Determination of the extreme reduction of concrete strength due to Acid Mine Drainage by laboratory tests on specimens located in a real environment.

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Abstract

The reduction in durability due to the drainage of acidic mine water is a serious problem that causes the deterioration of the structural materials located in this type of environment, spreading throughout all the sulphide mining operations of the world, and in particular, in the Iberian Pyritic Belt where there are a large number of abandoned mines.

In this research the evolution over time of the mechanical characteristics of concrete affected by acid mine drainage has been studied, as well as some properties of concrete that are closely related to durability. Several samples of concrete (40 MPa of compressive strength, w/c ratio of 0.45, 435 kg/m^3 of sulphate resistant cement), were subjected to a real acidic environment, allowing the harmful effects of erosion and the action of bacteria to be taken into account. The samples were subjected to this acidic environment for six months, five of them being extracted every two months.

From the two types of tests carried out, one destructive and the other non-destructive, the concrete strength was determined, as well as an estimate of its quality, porosity and air permeability. Through this process, it has been possible to obtain an approximate evolution of the deterioration of the concrete mechanical properties.

A significant deterioration of concrete has been confirmed, with a considerable loss of the surface cement paste and fine aggregate, together with a substantial reduction in the concrete strength (over 40% in just six months, this value being much higher than obtained in previous investigations carried out by other researchers in the synthetic environment) and an increase in porosity, all with a very rapid evolution over time.

Keywords: concrete, Acid Mine Drainage, durability, compressive strength, porosity, ultrasonic test, sulphate

1 Introduction

Acid Mine Drainage (AMD) is a process that is generated in conjunction with sulphide mining operations, accentuating in abandoned mines, which occurs in many of the existing mines in the Iberian Pyrite Belt, representing millions of cubic meters of waste. This process is characterized by extreme acidity, with water pH values in many cases below 4, and high concentrations of sulphates, metals and metalloids. These characteristics make this water unsuitable for human consumption [1,2].

The AMD process is hydrogeochemical contamination that starts when pyrites react with oxygen and water, resulting in ferrous oxide and sulphates. The ferrous oxide is rapidly oxidizes to ferric, which further oxidizes the pyrites. This process is repeated continuously and is accelerated by the activity of acidophilic bacteria that act as catalysts by increasing the speed of corrosion [3-5].

The basic reactions that explain this process (Eq. (1) and (2)) were defined by [6]:

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

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

Acid Mine Drainage has a significantly negative impact on water resources, affecting wetland biota [1,7,8], groundwater and damaging structural materials such as concrete and steel, with extremely high maintenance costs in mining operations [9]. Among other effects on structural elements, AMD causes detrimental impacts on different infrastructures, such as corrosion in pipes, tanks, conveyor belts, pumping equipment, thickeners, etc [3].

Focusing on concrete structures, among which would be affected by this problem, it can point out the building structures made with this material, pipes, tanks, containment elements in general (dikes, retaining walls and even rockfills that use concrete), gallery plugs, bridge pillars, foundation elements, hopper columns, etc. (Figure 1).

1.a. Retaining dike.   1.b. Gallery plug.

Figure 1. Structures altered by AMD.

Different processes affect the durability of concrete, such as physical, chemical, structural and even biological phenomena. In general, it can be said that concrete will be attacked depending on the strength of the acid, from weak acids to those produced by strong acids such as those found in situations with AMD.

However, even though there are significant advances in the study of concrete durability [10-13], there are almost no research works on the interaction between AMD and concrete, except for some works such as those of [3,14 and 15], and none of them have analysed the alteration of concrete in a real AMD environment. In some of these works, protection alternatives for concrete in acidic environments are even proposed, such as the use of concrete with silica fume, rice husks and recycled aggregates or different types of cement, recycled rubber tires [16- 20]. However, in most cases the results are not conclusive or definitive.

The durability of concrete is a topic of increasing interest, proof of this is the number of scientific publications that address this issue and the increasing extension that is devoted to it in the regulations on structural concrete, reflected in almost all of them with more demanding prescriptions.

The process by which corrosion occurs in concrete has been extensively explained. Thus, in the presence of sulphate ions, including those found in AMD environments [3], this anion reacts with the hydroxide of Ca released during the hydration of cement forming gypsum (eq. 3), and with the hydrated tricalcium aluminate forming ettringite (calcium aluminate sulphate - eq. 4). Both reactions result in expansion, loss of strength and cracking of concrete [21], increasing the permeability of concrete mass, mainly in the outer area, which allows the access of bacteria.

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

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

It can be said that the durability of the structural elements (particularly in concrete) put through to AMD is altered by the following factors [22]: the amount of dissolved oxygen in water, degree of acidity of water, concentrations of sulphate and magnesium and, finally, by the presence of microorganisms.

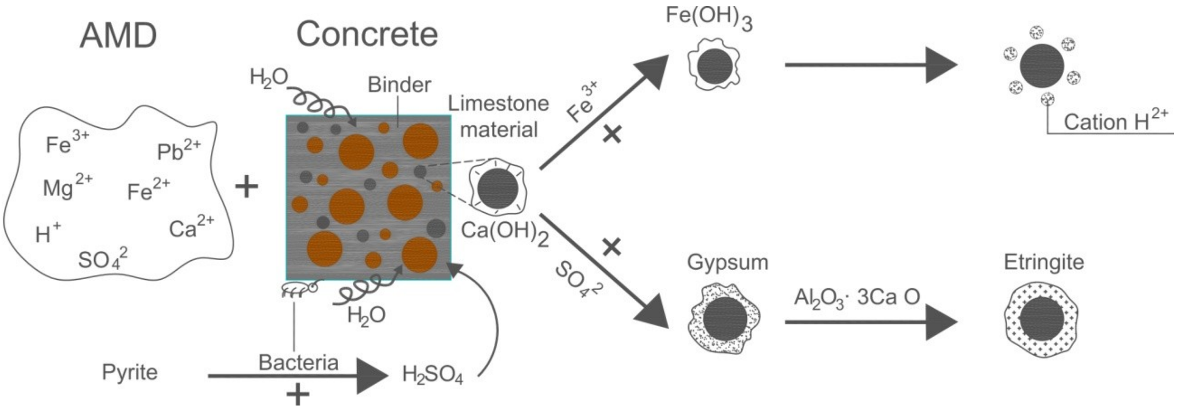


Figure 2. Scheme of concrete corrosion by AMD.

The phenomenon of concrete corrosion by AMD is summarised in Figure 2

In the present case, the attack on concrete occurs from the moment in which the samples are placed within the river course, taking into account that the samples were placed in water in July, when the level of water had dropped a lot and therefore had a very low pH, in addition to being subjected to erosion by the effect of the water current.

Even though there are not many works that have studied the affection of concrete by AMD, it is essential to highlight some engaging research papers. Thus, [3] carried out a study using micro analytical techniques on pieces of concrete from a dam located in a coal mine. They determined that due to the contact of concrete with the AMD, the breakage and fragmentation of concrete with the formation of gypsum on the surface and the appearance of micro fractures occurred. In this research, the concrete samples had a compressive strength of 20MPa and had been made without sulphur-resistant cement.

Some studies try to create a laboratory environment to accelerate corrosion, such as the one carried out by [23] and [24], that studied the behaviour of mass concrete in a synthetic acid environment prepared in the laboratory by adding nitric and sulphuric acid. The study concluded that resistance values decreased mainly in samples with a lower pH (1.5) subjected to the acid for six months.

[14] Carried out an investigation in different aggressive media, among others, in a synthetic AMD environment, as well as in waste water of the sewage system to evaluate the loss of mass in concrete specimens. However, this research was carried out with samples of 32 mm in diameter and with a non-sulphur-resistant cement.

[25] Has carried out two investigations in which he made a computer model of the attack on concrete in acidic environments (pH between 4 and 6.5). This attack was modelled by applying dissolution, precipitation and transport processes; thus, it was determined that deterioration is characterized by a significant increase in surface layer porosity, by the dissolution of calcium in the binder matrix and, in some cases, by aggregates and gypsum precipitation.

Also noteworthy are the contributions in which the participation of microorganisms to the phenomenon of corrosion in concrete has been studied. Thus, [22 and 26] indicated that some bacteria act as catalysts and accelerators of the oxidation of pyrite, which in turn contributes to an increase in the acidity of the water (see Figure 2).

The presence of surface gypsum and/or ettringite initially provides a protective layer against acid for the undisturbed inside the concrete. However, this type of bacteria finds in this porous paste the ideal medium to develop and is capable of penetrating it, producing more sulphuric acid next to the non-attacked concrete area [4]. This is one of the factors that influences the fast deterioration of the analysed samples.

The Acidithiobacillus ferooxidans and Acidithiobacillus thiooxidans bacterias have been shown to cause loss of mass in concrete and the appearance of microfractures in the binder mass and around the aggregate [14]. As will be seen in later sections, it is on the outer surface of samples that these processes initially take place.

In the current regulation of structural concrete, the type of environment is defined as "*the set of physical and chemical conditions to which it is exposed, and which may cause its degradation as a consequence of effects different from those of loads and solicitations considered in structural analysis*" [27].

In this sense, in the current concrete regulations (e.g. UNE-EN 206 [28] and ACI [29]) the different environments are defined by several factors, such as corrosion, freeze-thaw effects and chemical attack. Table 1 shows the exposure classes indicated by [13] related to chemical aggressiveness. Taking into account that the samples that have been analysed have been in contact with water with pH values variable between 2.2 (in August 2019) and 4.3, it would be the type of exposure XA3 or intense aggressiveness, which is the maximum value that an environment can achieve for concrete structures. As will be seen later, these pH values coincide within the studied range.

Parameters	**Testing method**	**XA1 Weak chemical aggressiveness**	**XA2 Moderate chemical aggressiveness**	**XA3 Strong chemical aggressiveness**
		WATER		
pH	ISO 4316	6.5 - 5.5	5.5 - 4.5	4.5-4.0
Mg^{2+} (mg/L)	EN ISO 7980	300 - 1000	1000 - 3000	>3000
SO_4^{2} (mg/L)	EN 196-2	200 - 600	600 - 3000	3000 - 6000
		SOILS		
SO_4^{2} (mg/kg)	EN 196-2	2000 - 3000	3000 - 12000	12000 - 24000
Degree of Bauman-Gully acidity (mg/kg)	EN 16502	>200	----	----

Table 1. Exposure class due to chemical aggressiveness of water or soil [28].

The environments defined in table 1 as XA1, XA2 and XA3 coincide with those indicated in the French standard [30] and correspond to the Qa, Qb and Qc defined in the Spanish standard EHE-08 [27], while in the ACI code [29] and in the Canadian Standard [31] the environment 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 will be seen later in this work). In the case of the Indian Standards [32], it includes four subclasses of exposure depending on the content of SO_3 (subclasses S0 to S4), which even though we cannot compare them in terms of exposure classes if we are interested in comparing them as for their demands.

The effect of corrosion is not only the produced by the low pH, by the action of sulphates and the addition of some bacteria, but also due to the erosion produced by the water current, in addition to the affection in real situation by bacteria. In addition, this study has been carried out on concrete samples that comply with the current international regulations regarding the use of sulphur-resistant cement, resistance, etc; when some of these parameters were not met in previous works. For it, this work is to fill a gap in the field of AMD, since the alteration of concrete structural elements in a real environment has never been studied before. The investigations carried out so far to study the evolution of the mechanical properties and porosity of concrete have only dealt with the subject through simulations or synthetic preparations in the laboratory.

Thus, the aim of this work is to carry out an initial assessment of corrosion due to the effects of real AMD on mass concrete structural elements. To achieve this objective, the evolution of the mass concrete strength subjected to real AMD will be analysed, as well as its quality and some concrete properties related to durability.

2 Materials and methods

2.1 Methodology

The procedure followed began with the choice of an appropriate site to place the samples that met certain requirements: easy access, it should have water throughout the year, but with little depth to allow collecting the samples and, of course, It should be a site with water affected by the AMD environment. That is why the Agrio river was chosen, which is part of the Oraque river basin that discharges its waters into the Odiel river (Figure 3). The Odiel river and its entire basin have historically been affected by serious AMD problems, with a large number of abandoned sulphide exploitations, a fact that accentuates this problem. This stream comes directly from the tailings of the Tharsis mines, which have been abandoned for many years and are still in the same situation. As can be seen in the Location setting (Figure 3), the chosen location is within the Iberian Pyrite Belt (FPI) and in the province of Huelva (SW Spain), therefore, the evolution of concrete properties could be studied in a real AMD environment, which had not been done until now.

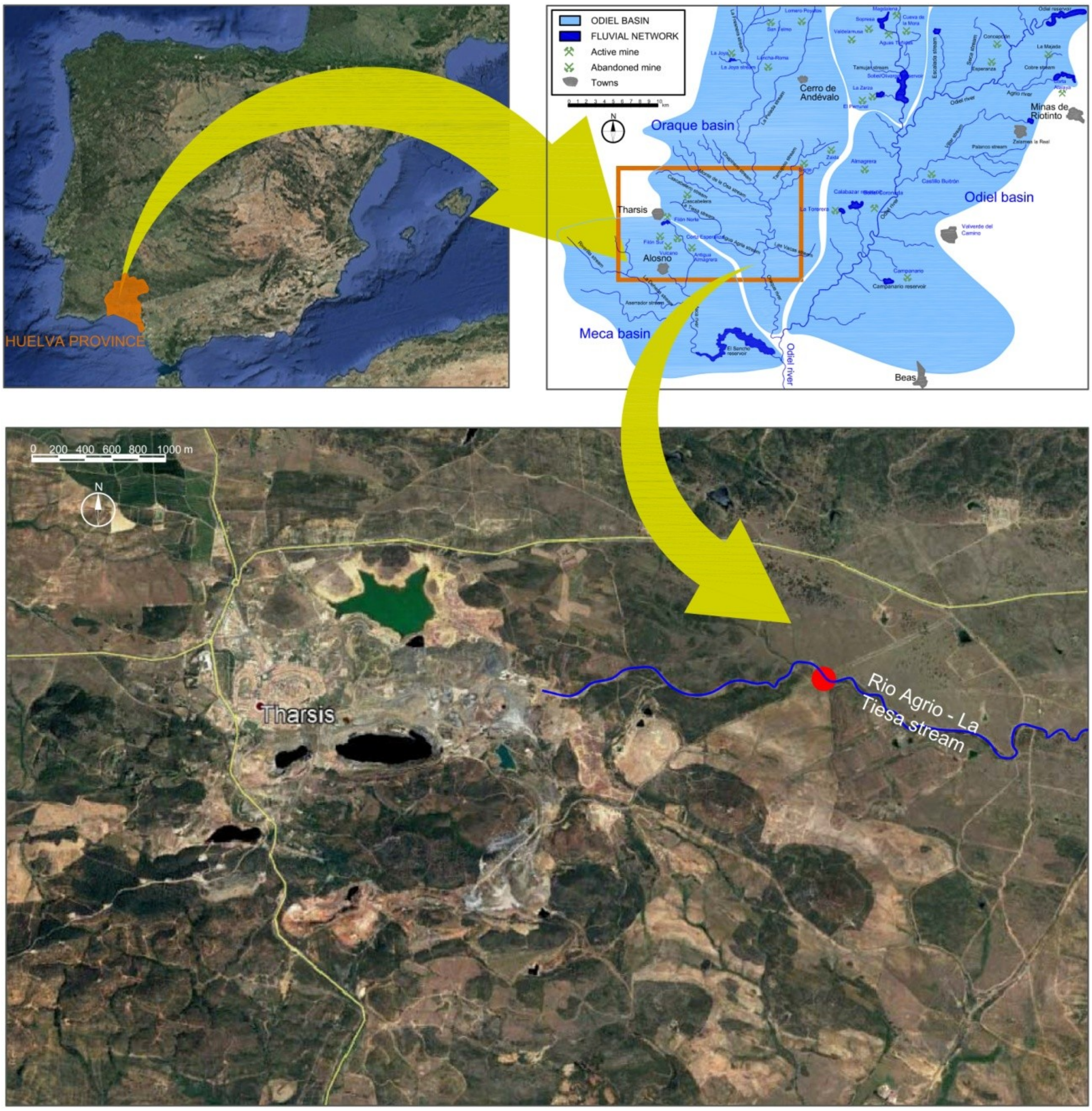


Figure 3. Samples location (Source: own creation and Google Earth).

To carry out this work, a total of 38 concrete specimens were elaborated, of which three were used to adjust the appropriate dosage, another five were left as a reference and the other 30 specimens were placed in the Agrio river (Figure 3) to be able to continue the investigation for a extended period of time, depending on the evolution and degradation of the properties of the concrete affected by AMD, with the withdrawal of five samples being scheduled every two months. Depending on how concrete was deteriorating, the extension that this experience should follow would be decided, so in practice, 15 specimens affected by AMD and 5 reference ones have been evaluated.

To study the effects of AMD on mass concrete, samples were introduced into the water affected by acid mine drainage in a real situation, in particular, close to Tharsis Mining Complex (Odiel Basin, Iberian Pyrite Belt, SW Spain; an area with more than 80 mines - much of them abandoned - and almost 5000 years of history), dated July 11, 2019 (see Figure 3).

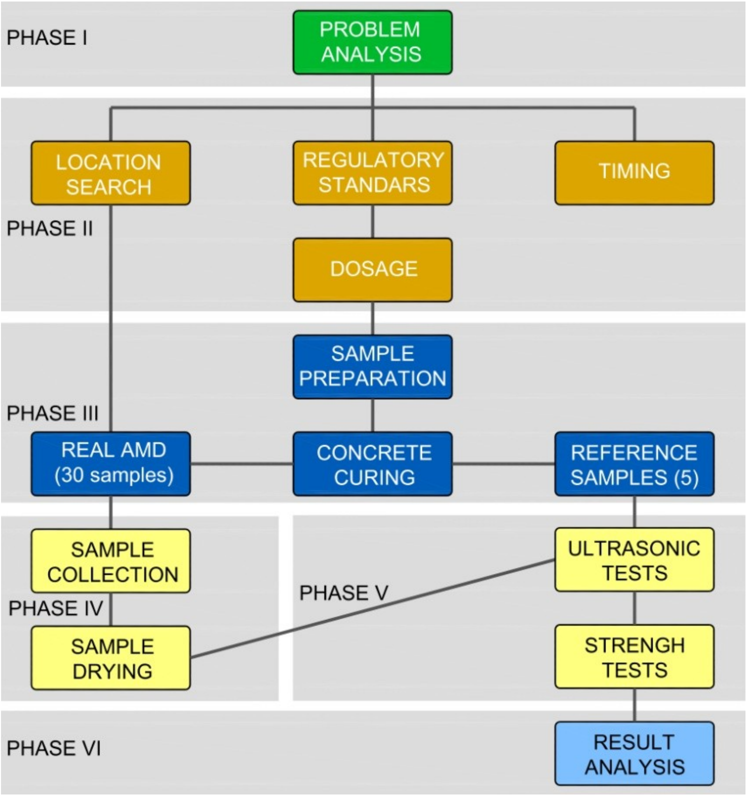


Figure 4. Work Diagram.

To better understand the procedure followed, a diagram is included with the entire process followed in the investigation (Figure 4).

To understand the situation in which the specimens were placed, the parameters determined by [33] for years (from 2002 to 2006) are summarized (Table 2), taking into account that the months form July to September correspond to the dry season, while the months from October to January are within the rainy season. In addition, it should be noted that the authors of this work have found lower pH values (-1.56 [34] and 1.32 [35]) and sulphate content higher than those found where the specimens were placed (16000 mg/L [36], 45000 mg/L [1] and 114322 mg/L [34]), which means even more aggressive situations in AMD environments.

Date	pH	Eh (mV)	EC (µS/cm)	TDS (mg/L)	Fe (mg/L)	FeII (mg/L)	FeIII (mg/L)	Mg (mg/L)	Pb (µg/L)	Ca (mg/L)	SO_4^2 (mg/L)
2002	2.48	n.d.	11600	n.d.	817.6	n.d.	n.d.	1044.0	136.0	145.1	13301.5
2003	2.71	648	11917	3.4	1262.5	169.4	658.3	873.9	262.9	165.3	9142.8
2004	2.72	668	9230	5.2	1146.5	607.1	317.6	1333.3	499.0	245.4	12123.8
2005	2.57	682	10260	12.0	1092.0	261.5	830.5	n.d.	n.d.	n.d.	n.d.
2006	2.63	650	9340	7.0	1168.5	604.2	564.3	864.5	81.5	206.8	8513.0

Eh: Redox; EC: Electrical conductivity, TDS: Total Dissolved Solids, n.d.: not determined

Table 2. Parameters determined in the Agrio River [33]

Table 2 also serves to understand the physical-chemical parameters of the environment in which the samples were placed. The values determined during the years 2002 to 2006 can be extrapolated to the current situation, since these will depend on the situation of the mines from which the stream starts (which have not changed for many years) and the rainfall regime. Thus, with the known rainfall data for the hydrological years (from September to August of the following years) included in the period 2002 to 2006 and 2019/20 (Table 3), obtained from the Alosno meteorological station, located at 6 km from the place where the samples were placed; the physicochemical parameters and the metallic concentrations have been validated, with the idea of understanding the characteristics of the acidic river water. As can be seen, the rainfall regime of the hydrological year 2019/20 would be in intermediate values between the years 2004/05 and 2005/06, but if we also look at the months in which the research was carried out (July to January), the situation would be very similar to the period 2004/05.

	2002/03	2003/04	2004/05	2005/06	2019/20
Hydrological year	803	887	302	656	460
From July to January	446	501	227	343	213

Table 3. Rainfall in L/m^2 (Alosno weather station)

Once the ideal location to carry out the experiment was decided, it was necessary to establish the dosage and requirements of the samples.

With the prepared samples (including a 28 day curing period), the reference tests were started and the rest were taken to the stream. Once the specimens had been progressively removed, they were dried at room temperature in the laboratory for 15 days prior to carrying out the tests.

Since the tests performed were both destructive and non-destructive, the ultrasonic tests were performed first, and the same samples were subsequently tested under compression. The methodology followed to evaluate the mechanical properties (strength and modulus of elasticity) and durability has been previously validated by various authors [37-39].

2.2 Materials

Dosing consists of determining the quantity of the substances that make up the material. Depending on the environment in which the structure is found, the quantity and proportion of the components can be defined in the regulations; in this case, the environment is the XA3 already mentioned in Table 1.

The minimum requirements for hardened concrete are shown in Table 4 for the different environments defined by chemical aggressiveness.

	Kind of environment **Chemically aggressive environments**		
	Qa	Qb	Qc[a]
Maximum ratio w/c	0.50	0.50	0.45
Minimum strength (MPa)	30	30	35
Minimum cement content kg/m^3	275	300	325
Other requirements	-	Sulphate resistant cement	

[a] This environment is equivalent to XA 3 in UNE-EN 206

Table 4. Minimum requirements depending on the type of environment [12].

As indicated, the concrete specimens have been prepared with the following data: w/c ratio of 0.45, minimum cement content of 435 kg/m^3, minimum strength 35 MPa and the use of sulphur-resistant cement (SR) (meeting the requirements of EHE-08), 150 mm in diameter and 300 mm in height.

In this same sense, the ACI and the Canadian Standard require w/c = 0.45 (for class S2), use of HS (sulphur-resistant) cement and a minimum resistance of 31 MPa, EN 206 requires 360 kg/m^3 of cement . The Indian standard (IS 456: 2000) recommends for the most demanding subclass for sulphate content (called S4) a w/c ratio of 0.4, a minimum cement content of 400 kg/cm^3, minimum resistance of 50MPa and the use of cement type SRPC (sulphur-resistant), the latter being the most demanding of the regulations analysed.

Among the dosing methods based on compressive strength, the most used are the ACI method and the La Peña method (1955). La Peña will be followed as it is the most widespread both in Spain and in other countries. To apply the method, the following parameters are used: maximum aggregate size (silicon-type rolled aggregate has been used, with a maximum size of 16mm) and desired strength of concrete, (higher than the 35 MPa required in the regulations) as starting data, obtaining the final dosage. Thus, for the maximum w/c ratio of 0.45 required, we would obtain a resistance more significant than 38 MPa

It starts from the value of the strength concrete, determined by the expression (Eq. 5):

$$Z = Kf_{cm} + 0.5 \qquad (5)$$

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 5).

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

Table 5. K parameter values.

The amount of water to be used is defined according to the consistency, type of aggregate and maximum size of the aggregate (Table 6). By means of Fuller's parabola (Eq. 6 - [40]) and Eq. (7) the quantities (by weight) of the concrete components are determined. Thus, for 1.025 m^3 of concrete these quantities are defined by: 435 kg/m^3 cement (type 42.5 SR - sulphate resistant), 0.193 m^3 of water, 836.9 kg of coarse sand and 1046.5 kg of fine sand.

		Abrams (cm)	Rounded aggregates (mm)			Crushed aggregates (mm)		
			80	40	20	80	40	20
Water (l)	Dry	0-2	135	155	175	155	175	195
	Plastic	3-5	150	170	190	170	190	210
	Soft	6-9	165	185	205	185	205	225
	Fluid	10-15	180	200	220	200	220	240

Table 6. Water amount

$$p = 100\sqrt{\frac{d}{D}} \qquad (6)$$

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

$$A+\frac{C}{\gamma_C}+\frac{G_g}{\gamma_g}+\frac{G_f}{\gamma_f}=1.025 \quad (7)$$

Where.

A is the amount of water,

C is the amount of cement,

G_g is the amount of coarse aggregate,

G_f is the amount of fine aggregate,

γ_C is the specific weight of the cement,

γ_g is the specific gravity of the coarse aggregate, and

γ_g is the specific gravity of the fine aggregate

In the consistency test the result was 85 mm (S2, as indicated by UNE-EN 206).

The method of identification of the test pieces was by marking them with holes, in order to be able to identify them once they were affected by the AMD, creating their own code, beginning to read from left to right, which is known from a mark made with a chisel, this mark remaining on the left side (Figure 5).

Figure 5. Example of specimens mark (after affecting by AMD).

It should be noted that the study has significant advantages over studies with synthetic acid, as in the real situation proposed it is taken into account the erosion by water flow and possible acceleration caused by the action of existing bacteria in the environment.

2.3 Tests

Two kinds of tests were carried out, one of resistance to compression by means of a press and non-destructive ultrasonic tests.

In this case, the compression test was carried out on cylindrical specimens of 150x300 mm (with a curing time of 28 days) using the Automax X5 compression equipment (Figure 6). To carry out the test, the following parameters were used, according to UNE EN 12390-3 standard [41]:

- Sensibility: 20 kN
- Velocity: 0.60 MPa/s

Figure 6. Specimens prepared for the compression test in the press.

Figure 7. Ultrasonic test

The ultrasonic tests have been used as an assessment of deterioration in concrete durability. This test consists of two transducers, so that one of them emits an ultrasonic pulse; therefore, the sample is travelled by the wave from one end to the other and the velocity is measured. The equipment used was the Pundit Plus from the CNS Farnell company (Figure 7).

Initial tests were carried out seven days after hardening the reference specimens, with the intention of checking whether the dosage that had been determined was adequate and we obtained the minimum resistance required by the regulations. From there, once the results were verified to be valid, obtaining a resistance higher than the 70% established in the regulations, all the specimens were for a period of 28 days hardening.

From the results obtained in the ultrasound equipment, the following parameters were determined approximately: concrete quality, damage depth, porosity and air permeability as indicated by [42]. With this, the evolution of the durability of the concrete affected by acid mine drainage can be analysed.

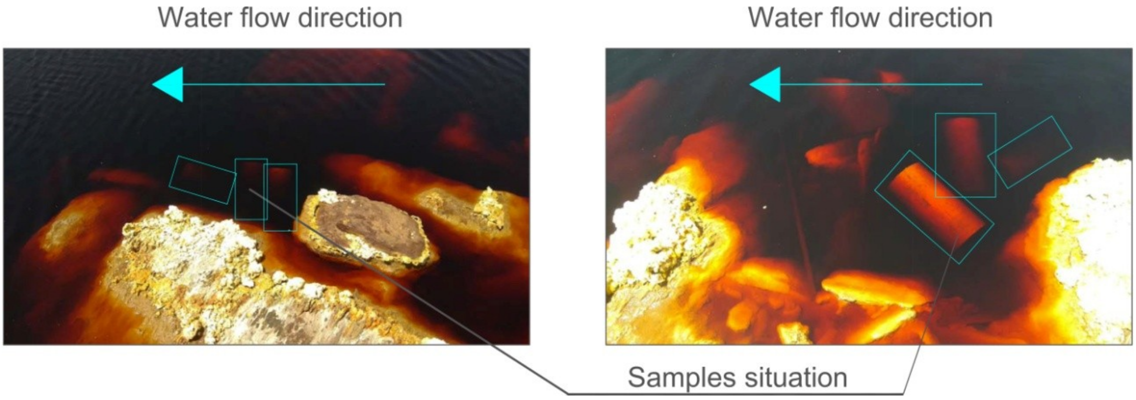


Figure 8. Specimens in water altered by AMD.

Thus, Figure 8 shows the high degree of affection and metallic concentrations due to the colouration of the water, as well as the sulphated salts formations on the stream sides.

The samples were deposited in the Agrio river that collects the water from the waste heaps near the Tharsis mines and forms part of the Oraque river basin, having water throughout the year, with the logical seasonal variations. The samples were placed near the river banks to allow their subsequent withdrawal. As can be seen in Figure 8, the samples were partially protected by rocks on the banks of the river, which represents a certain limitation to the effect of water erosion on the test tubes, so the effect of erosion could even be greater than in another situation.

As indicated in a previous section, the specimens were grouped as follows: 3 to carry out an initial test to validate the concrete dosage; once this aspect was confirmed, a total of 35 more samples were prepared, 5 to have reference values and five for each exposure period in AMD, of which the 15 samples corresponding to 2, 4 and 6 months of alteration were finally tested.

3 Results and discussion

Figure 9 shows the condition of the specimens taken out of the water after four months of exposure, appreciating outside a significant mass of gypsum paste.

Figure 9. Specimens taken from the water with AMD.

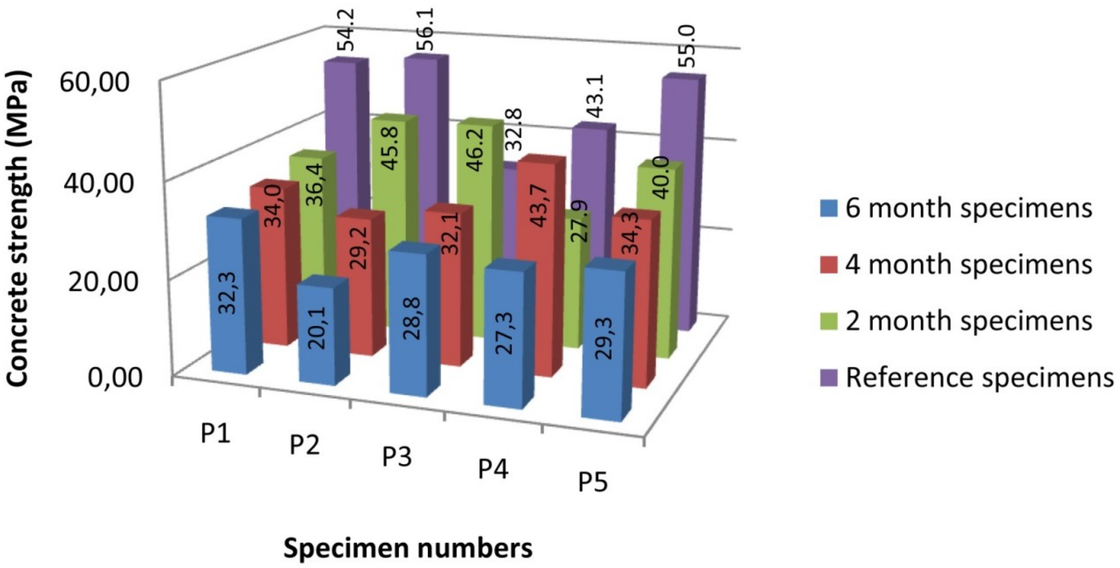


Figure 10. Compressive strength with different periods of exposure

Figure 10 graphically presents the results of the compressive strength of the specimens altered by AMD during different exposure periods. It can be already seen a clear reduction in the concrete strength over the months.

In Figure 11 it can see the evolution of the average concrete strength in the different phases. The reduction of the initial resistance value is 18.6%, 28.1% and 42.8% respectively, for 2, 4 and 6 months compared to the reference without alteration. As It can be seen in the same figure, the evolution of compressive strength has practically followed a linear evolution.

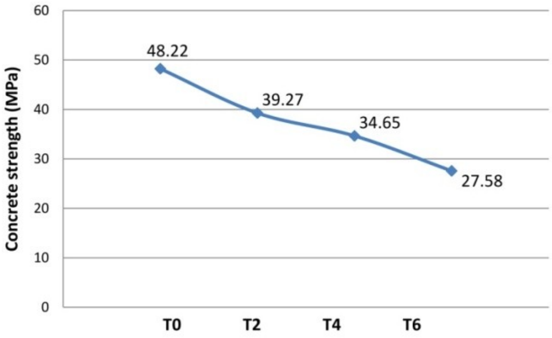
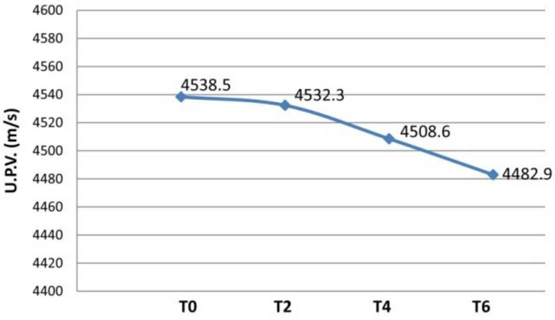


Figure 11. Average resistance of the specimens exposed to AMD and reference environment (T0).

It is important to highlight that, along with the aggressive effect of acidic water, there will have been an erosion on the surface of the test specimens, since they were in the course of a small stream. In any case, this effect will clearly have accelerated the deterioration of the concrete, but it is not the most important, since the specimens were placed close to the banks and protected by rocks. Moreover, this is an effect that occurs in practice in many mining installations and must be taken into account. Furthermore, as indicated above, the process will have been accelerated by the action of the bacteria in the environment.

Regarding the results obtained in the ultrasonic test (Figure 12), the estimated quality of the concrete can be obtained from the velocity of the ultrasonic pulse following the criteria established by Leslie y Cheesman, (1949) in [43] and [44 and 45], as indicated in Table 7.



U.P.V.: ultrasonic pulse velocity

Figure 12. Longitudinal velocity of ultrasonic tests.

The quality of the concrete with which we initially worked was excellent (U.P.V. greater than 4500 m/s). However, the value of this parameter decreases with the months of exposure in AMD, until reaching the average value at six months of exposure of 4482.9 m/s, with a minimum value of 4379.6 m/s. This decrease means that the quality of the concrete has dropped one level (good quality).

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

Table 7. Concrete quality by ultrasonic test from [45].

As indicated in the works of [46 and 47] porosity is closely related to the longitudinal velocity of the ultrasonic test. Although indeed, the results of both authors differ quite a bit, it is clear that the relationship between V_L (longitudinal velocity) and porosity follows an inverse almost linear law, in which a reduction in velocity of 100 m/s represents an increase between 1 and 3% of porosity.

Applying the expression (Eq. 8) indicated by [24], it has been possible to determine the estimated depth of the alteration in the concrete specimens (we understand that even when the exposed study is applied to mortars, it is valid to make a calculation estimated in concrete). Thus for specimens exposed for six months to AMD exposure, an alteration depth of 11.8 mm is obtained.

$$d_{fc} = \frac{l_0}{2}\sqrt{\frac{V_a - V_f}{V_a + V_f}} \qquad (8)$$

Where:

l_0 is the length of the specimen,

V_a is the ultrasonic pulse velocity in the unaffected specimens (reference), and

V_f is the ultrasonic pulse velocity in the specimens exposed to AMD.

The value obtained for h_f is much higher than that found in other studies, such as that of [48], in which several results are indicated in various acidic environments, reaching maximum values similar to the one obtained here but in a period of one year of exposure.

From the results of the ultrasonic pulse velocity it can be estimated [46] that the porosity has risen from an initial value of 12 up to 13 % at six months. Similarly, following the criteria set forth by [42], we can estimate that air permeability has increased approximately in $2 \cdot 10^{-18}$ m^2

Regarding the variation of the modulus of elasticity, this can also be estimated from the results of the ultrasonic pulse velocity applying the well-known equation (9) obtained from the work of Malhotra et al in [47]

$$V_L = \sqrt{\frac{E(1-\mu)}{\rho(1+\mu)(1-2\mu)}} \tag{9}$$

Where:

E is the modulus of elasticity in MN/m^2,

V_L is the speed of the ultrasonic pulse (km/s),

μ is the Poisson's ratio, and

ρ is the density of concrete (kg/m^3)

The variation in the modulus of elasticity between the undisturbed samples and those exposed for six months only represents a decrease of 2.5% with respect to the initial value (E0= 4.078321·E + 07, E6 = 3.979146·E + 07 kN/m^2).

4 Conclusions

The degree of concrete corrosion depends on several factors, mainly the w/c ratio and the composition of concrete. This research has followed the criteria established by the current regulations to determine the concrete dosage.

In the present work, the analysis of the alteration of the mechanical properties of concrete affected by the real AMD environment has been boarded in its initial phase. For this, the evolution of the concrete strength immersed in acidic water up to six months in this environment has been studied.

In view of the strength results of the mass concrete specimens, it can be affirmed that the concrete suffers a very severe deterioration, with a reduction in the resistance that reaches almost 43% after only six months. The evolution of the strength from the origin without affection and subsequent samplings at two, four and six months presents an almost linear distribution.

The deterioration of mass concrete by AMD is severe, with a very significant loss of the cement mass and part of the surface aggregate, in addition to the chemical alteration that the cement will present. This process has been confirmed to occur at high speed.

The ultrasonic tests have served to confirm the data obtained in the destructive tests, corresponding to the decreasing curve of the concrete quality and an increase in the porosity of the material.

The deterioration of the concrete has been obtained in this investigation is much higher than that determined by other investigations in several acid environments, which has been verified with the extreme reduction of concrete stength determined here, as well as with the depth of corrosion

In view of the results, it is clear that when designing structures in AMD environments, certain precautions must be taken into account, with a higher level of demand than that defined in most current regulations, for example, with values close to those required by IS 456-200: lower w/c ratio, higher compressive strength, also greater thicknesses in reinforced concrete coatings, higher cement content (this standard recommends values higher than 400 kg/m^3) and of course, the use of sulphur-resistant cement; and the inclusion of additions that improve the behaviour of the concrete against this attack.

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References

[1] J. M. Davila, A. M. Sarmiento, M. Santisteban, A. T. Luís, J. C. Fortes, J. Diaz-Curiel, C. Valbuena, J. A. Grande, 2019. The UNESCO national biosphere reserve (Marismas del Odiel, SW Spain): an area of 18,875 ha affected by mining waste. *Environ. Sci and Poll. Res.* 1-13, https://doi.org/10.1007/s11356-019-06438-7.

[2] S. O. Ekolu, F. Z. Azene, S. Diop, 2014. A concrete reactive barrier for acid mine drainage treatment. *Proceedings of the Institution of Civil Engineers. Water Management,* July, 167, 373-380, http://dx.doi.org/10.1680/wama.13.00035

[3] S. O. Ekolu, S. Diop, F. Azene, N. Mkhize N, 2016. Disintegration of concrete construction induced by acid mine drainage attack. *Journal of the South African Institute of Civil Engineering* 58, 34-42.

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

[5] C. Grengg, F. Mittermayr, G. Koraimann, F. Konrad, M. Szabó, A. Demeny, M. Dietzel, 2017. The decisive role of acidophilic bacteria in concrete sewer networks: A new model for fast progressing microbial concrete corrosion. *Cement and Concrete Research,* 101, 93-101, http://dx.doi.org/10.1016/j.cemconres.2017.08.020

[6] Nordstrom, K.; Alpers, C.N., 1999. Negative pH, efflorescent mineralogy, and consequences for environmental restoration at the Iron Mountain Superfund site, California. *Proceeding of the National Academic of Sciences*, 96: 3455-3462, https://doi.org/10.1073/pnas.96.7.3455

[7] K. L. Hogsden, J.S. Harding, 2012. Consequences of acid mine drainage for the structure and function of benthic stream communities: a review. *Freshwater Science*, 31, 108-120, https://doi.org/10.1899/11-091.1

[8] A. Olenici, S. Blanco, M. Borrego-Ramos, L. Momeu, C. Baciu, 2017. Exploring the effects of acid mine drainage on diatom teratology using geometric morphometry. *Ecotoxicology*, 26, 1018–1030, https://doi.org/10.1007/s10646-017-1830-3

[9] A. N. Shabalala, S. O. Ekolu, S. Diop, F. Solomon, 2017. Pervious concrete reactive barrier for removal of heavy metals fromacid mine drainage −column study. *Journal of Hazardous Materials* 323, 641-653.

[10] A. M. Aguirre, R. Mejía de Gutiérrez, 2013. Durability of reinforced concrete exposed to aggressive conditions. *Materiales de Construcción. 63*, 7-38, https://doi.org/10.3989/mc.2013.00313.

[11] S. W. Tang, Y. Yao, C. Andrade, Z. J. Li, 2015. Recent durability studies on concrete structure. *Cement and Concrete Research* 78, 143-154, http://dx.doi.org/10.1016/j.cemconres.2015.05.021.

[12] S. Demis, M. P. Efstathiou, V. G. Papadakis, 2014. Computer-aided modeling of concrete service life. *Cement & Concrete Composites.* 47, 9-18, http://dx.doi.org/10.1016/j.cemconcomp.2013.11.004.

[13] T. Krykowski and A. Aybura, 2013. Modelling of Reinforced Concrete Element Damage as a Result of Reinforcement Corrosion. *Procedia Engineering* 57, 614–623, https://doi.org/10.1016/j.proeng.2013.04.078.

[14] V.O. Harbulakova, A. Estokova, N. Stevulova, A. Luptakova, 2014. Different aggressive

media influence related to selected characteristics of concrete composites investigation. *International Journal of Energy and Environmental Engineering,* 5, 1-6, https://doi.org/10.1007/s40095-014-0082-8

[15] R. Javaherdashti and H. Nikraz, 2010. On the role of deterioration of structures in their performance; with a focus on mining industry equipment and structures. *Materials and Corrosion* 61, 1-6, https://doi.org/10.1002/maco.200905515.

[16] M. Mahdikhani, O. Bamshad, M.F. Shirvani, 2018. Mechanical properties and durability of concrete specimens containing nano silica in sulfuric acid rain condition. *Construction and Building Materials*, 167, 929–935, https://doi.org/10.1016/j.conbuildmat.2018.01.137

[17] M. Koushkbaghi, M.J. Kazemi, H. Mosavi, E. Mohseni, 2019. Acid resistance and durability properties of steel fiber-reinforced concrete incorporating rice husk ash and recycled aggregate. *Construction and Building Materials*, 202, 266-275, https://doi.org/10.1016/j.conbuildmat.2018.12.224.

[18] S. Dezhampanaha, I. Nikbin, S. Charkhtab, F. Fakhimi, S.M. Bazkiaei, R. Mohebbi, 2020. Environmental performance and durability of concrete incorporating waste tire rubber and steel fiber subjected to acid attack. *Journal of Cleaner Production*, 268, https://doi.org/10.1016/j.jclepro.2020.122216.

[19] I.N. Etim, J. Dong, J. Wei, C. Nan, E.F. Daniel, D.B. Subedi, D. Xu, A.P. Yadav, M. Su, W. Ke, 2020. Mitigation of sulphate-reducing bacteria attack on the corrosion of 20SiMn steel rebar in sulphoaluminate concrete using organic silicon quaternary ammonium salt. *Construction and Building Materials* 257, 1-17, https://doi.org/10.1016/j.conbuildmat.2020.119047.

[20] M. Mahedi, A. Y. Dayioglu, B. Cetin, S. Jones, 2020. Remediation of acid mine drainage with recycled concrete aggregates and fly ash. *Environmental Geotechnics*, 7, https://doi.org/10.1680/jenge.19.00150.

[21] A. Neville, 2004. The confused world of sulfate attack on concrete. *Cement and Concrete Research* 34, 1275-1296, https://doi.org/10.1016/j.cemconres.2004.04.004.

[22] J. C. Fortes, J. M. Davila, A. M. Sarmiento, A. T. Luís, M. Santisteban, J. Diaz-Curiel, F. Cordoba, J. A. Grande, 2020. Corrosion of Metallic and Structural Elements Exposed to Acid Mine Drainage (AMD). *Mine Water and the Environment* 1-9, https://doi.org/10.1007/s10230-020-00681-y.

[23] V. Patel, N. Shah, 2017. Durability Study of M70 Grade Structural Concrete, *Iranian Journal of Science Technology Transactions of Civil Engineering* 41, 241-248, https://doi.org/10.1007/s40996-016-0046-8.

[24] Q. Xiao, Q. Li, Z.Y. Cao, W.Y.Tian, 2019. The deterioration law of recycled concrete under the combined effects of freeze-thaw and sulfate attack. *Construction and Building Materials* 200, 344-355, https://doi.org/10.1016/j.conbuildmat.2018.12.066.

[25] R. B. Beddoe, 2016. Modelling acid attack on concrete: Part II. A computer model. *Cement and Concrete Research* 88, 20-35, http://dx.doi.org/10.1016/j.cemconres.2015.10.012

[26] R. Quatrini, D.B. Johnson, 2019. Acidithiobacillus ferrooxidans. *Trends in Microbiology* 27, 282-283, https://doi.org/10.1016/j.tim.2018.11.009.

[27] *Instrucción de Hormigón Estructural* (*EHE-08)*, Ministerio de Fomento, Madrid, Spain, 2011.

[28] *UNE-EN 206, Hormigón. Especificaciones, prestaciones, producción y conformidad*, CTN-83 Technical committee, ANEFHOP, Spain, 2018.

[29] *ACI Committee 318, Building code requirements for structural concrete (ACI 318-14) and commentary*. Farmington Hills, MI: American Concrete Institute, 2014.

[30] *CEB-FIP Model Code 2010 for Concrete Structures.* Comité Euro-International du Béton

[31] *Concrete materials and methods of concrete construction*, CSA A 23.1 and 23.2 2004, Canadian Standards Association, Toronto, Canada, M9W 1R3.

[32] *Indian standard for plain and reinforced concrete*, IS 456 : 2000, Bureau of Indian Standards, New Delhi.

[33] A. M. Sarmiento, *Ph.D. Thesis,* Estudio de la contaminación por drenajes ácidos de minas de las aguas superficiales en la cuenca del río Odiel (SO España), University of Huelva, Spain, 2007, http://rabida.uhu.es/dspace/handle/10272/7629

[34] A. M. Sarmiento, J. A. Grande, A. T. Luís, J. M. Davila, J. C. Fortes, M. Santisteban, J. Curiel, M. L. de la Torre, E. F. da Silva, 2018. Negative pH values in an open-air radical environment affected by acid mine drainage. Characterization and proposal of a hydrogeochemical model. *Science of the Total Environment* 644, 1244–1253, https://doi.org/10.1016/j.scitotenv.2018.06.381.

[35] M. L. de la Torre, J. A. Grande, M. Santisteban, T. Valente, J. Borrego, F. Salguero, 2014. Statistical Contrast Analysis of Hydrochemical Parameters Upstream of the Tidal Influence in Two AMD-Affected Rivers. *Mine Water and Environment* 33, 217–227, http://dx.doi.org/10.1007/s10230-013-0258-0.

[36] J. A. Grande, T. Valente, M. L. de la Torre, M. Santisteban, J. C. Ceron, E. Perez-Ostale, 2014. Characterization of acid mine drainage sources in the Iberian Pyrite Belt: base methodology for quantifying affected areas and for environmental management. *Environmental Earth Sciencse* 71, 2729-2738, https://doi.org/10.1007/s12665-013-2652-0.

[37] Q. Xia, H.Li, A. Lu, Q. Tiana, J. Liu, 2017. Damage analysis of concrete members containing expansive agent by mechanical and acoustic methods. *Engineering Failure Analysis* 74, 95-106, http://dx.doi.org/10.1016/j.engfailanal.2016.12.020

[38] J. Ongpeng, A. W. C. Oreta, S. Hirose, 2018. Characterization of Damage Using Ultrasonic Testing on Different Types of Concrete. *Materials evaluation* 76, 1534-1541.

[39] S. Guo, Q. Dai, X. Sun, Y. Sun, Z. Liu, 2017. Ultrasonic Techniques for Air Void Size Distribution and Property Evaluation in Both Early-Age and Hardened Concrete

Samples. *Applied Science* 7, 2-18, https://doi.org/10.3390/app7030290.

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

[41] *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, 2020.

[42] Z. Lafhaj, M. Goueygou, A. Djerbi, M. Kaczmarek, 2006. Correlation between porosity, permeability and ultrasonic parameters of mortar with variable water/cement ratio and water content. *Cement and Concrete Research* 36, 625–633, https://doi.org/10.1016/j.cemconres.2005.11.009.

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

[44] B.J.A.Y. Sogbey, S. Kwofie, E. Darko, A.A. Adiaottor, N. Allotey, 2015. Comparative structural strength analysis of Pozzolana-Portland cement using ultrasonic non-destrctive testing technique. *Journal of Science and Technology* 5, 125-136, http://hdl.handle.net/11400/6398.

[45] F. Saint-Pierre, A. Philibert, B. Giroux, P. Rivard, 2016. Concrete Quality Designation based on Ultrasonic Pulse Velocity. *Construction and Building Materials* 125, 1022-1027, http://dx.doi.org/10.1016/j.conbuildmat.2016.08.158.

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

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

[48] M. Wu, T. Wang, K. Wu, L. Kan, 2020. Microbiologically induced corrosion of concrete in sewer structures: A review of the mechanisms and phenomena. *Construction and Building Materials* 239, 1-17, https://doi.org/10.1016/j.conbuildmat.2019.117813