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Different evolution of tensile and compressive strength in concrete affected by acid mine drainage

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ABSTRACT

Although not many studies have analysed the effects of acid mine drainage (AMD) on the durability of concrete, it is clear that such an aggressive environment affects the different mechanical parameters of this material. AMD is an environmental problem that affects the five continents and is especially widespread in the south western part of the Iberian Peninsula, in an area known as the Iberian Pyrite Belt.

In this work, the effect of AMD on tensile and compressive strength of concrete has been evaluated, analysing the evolution of these two fundamental parameters on this structural material. For this purpose, a series of concrete samples were subjected to a controlled AMD environment in the laboratory, using water with pH 2.8 collected from the Tharsis Mine (SW Spain). The concrete samples were prepared in accordance with the parameters required by various international standards.

The samples were subjected to the aggressive environment by AMD for two periods of time (3 and 6 months), after which they were subjected to non-destructive testing and destructive testing until breaking the samples by means of compression and tensile (indirect tensile test). In addition, Emission Scanning Electron Microscopy studies were performed on samples before AMD influence and on samples affected by AMD for six months.

The obtained results using the ultrasonic equipment showed a decrease in concrete quality, an increase in porosity and permeability, the reduction of modulus of elasticity that reaches 8.5% after six months, as well as the appearance of microcracks. The destructive the tests showed that tensile strength is much more affected than the compressive strength: the tensile strength went from 4.31 MPa to 3.27 MPa (24%) after six months, while the compressive strength went from 48.22 MPa to 43.83 MPa (9%) in the same period of time. This different evolution means that the formulas used in international standards that relating compressive strength to tensile strength need to be modified by means of a correction factor.

1. Introduction

Metal sulphide mining produces acid mine drainage (AMD), an acid lixiviate generated by the extraction of iron sulphides, such us pyrite. With very well known cases throughout Europe, such as the Iberian Pyrite Belt; those located in South America, with examples, among others, in Peru (Antamina) and Chile (La Escondida mine); in Asia (Grasberg mine) and those known in the USA (Morenci), Canada (Abititi area) and in Africa (Kansanshi). This lixiviate originates not only in the mining operating facilities, but also more markedly, in abandoned facilities before to the entry into force of standard regulations governing liquid discharges, as a consequence of the absence of preventive measures and/or pollution correcting measures.

The characteristics associated with AMD are widely known, with low or very low pH values, even reaching negative values [1], presenting high concentrations of sulphates, metals, and metalloids.

Acid mine drainage is a consequence of the sulphides oxidation when they are exposed to oxygen from air and water. We can summarize it in

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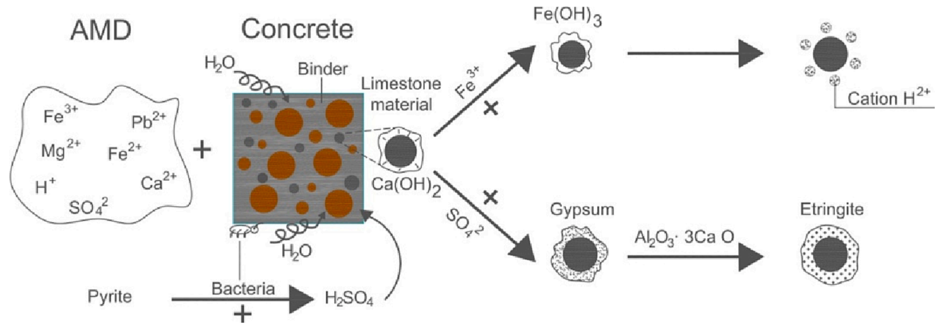

Fig. 1. Scheme of concrete corrosion by AMD (Modified from Davila et al, 2021).

this way [2]:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \tag{1}$$

The ferrous oxide is oxidized again to Ferric oxide (Fe III), which oxidizes the pyrite again, repeating again the cycle:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \tag{2}$$

These chemical reactions are accelerated by the biological action of acidophilic bacteria, which can act as catalysts for the oxidation of pyrite [3–6], that under certain pH conditions (between 2.5 and 3.5) and temperature (values between 15 °C and 35 °C) easily create surficial gypsum paste that is formed from the cement paste that contains the concrete, thus lowering even more the pH.

These polluting processes not only have a direct and negative effect on streams and rivers water quality [7], but also, indirectly, affecting the durability of structural materials such as steel and concrete [5,8] due to their highly aggressive character.

The corrosion of concrete in AMD media begins with the sulphates reacting with Ca hydroxide, in a way that gypsum paste is formed on the surface of the concrete Eq. (3). This last, can form ettringite by reacting with hydrated tricalcium aluminate by Eq. (4). By means of these reactions, and together with the action of erosion and the intervention of microorganisms [8], expansion, cracking and loss of resistance in the concrete are produced. In [8] the authors graphically summarised the alteration of concrete by AMD (Fig. 1).

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

$$Al_2O_3 \cdot 3CaO + CaSO_4 \cdot 2H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O \tag{4}$$

In addition, acid attack results in Ca dissolution in the binder, with a porosity increase in the external areas of concrete, leading in some situation to gypsum precipitation and aggregates, according to the work by [9].

There are not well-known cases that study the evolution of the concrete tensile strength in environments affected by AMD or its relationship with the compressive strength in this type of environment. There are authors who only analyse the possible improvements in tensile strength by adding some type of admixture to concrete, but it is essential to study previously how this strength is affected in order to know what improvements may be necessary.

In this sense, there are many works that propose different improvements in the concrete resistance, highlighting the most recent works, such as [10], in which the authors found improvements in mechanical properties and durability by adding fly ash and “effective microorganisms” to concrete.

Regarding the tensile strength, most authors propose the improvement by adding different types of fibres, as suggested by [11], by adding fibreglass and fly ashes to the concrete mass, which improves the mechanical properties of concrete (specially the tensile strength) and its durability; or [12] that proposes to add steel fibres to concrete and [13] that add “Forta-Ferro” fibres to concrete affected by sulphuric acid. In both cases, the tensile strength improves when mixed in low proportions. Other experience [14] have confirmed improvements in the mechanical properties of concrete (including its tensile strength) by partially replacing the fine aggregate with glass wastes, although in this case some properties related to concrete durability were reduced.

Table 1
Exposure class due to chemical aggressiveness of water [C.E. 2021].

Parameters	Testing method	XA1 Weak chemical aggressiveness	XA2 Moderate chemical aggressiveness	XA3 Strong chemical aggressiveness
		WATER		
pH	UNE 83952	6.5–5.5	5.5–4.5	<4.5
Mg^{2+} (mg/L)	UNE 83955	300–1000	1000–3000	>3000
SO_4^2 (mg/L)	UNE 83956	200–600	600–3000	>3000

There are works as [15] that evaluated the effects of acidic environments on compressive strength, but they are carried out with synthetic acid (therefore, without taking into account the effect of bacteria) and only evaluating the compressive strength.

When assessing tensile strength, most current regulations do so by relating it to compressive strength, the latter being the fundamental mechanical property of concrete. Thus, the current Structural Code 2021 [16], the Eurocode 2 [17] and the MODEL Code [18] use the Eq. (5) to estimate the tensile strength. Perhaps the only difference between these two regulations in what affects this work is that the 2021 Structural Code takes into account the effect of erosion in environments, which is not included in the Eurocode.

$$f_{ct} = 0.3f_c^{2/3} for f_c < 50MPa \tag{5}$$

The Indian standard [19] collects the relationship between the resistance to flexo-traction and the resistance to compression by means of the following expression (Eq. (6)):

$$f_{cf} = 0.7 \cdot f_c^{1/2} \tag{6}$$

The last, the Australian regulation [20] include two expressions, one for the relationship between the flexural and compressive strength (Eq. (7)) and another for the tensile and compressive strength (Eq. (8)), observing considerable similarity between Eq. (6) and (7), and with very similar results if Eq. (5) and (8) are applied.

$$f_{cf} = 0.6 \cdot f_c^{1/2} \tag{7}$$

$$f_{ct} = \left[0.36 \cdot f_c^{1/2}\right] \cdot 1.4 \tag{8}$$

Where:
f_{ct} is the uniaxial tensile strength,
f_c is the compressive strength, and
f_{cf} is the flexural strength

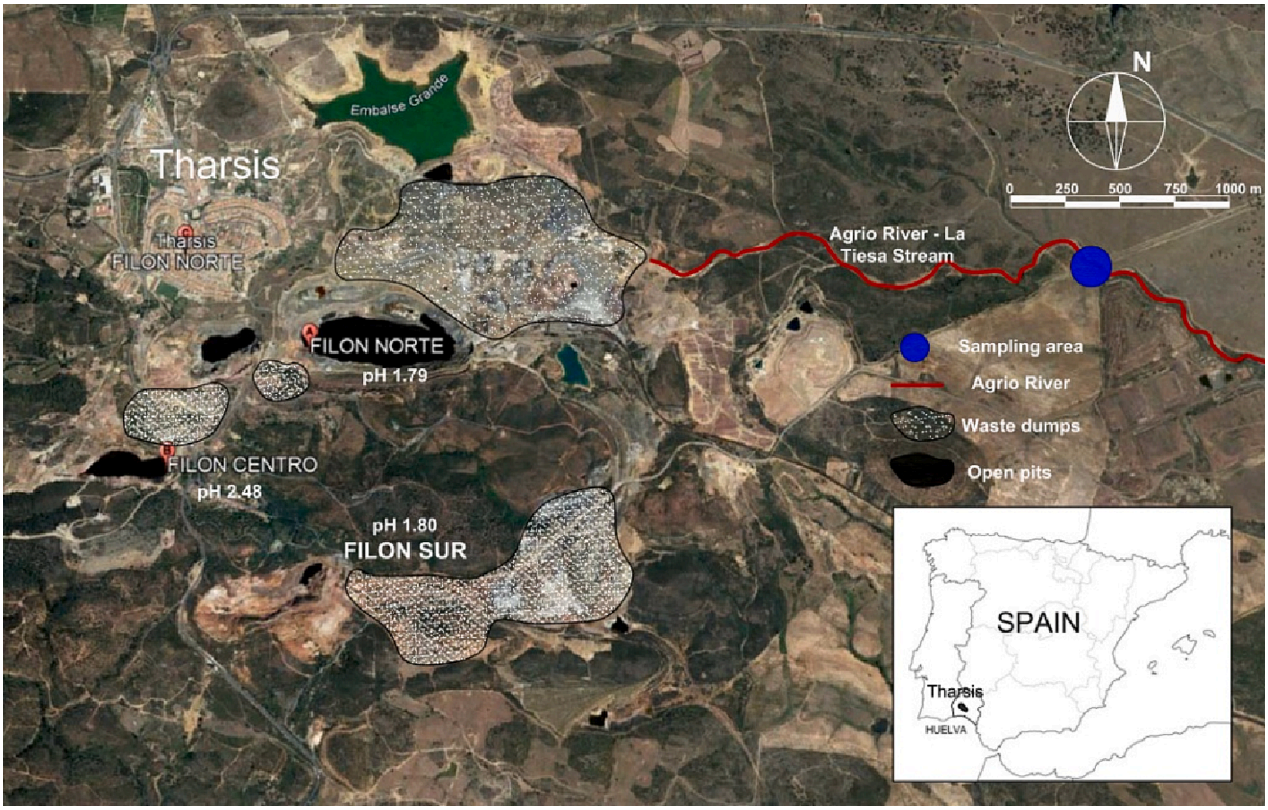

Fig. 2. Water samples location used in the experiences (Google Earth and own creation).

Taking into account that the analysed samples were in contact with waters of pH always below 4, the environment considered in the regulations (for example, in the Structural Code 2021 [16] or UNE-EN 206, 2022 [21]) would be the type of exposure XA3 or intense aggressiveness, which is the maximum value that an environment can achieve for concrete structures.

The environments defined in Table 1 as XA1, XA2 and XA3 coincide with those indicated in the French standard [18], while in the ACI code [22] and in the Canadian standard [23] the environments defined by the amount of sulphates, in mg/L of water, are grouped into four classes. In the case at hand, it would be an environment between S2 and S3 (considering the values determined for sulphates, as it will be seen later in this work). In the case of the Indian standards [19], it includes four exposure subclasses depending on the SO3 content (subclasses S0 to S4), although it is not possible to compare them in terms of exposure classes, because the interest here is to compare them based on their requirements.

The effect of low durability is not only produced by low pH, by the action of sulphates or by the action of some bacteria such as *Thiobacillus thiooxidans* [24], which can reduce the pH on the concrete surface to values between 1 and 3, but also, due to the effect caused by the erosion of the water flow.

In this study, the concrete samples used comply with the current international regulations regarding the use of sulphur-resistant cement, resistance, etc. Other authors did not take these parameters into account in their previous works.

The main aim of this work was to assess the durability evolution of concrete exposed to AMD-affected media in both, static and dynamic systems. For this purpose, compressive and tensile strength were evaluated as the most important mechanical properties of concrete.

2. Material and methods

To carry out the experiments in the laboratory, water affected by AMD from the Aguas Agrias stream was collected. This location was the same where other previous samples were already exposed to this highly aggressive environment ([8], Fig. 2), thus it was chosen to be able to compare the results obtained in the laboratory with those obtained in the river samples. The importance of this location choice was due to the data obtained for five years in the study by [25], with pH values below 3 over the whole period, concentration up to 13301 mg/L of sulphates, 4263 mg/L of Fe, 1333 mg/L of Mg, 245 ml/L of Ca, 499 μg/L of Pb, etc.

Table 2
Minimum requirements depending on the type of environment (table 43.2.1.a and b, [C.E. 2021]).

	Kind of environment Chemically aggressive environments XA1	XA2	XA3
Maximum ratio w/c	0.50	0.50	0.45
Minimum strength (MPa)	30	30	35
Minimum cement content kN/m^3	2.75	3.00	3.25
Other requirements	–	Sulphate resistant cement	

This water was taken to the Higher Technical School of Engineering laboratories of the University of Huelva (with an initial pH of 2.8) and 30 concrete samples of 150 mm in diameter and 300 mm in height were submerged in the water. The concrete was prepared with a dosage that complied with the regulations requirements of Spain [16], as indicated in the following tables (Tables 1 and 2).

The dosing (amount of each components) of the mass concrete was determined from the aggressiveness degree of the environment in which the structure is located; in this case, according to the chemical aggressiveness degree explained in the previous paragraphs. Therefore, for the XA3 environment, the resulting dosing that was used to knead the concrete was the one with the following parameters: w/c ratio of 0.45, minimum cement content of 435 kg/m^3, minimum compressive strength

Table 3
K parameter values.

Type of cement	Rounded aggregates	Crushed aggregates
22.5	0.072	0.045
32.5	0.054	0.035
42.5	0.045	0.030
52.5	0.035	0.026

of 35 MPa, as well as the obligation to use sulphide resistant (SR) cement. To determine the dosing of the concrete, the method of La Peña (1995) in [26] was followed, in which the water-cement ratio was obtained from a minimum resistance requested, as indicated in Eq. (9). Following this methodology, the water amount was determined based on the desired consistency, and the type and maximum size of the aggregate (a siliceous aggregate with a maximum aggregate size of 16 mm was used). With these parameters already obtained, using the Fuller's parabola (Eq. (10), [27]) and considering the specific weights of each material, the amount of each one in weight was determined (for more details, see the reference [8]).

$$Z = Kf_{cm} + 0.5 \quad (9)$$

Where:
Z is water-cement ratio (w/c), in weight,
f_{cm} is the average of concrete strength in MPa at 28 days and
K is a parameter that depends on the type of cement and aggregate. In our case it takes the value of 0.045 (see Table 3).

$$p = 100\sqrt{\frac{d}{D}} \quad (10)$$

Where:
p is the percentage by weight that passes through the sieve,
d is the diameter of each sieve, and
D is the maximum size of the aggregate

The requirements contemplated in the current Spanish regulations are very similar to those of other international standards, except for the Indian regulation (IS 456:2007) which is the most demanding of the revised ones, in which the w/c ratio is set at a lower value (w/c = 0.4), a minimum amount of cement of 400 kg/m^3 and a minimum compressive strength of 50 MPa.

In addition to all these indications, the UNE-EN 12390-1 standard [28] was followed for the preparation of the test samples.

Once the fresh concrete was prepared, consistency tests was carried out, following the procedure indicated in the UNE-EN 12350-2 [29] standard, obtaining a S2 class of consistency.

The 30 samples produced were distributed as follows:

- 5 Reference samples were tested with an ultrasonic equipment and subsequently were tested for compression, following the procedure of the UNE-EN 12390-3 [30] standard.
- 5 Reference samples were tested with an ultrasonic equipment and subsequently were tested for split-tensile strength, following the procedure of the UNE-EN 12390-6: 2010 [31] standard.
- 10 samples were subjected to AMD affected water contained in containers for three months and, subsequently, were tested with an ultrasonic equipment and then the compressive strength was determined in 5 of the samples and the split-tensile strength in the remaining 5.
- 10 samples were subjected to acidic water contained in containers for six months and, subsequently, were tested with an ultrasonic equipment and then the compressive strength was determined in 5 of them and the split-tensile strength in the remaining 5.

Once the 30 mass concrete samples were made, they were subjected to a curing process by immersion in water for 28 days, as determined in current regulations [CE 2021 and UNE-EN 12390-2], after which they were dried in air for 15 days and weighed on a precision scale. From the 30 samples, 10 of reference were saved for later testing. For the other 20, the followed procedure began with their introduction into buckets with acid water, keeping 10 of them exposed for three months and the other 10 for six months. During this exposure time, measurements of the different physico-chemical parameters (conductivity, temperature, total dissolved solids and pH) were taken.

When the samples were extracted from the acidic water, they were left to dry for 15 days at ambient temperature and from that moment on, the samples were weighed and the different non-destructive and destructive tests were carried out (until breakage).

The non-destructive tests were carried out with a H0370 equipment from Proetisa manufacturer to determine different mechanical parameters. Before beginning the test sessions, the equipment was calibrated with a sample of 42.5 μS, according to the manufacturer's instructions. Next, the parameter to be measured were selected: the ultrasonic pulse

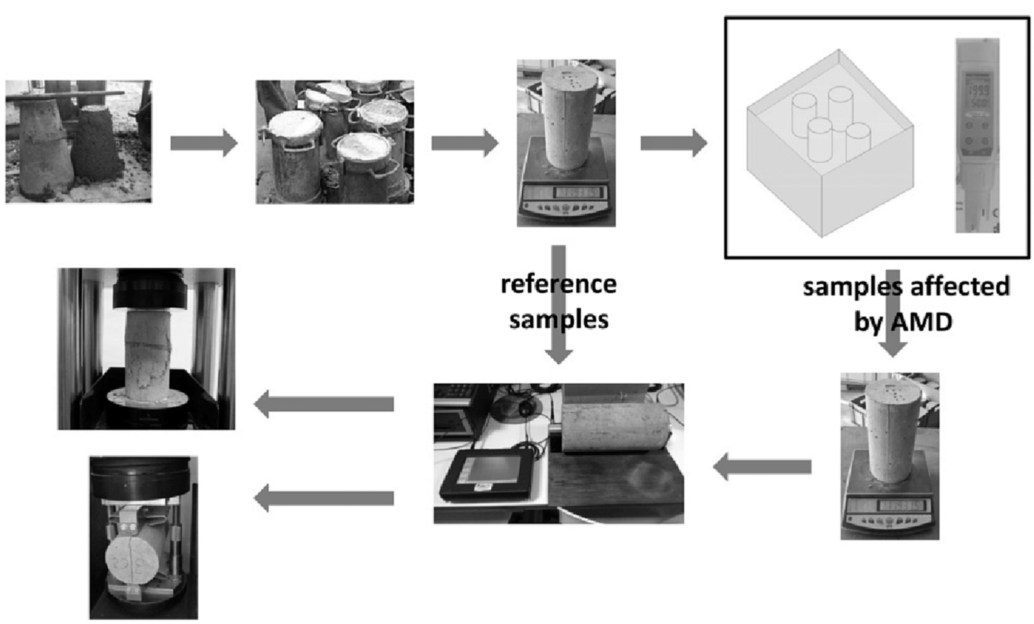

Fig. 3. Scheme of the methodology used.

Table 4
Evolution of the samples mass: reference (T0), after three months of exposure (T3) and after six months (T6).

	Mass (g.)	γ (kN/m^3)	D (%)
T_0	12328.6	22.79	—
T_3	12432.4	22.98	0.75
T_6	12480.1	23.07	1.32

γ is the apparent specific weight of the samples.

Fig. 4. Bacteria formation on the water surface.

speed (VPU in m/s), the estimated compressive strength (in MPa), the estimated elasticity modulus (in MPa).

From this technique, it was intended to evaluate some concrete parameters such as the quality of the material (obtained from the speed of the ultrasonic pulse - UPV) and the porosity.

The destructive tests were carried out in a Controls Automax X5 model press, using a sensitivity of 20 kN and a speed of 0.60 MPa/s in the compression tests, with a load limit of 1500kN. For the split-tensile tests, an accessory from the same manufacturer was used, with a sensitivity of 20 kN and a speed of 0.04 MPa/s, with a load limit of 500 kN, as established in UNE-EN 12390-3. Before carrying out the compression tests, it was necessary to face the face that was not in contact with the concrete cylinder moulds, to leave it sufficiently polished and flat, so that it adapts to the steel cylinder that the equipment has on the top.

The methodology used is summarised in the following figure (Fig. 3). This methodology has been used in the works of several authors [32–34].

Once the destructive tests were carried out, samples of both types of materials (reference concrete and concrete altered after 6 months of exposure to AMD) were taken and polished test samples were prepared for study using the JEOL JSM-Field Emission Scanning Electron Microscope. IT500HR coupled with Oxford X-Max 150 Energy Dispersive System (FESEM-EDS) to be able to analyse morphological changes, microstructure and compositional analysis.

3. Results and discussion

As explained in the methodology, we present the results as follows: the mass of the samples before and after their exposure, the results obtained directly from the non-destructive tests (VPU, modulus of elasticity and the estimation of the compression resistance data), as well as the parameters deduced from these (concrete quality and porosity), to finish with the results of the destructive tests. Thus, Table 4 shows the mass of the samples results in the different periods of exposure to AMD. A slight increase in mass was verified in the two exposure times related to neoformed materials on the outer surface of the samples.

Once the samples were subjected to the acidic water, it was possible to verify the formation of a superficial layer on the water, which confirmed the presence of bacteria that contribute to the acceleration of the alteration process of the concrete, which has been widely confirmed in AMD environment by works such as [35,36] (Fig. 4). The physico-chemical parameters measured are represented in Fig. 5, in which the decrease suffered in the exposure months can be verified, both in dissolved solids and in electrical conductivity, the latter being a direct consequence of the decrease in TDS. The pH value was maintained throughout the experience between 2.8 and 2.9 (except in the initial phase), which corresponds to an highly acidic environment, with the generated surface gypsum low capacity to modify this parameter and with the action of microorganisms in an AMD environment. In addition, it should be taken into account that the water collected from the Aguas Agrias stream has sulphate concentrations greater than 9000 mg/L throughout the year [25].

In Fig. 5 it can be observed that the TDS value follows a decreasing trend, which would justify the slight increase in the mass of the samples due to neoformed compounds adhered to the concrete, once the test samples do not suffer water erosion under static conditions. In addition to this, the Fe^{3+} would have precipitated at the bottom of the container during the entire exposure time, as demonstrated by the pH value above 3. Both the pH and the conductivity rise slightly in the initial phase when starting to react with the binder of the concrete, subsequently decreasing due to the Fe(III) hydrolysis, which precipitates as Fe(OH)3 and generating protons [37]. The measured Redox potential reached a mean value of 217 mV.

Fig. 5 also shows that the water temperature gradually increased from the 8th week of the experiment. This is due to the fact that the container was in a laboratory that is in permanent contact with the outside air as it has a ventilation hole in the roof of approximately 6 m2 in one of its corners, so this parameter increased progressively coinciding with the spring-summer period.

The 10 samples of each series (5 for the split-tensile tests and another 5 for the compression tests) were subjected to tests with the ultrasonic equipment, obtaining the results that appear in Fig. 6. With the measured values of UPV (ultrasonic pulse velocity) the quality of the concrete could be estimated using Table 5, established by [38] in [39,40]. According to the values of this table, the reference concrete would be of excellent quality, while those exposed for 3 and 6 months

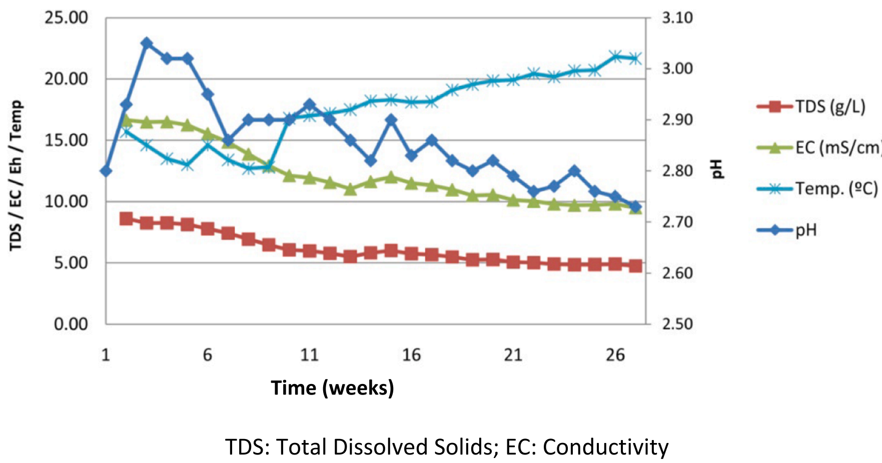

Fig. 5. Evolution of the physico-chemical parameters.

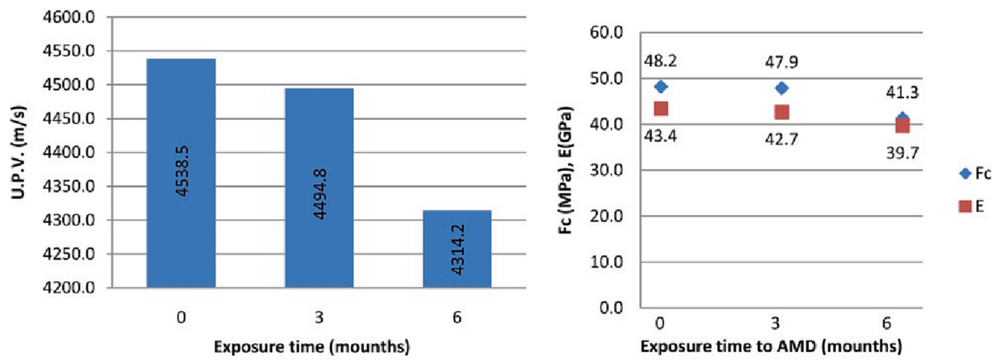

Fig. 6. Results of ultrasonic test: Left - U.P.V (m/s), Right - Average values of compressive strength and modulus of elasticity.

Table 5
Concrete quality by ultrasonic test from [40].

U.P.V. (m/s)	Concrete quality
More than 4500	Excellent
3600–4500	Good
3000–3600	Medium
2100–3000	Poor
1800–2100	Very poor
Less than 1800	Significant anomaly

would be of good quality.

The values determined for the parameter E (modulus of elasticity) by means of the ultrasonic equipment would correspond approximately to those obtained with the expression of Eq. (11), through which values around 7% lower were obtained, while in the case of compressive strength, the values measured by ultrasonic equipment at three and six months showed great correspondence with those obtained in the destructive tests, with a difference of less than 6% in the samples subjected to AMD for six months (47.2 MPa at three months and 43.8 MPa at six months).

$$V_L = \sqrt{\frac{E(1-\mu)}{\rho(1+\mu)(1-2\mu)}} \tag{11}$$

Where:
E is the modulus of elasticity in MN/m^2,
V_L is the speed of the ultrasonic pulse (km/s),

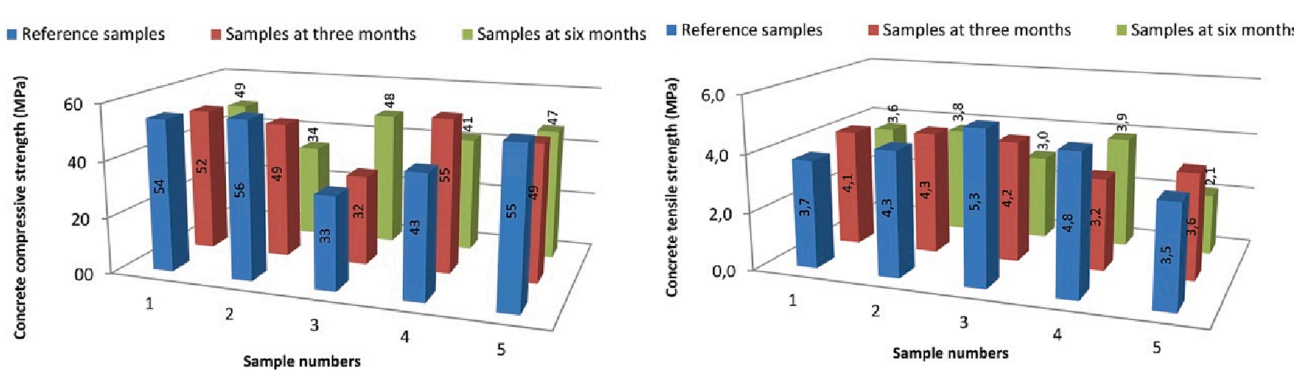

Fig. 7. Concrete strength results determined by destructive tests (compression - left, tensile - right).

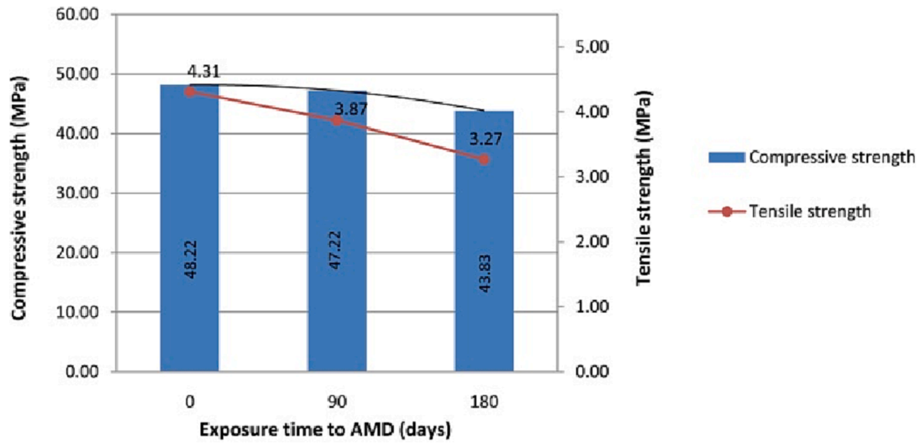

Fig. 8. Comparison of compressive and tensile strength of concrete.

μ is the Poisson's ratio, and

ρ is the density of concrete (kg/m^3)

Other parameters that it is possible to analyse from the ultrasonic results would be the porosity and the permeability to air. Thus, different authors [41,42] found an almost linear inverse relationship between the U.P.V value and the concrete porosity, which would mean that the porosity would go from 12% for the reference samples to 14.5% for the 6 months samples. Following the bibliographical reference of [43] it was possible to find that the air permeability would have increased by approximately $3{\cdot}10^{-18}$ m^2.

In Fig. 7, the results of the two destructive tests are indicated, both for compression strength (Fig. 6a) and for split-tensile strength (Fig. 7b), while Fig. 8 shows a comparison of the evolution followed by both parameters during the exposure time.

Regarding the results of the compressive and split-tensile strength over the time measured in the tests carried out until breaking (Figs. 7 and 8), it is clear that the changes due to AMD, affects in a much greater extent to tensile than to compression strength. This fact would invalidate equations (3) to (6), unless they are modified with a correction factor. Thus, the compressive strength was reduced in the affected periods (at 3 and 6 months) by 2.1% and 9.1% respectively, while the tensile strength was also reduced, but by 10.3% and 24.1% for the same period of time. In this sense, it must be taken into account that the formation of superficial gypsum, by creating a concrete-gypsum interface, can generate fracture points [44]. This is of special importance in those situations where the tensile strength of the concrete is taken into account when sizing or checking of a certain section, such as sections exposed to shear, torsion or punching forces. In addition, the uniaxial tensile strength values are likely to be somewhat lower, as found by [45].

In the case of the formula proposed by the Structural Code 2021, relating the tensile strength to the compression strength, the error reaches 14% (estimated a higher value than that determined by testing), while with the expression proposed by AS 3600 standard, the error reaches values between −11% and 2% higher than that found in this work.

In those situations in which the concrete is exposed to acidic water, two correction factors are proposed for the equations Eq. (13) and Eq. (14), which would be as follows:

$$Z = [1.091 - 0.443t]0.3f_c^{2/3} for f_c < 50MPa \quad (13)$$

$$f_{ct} = [1.244 - 0.557t]\cdot\left(0.36\cdot f_c^{1/2}\right)\cdot 1.4 \quad (14)$$

where t is the exposure period in years

The difference that can be seen in the correction factor is due to the accuracy of the two expressions proposed by the respective regulations, which corresponds to what was explained by [46] regarding the exponent of the variable f_c. In any case, it is a first approximation that should be confirmed with an analysis in which the samples are exposed for a longer time, although the expressions will not change too much. These expressions indicate that the tensile strength will be practically nil in a very short period of time.

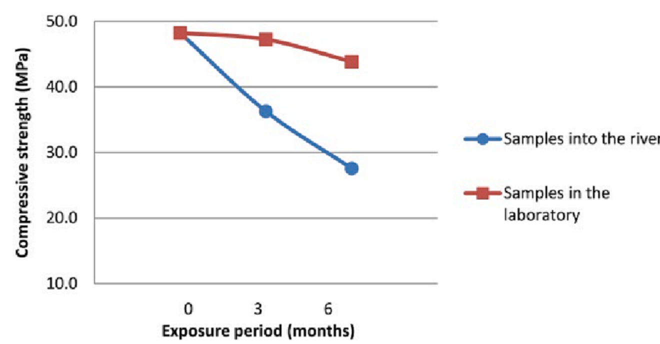

Fig. 9. Evolution of compressive strength in real environment and in laboratory.

If the results obtained in this work (exposed to AMD in the laboratory) are compared with those determined by the same authors in a real environment ([8] – Fig. 9), the different evolution of the compressive strength in both environments can be observed, with a reduction of more than 40% in samples exposed to the stream current while samples subjected to AMD in the laboratory, during the same period of time, had a resistance reduction of only 9.1%. These results show the great importance that erosion produced by the water current has on the durability of materials in mining environments, despite the fact that the samples placed in the stream were close to the shore and partially protected by rocks.

The results of the scanning electron microscope studies show that the reference samples (Fig. 10a and b) have a typical appearance and composition of concrete where 54.3% O, 28.5% Ca, 10.4% Si, 2.5% Al are the majority elements. Sporadic particles inclusions from the combustion of portland cement are also observed. The samples exposed to dynamic AMD in the Aguas Agria stream (Fig. 10c and d) confirm the appearance of micro cracks and detachment of the aggregate at the edges. In addition, the chemical composition of the concrete has been modified, decreasing the Ca content (22%) and increasing the content of other elements typical of AMD composition such as Al (up to 4.2%), Fe (2.1%) and S (1.8%). The precipitation of these elements at the pH of the experiment could indicate oxyhydroxysulphate formations, which could be Ca and Al oxyhydroxysulphate (ettringite), or Fe oxyhydroxisulphate, the latter being common minerals in AMD over a wide pH range.

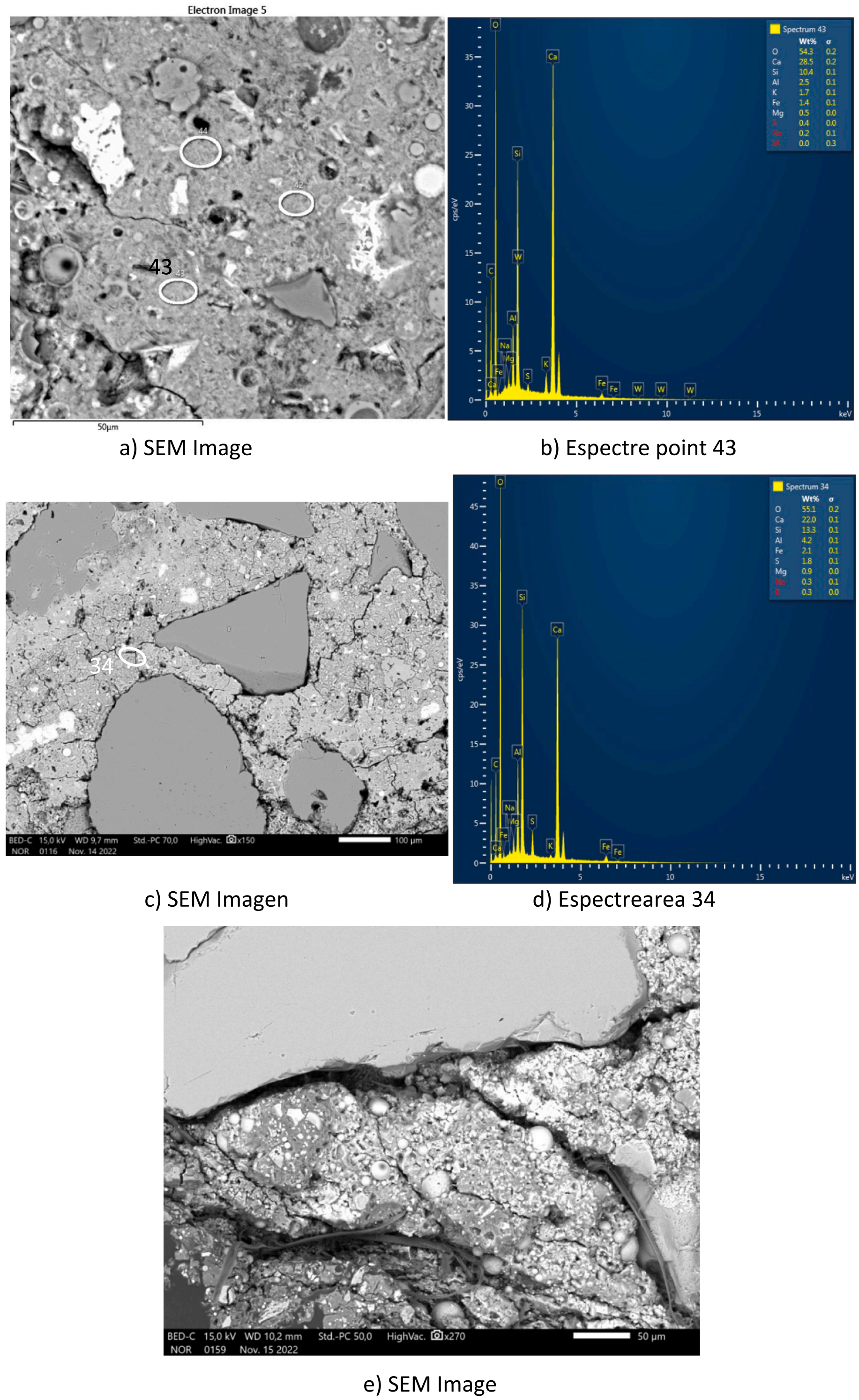

Fig. 10. Images taken with the scanning electron microscope (SEM): reference samples (a and b), samples exposed in the Aguas Agrias stream (c and d) and samples subjected to AMD in the laboratory (e).

Fig. 10e shows the presence of microorganisms in the existing micro cracks in the concrete binder area, appearing a multitude of small cracks in the same sample, which confirms the aggressive action of these microorganisms, that contribute to release fragments of aggregate from the concrete mass. The fact that they do not appear in the river samples may be due to the flow of water, especially in times of heavy rain, where these micro-organisms may be detached from the concrete paste.

4. Conclusions

In this work, mass concrete samples subjected to an AMD environment in the laboratory were studied, using water from the Aguas Agrias stream. The samples were tested with ultrasonic equipment and, subsequently, were subjected to destructive tests to evaluate the resistance to compression and tensile strength.

The tensile strength has been reduced by around 24% at 6 months, while the compressive strength was reduced by approximately 9%, which demonstrates the different evolution that these two parameters follow in a concrete affected by acid water. This is due to the cement mass loss in the external area of the concrete.

The formulas that relate the tensile strength to the compression strength cannot be applied in aggressive situations such AMD media, since the tensile strength is greatly influenced by the cement loss on the outside of the samples. Correction factors were proposed for some of the international standards. It would be interesting to see if the same thing happens in other similar and aggressive environments.

The samples exposed to the acid environment in the laboratory present a small increase in their mass due to the chemical and bacterial actions that have decomposed the surficial cement, forming gypsum paste.

Using ultrasonic tests, it was possible to demonstrate that the analyzed samples present a loss in the concrete general quality, going from excellent to good quality in the 6 months of exposure. This is reflected with an increase in porosity, air permeability, cracks appearance and the reduction of the modulus of elasticity.

It was possible to verify the great influence erosion had on the compressive strength loss, finding, for the same period of time (6 months), a difference of 34% between compressive strength loss of the samples subjected to AMD in laboratory compared to the samples exposed to the river current. It should be kept in mind, that the water used in the laboratory experiments was obtained from the same stream.

Scanning microscopy analysis confirmed the microcracks formation in the concrete binder paste, both in river and in laboratory samples, finding in the latter a multitude of microorganisms that accelerate the formation of these cracks.

CRediT authorship contribution statement

Jose Miguel Davila: Conceptualization, Methodology, Investigation. **Aguasanta Miguel Sarmiento:** Methodology, Validation, Investigation. **Jose Antonio Grande:** Project administration, Supervision, Writing – review & editing. **Ana Teresa Luís:** Writing – original draft, Formal analysis, Visualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

[1] A.M. Sarmiento, J.A. Grande, A.T. Luis, J.M. Davila, J.C., Santisteban M, Curiel J., de la Torre M.L. Ferreira da Silva E., Negative pH values in an open-air radical environment affected by acid mine drainage. Characterization and proposal of a hydrogeochemical model, Sci. Total Environ. 644 (2018) 1244–1253, https://doi.org/10.1016/j.scitotenv.2018.06.381.

[2] K. Nordstrom, C.N. Alpers, Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California, Proc. Natl. Acad. Sci. 96 (1999) 3455–3462, https://doi.org/10.1073/pnas.96.7.3455.

[3] D. Leduc, L.G. Leduc, G.D. Ferroni, Quantification of bacterial populationsindigenous to acidindrainage streams, Water Air Soil Pollut. 135 (2002) 1–21, https://doi.org/10.1023/A:1014778301817.

[4] C. Grengg, F. Mittermayr, G. Koraimann, F. Konrad, M. Szabó, A. Demeny, M. Dietzel, The decisive role of acidophilic bacteria in concrete sewer networks: A new model for fast progressing microbial concrete corrosion, Cem. Concr. Res. 101 (2017) 93–101, https://doi.org/10.1016/j.cemconres.2017.08.020.

[5] J.C. Fortes, J.M. Dávila, A.M. Sarmiento, A.T. Luís, M. Santisteban, J. Díaz-Curie, F. Córdoba, J.A. Grande, Corrosion of Metallic and Structural Elements Exposed to Acid Mine Drainage (AMD), Mine Water Environ. 39 (2) (2020) 195–203.

[6] R. Quatrini, D.B. Johnson, Acidithiobacillus ferrooxidans, Trends Microbiol. 27 (2019) 282–283, https://doi.org/10.1016/j.tim.2018.11.009.

[7] J.M. Davila, A.M. Sarmiento, M. Santisteban, A.T. Luís, J.C. Fortes, J. Diaz-Curiel, C. Valbuena, J.A. Grande, The UNESCO national biosphere reserve (Marismas del Odiel, SW Spain): an area of 18,875 ha affected by mining waste, Environ. Sci. Pollut. Res. 26 (2019) 33594–33606, https://doi.org/10.1007/s11356-019-06438-7.

[8] J.M. Davila, A.M. Sarmiento, J.C. Fortes, M. Santisteban, M. Leiva, F. Cordoba, J. E. Cabello, J.A. Grande, Determination of the extreme reduction of concrete strength due to acid mine drainage by laboratory tests on specimens located in a real environment, Constr. Build. Mater. 269 (2021) 1–10, https://doi.org/10.1016/j.conbuildmat.2020.121817.

[9] S.O. Ekolu, S. Diop, F.Z. Azene, N. Mkhize, Disintegration of concrete construction induced by acid mine drainage attack, J. South Afr. Inst. Civil Eng. 58 (2016) 34–42. https://doi.org/10.17159/2309-8775/2016/v58n1a4.

[10] G.F. Huseien, Z.H. Joudah, N.H.A. Khalid, A.R.M. Sam, M.M. Tahir, N.H.A.S. Lim, R. Alyousef, J. Mirza, Durability performance of modified concrete incorporating fly ash and effective microorganism, Constr. Build. Mater. 267 (2021) 1–15, https://doi.org/10.1016/j.conbuildmat.2020.120947.

[11] B. Ali, L.A. Qureshi, S.H. Ali Shah, S.U. Rehman, I. Hussain, M. Iqbal, A step towards durable, ductile and sustainable concrete: Simultaneous incorporation of recycled aggregates, glass fiber and fly ash, Constr. Build. Mater. 251 (2020) 1–12, https://doi.org/10.1016/j.conbuildmat.2020.118980.

[12] S.C. Moghaddam, R. Madandoust, M. Jamshidi, I.M. Nikbin, Mechanical properties of fly ash-based geopolymer concrete with crumb rubber and steel fiber under ambient and sulfuric acid conditions, Constr. Build. Mater. 281 (2021) 1–11, https://doi.org/10.1016/j.conbuildmat.2021.122571.

[13] J. Dashti, M. Nematzadeh, Compressive and direct tensile behavior of concrete containing Forta-Ferro fiber and calcium aluminate cement subjected to sulfuric d attack with optimized design, Constr. Build. Mater. 253 (2020) 1–14, https://doi.org/10.1016/j.conbuildmat.2020.118999.

[14] V. Tanwar, K. Bisht, K.I.S. Ahmed Kabeer, P.V. Ramana, Experimental investigation of mechanical properties and resistance to acid and sulphate attack of GGBS based concrete mixes with beverage glass waste as fine aggregate, J. Build. Eng. 41 (2021) 102372.

[15] V. Patel, N. Shah, Durability Study of M70 Grade Structural Concrete, Iran. J. Sci. Technol. Trans. Civil Eng. 41 (2017) 241–248, https://doi.org/10.1007/s40996-016-0046-8.

[16] C. Estructural, (2021). BOE núm. 190, de 10 de agosto de,, Ministerio de la Presidencia, Relaciones con las Cortes y Memoria Democrática, Spain, 2021.

[17] EN 1992-1-1 Eurocode 2 (2004). Design of concrete structures: General rules and rules for buildings. Directive 2004/18/EC.

[18] CEB-FIP Model Code 2010 for Concrete Structures. Federation Internationale du Beton.

[19] Indian standard for plain and reinforced concrete, IS 456 : Fourth revision 2007, Bureau of Indian Standards. New Delhi.

[20] Concrete Structures, AS 3600-2009 (incorporating Amendment 1-2010 and 2 of 2013), Standards Australia International.Sydney NSW 20001, Australia.

[21] UNE-EN 206: 2013+A2:2021/M (2022). Hormigón. Especificaciones, prestaciones, producción y conformidad. CTN-83 Technical committee, ANEFHOP. Spain.

[22] Aci 318–14,, Building Code Requirements for Structural Concrete, American Concrete Institute, USA, 2014.

[23] Design of Concrete Structures (2016). Canadian Standards Association, A23.3 Committee. Canada.

[24] J. Monteny, E. Vincke, A. Beeldens, N. de Belie, L. Taerwe, D. Van Gemert, W. Verstraete, Chemical, microbiological, and in situ test methods for biogenic sulfuric acid corrosion of concrete, Cem. Concr. Res. 30 (2000) 623–634, https://doi.org/10.1016/S0008-8846(00)00219-2.

[25] A.M. Sarmiento, J.M. Nieto, M. Olías, C.R. Cánovas, Hydrochemical characteristics and seasonal influence on the pollution by acid mine drainage in the Odiel River basin (SW Spain), Appl. Geochem. 24 (2009) 697–714, https://doi.org/10.1016/j.apgeochem.2008.12.025.

[26] Fernández M. (2007) Hormigones. Colegio de Ingenieros de Caminos, Canales y Puertos, ISBN: 978 380 0364 0. Spain.

[27] Fernández M.(1999). Hormigón", 5ª Edición adaptado a la Instrucción de Cementos RC-97 y a la Instrucción de Hormigón Estructural EHE-98. Madrid, Spain.

[28] UNE-EN 12390-1: 2022. Ensayos de hormigón endurecido. Parte 1: Forma, dimensiones y otras características de las probetas y moldes. CTN-83 Technical committee, ANEFHOP, Spain.

[29] UNE-EN 12350-2: 2020, Ensayos de hormigón fresco. Parte 2: Ensayos de asentamiento. CTN-83 Technical committee, ANEFHOP, Spain.

[30] UNE-EN 12390-3: 2020. Ensayos de hormigón endurecido. Parte 3: Determinación de la resistencia a compresión de probetas. CTN-83 Technical committee, ANEFHOP. Spain.

[31] UNE-EN 12390-6: 2010. Ensayos de hormigón endurecido. Parte 6: Resistencia a tracción indirecta de probetas. CTN-83 Technical committee, ANEFHOP. Spain.

[32] Q. Xia, H. Li, A. Lu, Q. Tiana, J. Liu, Damage analysis of concrete members containing expansive agent by mechanical and acoustic methods, Eng. Fail. Anal. 74 (2017) 95–106, https://doi.org/10.1016/j.engfailanal.2016.12.020.

[33] J.M.C. Ongpeng, A.W.C. Oreta, S. Hirose, Characterization of Damage Using Ultrasonic Testing on Different Types of Concrete, Mater. Eval. 76 (2018) 1534–1541.

[34] S. Guo, Q. Dai, X. Sun, Y. Sun, Z. Liu, Ultrasonic Techniques for Air Void Size Distribution and Property Evaluation in Both Early-Age and Hardened Concrete Samples, Appl. Sci. 7 (2017) 2–18, https://doi.org/10.3390/app7030290.

[35] D.C. Fernández-Remolar, D. Gómez-Ortiz, P. Malmberg, T. Huang, Y. Shen, A. Anglés, R. Amils, Preservation of Underground Microbial Diversity in Ancient Subsurface Deposits (>6 Ma) of the Rio Tinto Basement, Microorganisms 9 (2021) 1592, https://doi.org/10.3390/microorganisms9081592.

[36] D. Ayala-Muñoz, W.D. Burgos, J. Sánchez-España, E. Couradeau, C. Falagán, J. L. Macalady, Metagenomic and Metatranscriptomic Study of Microbial Metal Resistance in an Acidic Pit Lake, Microorganisms 8 (2020) 1350, https://doi.org/10.3390/microorganisms8091350.

[37] Ekolu S.O., Azene F.Z., Diop S. (2014). A concrete reactive barrier for treatment of acid mine drainage. Proceedings of the Institution of Civil Engineers (ICE) - Water Management Journal, 167, 373-380, 10.1680/wama.13.00035.

[38] Leslie J.R. and Cheesman W.J. (1949) in Vidaud E.J., Vidaud I.N. (2016). Ultrasonido: Aplicación para la determinación del módulo de elasticidad dinámico. Construcción y tecnología del concreto 31-35.

[39] B.J.A.Y. Sogbey, S. Kwofie, E. Darko, A.A. Adiaottor, N. Allotey, Comparative structural strength analysis of Pozzolana-Portland cement using ultrasonic non-destrctive testing technique, J. Sci. Technol. 5 (2015) 125–136. http://hdl.handle.net/11400/6398.

[40] F. Saint-Pierre, A. Philibert, B. Giroux, P. Rivard, Concrete Quality Designation based on Ultrasonic Pulse Velocity, Constr. Build. Mater. 125 (2016) 1022–1027, https://doi.org/10.1016/j.conbuildmat.2016.08.158.

[41] M.G. Hernández, M.A.G. Izquierdo, A. Ibáñez, J.J. Anaya, L.G. Ullate, Porosity estimation of concrete by ultrasonic NDE, Ultrasonics 38 (2000) 531–533, https://doi.org/10.1016/S0041-624X(99)00095-5.

[42] L.A. Quintero, J. Herrera, L. Corzo, J. García, Relationship between compressive strength and porosity of concrete evaluated from ultrasonic parameters, Revista ION 24 (2011) 69–76.

[43] Z. Lafhaj, M. Goueygou, A. Djerbi, M. Kaczmarek, Correlation between porosity, permeability and ultrasonic parameters of mortar with variable water/cement ratio and water content, Cem. Concr. Res. 36 (2006) 625–633, https://doi.org/10.1016/j.cemconres.2005.11.009.

[44] H. Haeri, V. Sarfarazi, M.F. Marji, Investigating the tensile strength of concrete-gypsum interface using the ring type bi-material specimens, Arab. J. Geosci. 14 (2021) 1–18, https://doi.org/10.1007/s12517-021-08096-x.

[45] H. Haeri, V. Sarfarazi, A.B. Shemirani, M.F. Marji, On the direct experimental measurement of mortar fracture toughness by a compression-to-tensile load transformer (CTLT), Constr. Build. Mater. 181 (2018) 687–712, https://doi.org/10.1016/j.conbuildmat.2018.06.066.

[46] F. Oluokun, Prediction of Concrete Tensile Strength from its Compressive Strength: an Evaluation of Existing Relations for Normal Weight Concrete, Mater. J. 88 (1991) 302–309.