

Evaluation of the behavior of concrete gravity dams suffering from internal sulfate attack

Comportamiento de presas de gravedad de hormigón con problemas de ataque interno por sulfatos



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Abstract

Herein is described a methodology developed to evaluate concrete expansion and consequent abnormal behavior in gravity dams suffering from internal sulfate attack. The work presented here encompasses the analysis, in different phases, of three Spanish dams plagued by sulfate reactions.

The aggregate and concrete of the Torán dam were characterized at a microscopic level. The principal iron sulfides and the products resulting from oxidation of the aggregate, and the products of the subsequent sulfate attack of the concrete were all identified. Moreover, macrostructural studies of the upstream displacement observed in the Graus and Tavascán dams were performed using a mathematical model.

Keywords: internal sulfate attack, expansion, gravity dam, pyrrhotite, aggregate.

Resumen

En este trabajo se presenta la metodología seguida con vistas a evaluar la expansión del hormigón debido al ataque sulfático interno y su repercusión en el comportamiento anómalo de presas de hormigón de gravedad. Para ello se presenta el análisis, en distintas fases del estudio, de tres presas españolas afectadas por las reacciones sulfáticas.

En el nivel microscópico se ha procedido a la caracterización del árido y del hormigón de la presa de Torán, identificando el principal sulfuro de hierro y los productos generados en el proceso de alteración del árido y su posterior ataque al hormigón. Por otro lado, el estudio en el nivel macroestructural de los movimientos remanentes observados se hace mediante un modelo matemático aplicado a las presas de Graus y Tavascán.

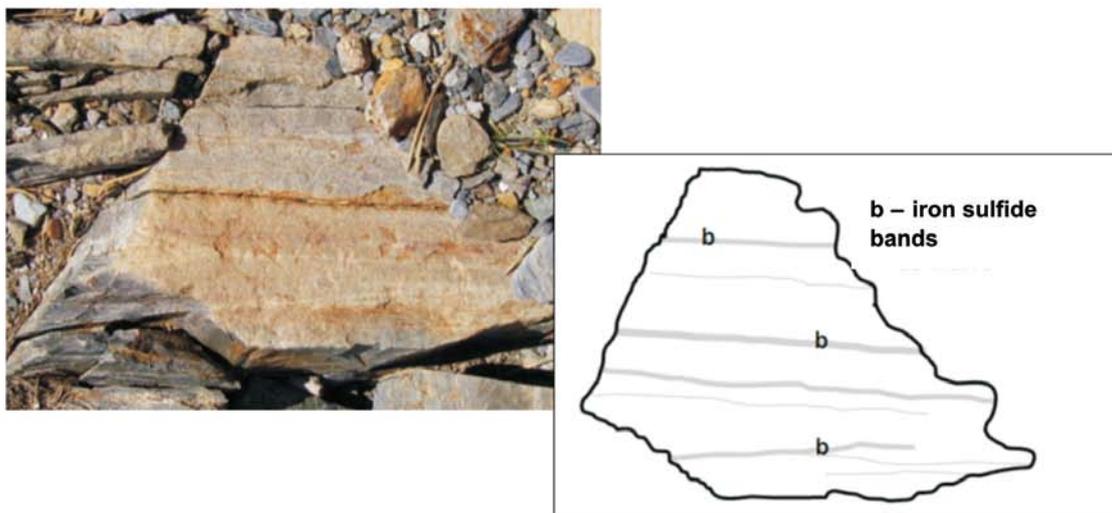
Palabras-Clave: ataque sulfático interno, expansión, presa de gravedad, pirrotina, árido.

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Figure 1 – A typical rock sample and a schematic of the sulfide bands



1. Introduction

Evaluating anomalies in the behavior of a concrete structure requires a firm understanding of the characteristics of the concrete and of its constituents. For projects that require large volumes of concrete, such as dams, special attention must be paid to the aggregate used, which may contain minerals that are potentially unstable during meteorization, and can thus react with cement components to give rise to expansive compounds. These compounds include iron sulfides, which, with the right amount of humidity and oxygen, can oxidize to give species which cause concrete expansion. In structures such as concrete gravity dams, said expansion is characterized by mapped cracks, changes in concrete surface color, breakdown of moving parts, and displacements.

The work presented proposes a methodology to study concrete dams that suffer from internal sulfate reactions, and explains that behavioral anomalies observed are a reflection of anomalies observed at the microstructural level. The work encompassed distinct phases, using three dams located in the Catalan Pyrenees (Spain) as case studies. The source of expansion was first determined by characterizing the aggregate and concrete of the Tórán dam through an arsenal of techniques: scanning electron

microscopy (SEM) with microanalysis (EDAX); X-ray diffraction (XRD); and X-ray fluorescence (XRF). The macrostructural consequences of the expansion were then evaluated by applying a mathematical model to the upstream displacement of the Graus and Tavascán dams.

2. Experimental methods

This section summarizes the results from laboratory analyses of rock and concrete from the Torán dam, which were performed to determine the precise cause of the abnormal behavior observed. Rock samples were taken from the dam area where the aggregate used for the dam concrete is located. Moreover, products from possible reaction between the aggregate and the cement matrix were searched for in samples taken from the dam.

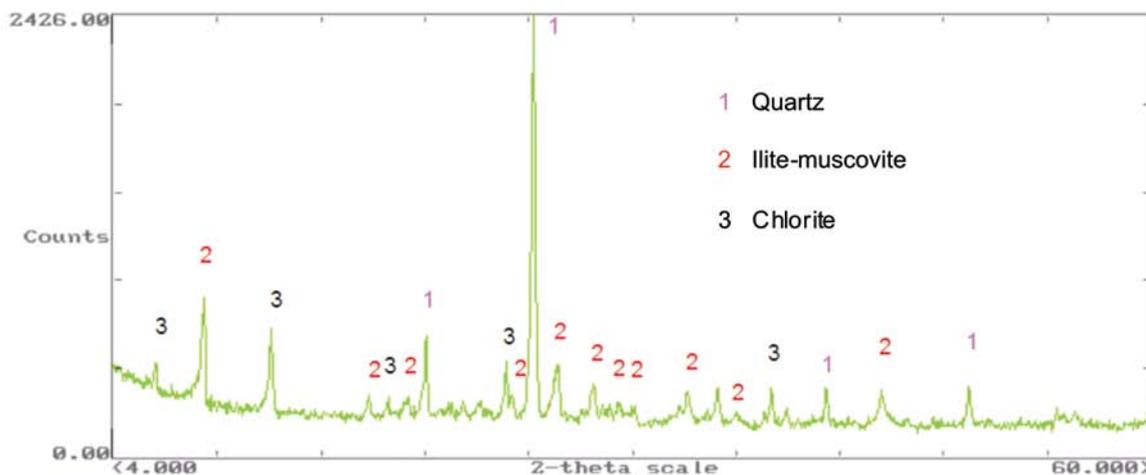
2.1 Characterization of the aggregate

This section summarizes the results of the experimental portion of the project in which the aggregate used in the Torán dam was analyzed—above all—for the presence of potentially reactive minerals. Figure 1 shows a typical rock from the quarry close to the dam, in which streaks of iron sulfides cutting through the schists are clearly observed. Figure 2

Figure 2 – Samples of analyzed rock



Figure 3 - Diffractogram of the rock



shows the samples taken from the quarry and subjected to laboratory analysis.

First, XRD was used to identify crystalline compounds in the rock. Figure 3 shows the diffractogram of the rock, which reveals that the rock is composed of quartz, mica and an apparently non-expansive type of clay.

The schists were thus expected to be primarily made up of compounds containing oxides such as SiO_2 , Al_2O_3 , Fe_2O_3 , as well as calcium, magnesium, potassium and sodium oxides from clay and mica.

To detect and quantify other compounds in the rock, the sample was chemically analyzed using XRF. The results of this analysis are shown in Table 1. In addition to finding the expected compounds, we also observed a certain percentage of sulfur compounds that were not in the mineral phases identified by XRD. XRF revealed that 2% of said compounds must stem from the iron sulfides (pyrites and/or pyrrhotites) contained in the schists.

In agreement with the aforementioned results, the ground rock used as aggregate was found to contain large quantities of sulfur compounds—the compounds responsible for the formation of expansive phases in the concrete of the Torán dam.

2.2 Characterization of the iron sulfides

Once the presence of sulfur compounds was confirmed, the respective minerals which contained them were identified by scanning electron microscopy (SEM) with microanalysis (EDAX), and X-ray diffraction (XRD). During sample preparation, the samples were observed to be attracted to a magnet. As opposed to pyrite, pyrrhotite crystals exhibit permanent internal magnetism [1]. Hence, this simple observation was a first sign that the sample contained a significant quantity of pyrrhotite.

XRD of the sample yielded the diffractogram shown in Figure 4, in which the major peaks corresponding to pyrite and to pyrrhotite are observed. The presence of quartz, chlorite and other clay minerals is a result of the mineralogy of the schists which accompany the iron sulfides in the analyzed samples.

The samples were then studied by SEM; the results of which are shown in Figure 5. The constituent elements in the sample were identified by microanalysis using SEM coupled to an X-ray spectrometer. Semi-quantitative analysis of the studied zone was likewise performed. A non-metallic sampled was used for these studies to avoid interference

Table 1 - Chemical analysis of the rock via X-ray fluorescence

| X-RAY FLUORESCENCE | | | | | |
|--------------------|-------------------------|-------------------|---------|-------------------------|-------------------|
| Element | Oxide | Concentration (%) | Element | Oxide | Concentration (%) |
| Na | Na_2O | 2.986 | S | SO_3 | 2.032 |
| Mg | MgO | 2.487 | K | K_2O | 3.175 |
| Al | Al_2O_3 | 17.378 | Ca | CaO | 3.130 |
| Si | SiO_2 | 59.403 | Fe | Fe_2O_3 | 7.881 |

Figure 4 - Diffractogram of the sample with a high concentration of sulfides

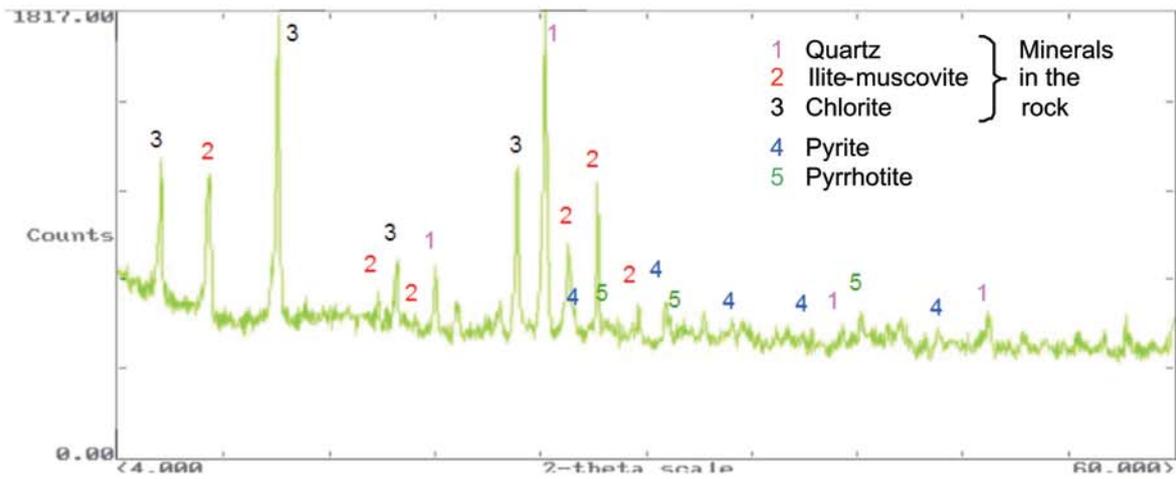


Figure 5 - Image, spectrum and microanalysis of the iron sulfides in the rock sample

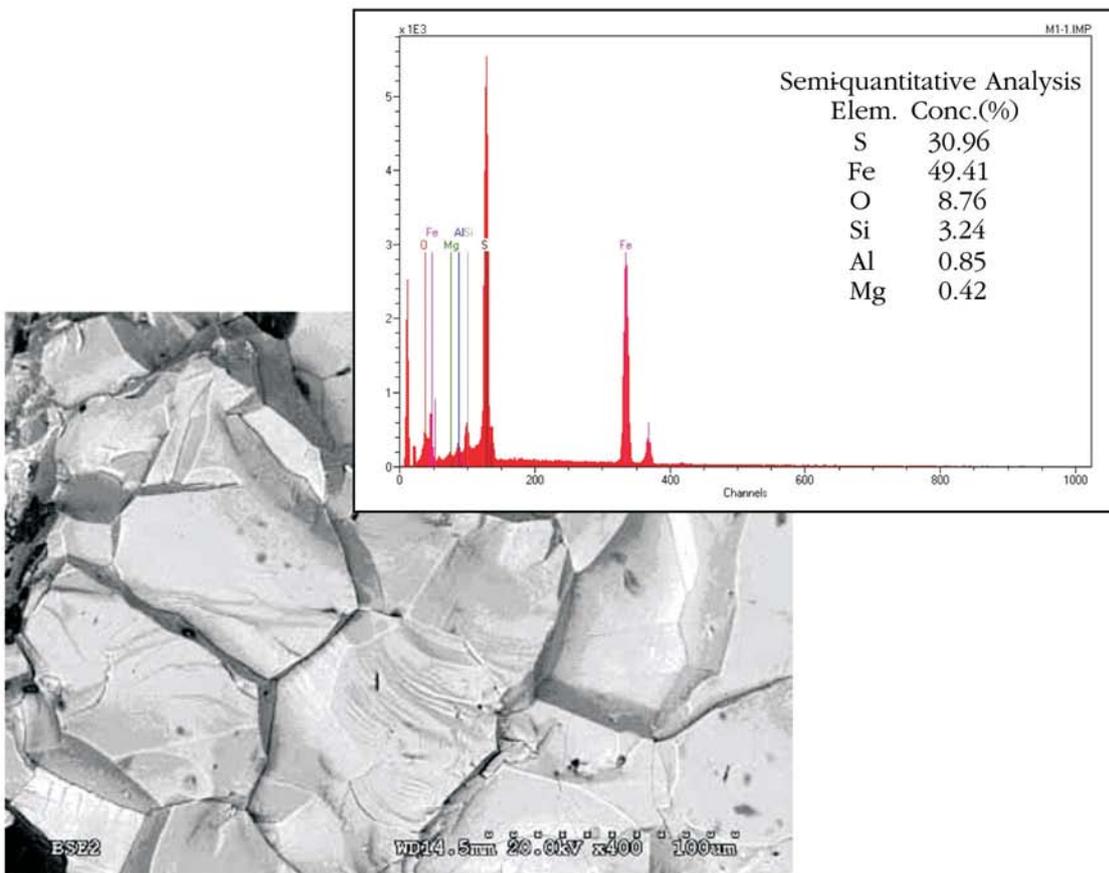
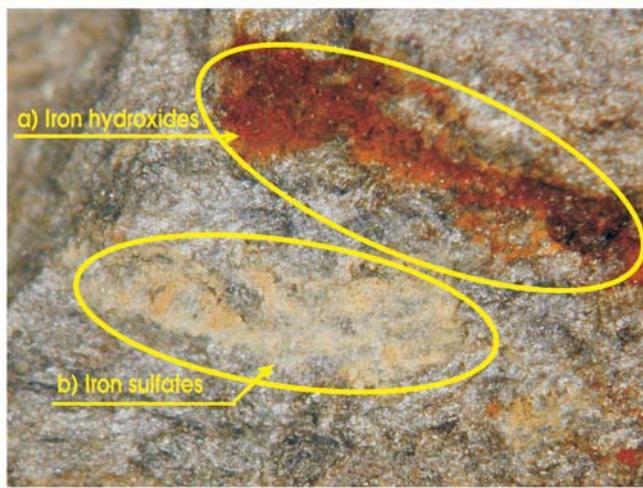


Figure 6 – Iron hydroxides (a) and iron sulfates (b) on the surface of the sample rock



of the gold peak from the metallization with the sulfur peak. The magnetism of the studied material, and its sulfur to iron ratio of 0.62, which most closely resembles that of pyrrhotite, indicate that iron sulfides are the predominant species. Nonetheless, observation by XRD of characteristic pyrite peaks meant that the presence of this mineral could not be ruled out.

2.3 Alteration of the aggregate

Once we identified the primary iron sulfide in the rock, we set about to study its oxidation, including the external factors that influence the reaction.

2.3.1 Chemical species resulting from the oxidation of sulfur compounds

Oxygen and ferric ions (Fe^{3+}) are major oxidants of pyrites and pyrrhotites [2]. At pH levels above 4, oxygen is the primary oxidant of sulfur compounds [3]. Given that the normal pH of concrete is 12.5 to 13.5, and of carbonated concrete, 9, we concluded that oxygen is the primary oxidant of the iron sulfides found in the aggregate of the Torán dam. Thus, under high levels of oxygen and ambient humidity, these sulfur compounds can undergo oxidation to generate hydroxide ion, iron sulfate, and sulfuric acid. The acid causes the system pH to become less alkaline (H^+) [4]. In addition to oxygen and humidity, which are required for oxidation of iron sulfides, factors such as temperature can accelerate the process. Steger [5] concluded that an increase in temperature leads to a major increase in the extent of oxidation of pyrrhotite. Apart from causing oxidation, Fe^{3+} can, under certain conditions and provided that it is not the primary oxidant, catalyze the process. [2].

2.3.2 Characterization of the products generated by alteration of the aggregate

To determine if the compounds formed in the alteration of the rock are present in the aggregate used in the Torán dam, we studied the rock samples taken from the quarry by XRD and by EDAX-coupled SEM (Figure 2). Analysis of the fragments enabled us to identify surface spots indicating the presence of altered sulfur compounds. Figure 6 provides close detail of a grayish-brown product characteristic of iron hydroxides (a), and another, lighter green stain typical of iron sulfates (b).

The diffractogram shown in Figure 7, and the spectrum shown in Figure 8, revealed the presence of iron hydroxide in the form of goethite, $FeO(OH)$.

The XRD results shown in Figure 9, and the presence of potassi-

Figure 7 – Diffractogram of iron hydroxide

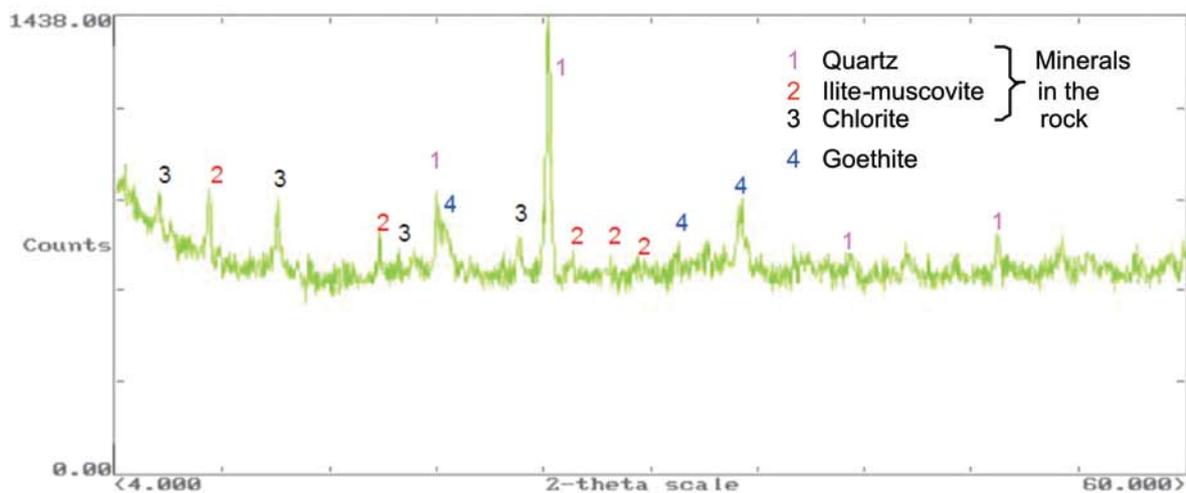


Figure 8 - Image and spectrum of iron hydroxide

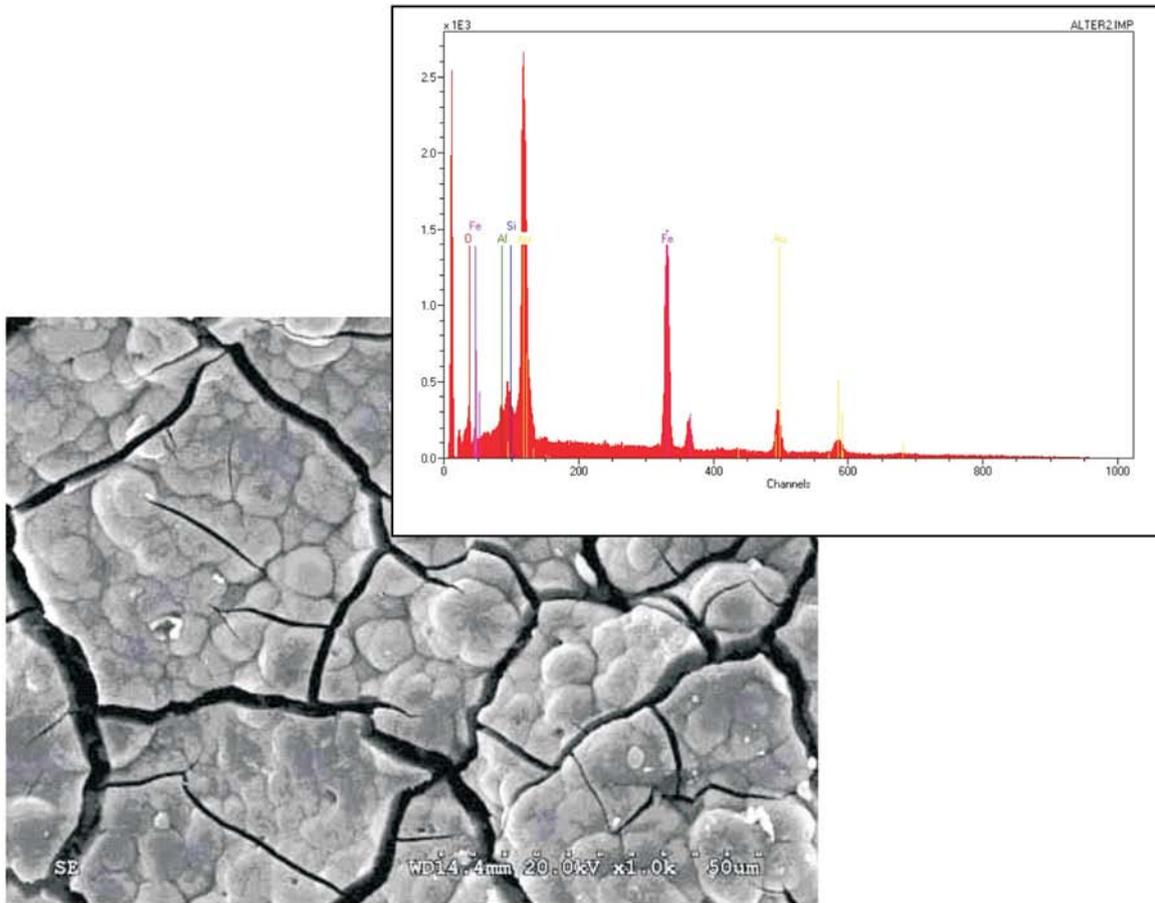


Figure 9 - Diffractogram of iron sulfates

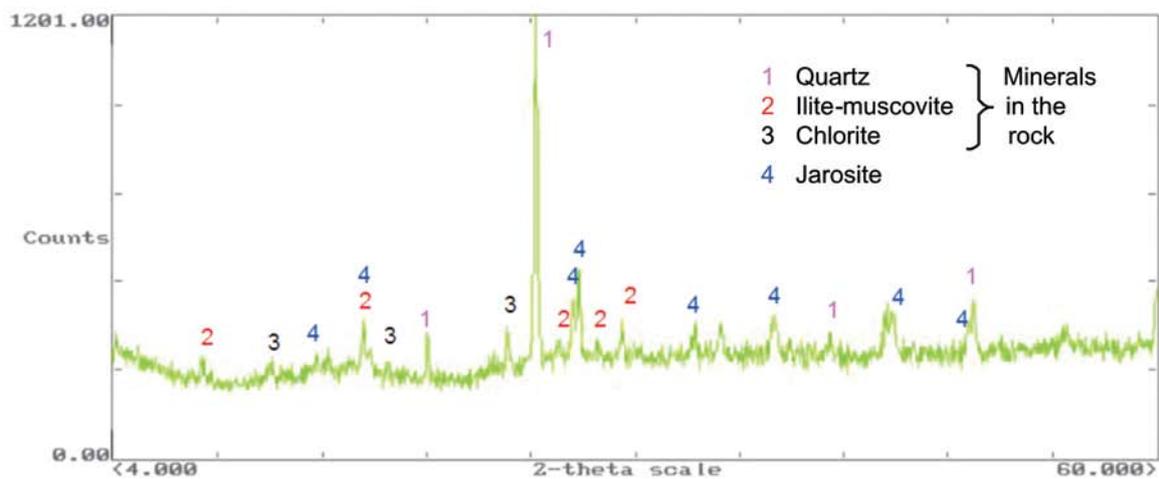


Figure 10 - Image and spectrum of iron sulfates

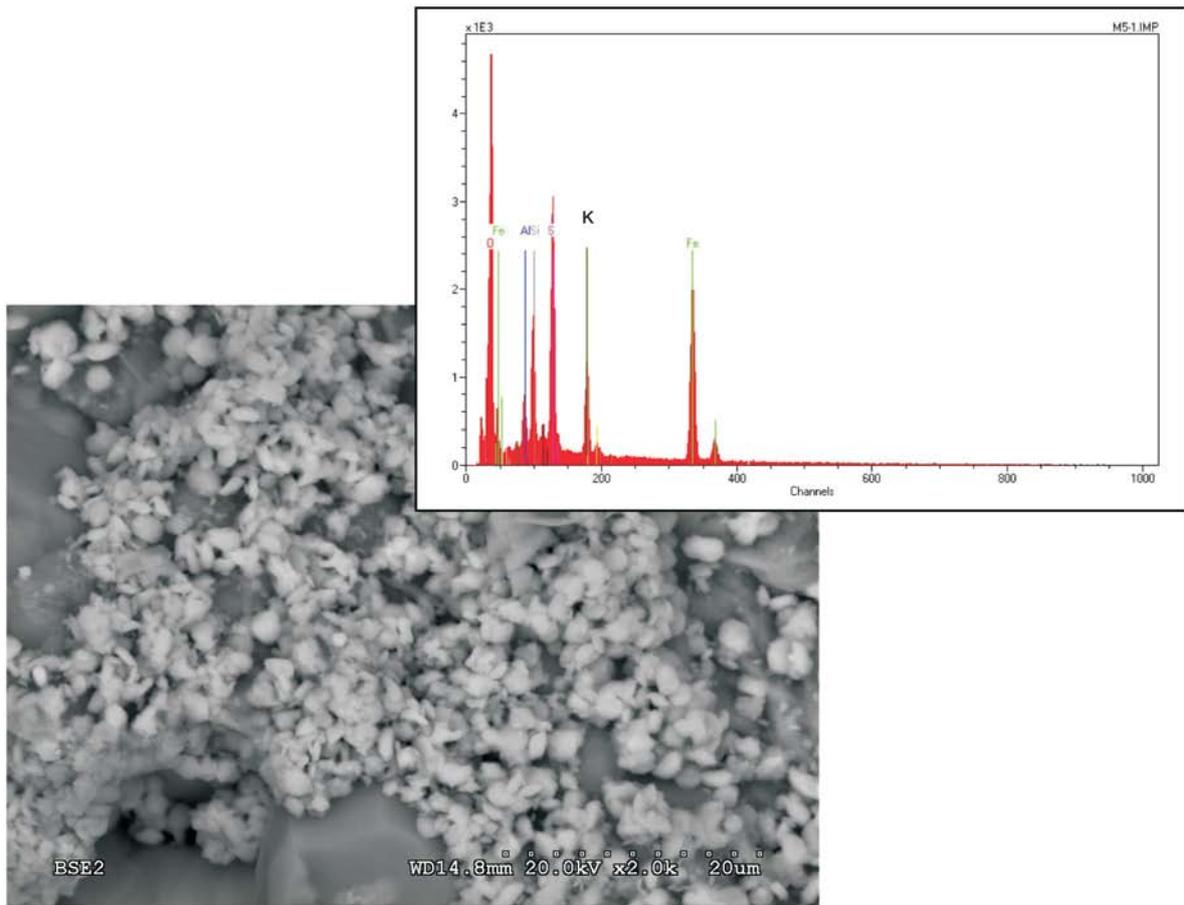


Figure 11 - Details of crystalline mineral on the rock surface

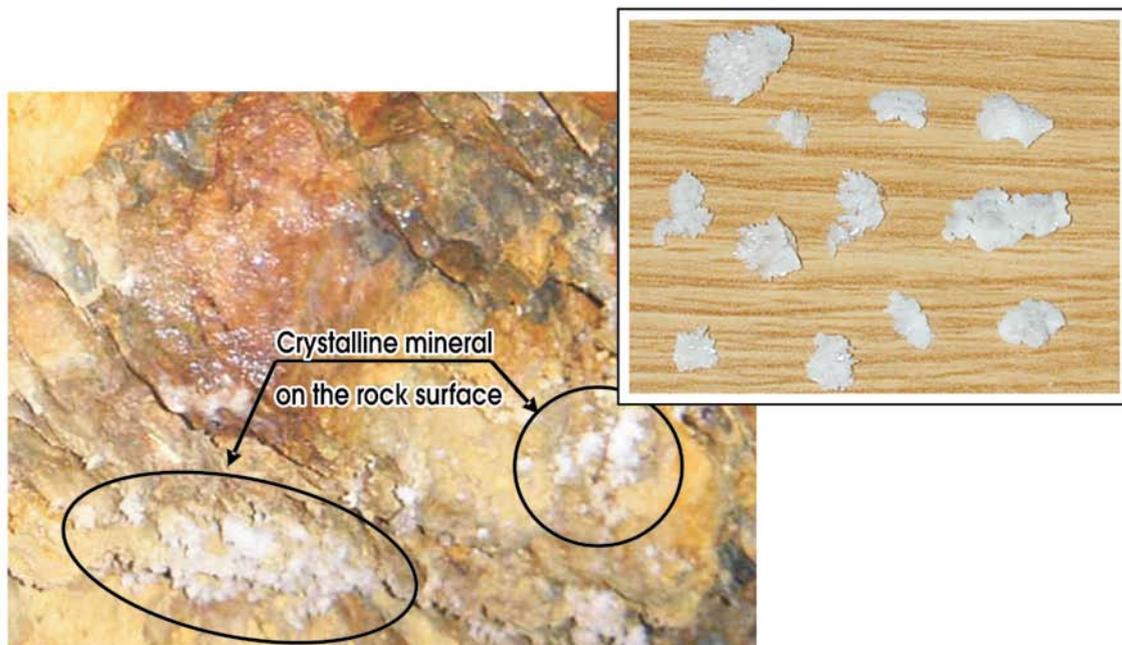
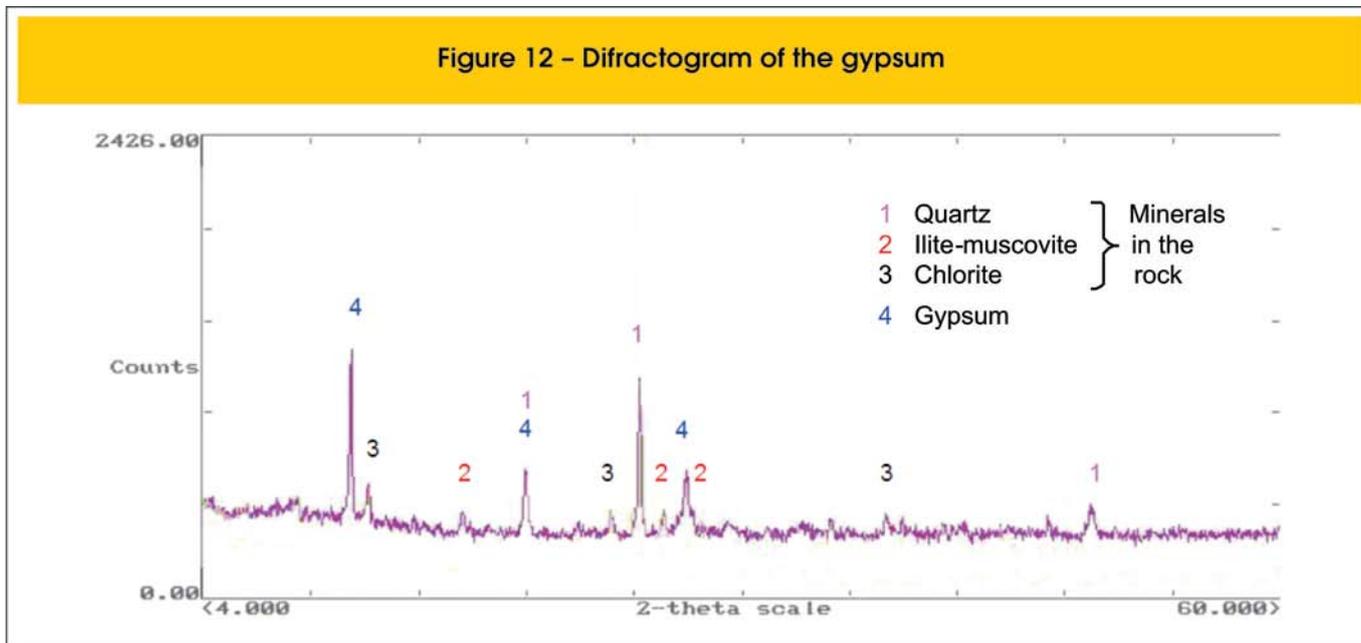


Figure 12 - Diffractogram of the gypsum

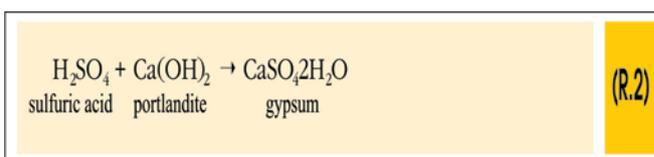
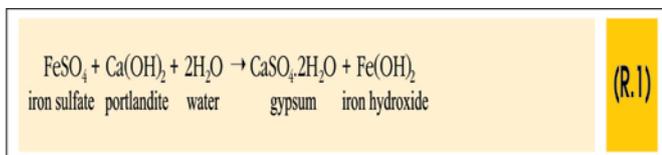


um as illustrated in Figure 10, indicated that the predominant iron sulfate in the sample is jarosite, $KFe_3(SO_4)_2(OH)_6$. Likewise, we studied the efflorescence found in the rock from the Torán dam quarry (Figure 11), the appearance of which can be observed in detail in the Figure. The XRD diffractogram (Figure 12), the needle-shaped crystals, and the presence of calcium identified by microanalysis (Figure 13) all indicated that the rock had undergone sulfate attack to produce gypsum ($CaSO_4 \cdot 2H_2O$). The filaments that appear in the Figure are due to spider webs deposited together with the alteration products.

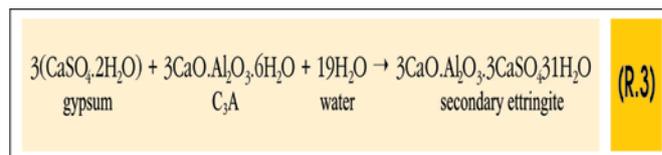
The results obtained from the characterization of the alteration products in the Torán dam area rock are in agreement with those of McGregor and Blowes [6], and Valente and Leal Gomes [7]. These researchers studied the physical, chemical and mineralogical properties of rocks containing pyrrhotite, and determined that alteration of these rocks by sulfate attack produces gypsum, goethite and jarosite.

2.4 Sulfate attack of concrete

In the presence of oxygen and humidity, the pyrrhotite that exists in aggregates can be oxidized in a primary reaction to form the alteration compounds described in the previous section. If this oxidation occurs in aggregate used in concrete, said compounds can undergo a secondary reaction with the products of the cement paste hydration, to produce sulfate attack. This in turn generates expansive compounds according to the following reactions [8]:



Reactions (R.1) and (R.2) can be considered intermediate reactions in concrete expansion, given that the gypsum formed in the presence of water will go on to react with tricalcium aluminate (C_3A) to generate expansive secondary ettringite, as shown below in (R.3) [9]:



Once we identified the oxidation products in the rock used for the Torán dam aggregate, we set about to determine if these products indeed react with cement paste compounds to form secondary ettringite. This was accomplished by studying samples of concrete taken from the dam by optical microscopy and EDAX-coupled SEM.

Optical microscopy revealed important details about the dam samples. Figure 14.a shows the internal area of a rock sample, in which non-oxidized pyrrhotite is observed. However, Figure 14.b shows that, in a more external area of the same sample close to the face, oxidation has begun at the aggregate edges, as revealed by the change in local coloration.

Optical microscopy also enabled discovery of needle shaped crystals in the pores (Figure 15.a) and paste-aggregate interfaces (Figure 15.b). Cracks in the paste were also identified, as shown in the highlighted area of Figure 15.b.

Figure 13 - Image and spectrum of the gypsum

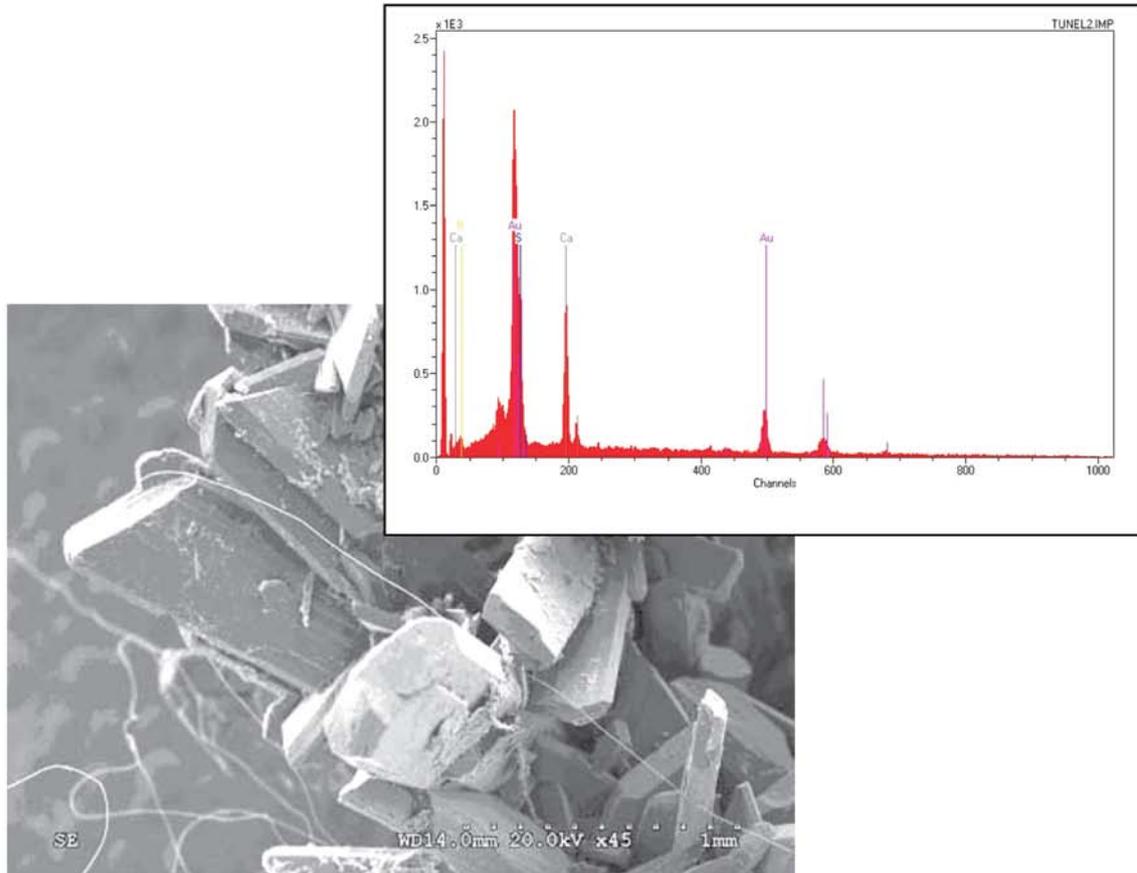


Figure 14 - Iron sulfate (a) and oxidized edge of aggregate (b)

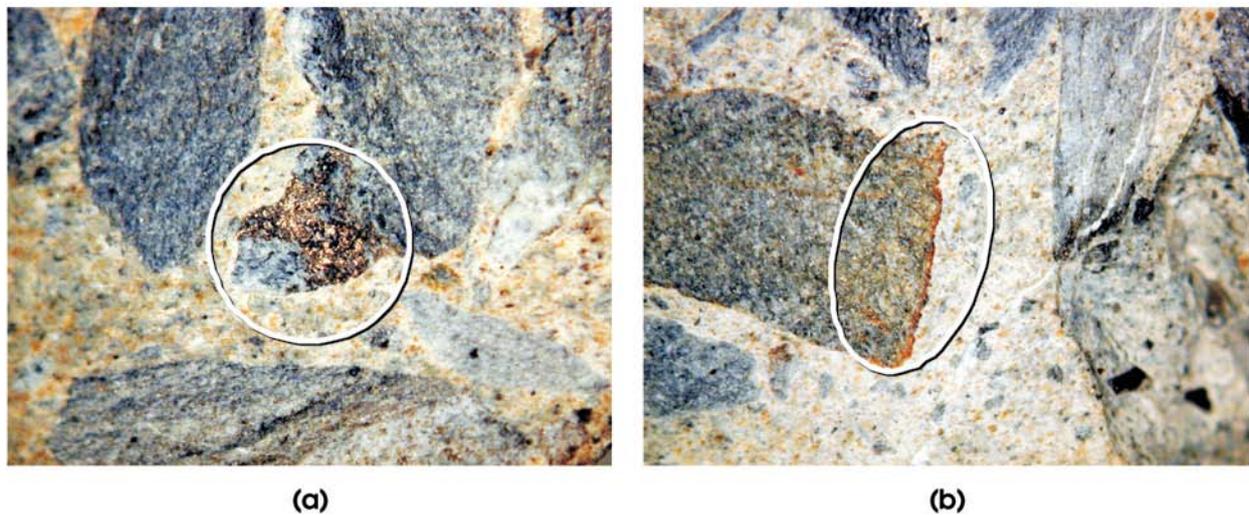
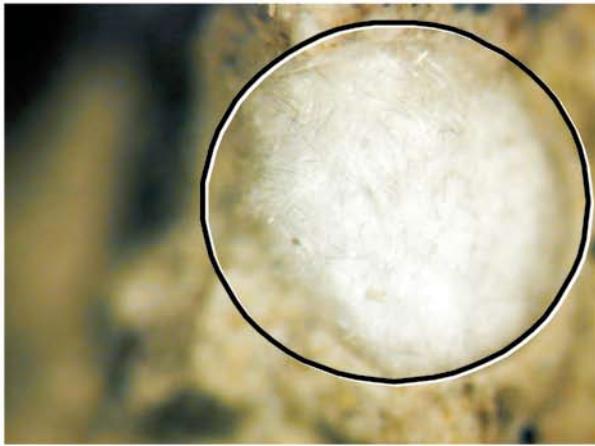
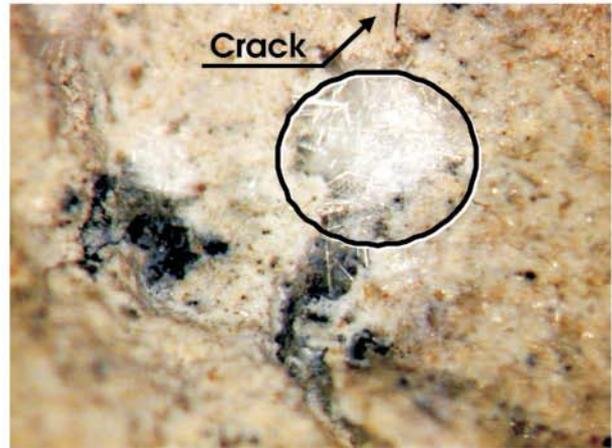


Figure 15 - Needle-shaped crystals in the pores (a) and in the paste-aggregate interface (b)



(a)



(b)

Figure 16 - Image and spectrum of the ettringite

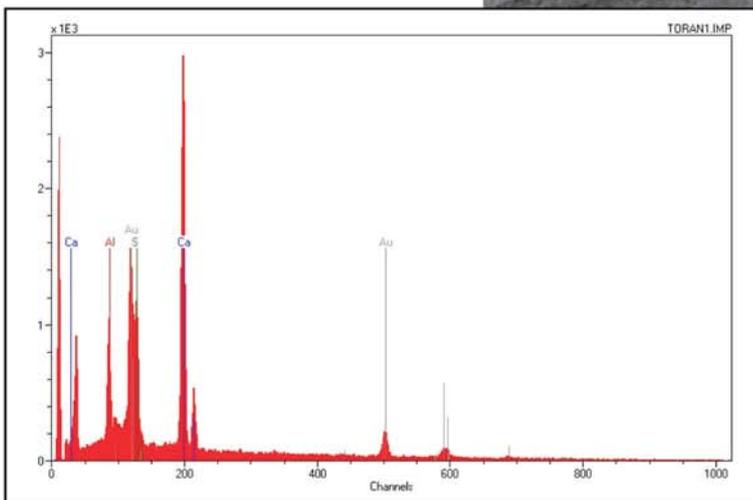
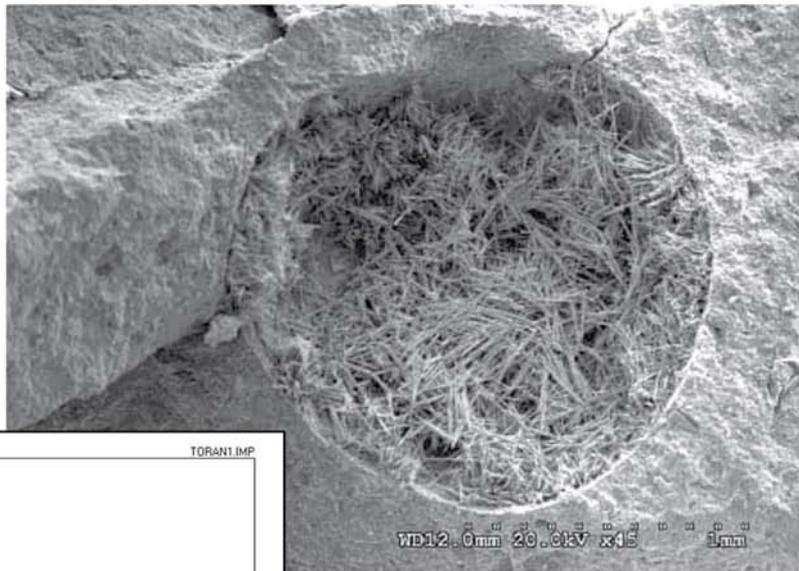
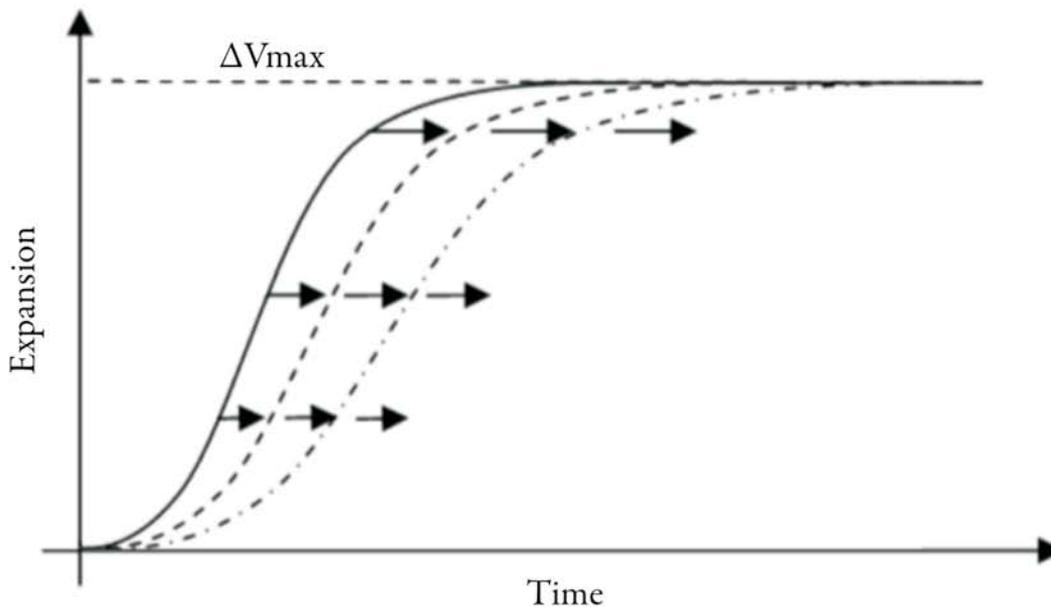


Figure 17 - Change in concrete expansion due to sulfate attack (10)



The results of the SEM-EDAX studies on the needle-shaped crystals (shown in Figure 15) confirmed the presence of ettringite, $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 31\text{H}_2\text{O}$ (Figure 16).

The formation of secondary ettringite is characteristic of sulfate attack. In the case of the Torán dam, this attack stems from oxidation of iron sulfides in the aggregate of the concrete. The oxidation leads to hydroxides and sulfates of iron, as well as sulfuric acid, in a primary reaction. Once inside the concrete mass, these products enter a secondary reaction with cement paste compounds to form expansive secondary ettringite.

3. Expansion associated with oxidation of iron sulfides and sulfate attack

The products from the oxidation of iron sulfides, as well as those generated in the subsequent attack on the cement paste, have greater volumes than their respective original compounds. This leads to an increase in the internal tensions of the concrete, which produces cracks. According to Casanova et al. [10], the increase in volume resulting from primary oxidation of iron sulfides is $6.04 \text{ cm}^3/\text{mol}$, whereas the increase due to sulfate attack can reach values of $172.19 \text{ cm}^3/\text{mol}$. The authors developed a numerical model that allows calculation of the maximum expansion caused by primary and secondary reactions, as well as of the velocity of the expansion. The model is outlined in Figure 17. The plots represent the increase as a function of grain size, given that the kinetics of the reactions are inversely proportional to aggregate diameter.

Certain aspects of Figure 17 should be underscored:

- The curve has an exponential shape and covers three distinct phases. In the first, the expansions begin slowly at roughly constant rates. In the second, the expansions accelerate due

to an increase in volume. Finally, in the third phase, the increases in volume begin to fall off and, at a certain point onwards, the expansions stop.

- The expansion becomes stabilized. This is quite logical given that, once all potentially reactive minerals are consumed, the oxidation reactions—and consequently, the expansions—cease. In certain cases it is of special interest to characterize the unit deformations that occur in the different directions analyzed based on the increase in volume of the material. Said deformations can be isotropic or anisotropic. As such, the spatial distribution of the potentially expansive minerals in the structure of interest must be studied using geometric models. A concrete structure with expansion problems may suffer from behavioral effects depending on factors such as design, and the availability of oxidizing agents and potentially reactive minerals.

4. Consequences of sulfate attack in dams

This section provides a qualitative explanation of abnormal behavior observed in concrete gravity dams that results from expansion of compounds formed by the oxidation of pyrrhotite, and by subsequent sulfate attack. Macrostructural behavior is thus a reflection of the microstructure of the concrete.

The model shown in Figure 18 demonstrates the need to integrate distinct levels of study to obtain satisfactory conclusions on macrostructural behavior [11]. Said model consists of solving the problem of concrete expansion due to sulfate attack at three levels (micro-, meso- and macro-structural), such that the results from one level can be used as data for the following level.

Initially, at the microscopic stage, the kinetics of reactions which can lead to unit deformations are simulated numerically, thereby providing a starting parameter for the second stage. Next, in the

mesostructural stage, a numerical model is used to predict the deformations and tensions that correspond to distinct confinement conditions. These deformations, which stem from expansion at the mesostructural level, are then used as starting data in the final stage, the macrostructural analysis stage.

5. Movements observed in dams suffering from internal sulfate attack

As previously explained, the abnormal behavior seen in concrete dams is a consequence of phenomena occurring at the material

level. Before analyzing the real behavior of a given structure, it is utile to determine the expected movements of a gravity dam suffering from expansive reactions caused by aggregate oxidation. For concrete gravity dams, geometry is the principal factor that determines the extent of the oxidation reactions, as it dictates the availability of oxidizing agents. Hence, in the upstream face of the dam, which is submerged for long periods of time, the availability of oxygen is much lower than in the downstream face. However, ambient humidity and rainwater are sufficient sources of moisture to start and drive oxidation at the downstream face. Likewise, depending on the orientation of the dam, the large sur-

Figure 18 – Model for analyzing dam behavior at different structural levels (10)

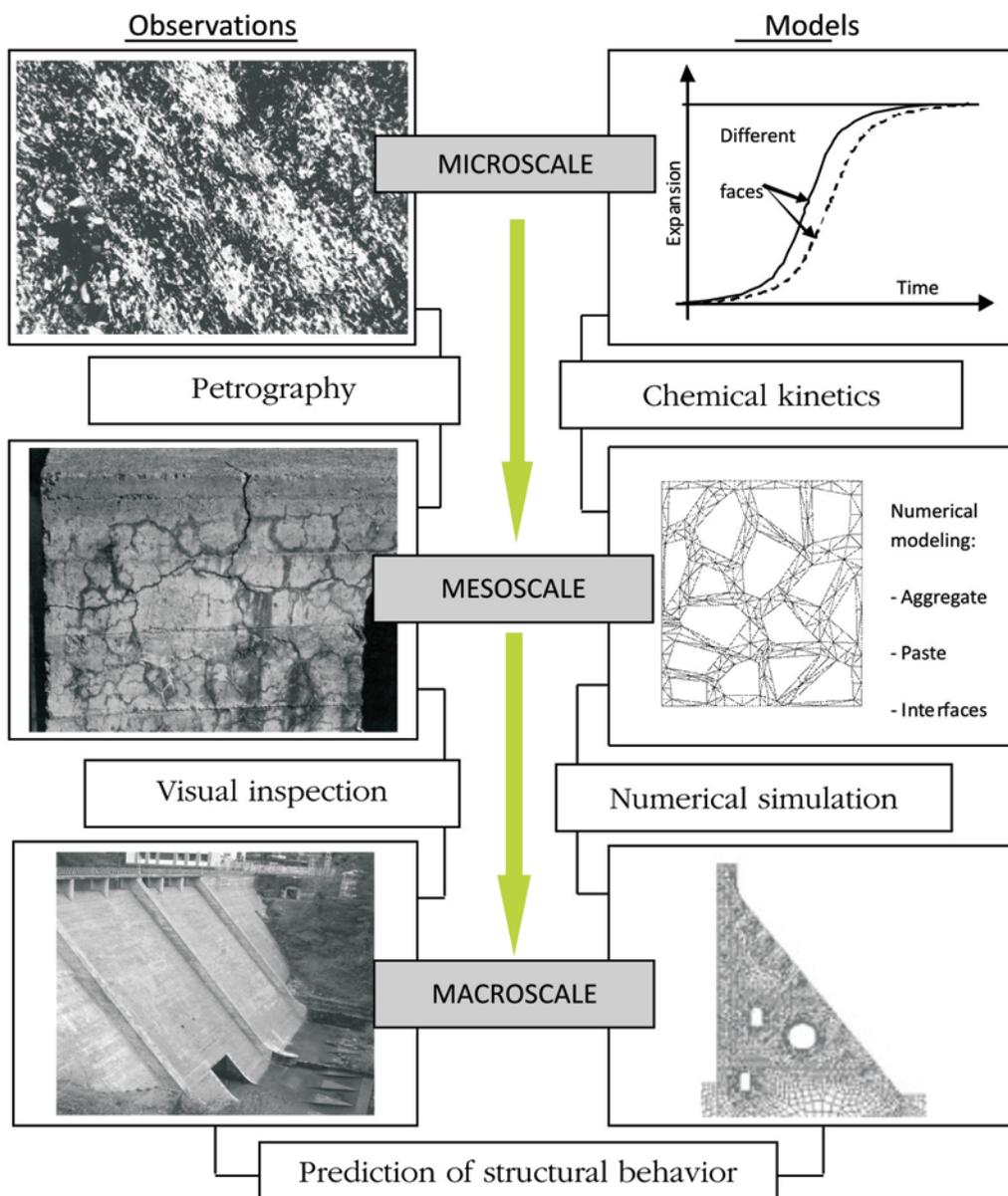
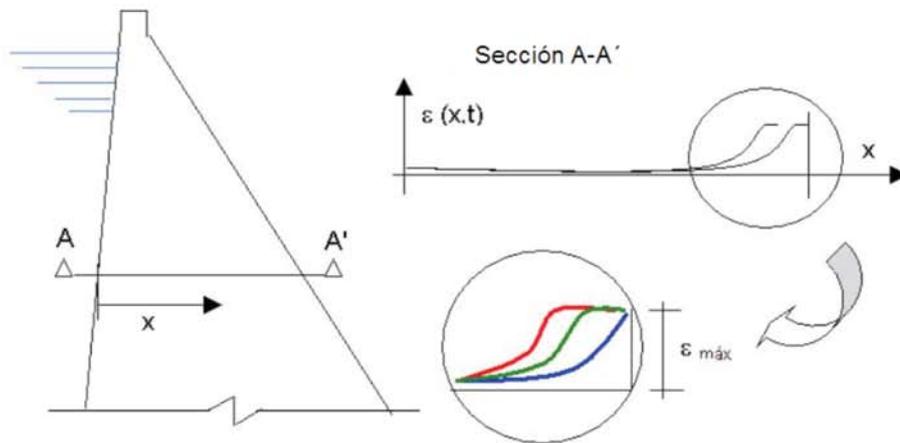


Figure 19 - Non-linear distribution of the deformations (12)



face area of the downstream face can leave it more exposed to higher temperatures. As such, the downstream face is exposed to conditions which favor faster, more intense oxidation reactions than those in the upstream face. It can therefore be concluded that expansions in the former will also be more dramatic than in the latter. Consequently, dams are expected to move in the upstream direction. Indeed, disalignment towards the upstream side is a direct consequence of expansions observed at the material level.

Figure 19 shows a schematic of the non-linear distribution of the expansions of a representative section of the dam [12]. It must be pointed out that inwards expansion from the downstream face tends to stabilize with time. This is because the availability of oxidizing agents decreases from the most exposed areas of the dam towards the interior.

A mathematical model can be used to study the remaining disalignments observed in concrete dams suffering from sulfate attack. To adjust an equation that adequately represents the abnormal behavior of these structures, Aguado et al. [13] proposed the following exponential function:

$$y = A + B \left(1 - e^{-\frac{t}{c}} \right) \tag{E.1}$$

whereby A is the value of ordinate at the origin (i.e. the initial value of the movements); B is the value of the ordinate of the maximum predicted movements; C is the value of the abscissa of the inflection point, at which the expansion effects begin to stabilize; t is the time in months; and p is the parameter that influences the shape of the curve.

We set about to apply this equation to our case studies. However, given that we lacked sufficient movement measurements to evaluate the equation for the Torán dam, we validated it using data from the Graus and Tavascán dams, each of which has extensive

measurement records of over 400 months. These structures suffer from internal concrete expansion problems due to alteration of iron sulfides in the aggregate used for the concrete mix. Similarly to the Torán dam, both dams exhibit symptoms of mapped cracks, changes in surface coloring, and upstream displacements.

Using the least-squares methods, we adjusted the function (E.1) to obtain the parameters required for distinct stabilization times of the process. Upon analyzing the results, we concluded that, of the various adjusted curves, that which best represents the movements is the curve with the inflection point near 350 months. Figures 20 and 21 show actual movement measurements (solid lines), and adjusted curves at 350 months (dashed lines), for the Graus and Tavascán dams, respectively.

As seen in the figures, the curves provide a highly satisfactory representation of the horizontal movements observed in each of the analyzed dams. In addition to the stabilization times of the remaining movements, the mathematical model also enables prediction of

Figure 20 - Disalignment movements and adjusted curves for the Graus dam

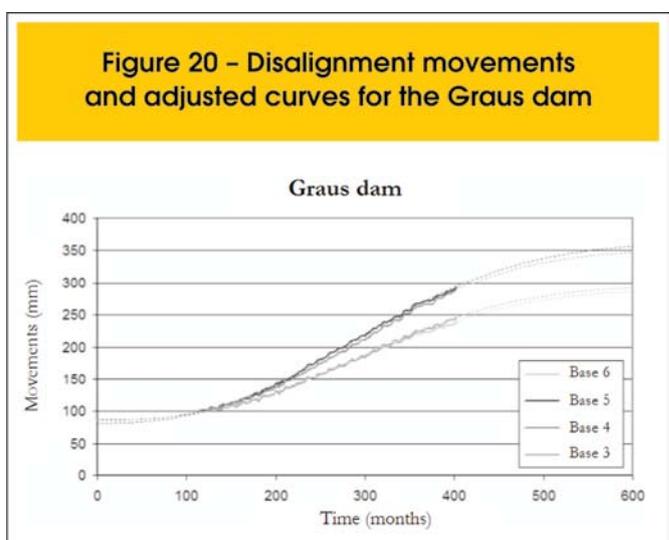
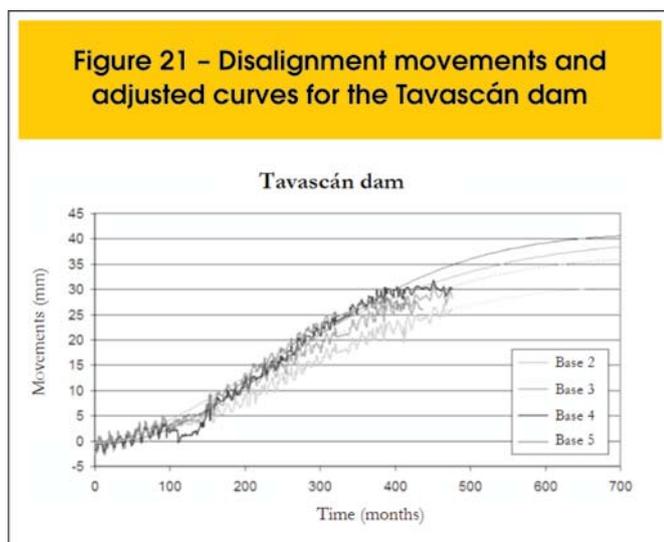


Figure 21 – Disalignment movements and adjusted curves for the Tavascán dam



the order of magnitude of the maximum expected movements.

The advantage of this type of function is that it represents movements observed in the structures as an exponential component of the equations that dictate concrete expansion (as explained in Section 3).

6. Final considerations

This study led us to the following major conclusions:

- The alteration products resulting from oxidation of iron sulfides in aggregate pyrrhotite, and from subsequent sulfate attack of the concrete paste, are the principal agents responsible for the expansions observed in the Torán dam.
- The primary symptoms of expansion are mapped cracks and non-recoverable movements.
- The more dramatic expansion observed in the downstream face of the dams is responsible for upstream displacement of the crest.
- The mathematical model described herein has allowed adequate representation of the displacements observed in the Graus and Tavascán dams, also enabling prediction of the stabilization times for this behavior, and of the maximum movements.

7. Acknowledgements

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8. References

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