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

I. Segura [a,*], E. Sánchez [b], A. Moragues [c], M.G. Hernández [d]

[a] *Mechanical Engineering Division, Cartif Technology Centre, Parque Tecnológico de Boecillo, Valladolid 47151, Spain*
[b] *Dept of Science and Technology Applied to Agricultural Technical Engineering, School of Agricultural Technical Engineering, Polytechnic University of Madrid, 28040 Madrid, Spain*
[c] *Dept of Civil Engineering: Construction, School of Civil Engineering, Polytechnic University of Madrid, 28040 Madrid, Spain*
[d] *CAEND - CSIC/UPM, 28500 Arganda del Rey, Madrid, Spain*

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ABSTRACT

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.

## 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 $\approx$ 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 ($V_l$) is:

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

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[*] Corresponding author. Address: Cartif Technology Centre, Parque Tecnológico de Boecillo, 205, 47151 Boecillo, Valladolid, Spain. Tel.: +34 983 54 65 04; fax: +34 983 54 65 21.
*E-mail address:* ignseg@cartif.es (I. Segura).

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**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.<br>7.43 | Ave.<br>7.94 | Max.<br>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° $2\theta$ with a scan rate of 0.6° $2\theta$/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