

# Microstructural characterization of aged mortar by destructive and non-destructive testing

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## 1. Introduction.

Degradation of concrete structures by effect of different aggressive environments is one of the most important reasons of failure in service. Characterization of these degradation processes and the effects in the microstructure is necessary in order to establish the ways to avoid and prevent the failure of concrete structures.

Accelerated ageing processes are widely used in order to allow the characterization of the degradation process which takes place in cement based materials by the action of environmental conditions, aggressive chemicals and other factors. Several works have been done in the field of microstructural characterization of aged mortars by means of destructive testing [1-3], but less work has been done in the field of non-destructive testing of this kind of processes [4-6]. Recently some works have been presented relating destructive and non-destructive testing of this materials and modeling the variation of microstructural characteristics [7, 8], but there is still work to do in order to correlate non-destructive testing and deeply microstructural characterization.

The focus of this work has been the microstructural characterization of aged mortar samples. Samples were aged by immersion under an ammonium nitrate solution. Microstructural characterization was approached by destructive testing (porosimetry and scanning electron microscopy) and non-destructive testing (analysis of ultrasonic pulse velocity).

## 2. Experimental program.

### 2.1 Materials and ageing process.

Four series of mortar samples were cast on prismatic moulds of size 40 x 40 x 160 mm. Table 1 presents mortars dosage. This materials were made from commercial cement (Cem III/B 32.5N/SR/BC; 69% BFS and 31% Clinker) and silicon sand (CEN-Standard Sand EN 196). Mortars

were stored during 24 hours in their moulds, in a climatic chamber (96% RH / 20° C), and cured during 28 days under water at 20° C.

Table 1 – Mortars used on the analysis

Sample	w/b	s/b	Sample	w/b	s/b
MC45303X	0.45	3:1	MC45201X	0.405	2:1
MC45304X			MC45202X		
MC55301X	0.55		MC55201X	0.505	
MC55302X			MC55202X		

The ageing process was made with ammonium nitrate, which creates a soft acid medium (pH  $\approx$  4.5-5) and accelerates calcium leaching by formation of highly soluble calcium nitrate salts. This ageing process has been widely described in other papers [2, 9]. Cubic mortar samples (40 x 40 mm) were immersed under an ammonium nitrate solution (300 g per liter) during 31 days. Samples were taken out at 5, 10, 20 and 31 days of immersion. After each time of ageing, ultrasonic velocity and open water porosity measurements were done.

## 2.2 Destructive characterization.

Destructive characterization of aged mortar samples was made by the author at the Chemistry Department of the University of Aberdeen. Several destructive techniques were used in order to characterize the microstructure of aged mortars: Mercury Intrusion Porosimetry (*MIP*) and Scanning Electron Microscopy (*SEM*). Open water porosity measurements (*OPW*) were also made at the School of Civil Engineering of Madrid. Thermogravimetry and Differential Thermal Analysis (*TG/DTA*) and X-Ray Diffraction (*XRD*) analyses of the samples were also made. That results are currently been analyzed and will be presented in further publications.

*MIP* analyses were conducted in a Micromeritics PoreSizer 9300, operating in a range of pressures from 0.01 to 31 MPa, which measures pores diameters in the range of 125 to 0.04  $\mu$ m. *SEM* analyses were conducted in an ISI ABT-55 electronic microscope. Samples for *MIP* and *SEM* analyses were cut from the mortar cubes, with a low speed diamond saw, cooled with liquid paraffin. *MIP* samples were cut in 5 mm intervals and *SEM* samples were cut in 10 mm intervals. Samples always come from the middle part of the cube, in order to avoid wall effects.

The main objective of the destructive characterization is to obtain profiles of different microstructural characteristics, in order to obtain a whole picture of the microstructure variation with depth. This characterization is necessary in order to achieve a good interpretation of the non-destructive characterization results.

### 2.3 Non-destructive characterization of samples.

Non destructive characterization was made by ultrasonic testing. Ultrasonic longitudinal velocity was measured using broad band transducer of 2 MHz of central frequency, Krautkramer H2K, emitting in longitudinal mode. Ultrasonic signals have been acquired at 80 MHz of sampling frequency with an equipment of high precision, SENDAS system. Inspections have been made with samples immersed in a water tank with controlled axis. Samples are aligned in the bottom of the tank and the two ultrasonic transducers scan all the samples surfaces with a spatial resolution of 1 mm in the horizontal and vertical direction.

A transmission inspection was made to calculate ultrasonic velocity of saturated samples. The following expressions have been used:

$$v_L = \frac{X_c}{t_c - t_{water} + \frac{X_c}{v_{water}}} \quad (5)$$

$X_c$  represents the path length of the specimen,  $t_c$  is the traveling time of the signal through the specimen,  $t_{water}$  is the traveling time in water (with the specimen absent) and  $v_{water}$  is the velocity in water at inspection temperature. It has been used zero crossing algorithm to know the traveling time of the ultrasonic signal. Due to the leaching process can modify the dimensions of mortar samples, two pulse-echo inspections (from both sides) have been realize to know exactly  $X_c$  in each point.

### 3. Results and discussion.

#### 3.1 Destructive characterization.

Prior to the destructive testing, all the samples where tested with in order to determine the depth of acid attack, as can be seen by the variation in the pH of the pore solution. Some of them can be seen in figure 1. The zone that appears in pink color has a pH > 8.

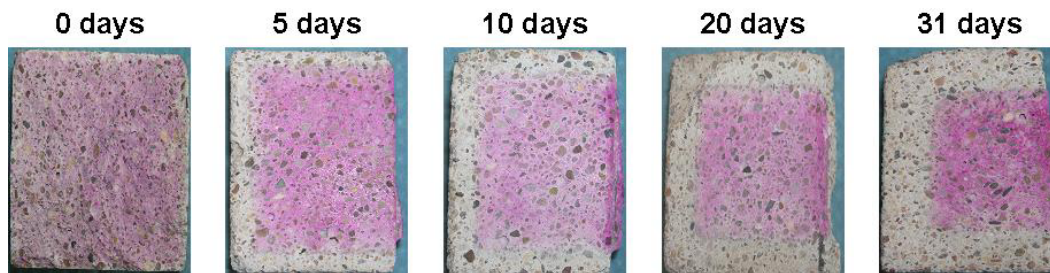


Fig. 1 – Phenolphthalein tests in some degraded and non-degraded mortar samples. S/b: 3/1; w/b: 0.45.

The pH diminution is a direct effect of the leaching process as the ammonium nitrate creates a buffer solution. It can indicate how the leaching process progresses but it can not be used as a direct measure of calcium depleting. Results of measuring the thickness of the leaching front from the phenolphthalein test are presented in table 2. These results will be correlated with *SEM* analyses in order to establish the leaching front and if phenolphthalein test can measure it.

Table 2 – Thickness of the leaching front from phenolphthalein tests.

<b>S/b: 3/1; w/b: 0.45</b>		<b>S/b: 3/1; w/b: 0.55</b>	
<b>Time (days)</b>	<b>Leaching Front (cm.)</b>	<b>Time (days)</b>	<b>Leaching Front (cm.)</b>
<b>5</b>	0,42 ± 0,02	<b>5</b>	0,40 ± 0,01
<b>10</b>	0,49 ± 0,01	<b>10</b>	0,52 ± 0,01
<b>20</b>	0,67 ± 0,01	<b>20</b>	0,67 ± 0,01
<b>31</b>	0,89 ± 0,01	<b>31</b>	0,87 ± 0,01
<b>S/b: 2/1; w/b: 0.405</b>		<b>S/b: 2/1; w/b: 0.505</b>	
<b>Time (days)</b>	<b>Leaching Front (cm.)</b>	<b>Time (days)</b>	<b>Leaching Front (cm.)</b>
<b>5</b>	0,28 ± 0,01	<b>5</b>	0,34 ± 0,01
<b>10</b>	0,36 ± 0,01	<b>10</b>	0,46 ± 0,01
<b>20</b>	0,55 ± 0,01	<b>20</b>	0,64 ± 0,01
<b>31</b>	0,72 ± 0,01	<b>31</b>	0,81 ± 0,01

Measurements of *OPW* of non degraded and degraded mortar samples are showed in table 3. It can be observed how open porosity increases with leaching time. This growing is related with the leaching of portlandite from the cement matrix, although for long ageing times there must be considered a contribution from CSH leaching. This fact is important as leaching of portlandite, CSH and other cement matrix compounds will influence the elastic constants of the degraded mortar and will determine the ultrasonic response of these materials [8].

Table 3 – *OWP* of degraded and non-degraded mortar samples.

<b>Groups</b>	<b>0 days</b>	<b>5 days</b>	<b>10 days</b>	<b>20 days</b>	<b>31 days</b>
<b>3/1 0.45</b>	15.04	20.16	21.34	22.42	22.75
<b>3/2 0.55</b>	18.23	21.42	22.39	23.7	24.56
<b>2/1 0.405</b>	17.87	21.32	22.01	24.63	25.24
<b>2/1 0.505</b>	21.01	24.76	25.78	27.17	28.36

MIP results show how porosity microstructure is influenced by the ageing process. In figure 2 can be observed the variation of medium pore diameter with depth and with ageing time expressed as the pore diameter in which 50 % of the total volume is intruded. Medium pore diameter (MPD) can give a comparative value of the effect of leaching in the microstructure and can provide comparative analysis of how the microstructure varies with depth.

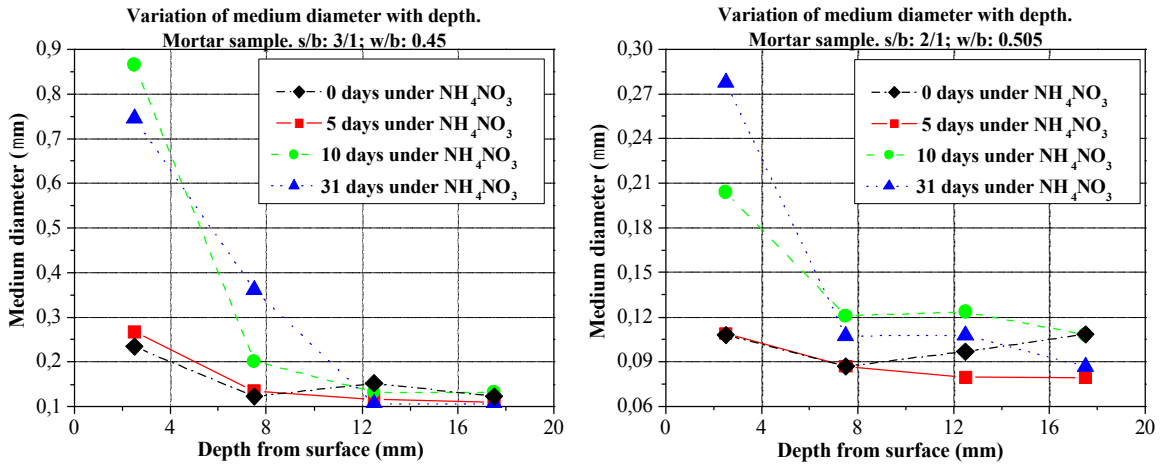


Fig. 2 – Variation of MPD in the samples analyzed.

MPD changes can be analyzed in two ways. In one hand there is a variation of medium pore diameter with depth in all the samples. For degraded and non-degraded samples this variation shows a leaching front no bigger than 10 mm for all the samples studied, which is in good agreement with the phenolphthalein test results. In the other hand there is the variation of the MPD with the leaching time. The larger increases are concentrated in the first 10 mm in which there can be appreciated an increasing of the MPD of more than 100 %. These data are statistical expressions of the pore size distributions and can point out how the distribution is moving towards to wider or narrower pore sizes but must be taken in account with the pore size distributions (PSD). In figures 3 and 4 are presented the PSD of the mortar samples analyzed by PIM.

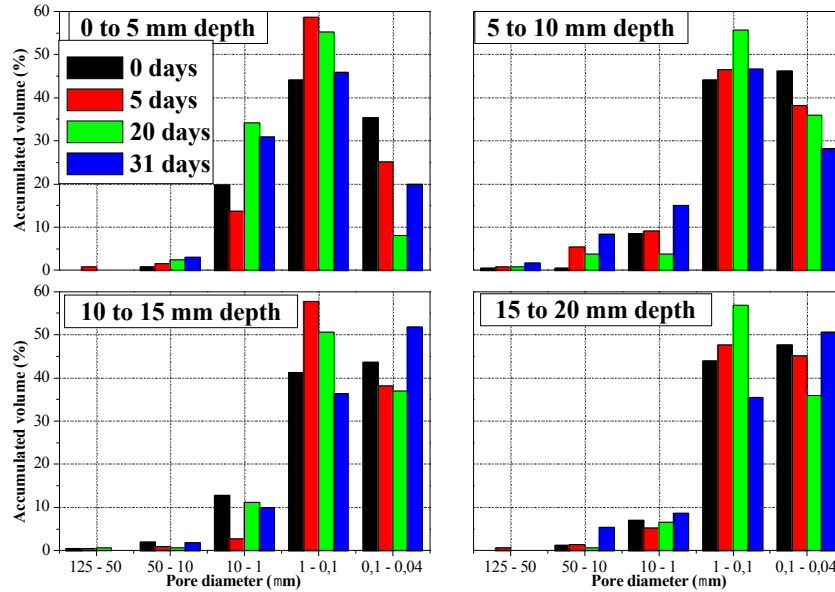


Fig. 3 – PSD of degraded and non-degraded mortar samples. S/b: 3/1; w/b: 0.45.

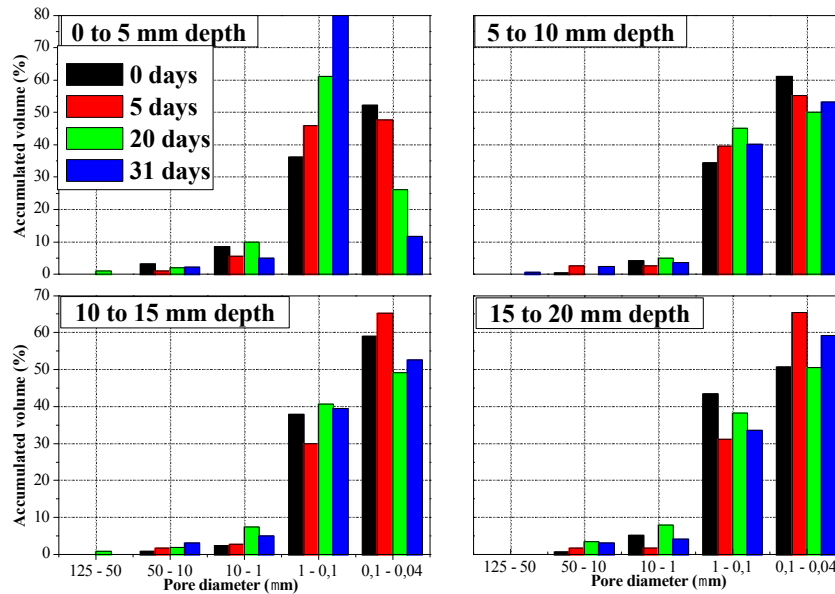


Fig. 4 – PSD of degraded and non-degraded mortar samples. S/b: 2/1; w/b: 0.505.

From the PSD we can observe that the larger increases in the accumulated volume are concentrated in the 0 to 5 mm depth. Going to further depths does not show us significant changes in the PSD, apart from the normal heterogeneity that will be found in cement mortar samples. The changes in the porosity are mainly in the zone of small

capillary porosity (1 to 0.01  $\mu\text{m}$ ) and in less extent in the larger capillary zone.

*SEM* analyses allowed us to identify calcium variation with depth by studying the X-Ray emitted by the sample and filtering only the signal arising from the calcium of the sample. The images obtained have an area of  $2029 \times 2029 \mu\text{m}^2$  and the step beside each image was near 0.2 cm, so consecutive images in depth were obtained. In figure 5 are presented some images of these analyses in which can be seen the calcium content variation that the leaching process creates in the mortar samples. It can be seen that the calcium variation is not an abrupt change and there is a continuous change in the calcium content.

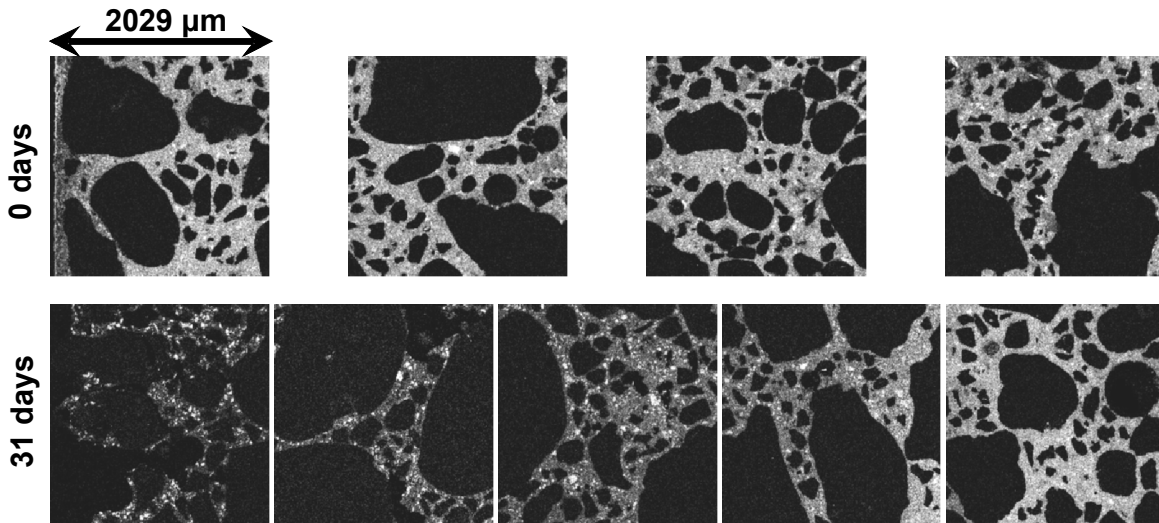


Fig. 5 – Calcium content images obtained by filtering the calcium peak in the X-Ray emitted during *SEM* analyses. S/b: 3/1; w/b: 0.45.

Basing on these images there have been made attack profile analyses, in order to calculate the thickness of the leaching front. Results form these analyses are presented in table 4

Table 4 – Thickness of the leaching front from *SEM* images.

<b>S/b: 3/1; w/b: 0.45</b>		<b>S/b: 2/1; w/b: 0.505</b>	
<b>Time (days)</b>	<b>Leaching Front (cm.)</b>	<b>Time (days)</b>	<b>Leaching Front (cm.)</b>
<b>5</b>	0,24	<b>5</b>	0,41
<b>10</b>	0,47	<b>10</b>	0,48
<b>31</b>	0,84	<b>31</b>	0,73

There is good agreement between these results and those obtained by analyzing the phenolphthalein tests excluding the value calculated for the

sample s/b: 3/1; w/b: 0.45 at 5 days of leaching. This difference may arise from the fact that the SEM analyses give local information and the phenolphthalein test can give a general view of the leaching profile.

### 3.2 Non-destructive characterization

In figure 6 are presented different maps obtained from the ultrasonic inspections for a 3/1 0.55 aged mortar sample. Thickness map can show the variation of dimensions in the sample as consequence of the leaching process. It can not be observed an important change in thickness of the samples. But instead of this, longitudinal velocity maps show important variations of ultrasonic velocity with leaching time.

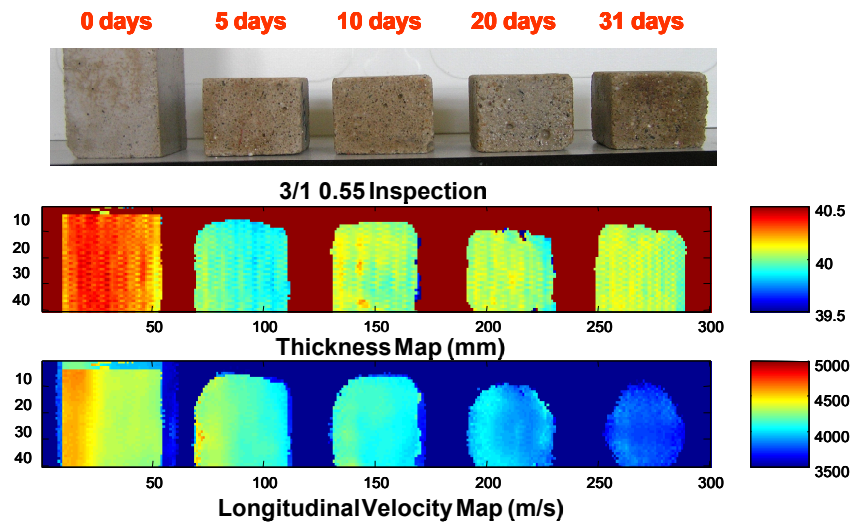


Fig. 6 – Maps of thickness and ultrasound velocity for a mortar aged sample. S/b: 3/1; w/b: 0.55.

If we make an inspection in a homogeneous degraded mortar probe by an ultrasonic transmission experiment, as in figure 7, where we can ideally assume that there is an external degraded zone (D) with thickness  $X_D$  and an internal non-degraded zone (U) with thickness  $X_U$ , we will find that the ideal profile of velocities will be a step function which depends on the thickness ( $X_B$ ) of the ultrasonic beam (B), widths and ultrasonic velocities in the degraded ( $V_D$ ) and non-degraded zone ( $V_U$ ), being the maximum velocity  $V_M$  and the minimum  $V_m$ :

$$V_M = (V_D \cdot X_D + V_U \cdot X_U) / (X_D + X_U) \quad \text{Eq. (1)}$$

$$V_m = V_D$$

As  $X_B$  and the thickness of the probe ( $X_D + X_U$ ) are known it can be easily determined from this profile the other variables which appear in the process. In this way two important parameters in order to measure the degradation can be obtained, the attack thickness and the velocity in the



degraded zone. Velocity can help us to calculate velocity and elastic constants of the cement matrix using micromechanical models [8, 10, 11].

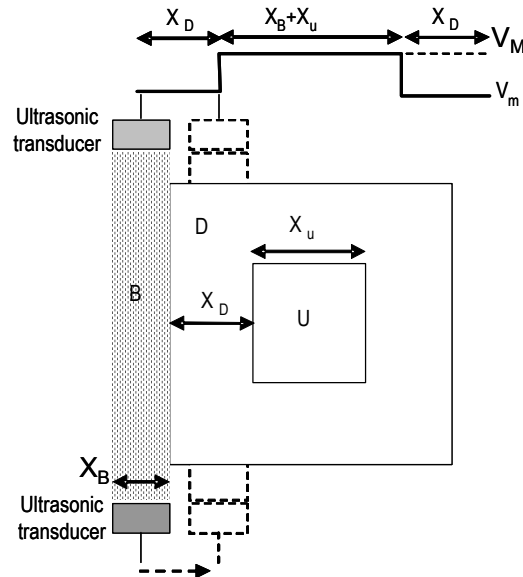


Fig. 7 – Ideal velocity profile during ultrasonic inspection of degraded mortar.

However, when we have a real situation as in figure 8, there will appear some difficulties which impede the exact determination of the degraded thickness and velocity. Cement mortar are inhomogeneous materials and so the ultrasonic velocities are not constant and it is not so easy the calculation in the profile of  $V_M$  y  $V_m$ . Also it is hard to find  $X_D$  as the transition zone between the degraded and non-degraded zone is not an abrupt change as showed in some of the destructive characterization. Finally it is necessary that the energy that goes through the material exceeds a threshold value so it can be measured. Degraded zones are highly attenuating for high frequencies so normally it is no possible to measure  $V_m$ . Lowering the frequencies of the transducer is not a good solution as it produces loosing of lateral resolution and sensibility and consequently the transition zones increases.

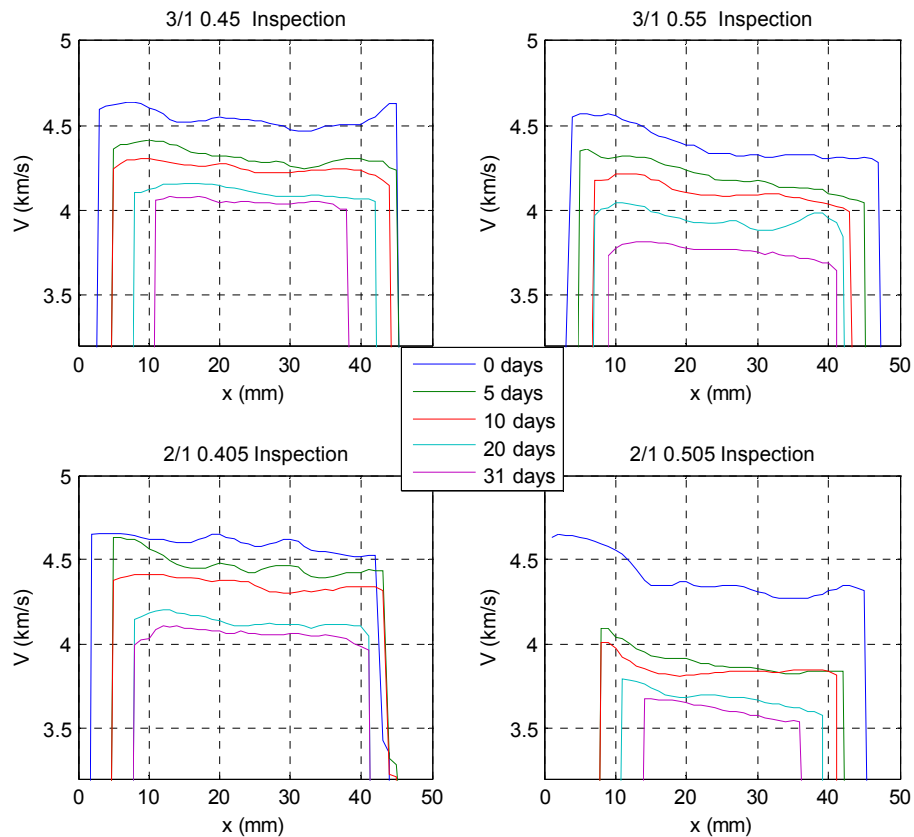


Fig. 8 – Velocity profiles in degraded mortar samples.

Leaching depth is shown in figure 9 A using velocity profiles from figure 2. In order to make this probe dimension is assumed as a known value and by using non-degraded velocity profiles  $X_B$  is obtained. In the other velocity profiles the thickness of non-degraded zone is measured by assuming that with the frequency used the ultrasonic signal can not go through the degraded material. If the results obtained in this way are compared with the results obtained from the destructive measurements it can be observed that there is a large error, which is larger when measuring narrower thickness. Mainly this arises from the fact that the precision of this method depends on the transducer lateral resolution and on the inspection step, which in this case is near 3 mm.

Figure 9 B shows the thickness calculated by using equation (1). In order to calculate the thickness  $V_M$  and  $V_m$  must be known. The calculation of the first variable has been done by using the medium value of the central 10 mm from the probe velocity profiles. However  $V_m$  can not be calculated with the ultrasonic inspection made as the ultrasonic waves have not gone through the degraded material. In order to have an estimation of these values, thickness results from phenolphthalein tests at 31 days were used. Results of this estimation are shown in table 5.

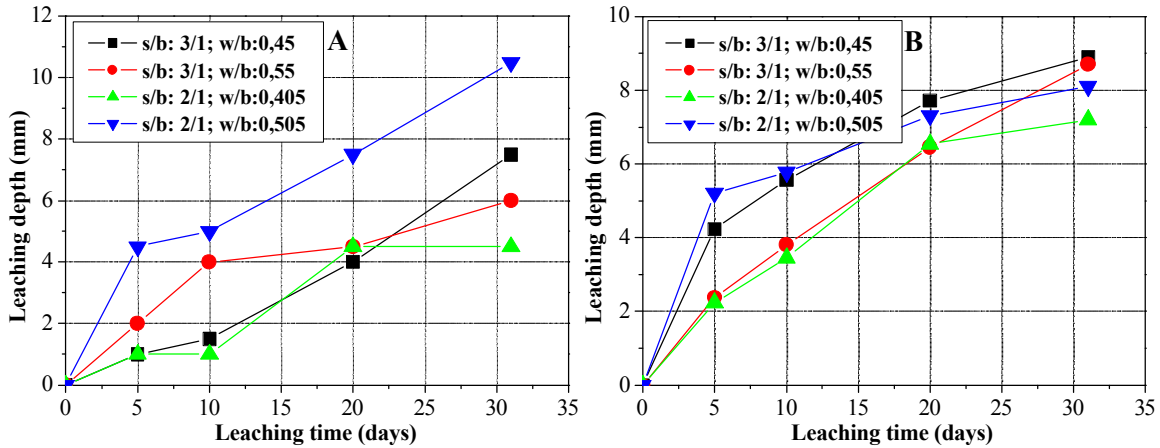


Fig. 9 – Leaching depths calculated from ultrasonic measurements.

Table 5 – Ultrasonic longitudinal velocity.

Groups	$V_M$ (m/s)					$V_m$ (m/s)
	0 d.	5 d.	10 d.	20 d.	31 d.	31 d.
<b>3/1 0.45</b>	4521	4324	4245	4130	4046	3462
<b>3/1 0.55</b>	4485	4205	4103	3935	3786	3045
<b>2/1 0.405</b>	4605	4464	4360	4121	4056	3094
<b>2/1 0.505</b>	4330	3879	3825	3691	3640	2557

It can be seen that the values obtained by using this method have been improved considerably. The medium error calculating leaching depth is 0.09 cm and the maximum error is lower than 0.18 cm in all cases as can be seen in figure 10.

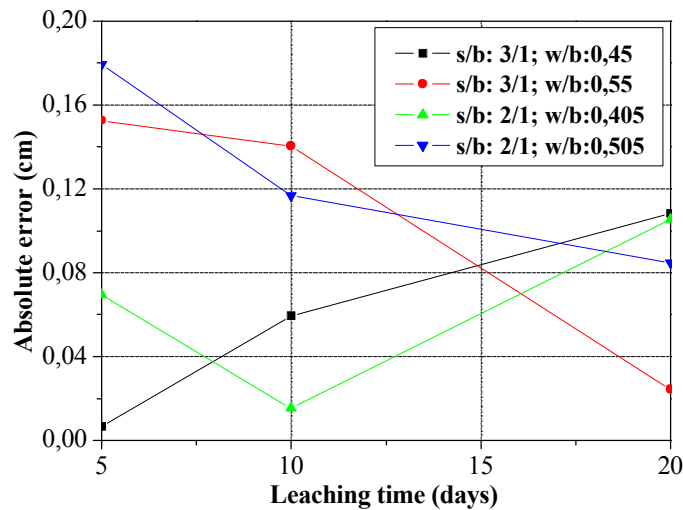


Fig. 10 – Absolute error made in the calculation of leaching depth from ultrasonic measurements, compared with phenolphthalein tests.

#### **4. Conclusions.**

Results from microstructural characterization of degraded mortar samples by means of destructive and non-destructive testing have been presented. Microstructural characterization by means of Mercury Intrusion Porosimetry has showed the variation of the porosity with leaching time and also it has shown that the changes in the microstructure are limited to the first 10 mm depth. This result arises from the analyses of the medium pore diameter and from the pore size distribution and is consequent with the leaching profiles calculated from phenolphthalein tests. Scanning Electron Microscopy analyses had allowed obtaining images of the calcium variation with depth and have made possible to make calculations of leaching profiles with depth, which are in good agreement with the other leaching profiles calculated by Mercury Intrusion Porosimetry and by phenolphthalein tests.

Non-destructive characterizations of degraded mortar samples have been made using ultrasonic transmission inspections. The analyses of the velocity profiles allow us to calculate the leaching depths. These calculations have good agreement with destructive characterization but are limited by the lateral resolution of the transducers and by the characteristics of the ultrasonic inspection. These results can be improved by using the results from destructive characterization.

At this moment further analyses of destructive results is being in process and it will be correlated with the ultrasonic measurements in order to apply a micromechanical three-phasic model to estimate the elastic constants and porosity of the degraded samples.

The combination of destructive and non-destructive testing analyses gives a better comprehension of the degradation process and can help the characterization of degraded structures by making inspections of the structures and extraction of test probes in order to calculate the depth of attack and determine the elastic constants of the material by application of micromechanical models.

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