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Preliminary study on short-term sulphate attack evaluation by non-linear impact resonance acoustic spectroscopy technique

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HIGHLIGHTS

- Durability of concrete was tested by Nonlinear Impact Resonance Acoustic Spectroscopy.
- NIRAS technique was successfully tested for external sulphate attack.
- Good relationship was established between expansion and vibrational tests.
- Frequency shift, quality factor and α parameter were evaluated for damaged specimens.
- Microstructural analysis supported linear and non-linear parameters from NIRAS.

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ABSTRACT

The scope of this paper is to study the sulphate attack on concrete with new testing methods based on vibrational spectroscopy with mechanical waves. These are based on Non-linear Impact Resonance Acoustic Spectroscopy (NIRAS) that allows detecting the frequency shift of its resonant modes. Both, signal quality factor and alpha, are measured to monitor the increase of the non-linearity of the material due to the stiffness change on the matrix after being attacked. Different Portland cement matrices were assessed and results between vibrational tests and the traditional expansion ASTM method were compared. Two types of cement with different C_3A content were tested for external sulphate attack and one cement with high C_3A content with different amount of addition of SO_3 on the original mix was tested for internal attack. NIRAS was suitable for monitoring external sulphate attack process. A microstructual analysis was carried out with thermogravimetry (TG), scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques in order to detect harmful products on damaged series.

1. Introduction

Ettringite is an expansive compound formed during the Portland cement hydration process (primary ettringite, Eq. (1)) and also during the lifetime of the concrete structures (secondary ettringite, Eq. (2)) [1]. Primary ettringite has no harmful effect on concrete because expansions produced by the reaction are absorbed by fresh concrete. Secondary ettringite is formed for months, or even years after concrete has been hardened. The stresses that appear when an external or internal source of sulphate salts reacts with calcium aluminates hydrates can spoil the matrix, causing micro cracks, expansion and spalling. Additionally gypsum is also formed by reaction of sulphate and portlandite (Eq. (3)).

$$C_3A + (CaSO_4 \cdot 2H_2O) + 26H_2O \rightarrow 3CaSO_4 \cdot 3CaO \cdot Al_2O_3 \cdot 32H_2O \quad (1)$$

$$3CaSO_4 \cdot 2H_2O + C_3A \cdot 6H_2O + 24H_2O \rightarrow 3CaSO_4 \cdot 3CaO \cdot Al_2O_3 \cdot 32H_2O \quad (2)$$

$$Ca(OH)_2 + SO_4^{-2} + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2OH^- \quad (3)$$

Initially, sulphate products fill the voids, capillary net and also promote a compressive resistance increment [2]. When the voids and free space inside the element are full, micro cracks start to appear and compressive strength and Young's modulus decrease. When this mechanism is too aggressive, the cement paste could loss strength and adhesion capacity due to decalcification of C–S–H [3]. On one hand, external sulphate attack (ESA) is determined by the chemical interaction between sulphate-rich sources with the cement paste. The sulphate anion may be contained on soils and water as different sulphate salts such as sodium, potassium, magnesium and calcium [1,2]. The next three conditions must be satisfied for ESA [1]

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- Porous cement matrix.
- Presence of water.
- High percentage of SO_3.

If any of the above conditions are not fulfilled ESA does not occur. For instance, if concrete structure's foundation is placed on sulphate-rich soil having high humidity or containing groundwater but the cement matrix is not porous enough, then the sulphate external attack will not occur.

On the other hand, internal sulphate attack (ISA) is due to an initial content of SO_3 in high percentages on the original mix or in raw materials. Also, combined sulphates on clinker are released slowly when they are in a liquid phase with possibility to form ettringite and other expansive compounds. It damages the matrix if enough sulphate were added to the initial mix. The next two conditions must be satisfied for ISA [1].

- High percentage of SO_3 in the original matrix.
- Presence of water.

Traditional methods to detect damage and expansion of the material were used in this experimental program following the ASTM standard [4]. These techniques evaluate the potential expansion of a mortar bar for fifteen weeks as it remains immersed in a Na_2SO_4 solution. During the last few years, alternative methods with thermogravimetry and XRD on cement/pozzolane systems [5–9], numerical models [10] and also micrography techniques in real structures [11] had been developed in order to detect and monitor damage due to sulphate attack on concrete and mortar elements.

Several authors focused their research on characterizing concrete matrices with different NDT techniques. Garnier et al. were studying different concrete matrices with varying w/c ratio, compressive strength and density using non destructive testing techniques, such as pressure waves, surface waves, back-scattered waves, impact echo and non linear analysis [12]. Gudra and Stawiski, used surface waves to study the influence of surface roughness and inclination angle on the measurement of the concrete specimens [13].

It is known that NDT techniques have the capability of obtaining a widerange of physical properties of cementitious materials like dynamic Young's modulus, porosity and compressive strength [14–18].

Leśnicki et al. and Chen et al. studied alkali-silica reaction on concrete and mortar showing several changes of non-linear parameters for damaged specimens [19,20]. Those authors monitored the microcracking process evaluating the frequency shift of its resonant vibrational modes using Non-linear Impact Resonance Acoustic Spectroscopy (NIRAS) method. This technique was developed by Chen et al. who used a cantilevered test disposition for mortar specimens to excite the principal modes and evaluate the non linear effects on the frequency. A subsequent study by Leśnicki et al. used a free vibration specimen configuration to evaluate the same parameters of concrete specimens showing better results with this model.

The scope of this paper is to compare two methods (traditional expansion test and NIRAS) in order to evaluate sulphate attack on Portland cement matrices with different C_3A content.

2. Experiment

Several tests were done on this study in order to compare the performance of NIRAS tests and other characterization techniques. Expansion tests (Mitutoyo digital indicator 0.001 mm resolution), scanning electron microscopy (JEOL JSM 6300 aplying a 20 kV voltage), thermogravimetry and X-ray diffraction. On thermogravimetry analyses, portions of the samples were taken and pulverized with an agate mortar adding a small amount of acetone. The solid was filtered and dried at 60 °C for 15 min. The equipment used were a Mettler TGA 850. Sealed aluminium crucibles of 100 μm were used with a lid that has a micro hole to create a water vapour self-generated atmosphere. The analysis was carried out in dry nitrogen atmosphere with a flow of 75 mL/min, a heating rate of 10 °C/min, and a temperature interval of 35–300 °C. For high resolution thermogravimetric analysis (MaxRes), the lowest heating rate was 0.1 °C/min and the highest one 10 °C/min. The heating rate was changed according to the mass loss rate. The highest heating rate was achieved for mass loss rate lower than 1 $\mu g\,s^{-1}$, and the lowest heating rate was achieved for mass loss rate higher than 3 $\mu g\,s^{-1}$. The X-ray diffractometer model used is a Brucker AXS D8 Advance. $K\alpha$ of Cu radiation was used and secondary monochromator (Ni filter) that eliminates the Cu $K\beta$ radiation. The intensity and voltage generator X-ray tube was set to 20 kV and 40 mA respectively. Diffractograms were recorded for 2Θ range between 5° and 70° with a step angle of 0.02 and 2 s accumulation time.

2.1. Materials

As commented earlier, the main sulphate attack process is the formation of secondary ettringite due to free SO_4^{-2} ions on the solution and calcium aluminate hydrates on the cement matrix. Other variable for this mechanism is the porosity of the cement matrix.

For that reason, for ESA investigation two types of cement to prepare mortars with two different w/c ratios (Tables 1 and 2) were chosen, while for ISA study one cement type and two different amounts of addition of SO_3 (by adding anhydrous $CaSO_4$) in the original mix were considered.

Table 2 shows the chemical composition of every type of cement used on this experiment. The main difference between the two cements is the C_3A content: the sulphate resistant cement was a Spanish cement CEM I-52,5 SR and it has 2.33% of C_3A and the white cement, BL II A-LL 42.5 R, has 9.84% C_3A.

The specimens prepared for the tests had different geometries: 40x40x160 mm^3 for vibrational tests (three specimens for each series) and 25.6 × 25.6×280 mm^3 for ASTM C452/ C452M potential expansion tests (four specimens for each series). The sulphate solution had 15% of Na_2SO_4.

Table 1
Dosages (in grams) used to manufacture the specimens in grams.

	ESA				ISA	
Code	0.5-G	0.5-W	0.6-G	0.6-W	0.6–0%	0.6–3%
w/c	0.5	0.5	0.6	0.6	0.6	0.6
Sand	1350	1350	1350	1350	1350	1350
$\%SO_3$	-	-	-	-	0	3
Cement type	SR	BL	SR	BL	BL	BL

2.2. NIRAS method and test disposition

NIRAS method is a relatively new NDT technique which can detect changes in materials from the resonance frequency shifts of the vibrational modes of a specimen made from this material as the impact energy increases [20] This change is simply due to the non-linearity of the material. This technique has been shown to be highly sensitive to material defects, specifically to the micro-cracks of the material. It is well-known that defects in a material can be detected from the vibrational frequency resonance values of a specimen made of that material. Distributed cracks reduce the stiffness of the specimen, and therefore, the natural frequency of the structural element made of that material. Besides this linear effect ($f = \sqrt{k/m}$, where k is the stiffness and m the mass of the specimen) cracks also change non-linear properties of the material: those cracks form imperfect matrix and non-homogeneity zones and thus creates, for instance, pores or voids, micro pores, paste-aggregate interface and other mesoscopic effects [20,19].

Table 2
Cement composition by % weight.

Cement type	LOI[a]	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	C_4AF	C_3A	C_3S	C_2S
CEM I-52,5 SR	2.05	20.52	3.37	3.92	63.36	1.96	2.59	11.93	2.33	55.7	16.94
BL II A-LL 42.5 R	9.75	16.55	3.88	0.26	62.91	1.39	4.28	0.8	9.84	51.73	8.56

[a] Loss on ignition.