Study of Aggregates with Sulphides in Cement Composites

Estudo de Agregados contendo Sulfetos em Compósitos de Cimento

M.J. GOMIDES [a]
gomides@furnas.com.br

M.A. CINCOTTO [b]
maria.cincotto@poli.usp.br

N.P. HASPARYK [c]
nicole@furnas.com.br

H. CARASEK [d]
hcarasek@eec.ufg.br

Abstract

Aggregates from rocks containing sulphide mineral may cause the occurrence of deleterious expansive products generated by the oxidation-hydration process of these minerals. This study was performed in cement paste and mortar produced with three types of cement containing limestone filler and blast-furnace slag (content ranging from 40% to 60%) and aggregates containing sulphide mineral. The sulphide oxidation-hydration process and the chemical interactions with hydrated compounds of cement paste and mortar were evaluated for 18 months, using two different methodologies, X-ray diffraction and thermogravimetric analyses, which were considered for both. Thus, after 180 days, a progressive increase of compounds, such as ettringite and gypsum was observed, along with a decrease in the portlandite content, as well as different growth trends, according to the cement type.

Keywords: deterioration, ettringite, gypsum, expansion, mortar, oxidation, sulphide

Resumo

Agregados provenientes de rochas contendo sulfetos podem propiciar a formação de produtos expansivos e deletérios resultantes do processo de oxidação-hidratação destes minerais. O estudo apresentado neste trabalho foi desenvolvido utilizando-se pastas de cimento e argamassas produzidas com três tipos de cimentos compostos por fíler calcário e adição de escória granulada de alto-forno (nas proporções de 0%, 40% e 60%) na presença de agregados contendo sulfetos. O processo de oxidação-hidratação do sulfeto e as alterações químicas com os compostos hidratados das pastas de cimento e das argamassas foram avaliados durante 18 meses, através de duas diferentes metodologias, difração de raios X e análises termogravimétricas. Os resultados indicam um progressivo aumento dos compostos, tais como etringita e gipsita, com uma conseqüente redução do teor de portlandita,, após 180 dias de avaliação em laboratório, sendo este comportamento dependente do tipo de cimento utilizado.

Palavras-chave: deterioração, etringita, gesso, expansão, argamassa, oxidação, sulfeto

[a] *Federal University of Rio Grande do Sul, Porto Alegre, Brazil;*
[b] *São Paulo University, São Paulo, Brazil;*
[c] *FURNAS Centrais Elétricas S.A., Goiânia, Brazil;*
[d] *Federal University of Goiás, Goiânia, Brazil*

1   introduction

The type of sulphides found in rocks, in the form of pyrite, pyrrotite and calcopyrite, is not insignificant. Therefore, it is difficult to avoid using aggregates containing sulphide for concrete production, especially because there are regions where another source is not easy to find either because the material is not economically feasible or because it is simply inexistent. This causes a lot of problems for building structures, such as dams, where a great deal of aggregates is needed [1,2].

Concrete deterioration caused by the presence of aggregates can occur as a result of expansion, triggered by the formation of products generated by the changing process suffered by sulphide [3].

This expansion phenomenon can take place through two different mechanisms. The first one may be the result of an oxidation-hydration process that the sulphide goes through that can result in iron hydroxide and other compounds having expansive characteristics.

The second mechanism is related to the internal attack concrete suffers from sulphate. According to research done by several authors [4,5,6], aggregates containing sulphide can become an internal source of sulphate ions. These ions can favor the development of harmful chemical reactions with the cement paste compounds, which can result in typical expansive products of the sulphide attack: ettringite and gypsum [7,8].

1.1 Characteristics and chemical reactions related to the changes sulphide undergoes in natural aggregates

According to several authors [2,9,10,11,12,13], the oxidation process of sulphide is complex and not entirely understood, but it is known that for this process to take place, moisture and oxygen must be present in the system.

Several chemical reactions have been suggested to express the oxidation of pyrite [1,4,14,15,16,17]. The oxidative reactions of this type of sulphide, as well as the pertinent information on each one are presented in Equations (1) to (5), below [15,16].
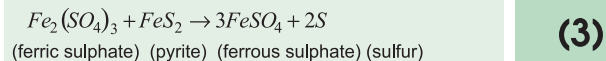
In the presence of water and oxygen, pyrite oxidizes forming ferrous sulphate and sulphuric acid. Equation (1) is defined as being purely chemical in nature.

$$FeS_2 + H_2O + 7/2O_2 \rightarrow FeSO_4 + H_2SO_4 \qquad (1)$$
(pyrite)   (ferrous sulphate)   (sulphuric acid)
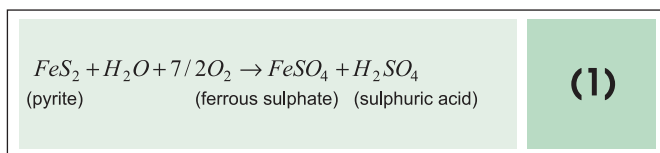
Ferrous sulphate can react with sulfuric acid, in the presence of oxygen resulting in ferric sulphate, as seen in Equation (2). This reaction can be accelerated by the catalytic action of bacteria of the Ferrobacillus-Thiobacillus class, when present.

$$2FeSO_4 + 1/2O_2 + H_2SO_4 \rightarrow Fe_2(SO_4)_3 + H_2O \qquad (2)$$
(ferrous sulphate) (sulphuric acid) (ferric sulphate)
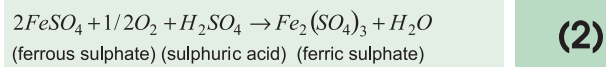
Ferric sulphate (a strong oxidative agent) can react again with pyrite to form more ferrous sulphate and release sulfur, according to Equation (3).

$$Fe_2(SO_4)_3 + FeS_2 \rightarrow 3FeSO_4 + 2S \qquad (3)$$
(ferric sulphate) (pyrite) (ferrous sulphate) (sulfur)

The sulfur that is released can be rapidly converted into sulfuric acid, in the presence of water, oxygen and these bacteria, which act as catalysts, triggering Equation (4).

$$S + 3/2O_2 + H_2O \rightarrow H_2SO_4 \qquad (4)$$
(sulfur)   (sulphuric acid)
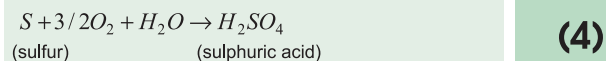
The oxidation of pyrite can also result in iron hydroxide in the presence of high concentrations of water and oxygen, as shown in Equation (5).

$$FeS_2 + 7/2H_2O + 15/4O_2 \rightarrow Fe(OH)_3 + 2H_2SO_4 \qquad (5)$$
(pyrite)   (iron hydroxide) (sulphuric acid)
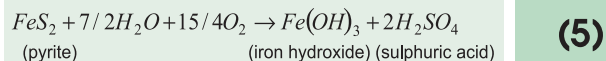
The speed with which sulphide oxidizes in natural aggregates can be associated both to the specific surface and to the iron ion content in the chemical composition of this mineral.

It is known that the larger the specific surface of sulphides is, the faster the oxidation process for this mineral takes place. The same effect is observed with regards to its iron content [1,18,19,20].

Another significant factor influencing the speed with which sulphide oxidation takes place is the environment/system pH. With a pH higher than 10, sulphides become unstable. Some researchers [19] report on experimental evidence showing that in a highly alkaline environment (12.5 < pH < 13.7) the oxidation time for sulphide is accelerated. However, if pH values range from 7.5 to 8.5, oxidation does not really depend on alkalinity and is controlled by the degree of oxygenation and by grain dimension.

2   Experimental program

2.1 Cementitious materials

- Portland cement with carbonate filler (6%-10%), CP II F-32, denominated CPII;
- Portland cement CP II F-32 containing 40% of ground blast-furnace slag (CP II F-32+40GBFS, similar to American cement ASTM Type IS - denominated CP40);

Table 1 – Chemical characteristics of cementitious cementitious materials (%)												
Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	Na_2Oeq Total	Loss of ignition	SO_3	Free Lime	Insoluble residue
CP II F-32	19.44	5.48	3.73	62.88	1.39	0.24	0.41	0.51	3.13	2.52	2.23	0.93
CP II F-32 + 40GBFS	25.91	7.79	2.66	54.48	3.93	0.19	0.45	0.49	2.45	1.93	1.30	0.73
CP II F-32 + 60GBFS	29.11	9.05	2.40	50.54	4.82	0.23	0.55	0.59	1.14	1.38	0.90	0.52
GBFS	35.04	12.43	0.16	41.58	8.68	0.31	0.55	0.67	0.31	0.12	-	-

Note: $Na_2Oeq = 0.658.K_2O + Na_2O$

- Portland cement CP II F-32 containing 60% of ground blast-furnace slag (CP II F-32+60GBFS, similar to American cement ASTM Type IS - denominated CP60).

It is important to point out that the incorporation of ground blast furnace slag (GBFS) was done to CPII in laboratory, in this manner both cements CP40 and CP60 were experimental ones. On the other hand, CPII is commercially available in Brazil.
The chemical and physical characteristics of cementitious materials used in the experimental study are presented in Tables 1 and 2.

2.2 Aggregates

- Muscovite-quartz-schist aggregate containing sulphides and a maximum of 19 mm grain size (Fineness modulus = 6.41);
- Artificial sand from muscovite-quartz-schist aggregate containing sulphides (Fineness modulus =2.59);
- Natural quartz sand (Fineness modulus = 2.99).

According to analyses performed with the aid of transmitted light microscopy, the aggregate was classified as muscovite-quartz-schist containing basically 60%-65% quartz, 30% muscovite mica, less than 10% opaque minerals and carbonated materials, and less than 5% garnet, biotite and chlorite. While investigating opaque minerals with transmitted light microscopy, the following sulphides were identified: pyrrotite ($Fe_{1-x}S$) the main sulphide present, pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and marcasite (FeS_2). However, there were only few oxides present, namely, hematite and magnetite. Quantitative analyses indicated 3.89% total sulphides in aggregates with a standard deviation of 0.3%, after three verifications.

2.3 Cement pastes containing sulphide aggregates

Test specimens of paste bars (25 x 25 x 285) mm in size were prepared with the three cements, water/cement ratio of 0.37, and three grains of aggregate with high pyrrotite content (about 10%), and about 10 mm. Those

Table 2 – Physical characteristics of cementitious cementitious materials (%)								
Materials	Density (g/cm^3)	Blaine Fineness (cm^2/g)	Average dimension size (µm)	Setting time (hour:min) Initial	Final	Compressive Strength (MPa) 3 days	7 days	28 days
CP II F-32	3.09	3540	16.47	02:10	03:20	23.6	27.9	34.4
CP II F-32 + 40GBFS	2.99	3160	13.70	02:50	04:20	15.4	23.5	40.0
CP II F-32 + 60GBFS	2.96	3100	13.67	03:10	04:40	9.6	19.4	36.4
GBFS	2.90	3330	12.05	-	-	-	-	-

Figure 1 – Two cement paste bars containing sulphides aggregates

grains were inserted in the paste according to Figure 1. The specimens were cured in a moist room for 2 days and then submitted to wetting and drying cycles, remaining immersed in water for 3 days, at (23±2)ºC, followed by 4 days of drying in a stove at (50±2)ºC.

After 70 days of cycling, the samples were analyzed by scanning electron microscopy, using a LEICA, S440i, to evaluate qualitative modifications caused by changes in the sulphide grains inserted in the paste.

2.4 Concrete

Prismatic specimens measuring 7.5 x 7.5 x 28.5 cm were cast with the three cements using the following mix proportion: cement 467 kg/m³; coarse aggregate containing sulphides with maximum size 19 mm: 1,018 kg/m³; artificial sand from sulphide rock: 183 kg/m³; natural sand: 495 kg/m³; water/cement ratio: 0.45 and slump about 95 mm.

To evaluate expansion, specimens were cured for 18 months, in two different exposure conditions: a) in a moist room (MR), relative humidity equal to or above 90% and temperature of (23±2)ºC; b) wetting and drying cycles (WD) consisting of 7 days of water immersion at (23±2)ºC, and 21 days of drying at 40ºC, after curing of 28 days in moist room. The time for wetting and drying cycles was established after evaluation about the number of days in which concrete can absorb water until the weight become constant. The same process was led to assess the period of drying of concrete.

Expansion was determined by the length change of the specimens, using a specific apparatus, according to ASTM C-490/2004.

In order to perform X-ray diffraction analyses, cylindrical specimens measuring (10 x 20) cm were cast with the same mixture and kept in moist room (MR) for the expansion tests. The main purpose of these analyses was to determine some changes in the cement paste due to formation of deleterious products in concrete cast with the cements studied.

Specimens were analyzed at 28, 90 and 180 days, after selecting an internal portion of the mortar and discarding the coarse aggregates by extracting it manually and with proper tools from concrete in order to reduce mineral influence in the XRD analyses.

The samples were ground to less than 0.037 mm for the tests, which were performed by using a Siemens D5000 X-Ray Diffractometer.

The evolution of hydration and chemical change due to interaction with mortars extracted from the concrete, D-dried, was submitted to thermogravimetric (TG/DTG) analysis, using a NETSZCH equipment, model TG 209-C, 30 ml/min N_2-gas flux, at a heating rate of 10ºC/min, in a Pt crucible, up to 1,000ºC. These results were compared to data obtained from pure cement pastes, cured under the same conditions.

Additionally, a chemical analysis was performed with mortars extracted from concrete to determine sulphate content. The total sulphate content was gravimetrically determined with the use of barium chloride at 28, 90, 180 and 540 days, in two different exposure conditions.

3 Results

3.1 Microstructure of cement pastes containing sulphide aggregates

SEM analyses made it possible to identify sulphides in aggregates (Fig. 2) as well as some neoformed products, mainly in the transition zone (Fig. 3), due to aggregate change and chemical reactions with the paste. The presence of needles containing mainly calcium, sulfur and aluminium, suggestive of ettringite, is significant for all types of cement studied, as can be seen in Figures 4 to 7.

The literature contains reports from Spanish researches [5] associating the formation of ettringite to the process of iron sulphide oxidation. Their studies were carried out with aggregates with a high sulphide content (0.7% of pyrite and 4.2% of pyrrotite) used for preparing mortar.

3.2 Expansion assessment in concrete containing sulphide aggregates

An expansion phenomenon was observed for concrete, regardless of the type of cement used and of exposure conditions (moist room or cycles), as can be seen in Fig. 8, presenting complementary expansion data from [21].

Shrinkage (negatives values) was observed in the prismatic specimens submitted to these cycles till approximately the first 214 days of the experiment, due to hydraulic shrinkage resulting from the drying period at 40ºC. Consequently, the expansion phenomenon in concrete submitted to these cycles was less intense, relative to the changes taking place in the concrete left in a moist room. Regarding concretes stored in the moist room, more expressive expansions were noted starting from 272 days, representing almost 0.04%, regardless of the type of cement used. For the same period, it was also possible to observe expansion in concretes submitted to the wetting and drying cycles.

In relation to the changes in sulphide, another study [22] performed in concrete beams with a high sulphide content (15% to 20%) show unquestionable symptoms of deterioration, such as expansion and stains.

Figure 2 – Cement paste with
CP II F-32 + 40GBFS (CP40)Presence of sulphide (S)
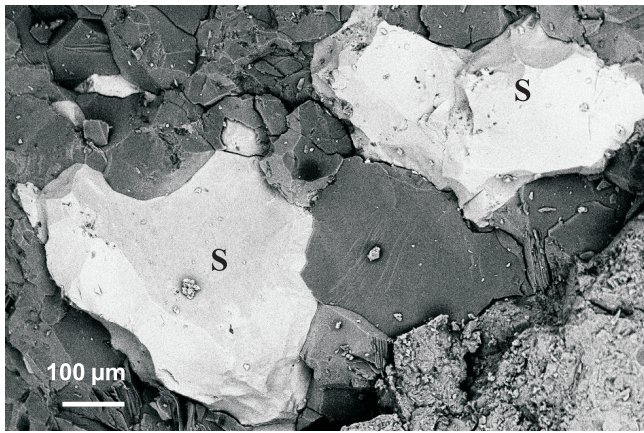in aggregate (BSE Detector)

Figure 3 – Cement paste with
CP II F-32 (CPII) – Neoformed products in
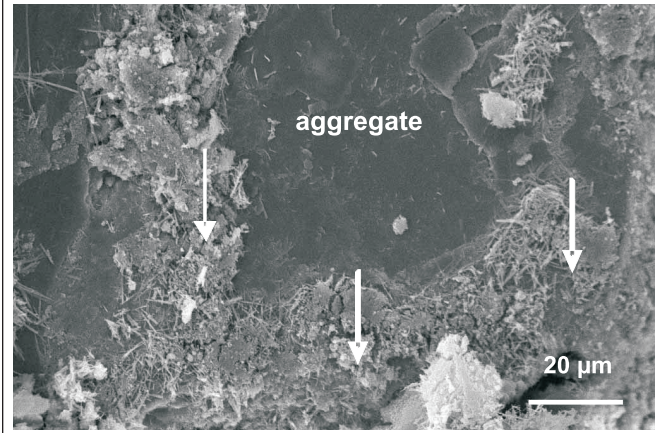the transition zone (BSE Detector)

Figure 4 – Cement paste with CP II F-32 (CPII)
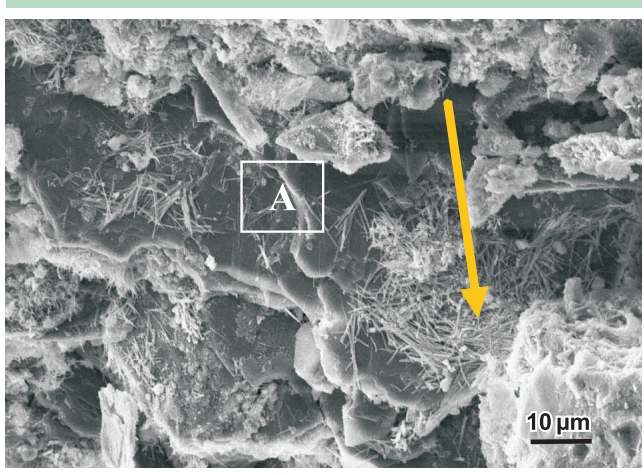Presence of needle rods over
aggregate (A) – SE Detector

Figure 5 – Spectrum of chemical elements
of the rods (Ca, Sand Al) over mineral
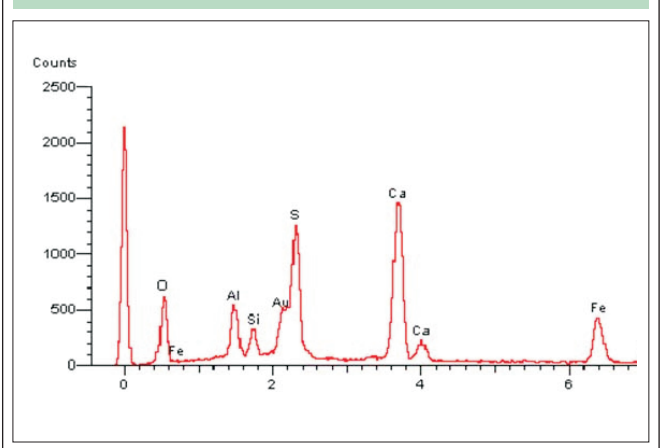quartz (Si) and sulphide (S and Fe) of aggregate

Figure 6 – Cement paste with CP II
F-32 + 40GBFS (CP40) Significant presence
of needles suggesting ettringite (SE detector)
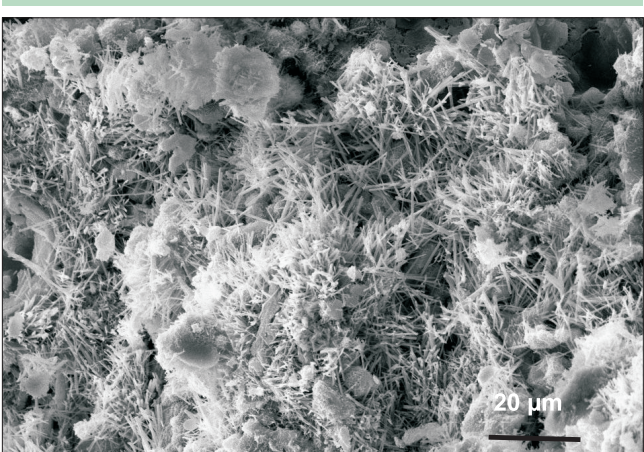
Figure 7 – Cement paste with CP II
F-32 +60GBFS (CP60) – Large concentration
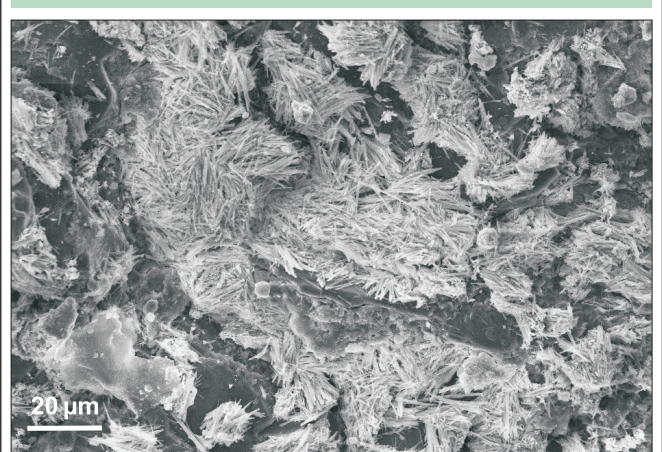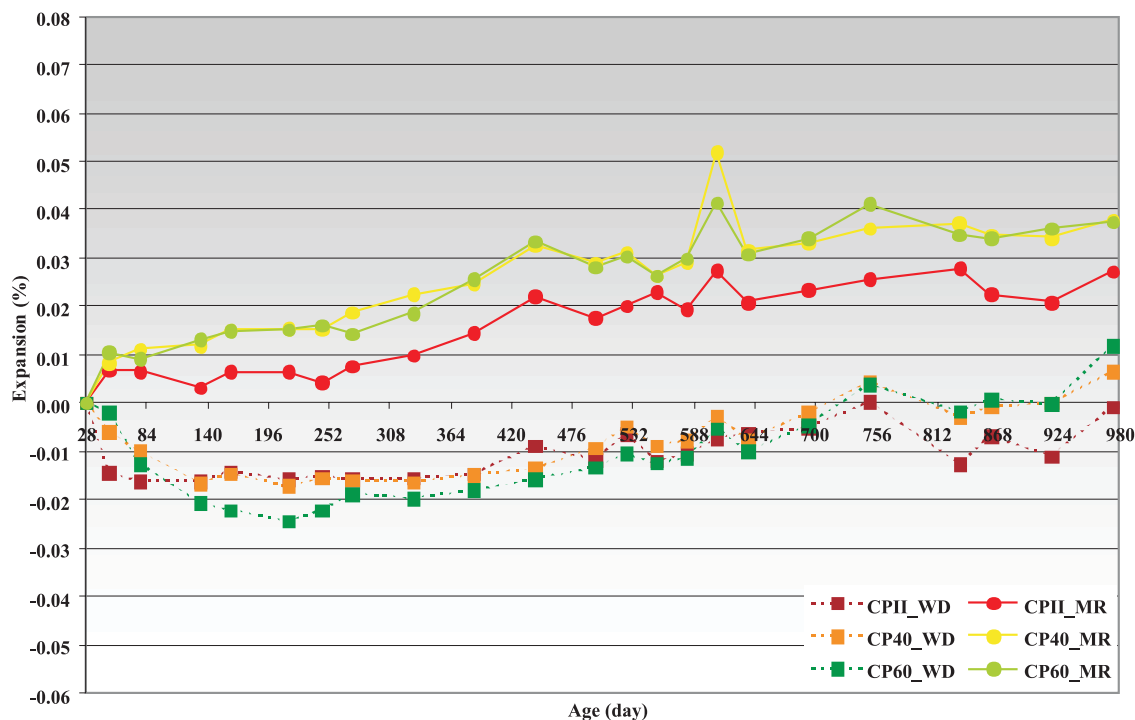of neoformed products (SE detector)

Figure 8 – Concrete expansions in both conditions: wetting and drying cycles (WD) and moist chamberroom (MR): CP II F-32 (CPII), CP II F-32 + 40GBFS (CP40) and CP II F-32 + 60GBFS (CP60)

3.3 Assessment of mortar extracted from concrete by means of X-Ray diffraction

X-ray diffraction analyses also contributed to the understanding of the chemical mechanisms involved in deleterious reactions. Qualitative and semi-quantitative analyses of the compounds were performed. Many of the products found in the samples exposed to moist room (MR) are compounds usually present in hydrated cement paste or even in minerals that make up fine and coarse aggregates. However, the appearance of compounds with time or their increase indicated that intrinsic changes were taking place in the concretes due to sulphide oxidation and the consequent combination with other compounds to form deleterious products.

This behavior was observed in samples of all concretes studied, as can be seen in Figures 9, 10 and 11.

These semi-quantitative analyses were expressed in terms of intensity, as can be seen in the figures below. The following notation was used to indicate the intensity of detected compounds: 0 - undetected, 1 - small, 2 - moderate, 3 - excessive.

X-ray diffraction analyses indicated an increase in ettringite and calcite content from 90 to 180 days in concrete mortar prepared with CP II F-32. Portlandite is also present, but did not increase with time. (Figure 9)

A similar occurrence was observed for concrete prepared

with CP II F-32 + 40 GBS (Fig. 10). An increase in calcite and ettringite content after 30 days was verified. Additionally, an increase in the intensity of gypsum from 90 to 180 days was also observed associated to a reduction of the intensity of portlandite indicating that it is consumed and suggesting a possible internal attack in concrete.

According to Fig. 11, concrete with 60% of ground blast furnace slag showed an increase in ettringite and gypsum

Figure 9 – Evidence of microstructural changes in concrete mortar prepared with CP II F-32 (CPII)
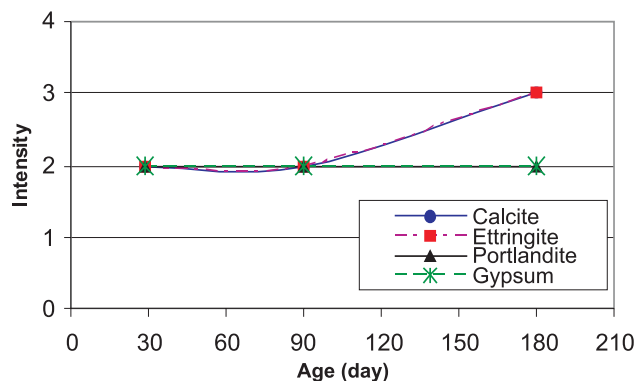
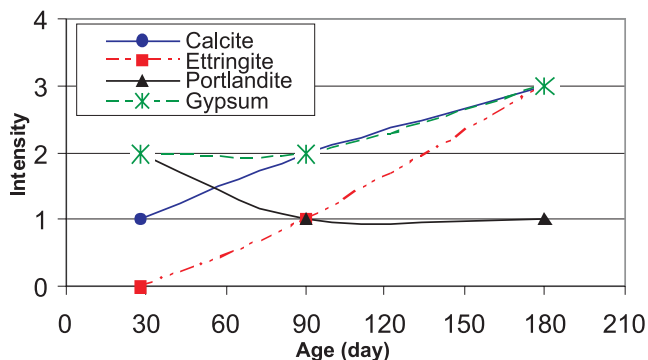**Figure 10 – Evidence of microstructural changes in concrete mortar prepared with CP II F-32 + 40 GBS (CP40)**
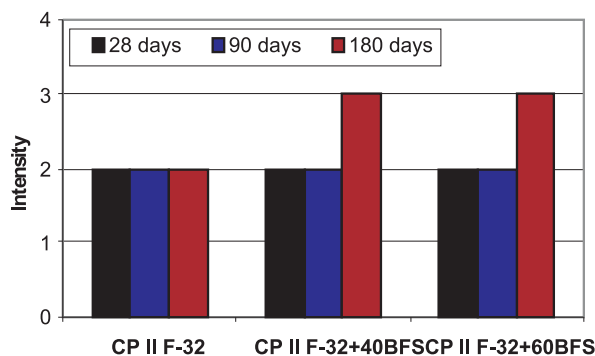

Figure 11 – Evidence of microstructural changes in concrete mortar prepared with CP II F-32 + 60 GBS (CP60)

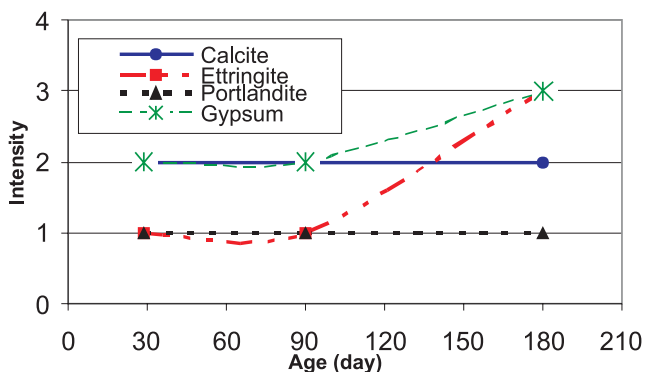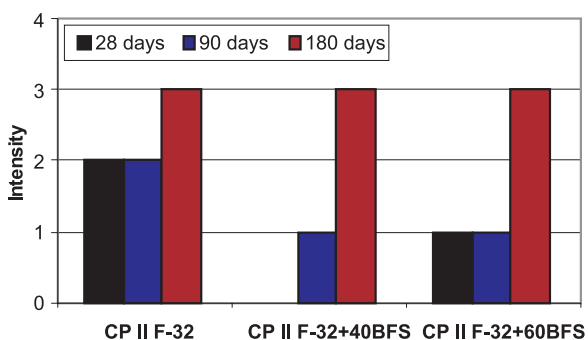**Figure 12 – Behavior of ettringite in the mortar, with time**

Figure 13 – Behavior of gypsum in the mortar, with time

content between 90 and 180 days after being cast. For compounds such as calcite and portlandite content was constant up to 180 days.

Figures 12 and 13 show grouped results for the three concrete mixes, a comparative analysis of the three cements studied. An increase in the content for the compounds ettringite and gypsum were observed with time, in almost all cases.

3.4 Determination of sulphate in mortar extracted from concrete

Fig. 14 shows an increase in sulphate content on mortar caused by sulphide oxidation, after curing for three to eighteen months. Under moist room conditions, oxygen diffusion becomes difficult resulting in less sulphate formation, when compared to results from wetting and drying cycles. For the cement with blast furnace slag, results were lower. The slight decrease of sulphate on CPII-WD and CPII-MR was attributed to the inhomogeneity of the sulphide present in the aggregate.

3.5 Thermogravimetry results

Results of the thermogravimetric analysis of cement paste and mortar were used to calculate the increase of combined water up to 325°C, including the gypsum and ettringite formed from a oxidative reaction of sulphide, as well as the normal hydrated compounds of the cement. These results were considered to be in agreement with those obtained from the determination of sulphate.

4   Conclusions

The methodology used confirmed that the presence of moisture is essential to accelerate the oxidation of sulphide and, consequently, the deleterious chemical reactions in the system being studied. Expansion and other pathological symptoms associated to changes taking place in sulphides were observed in concrete stored in a moist environment.

Figure 14 – Increase in sulphate content of concrete mortar in moist chamberroom (MR) and wetting and drying cycles (WD) for CP II F-32 (CPII), CP II F-32 + 40GBFS (CP40) and CP II F-32 + 60GBFS (CP60)
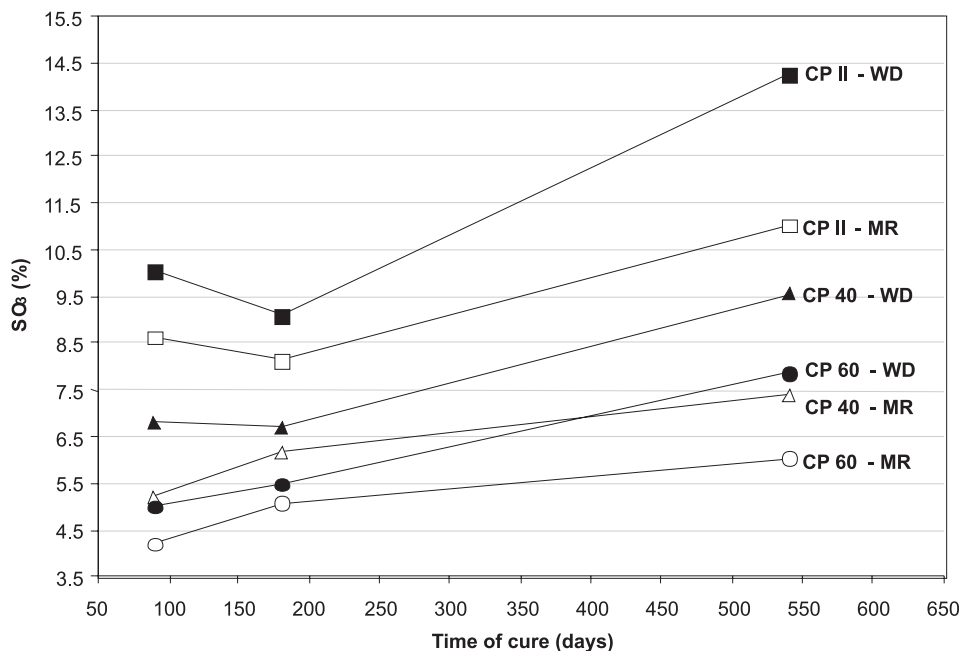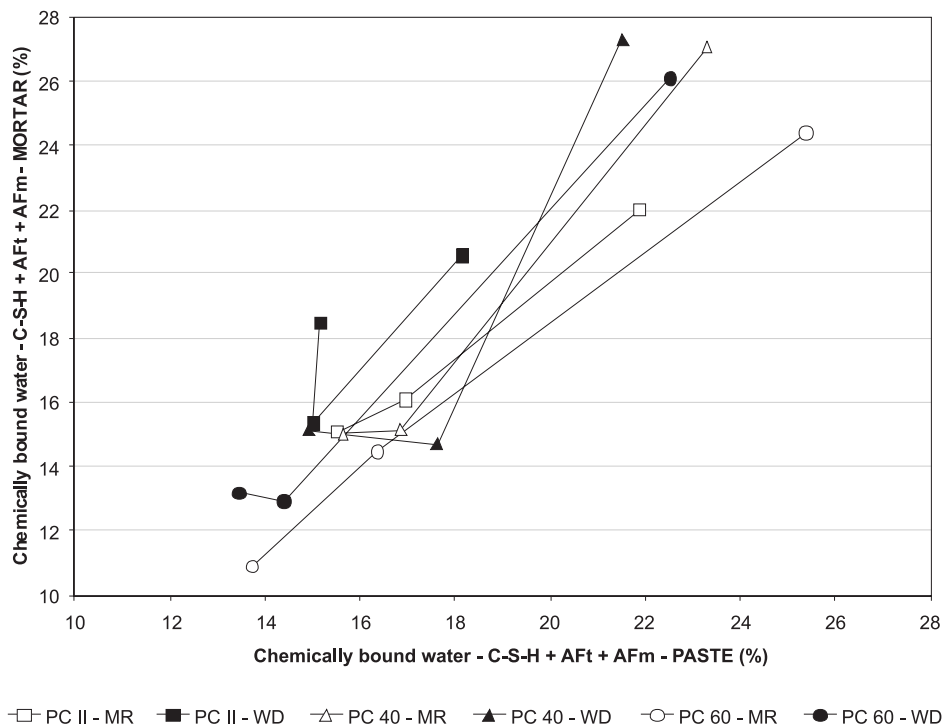

Figure 15 – Relationship between combined water for paste and mortar in moist chamberroom (MR) and wetting and drying cycles (WD) determined by TG/DTG up to 325° C, for CP II F-32 (CPII), CP II F-32 + 40GBFS (CP40) and CP II F-32 + 60GBFS (CP60)

In this study, the ground blast furnace slag used as a mineral addition in the preparation of concrete, with CP II F-32 (40% and 60%), did not contribute to the reduction of expansion or changes in sulphides, relative to cement without this addition (CP II F-32).

X-ray diffraction analyses indicated the presence of ettringite and gypsum almost from the moment the concrete is mixed. These products, especially the gypsum, can be formed as a result of sulphate attack. Additionally, an increase of ettringite content was observed with time, for all cases. For concrete prepared with ground blast furnace slag (40% and 60%), there an increase in gypsum content was also noted. This information indicates that even in the early stages, an internal process of microstructural change is taking place in the cement paste, as a consequence of sulphide oxidation.

All the corresponding expansion processes were considered significant, in the cure period studied. New studies have been performed to evaluate the behavior of commercial cements containing slag (e.g. Brazilian cement type CP III similar to American cement type IS, ASTM C595).

5   References

[01] CASANOVA, I., AGULLÓ, L., AGUADO, A, Aggregate expansivity due to sulfide oxidation – I. Reaction system and rate model, Cement and concrete research 26 (7) (1996) 993-998.

[02] LUGG, A., PROBERT, D, 'Mundic'-type problems: a building material catastrophe, Construction and Building Materials (10) 6 (1996) 467 - 474.

[03] GOMIDES, M. J., HASPARYK, N. P., ANDRADE, M. A. S., BITTENCOURT, R. M. Investigação de Agregados Contendo Sulfetos para Utilização em Estruturas de Concreto, XXVI Seminário Nacional de Grandes Barragens, Goiânia, CD ROM. Goiânia ,Goiás, CBDB, (2005).

[04] CHINCHÓN, J.S., AYORA, C., AGUADO, A., GUIRADO, F, Influence of weathering of iron sulfides contained in aggregates on concrete durability, Cement and Concrete Research (25) 6 (1995) 1264-1272.

[05] CHINCHÓN, J. S., LOPEZ, A., SORIANO, J., VAZQUEZ, E, La cantera de Mont Palau II Formación de compuestos expansivos generados en la reacción árido-hormigón, Enginieria Civil (72) s.d. 109- 113.

[06] VÁZQUEZ, E., Relatório Técnico de Consultoria – Informe sobre la influencia de la presencia de pirita y de sus procesos degradativos en los materiales de construcción, 1999.

[07] AYORA, C., CHINCHÓN, S., AGUADO, A., GUIRADO, F., Weathering of iron sulfides and concrete alteration: thermodynamic model and observation in dams from Central Pyrenees, Spain, Cement and concrete research (28) 9 (1998) 1223-1235.

[08] CASANOVA, I., LÓPEZ, C.M., AGUADO, A., AGULLÓ, L., Micro and mesoscale modeling of expansion in concrete dams. Dam Safety. In: Proceedings of International Symposium on New Trends and Guidelines on Dam Safety. Barcelona, ed. L. Berga, 1, 1998, 661-667.

[09] QUIGLEY, M. R., VOGAN, R. W., Black shale heaving at Ottawa, Canada, Canadian Geotechnical Journal (7) (1970) 106- 112.

[10] BUILDING RESEARCH ESTABLISHMENT Special Digest 1. Concrete in aggressive ground. London, England, BRE Centre for Concrete Construction - BRE Centre for Ground Engineering and Remediation, Construction Research Communications Ltd., 2001.

[11] HASPARYK, N. P., MUNIZ, F. C., NASCIMENTO, J. F. F., ANDRADE, M. A. S., BITTENCOURT, R. M., PACELLI DE ANDRADE, W. Estudo de laboratório com concreto contendo agregados obtidos a partir de rocha com sulfetos, XV Reunión Técnica de la Asociación Argentina de Tecnología del Hormigón, Seminario sobre Hormigones Especiales, Anais, Santa Fé, Argentina, (2003).

[12] HASPARYK, N. P., MUNIZ, F. C., ARMELIN, J. L., NASCIMENTO, J. F. F.; SANTOS, M. C., BITTENCOURT, R. M.; PACELLI DE ANDRADE, W., CARASEK, H., CASCUDO, O., MINICUCCI, L.A. Contribuição ao Estudo da Influência de Sulfetos Presentes no Agregado nas Propriedades e Durabilidade do Concreto, Congresso Brasileiro do Concreto, 44, Belo Horizonte, CD Rom. Belo Horizonte: IBRACON, (2002).

[13] HASPARYK, N. P., MUNIZ, F. C., ANDRADE, M. A. S., BITTENCOURT, R. M., GOMIDES, M. J., CARASEK, H. A. Deterioração de Estruturas de Concreto Contendo Agregados com Sulfetos, Simpósio sobre Estruturas de Concreto, 5, São Paulo, CD ROM. São Paulo: EPUSP, (2003).

[14] SINGER, P. C., STUMM, W., Acidic mine drainage: The rate-determining step, Science 167 (2) (1970) 1121-1123.

[15] PYE, K., MILLER, J. A., Chemical and biochemical weathering of pyritic mud rocks in a shale embankment, Quarterly Journal of Engineering Geology (23) (1990) 365-381.

[16] CZEREWKO, M. A.; CRIPPS, J. C. Sources of sulfur species – Identification and quantification. Thaumasite and other forms of concrete deterioration and protection. The Centre for Cement and Concrete. Halifax Hall, University of Sheffield, 1999.

[17] IGARASHI, T., OYAMA, T., Deterioration of water quality in a reservoir receiving pyrite-bearing rock drainage and its geochemical modeling, Engineering Geology (55) (1999) 45-55.

[18] NICHOLSON, R. V., GILLHAM, R. W., REARDON, E. J., Pyrite oxidation in carbonate-buffered solution: 2. Rate control by oxide coatings, Geochimica et Cosmochimica Acta (54) (1990) 395-402.

[19] CASANOVA, I., AGULLÓ, L., AGUADO, A. Aggregate expansivity due to sulfide oxidation – II. Physical-chemical modeling of sulphate attack, Cement and concrete research (27) 11 (1997) 1627-1632.

[20] AGUADO, A., AGULLÓ, L., CÁNOVAS, M.F., SALLA, J.M., Diagnóstico de daños y reparación de obras hidráulicas de hormigón, Colegio de Ingenieros de Caminos, Canales y Puertos, Almagro, Madrid, 1996.

[21] HASPARYK, N. P., GOMIDES, M. J., ANDRADE, M. A. S., SILVA, H. H. A. B., CARASEK, H. Estudo em laboratório de concretos contendo agregados com sulfetos, Congresso Brasileiro do Concreto, 47, Olinda, Anais. São Paulo: IBRACON, (2005).

[22] HARGEMAN, T., Chemical reactions involving aggregate: Discussion, In: International Symposium on the Chemical of Cement, 4., Washington, 1960, 783.