

# Evaluation of pyrite and pyrrhotite in concretes

## Avaliação de pirita e pirrotita em concretos

A. P. MARCELINO <sup>a</sup>  
anaborgesmarcelinoapple@gmail.com

J. M. CALIXTO <sup>b</sup>  
calixto@dees.ufmg.br

A. G. GUMIERI <sup>c</sup>  
adriana@demc.ufmg.br

M. C. FERREIRA <sup>d</sup>  
mceciliafirms@gmail.com

C. L. CALDEIRA <sup>e</sup>  
claudia@demet.ufmg.br

M. V. SILVA <sup>f</sup>  
vinicio@cemig.com.br

A. L. COSTA <sup>g</sup>  
naluvmsc@gmail.com

### Abstract

It is well known that aggregate characteristics can intensively interfere in concrete behavior especially when sulfides are presented in the aggregates. The lack of consensus to content limit value of these deleterious sulfur compounds in concrete structures for dams has motivated several investigations worldwide. Within this scenario, this work presents a methodology to evaluate the presence of pyrite and pyrrhotite in concretes produced with aggregates containing sulfides. For the study, rock samples from the Irapé hydroelectric power plant area in Minas Gerais (Brazil) were used. This plant was built in a geological site where the rock presented sulfide levels of at least 3%. These rock samples were first ground and then used as aggregates in mortars, which were, during almost one year, subjected to three different exposed conditions: temperature of  $23 \pm 2^\circ\text{C}$  and relative humidity of 95 to 100%; calcium hydroxide solution diluted in water kept at two different temperatures: room temperature and  $50^\circ\text{C}$ . The presence and amount of pyrrhotite were obtained from a leaching process of the material (aggregate or mortar) in a solution of hydrochloric acid. This procedure allowed also the evaluation of the pyrite content. The results showed that the amount of pyrite has remained virtually constant over time in the three exposure situations. This finding indicates that sulfur limits in aggregates should be set according to the type of iron sulfide presented and not solely by the total amount of sulfur.

**Keywords:** sulfide aggregates, concrete, behavior, dams.

### Resumo

As características dos agregados podem interferir intensamente no comportamento do concreto, especialmente quando sulfetos, como pirita e pirrotita, estão presentes nos agregados. A falta de consenso para o valor limite do teor desses compostos de enxofre em estruturas de concreto de barragens tem motivado várias investigações em todo o mundo. Dentro desse cenário, este trabalho apresenta uma metodologia para a avaliação da presença desses compostos de enxofre em concretos fabricados com agregados contendo sulfetos. Para o estudo, foram utilizadas amostras de rochas da área de usina hidrelétrica do Irapé, em Minas Gerais (Brasil). Esta usina foi construída em um sítio geológico onde a rocha apresentava níveis de sulfeto de pelo menos 3%. Essas amostras de rochas foram moídas e depois utilizadas como agregados em argamassas submetidas durante aproximadamente um ano a três diferentes condições de exposição: temperatura de  $23 \pm 2^\circ\text{C}$  e umidade relativa de 95 a 100%; solução de hidróxido de cálcio diluída em água mantida em duas temperaturas diferentes: temperatura ambiente e  $50^\circ\text{C} \pm 2^\circ\text{C}$ . A presença e quantidade de pirrotita foram obtidas a partir de um processo de lixiviação do material (agregado ou argamassa) numa solução de ácido clorídrico para dissolução desta, o que permitiu a avaliação do teor de pirita, sulfeto esse não dissolvido pelo ácido clorídrico. A quantidade de pirrotita foi obtida pela diferença entre o valor inicial de enxofre total da amostra e o valor após essa lixiviação. Como resultado desse estudo, observou-se que a quantidade de pirita se manteve praticamente constante ao longo do tempo nas três situações de exposição. Este resultado indica que limites de enxofre em agregados devem ser estipulados de acordo com o tipo de sulfeto de ferro presente e não unicamente pela quantidade total de enxofre.

**Palavras-chave:** agregados sulfetados, concreto, comportamento, barragens.

<sup>a</sup> Programa de Pós-Graduação em Engenharia de Estruturas, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil;

<sup>b</sup> Departamento de Engenharia de Estruturas, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil;

<sup>c</sup> Departamento de Materiais para a Construção Civil, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil;

<sup>d</sup> MC Soluções Engenharia, Belo Horizonte, MG, Brasil;

<sup>e</sup> Departamento de Metalurgia e de Materiais, Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil;

<sup>f</sup> Companhia Energética de Minas Gerais - CEMIG, Belo Horizonte, MG, Brasil;

<sup>g</sup> Universidade Federal de Minas Gerais, Belo Horizonte, MG, Brasil.

## 1. Introduction

Sulfate attack to concrete is a pathological phenomenon that has been investigated since the 1920's. The deleterious effects related to this kind of chemical attack are usually expansion, which causes considerable cracking and progressive reduction of stiffness and strength of the concrete, as well as aesthetic aspects such as efflorescence. These factors reduce significantly the service life of concrete structures, and could even lead to their complete deterioration [1].

The most common sources of sulfate attack in concrete are the contact with natural and seawaters, with sewer effluents and with soil or rocks containing sulfides. However, in some cases, sulfates appeared in the concrete constituents themselves. Aggregates containing sulfur compounds, usually in the form of sulfides, can be deleterious internal sources of sulfate attack to concrete [2].

In large dams, which are usually located in remote areas, this problem can easily occurred, because, in most cases, the sulfide rocks are the only available aggregates [2].

The vast majority of the studies related to the use of sulfide aggregates in concretes were carried out in Spain and showed severe concrete decay in dam structures. Aggregates containing iron sulfides were used in Graus and Tavascán dams in Spain in 1992, as well as in buildings in Maresme also in Spain in 1970. Chinchón et al. [3], Ayora et al. [4] and Araújo et al. [5] reported serious concrete cracking and degradation in all the above-mentioned structures. To investigate further this pathological phenomenon, these authors carried out microscopic tests in extracted samples from these structures and found compounds different from those usually produced in the cement hydration of cement. These compounds incurred as a result of a chemical reactions caused by the presence of sulfides and sulfates in the aggregates.

In Brazil, the concerning in the use of sulfide aggregates is relatively recent, and only during the design phase of the Irapé hydroelectric power plant, in Minas Gerais, where rocks were found with high levels of sulfides, with predominance of pyrite and pyrrhotite, studies began to emerge about the subject. A trend of these studies was the correlation of the sulfide type rocks with pathologies in the concrete.

The choice to use the Irapé sulfide aggregates for this investigation is associated exactly with the interest of technical community in achieve a better understanding of the behavior of these rocks when embedded in concrete. The relevance of this work is to identify and quantify the levels of pyrite and pyrrhotite in concretes made with sulfide aggregates at any stage after its cure. This methodology will allow the feasibility analysis on the use of these types of aggregates in the studies of concrete elements of hydroelectric power plants and other structures subject to this kind of internal sulfate attack.

## 2. Sulfate attack

The sulfate attack to concrete is a complex process, often involving different chemical reactions that depend on various parameters including the cement composition, the nature of the aggregates, admixtures and environmental factors [6].

The attack usually occurs when hardened concrete is exposed to sulfate ions from external or even internal sources. In general, the

sulfate ions react with cement hydrous products such as calcium hydroxide and aluminates forming the delayed ettringite, which is extremely expansive [7]. At this stage, the concrete no longer has good deformation capacity, and consequently, the expansion caused by delayed ettringite formation may cause cracking and degradation of hardened concrete.

### 2.1 Internal sulfate attack in concrete

#### 2.1.1 Aggregates containing sulfates and sulfides

Rocks containing sulfates and sulfides can be harmful to concrete in two ways. First when the concrete is in direct contact with the rock formation containing sulfides. Secondly, when these rocks are used as aggregates in the concrete composition. In this latter way, the sulfates and sulfides presented in the aggregates may cause changes in the cement hydration process, which may lead to the emergence of efflorescence and expansions [8]. Thus, the use of such aggregates in concrete should be carefully studied not only in the content to be employed but also in the in consequences it may bring.

The delayed gypsum and ettringite formation due to the presence of iron sulfides and the effects on the durability of concrete has been well studied and documented over the last 50 years. However, there are not so many studies on effects of oxidation of ferrous sulfides when the predominant source is the aggregate itself. Most of the design specifications that deal with the subject prescribe a threshold value for the total sulfur in the aggregates and do not differentiate the type of sulfide: pyrite or pyrrhotite. An exception is the European standard EN 12620:2008 [9], which recommends that, if pyrrhotite (an unstable form of iron sulfide  $\text{FeS}$ ) is detected in the aggregate composition, the maximum value of total sulfur should not exceed 0.1 %. This value is 10 times smaller than the usually accepted one for aggregates containing iron sulfides. According to Chinchón-Payá *et al.* [10], this value is considered extremely small by many engineers and may have caused the unnecessary disposal of aggregates that could be suitable for producing concrete. Research has also shown that there is a significant difference between the oxidation products derived from pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) and pyrite ( $\text{FeS}_2$ ). Pyrite is generally more stable than the pyrrhotite [6]. Thus, it is important to identify the different types of sulfides present in the concrete and the consequences of their presence on its behavior.

#### 2.1.2 Concrete produced with aggregates containing sulfates and sulfides

When the oxidation of aggregate iron sulfides occurs within the concrete, the generated compounds undergo a secondary reaction with the cement hydration products, promoting the internal sulfate attack [5]. In this process, in addition to the expansive products due to the own oxidation of sulfides, sulfates ions are produced that react secondarily leading also to the concrete decay [11].

The sulfate attack rate from sulfide aggregates is affected not only by aggregate characteristics (composition, shape and size) and by the kinetics of the sulfide oxidation reactions, but also by cement type and content used in the concrete [6]. When the external sulfate supply is null, or minimal, and may be ignored, concrete

deterioration will be controlled mainly by the rate of aggregate sulfide oxidation, which is limited by the speed of this chemical reaction. Once the sulfate ions are released, the attack is much faster [2] [4]. The rate of aggregate sulfide oxidation depends on the oxygen diffusion through the oxide layer (hydroxide) formed around the sulfide grains and the subsequent change of their surface area. Inside the concrete, these reactions are also function of the oxidizing agents' availability, which may vary for each type of concrete since it is dependable on various parameters such as the amount of oxygen and its diffusion through the pores of the concrete and of the aggregates [2].

In the specific case of hydroelectric dams, Araújo et al. [5] state that the dam position is the main controlling factor related to the extent of oxidation reactions, since it determines the availability of oxidizing agents. In this way, the underwater part of the dam will deteriorate less since it has less oxygen available. On the other hand, the part of the dam above the water level needs only the environment relative humidity or rain for the occurrence of the reactions. In addition, depending on the orientation of the dam, this part is also exposed to higher temperatures, further accelerating the reactions. As a result, the dam tends to move to the face in contact with oxygen, where the reactions are more significant causing a misalignment in the dam. It is important to point out that the expansion will be greater in these external surface layers and not throughout the dam due to the lower availability of oxygen in the internal parts.

### 3. Materials and methods

The purpose of this research investigation was the development of a methodology to identify and quantify the levels of pyrite and pyrrhotite in concretes made with sulfide aggregates at any time after the curing period [12].

In the case of concretes, mortars and cement pastes, aspects related to the constitutive materials and the analysis of the behavior involve access to the structure at various levels. In this investigation, the approach used was based in two criteria: objectivity in the choice

of the parameters relevant to the problem and different methods to obtain the results. Objectivity aimed at minimizing the amount of experimental work. On the other hand, in a complex material as mortars and concretes, it is not advisable to draw conclusions from the application of a single characterization and experimental method: so alternative techniques were used, with good reproducibility that, independently, help verify and/or confirm the results.

In this study, aggregates containing iron sulfides were used. These aggregate were produced from rock samples, consisting of predominantly shale, extracted from the deployment area of the Irapé hydroelectric power plant, located in Minas Gerais. This plant was built in a geological site where the rock featured sulfide levels of at least 3%; therefore, this rock was not used as aggregate source for the concrete employed in the dam.

#### 3.1 Characterization of the materials

##### 3.1.1 Aggregates

Aggregates were first crushed and sieved from the Irapé rock samples to achieve the size distribution according to the requirements of NBR 15577 – part 4 (ABNT, 2008) [13]. However, after crushing and sifting, the produced material did not meet this code prescribed size distribution. Due to this fact, it was decided to employ the actual size distribution of the material obtained after the following crushing and sieving procedures. Approximately 100 kg of rock samples were first triturated in primary and secondary jaw crushers. The material was then split in sieves with mesh openings of 6.3, 4.8, 2.4, 1.2, 0.6, 0.3, 0.15 and 0.10 mm. All material retained in the 6.3 mm sieve was crushed again in the secondary jaw crusher. This procedure was repeated several times until the percentage retained in 6.3 mm sieve was less than 10% of the initial rock sample amount.

In order to investigate the fresh state rheology, mortars were produced with different aggregate size distributions. For each mortar, fresh state consistency tests were carried out according to NBR 7215 (ABNT, 1997) [14]. The best result was found for the following aggregate size distribution: 80 % of aggregates retained between the 4.8 and 0.6 mm sieves and the rest, 20 %, consisting of material retained on sieves with mesh openings equal or less than 0.3 mm. The final aggregate size distribution obtained from crushing procedure and used in the mortar production are shown in Table 1. The aggregate density was determined in accordance with NBR NM 52 (ANBT, 2009) [15]: the measured value was 2.81 g/cm<sup>3</sup>. Aggregate water absorption, determined according to NBR NM 30 (ABNT, 2001) [16], was equal to 1.67 %.

Aggregate microstructure analysis was conducted to evaluate qualitatively and quantitatively the presence of pyrite and pyrrhotite. For qualitative verification of the presence of these sulfides, RAMAN spectroscopy [17] was used. The Raman spectrum provides information on the modes of vibration of a material. The ability to perform non-destructive analyses on the microscopic areas of several minerals has made confocal laser RAMAN spectroscopy a technique intensively employed [17]. Its application includes practically all types of rock samples and it has been used mainly in cases where analyses with TiO<sub>2</sub> or with x-ray spectroscopy do not provide good results. Another great advantage of this method is that no special sample preparation is required. Based on all these aspects, RAMAN spectroscopy was chosen in the qualitative

**Table 1 - Aggregate particle size distribution**

Mesh opening size (mm)	Final aggregate particle size distribution after crushing (%)	Aggregate size distribution used in the mortars (%)
6.3	7.5	-
4.8	28.4	26.9
2.4	20.1	26.4
1.2	14.1	17.4
0.6	7.0	9.3
0.30	3.4	3.9
0.15	3.4	4.4
0.10	2.7	2.7
< 0.10	8.6	9.0

evaluation of the presence of pyrite and pyrrhotite. In these tests, RAMAN spectrometer LAB-RAM HR 800 model coupled with an optical microscope Olympus BX model 41 was used.

For the quantitative assessment of pyrite and pyrrhotite, a sample of aggregate (containing its final size distribution) was ground to a grain size equal or smaller to 0.15 mm. In part of ground sample, the total sulfur content was determined by direct combustion (with infrared detection) using the LECO CS equipment 632.

The pyrrhotite and pyrite quantitative evaluation was conducted employing two different leaching procedures [18]. For the dissolution and leaching of pyrrhotite, one gram of crushed aggregate sample was mixed in a flask bottle to 100 ml of hydrochloric acid (HCl) in the proportion 1:1. This solution was agitated during 1 hour at a temperature of 60°C. The solution was then placed in a funnel with a filter paper for its drainage. The remaining solid material was then washed in distilled water to remove the residual HCl and oven dried at 40°C for 24 hours. The total sulfur amount in part of this dried material, which corresponds to the pyrite content, was determined by direct combustion (LECO). The difference between the aggregate total sulfur amount and this pyrite content is equal to the pyrrhotite. To verify the efficiency of this methodology, pyrite must be dissolved and leached. For this, one gram of material first dissolved in the HCl solution and then oven dried was mixed in a conical flask bottle to 100 ml of *aqua regia* (proportion of 75 ml of HCl with 25 ml of HNO<sub>3</sub>). This solution was agitated during 1 hour at a temperature of 60°C. The material was then filtered and washed with *aqua regia*. Next, it was oven dried at 40°C for 24 hours. The residual sulfur in part of this dried material was then determined by direct combustion (LECO). The residual sulfur content in this case must be equal or close to zero.

### 3.1.2 Portland cement

Brazilian type CP V Portland cement, produced by the National Cement Company, was used in all mortars. The manufacturer provided this cement physical, chemical and mechanical characterization. The cement total sulfur content was determined by of direct combustion using the LECO CS equipment 632.

### 3.1.3 Water

The employed water was supplied locally by COPASA. Its SO<sub>4</sub> content was determined by chromatography of ions [19].

## 3.2 Investigated mortars

### 3.2.1 Mix design

The mortar mix design followed the requirements of NBR 15577 (ABNT, 2008) [13]. The used proportion was 1:2.25 (cement: aggregate), by weight, with a water/cement ratio equal to 0.47.

### 3.2.2 Fresh state evaluation

The mortar workability was evaluated according to NBR 7215 (ABNT, 1997) [14]. All mortars presented good workability, and a mean spreading diameter equal to 265 mm.

### 3.2.3 Mortar behavior evaluation

After curing, mortar specimens were subjected to three different exposed conditions. The first one, called reference, corresponded to placement in a curing room with relative humidity between 95 and 100 and temperature of about 23° C ± 2°C. The other two conditions were: specimen's immersion in a calcium hydroxide Ca(OH)<sub>2</sub> solution (30g/l) at room temperature and at 50° ± 2°C.

For each exposed condition, a total of 30 cylindrical specimens (50 x 100 mm) and 5 prismatic bars (25 x 25 x 300 mm) were cast according to the NBR 7215 (ABNT, 1997) [14] and NBR 15777 (ABNT, 2008) [13] respectively. The cylindrical specimens were employed in the splitting tensile strength tests and in the microstructure analysis. The prismatic bars were used in the expansion evaluation. The specimens were removed from the molds 24 hours after casting and immediately subjected to each exposure condition.

### EXPANSION EVALUATION

The prismatic cast bars were used in the mortars' expansion evaluation over time. Each bar initial length (L<sub>0</sub>) was determined 24 hours after casting using the equipment shown in Figure 1. After this initial length measurement, the bars were then subjected to





three different exposed conditions. Mortar bar lengths were measured weekly from which the corresponding strains were calculated. The corresponding strain at each age was determined according to the following equation:

$$\epsilon = (L_t - L_0) / L_0 \quad (1)$$

where:

$L_t$  is the bar length, in mm, after t days of exposure to a certain condition;

$L_0$  is the initial bar length in mm; and

$\epsilon$  is the corresponding strain.

To minimize the moisture changing effects, the bars removed from the curing room were wrapped in a wet towel and placed in a plastic box with a lid. Each bar was only taken from this box at the moment of its length measurement and put back immediately after this. An air humidifier was also placed next to length measuring device in order to maintain a high value of the relative humidity and reduce shrinkage effects. The bars placed in the calcium hydroxide solutions, both at room temperature and at 50° C, were transported in covered Styrofoam box containing some of the solution taken from the tank in such a way that they were always submerged. Each bar was only removed from this box at the moment of measurement and placed back immediately after this.

E 251 specification [20] prescribes that aggregates for concretes behave satisfactorily when after two months of exposure, the expansive strains do not exceed 0.03 or at the end of six months, these strains are smaller than 0.05 and no cracks are found.

**SPLITTING TENSILE STRENGTH**

The splitting tensile strength was determined according to NBR 7222 (ABNT, 2011) [21] for the mortars subjected to the three

different exposed conditions. Cylindrical specimens (ϕ 5 x 10 cm) were used. The splitting tensile strength tests were done after different periods of exposure. The first one corresponded to 27 days; the other ones were selected according the measured expansive strains. All tests were performed under displacement controlled at a rate of 0.25 mm/min in a 100 kN Instron servo hydraulic machine.

**MICROSTRUCTURE**

Cylindrical specimens (ϕ 5 x 10 cm) were used for the mortar microstructure analysis. The day after the mortars were cast, they were sliced into four parts. These slices were then placed under the three different exposed conditions from where they were taken at certain dates for the microstructure evaluation.

In assessing the pyrite and pyrrhotite rates in the mortars, the same dissolution and leaching procedures used for the analysis of aggregates were employed. Firstly, a mortar sample was ground and oven dried at 40° C for approximately 24 hours. This process intended to evaporate the water before the start of the total sulfur, pyrrhotite and pyrite content evaluation. The dry sample was then split into two parts: in one part, the total sulfur amount was determined by direct combustion while the other part was subjected to leaching process with hydrochloric acid solution (to dissolve all pyrrhotite). This way the total sulfur and pyrite contents were assessed. The difference between these two corresponded to pyrrhotite.

For mortars exposed to calcium hydroxide solution diluted in water, the sulfur content in the water and in the precipitated material formed in this water was also carried out. These evaluations aimed to verify if the leaching of sulfur compounds from the mortar to the calcium hydroxide solution had occurred. Ion chromatography was used for the determination of SO<sub>4</sub><sup>2-</sup> in the water. The precipitated material formed in the solution of the tanks was first oven dried at 40° C for approximately 24 hours. This process also intended to evaporate the water before the beginning of sulfur content determination procedure.

Figure 2 – Pyrrhotite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample

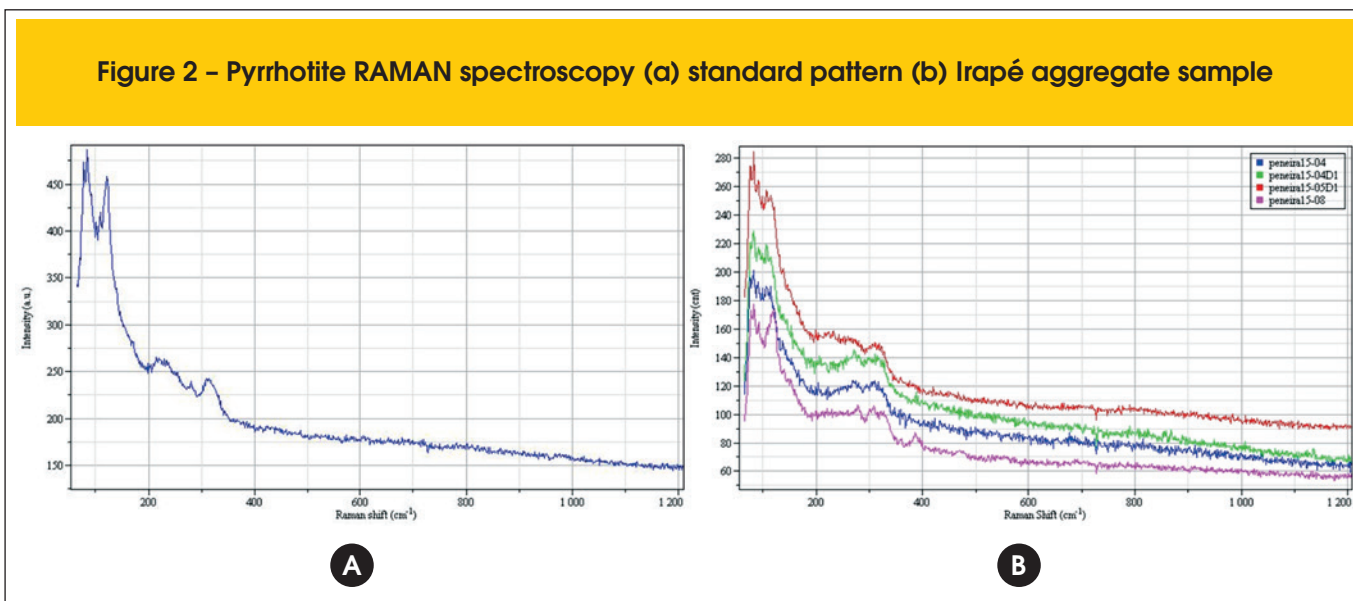
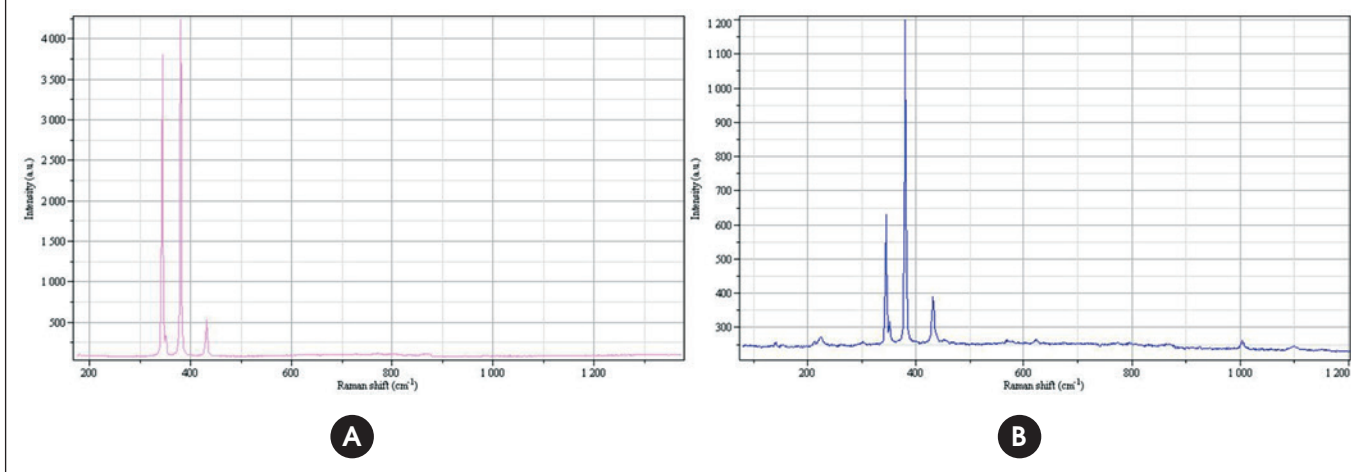


Figure 3 - Pyrite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample



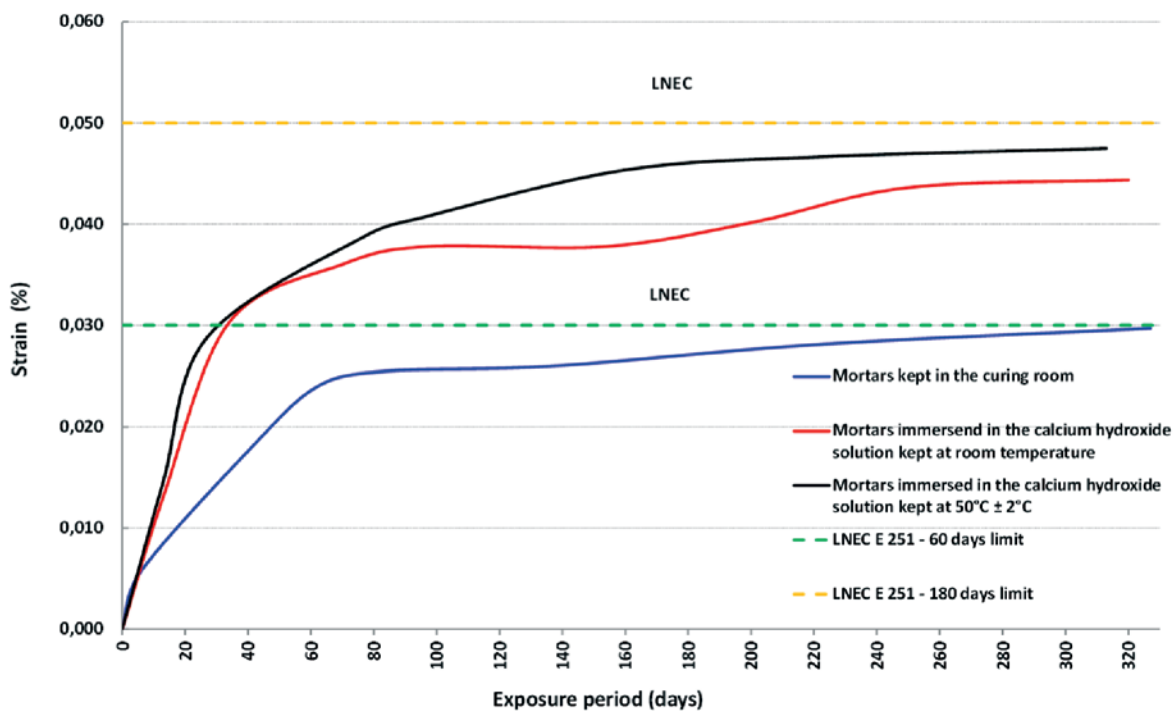
## 4. Results and analysis

### 4.1 Characterization of the constituent materials

#### 4.1.1 Aggregates

The presence of pyrrhotite and pyrite was detected in the RAMAN spectroscopy as shown in Figures 2 and 3. The RAMAN analysis also revealed a higher pyrrhotite occurrence with respect to pyrite. This fact was confirmed as well by the pyrrhotite content determined from direct combustion.

Figure 4 - Strain versus time relationships for the mortars subjected to the three different exposure conditions



**Figure 5 – Prismatic bars used in the expansion evaluation (a) placed in curing room after 327 days – (b) placed in the Ca(OH)<sub>2</sub> solution kept at room temperature after 320 days (c) placed in the Ca(OH)<sub>2</sub> solution kept at 50°C after 313 days**



The average total sulfur and pyrite contents in the aggregates were equal to 2.02 % and 0.6 % respectively. Consequently, the percentage of pyrrhotite (1.42 %) was much larger than the pyrite. This fact confirmed the results found in studies conducted during the construction of the Irapé hydroelectric power plant contained in the P&D 122 [22] final report.

**4.1.2 Portland cement**

The average total sulfur rate in the cement corresponded to 1.07 %. This value was consistent with the content provided by the cement’s manufacturer, which indicated a 2.65% of sulfur trioxide (SO<sub>3</sub>).

**4.1.3 Water**

The water used in the mortars’ production presented an average SO<sub>4</sub> content equal to 25.7 mg/liter. According to the SO<sub>4</sub> molar ratio, every 3 mg/liter of SO<sub>4</sub> has 1 mg/liter of sulfur; thus, the total

sulfur content was equal to 8.57 mg/liter or 0.000857 %.

**4.2 Studied mortars**

**4.2.1 Expansion**

The average expansive strain values for the mortars are presented in Figure 4. The values were measured up to 327 days for the mortars stored in the curing room, 320 and 313 days for the mortars immersed in the calcium hydroxide solution kept at room temperature and at 50° C respectively.

The analysis of these strains indicates that the mortars placed in the curing room almost reached the value of 0.03 % after 328 days. For the mortars immersed in the Ca(OH)<sub>2</sub> solution, both at room temperature and at 50° C, the expansive strains exceeded this value after 30 days of exposure. However, no cracking was observed in the specimens regardless of exposure condition. These results also revealed that, after a period of 10 months of exposure to the three different conditions, the

**Table 2 – Splitting tensile strength of the mortars**

Exposed condition	Exposure period (days)	Mean splitting tensile strength (MPa)	Standard deviation (MPa)
Exposed condition	27	3.67	0.64
	327	4.34	0.41
Curing room	27	3.78	0.27
	63	3.50	0.37
Ca(OH) <sub>2</sub> solution kept at room temperature	320	4.42	0.37
	27	4.43	0.32
Ca(OH) <sub>2</sub> solution kept at 50° ± 2°C	63	4.84	0.25
	313	4.31	0.63

**Table 3 - Contents of sulfur compounds in mortars kept at the curing room**

Exposure period (days)	Total sulfur content in the mortars (%)	Total sulfur content in the cement paste (%)	Pyrite content in the mortars (%)	Pyrrhotite content in the mortars (%)
0	1.50	0.29	0.39	0.82
27	1.49	0.29	0.37	0.83
79	1.48	0.29	0.33	0.82
327	1.05	0.29	0.33	0.43

measured strains did not exceed the E 251 [20] limiting value of 0.05 % in any case and that no apparent mortar deterioration was found (Figure 5).

#### 4.2.2 Splitting tensile strength

Table 2 presents the mortars' splitting tensile strength subjected to the three different exposure conditions. These results showed that the temperature affected significantly this tensile strength: a 21 % increase in strength was found after 27 days of exposure. The 50° C solution temperature during the initial stage of the cement hydration reactions affects not only the rate of hydration, but also the characteristics and quantity of the products formed in these reactions. These effects can interfere with the initial splitting tensile strength of the mortars. Over time, this effect was reduced: the tensile strength of the mortars kept in the calcium hydroxide solution at 50° C was not significantly different from the others.

#### 4.2.3 Microstructure analysis

The values of the total sulfur, pyrite and pyrrhotite contents for the mortars under the three different exposure conditions over time are presented in Tables 3 to 5. The results from the sulfur content evaluation in the Ca(OH)<sub>2</sub> solution and in the precipitated material formed in this solution are shown in Tables 6 to 9.

A theoretical total sulfur content was initially estimated based on the chemical analysis of the constituent materials and their mix proportion in the composition of the mortars. This estimate was calculated as follows:

Initial theoretical  $S_{total}$  content in mortars (%) =  $100 \times [(cement\ proportion \times S_{total}\ content\ in\ the\ cement) + (aggregate\ proportion \times S_{total}\ content\ in\ the\ aggregates) + (water\ proportion \times S_{total}\ content\ in\ the\ water)] / (total\ mass\ of\ mortar)$ .

The used mortar mix proportion, by weight, was equal to: 1: 2.25 : 0.47 (cement : aggregates : water). Based on this mix proportion,

**Table 4 - Contents of sulfur compounds in mortars immersed in Ca(OH)<sub>2</sub> solution kept at room temperature**

Exposure period (days)	Total sulfur content in the mortars (%)	Total sulfur content in the cement paste (%)	Pyrite content in the mortars (%)	Pyrrhotite content in the mortars (%)
0	1.50	0.29	0.39	0.82
27	1.52	0.29	0.43	0.80
90	1.58	0.29	0.43	0.86
320	1.27	0.29	0.42	0.61

**Table 5 - Contents of sulfur compounds in mortars immersed in Ca (OH)<sub>2</sub> solution kept at 50 ± 2°C**

Exposure period (days)	Total sulfur content in the mortars (%)	Total sulfur content in the cement paste (%)	Pyrite content in the mortars (%)	Pyrrhotite content in the mortars (%)
0	1.50	0.29	0.39	0.82
27	1.62	0.29	0.37	0.96
63	1.72	0.29	0.43	1.00
313	1.34	0.29	0.42	0.63



**Table 6 – Sulfur content in Ca (OH)<sub>2</sub> solution kept at room temperature**

Exposure period (days)	SO <sub>4</sub> content (mg/l)	Sulfur content (mg/l)	Sulfur content (%)
0	43.43	14.48	0.01
27	46.00	15.33	0.01
313	50.42	16.81	0.02

**Table 7 – Sulfur content in in Ca (OH)<sub>2</sub> solution kept at 50 ± 2°C**

Exposure period (days)	SO <sub>4</sub> content (mg/l)	Sulfur content (mg/l)	Sulfur content (%)
0	44.33	14.78	0.01
27	61.60	20.53	0.02
335	85.97	28.66	0.03

the theoretical initial S<sub>total</sub> content is equal to 1.47 %. This result is very close to the determined value in the direct combustion procedure of 1.50 % as shown in tables 3 to 5 for the exposure period of zero days.

The pyrite content on the mortars can be estimated as:  $100 \times 0.0202 \times (2.25/3.72) \times (0.6/2.02) = 0.37 \%$  of the total mortar mass. This result is also very close to the measured values shown in the tables 3 to 5. It is important to emphasize that the pyrite content remained practically constant along the evaluated period independently of the exposure condition.

The analysis of these test results also reveals that the total sulfur content was reduced after a period of 300 days of exposure in the three different conditions. This reduction was due to sulfur leaching that migrated to the Ca(OH)<sub>2</sub> solution or to the precipitated material formed in this solution or to the air. This fact can be verified by the increase in the total sulfur content measured in the calcium hydroxide solution and in the precipitated material deposited on the bottom of the tanks after 300 days of exposure. In the case of the curing room, the sulfur leaching must have occurred to the environment.

### 5. Concluding remarks

The results of the experiments conducted herein reveal that the three exposure conditions used were conducive to the sulfide’s oxidation. The mortars kept in the curing room showed a larger reduction in total sulfur content in relation to the mortars immersed in the calcium hydroxide solution. This fact indicates that the presence of oxygen is needed to accelerate the iron sulfide oxidation rate

In terms of the evaluated mechanical properties, the test results show no significant difference in splitting tensile strength of the

mortars over time independently of the three different exposed conditions.

The results also indicated that, for the specimens immersed in Ca(OH)<sub>2</sub> solution, sulfur migrated from the mortars to this solution after 300 days of exposure. This fact was confirmed by the increase in the total sulfur content measured in the calcium hydroxide solution and in the precipitated material deposited on the bottom of the tanks over time.

On the other hand, mortar expansion occurred more significantly in the first 60 days of exposure, while the pyrrhotite content remained constant. The only exception was the mortars immersed in the calcium hydroxide solution kept at 50° ± 2°C.

The pyrite content in the mortars remained virtually constant over time independently of the three exposure situations. This result indicates that the sulfur content limits in aggregates to be used in concretes should be prescribed according to the type of iron sulfide presented in these aggregates and not solely by the total amount of sulfur.

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**Table 8 – Sulfur content in the precipitated material formed in Ca (OH)<sub>2</sub> solution kept at room temperature**

Exposure period (days)	Sulfur content (%)
0	< 0.01
27	0.04
343	0.08

**Table 9 – Sulfur content in the precipitated material formed in Ca (OH)<sub>2</sub> solution kept at 50 ± 2 °C**

Exposure period (days)	Sulfur content (%)
0	< 0.01
27	0.03
335	0.10

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