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Short communication

Carbonation assessment in concrete by nonlinear ultrasound

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ABSTRACT

The carbonation process results in a change in the elastic properties of concrete, resulting in a variation of standard acoustic indicators such as wave speed. However, this evolution is too low to ensure an efficient carbonation assessment. The present communication focuses on the feasibility of carbonation assessment in concrete by applying Nonlinear Resonant Ultrasound Spectroscopy (NRUS). The results show that the nonlinear parameter is significantly affected by the presence of carbonation, which is interpreted with respect to the evolution of concrete microstructure in the presence of this pathology.

Carbonation is a chemical reaction in concrete between the calcium hydroxide ($Ca(OH)_2$) contained in cement and the carbon dioxide (CO_2) in the air. The following chemical reactions can be identified:

- Dissolution of carbon dioxide in water:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+$$

$$HCO_3^- + H_2O \rightarrow CO_3^{2-} + H_3O^+$$

- Reaction of carbonic acid with calcium hydroxide $Ca(OH)_2$, after its dissolution:

$$H_2CO_3 + Ca(OH)_2 \rightarrow CaCO_3 + 2H_2O \tag{1}$$

One of the consequences is the decrease of the pH due to the liberation of ions H_3O^+. The pH value of concrete ranges from 12 to 13 and after carbonation, the pH drops to 9 for fully carbonated concrete. It was observed that the ability of carbon dioxide to be fixed by calcium hydroxide depends on the quantity of alkalis (NaOH, KOH) contained in the cement because the alkalis decreases the solubility of calcium hydroxide. But once the alkalis are carbonated higher amounts of calcium hydroxide can be carbonated [1].

Carbonation also affects the other hydrates of the cement paste (silicates and aluminates). Particularly, it was observed that the C–S–H can be carbonated following the reaction:

$$1.7H_2CO_3 + 1.7CaO.SiO_2.2.5H_2O \rightarrow 1.7CaCO_3 + 1.7SiO_2.2.5H_2O + 1.7H_2O$$

Nevertheless it must be noticed that the carbonation of calcium hydroxide is faster than for the other hydrates. The speed of carbonation essentially depends on the humidity of concrete and is maximal for values about 65%.

After carbonation it was observed that the porosity of concrete decreases due to a highest molar volume of carbonation products in comparison to the volume of hydrates. For instance, the molar volume of $Ca(OH)_2$ is about 33.2 cm^3/mol while the molar volume of $CaCO_3$ is about 36.9 cm^3/mol which corresponds to an increase of 11%. The consequence of this difference was observed on cement pastes [2] and on concrete [3], essentially by Mercury Intrusion Porometry (MIP). For concrete, the difference of porosity between non carbonated and carbonated concrete is higher for concrete with low porosities and can attain 10% [3]. The same studies emphasized that carbonation also modifies the size distribution and it was generally observed a coarsening of the pore structure after carbonation. For instance, it was observed an increase of the volume of capillary pores after full carbonation of cement pastes mixed with different cements [2]. For the authors the coarsening of the pore structure may be associated with the formation of additional silica gel due to the decomposition of the C–S–H gel in the matrices following prolonged exposure to CO_2. Another study aiming to compare the effect of CO_2 concentration on the carbonation process demonstrated that the carbonation of C–S–H is significantly enhanced when high concentration is used (50% of CO_2 in this study) [4]. This consideration again supports the assumption that the reduction of porosity is due to the carbonation of C–S–H, but specifically at high pressure of CO_2.

The most important consequence of carbonation for reinforced concrete structures is the decrease of pH. In fact, it will lead to a destruction of the passive film which is formed by non-carbonated concrete around the reinforcing steel [5]. Then, in presence of oxygen and water the corrosion process can be initiated. Such corrosion products are expansive, so very quickly the concrete is mechanically damaged and a spalling of cover can be observed with the reinforcement

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directly exposed to the environment. A very usual and reliable tool for assessing the phenomenon consists in measuring the carbonated depth by means of phenolphthalein [6]. But this needs to extract a sample or to drill the concrete which is slightly destructive. The aim of this paper is to provide a non-destructive indicator of carbonation, absolutely non intrusive, allowing the characterisation of an important quantity of points on large structures.

Chang et al. [7] have shown that for a Portland cement based concrete, standard mechanical indicator such as elastic modulus is slightly increased by carbonation. This evolution results in an increase of wave speed (linear indicator) to a 2% order magnitude. This poor sensitivity makes difficult the use of standard ultrasonic non destructive techniques to discern this pathology. Therefore, this study focuses on the potentialities of nonlinear ultrasonic indicators to discern the presence of carbonation.

The complex nonlinear mechanical behaviour of nonlinear mesoscopic media such as concrete [8] is not well described as regards physics. The origin of this so called “non-classical” nonlinearity is thought to come from the mesoscopic scale by the breakage/overlap phenomena of the cohesive properties of grains bonds, contact friction, and the opening/closing of micro-cracks. The nonlinear elastic theory, introduced in the 1960's by Landau and Lifchitz [9], provides no explanation about phenomena such as hysteresis, end point memory effect observed in these materials [10]. However, the introduction of a phenomenological stress strain relationship allows one to describe nonlinear elasticity [10]:

$$\sigma = K_0\varepsilon\left[1+\beta\varepsilon+\delta\varepsilon^2...\right]+\alpha(\varepsilon, sign(\dot{\varepsilon})), \quad (2)$$

where K_0 is the elastic modulus, ε is the strain, β and δ represent the classical Landau and Lifchitz [9] type of nonlinearity, the dot relates to the time derivative of ε , and α is the non-classical nonlinear parameter. The *sign* function is equal to $+1$ when the time derivative of the strain is positive, and -1 when it is negative.

Extensive studies of the nonlinear parameter α, have highlighted its sensitivity to damage in various media and fields of applications, and in civil engineering for the monitoring of thermal damage [11] and mechanical damage [12,13]. The influence of structural changes in concrete such as water saturation [14] or alkali silicate reaction [15] has been recently shown. On the other hand, to our knowledge, no former studies have dealt with the effect of carbonation on the nonlinear behaviour of concrete.

In this study, to gain more insight into the influence of carbonation on the nonlinear behaviour of concrete, the nonlinearity of carbonated and non-carbonated samples are compared. The six samples under study are cylindrical cores (5 cm in diameter, 12 cm in length), extracted from slabs prepared in laboratory. Table 1 gives the samples characteristics. Note that the samples S1 and S2 have exactly the same composition but are manufactured in two different batches. The slabs destined to carbonation were exposed to particular conditions with 50% of CO_2 and a 65% relative humidity so as to accelerate their carbonation process. After acoustic measurements, the carbonation depth has been measured by spraying the samples with phenolphthalein after having split them.

To assess the nonlinearity, we develop an experimental device based on NRUS technique. It consists on the measure of the resonance frequency shift versus the resonance peak amplitude for a given resonance mode, while increasing excitation amplitude. From Eq. (2), the nonlinear α parameter is evaluated by $\Delta f/f_0 = \alpha.\Delta\varepsilon$ [11], where f_0 is the linear (low amplitude) resonant frequency and $\Delta\varepsilon$ the strain wave amplitude. Based on the method proposed by Chen et al. [15], the samples were clamped at one end with a chuck and let free at the other end in order to favour the first flexural mode (around 11 kHz for our samples). The vibrations are recorded via an accelerometer (B&K 8339), a signal conditioner (B&K 4416B) connected to an A/D converter (Picoscope 3204) and stored by a computer. The linearity of the acquisition system has been checked by using a cylindrical Aluminium sample. Each concrete sample was subjected to sixteen impacts with an intensity progressively increased.

Table 1
Concrete samples characteristics. C: Carbonated samples, NC : Non-carbonated samples.

Aggregate	Siliceous				Limestone	
Codification	S1-NC	S1-C	S2-NC	S2-C	L-NC	L-C
Carbonation depth (mm)	–	~15	–	~20	–	~30
Cement CEM I (kg)	370		370		370	
Sand 0/2 or 0/4 (kg)	774		774		474	
Gravel 4–14 or 10–14 (kg)	1069		1069			
Fine gravel 2/4 (kg)					284	
Gravel 4–6 (kg)					284	
Gravel 6–10 or 6–14 (kg)					854	
Water (kg)	212		212		214	

Fig. 1 shows that the distribution followed by the variation of the relative frequency shift versus the resonance peak amplitude (acceleration) is linear. The slopes of the dashed lines provide the nonlinear parameter for each sample. Note that the nonlinear parameter is a quantity proportional to α but not an absolute value. The summary of the whole set of results presented Fig. 2a highlights the impact of carbonation on the nonlinear parameter. The amplitude on the nonlinearity is not significantly affected by the concrete composition but we can notice that the L samples are less sensitive to the presence of carbonation.

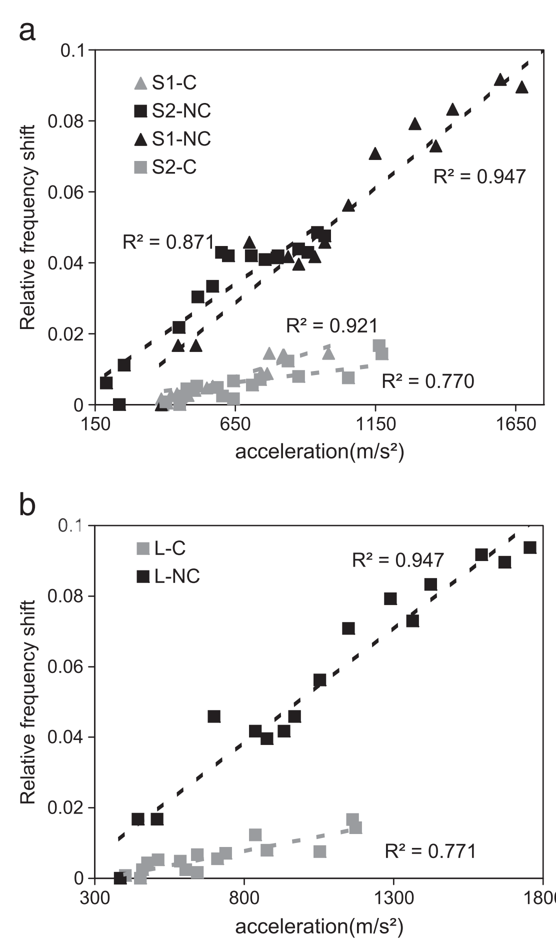

Fig. 1. Relative frequency shift as a function of amplitude. (a) Siliceous aggregates samples, (b) limestone aggregates samples. Dashed lines are the linear fits of these evolutions.

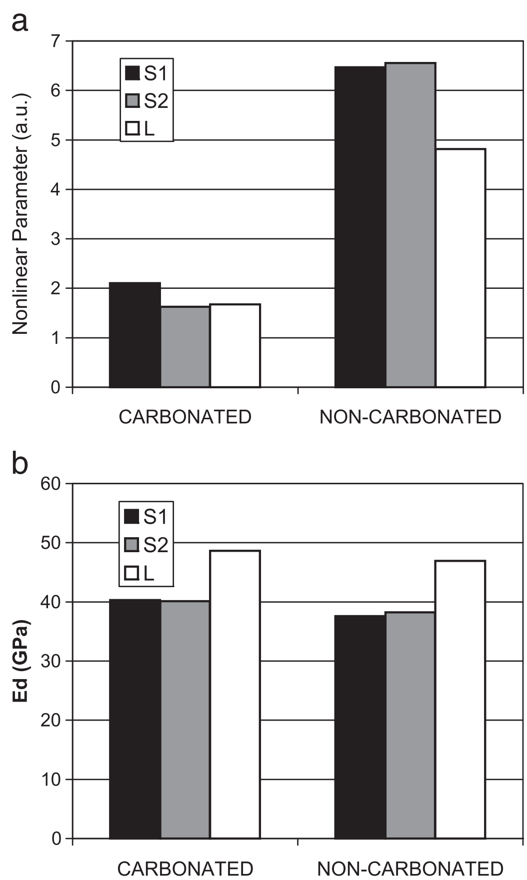

Fig. 2. Comparison of nonlinear (a) and linear (b) parameters of carbonated and non-carbonated samples.

The general decrease of the nonlinear parameter can be explained by the change of concrete microstructure as follow:

- SEM pictures from Chang et al. [7] show that cubic shapes of $CaCO_3$ are deposited in the concrete pores and micro-cracks. This should reduce the contact between grains and micro-cracks lips which is thought to be one of the main sources of nonlinear phenomena.
- It is worth noticing that C–S–H gel plays a key role in the viscoelastic nature of cement pastes [16]. Even if the linear global viscoelastic nature of concrete do not influence the measured nonlinearity (amplitude dependant), the presence of soft inclusions into hard matrix [10] is known to cause some non classical nonlinear phenomena. Since our samples have been carbonated in accelerated conditions, the carbonation of C–S–H gel is a central reaction that can contribute to the decrease of the nonlinear parameter.

For comparison, the dynamical Young modulus has been evaluated (see Fig. 2b) by shear and compressional wave velocities measurements. As in previous studies [7], the presence of carbonation affects slightly this indicator with a maximum increase of 5%, corresponding to a 100 m/s wave speed variation, while the mean variation of the nonlinear parameter reaches more than 300%.

Further to this qualitative study that shows that the presence of carbonation has a large influence on the nonlinear parameter, it can be considered as a good indicator for the detection of this pathology. To have a quantitative result, it would be worth studying the variations of the nonlinear parameter versus carbonation depth. That is uneasy because the sample response characterised by the NRUS method is not a local but a global one. Thus future study will be aimed at identifying a method able to provide the nonlinear parameter as a function of the wave propagating depth. In addition, that would be worth studying an extended carbonation depth scale, up to fully carbonated samples.

It is likely that the study of carbonation phenomenon within materials and rocks would have numerous applications in the CO_2 storage field, which is among the very important current topics [17].

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