry, at least by the results presented here (48 months of immersion). Compressive strength and ultrasonic measurements of samples immersed in pig slurry for 48 months do not allow us to state that there is an appreciable degradation of those samples. Furthermore, the results indicate the continuation of the hydration reactions of both cement and fly ash. Similar conclusions are obtained when examining XRD analyses of those samples. This hydration is lowered when compared with the same process in water, because of the temperature variations during the field experiment.

Ultrasonic velocity variation with immersion time, in both water and pig-slurry immersed samples, has been successfully modelled using Knudsen parabolic model for cement hydration. Furthermore, compressive strength variation with immersion time has been successfully modelled using ultrasonic velocity. Accurate and precise ultrasonic velocity measurements were made by automated ultrasonic inspections in transmission mode in water-submerged samples. It has been shown that with precise ultrasonic measurements characterization of cementitious materials is possible, helping to assess its degradation state.

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