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**A FEASIBLE EVALUATION PROTOCOL TO DETERMINE THE REACTIVITY OF
SULFIDE-BEARING AGGREGATES FOR USE IN CONCRETE**

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Ana Paula Borges Marcelino

**“A FEASIBLE EVALUATION PROTOCOL TO DETERMINE THE REACTIVITY
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Versão final

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ATA DA DEFESA DE TESE DE DOUTORADO EM ENGENHARIA DE ESTRUTURAS Nº: 75 da aluna Ana Paula Borges Marcelino

Às **14** horas do dia **22** do mês de **Julho** de **2020**, reuniu-se, totalmente por videoconferência para atender aos novos protocolos de distanciamento social adotados pelo governo federal e pela prefeitura de Belo Horizonte, que integram medidas para combater o avanço da pandemia de Covid-19, provocada pelo novo coronavírus, a Comissão Examinadora indicada pelo Colegiado do Programa em **28 de Abril de 2020**, para julgar a defesa da tese de doutorado intitulada "**A Feasible Evaluation Protocol To Determine The Reactivity Of Sulfide-Bearing Aggregates For Use In Concrete**", cuja aprovação é um dos requisitos para a obtenção do Grau de DOUTOR EM ENGENHARIA DE ESTRUTURAS na área de ESTRUTURAS.

Abrindo a sessão, o Presidente da Comissão, **Prof. Dr. José Márcio Fonseca Calixto**, após dar a conhecer aos presentes o teor das Normas Regulamentares passou a palavra à candidata para apresentação de seu trabalho. Seguiu-se a arguição pelos examinadores, com a respectiva defesa da candidata. Logo após, a Comissão se reuniu, sem a presença da candidata e do público, para julgamento e expedição do resultado final. Foram atribuídas as seguintes indicações:

Prof. Dr. José Márcio Fonseca Calixto - DEES - UFMG (Orientador)

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Dr. Cláudio Sbrighi Neto - IBRACON

Pelas indicações acima, a candidata foi considerada aprovada, conforme pareceres em anexo.

O resultado final foi comunicado publicamente à candidata pelo Presidente da Comissão.

Nada mais havendo a tratar, o Presidente encerrou a reunião e lavrou a presente ATA, que será assinada por todos os membros participantes da Comissão Examinadora. Belo Horizonte, 22 de julho de 2020.

Observações

1. A aprovação da candidata na defesa da Tese de Doutorado não significa que a mesma tenha cumprido todos os requisitos necessários para obtenção do Grau de Mestre em Engenharia de Estruturas;
2. Este documento não terá validade sem a assinatura e carimbo do Coordenador do Programa de Pós-Graduação.



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*Dedico este trabalho a
minha família e a todos
que contribuíram para a
sua realização.*

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RESUMO

Existem muitos mecanismos de degradação no concreto armado. Esses mecanismos podem ser divididos em degradação da própria estrutura, deterioração da armadura e deterioração do concreto. O ataque interno de sulfatos pertence ao último grupo. O ataque interno por sulfatos é um dos mecanismos mais nocivos ao concreto, pois quando sulfetos (que depois de oxidados liberam sulfatos) provenientes de algum componente do concreto, tal como o agregado, encontram-se de maneira dispersa no interior do material, há um ataque de maneira generalizada em todo o elemento estrutural. Esse ataque ocasiona a formação de produtos expansivos que geram fissuração que podem levar a sérios problemas estruturais no concreto. A utilização de materiais rochosos que contenham sulfetos na produção de agregados vem se tornando cada vez mais comum em todo o mundo, pois esses minerais estão presentes na maioria das litologias e as reservas naturais de materiais desprovidos de sulfetos estão cada vez mais exauridas e escassas. Poucos estudos de caráter científicos sobre a utilização de agregados sulfetados em estruturas de concreto associados à resistência do meio técnico na utilização desse material justificam o aprofundamento nesse tema. A principal contribuição desta pesquisa é a avaliação da reatividade de agregados que contêm sulfetos usando para isso a combinação de diferentes técnicas de rápida execução e de custo reduzido. Para isso foram utilizados agregados fabricados a partir de rochas provenientes da região de implementação da UHE de Irapé, em Minas Gerais, com amostras contendo sulfetos na ordem de 5% em sua composição. Inicialmente buscou-se avaliar a granulometria mais reativa desse material. Baseado em investigações anteriores partículas entre 0,15mm e 4,80 mm foram analisadas e as quantidades de sulfeto pirita (FeS_2) e pirrotita ($\text{Fe}_{(1-x)}\text{S}$) determinadas através de ensaio de combustão direta. A superfície livre de cada sulfeto também foi determinada através da técnica MLA (Mineral Liberation Analysis). Em seguida amostras de cada granulometria escolhida foram submetidas ao ataque de uma solução de peróxido de hidrogênio (H_2O_2) e o sulfato, produto da oxidação dos sulfetos, liberado na solução foi quantificado pela técnica de turbidimetria indicando assim em qual granulometria o sulfeto reagiu mais. Os resultados também mostraram que quanto maior a superfície exposta do sulfeto e menor o tamanho do agregado, mais efetiva é a oxidação e conseqüentemente mais reativo é o agregado para o concreto. Com esses resultados os tamanhos de partícula 0,15 a 2,40 mm foram definidos como os mais propícios à oxidação: portanto não devem ser utilizados na produção de concreto. Agregados maiores que 4,80 mm

podem não ser reativos para o material analisado; no entanto, serão necessários testes adicionais para verificar sua possível utilização em concreto.

Palavras-chave: ataque interno de sulfatos, agregados sulfetados, métodos de ensaios, concreto.

ABSTRACT

There are many degradation mechanisms in reinforced concrete. They can be divided into degradation mechanisms of the structure itself, in deterioration of the reinforcement, and deterioration of the concrete. Sulfate attack belongs to the latter group. Internal sulfate attack is one of the most harmful deterioration mechanisms to concrete. Sulfide-bearing aggregates when oxidized release sulfates which are dispersed inside the hardened concrete leading to generalized expansion and cracking of the material. These effects could cause serious structural problems in concrete. The use of this type of aggregates in concrete production is increasing worldwide since sulfides are present in most rock lithology. Moreover, the natural reserves of rocks without sulfides are becoming depleted and scarce. Few scientific studies on the use of sulfide-bearing aggregates in concrete structures associated with the resistance of the technical community in using this material justify more investigations. The main contribution of this research is to evaluate the sulfide-bearing aggregate reactivity using the combination of different procedures with reduced cost and time. Aggregates derived from rocks of the Irapé hydroelectric power plant area in Minas Gerais were used. These rock samples contained sulfides in the order of 5% in their composition. Initially, the more reactive grain size was evaluated. Based on previous investigations, grain sizes between 0.15- and 4.80-mm were selected for the study. For each particle size, the quantities of pyrite (FeS_2) and pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$) were first determined by the direct combustion test (LECO). The exposed surface of each sulfide was also quantified by the mineral liberation analysis (MLA) technique. Samples of each particle size were then immersed in an H_2O_2 solution and the released sulfate (from the sulfide oxidation) was quantified by turbidimetry, thus indicating in which particle size the sulfide reacted more. The results also showed that the larger the sulfide exposed surface and the smaller the aggregate particle size are, the more effective is its oxidation and consequently more reactive the aggregate. With these results, the particle sizes 0.15- to 2.40-mm were defined as the most likely to be oxidized: thus, it should be discarded for use in concrete. Particle sizes larger than 4.80 mm may not be reactive for the analyzed material; however additional tests will be needed to verify their possible use in concrete.

keywords: internal sulfate attack, sulfide-bearing aggregates, testing method, concrete.

FIGURES LIST

Figure 2. 1: Micrograph of mortar produced with sulfate aggregate - age 315 days (MARCELINO, 2015).	15
Figure 2. 2: Extensive cracking and stains at the Tascaván dam gate (ARAÚJO, 2008 apud GOMIDES 2009).	19
Figure 2. 3: Structural displacement at Graus dam (ARAÚJO, 2008 apud GOMIDES 2009)	19
Figure 2. 4: Ettringite in the pore cavity. (ARAÚJO <i>et al</i> 2008).	20
Figure 2. 5: Appearance of Barragem Rio Descoberto: a) crack due to the presence of acidic water and pyrite in the concrete aggregate, b) construction of the diaphragm wall (ECL, 2003 apud BATISTA, 2013).	21
Figure 2. 6: Extensive cracking on the foundation blocks of a house in Quebec, Canada (RODRIGUES <i>et al.</i> 2012b).	22
Figure 2. 7: Typical degradation signs observed in foundation concrete containing sulfide-bearing aggregates in the Trois-Rivières area (RODRIGUES <i>et al.</i> , 2016b)	22
Figure 2. 8: Typical concrete foundation replacement process in the Trois-Rivières area: a) coating removal; b) foundation concrete demolition; c) shored house; and d) placement of the new concrete foundation (RODRIGUES <i>et al.</i> , 2016b).	23
Figure 2. 9: Basement wall affected by internal sulfate attack. (GEISS and GOURLEY, 2019)	23
Figure 2. 10: Symptoms of deteriorated concrete foundation. (ZHONG and WILLE, 2018).	24

Figure 2.11: Pyrrhotite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample (MARCELINO, 2015).....	26
Figure 2.12: Pyrite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample (MARCELINO, 2015).....	26
Figure 2.13: (a) Aggregate sample for direct combustion test (b) Equipment LECO SC 632 (MARCELINO, 2015).....	27
Figure 2.14: Iron sulfides leaching process (MARCELINO, 2015).	28
Figure 2.15: Oxygenation of pyrite and pyrrhotite samples (Chincón-Payá <i>et al.</i> , 2012).....	29
Figure 2.16: Aggregate samples with different pyrite contents oxidized in hydrogen peroxide	31
Figure 2.17: pH variation in samples with different pyrite contents and for the Pedreira aggregate in relation to time – paste pH determination test (PEREIRA, 2015).....	32
Figure 2.18: Test setup (RAMOS <i>et al.</i> , 2015)	33
Figure 2.19: Results of the test after 8 days for a H ₂ O ₂ solution: A) MSK; B) B&B; C) GGP; D) SB; E) SW; F) SPH; G) PKA; H) HPL. (RAMOS <i>et al.</i> , 2015)	34
Figure 2.20: Results of the three-day test using NaClO solution. The images to the left show the aspect of the aggregates at the end of the test and the images to the right show the aspect of the chemist cloth gown after the removal of the particles, rinsed with distilled water and dried in an oven: A and B) MSK; C and D) B&B; E and F) GGP; G and H) SB. (RAMOS <i>et al.</i> , 2015).....	35
Figure 2.21: Results of the three-day test using NaClO solution. The images to the left show the aspect of the aggregates at the end of the test and the images to the right show the aspect of the cloth after the removal of the particles, rinsed with distilled water and dried in an oven: I	

and J) SW; K and L) SPH; M and N) SDBR; O and P) PKA; and Q and R) HPL. (RAMOS <i>et al.</i> , 2015)	36
Figure 2.22: Oxygen consumption test (RODRIGUES <i>et al.</i> , 2016a).....	37
Figure 2.23: Test with different aggregates particle sizes immerse in a) alkaline solution and b) neutral solution (GOTO <i>et al.</i> , 2016).....	38
Figure 2.24: Variation in the measured pH values for the different solutions and particle sizes (GOTO, 2016).....	39
Figure 2.25: Electrical potential for different solutions and particle sizes (GOTO, 2016).....	39
Figure 2.26: Electrical potential for the different solutions and SO ₃ contents (GOTO, 2016).	40
Figure 3. 1: Blocks of aggregate samples for MLA analysis. Samples a) 0.15, b) 0.30, c) 0.60, d)1.20, e)2.4 and f) 4.80.....	48
Figure 3. 2: SEM image. Source: UFMG Microscopy Center.....	49
Figure 3. 3: Identification of mineral phases by MLA mapping. Source: UFMG Microscopy Center.....	49
Figure 3. 4: SEM equipment with the MLA software package. Source: UFMG Microscopy Center.....	50
Figure 3.5: Scheme of the basic operation of a spectrophotometer. Source: http://www.kasvi.com.br/espectrofotometria-principios-aplicacoes/espectrofotometro/	52
Figure 3. 6: Example of a calibration turbidimetric curve.	53

Figure 3. 7: Spectrophotometer of the Laboratório Prof. José Marcelino de Oliveira, DESA, UFMG.....	54
Figure 4. 1: Sample 0.15 - MLA analysis.	57
Figure 4. 2: Sample 0.30 - MLA analysis.	58
Figure 4. 3: Sample 0.60 - MLA analysis.	58
Figure 4. 4: Sample 1.20 - MLA analysis.	59
Figure 4. 5: Sample 2.4 - MLA analysis.....	59
Figure 4. 6: Sample 4.80 - MLA analysis.	60
Figure 4. 7: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases of a 0.15-mm sample: Pyrite (1) and Pyrrhotite (2) with exposed surfaces.	61
Figure 4. 8: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.15-mm sample: Pyrite (1), Pyrrhotite (2) and Albite grains (3) disseminated in a matrix of Quartz (4). No exposed surface of sulfide.	61
Figure 4. 9: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.30-mm sample: Pyrrhotite grains (1) disseminated in a matrix of Quartz (2) and Muscovite (3). A little exposed surface of sulfide.	62
Figure 4. 10: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.60-mm sample: Pyrite (1) and Pyrrhotite (2) grains disseminated in a matrix of Muscovite (3) and Quartz (4). A little exposed surface of sulfide. Pyrrhotite with oxidation signals.....	62
Figure 4. 11: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 1.20-mm sample: Pyrrhotite (1) and Pyrite (2) grains	

disseminated in a matrix of Quartz (3) and Clinocllore (4). Presence of exposed surface of Pyrite and a little of Pyrrhotite..... 62

Figure 4. 12: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 2.40-mm sample: Pyrrhotite (1) and Pyrite (2) grains disseminated in a matrix of Quartz (3), Clinocllore (4) and Spessartine. No exposed surface of Pyrite and a little of Pyrrhotite..... 63

Figure 4. 13: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 4.80-mm sample: Pyrrhotite (1) and Pyrite (2) grains disseminated in a matrix of Quartz and Muscovite (3). No exposed surface of Pyrite or Pyrrhotite..... 63

Figure 4. 14: Pyrrhotite Exposed Surface. 64

Figure 4. 15: Pyrite Exposed Surface..... 64

Figure 4. 16: Sulfur contents in solid residue and in the solution after oxidation processes ... 68

Figure 4. 17: Sulfur contents in initial and after oxidation (solution and residues)..... 69

Figure 4. 18: Pyrite and pyrrhotite contents in solid residue after oxidation processes. 69

Figure 4. 19: MLA analysis after oxidation– 0.15-mm size particle. 70

Figure 4. 20: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.15-mm sample: Pyrrhotite grains (1) involved by an iron-sulfide oxide (2)..... 71

Figure 4. 21: MLA analysis after oxidation – 0.30-mm size particle. 71

Figure 4. 22: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.30-mm sample: Pyrrhotite grains (1)

disseminated in a matrix of Almandine (2), Quartz (3) and Biotite (4). No exposed surface of sulfide and no iron-sulfide oxide.	72
Figure 4. 23: MLA analysis after oxidation – 0.60-mm size particle.....	73
Figure 4. 24: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.60-mm sample: Pyrrhotite grains (1) involved by an iron-sulfide oxide (2).	73
Figure 4. 25: MLA analysis after oxidation – 1.20-mm size particle.....	74
Figure 4. 26: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 1.20-mm sample: Pyrrhotite grains (1) with an iron-sulfide oxide (2) only in edge exposed. Most part of the pyrrhotite is preserved since it is inserted in an Albite (3) and Kyanite (4) matrix.	74
Figure 4. 27: MLA analysis after oxidation – 2.40-mm size particle.....	75
Figure 4. 28: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 2.40-mm sample: Pyrrhotite grains (1) with no iron-sulfide oxide surrounded by a Quartz and Muscovite (3) matrix.	75
Figure 4. 29: MLA analysis after oxidation – 4.80-mm size particle.....	76
Figure 4. 30: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 4.80-mm sample: Pyrrhotite grains with (1) and without (2) iron-sulfide oxide surrounded by Quartz and Muscovite (3) matrix.	76
Figure 4. 31: Block sawn of sample 4.80 oxidized for MLA analysis.	77
Figure 4. 32: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of sliced 4.80-mm sample: Pyrrhotite grains (1) with no iron-sulfide oxide disseminated in a Quartz and Muscovite (2) matrix and biotite grains (3). Only at the aggregate edge, there is pyrrhotite with some iron-sulfide oxidation (4).	77

TABLES LIST

Table 1-1: Maximum sulfur content in aggregates for concrete use. (CEMIG, 2007)	6
Table 2. 1: Formation of C ₃ A hydration products (adapted from CASANOVA <i>et al</i> , 1997) .	16
Table 2. 2: Deteriorated concrete structures due to sulfide-bearing aggregate use.	24
Table 2. 3: Aggregate particle size distribution (MARCELINO, 2015).....	25
Table 2. 4: Fe ²⁺ and SO ₄ ²⁻ concentration in the samples. Aggregates: M- Marlstone, L- Limestone, S-Schist. Sulfides: Py – pyrite, Po – pyrrhotite. (Chincón-Payá <i>et al.</i> , 2012)	29
Table 2. 5: Characteristics of the investigated aggregates. (RAMOS <i>et al.</i> , 2015)	33
Table 2. 6: Aggregate mineralogy and total sulfur content. (GUIRGUIS and SHEHARA, 2017)	41
Table 2. 7: Change in pH, sulfur, and iron in bleach after one cycle of 12 days soaking at 40°C. The cycle reported here is cycle # 1. The initial pH of the solution was 12.2. (GUIRGUIS and SHEHARA, 2017)	42
Table 2. 8: Mass loss results and total Sulfur (S _T %) for aggregates tested at 23°C using particle size from 2.36 mm to 1.18 mm after cycles 1, 2, 3. (GUIRGUIS and SHEHARA, 2017)	43
Table 3. 1: Aggregate by particle size.....	45
Table 4. 1: Aggregate sulfur content by particle size	57
Table 4. 2: Aggregate solution pH.....	65

Table 4. 3: Actual concentrations of the SO_4 (mg/l).	66
Table 4. 4: Sulfur released in solution.	67
Table 4. 5: Sulfur in initial and after oxidation for samples.	67

ACRONYMS AND ABBREVIATIONS LIST

ABNT - Associação Brasileira de Normas Técnicas

Al Aluminum

Al₂O₃ Aluminum oxide

ASTM American Society for Testing and Materials

C₂S Dicalcium silicate

C₃A Tricalcium aluminate

C₃S Tricalcium silicate

C₄AFe Tetracalcium ferroaluminate

Ca Calcium

CaCO₃ Calcite

Ca(OH)₂ Calcium hydroxide

CaO Calcium oxide

CAESB Companhia de Saneamento Ambiental do Distrito Federal

CEMIG Companhia Energética de Minas Gerais

COPASA Companhia de Saneamento de Minas Gerais

CO₂ – carbon dioxide

CP-V Brazilian type V Portland cement

C-S-H Hydrated Calcium Silicate

DRX X-ray diffractometer

EDS Electronic Data Systems

ERX X-ray spectrometer

Fe Iron

Fe(OH)₃ Iron hydroxide

FeO(OH) Goetia

Fe_(1-x)S Pyrrhotite

FeS₂ Pyrite

FeSO₄ ferrous sulfate

H₂O₂ Oxygen peroxide

H₂SO₄ Sulfuric acid

HCl Hydrochloric acid

HPP Hydro Power Plant

L₀ Initial length

L_t Length at the end of time t of exposition

MEV Scanning electron microscopy

MLA Mineral Liberation Analyze

mg milligram

mol Unit for the quantity of matter or substance

NAG Net Acid Generation

NaOH Sodium hydroxide

NBR Brazilian Standard

NM Mercosul Standard

O Oxygen

pH Magnitude indicating the acidity, neutrality, or alkalinity of an aqueous solution

P&D Research and development project

S Sulfur

SEM Scanning Electron Microscope

Si Silicon

SO₃ Sulfur trioxide

SO₄ Sulfate

UFMG Universidade Federal de Minas Gerais

µm Micrometer

°C Celsius Degree

% Percentage

ε Specific deformation

SUMÁRIO

AGRADECIMENTOS.....	i
<i>RESUMO</i>	iii
ABSTRACT.....	v
FIGURES LIST.....	vi
TABLES LIST	xii
ACRONYMS AND ABBREVIATIONS LIST	xiv
1. Introduction	3
1.1 General Considerations.....	3
1.2 Relevance	5
1.3 Objectives.....	7
1.4 Methodology.....	7
2. Literature Review	9
2.1 Preliminary Considerations	9
2.2 Sulfide oxidation.....	10
2.3 Internal sulfate attack (ISA) in concrete.....	13
2.3.1 Concrete - microstructure.....	14
2.3.2 Deleterious action of the sulfides present in the aggregates	17
2.4 Sulfide-bearing aggregates attack cases	18
2.5 Aggregate reactivity – sulfide oxidation potential	24
3. Experimental Program.....	44
3.1 General considerations	44
3.2 Determination of the aggregate most reactive grain size	44
3.2.1 Determination of the aggregate sulfur content.....	46
3.2.2 Determination of the pyrite and pyrrhotite spatial distribution.....	47
3.2.3 Sulfide oxidation with H ₂ O ₂ solution	50

3.2.4	Sulfate Determination by Turbidimetry	52
3.2.5	Protocol Summary	55
4.	Results and Analysis.....	56
4.1	Aggregate sulfur content by particle size	56
4.2	Pyrite and pyrrhotite spatial distribution	57
4.3	Oxidation with H ₂ O ₂ solution.....	65
4.3.1	Sulfate determination by pH	65
4.3.2	Sulfate determination by spectrophotometry	66
4.3.3	Sulfur content in the solid residues.....	67
4.3.4	Verification of oxidation with H ₂ O ₂ efficiency	68
5.	Conclusions and Suggestions	78
5.1	Suggestions for future investigations	80
6.	References	81
7.	Appendix	90
	Appendix A: Free Surface (Exposed Surface).....	91
	Appendix B: Mineral Association	110
	Appendix C: Publications.....	117

1

INTRODUCTION

1.1 General Considerations

Concrete is the most used construction material worldwide. It is employed in small houses and large buildings as well as in hydroelectric and nuclear power plants. According to the Global Cement Report 11th edition, the world market consumed 4.1 billion tons of concrete in 2014. From this volume, 86% is concentrated in 20 countries from which Brazil is in fourth place, behind China, India, and the USA. In this report, 171 countries were surveyed and concrete production was recorded in 154 of them. (REVISTA GRANDES CONSTRUÇÕES, 2016)

According to Metha and Monteiro (2014), there are at least three main reasons that justify concrete being the most used engineering material. The first one is the concrete's capacity to resist water action without serious deterioration. Thus, it makes the concrete ideal for structures used for transportation, purification, and storage of water. The second reason is that structural elements with different shapes and sizes can be built with it since in the fresh state concrete has the necessary plasticity to flow into the interior of formwork. The third characteristic that makes concrete so popular in the construction market is its low cost associated with the easy availability of its components. In general, the main components of concrete (aggregate, water, and Portland cement) are cheap and easy to find. However, in large structures built far away from large population centers and in places of difficult access, the use of local aggregates from the obligatory excavations is mandatory since it reduces the concrete cost. In addition to diminishing concrete cost, it also decreases environmental impact. The use of the excavations eliminates the need for the area to discard the material and avoids the extraction of natural material from another region.

In nature, the lithological variety is huge and, consequently, aggregates have different mineralogical constitutions. There are aggregates containing minerals that are potentially

reactive with the alkalis of the cement. These reactions may be the alkali-aggregate type, a phenomenon already well known, that causes expansion resulting in concrete deterioration (HASPARYK *et al.*, 2003).

However, there are other reactive aggregates such as rocks with sulfides in their mineralogical composition. These sulfides are pyrite, pyrrhotite, marcasite, chalcopyrite, arsenopyrite, sphalerite, galena, among others. Depending on the sulfide conditions, they can oxidize and cause internal expansion and deterioration of the hardened concrete.

The use of non-reactive aggregates in concrete is even more difficult in places where the availability of another source of material is economically impracticable or non-existent as in the case of concrete dams where large volumes of aggregates are needed (CASANOVA *et al.*, 1996; HASPARYK *et al.*, 2005). Concerning sulfide oxidation, their deleterious potential and the allowable limits on the total amount of sulfur in these aggregates need further investigations.

Cases of severe concrete damage due to the oxidation of iron sulfide-bearing aggregates in concrete have been identified in Spain [Chinchón *et al.* (1995), Ayora *et al.* (1998), and Araújo *et al.* (2008)], England [Bromley (2002)], Brazil [SOARES *et al.*, (2003), BATISTA (2013)], Switzerland [Schmidt *et al.* 2011], Canada [RODRIGUES *et al.* 2012a, 2012b, 2013, 2016] and most recently in the United States [Zhong and Wille (2018), Geiss *et al.* (2019)].

Due to cases such as those, there is great resistance by the technical community in the use of sulfide-bearing aggregates. This is reinforced by the limited number of standards and specifications that address the issue and the ones that do are extremely conservative. On the other hand, it is believed that not every sulfide-bearing aggregate should be discarded and that this behavior may be generating unnecessary environmental and economic liabilities.

In Brazil, the concern with the use of sulfate aggregates began during the implantation phase of the Irapé Hydroelectric Power Plant (HPP), located in the Jequitinhonha Valley in Minas Gerais. At this site, rock formations with high iron sulfide contents were found with the predominance of pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$). Such studies were conducted by CEMIG Geração e Transmissão S.A., the Irapé HPP Complex owner, and by CCI – Irapé Construction Consortium formed by Builder Andrade Gutierrez, Builder Norberto Odebrecht, Brazil Hochtief International, Ivaí Construction Engineering, Voith Siemens Hydro Power Generation, and by

the Consortium Leme-Intertechne responsible for the Basic Project, in partnership with universities (MARCELINO, 2015).

Based on the studies carried out by CEMIG and the Leme-Intertechne Consortium, aggregates from the obligatory excavations of the Irapé rock were not used. This resolution was due to the lack of national standards and information about materials that could effectively contribute to minimize or prevent the deleterious phenomenon of sulfide oxidation present in the aggregates. Thus, materials from the Olhos d'Água and Córrego do Bonito quarries were investigated for the preparation of the concretes. The studies determined the use of aggregates from the Olhos d'Água quarry located six kilometers from the Irapé HPP. These aggregates contained less than 0.5% in sulfide content. (CONSÓRCIO LEME-INTERTECHNE, 1999)

1.2 Relevance

The human capacity to exploit mineral resources is far greater than the ability of the environment to recover. Therefore, the environment and sustainable development have become vital issues.

Sustainability in construction is an extremely important issue. The construction industry causes great environmental impact such as land occupation, raw materials extraction, production and transportation of materials, construction of buildings, generation and disposal of solid waste.

It is observed that there has been a great advance in the quality of construction in recent years, which were obtained mainly through loss reduction programs and quality management systems implementation. There is no doubt, however, that in the coming decades, besides quality (implemented to guarantee user satisfaction with a specific product) there will also be a great concern for sustainability, above all, to guarantee the future of humanity.

The use of residual waste as construction materials is one of the actions that should be included in common practice which in turn will preserve natural resources and minimize environmental impact. Thus, the potential for reuse and recycling of residual wastes in construction is enormous.

A good example of great environmental and economic impact is concrete dams where excavation rocks are used as aggregates. Hydroelectric power concrete dams demand a high volume of material due to their large size. Economic issues practically require the use of the surrounding rocks as aggregates of the concrete, which demands previous studies of the rocks for their possible incorporation (MARCELINO, 2015). These studies are based on the analyses of the physical and chemical characteristics of the rock matrix, as well as the identification of its mineralogical composition. This makes it possible to decide on the use of this material in the concrete avoiding future pathological manifestations.

Most often large dams are located in remote areas and where sometimes rocks containing sulfides are the only available aggregate (CASANOVA et al., 1996). In Brazil, the verification of these minerals in geological sites of hydroelectric power plants is mandatory (GOMIDES, 2009). Thus, studies on the possibility of using this material are necessary. On the other hand, there is still no consensus on the limiting amount of sulfur compounds in aggregates. Investigations and standards found in the technical literature environment have recommendations of sulfur-bearing compound limits in aggregates, but they, generally, do not differentiate the origin of the sulfur as shown in Table 1-1.

Table 1-1: Maximum sulfur content in aggregates for concrete use. (CEMIG, 2007)

Specification / Author	Sulfur maximum content	Sulfur compound
German General Assembly for Quarries Study (1960)	1% of the total aggregate mass content	Sulfate
International Commission on Large Dams (1965)	0,5% of the total coarse aggregate mass content	Sulfide + Sulfate
Portuguese Concrete Regulation (1971)	Relatively to the cement mass content:	Sulfide
	0,2% - concrete with pozzolanic addition	
	0,5% - plain concrete	
	0,2% - reinforced concrete	
	0,05% - prestressed concrete	
British Standard n° 1047 for slag aggregates	0,7% of the total aggregate mass content	Sulfate
AFNOR P 18-542 (1994)	0,4% of the total aggregate mass content	Total sulfur
	0,15% of the total aggregate mass content	Sulfate
Hageman e Roosarr (1995)	1% of the total aggregate mass content	Sulfide (pyrite)

An exception is a European standard, EN12620:2008. This standard recommends that if the pyrrhotite is detected in the aggregate, the maximum value of the sulfur element must not

exceed 0.1%. This value is 10 times lower than the limit usually accepted by the technical community for aggregates containing iron sulfides in general. According to Chinchón-Payá *et al.* (2012), it is an exaggeration to set such a low limit of sulfur (0.1%) and this may be leading to the unnecessary aggregates disposal that would be suitable for concrete production.

In Brazilian specifications, ABNT NBR 7211 (2009) is the only one to set limits on the amount of sulfide-bearing aggregates for concrete. This standard limits the maximum levels of sulfates (SO_4) present in the aggregates to 0.1% of the total aggregate mass content. This limit is only valid for the water-soluble sulfates. ABNT NBR 9917 (2009) does not refer to the mineral content of sulfides or total sulfates present in the aggregates.

There are no laboratory tests capable of satisfactorily predicting the sulfide-bearing potential deleterious character [RODRIGUES *et al.*, 2016a]. Thus, investigations that guide methodologies to determine the possible use of sulfide-bearing aggregate in mortars and concretes are necessary. It is also important to point out that this assessment of the aggregate reactivity must be carried out as expeditiously as possible since it will help engineers and builders take decisions early on.

1.3 Objectives

In this scenario, the objective of the present work is the development of a feasible evaluation protocol to determine the most reactive sulfide-bearing aggregate for use in concrete. The main contribution of this research is the evaluation of the sulfide-bearing aggregate reactivity using the combination of different procedures (Direct Combustion, Mineral Liberation Analyzer, Static Net Acid Generation, and Turbidimetry) with reduced cost and time-consuming.

1.4 Methodology

To accomplish the objective, aggregates derived from rocks of the Irapé hydroelectric power plant area in Minas Gerais were used. Schistosity is the most conspicuous geological feature of the rocky formation of the Irapé hydroelectric power plant area. This schist formation has a unique characteristic given by the existence of iron sulfide (pyrrhotite and pyrite) as well as iron and copper sulfide (chalcopyrite) and zinc sulfide (sphalerite) disseminated in the rock matrix: pyrrhotite predominates over the others [CEMIG, 2007; Lima, 2009]. According to the

results from these investigations, drill holes samples were selected to make the aggregates. The collected material was degradation-free, which is without sulfide oxidation or any stain. It also had a total sulfur content between 1.5 and 3%. The drill holes samples were first crushed and sieved. The materials retained in sieves between 4.8- and 0.15-mm were selected for analysis. The sulfide oxidation evaluation procedure started with the determination, for each particle size, of sulfur concentration in sulfide-bearing aggregate (pyrite and pyrrhotite), using a direct combustion method. The exposed surface of each sulfide was then calculated by the Mineral Liberation Analyzer (MLA). To promote the sulfide oxidation an oxidative dissolution process was carried out as described in the protocol known as The Static Net Acid Generation (NAG) test [AMIRA, 2002]. The NAG test is usually applied to evaluate the potential of an acid generation of waste and tailings in the mining industry. In the present work, the protocol's first step promoted the reaction between the solid sample (aggregate) and a hydrogen peroxide solution (H_2O_2). The aggregate was soaked in the solution. The amount of sulfate released in solution was determined by turbidimetry, and the sulfur content remaining in the residue after oxidation was quantified by direct combustion method.

2

LITERATURE REVIEW

2.1 Preliminary Considerations

According to Isaia (2011), the wide use of concrete is mainly due to its constitution as a ceramic material, whose raw materials are available in practically all corners of the globe. The advantages that are inherent to this material have led it to become the flagship of construction, for it adapts to a wide range of distinct environments and circumstances due to properties such as versatility, durability, and performance, which grant adequate service life to structures at competitive costs in comparison to other structural materials. In the face of that, studies on degradation mechanisms and durability of concrete have experienced an increasing demand.

Studies on the durability of concrete structures generally take into account aspects related to its constituents, contents of incorporated materials, execution and service conditions, as well as the environment (LIMA, 2011). Such studies have evolved considerably through the years as a result of increasing knowledge of the liquids and gases transport mechanisms through the pores (MEDEIROS *et al.*, 2011) and of how aggressive agents affect the concrete.

There are many degradation mechanisms in reinforced concrete, the most important being described by the NBR 6118 (ABNT, 2014) and NBR 12655 (ABNT, 2015) standards. They can be divided in degradation mechanisms of the structure itself, in deterioration of the reinforcement (active and/or passive), and deterioration of the concrete (MEDEIROS *et al.*, 2011). Sulfate attack belongs to the latter group, causing degradation directly on the concrete, even if the expansion unleashed by the phenomenon can lead to cracking and facilitate the corrosion of the reinforcement.

2.2 Sulfide oxidation

A great variety of sulfides is present in the rocks, mainly in the form of pyrite (FeS_2), pyrrhotite ($\text{Fe}_{(1-x)}\text{S}$), marcasite (FeS_2), chalcopyrite (CuFeS_2), arsenopyrite (FeAsS), sphalerite (ZnS), and galena (PbS). Aggregates containing sulfides cannot always be replaced due to a lack of other available materials and to economic factors (HASPARYK *et al.*, 2003).

Concrete containing sulfide-bearing aggregates can degrade due to the appearance of expansive products formed inside the hardened concrete and originating from the oxidation of the sulfide minerals. Many factors can interfere in the oxidation of the sulfides, of which the most relevant are: high concentration of oxygen, high temperature and humidity (BROMLEY e PETTIFER, 1997), apart from the high specific surface area of aggregates (CASANOVA *et al.*, 1997).

In the sulfide alteration process, the most commonly mentioned are those involving the iron sulfides: pyrite and pyrrhotite (HASPARYK *et al.*, 2003). Pyrite is a mineral whose approximate chemical composition consists of 46.6% Fe and 53.4% S; its molecular formula is FeS_2 . It is golden-yellow and its hardness is relatively high - between 6.0 and 6.5. It is insoluble in hydrochloric acid and soluble in concentrated nitric acid. Pyrrhotite is a mineral whose simplified composition is $\text{Fe}_{(1-x)}\text{S}$ ($0 \leq x \leq 0.17$); it stands out from other sulfides for its high degree of alterability, for it oxidizes easily when exposed to atmospheric agents, it is also magnetic and sticky to the touch. It possesses a dark, blackish color and metallic luster. Unlike pyrite, it is soluble in hydrochloric acid and releases a sulfur odor when reacts with it (GOMIDES, 2009; ANTHONY *et al.*, 2015).

Oxygen and iron are the main pyrite and pyrrhotite oxidizing agents. At pH levels higher than 4, oxygen is the primary oxidant of concrete sulfur compounds because of the alkalinity of this material. At pH levels lower than 4, iron can function as a catalyst for the oxidation process (BELZILE *et al.*, 2004 e ARAÚJO *et al.*, 2008).

Reaction rate, on its turn, depends on several other factors as sulfur content, surface area, size and shape of the sulfur particles, temperature and pH, rock mass permeability, and action of specific microorganisms (CASANOVA *et al.*, 1996; AYORA *et al.*, 1998; ARAÚJO *et al.*, 2008). Still, concerning oxidation rates of iron sulfides, Belzile *et al.* (2004) observed that an

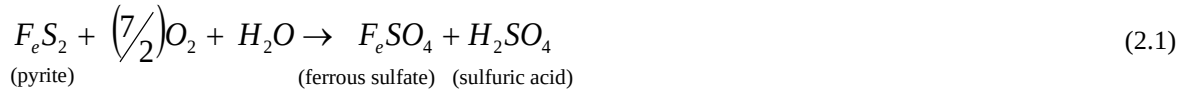
increase of 20°C in temperature, with oxygen as the oxidizing agent, the reaction rate is 3 to 5 times higher.

According to Casanova *et al.* (1996), the sulfide oxidation rate depends on the ambient pH in the range between 4.5 and 6.5 and is independent of the pH when it falls below 3.5. Other researchers suggest that the rate is independent of the pH when it falls between 7.5 and 8.5 (neutral); in this interval, the rate depends solely on the surface area, which in its turn depends on grain size and on the balance between the decomposition of the oxidized products and oxygen absorption on the sulfide surface (Nicholson *et al.*, 1988 *apud* Casanova *et al.*, 1996). Furthermore, Casanova *et al.* (1997) suggest that the oxidation rate is increased to a high degree in strongly alkaline environments ($12.5 < \text{pH} < 13.7$), growing at a rate of 50 times for each 1.2 pH unit. According to Rodrigues *et al.* (2012a), sulfide oxidation reactions are much more easily to occur at high pH levels. Therefore, concrete favors this kind of process, since its pH is higher than 12 under normal conditions.

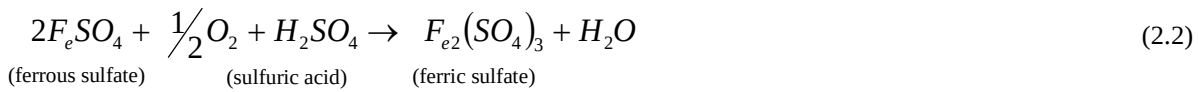
The type and origin of the rocks play an important role in the development of the sulfide reactions over time: while the expansive iron sulfates typical of more acidic environments form in black schists, the capacity of neutralization of the pH of calcite (CaCO_3) dissolution in limestone prevents the forming of aggressive materials in these rocks, with the formation of iron hydroxides only (CHINCHÓN *et al.*, 1995). As stated by Blowes *et al.* (2003) *apud* Lima (2009), the carbonate content on the substrate needs to be higher than the sulfide content to ensure the control of the pH levels next to neutral values.

Several researchers such as Casanova *et al.* (1996, 1997), Belize *et al.* (1997), Lima (2009), Rodrigues *et al.* (2012b), Marcelino (2015) among others, have studied the oxidation behavior of oxidized sulfide minerals, particularly the iron sulfides pyrite and pyrrhotite along with their particularities. The alteration reactions of the aforementioned sulfides are extremely complex and present, as reported by some authors (AYORA *et al.*, 1998; CHINCHÓN *et al.*, 1995; (CASANOVA *et al.*, 1996; GOMIDES *et al.*, 2007; LIMA, 2009), small divergences in the stoichiometry of the equations, depending mainly on the reaction medium, on the oxidants present and the pH values.

In this context, Gomides (2009) presents the most common pyrite oxidation reactions. In the presence of water and oxygen, pyrite oxidizes, leading to the formation of ferrous sulfate and sulfuric acid, as shown in Equation (2.1).



Still, in the presence of oxygen, ferrous sulfate can react with sulfuric acid resulting in ferric sulfate, as represented in Equation (2.2).



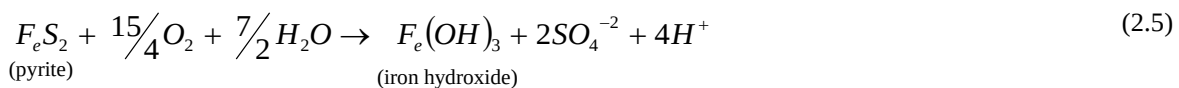
Ferric sulfate, which is a strong oxidizing agent, can react with pyrite one more time in its initial state to form more ferrous sulfate and release sulfur, according to Equation (2.3).



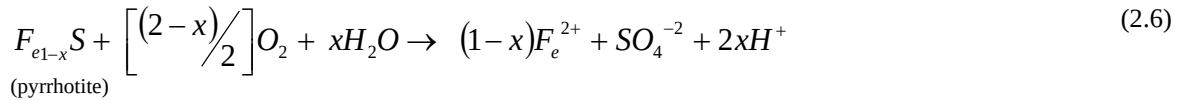
In the presence of water and oxygen, the sulfur which was released can rapidly turn into sulfuric acid, as in Equation (2.4).



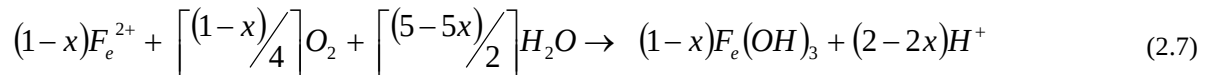
When in the presence of large amounts of water and oxygen, pyrite oxidation generally results in iron hydroxide and sulfuric acid, which dissociates almost completely in (H^+) and (SO_4^{-2}) ions, as can be observed in Equation (2.5). Many authors consider this equation as the global pyrite oxidation equation.



For pyrrhotite oxidation, studies have shown that this iron sulfide oxidation results in the release of a considerable amount of sulfur (MIKHILIN *et al.*, 2002; BELZILE *et al.*, 2004). Nicholson (1970 apud AYORA *et al.*, 1998) claims that the pyrrhotite oxidation equation can be described by Equation (2.6), with x ranging from 0 to 0.125.



The released iron (Fe^{2+}) and the precipitation of iron hydroxide ($Fe(OH)_3$) can raise the acid production as shown by Equation 2.7, in which 1 mole of pyrrhotite can generate more than 1 mole of sulfuric acid according to Nicholson (1970 apud AYORA *et al.*, 1998).



2.3 Internal sulfate attack (ISA) in concrete

In the earliest studies about Portland cement concrete, it was a common belief that the aggregate was an inert component whose only function was filling space, and consequently reducing the final cost of concrete. However, as time passed, many of the concrete properties were found to be influenced by the characteristics of the aggregates, such as shape, size, texture, granulometric distribution, water absorption, strength, and the presence of deleterious substances (SBRIGHI NETO, 2011). Some of the substances in aggregates that may be harmful to the concrete are impurities of organic origin, alkali-reactive minerals, and salts as chlorides, sulfates, and sulfides.

Rocks that are morphologically characterized with the presence of sulfides, in a favorable medium, oxidize releasing sulfate ions and sulfuric acid, which in contact with the Portland cement paste react to produce neoformed compounds, which cause expansion (Lima (2009) and Pereira (2015)).

To approach the effects of sulfide-bearing aggregates, it is crucial to understand the cement hydration mechanisms in the microstructure of concretes. They will be presented here in general terms to contribute to the comprehension of the deterioration mechanisms of concrete by internal sulfate attack.

2.3.1 Concrete - microstructure

Concrete is a material composed mainly of Portland cement, water, and aggregates. The water-cement mixture results in a cement matrix whose aim is to agglomerate the aggregates and bind them through the formation of hydrated products and, hence, develop its strength (CINCOTTO, 2011).

Portland cement is predominantly composed of clinker, a result of calcination, at 1450°C approximatively, of a mixture containing limestone and clay. Corrective chemicals of siliceous, aluminous, or ferriferous nature can also be added. The heat input of the mixture in the kiln causes decarburization of the limestone and restructuration of clay minerals, resulting in four main elements (Ca, Si, Al e Fe) which recombine along with the rotary kiln temperature profile, under negative pressure and alkaline oxidizing environment. The clinker components are then sintered: $3\text{CaO} \cdot \text{SiO}_2$ (alite), $2\text{CaO} \cdot \text{SiO}_3$ (belite), $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ and $4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$. They are stable under such conditions (BATTAGIN, 2011).

In cement chemistry, the adoption of a simplified nomenclature to refer to cement anhydrous or hydrate chemical compounds is usual. This occurs replacing the oxides by letters and using $\text{C}=\text{CaO}$, $\text{S}=\text{SiO}_2$, $\text{A}=\text{Al}_2\text{O}_3$, $\text{F}=\text{Fe}_2\text{O}_3$, $\text{H}=\text{H}_2\text{O}$, $\bar{\text{S}}=\text{SO}_3$. On that account, the main constituents of Portland cement can be expressed as:

- $\text{C}_3\text{S} - 3\text{C}_a\text{O} \cdot \text{S}_i\text{O}_2$ – Tricalcium silicate;
- $\text{C}_2\text{S} - 2\text{C}_a\text{O} \cdot \text{S}_i\text{O}_2$ – Dicalcium silicate;
- $\text{C}_3\text{A} - 3\text{C}_a\text{O} \cdot \text{A}_{12}\text{O}_3$ – Tricalcium aluminate; and
- $\text{C}_4\text{AF} - 4\text{C}_a\text{O} \cdot \text{A}_{12}\text{O}_3 \cdot \text{F}_{e2}\text{O}_3$ – Tetracalcium ferroaluminate.

In short, the hydration of C_3S and C_2S creates hydrated calcium silicates (of much-varied chemical composition and generically represented by C-S-H) and calcium hydroxide ($\text{Ca}(\text{OH})_2$ or CH), also known as portlandite. C-S-H grants strength properties to the cement and represents 50% to 60% of the completely hydrated cement paste solid volume. Portlandite

occupies around 20% to 25% of such volume and maintains the basic pH of the cement material. However, as it is extremely soluble, it can negatively affect concrete durability (METHA and MONTEIRO, 2014).

Aluminates (C_3A and C_4AF) act on cement setting time since they react quickly with the water promoting the hardening of the material. For this reason, gypsum ($CaSO_4 \cdot 2H_2O$) is added to the clinker in the production process to retard the setting time and increase the time during which concrete is workable.

The reaction of gypsum, calcium aluminates and water gives origin to calcium trisulfoaluminate, known as ettringite ($C_6\bar{A}\bar{S}_3H_{32}$). With the passing time, hydration reactions continue to occur and when no more sulfate is left to be consumed, the remaining aluminate converts part of the ettringite into a more stable form, calcium monosulfoaluminate ($C_4\bar{A}\bar{S}H_{12}$) (CINCOTTO, 2011). The aforementioned reactions are shown in Equations (2.8) and (2.9), respectively, presented by Taylor (1997). Figure 2. 1 shows a micrograph of mortar at the age of 315 days, produced with sulfide-bearing aggregates (MARCELINO, 2015).

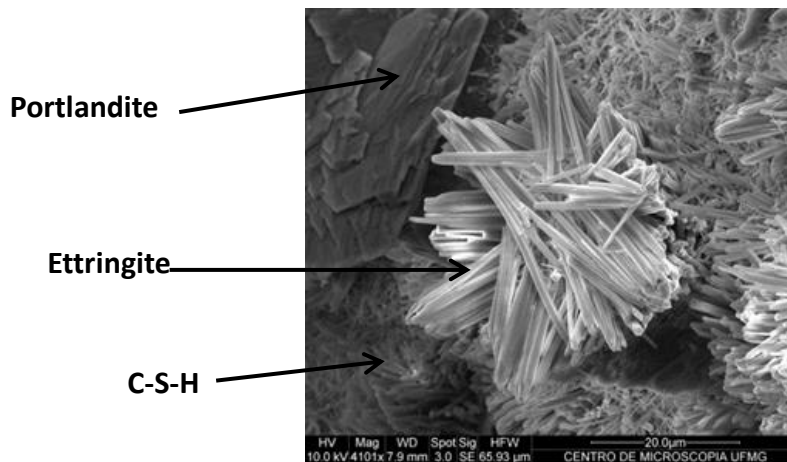
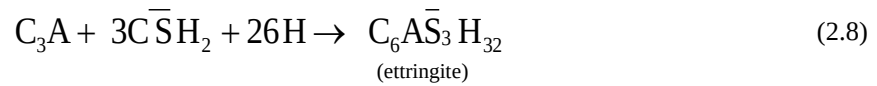


Figure 2. 1: Micrograph of mortar produced with sulfate aggregate - age 315 days (MARCELINO, 2015).

The formation of one or another product following equations (2.8) and (2.9) is essentially controlled by gypsum/C₃A (or another sulfate/C₃A) proportion of a given system. Ettringite becomes a stable hydration product only when sulfate is present in abundance, i.e., high gypsum/C₃A ratio. When the cement presents a low gypsum/C₃A ratio (little sulfate and/or high C₃A content), ettringite becomes unstable and turns into monosulfoaluminate (CASANOVA *et al.*, 1997). Table 2. 1 shows the formation of hydration products for different gypsum/C₃A ratios.

Table 2. 1: Formation of C₃A hydration products (adapted from CASANOVA *et al.*, 1997)

$\bar{C}\bar{S}H_2 / C_3 A$	Hydration products formed
3,0	Ettringite
3,0 - 1,0	Ettringite + Monosulfoaluminate
1,0	Monosulfoaluminate
0	Hydrated calcium aluminate

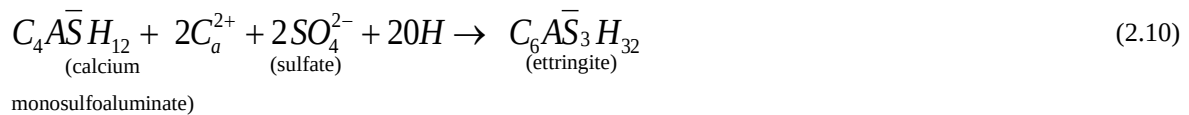
As mentioned before, ettringite is formed in the first hydration hours (it originates from the reaction of gypsum in the cement) and is called primary ettringite. Despite being an expansive product, primary ettringite causes no damage to the concrete since in the fresh state it has the capacity of absorbing the expansion (PRISZKULNIK, 2011; CINCOTTO, 2011). This nomenclature will be adopted herein to distinguish it from delayed ettringite, which is formed in the hardened material due to sulfate attack (COLLEPARDI, 2003).

Mehta and Monteiro (2014) claim that if the predominant phase formed following the hydration process is monosulfoaluminate, the material will be prone to sulfate attack, for these compounds tend to transform into delayed ettringite with time. If ettringite happens to be the predominant phase, shortly after hydration, concrete tends to present good resistance to sulfate attack (DHOLE *et al.*, 2011).

2.3.2 Deleterious action of the sulfides present in the aggregates

A particular form of sulfate attack is internal, deriving from the deleterious action of sulfide-bearing aggregates used in concrete. The referred sulfides, when oxidized, release sulfate ions, which become available in the concrete internal structure (HASPARYK *et al.*, 2005). As described above, the sulfate ions chemically react with some of the compounds of the cement paste as portlandite and C_3A , leading to the formation of expansive products such as calcium monosulfoaluminate and/or calcium trisulfoaluminate also known as ettringite. Studies carried out by Hasparyk *et al.* (2003), Gomides (2009) and Marcelino (2015) investigated the formation of such ettringite crystals in the transition zone between the cement paste and aggregates. After the concrete has hardened, the ettringite formation unchains the phenomenon of internal expansion, which can irreversibly impair the integrity and the structural performance, especially in the case of big-sized hydraulic structures as concrete dams (CASANOVA *et al.*, 1996, 1997).

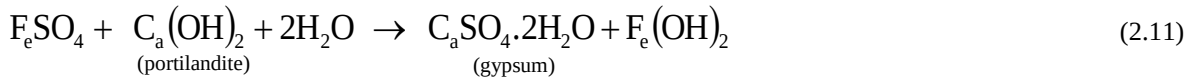
The predominant sulfate attack reaction occurs as shown by Equation (2.10), in which sulfate ions react with the monosulfoaluminate in the cement matrix of the concrete in the presence of calcium, leading to the emergence of ettringite (TAYLOR, 1997).



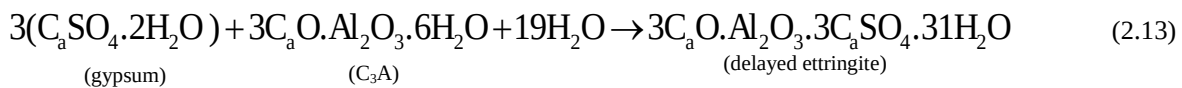
The sulfate ions in Equation (2.10) are in this case supplied by the oxidation of the sulfides present in the aggregates. The calcium ions come from the portlandite; and, after their complete consumption or when they are less available, it can come from C-S-H, which is partially decalcified. This last reaction is much more problematic because of the low solubility of C-S-H in relation to portlandite as well as the consumption of C-S-H leads to concrete to severe deterioration and strength loss (TAYLOR, 1997).

Another product likely to be formed from the aggregates iron sulfides oxidation is gypsum ($CaSO_4 \cdot 2H_2O$). Araújo *et al.* (2008) present these other possible reactions consonantly with equations (2.11) and (2.12). Equation (2.11) shows the reaction of iron sulfate coming from sulfide oxidation with portlandite and water present in the cement, creating gypsum and iron hydroxide. Equation (2.12) presents sulfuric acid (oxidation product) reacting with portlandite

(from hydrated cement) to form gypsum as well. Taylor (1997) states that the reaction forming gypsum (Equations (2.11) and (2.12)) occurs at a stage posterior to Equation (2.10) reaction and also requires the presence of calcium ions.



Gypsum formed in Equations (2.11) and (2.12) in the presence of water can react with tricalcium aluminate (C_3A) to generate expansive delayed ettringite, as shown in Equation (2.13).



This delayed ettringite creates tensile stresses on the hardened concrete, resulting in cracking and deterioration due to its low tensile strength.

Sulfate internal attack reveals itself through extensive cracking, stains, and efflorescence on the surface of the concrete structures. This pathological phenomenon can also lead to a progressive decrease in strength, mass loss, and disaggregation of the concrete caused by cohesion loss of the hydration products. Furthermore, it can cause structural displacement, specifically in dams (CASANOVA *et al.*, 1997; HASPARYK *et al.*, 2005; PRISZKULNIK, 2011).

In structural diagnosis, the main difference between aggregate sulfide oxidation attack and external sulfate attack is that in the former, concrete deterioration spreads through the entire concrete depth or can be more acute in higher humidity zones, whereas in external attack the deterioration advances from the elements surface towards the inner areas, being dependent, hence, of surface porosity and permeability of concrete (RODRIGUES *et al.*, 2012a).

2.4 Sulfide-bearing aggregates attack cases

Studies on the use of sulfide-bearing aggregates in concrete and mortar are usually carried out after the identification of their pathology. Aggregates containing iron sulfides were used in the Graus, Tavascán and Torán dams in Spain in 1992. Chinchón *et al.* (1995), Ayora *et al.* (1998),

and Araújo *et al.* (2008) reported concrete degradation problems in the above-mentioned structures mainly related to severe cracking. To study this pathological phenomenon, these authors conducted microscopic tests from *in situ* samples. These tests aimed to find different concrete compounds from those normally found in cement hydration, which were produced due to the alterations caused by the presence of sulfides and sulfates.

The Graus and Tascaván dams (Figure 2. 2) are the most deeply studied and reported cases found in the literature. A research group at the *Universitat Politècnica de Catalunya* was hired by the electrical company that owned the dams to investigate the cause of the deterioration.



Figure 2. 2: Extensive cracking and stains at the Tascaván dam gate (ARAÚJO, 2008 apud GOMIDES 2009).

Figure 2. 3 shows structural displacement caused by concrete expansion at the Graus dam. The observed displacement was evaluated by the movement of the metallic structure, which was equal to approximately 8 cm horizontally (Figure 2. 3a) and 3 cm vertically (Figure 2. 3b).



Figure 2. 3: Structural displacement at Graus dam (ARAÚJO, 2008 apud GOMIDES 2009)

Concrete samples were extracted from the deteriorated structures of both dams to have their microstructure carefully analyzed. Scanning electronic microscopy examination identified needle-shaped crystals filling cavities and cracks in the cement paste, indicating the formation of delayed ettringite created in the alteration process. Needle-shaped gypsum crystals composing a radial aggregate were also found. Besides visual identification, chemical analyses confirmed that calcium and sulfur were part of such crystals (AYORA *et al.*, 1998).

From the Torán dam concrete samples were taken and examined via optical microscopy and scanning electronic microscopy coupled to an X-ray spectrometer (SEM/EDX). From the micrographs, needle-shaped crystals identified as delayed ettringite were detected in the concrete pores (Figure 2. 4) and at the cement paste-aggregate interface. Cracking on the paste was also found.

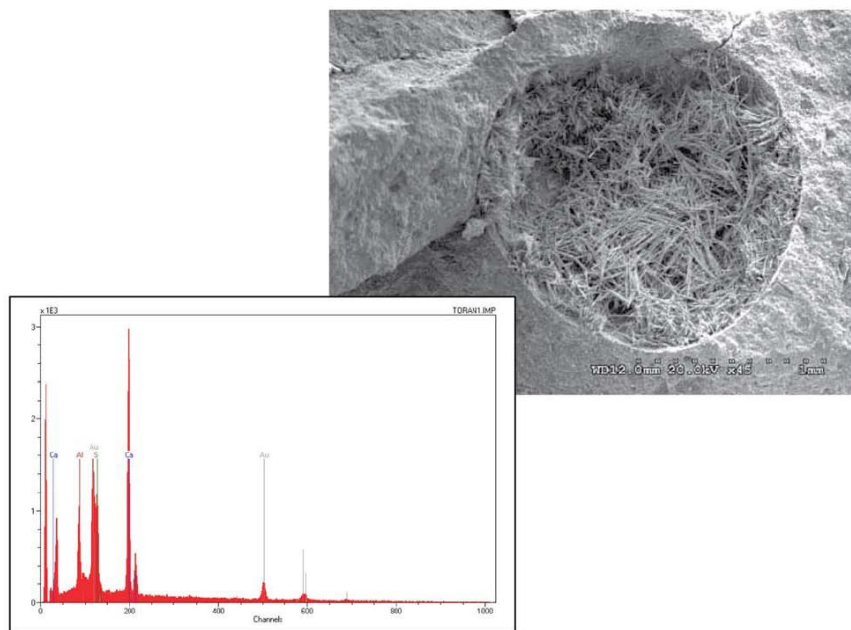


Figure 2. 4: Ettringite in the pore cavity. (ARAÚJO *et al* 2008).

In Brazil, one reported case of a concrete structure presenting sulfide-aggregate-use-related pathologies is the Rio Descoberto dam, built in 1974. Located in Brasília, the dam presented cracks and leakages (Figure 2.5) shortly after its construction, which increased over time. After several interventions and repair attempts, CAESB (Brasilia District Environmental and Sanitation Company) investigated further the causes of the cracks and the conclusion was that they were the result of the expansion due to the use of sulfide-bearing aggregates. The dam was subsequently repaired with the construction of a large diaphragm wall (SOARES *et al.*, 2003).

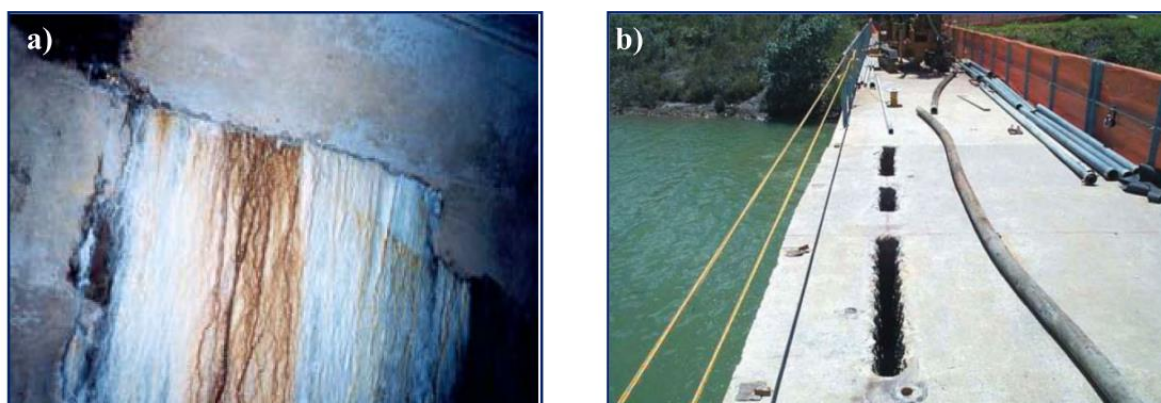


Figure 2. 5: Appearance of Barragem Rio Descoberto: a) crack due to the presence of acidic water and pyrite in the concrete aggregate, b) construction of the diaphragm wall (ECL, 2003 apud BATISTA, 2013).

In Switzerland, a dam built in the early 1970s used sulfide-bearing aggregates. Since the early 1980s, the concrete in this dam has been constantly expanding. The dam has been monitored continuously and in 1998 the upstream displacement was 20mm at the top a 5mm in the middle gallery. In 2011 the respective values were 45 and 10mm [Schmidt *et. al.* 2011]. The extracted and quarried aggregates consisted mainly of schists. The content of ores in the aggregate was analyzed and pyrite and pyrrhotite were the most frequent ones. Schmidt *et. al.* (2011) investigated the physical and microstructural aspects of iron sulfide degradation in concrete and concluded that the degree of reaction of the iron sulfides did seem to be related to the position of the particles within the aggregates. The microstructure of the concrete samples was examined by scanning electron microscopy SEM (FEI QUANTA 200) using backscattered electron imaging (BSE) and energy-dispersive X-ray spectroscopy (EDS).

Another reported case refers to houses and buildings built between 2004 and 2008 in the area of Trois-Rivières, Quebec, Canada (Figure 2. 6). They presented severe deterioration of the concrete used in their foundations after three to five years of construction. Norite or hypersthene gabbro aggregates (designated MSK) obtained at a nearby mine were used. This aggregate contained pyrite and pyrrhotite with a total sulfur content ranging from 0.73% to 1.28%, (RODRIGUES *et al.* 2012a, 2012b, 2013, 2016). Extensive cracking, pop-outs, and yellow stains were observed on the foundation concrete surface (Figure 2. 7).



Figure 2. 6: Extensive cracking on the foundation blocks of a house in Quebec, Canada (RODRIGUES *et al.* 2012b).



Figure 2. 7: Typical degradation signs observed in foundation concrete containing sulfide-bearing aggregates in the Trois-Rivières area (RODRIGUES *et al.*, 2016b)

Rodrigues *et al.* (2012a, b, 2013, 2016b) highlight that most of such affected foundations were demolished and replaced, given the severe concrete deterioration (Figure 2. 8).



Figure 2. 8: Typical concrete foundation replacement process in the Trois-Rivières area: a) coating removal; b) foundation concrete demolition; c) shored house; and d) placement of the new concrete foundation (RODRIGUES *et al.*, 2016b)

Recently it was reported in the United States, in the region of Eastern Connecticut, severe premature deterioration of concrete foundations (Figure 2.9). Aggregate containing pyrrhotite was unwittingly used in concrete construction for over twenty-five years in this region. The symptoms observed included map cracking, as well as whitish deposits at the vicinity of cracking surfaces and wide crack openings (Figure 2.10). The affected structures required immediate remedial action (ZHONG and WILLE, 2018; GEISS and GOURLEY, 2019).



Figure 2. 9: Basement wall affected by internal sulfate attack. (GEISS and GOURLEY, 2019)



Figure 2. 10: Symptoms of deteriorated concrete foundation. (ZHONG and WILLE, 2018)

Table 2. 2 groups the structures presented in this item, with the sulfide contents found in the aggregates used, as well as their main concrete pathologies.

Table 2. 2: Deteriorated concrete structures due to sulfide-bearing aggregate use.

Structure	Aggregate sulfide content and type	Concrete deterioration	Reference
Graus and Tavascán dams (Espanha)	0,8% (Pyrrhotite)	Cracking, concrete degradation, structural displacements	AYORA <i>et al.</i> , 1998
Rio Descoberto Dam (Brasil)	Low levels (Pyrite)	Cracks, leaks, percolation planes	SOARES <i>et al.</i> , 2003
Torán Dam (Espanha)	2% (Pyrrhotite + Pyrite)	Extensive cracks, surface color changes, structural displacements	ARAÚJO <i>et al.</i> , 2008
Dam (Switzerland)	0.28% by aggregate volume (Pyrrhotite + Pyrite)	Cracking in aggregates and concrete	Schmidt <i>et. al.</i> 2011
Trois-Rivières house foundations (Quebec – Canadá)	≈1% of S by aggregate mass (Pyrrhotite + Pyrite)	Extensive cracks, concrete deterioration - need to demolish and replace foundation	RODRIGUES <i>et al.</i> , 2012a, b, 2013, 2016b
Foundation Houses (Connecticut – USA)	2.54% by aggregate mass (Pyrrhotite)	Map cracking, whitish deposits at the vicinity of cracking surface and wide crack openings	ZHONG and WILLE, 2018

2.5 Aggregate reactivity – sulfide oxidation potential

Studies on the reactivity of sulfide-bearing aggregates, regarding their oxidation potential, have contributed to the evaluation of the deleterious potential this material might have if used in mortar and concrete. In this item, research and test results on this matter are presented.

In the 1950s, Midgley (1958 apud RAMOS *et al.*, 2015) proposed a quick qualitative test for the verification of aggregates containing sulfide. This test was based on the observation of samples immersed in a saturated lime solution. After 30 minutes, the deemed reactive materials presented a greenish-blue-colored sulfide oxidation product on their surface, which turned brown when exposed to oxygen. No particle size or sample quantity was mentioned by the author. MacDonald (2014), in private communication with Ramos *et al.* (2015), claims that this method cannot be considered effective for all sulfide-bearing rock types.

To evaluate the deleterious effects of sulfide-bearing aggregates in concrete is important to identify and quantify the main sulfides present in the aggregate. Marcelino (2015) has developed a protocol to identify and quantify pyrite and pyrrhotite sulfides in aggregates produced from drill holes of the Irapé HPP area. Aggregates were first crushed and sieved to achieve the size distribution according to the requirements of NBR 15577 – part 4 (ABNT, 2008). 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. The final aggregate size distribution obtained from the crushing procedure are shown in Table 2.3.

Table 2. 3: Aggregate particle size distribution (MARCELINO, 2015).

Mesh opening size	Final aggregate particle size distribution after crushing
(mm)	(%)
6.3	7.5
4.8	28.4
2.4	20.1
1.2	14.1
0.6	7.0
0.30	3.4
0.15	3.4
0.10	2.7

< 0.10	8.6
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For qualitative verification of the pyrite and pyrrhotite presence, RAMAN spectroscopy analyses were performed. The Raman spectrum provides information about the vibration modes of a material generating specific spectral patterns. Comparison with these standards allows qualitatively to identify the presence of atoms and their compounds (NASDALA *et. al.*, 2001). The pyrrhotite spectrum is characterized by peaks in the 80 and 120 cm^{-1} spectral bands and approximately constant intensity between the 220 and 300 cm^{-1} bands (Figure 2.11(a)). The pyrite spectrum is characterized by the presence of intense and fine peaks, typical of very crystalline material (CALDEIRA *et al.*, 2005). This sulfide has its main spectral bands at 343, 379 and 430 cm^{-1} as shown in Figure 2.12 (a). Figures 2.11(b) and 2.12(b) show the spectra found for the samples analyzed by Marcelino (2015) confirming the presence of sulfides.

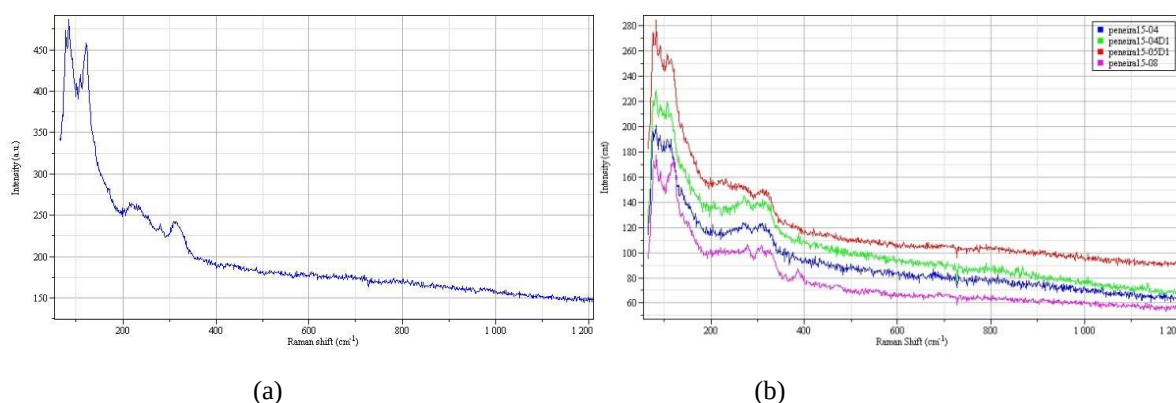


Figure 2.11: Pyrrhotite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample (MARCELINO, 2015).

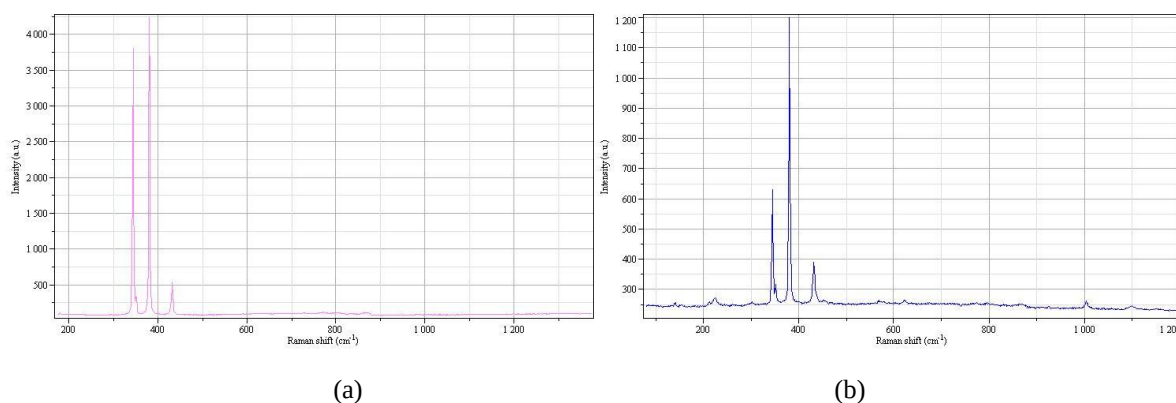


Figure 2.12: Pyrite RAMAN spectroscopy (a) standard pattern (b) Irapé aggregate sample (MARCELINO, 2015).

The total sulfur and that from pyrite and pyrrhotite content in aggregate were evaluated by Marcelino (2015) as follows. First, aggregate samples were crushed to a grain size smaller than or equal to 0.15 mm. They were then dried in an oven at 40°C, for approximately 24 hours for water evaporation. The total sulfur content was then determined through direct combustion (with infrared detection) using the equipment LECO SC 632 (Figure 2.13). This material had an average sulfur content of 2%, which is equivalent to average iron sulfide content (pyrite + pyrrhotite) of 5%, due to the stoichiometry of these compounds.



Figure 2.13: (a) Aggregate sample for direct combustion test (b) Equipment LECO SC 632 (MARCELINO, 2015).

For the evaluation of the content of the different iron sulfides, a leaching process (LOREZEN, 1995) was employed. For the selective dissolution of the pyrrhotite, 1g of the smashed aggregate sample was blended with a 100ml hydrochloric acid solution (HCl), in the proportion of (1:1) in an Erlenmeyer flask, and agitated for an hour at 60°C. Next, the material was put in a funnel containing a filter paper to drain the solution (Figure 2.14). The material was then washed with distilled water, so all HCl could be removed. Then it was dried in an oven at 40°C for 24 hours. A portion of this dried material was subjected to direct combustion testing (LECO) for the determination of total residual sulfur content, which corresponds to the sulfur from pyrite. The value found was 0.60%. The difference between the total initial sulfur content (not leached) and the residual content (pyrite) corresponds to the sulfur content from the pyrrhotite, ie 1.40%.



Figure 2.14: Iron sulfides leaching process (MARCELINO, 2015).

To verify the efficiency of this methodology, pyrite must be dissolved and leached. For this, 1g 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_3). This solution was agitated for 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. Marcelino (2015) performed direct combustion analysis after this dissolution in *aqua regia* and found values very close to zero, validating the method.

Gomides (2009) researched the effects of sulfide-bearing aggregates on concrete and reached the conclusion that the fine aggregates altered more in comparison with the coarse aggregates. Gomides attributes this phenomenon to the larger sulfide specific surface area and higher oxidation rates and deterioration mechanisms as a consequence.

Chinchón-Payá *et al.* (2012) verified that aggregates containing pyrrhotite oxidize at a higher rate than those having the same amount of pyrite. The authors carried out an experiment in which they evaluated the reaction potential of samples containing 95% aggregates with none to the little amount of sulfur and 5% sulfides (pyrite or pyrrhotite) with granulometry between 1 mm and 0.5 mm. Sulfide-aggregate mixture samples weighing 15g were put into recipients with 200 mg water and exposed to oxygen flowing at a 120 mbar pressure. Pure pyrite and pyrrhotite samples of 10 g were also analyzed under identical conditions (Figure 2.15). Fifty days after the beginning of the experiment, the SO_4^{2-} and Fe^{2+} ions released into the water were measured using ion chromatography (

Table 2. 4).



Figure 2.15: Oxygenation of pyrite and pyrrhotite samples (Chincón-Payá *et al.*, 2012)

Table 2. 4: Fe^{2+} and SO_4^{2-} concentration in the samples. Aggregates: M- Marlstone, L-Limestone, S-Schist. Sulfides: Py – pyrite, Po – pyrrhotite. (Chincón-Payá *et al.*, 2012)

Sample	Sulfur g	Aggregate g	% S	% Fe	SO_4^{2-} ppm	Fe^{2+} ppm
Po	10	–	35.18	61.12	1517.8	455
Py	10	–	49.03	46.37	1238.7	270
M-Po	0.757	14.261	1.77	5.91	36.36	0
M-Py	0.769	14.251	2.50	5.17	24.74	0
L-Po	0.752	14.298	1.76	3.87	36.61	0
L-Py	0.759	14.260	2.48	3.13	23.31	0
S-Po	0.751	14.260	1.77	10.71	37.89	0
S-Py	0.753	14.300	2.45	9.97	20.43	0

From these results, Chinchón-Payá *et al.* (2012) concluded that the oxidation dynamics is different for different sulfides: pyrrhotite generates more sulfates than pyrite (in proportion to the initial amount of sulfur), which indicates that the pyrrhotite oxidation is more deleterious to concrete. This is explained by the fact that when more sulfate is released the chances of secondary ettringite formation in the hardened concrete increase, which can cause damage such as cracking. In the case of an aggregate-sulfide mixture, this behavior was the same: solutions containing pyrrhotite released a greater amount of sulfates despite having a smaller amount of the total initial sulfur than that observed in the solutions containing aggregate and pyrite.

Pereira (2015) developed another study on the reactivity of sulfide-bearing aggregates and sought to analyze the reactivity of such aggregates through the static Net Acid Generation

procedure, also known as pH NAG, and by paste pH determination. The material analyzed was fine aggregate conforming to the following specifications:

- i) crushed limestone sand (control aggregate);
- ii) control aggregate with 1% pyrite;
- iii) control aggregate with 5% pyrite;
- iv) control aggregate with 10% pyrite;
- v) quarry sand, composed of a heterogeneous rock with 1% - 5% pyrite content;
- vi) pure pyrite.

Net Acid Generation test (pH NAG) consists of oxidizing minerals in a 15% hydrogen peroxide (H_2O_2) solution. This solution is heated until the complete decomposition of the hydrogen peroxide (bubbles are no longer seen), and when the solution has cooled the pH is read. The sample is then titrated with a solution of 0.01 mole/l of NaOH until the pH reaches 4.5. In Pereira's work (2015), the acidic potential (NAG), expressed in kg of H_2SO_4 /t, was determined using the methodology proposed by Lima (2009) as shown in Equation (2.14):

$$NAG = \frac{49 \cdot V \cdot M}{W} \quad (2.14)$$

Where:

V= volume of titrated NaOH (ml)

M= Molarity of NaOH used in the titration (moles/ liter)

W= Mass of the sample (g)

The pH NAG results were very similar, in the sense that the methodology did not turn out to be effective in the distinction among the different sulfur contents in the aggregate mixtures.

Pereira (2015) highlights that the solutions diverse colors can be attributed to the pyrite content and indicates the solubilization of the compounds, suggesting as further development the quantification of iron and sulfur contents available in the solution. The author claims this is a

parameter of relevance to the analysis of the aggregate reactivity when they are used in concrete and mortar (Figure 2.16).

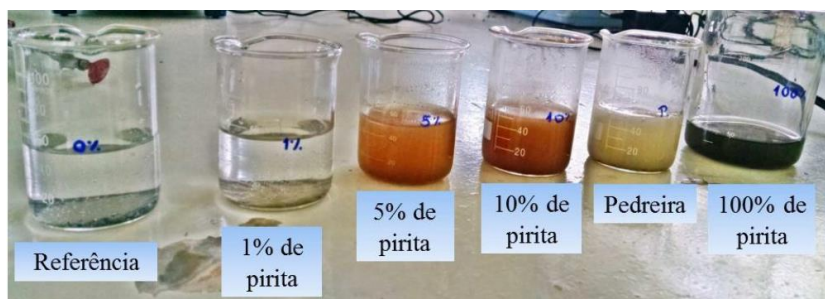


Figure 2.16: Aggregate samples with different pyrite contents oxidized in hydrogen peroxide (PEREIRA, 2015).

The other method Pereira (2015) used to analyze the aggregate reactivity was named paste pH, as explained by the author:

The determination of the “paste pH”, presented by Sobek *et al.* (1978), identifies the degree of alkalinity of the samples, providing an indication of the acidic character of the material. The results are obtained through the direct pH measurement of a mixture containing distilled water and the aggregate, in different observation times. The methodology proposed by Sobek indicates measurements every 15 minutes after the mixture preparation until the test completes 1 hour, comprising 4 measurements total. In this work, hourly measurements after the first hour were also taken until the pH values became stable. (PEREIRA, 2015, my translation)

The results from the paste pH determination test are shown in Figure 2.17, with 15-minute intervals (initially) and subsequent hourly readings, in a total analysis time of 7 hours.

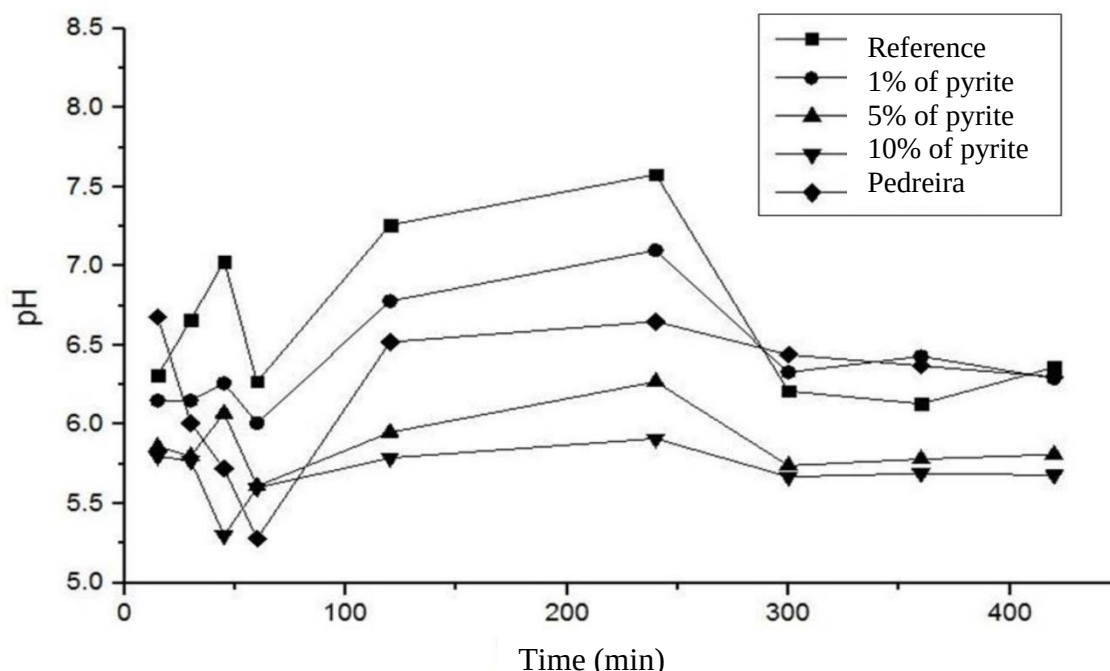


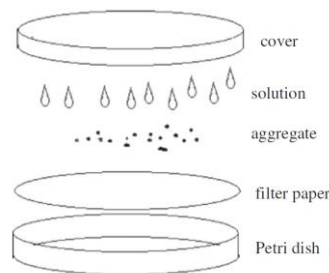
Figure 2.17: pH variation in samples with different pyrite contents and for the Pedreira aggregate in relation to time – paste pH determination test (PEREIRA, 2015).

The stability of the pH values was reached after five hours of test and the values found were not enough to distinguish aggregates with different pyrite amounts.

Research carried out in Canada by Ramos *et al.* (2015) presented a quick chemical test to assess the deleterious potential of a sulfide-bearing aggregate. The authors used six sulfide-bearing aggregates (MSK, B&B, GGP, SB, SW, SPH – Table 2. 5) originating from distinct rocks and diverse iron sulfide contents and two control aggregates (PKA and HPL) whose characteristics and sulfur content are in Table 2. 5. The aggregate particle size ranged from 9.5mm and 600 μm . The test procedure was: 20 g of each aggregate were carefully spread on a Petri dish (150mm x 15mm) over a Whatman n° 42 (125 mm) filter paper. Sixty ml of oxidizing solution was added to the samples and the Petri dish was covered with a lid for protection (Figure 2.18). This procedure was repeated for four distinct types of oxidizing solutions: lime-saturation solution, 3% NaCl, 3% H_2O_2 and 6% NaClO. After 8 days, the filter was washed with distilled water to remove both the solution and the aggregate particles. It was then dried in an oven at 60°C and had its color analyzed.

Table 2. 5: Characteristics of the investigated aggregates. (RAMOS *et al.*, 2015)

Aggregate	Rock type		Mineralogy		% S _T by mass
			Main mineral constituents	Iron sulfur minerals	
Sulfide-bearing aggregates	MSK	Norite or hypersthene gabbro	Plagioclase Biotite Pyroxene Quartz	Pyrrhotite Pyrite Chalcopyrite Pentlandite	0.73–1.28
	B&B	Gabbro	Pyroxene Plagioclase Quartz Biotite K-Feldspar	Pyrrhotite Pyrite Chalcopyrite	2.13–4.22
	GGP	Granitic gneiss	Quartz Hornblende Pyroxene Plagioclase	Pyrrhotite Pyrite Chalcopyrite	0.24–0.33
	SB	Hornfel	Feldspars Quartz Clays Organic matter	Pyrrhotite Pyrite Chalcopyrite Sphalerite	0.75–0.87
	SW	Mica Schist	Quartz Feldspars White mica Amphibole	Pyrrhotite Pyrite Chalcopyrite	0.05–0.07
	SPH	Phyllite	Quartz Feldspar White mica Chlorite	Pyrrhotite Pyrite Chalcopyrite	0.09–0.32
	SDBR	Gabbro	Plagioclase Pyroxene Biotite Epidote Apatite	Pyrrhotite Pyrite Ilmenite Chalcopyrite Pentlandite	13.86–14.46
	PKA	Anorthosite	Plagioclase Hornblende Biotite	–	0.04–0.06
	HPL	Limestone	Carbonates	–	0.02

Figure 2.18: Test setup (RAMOS *et al.*, 2015)

The test using lime solution resulted in weak rust stains for all filters after 8 days of storage, except those with control aggregates PKA and HPL, which bore no stains at all. In the test using NaCl as an oxidizing agent, the filters with aggregates SPH, MSK, SB, and B&B had weak rust stains right after 4 days; and after 8 days, the PKA filter also contained a weak rust stain. Stains

were already evident right after 3 days on the filters of MSK, GGP, SB, and B&B aggregate with H_2O_2 as an oxidizing agent and light staining for SB and B&B. The same observations were made after 8 days, except for the filter of B&B aggregate, which presented heavy staining. Some filters with the H_2O_2 solution disintegrated as shown in Figure 2.19.

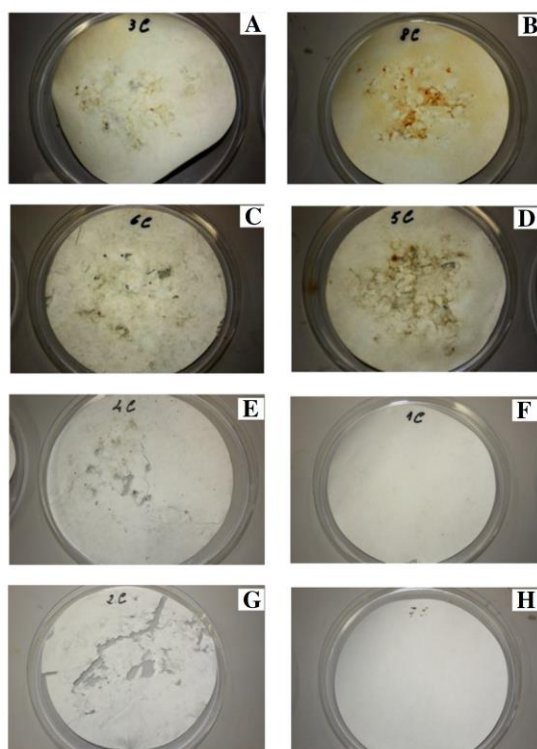


Figure 2.19: Results of the test after 8 days for a H_2O_2 solution: A) MSK; B) B&B; C) GGP; D) SB; E) SW; F) SPH; G) PKA; H) HPL. (RAMOS *et al.*, 2015)

The use of the $NaClO$ solution led the formation of rust on the surface of aggregates SPH, SB, GGP, MSK e B&B (Figure 2.20 and 2.21) with 30 minutes of testing, and by the third day, there was heavy staining on the filters of MSK e B&B. However, after 8 days, the filters were completely destroyed and effective removal of the solid particles for evaluation was made impossible. The filters were, then, replaced by chemist cloth gown, and the test period was reduced to 3 days for the $NaClO$ solution.

During this phase, a volume of 4.75 ml of aggregate with particles varying from 1 mm to 5 mm was used aiming to reduce the number of particles on each Petri dish and the high variability of the former samples. Both chemist cloth gown and paper filters were used. The SW, HPL, and PKA (Figure 2.21) aggregate samples showed no sign of rusting while MSK e B&B (Figure 2.20) presented heavy staining on the cloth gown. For the SDBR sample (Figure 2.21), the

staining observed was not very strong after the removal of the solids and washing the cloth with distilled water, despite this sample have the highest sulfur content. Nevertheless, a dark oxidation product was observed before washing.

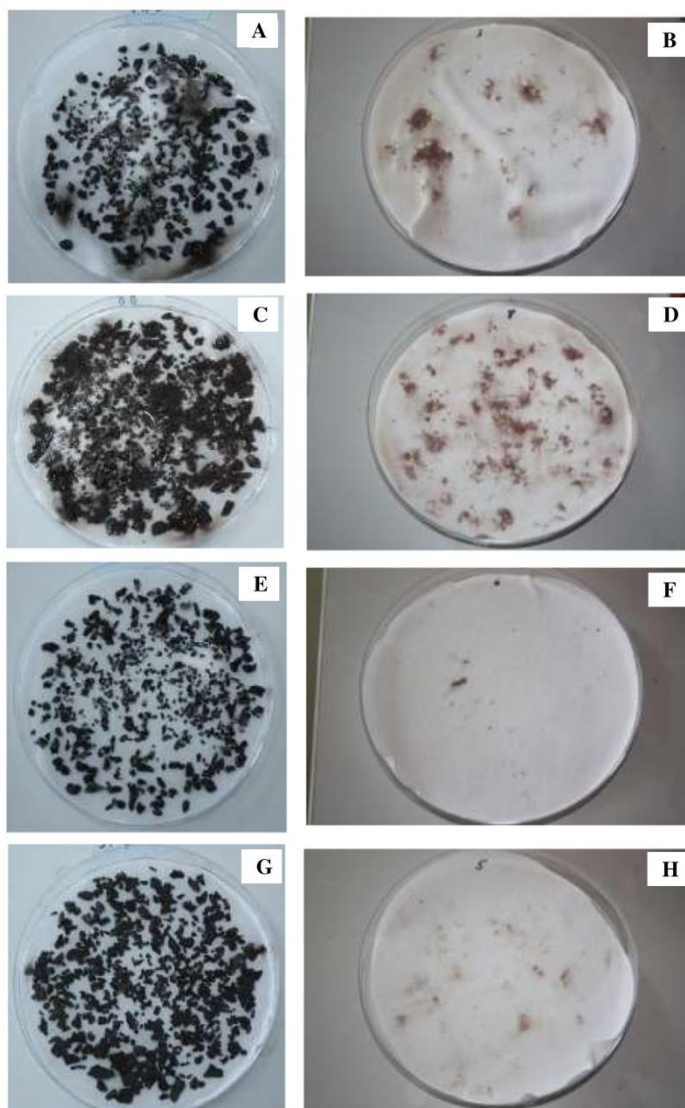


Figure 2.20: Results of the three-day test using NaClO solution. The images to the left show the aspect of the aggregates at the end of the test and the images to the right show the aspect of the chemist cloth gown after the removal of the particles, rinsed with distilled water and dried in an oven: A and B) MSK; C and D) B&B; E and F) GGP; G and H) SB. (RAMOS *et al.*, 2015)

Ramos *et al.* (2015) concluded that the saturated solution and the NaCl solution are not good oxidant agents due to their weak formation of stains in the filters of all sulfide-bearing aggregates (Figure 2.21). The results with H₂O₂ were slightly more efficient but not satisfactory, as they did not reveal the deleterious potential of the MSK. The test results also indicated that

the three-day test using a 6% NaClO solution was more effective, though for a complete analysis both the Petri dish containing the oxidized aggregates and the piece of chemical cloth washed and dried should be analyzed. The analysis also revealed that the results are in agreement with the total amount of sulfur present in each aggregate, as shown in Table 2. 5. The conclusion regarding the reactivity potentiality of the aggregates using this method was: first, among the aggregates containing sulfide, only the SW, with approximatively 0.06% of total sulfur, was considered non-reactive; second, all the others must undergo additional analysis to verify their deleterious potential.

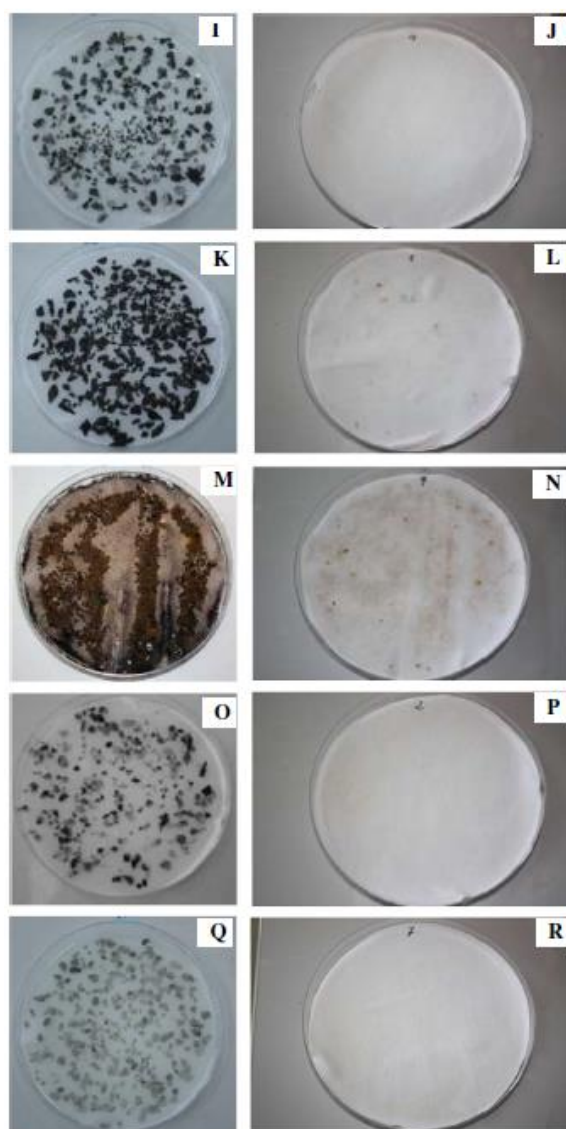


Figure 2.21: Results of the three-day test using NaClO solution. The images to the left show the aspect of the aggregates at the end of the test and the images to the right show the aspect of the cloth after the removal of the particles, rinsed with distilled water and dried in an oven: I and J) SW; K and L) SPH; M and N) SDBR; O and P) PKA; and Q and R) HPL. (RAMOS *et al.*, 2015)

Rodrigues *et al.* (2016a) studied the reactivity of the same aggregates studied by Ramos *et al.* (2015) (Figure 2. 3), evaluating the potential of oxygen consumption of the material. To do so, an aggregate layer was exposed to oxygen (O_2) inside of a hermetically closed cell and the consumption of O_2 was monitored. Aggregates with particle size, varying between 1.18 mm and smaller than 150 μm were evaluated. The results showed that the distribution of the particle sizes is an important factor in the oxidation reaction of the sulfides and that the smallest particle size studied showed the highest oxygen consumption. After several tests, the authors concluded that the optimal parameters for the realization of this experiment are as follows: a 10 cm aggregate layer with particles smaller than 150 μm , kept in a saturation degree of 40% and a space of 10 cm to the top of the cell (Figure 2.22). The oxygen consumption present in this space between the aggregate and the cell lid was monitored for 3 hours of testing, at a temperature of 22°C. The authors verified that the highest O_2 consumptions were obtained for the aggregates with a higher sulfur percentage and that they reached a limit, for the studied aggregates, of 5 % of O_2 consumption, which would allow considering the material as non-reactive regarding the oxidation of sulfides. However, the authors highlight that the threshold value is still preliminary and must be validated through tests with a larger number of different aggregates.



Figure 2.22: Oxygen consumption test (RODRIGUES *et al.*, 2016a).

Goto *et al.* (2016) evaluated the sulfide oxidation processes in which the effects of the aggregate sizes (Phase 1) and the quantity of pyrite (Phase 2) were investigated. Aggregates containing between 1% and 3% of total sulfur were used.

Three aggregates particle sizes were analysed in Study 1: small ($2.36 \text{ mm} < \Phi < 4.75 \text{ mm}$), medium ($6.30 \text{ mm} < \Phi < 9.50 \text{ mm}$) and large ($19.00 \text{ mm} < \Phi < 37.50 \text{ mm}$). Each group was subjected to two types of immersion for 30 days: distilled water (neutral solution) and a

saturated solution of calcium hydroxide (alkaline solution), both constantly aerated by an air compressor with a pressure of 100mbar (Figure 2.23) and at a temperature of $24 \pm 2^\circ\text{C}$. Goto *et al.* (2016) justify the use of the calcium hydroxide solution with its high pH that is similar to the one found in the interior of concrete structures. The pH and electric conductivity were monitored over time.

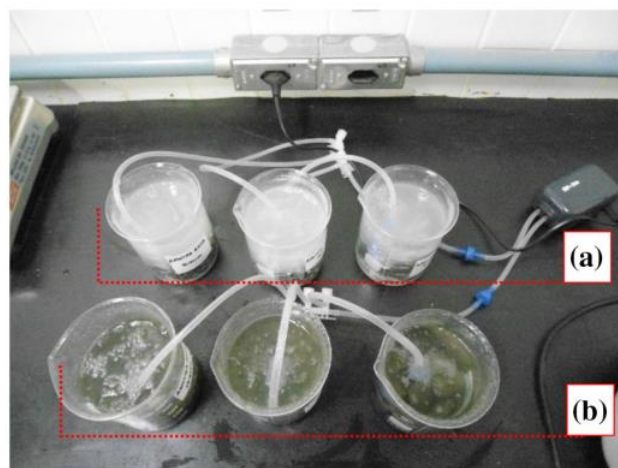


Figure 2.23: Test with different aggregates particle sizes immerse in a) alkaline solution and b) neutral solution (GOTO *et al.*, 2016).

During the exposition in Phase 1, the oxidation reaction of the sulfides caused the hydrogen to be released to the solution, decreasing the pH in both exposition series, in the distilled water, and in the calcium hydroxide solution ($\text{Ca}(\text{OH})_2$). The small and medium particle sizes showed a decrease in the pH very close to and higher than the one observed for the large-sized-particle aggregate. The authors claim that such behavior is due to the difference of specific surface area, for the smallest particle has the largest area and consequently greater effect on the internal attack by sulfate. The samples immersed in water did not show any difference in the pH variation, as can be verified in Figure 2.24.

The monitoring results of the electric conductivity showed similar behavior to the ones obtained in the pH monitoring: the alkaline solutions containing the submerged small and medium-size aggregates showed great variation in the electric potential during the study time. The large-sized aggregate in alkaline solution and all sizes aggregates in neutral solution (distilled water) did not show any significant variation in the electric conductivity values (Figure 2.25).

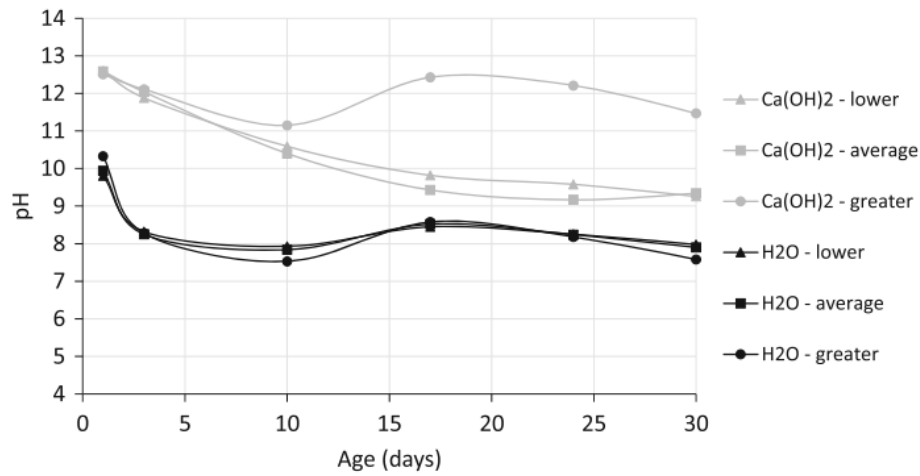


Figure 2.24: Variation in the measured pH values for the different solutions and particle sizes (GOTO, 2016).

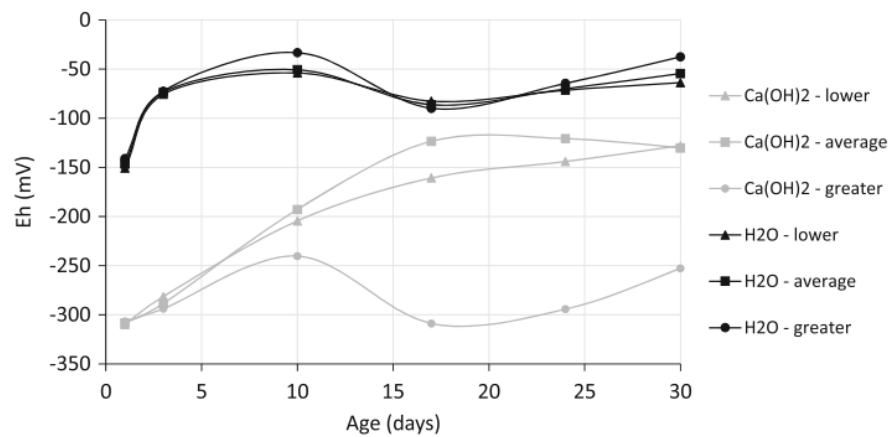


Figure 2.25: Electrical potential for different solutions and particle sizes (GOTO, 2016).

This way, it is possible to conclude that, regarding the granulometric variation of the aggregates, the smaller the particle, the larger the oxidation propensity of the sulfide. It is concluded too that the alkaline medium is more influential in the oxidation reactions, since in neutral solution there was no variation in the behavior, independently of the aggregate granulometry.

In Phase 2, natural sand was analyzed, without the presence of sulfur oxides in its composition, as well as with the addition of pyrite in four different theoretically calculated rates of SO_3 : reference (0%); 0.5%; 1.0%, and 5.0% in aggregate mass. Crushed sand containing $\text{SO}_3 \approx 0.3\%$, originated from the same rock used in Phase 1 was also evaluated: however, it had a smaller size, so it could resemble the granulometry of the natural sand contaminated with pyrite. The samples were kept submerged for 30 days in distilled water, constantly aerated by an air compressor with the pressure of 100 mbar and a temperature of $24 \pm 2^\circ\text{C}$. It was observed that

the pH of the samples contaminated with 0.5, 1.0 and 5.0% of pyrite in mass showed values between 3 and 4, while the artificial sand (<0.5%) and the control sand (0%) showed pH close to 7.0.

The results of the electrical potential variation showed different values, however similar to all samples, except to the one contaminated with 5.0% of SO_3 , that presented higher values and more accentuated growth (Figure 2.26). Based on these results, Goto *et al.* emphasized that the electrical potential measurement allowed the evaluation of the different levels of SO_3 contamination in the samples.

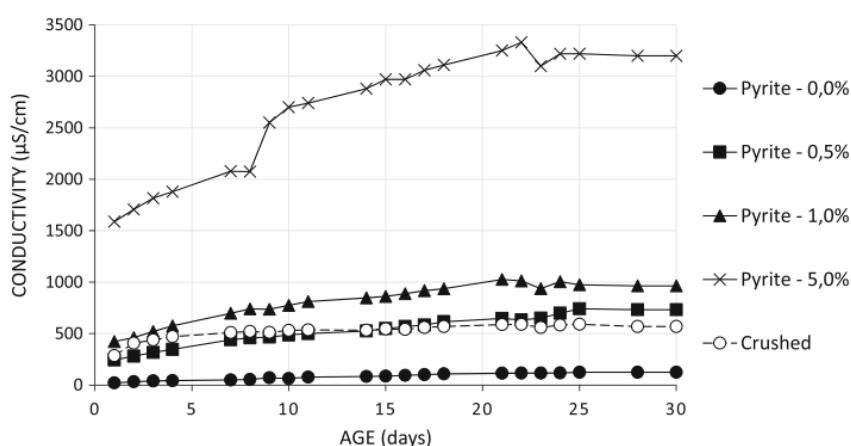


Figure 2.26: Electrical potential for the different solutions and SO_3 contents (GOTO, 2016).

Guirguis and Shehata (2017) developed a simple screening test to evaluate aggregates for their potential to cause damage when used in concrete due to the oxidation of sulfide phases. The test consisted of soaking aggregates in an oxidizing agent for some time and measuring mass loss. Aggregates with different sulfur contents were used in this study and they were divided into three categories: (1) aggregates that are known to have sulfide content or have caused deterioration when used concrete; (2) aggregates that are alkali-reactive; (3) aggregates that have no known issues related to sulfide (Table 2.6).

Table 2. 6: Aggregate mineralogy and total sulfur content. (GUIRGUIS and SHEHARA, 2017)

Cate-gory #	Agg. ID	Primary rock type	Composition [*]	Iron sulphur mineral	Total sulphur(S _T %)
1	GAB 1	Gabbro	Entirely ore mineral	Po, Py, Ccp, Pn ^{**}	20
1	GAB 2	Gabbro	Entirely ore mineral	Po, Py, Ccp, Pn	20
1	QTZ 1a	Quartz-biotite schist	Qz, Fsp, Bt, Ms	Po, Py, Jrs, Lm	1.50
1	QTZ 1b	Quartz-biotite schist	Qz, Fsp, Bt, Ms	Po, Py, Jrs, Lm	0.54
1	GAB 3 ^{***}	Gabbro	Pl, Bt, Qz	Po, Py, Ccp, Pn	0.73–1.28
1	GAB 4 ^{***}	Gabbro	Pl, Bt, Qz, K-Fsp	Po, Py, Ccp	2.13–4.22
2	LIM 1	Dolomitic limestone	Cal, Dol, Clay minerals	–	0
2	LIM 2	Siliceous limestone	Cal, Dolomite Cht, Clay minerals	–	0
2	GRAV 1	Siliceous gravel	Sst, Qz, Grt, Db, Gns	–	0
3	DOL 1	Dolostone	Dol	Gp, Py	0.150
3	LIM 3	Limestone	Cal	–	0.038
3	DOL 2a ^{****}	Dolostone	Dol	–	0.007
3	DOL 2b ^{****}	Dolostone	Dol	–	0.007
3	LIM 4	Limestone	Cal	–	0.046
3	DOL 3	Dolostone	Dol	Gp, Py	0.140
3	DOL 4	Dolostone	Dol	–	0.017
3	GRAV 2	Carbonate dominant gravel	90% Cb, 10% Siliceous	Py	0.180
3	GNS 1	Mafic gneiss	Pl, Bt, Qz, Amb	Py	0.110
3	GAB 5	Gabbro	Act, Pl, Chl, Mag	–	0.039
3	ANRS ^{***}	Anorthosite	Pl, Hbl, Bt	–	0.04–0.06
3	DOL 5	Dolostone	Dol	–	0.007
3	DOL 6	Dolostone	Dol	Py	0.30
3	LIM 5	Limestone	Cal	–	0.059
3	GAB 6 ^{****}	Gabbro	Amp, Pl, Mag, Bt	Po, Py	0.15
3	BAS 1a ^{****}	Basalt	Act, Pl, Bt, Chl, Mag	–	0.027
3	BAS 1b ^{****}	Basalt	Act, Pl, Bt, Chl, Mag	–	0.027
3	QTZT	Quartzite	Qz	–	0.024
3	LIM 6	Limestone	Cal	–	0.06
3	GNS 2	Granite to granite gneiss	K-Fsp, Qz, Pl, Bt	–	0.009
3	GRAV 3	Siliceous gravel	Gns, Grt, Gab	–	0.010
3	GRAV 4	Siliceous gravel	Mafic to intermediate granite gneiss	–	0.050

^{*} Main rock and/or mineral compositions in decreasing order of abundance (listed most to least abundant).

^{**} Minerals abbreviations [31]: Pyrrhotite = Po, Pyrite = Py, Chalcopyrite = Ccp, Pentlandite = Pn, Quartz = Qz, Feldspar = Fsp, Biotite = Bt, Muscovite = Ms, Jarosite = Jrs, Limonite = Lm, Plagioclase = Pl, Calcite = Cal, Dolomite = Dol, Chert = Cht, Sandstone = Sst, Granite = Grt, Diabase = Db, Gneiss = Gns, Gypsum = Gp, Carbonate = Cb, Amphibole = Amp, Actinolite = Act, Chlorite = Chl, Magnetite = Mag, Hornblende = Hbl.

^{***} GAB 3, GAB 4 and ANRS aggregates are the same aggregates defined as MAS, B&B, and P, respectively in Ref. [11].

^{****} DOL 2a and DOL 2b are from the same source but different samples; this is also the case for BAS 1a and BAS 1b.

The samples were crushed into different sand-size: passing 4.75 mm and retained on 2.36 mm and passing 2.36 mm and retained on 1.18 mm. The aggregates were first washed and then oven-dried at 100°C for 24h and then cooled for 5 hours. From each aggregate size, a mass of 100g (of specific particle size) was washed to one liter of 6% sodium hypochlorite solution (household bleach). The samples were then soaked in the oxidizing solution for 12 days at 40°C. After that, the samples were taken out of the solution and placed in an oven at 80°C for one day followed by 5 hours of cooling at room temperature. After this first cycle, others were performed. The mass loss of the aggregates $\Delta m(\%)$ after several wetting-drying cycles was calculated as follows:

$$\Delta m (\%) = [(m_0 - m_1)/m_0] \times 100\%$$

where: m_0 (g) = original or zero mass of the aggregate at 0 cycles

m_1 (g) = mass of aggregate after several wetting-drying cycles

To evaluate the particle size effect on mass loss the aggregate GAB4 was tested. This aggregate has 2.13 - 4.22 % of total sulfur that are from pyrite, pyrrhotite, and chalcopyrite. Three different particle sizes of GAB4 were tested: (i) 9.5–4.75 mm, (ii) 4.75–2.36 mm, and (iii) 1.18–0.60 mm. It was clear that the smaller the aggregate size, the higher was the expected oxidation rate, especially at the beginning.

In addition to measuring the mass loss, selected solutions were tested for pH. The total iron (Fe) and sulfate (SO_4^{2-}) ions in solution after the first cycle (two weeks) of the testing were evaluated using spectrophotometry. As shown in Table 2.7, the pH dropped significantly for aggregates that are known to have high contents of total sulfur; i.e. GAB 1, and GAB 2. For GAB 3 and QTZ 1b, which are also known to have low contents of total sulfur, the reduction in pH was not significant; suggesting that monitoring the pH was not suitable for all sulfide-bearing aggregates.

Table 2. 7: Change in pH, sulfur, and iron in bleach after one cycle of 12 days soaking at 40°C. The cycle reported here is cycle # 1. The initial pH of the solution was 12.2. (GUIRGUIS and SHEHARA, 2017)

Aggregate	GAB 1	GAB 2	GAB 3	QTZ 1b	DOL 6	DOL 1	BAS 1a	DOL 2a	ANRS
Total Sulphur $S_T\%$	20.0	20.0	1.0	0.54	0.30	0.15	0.027	0.007	0.04
Mass loss after cycle #1	6.0	4.0	3.0	3.1	0.2	0.5	0	0	0
pH	8.0	8.5	11.9	12.0	12.1	12.1	12.1	12.0	12.0
Total iron ion (Fe) (mg/L)	600	525	75	29	10	4.5	3.0	1.0	0
Total sulphate ion (SO_4^{2-}) (mg/L)	5200	4500	700	310	160	400	0	0	0
Sulphate/Iron	8.7	8.6	9.33	10.7	16	88.9	0	0	0

Guirguis and Shehara (2017) observed that the higher the mass loss, the higher the level of sulfate and iron ions in solution.

Beyond particle size, effects of testing temperature and cycle length were evaluated. The results revealed that the test was able to distinguish aggregates with oxidizable sulfide from those without. Quicker results were obtained when the test was run at room temperature using a particle size of 2.36–1.18 mm and may result in more oxidation for materials with very high sulfur contents such as GAB 1 and GAB 2. The mass loss at room temperature after cycles 1, 2, and 3 are shown in table 2.8.

Table 2. 8: Mass loss results and total Sulfur ($S_T\%$) for aggregates tested at 23°C using particle size from 2.36 mm to 1.18 mm after cycles 1, 2, 3. (GUIRGUIS and SHEHARA, 2017)

Cat. #	Aggregate ID	Total sulphur ($S_T\%$)	Mass loss% Cycle 1	Mass loss% Cycle 2	Mass loss% Cycle 3
1	GAB 1	20.00	14	29.5	41.8
1	GAB 2	20.00	13	28.0	40.8
1	QTZ 1a	1.500	5.3	9.10	12.4
1	GAB 3	1.000	4.5	6.70	8.90
1	QTZ 1b	0.540	3.6	5.70	7.10
3	DOL 6	0.300	0.0	0.20	0.20
3	GRAV 2	0.180	0.0	0.00	0.00
3	DOL 1	0.150	0.8	1.00	1.30
3	GAB 6	0.150	0.2	0.40	0.60
3	DOL 3	0.140	0.0	0.00	0.00
3	GNS 1	0.110	0.6	1.00	1.30
3	LIM 6	0.060	0.1	0.20	0.30
3	LIM 5	0.059	0.0	0.00	0.10
3	GRAV 3	0.050	0.4	0.80	1.20
3	LIM 4	0.046	0.0	0.00	0.00
3	ANRS	0.040	0.0	0.00	0.10
3	GAB 5	0.039	0.0	0.10	0.20
3	LIM 3	0.038	0.0	0.20	0.30
3	BAS 1a	0.027	0.2	0.20	0.70
3	BAS 1b	0.027	0.4	0.60	1.60
3	QUITZT	0.024	0.0	0.00	0.00
3	DOL 4	0.017	0.0	0.00	0.00
3	GRAV 3	0.010	0.0	0.00	0.00
3	GNS 2	0.009	0.0	0.00	0.00
3	DOL 2a	0.007	0.0	0.00	0.00
3	DOL 2b	0.007	0.0	0.00	0.00
3	DOL 5	0.007	0.0	0.00	0.00
2	GRAV 1	0.000	0.0	0.00	0.20
2	LIM 1	0.000	0.0	0.00	0.10
2	LIM 2	0.000	0.0	0.00	0.00

Guirguis and Sherara (2017) concluded that while a low level of total sulfur in aggregate has been suggested by some standards, e.g. 0.10% as proposed by Annex P of Canadian Standards Association CSA A23.1-2014, aggregate with higher sulfur content can have little or no oxidizable sulfide. Six of the aggregates tested with no known oxidizable sulfide had a total sulfur content $>0.10\%$. Four of these aggregates met the 0.50% mass loss limit while the other two had a mass loss between 0.5% and 1.0%. There was no direct relationship between mass loss and total sulfur. This shows the benefit of using the proposed test as a second step after total sulfur.

In this scenario, it is concluded that limiting the use of sulfide-bearing aggregate only by the sulfur amount may be a mistake. Studies have shown that other parameters are important. The sulfide type influences since pyrrhotite is more reactive than pyrite (MARCELINO, 2015; CHINCHÓN-PAYÁ *et al.*, 2012). The particle size of the aggregate has proved to be an important characteristic for the sulfide oxidation inside the concrete and consequently in causing damage (GOTO *et al.*, 2016; GUIRGUIS and SHERARA, 2017). For different aggregates sizes, in the larger ones, there are less exposed areas of sulfides. This is because most of the sulfides are occluded in the rock matrix which reduces the chance of oxidation, even with the same amount of sulfur.

3

EXPERIMENTAL PROGRAM

3.1 General considerations

The reactivity of aggregates with respect to the particle size has been investigated in the last years [RODRIGUES *et. al.*, 2016a, GUIRGUIS and SHEHATA, 2017]. The results showed that the distribution of the particle sizes is an important factor in the oxidation reaction of the sulfides and that the smallest particle size studied showed the highest oxidation rate.

According to Rodrigues et al. (2016b), there are no currently available specific guidelines to point out more precisely the deleterious potential of aggregates containing iron sulfide minerals. This study aimed at the development of a testing procedure to evaluate how reactive is a sulfide-bearing aggregate to use in concrete considering not only the size of aggregates particles. Drill hole samples of rock containing iron sulfide were used in this study to produce the aggregates. These samples were from the Irapé HPP area in Minas Gerais. These aggregates had at least 1.5 % of total sulfur content.

3.2 Determination of the aggregate most reactive grain size

Schistosity is the most conspicuous geological feature of the rocky formation of the Irapé Hydroelectric Power Plant area. The schist of the Chapada Acauã formation has a unique characteristic given by the existence of iron sulfide (pyrrhotite and pyrite) as well as iron and copper sulfide (chalcopyrite) and zinc sulfide (sphalerite) disseminated in the rock matrix. Pyrrhotite predominates over the others. These minerals exhibit fine grain size and occur mostly in the form of thin laminae that are disposed of according to the rock foliation. Besides, they are associated with quartz veins, which vary in size from centimeters to meters, which form well-developed crystals and display a larger grain size (CEMIG, 2007).

Lima (2009) analyzed the sulfur distribution in the study area. Marcelino (2015) used this guidance to collect drill hole samples to make aggregates. The collected material was degradation-free, which is without sulfide oxidation or any stain. Moreover, it was mandatory to have a total sulfur content between 1.5 and 3%.

Aggregates were first crushed and sieved from the Irapé rock samples. The material retained in sieves between 4.8-mm and 0.15-mm was selected for analysis and future use. The samples were identified according to Table 3.1. The total sulfur, pyrite, and pyrrhotite contents for each selected aggregate size (between 4.8 and 0.15-mm) were determined by a leaching procedure followed by a direct combustion test. The pyrite and pyrrhotite spatial distribution for each selected aggregate size was next evaluated using the Mineral Liberation Analysis (MLA) technique.

Table 3. 1: Aggregate by particle size

Sample ID	Particle size (mm)
0.15	$0.15 \leq \Phi < 0.30$
0.30	$0.30 \leq \Phi < 0.60$
0.60	$0.60 \leq \Phi < 1.20$
1.20	$1.20 \leq \Phi < 2.40$
2.40	$2.40 \leq \Phi < 4.80$
4.80	$4.80 \leq \Phi < 6.30$

The sulfide oxidation evaluation is an important tool to determine the reactive potential of the aggregate. Initially, each sample was exposed to a hydrogen peroxide solution (H_2O_2). The sulfate, originated by the sulfide oxidation, migrates from the sample to the solution. Turbidity analysis was then used to quantify the migrated sulfate portion. The remaining amount of iron sulfide (after the H_2O_2 solution exposition) was evaluated by the direct combustion test. Mineral Liberation Analysis (MLA) technique was also used to observe the presence or not the iron sulfide and how its grains are exposed.

In the next sections, each one of these analysis techniques is explained in more detail.

3.2.1 Determination of the aggregate sulfur content

For the quantitative determination of the total sulfur content, a fraction of each aggregate size sample was ground to a grain size smaller or equal to 0.45 μm . The sulfur content is then determined by direct combustion (with infrared detection). In this method, the sample is previously weighed and packed in a ceramic crucible (combustion boat), added a flux (com-cat accelerator). It is then introduced into a furnace, in an oxygen atmosphere, where combustion is processed at a temperature of 1400 °C. The sample combusts, releasing carbon as CO_2 gas with the sulfur forms being oxidized and released as SO_2 gas. After a preset time, additional oxygen is introduced via a ceramic lance directly above the sample to accelerate the combustion of refractory materials. The combustion gases are swept to the back of the furnace and then forward through the inner and outer furnace tubes, allowing the combustion gases to remain in the high-temperature zone of the furnace ensuring efficient oxidation. Upon exiting the furnace, the combustion gases flow through anhydrous tubes removing moisture and on to the flow controller, setting the flow of the combustion gases through the NDIR (Nondispersive Infrared Sensor) sulfur and/or carbon detection cells.

Non-dispersive infrared cells are based on the principle that CO_2 and SO_2 absorb infrared (IR) energy at unique wavelengths within the IR spectrum. Incident IR energy at these wavelengths is absorbed as the gases pass through IR absorption cells with the absorption being dependent upon the path length of the cell. The software automatically selects which cell to use for optimum measurement. The concentration of unknown samples is determined relative to calibration standards. An external PC with LECO Cornerstone brand software manages all of the quantitative calculations and saves all of the data. In this research it was used the LECO SC analyzer, model 632, from the Laboratory of Chemical Analyses of the Metallurgy and Materials Department of the UFMG.

In a previous work (LIMA, 2009), the mineralogical characterization of aggregate samples was done, which showed that sulfate compounds were not found: pyrite and pyrrhotite were found. To confirm that no sulfates were present, a leaching procedure was done. Many sulfates are soluble in water, so a leaching procedure with water was performed, and the residue was analyzed by LECO. The difference between the initial sulfur percentage and the remaining sulfur in the water solution corresponds to the initial sulfide percentage. In the analyzed

samples, the remaining sulfur in the water solution was zero, confirming that there were no sulfates in the aggregate under scrutiny.

It is important to know the mineralogy of aggregate to apply the protocol: if the sulfur from pyrrhotite is overestimated due to the presence of sulfate, the sulfide oxidation will be also overestimated. In this way, the decision-making will be more conservative.

The determination of pyrrhotite and pyrite contents was performed according to leaching procedures described by Marcelino (2015). 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 1:1:00 pm. This solution was agitated for 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 with distilled water to remove the residual HCl and oven-dried at 40°C for 24 hours. The total sulfur amount 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 sulfur content.

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 HNO₃). This solution was agitated for 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.

3.2.2 Determination of the pyrite and pyrrhotite spatial distribution

The iron sulfides reaction degree did seem to be related to the position of the particles within the aggregates. Particles near the center of the aggregates showed a lower degree of reaction than those close to the surface (SCHMIDT, 2011).

In the mortar and concretes, the region near the iron sulfide particles is the zone in which the oxidation occurs, releasing excess sulfuric acid and iron ions by diffusion toward the cement paste. This sulfuric acid in contact with the compounds of the cement paste reacts forming

gypsum and then secondary ettringite (CAMPOS et al., 2016). Thus, it can be inferred that the more exposed sulfide surface available in the aggregate the higher is the potential of sulfide oxidation.

The pyrite and pyrrhotite spatial distribution for each selected aggregate size was next evaluated using the Mineral Liberation Analyzer (MLA), a scanning electron microscopy SEM-based automated image analysis system. The MLA technique consists of the combination of Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray Spectroscopy (EDS) and a software package specially developed to perform SEM control, sample image capture, and analyses among other things. The MLA transforms raw particle images with x-ray data into particle mineral maps and calculates bulk and liberation data from these maps (GU, 2003).

Initially, a portion of each selected aggregate size is mixed with epoxy resin and inserted into a round mold to form a hardened block of 30 mm in diameter. The blocks were vibrated to remove air and avoid bubbles after the hardening of the resin. The block surface was polished (abrasive paper with grain 240, 320, 400, and 600 in this sequence) and covered with carbon (Figure 3. 1).

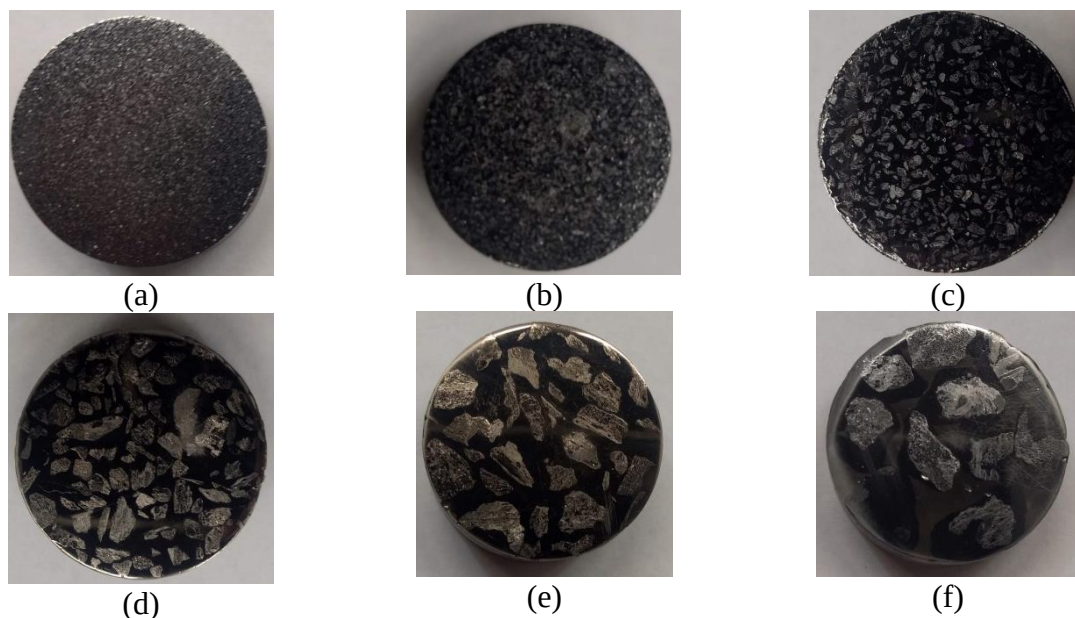


Figure 3. 1: Blocks of aggregate samples for MLA analysis. Samples a) 0.15, b) 0.30, c) 0.60, d) 1.20, e) 2.4 and f) 4.80.

The MLA analysis allows the identification of mineral phases (grains) and the determination of the boundaries of each particle image and consequently the spatial distribution of each mineral in each material grain. Initially, by SEM technique the image acquisition by backscattered electrons is performed (Figure 3. 2). A specific color is assigned to each homogeneous grayscale region by selecting the grains that make up the particle (Figure 3. 3). The mineral identification is achieved by x-ray analysis, comparing EDS-spectra of the found mineral patterns with those contained in an existing library. The library construction demands the collection of high-quality x-ray spectrum for each mineral in the sample (FANDRICH *et al.*, 2006).

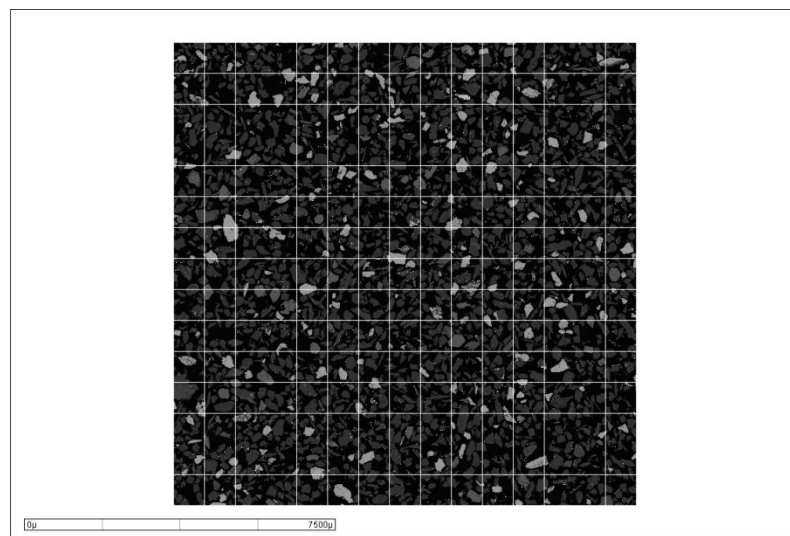


Figure 3. 2: SEM image. Source: UFMG Microscopy Center.

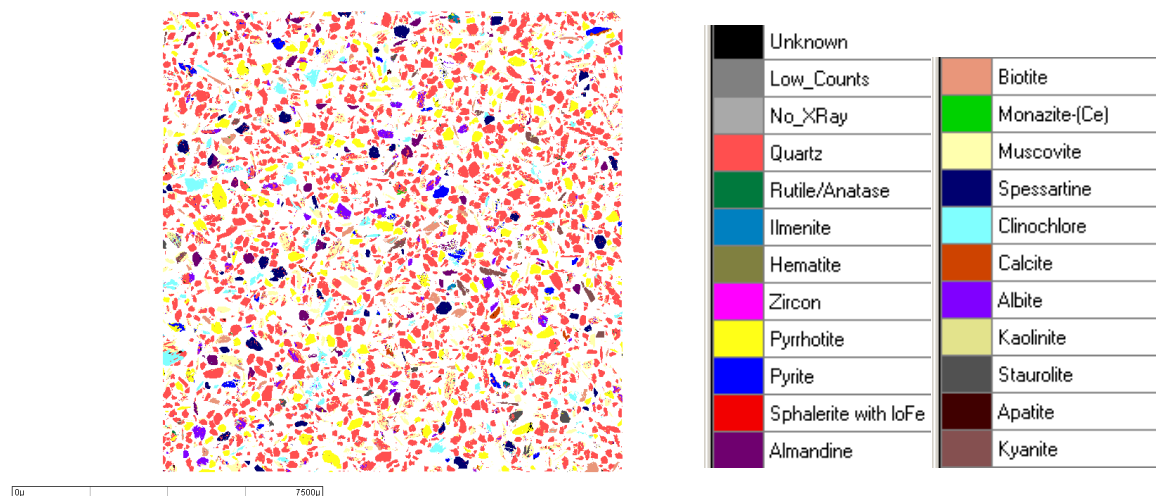


Figure 3. 3: Identification of mineral phases by MLA mapping. Source: UFMG Microscopy Center.

The MLA software provides, among other information, quantification of the mineral phases present in the sample, mineral association, mineral grain size distribution, and determination of mineral release spectrum. It is important to emphasize that mineralogical characterization and determination of the release spectrum are essential steps to define the optimal processing route of any mineral asset of economic interest. More detailed information about the functionality of the MLA system can be found in Gu (2003) and Fandrich et al. (2006).

MLA analyses were performed at the UFMG Microscopy Center and the system consists of a FEI Quanta 650F manufactured SEM-FEG, equipped with two Bruker EDS Xflash 6130 detectors and an MLA software package version 3.1.4. Figure 3. 4Figure 3. 4 shows the SEM equipment coupled with the MLA software package.

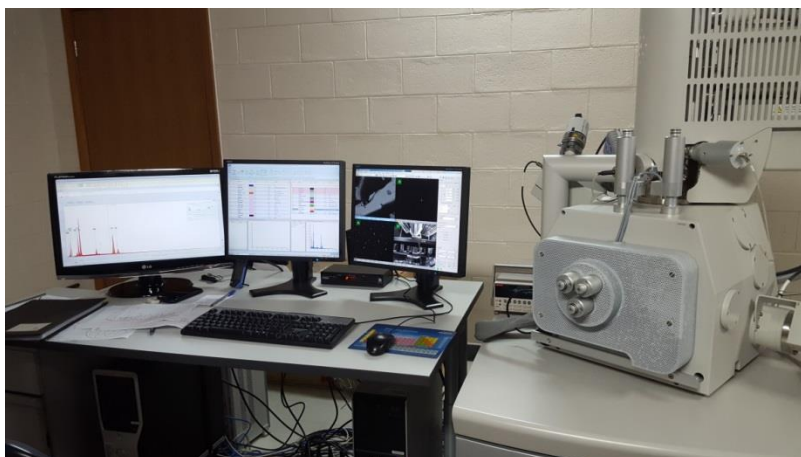


Figure 3. 4: SEM equipment with the MLA software package. Source: UFMG Microscopy Center.

3.2.3 Sulfide oxidation with H₂O₂ solution

Oxygen and humidity are indispensable for the sulfide oxidation process (KNIPE, *et al.*1995; LOWGWORTH, 2003; CHINCHÓN-PAYÁ *et al.*, 2012). Knipe *et al.* (1995) used XPS (x-ray photoelectron spectroscopy) to confirm that oxygen is the primary oxidizer of pyrrhotite. Moreover, no sulfide oxidation is detected when water containing little oxygen is used. According to Casanova *et al.* (1997), the oxidation of the sulfide-bearing aggregate inside concrete or mortar depends strongly on the alkalinity of the solution inside the cement matrix pores, oxygen availability, and aggregate particle size. Regarding the aggregate, the specific surface area of sulfides is the main factor to govern the oxidation process and the reaction rate (Casanova *et al.* 1996 and 1997).

Temperature is another factor that influences the oxidation speed of iron sulfides because the liberation rates of elemental iron and sulfur also increase with temperature (BELZILE, 2004).

To accelerate the oxidation of iron sulfide and determine the most reactive grain size, the carried-out dissolution process was adapted from the protocol Net Acid Generation - NAG test (AMIRA, 2002). Two kilograms of each selected grain size under scrutiny were split into 100-gram portions. These were divided again to provide twenty 5-gram aggregate samples for each selected size.

For each particle size, six 5-gram samples were placed in six 1,000-ml Erlenmeyer flasks. Each flask contained 500 ml of an H_2O_2 solution containing de-ionized water at 15% concentration and pH between 4.5 and 6. If the pH was smaller than 4.5, drops of a 0.25mol/l solution of NaOH were added until a pH next to 5.3 was reached. The solution was kept under agitation when adding the NaOH solution to correct the pH of the H_2O_2 solution.

The Erlenmeyer flasks containing aggregate and the H_2O_2 solution were shaken by hand. The solution level was indelibly indicated on the glass. The flasks were then placed on a heated plate for 90 minutes. The plate temperature was between 150°C and 200°C to obtain solution temperatures between 90°C and 100°C.

After that heating period, the flasks were removed from the plate and their solution levels checked. If necessary, de-ionized water was added to keep the initial volumes. Next, the flasks were immersed in a water-bath until the solutions reach room temperature. After cooling, the samples were filtered to separate the solid phase from the liquid one (or liquor).

Three portions of liquor for each selected aggregate grain size were separated to determine the amount of released sulfate. Additionally, three samples of the remaining solid phase, which had been previously oxidized by the H_2O_2 solution, were submitted to a second oxidation stage, following the same procedure.

Turbidimetry was used to determine the amount of released sulfate in liquor samples from the first and second oxidation. The direct combustion test was employed to quantify the sulfur content in each solid phase after the oxidation steps. To quantify the remaining sulfur of pyrite and pyrrhotite it was necessary to remove the sulfate which may have precipitated in solid. Thus

the samples were placed in Erlenmeyer flasks and for each one gram were added 100 ml of deionized water. The solution was kept under agitation for one hour and then filtered to separate the solid phase. Then, the sulfur from pyrite and pyrrhotite contents for each remaining solid was determined by the leaching procedure described earlier (item 3.2.1) followed by direct combustion analyses.

3.2.4 Sulfate Determination by Turbidimetry

Molar extinction coefficient or molar absorptivity (ϵ) is a measure of how well a mol of a chemical species absorbs a given wavelength of light. Molar absorptivity varies according to the substance at issue and its solvent, wavelength, and temperature among others. According to Lambert-Beer Law, the absorbance (A) of a substance depends on the wavelength (L), substance concentration (C), and its molar extinction coefficient (ϵ) as shown in Equation 3.1 below.

$$A = \epsilon CL \quad (3.1)$$

Currently, spectrophotometry devices present wavelength as a function of absorbance through the following equation:

$$A = \log \frac{I_0}{I_t} \quad (3.2)$$

where I_0 represents the intensity of the incident light and I represents the intensity of the transmitted light (Figure 3. 5).

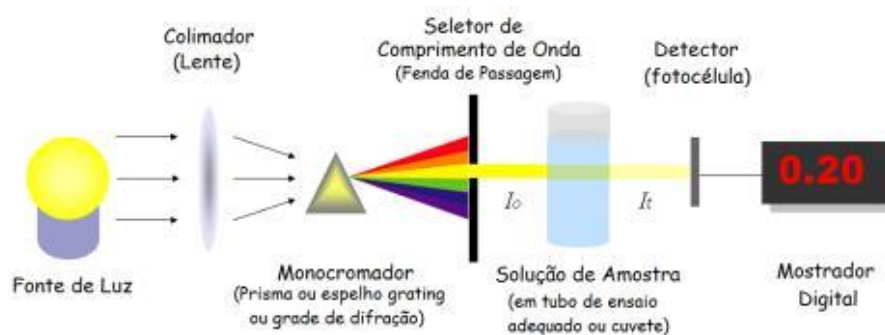


Figure 3. 5: Scheme of the basic operation of a spectrophotometer.

Source: <http://www.kasvi.com.br/espectrofotometria-principios-aplicacoes/espectrofotometro/>

Sulfate forms few color substances that absorb radiation in the length of visible and ultraviolet waves. This restricts the use of spectrophotometry analysis to sulfate solutions. In the 1950s, barium chloranilate ($\text{BaC}_6\text{Cl}_2\text{O}_4$) was proposed for sulfate determination purposes. When it reacts with $(\text{SO}_4)^{2-}$ in an acidic medium, the chloranilate dislocates an equivalent quantity of chloranilic ions because of the smaller solubility of the barium sulfate. (CRNKOVIC and JACINTHO, 2002).

The method described in APHA (2005) is based on the measurement of the turbidity caused by the reaction of barium chloride with sulfate of the sample. The resulting barium sulfate stays in suspension and darkens the solution as a consequence. This method was used in this study.

The absorbance light of the BaSO_4 suspension is measured by photometry and the $(\text{SO}_4)^{2-}$ is determined by comparing the spectrophotometer reading with reference curves from a standard sulfate solution. This solution is such that $1\text{ml} = 100\mu\text{g } (\text{SO}_4)^{2-}$ (APHA, 2005). It allows the construction of the calibration turbidimetric curve (Figure 3. 6) within the interval that varies from 0 to 40 mg/l of $(\text{SO}_4)^{2-}$.

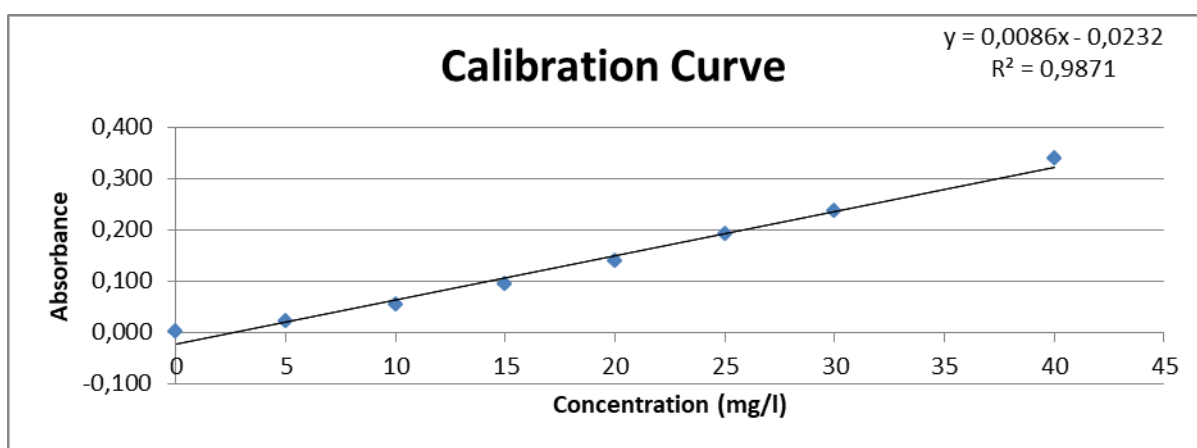


Figure 3. 6: Example of a calibration turbidimetric curve.

Two reagents are required for the execution of these reactions as described below.

- 1) Buffer solution: 30 g of magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$), 5g of sodium acetate ($\text{CH}_3\text{COONa} \cdot 3\text{H}_2\text{O}$), 1g of potassium nitrate (KNO_3), 20 ml of acetic acid (CH_3COOH , 99%), and 500 ml of de-ionized water are put in a 1,000-ml volumetric balloon. De-ionized water is added until obtaining a 1,000-ml solution.

- 2) Barium chloride (BaCl_2): Crystals of dihydrated barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) with grain sizes between 20 and 30 mesh (0.841 to 0.595 mm) are used.

These analyses were performed at Laboratório Prof. José Marcelino de Oliveira (Laboratory of Physical and Chemical Analyses) of the Environmental Engineering Department (DESA) at UFMG (Federal University at Minas Gerais).

Initially, the turbidity of a blank solution was measured by putting 50 ml of de-ionized water and a small magnetic bar into a 125-ml Erlenmeyer flask. This flask was submitted to moderate agitation provided by a magnetic agitator. Ten milliliters of the tampon solution and between 0.2 and 0.3 g of barium chloride crystals (BaCl_2) were added. Soon after the BaCl_2 addition, the solution was continuously agitated for 60 ± 2 seconds. The Erlenmeyer flask was removed from the agitator and laid to rest for 300 ± 30 seconds before a spectrophotometer reading was obtained. Figure 3. 7 shows the spectrophotometer equipment.

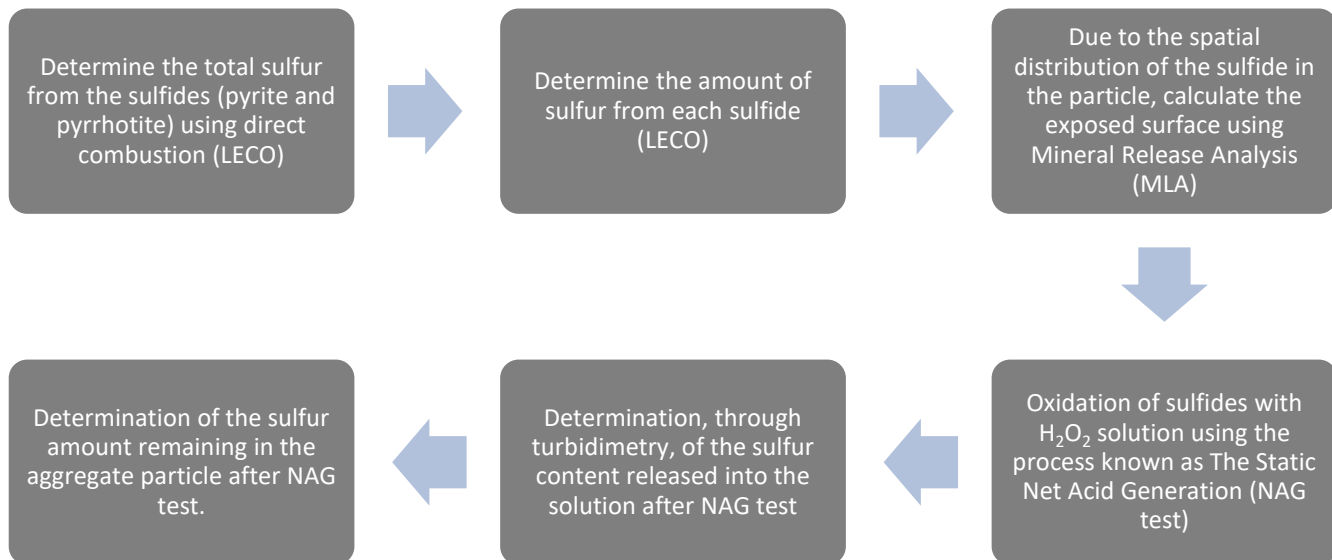


Figure 3. 7: Spectrophotometer of the Laboratório Prof. José Marcelino de Oliveira, DESA, UFMG.

The amount of sulfate in the sample is determined after obtaining the blank-solution reading. Fifty milliliters of the sample, free of solid particles, is placed in a 125-ml Erlenmeyer flask and submitted to identical procedures described for the blank solution. The spectrophotometer readings were the input values in the calibration curve to obtain the amount of sulfate. This type of technique was also used by Guirguis and Shehata (2017) to quantify the presence of oxidizable sulfide minerals in coarse aggregates.

3.2.5 Protocol Summary

The proposed protocol to evaluate sulfide-bearing aggregates included the following steps:



4

RESULTS AND ANALYSIS

The reactivity of aggregates with respect to the particle size has been investigated in the last years [SCHMIDT et al. (2011), RODRIGUES et al. (2016), GUIRGUIS AND SHEHATA (2017)]. The results showed that the distribution of the particle sizes is an important factor in the oxidation reaction of the sulfides and that for investigated rocks the smallest particles showed the highest oxidation rate. In this study, the combination of four different types of analysis (direct combustion, MLA, oxidation with H₂O₂ solution, and turbidimetry) was used for different aggregate sizes, to evaluate the extension of the sulfide oxidation. The results are presented below.

4.1 Aggregate sulfur content by particle size

To define the aggregate size distribution to be used in mortar and concrete, direct combustion tests (LECO) were performed on the sulfide-bearing aggregates. Particle size fractions bigger or equal than 0.15- and smaller than 6.30-mm were selected for the study. The percentage amount of total sulfur, sulfur from pyrite and pyrrhotite for each particle size is presented in Table 4.1. The sulfur content increases when the sizing fraction decreases from 4.8 to 0.15 mm, except for sample 0.60, in which the sulfur content slightly decreased (1.93 % S). No constant ratio between sulfur from pyrrhotite and pyrite was observed in the sizing fractions. The ratio varies from 1.1 to 2.1.

The European standard EN 12620:2008 specifies that if pyrrhotite is found, the maximum total sulfur content is less than 0.1%. This amount is 10 times lower than would be permitted for aggregates containing other iron sulfides (Chinchón-Payá et. al, 2012).

Table 4. 1: Aggregate sulfur content by particle size

Sample ID	Particle size (mm)	Total Sulfur (%)	Sulfur from Pyrite (%)	Sulfur from Pyrrhotite (%)
0.15	$0.15 \leq \Phi < 0.30$	2.93	0.95	1.98
0.30	$0.30 \leq \Phi < 0.60$	2.60	1.16	1.44
0.60	$0.60 \leq \Phi < 1.20$	1.93	0.93	1.00
1.20	$1.20 \leq \Phi < 2.40$	2.14	0.79	1.35
2.40	$2.40 \leq \Phi < 4.80$	1.87	0.72	1.15
4.80	$4.80 \leq \Phi < 6.30$	1.59	0.51	1.08

It is important to note that, for the analyzed samples, the sulfur from pyrrhotite content is at least 1% in all sizes.

4.2 Pyrite and pyrrhotite spatial distribution

A general view of the spatial particle composition distribution resulting from the MLA analysis is shown in Figure 4.1 to 4.6. In figures, each grain color corresponds to a different compound described in the legend. In this way, the arrangement of the pyrite (blue) and pyrrhotite (pink) can be easily observed. Despite being an overview, it is possible to identify free particles composed only by pyrite or pyrrhotite in MLA analysis of sample 0.15 (Figure 4.1), 0.30 (Figure 4.2), and 0.60 (Figure 4.3). In this case, the sulfides have their whole surface exposed.

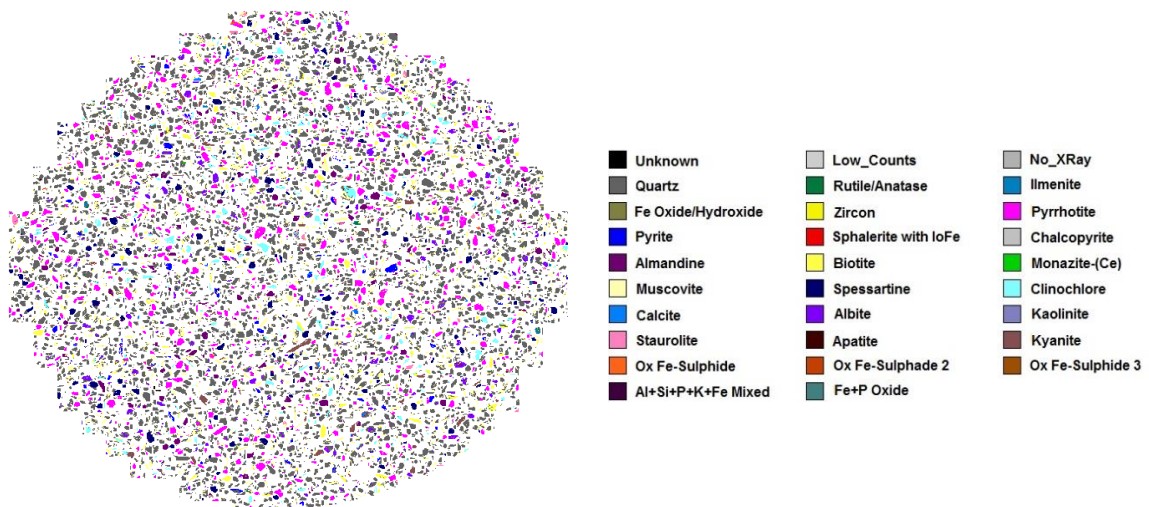


Figure 4. 1: Sample 0.15 - MLA analysis.

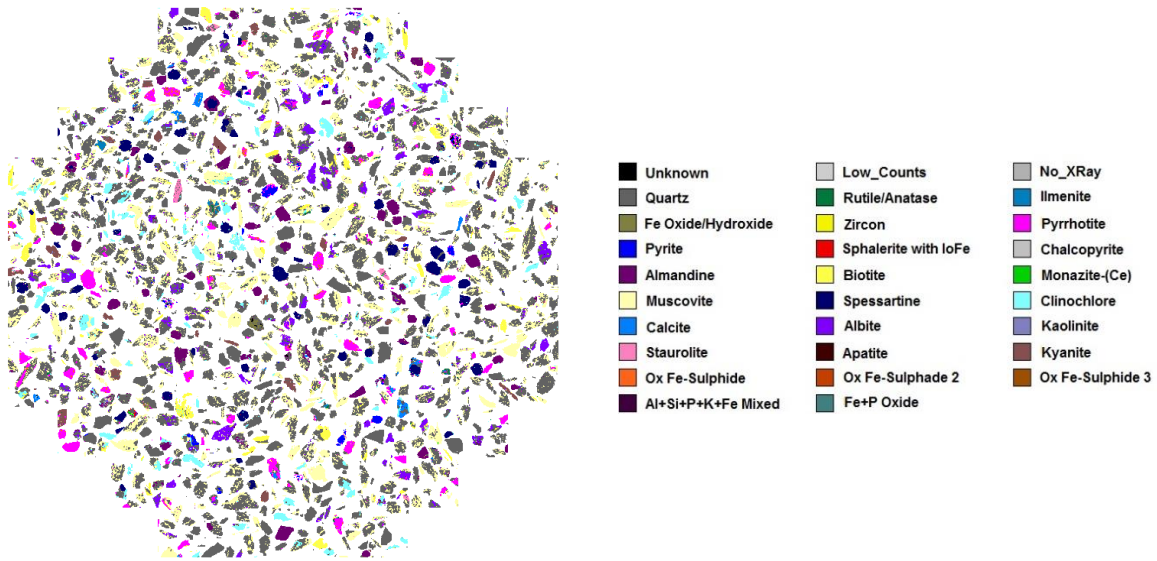


Figure 4. 2: Sample 0.30 - MLA analysis.

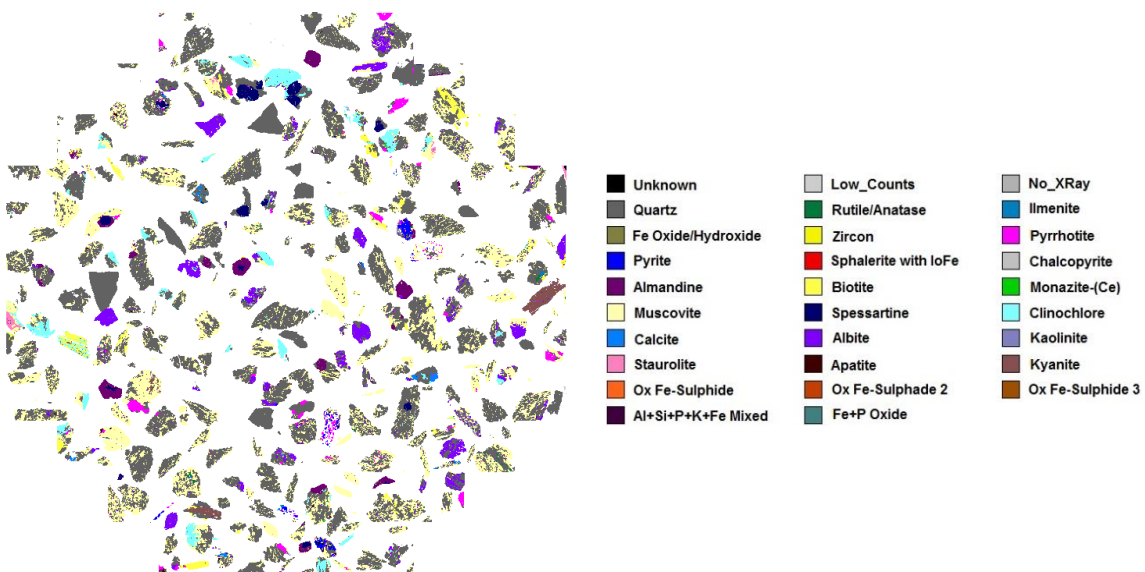


Figure 4. 3: Sample 0.60 - MLA analysis.

The MLA analysis of samples 1.20, 2.40, and 4.80 (Figures 4.4 to 4.6) shows that most parts of sulfides (pyrite and pyrrhotite) are surrounded by other minerals, such as quartz and muscovite.

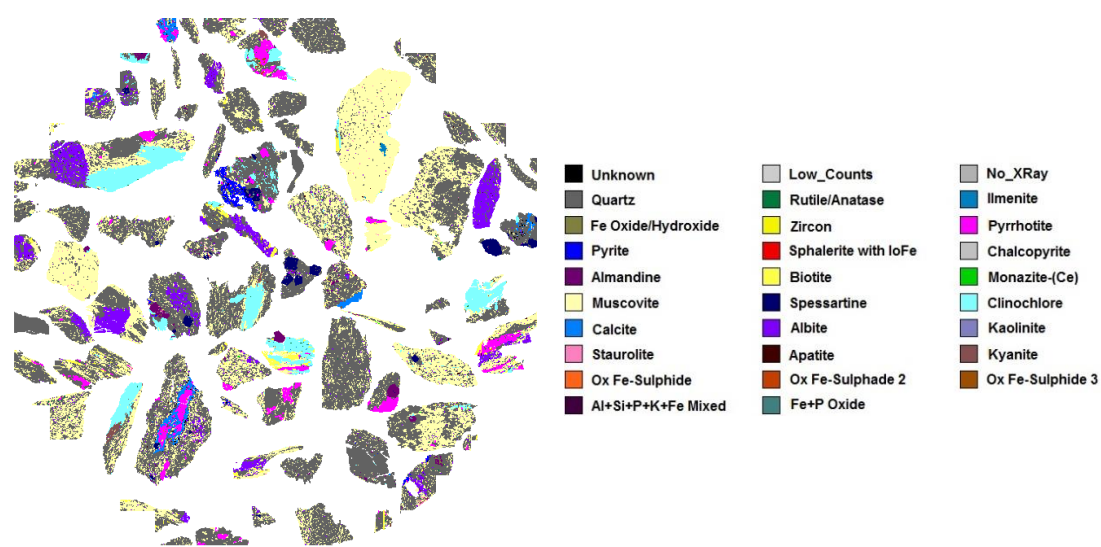


Figure 4. 4: Sample 1.20 - MLA analysis.

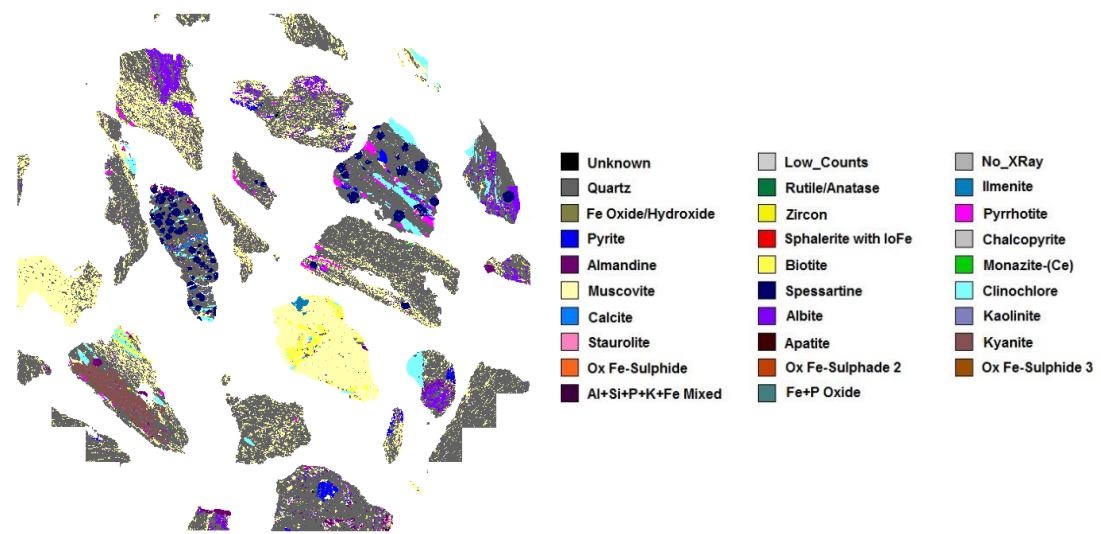


Figure 4. 5: Sample 2.4 - MLA analysis.

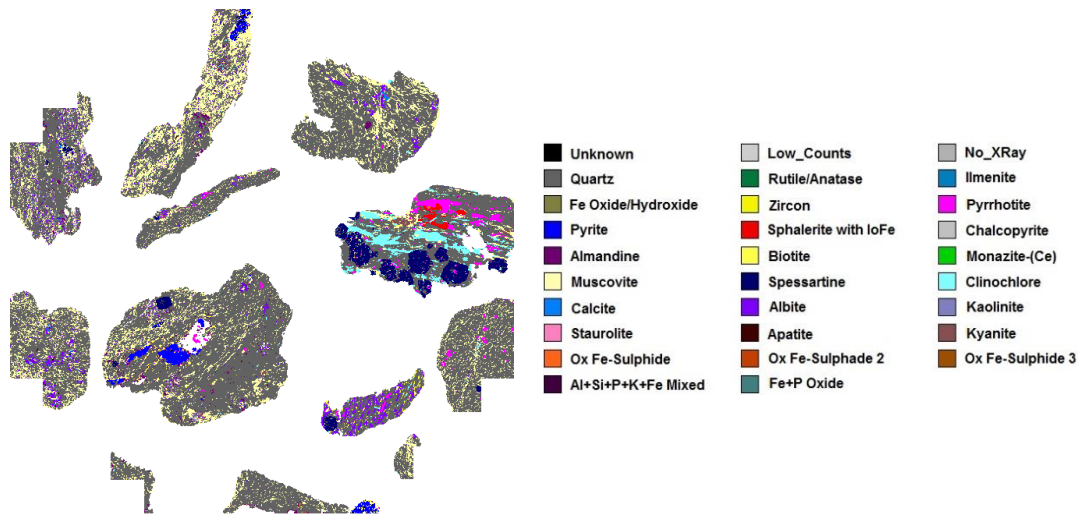


Figure 4. 6: Sample 4.80 - MLA analysis.

A close-up image of particles containing pyrite and pyrrhotite can be seen in Figures 4.7 to 4.13. The figures show the images obtained by SEM and MLA. As previously explained, MLA analysis identifies minerals/compounds based on information from a pre-existing library. Figure 4.7 shows the presence of an associated grain of pyrite and pyrrhotite. The MLA table of pyrite and pyrrhotite mineral association is in the appendix. It is observed that the pyrite and pyrrhotite are exposed since they are not bordering on any other mineral: thus, they are totally available to oxidation. Otherwise, Figure 4.8 shows grains of pyrite and pyrrhotite occluded and disseminated in a quartz matrix, which can difficult access to reagents (water and oxygen) to sulfide particles. Therefore, in this case, the pyrrhotite grains are not available for a potential oxidation reaction.

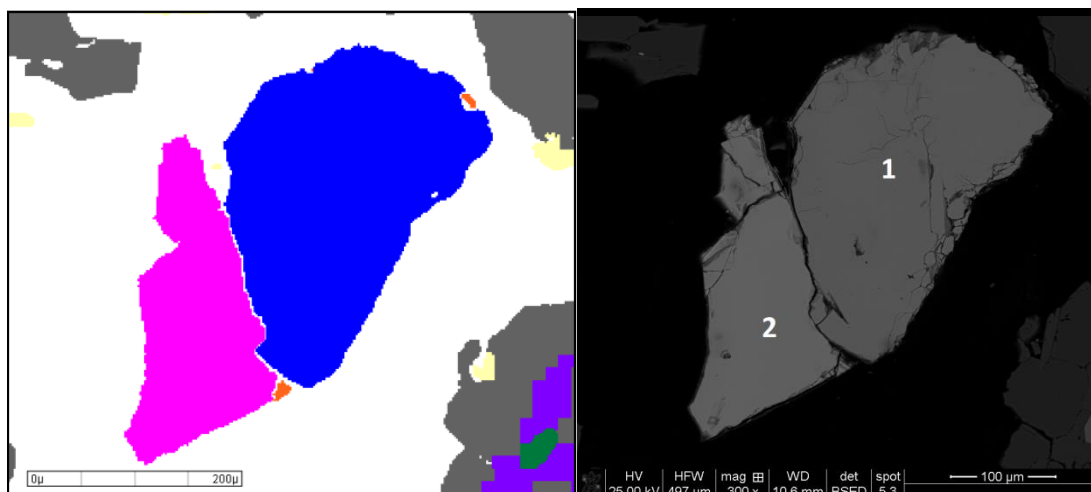


Figure 4. 7: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases of a 0.15-mm sample: Pyrite (1) and Pyrrhotite (2) with exposed surfaces.

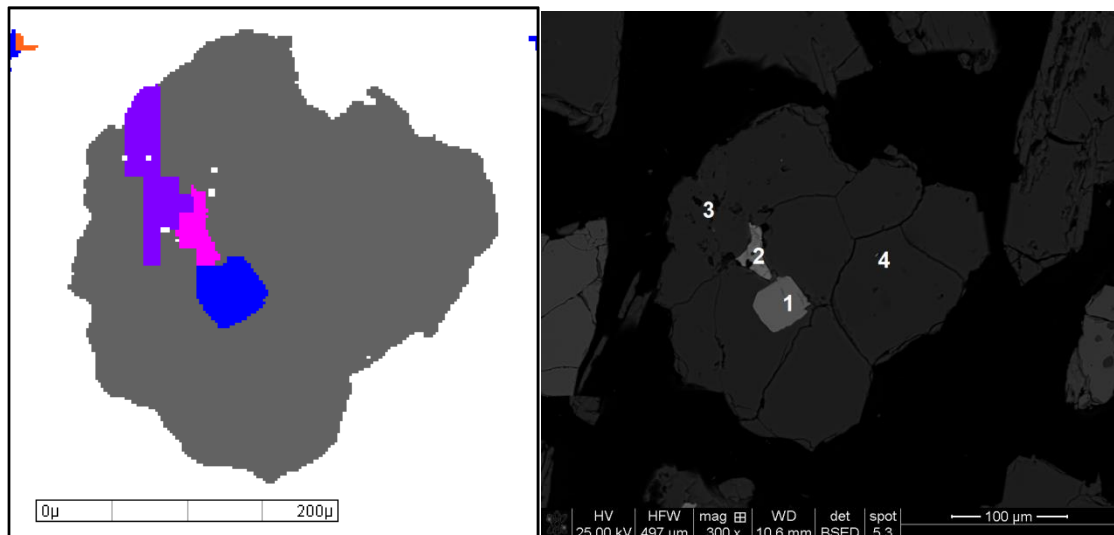


Figure 4. 8: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.15-mm sample: Pyrite (1), Pyrrhotite (2) and Albite grains (3) disseminated in a matrix of Quartz (4). No exposed surface of sulfide.

Figure 4.9 shows grains of pyrrhotite occluded or partially occluded. They are disseminated in a quartz and muscovite matrix. Except for partially occluded grain, it is also difficult to access to reagents (water and oxygen) to pyrrhotite.

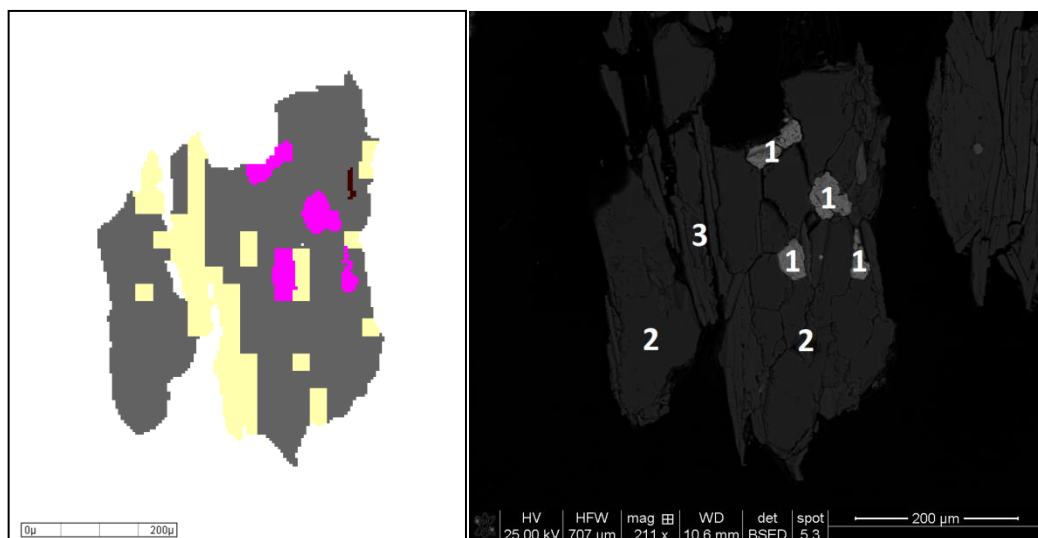


Figure 4. 9: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.30-mm sample: Pyrrhotite grains (1) disseminated in a matrix of Quartz (2) and Muscovite (3). A little exposed surface of sulfide.

In Figure 4.10, the pyrite and pyrrhotite grains are on the edge of the quartz and muscovite matrix. The sulfides are with part of their surface exposed.

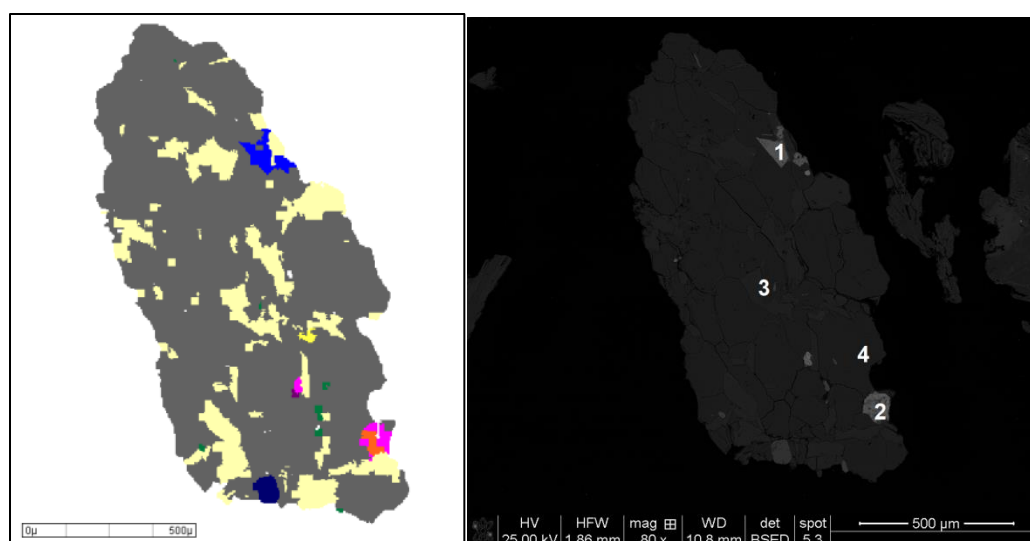


Figure 4. 10: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.60-mm sample: Pyrite (1) and Pyrrhotite (2) grains disseminated in a matrix of Muscovite (3) and Quartz (4). A little exposed surface of sulfide. Pyrrhotite with oxidation signals.

In Figure 4.11, the pyrite and pyrrhotite grains are disseminated in a matrix of quartz and clinochlore: only pyrite has a substantial exposed area.

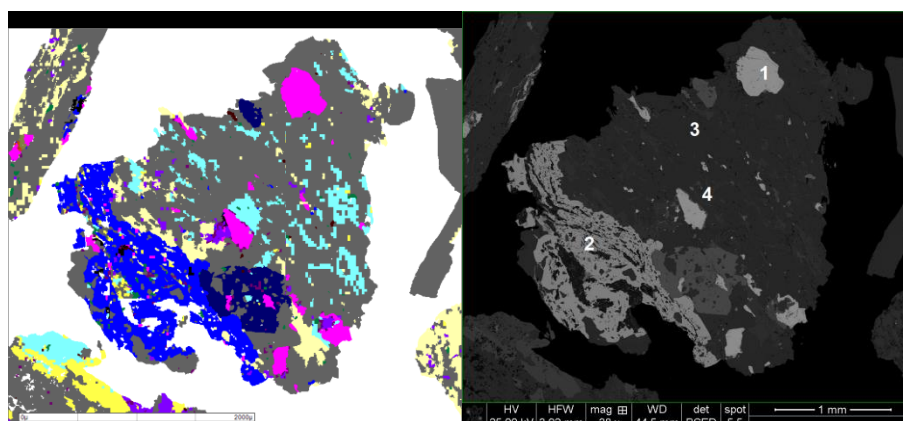


Figure 4. 11: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 1.20-mm sample: Pyrrhotite (1) and Pyrite (2) grains disseminated in a matrix of Quartz (3) and Clinochlore (4). Presence of exposed surface of Pyrite and a little of Pyrrhotite.

In Figure 4.12, the pyrite and pyrrhotite grains are disseminated in a matrix of quartz, clinochlore, and spessartine. The pyrite grains are completely occluded. Pyrrhotite next to the matrix edge have some exposed area.

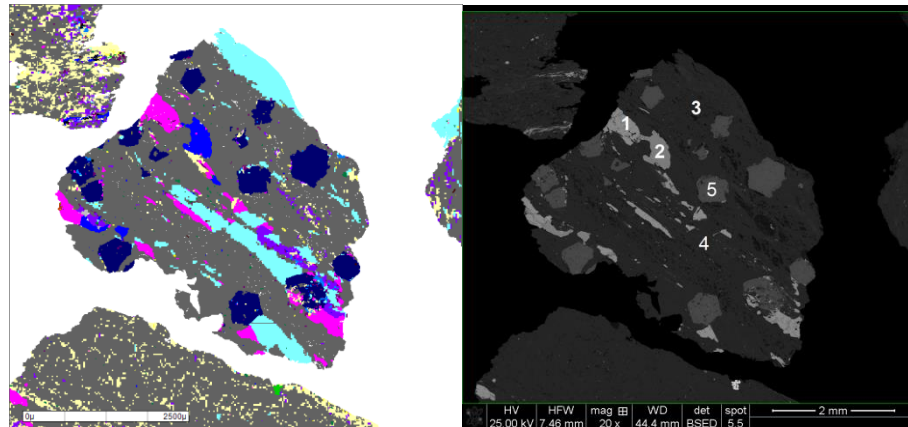


Figure 4. 12: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 2.40-mm sample: Pyrrhotite (1) and Pyrite (2) grains disseminated in a matrix of Quartz (3), Clinochlore (4) and Spessartine. No exposed surface of Pyrite and a little of Pyrrhotite.

In Figure 4.13, it is possible to observe pyrite and pyrrhotite grains completely occluded in a matrix of quartz and muscovite.

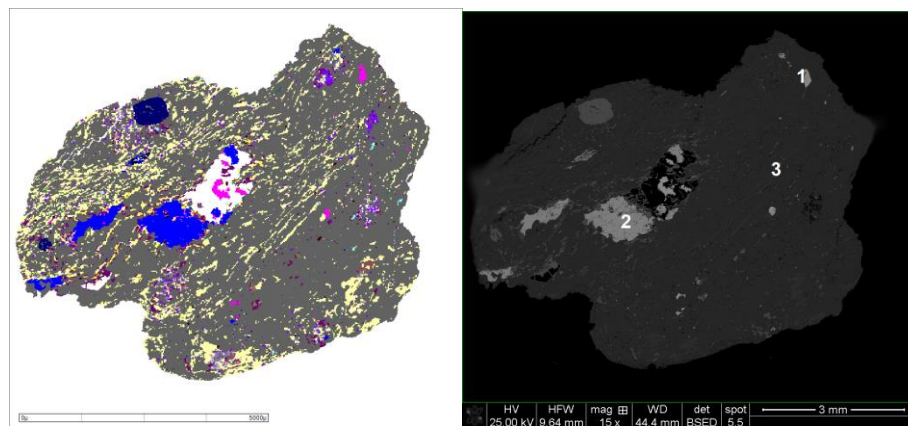


Figure 4. 13: Segmented particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 4.80-mm sample: Pyrrhotite (1) and Pyrite (2) grains disseminated in a matrix of Quartz and Muscovite (3). No exposed surface of Pyrite or Pyrrhotite.

From these images, the MLA analysis can determine the exposed surface (x) corresponded to pyrite and pyrrhotite. For example: $x > 60\%$ means that for that particle at least 60% of the sulfide is exposed. When this procedure is repeated for each particle in the sample, the relationship between the percentage of each iron sulfide compound (pyrite and pyrrhotite) with

respect to its exposed surface can also be established. These relationships for the sulfide-bearing aggregates with particle size from 0.15- to 4.8-mm are presented in Figures 4.14 and 4.15 for pyrrhotite and pyrite respectively. For 1.20 to 4.80-mm particle sizes, three blocks for MLA analysis were made. The free surface value for these samples is an average of the three results to improve sample representability. The data provided by the MLA analysis for each block are presented in the Appendix.

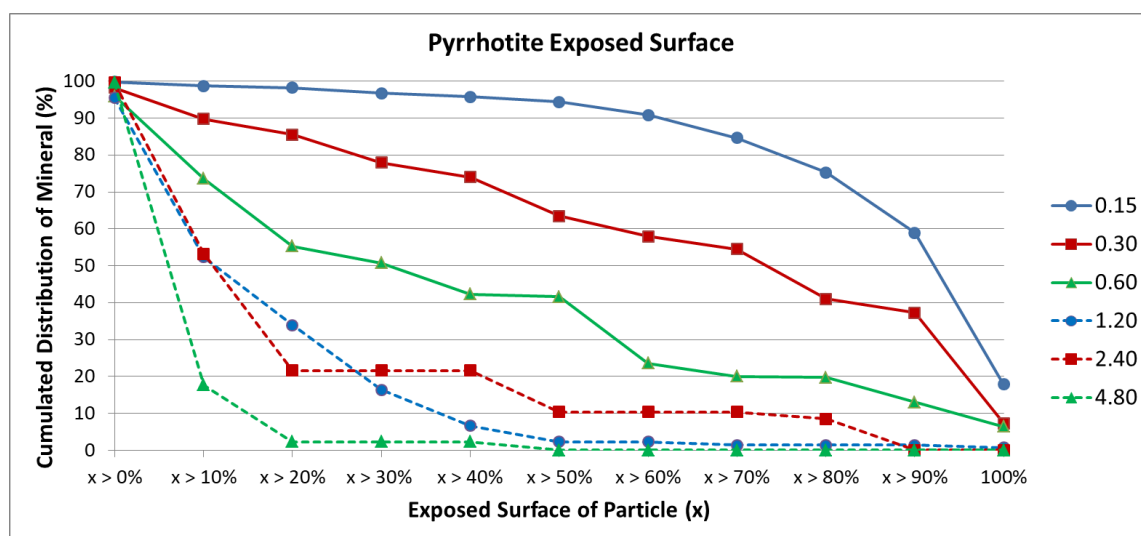


Figure 4. 14: Pyrrhotite Exposed Surface.

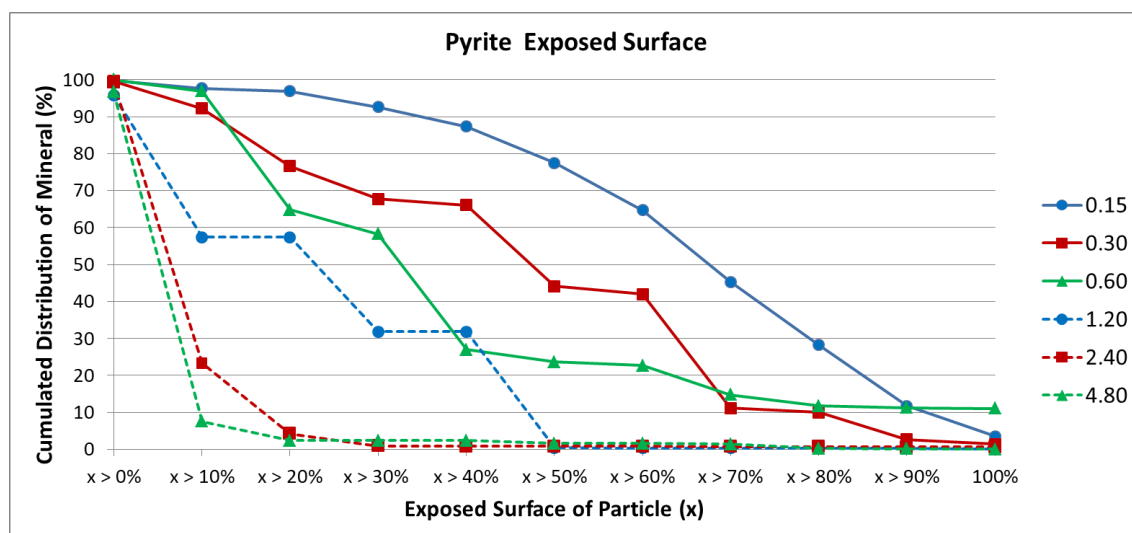


Figure 4. 15: Pyrite Exposed Surface.

These results show a difference between pyrrhotite and pyrite. For pyrite, only particles 0.15- to 1.20-mm present a significant percentage of exposed surfaces. For larger size particles (>2.40 mm), the percentage of the exposed surface was smaller than 20 %. For pyrrhotite, this was not

the same. For particles 0.15- to 2.40-mm, pyrrhotite has in all cases larger exposed surface than pyrite. For example, the 0.15-mm size particles have 85 % of its particles with more than 70% of their surface exposed (Figure 4.14) while for pyrite this value was only 45% (Figure 4.15).

The combination of the MLA (Figure 4.14) and sulfur content (Table 4.1) indicates that despite all aggregate particle sizes have high amounts of sulfur from the pyrrhotite, their exposed surface are different. The particles 0.15-, 0.30-and 0.60-mm have 70% or more of exposed pyrrhotite surface. The 1.2- and 2.4-mm have at least 50% of this sulfide with exposed surfaces. On the other hand, the sample 4.8-mm, despite having about the same quantity of sulfur coming from the pyrrhotite to the other sizes, has almost no exposed surface of this sulfide. According to Janzen *et al.* (2000), an increase in the specific surface area of the iron sulfides significantly intensifies the rate of sulfide oxidation.

4.3 Oxidation with H₂O₂ solution

4.3.1 Sulfate determination by pH

Initially, six samples of 5-g of 0.15 to 0.60-mm grain sizes were subjected to the oxidation process with an H₂O₂ solution as described in 3.2.3. Each sample was oxidized three times and at each stage, the pH of the solution was measured. These results are shown in Table 4.2.

Table 4. 2: Aggregate solution pH after H₂O₂ oxidation.

Sample ID	pH after stage 1	pH after stage 2	pH after stage 3
Blank solution	4.79	4.60	4.90
0.15	2.18	2.44	3.19
0.30	2.37	2.63	3.25
0.60	2.34	2.65	3.28

The sulfide oxidation reactions led to a decrease in the acidity of the solution, comparing the blank solution and the remaining solution after the process. The released acid suggests that sulfide particles are still available to oxidation (qualitative information). However, the measured pH values are very close for a particle size at stage 1 and stage 2 and also for particles of different sizes at each stage, although the amounts of released SO₄ differ, as will be seen next. This indicates that the solution pH is not a suitable parameter to quantify the oxidation

potential in relation to the size of the aggregate particle as observed by Guirguis and Shehara (2017).

4.3.2 Sulfate determination by spectrophotometry

The sulfate content released in the solutions was determined by spectrophotometry (turbidimetry). The test has a calibration curve ranging from 0 to 40 mg/l of sulfate, as explained in Section 3.2.4. Consequently, it is interesting that the samples under analysis have concentrations within this range to guarantee the reliability of the results. To check the magnitude of sulfate released into the solution, a sample of 0.15-mm size particle after stage 1 was diluted 10 times and then subjected to the test. The value found was 42.28 mg/l, which is outside the calibration curve. After the initial tests, it was decided to dilute 20 times the solution samples after stage 1 and 10 times after stage 2 for samples 0.15 to 0.60-mm; for samples 1.20 and 2.40-mm, the solution was diluted 10 times after stage 1 and 5 times after stage 2. No dilution was used for sample 4.80-mm. The solution concentrations, after stages 1 and 2, are presented in Table 4. 3.

Table 4. 3: Actual concentrations of the SO_4 (mg/l).

Sample ID	A- SO_4^{2-} after Stage 1	B - SO_4^{2-} after Stage 2	Total SO_4^{2-} (A+B)
0.15	492.15	211.35	703.50
0.30	414.61	159.33	573.94
0.60	314.70	100.30	415.00
1.20	295.60	85.01	380.61
2.40	216.03	54.61	270.64
4.80	30.32	0.75	31.07

The results of sulfate concentrations in the solutions indicate a more significant difference after Stage 2 for the different size particles under scrutiny. Thus, this test was more appropriate than the pH to check reactivity for the sulfide oxidation.

Turbidimetry analysis was also performed on solutions after a third Stage. The measured sulfate concentration values were close to stage 2. Thus, it was decided that the values of stages 1 and 2 were sufficient for purposes of comparison of reactivity.

From Table 4.3 values, the total amount of sulfur in the solution was calculated using stoichiometry. The results are presented in Table 4.4. It is observed that there is a decrease in

the sulfate concentration released as the particle size increases. This suggests lower reactivity of sulfides for larger size particles, which corroborates the results obtained for the MLA analyses: the larger the particle is, there are less exposed sulfides.

Table 4. 4: Sulfur released in solution.

Sample ID	Particle size (mm)	After Stage 1 (A)	After Stage 2 (B)	Total S in the solution (A+B)	Total S released in the solution
		(mg/l)	(mg/l)	(mg/l)	(%)
0.15	$0.15 \leq \Phi < 0.30$	164.1	70.5	234.5	2.34
0.30	$0.30 \leq \Phi < 0.60$	138.2	53.1	191.3	1.91
0.60	$0.60 \leq \Phi < 1.20$	104.9	33.4	138.3	1.38
1.20	$1.20 \leq \Phi < 2.40$	98.5	28.3	126.9	1.27
2.40	$2.40 \leq \Phi < 4.80$	72.0	18.2	90.2	0.90
4.80	$4.80 \leq \Phi < 6.30$	10.1	0.3	10.4	0.10

4.3.3 Sulfur content in the solid residues

The remaining total sulfur content in the solid residues of the aggregates after the oxidizing procedure (stage 1 and 2) was determined by the direct combustion test as described in 3.2.1. To quantify the remaining sulfur of pyrite and pyrrhotite it was necessary to remove the sulfate which may have precipitated in solid leaching the samples with deionized water (item 3.2.3). These results are shown in Table 4.5. For comparison, the values before the oxidation are also presented.

Table 4. 5: Sulfur in initial and after oxidation for samples.

Sample ID	INITIAL			AFTER OXIDATION			
	Total Sulfur (%)	Sulfur from Pyrite (%)	Sulfur from Pyrrhotite (%)	Total Sulfur (%)	Sulfur from Pyrite (%)	Sulfur from Pyrrhotite (%)	Sulfur from precipitated sulfate in the solid residue (%)
0.15	2.93	0.95	1.98	0.40	0.09	0	0.31
0.30	2.60	1.16	1.44	0.43	0.12	0.01	0.30
0.60	1.93	0.93	1.00	0.44	0.12	0.11	0.21
1.20	2.14	0.79	1.35	0.81	0.13	0.63	0.05
2.40	1.87	0.72	1.15	0.84	0.15	0.56	0.13
4.80	1.59	0.51	1.08	1.40	0.35	0.97	0.08

These results indicate the oxidation process with the H_2O_2 solution is efficient since the values of sulfur content after oxidation are much smaller. However, the larger the particle size is, the less effective was the oxidation procedure. For example, the 0.3-mm sample had in the solid residues approximately 17 % of its initial sulfur content; for the 4.80-mm, this value was 88 %.

Figure 4.16 shows the relationship between the total sulfur content in solutions after the oxidation process with respect to the remaining sulfur on the solid portion for each aggregate particle size. The analysis of the figure indicates that, for aggregate investigated, the larger the particle size is the less effective is the oxidation procedure.

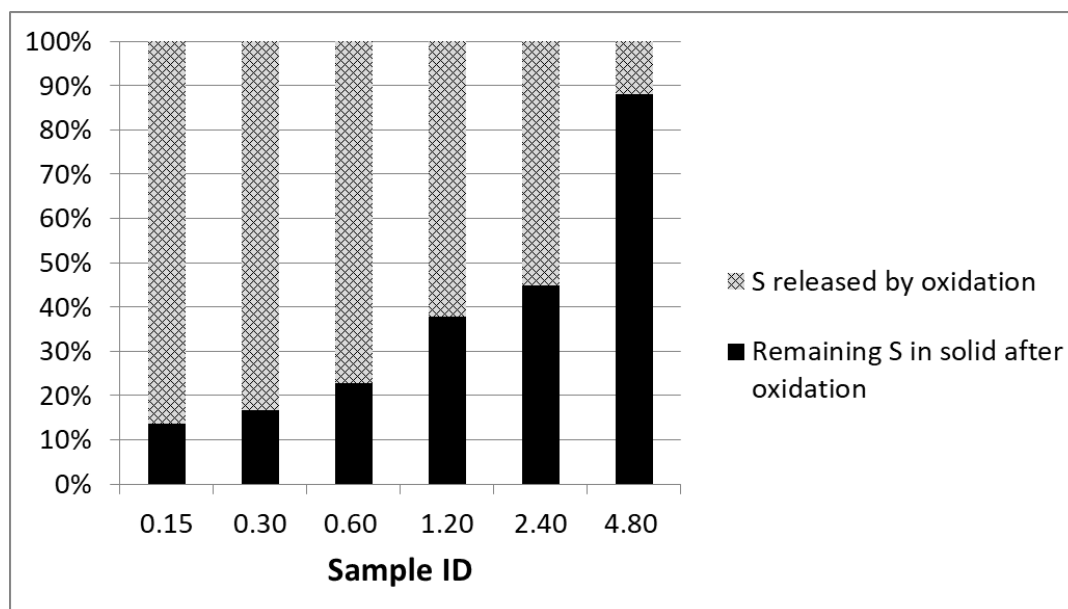


Figure 4. 16: Sulfur contents in solid residue and in the solution after oxidation processes

4.3.4 Verification of oxidation with H_2O_2 efficiency

To verify the efficiency of the oxidation process, the sulfur content was calculated by adding the sulfur content released to the solution (Table 4.4) and the sulfur content presents in the solid residue (Table 4.5). The correlation between the amount of sulfur in the aggregate in its natural state and the sum of the amounts of sulfur in solution and solid after oxidation shows that these values are close regardless of the particle size range, which demonstrates the effectiveness of the process (Figure 4.17).

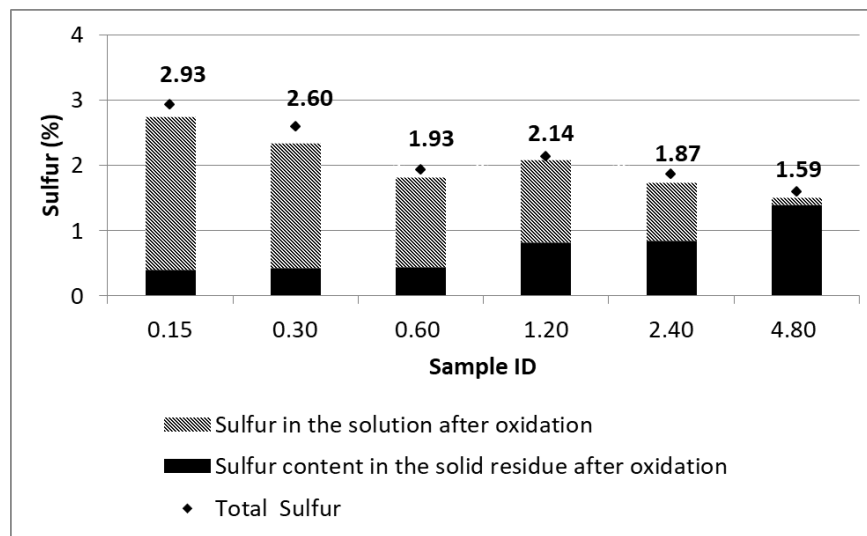


Figure 4. 17: Sulfur contents in initial and after oxidation (solution and residues)

The efficiency of the process can also be verified by the remaining amount of pyrrhotite. These results are shown in Figure 4.18. For 0.15 and 0.30 the pyrrhotite oxidized completely. In these samples, 60% and 90% of particles, respectively, had at least 50% of the pyrrhotite surface exposed (Figure 4.14). For 0.60 the same level of exposure occurs in 40% of the particles (Figure 4.14) and about 89% of pyrrhotite was oxidized (Table 4.5). It was observed that the oxidation process was efficient for both sulfides.

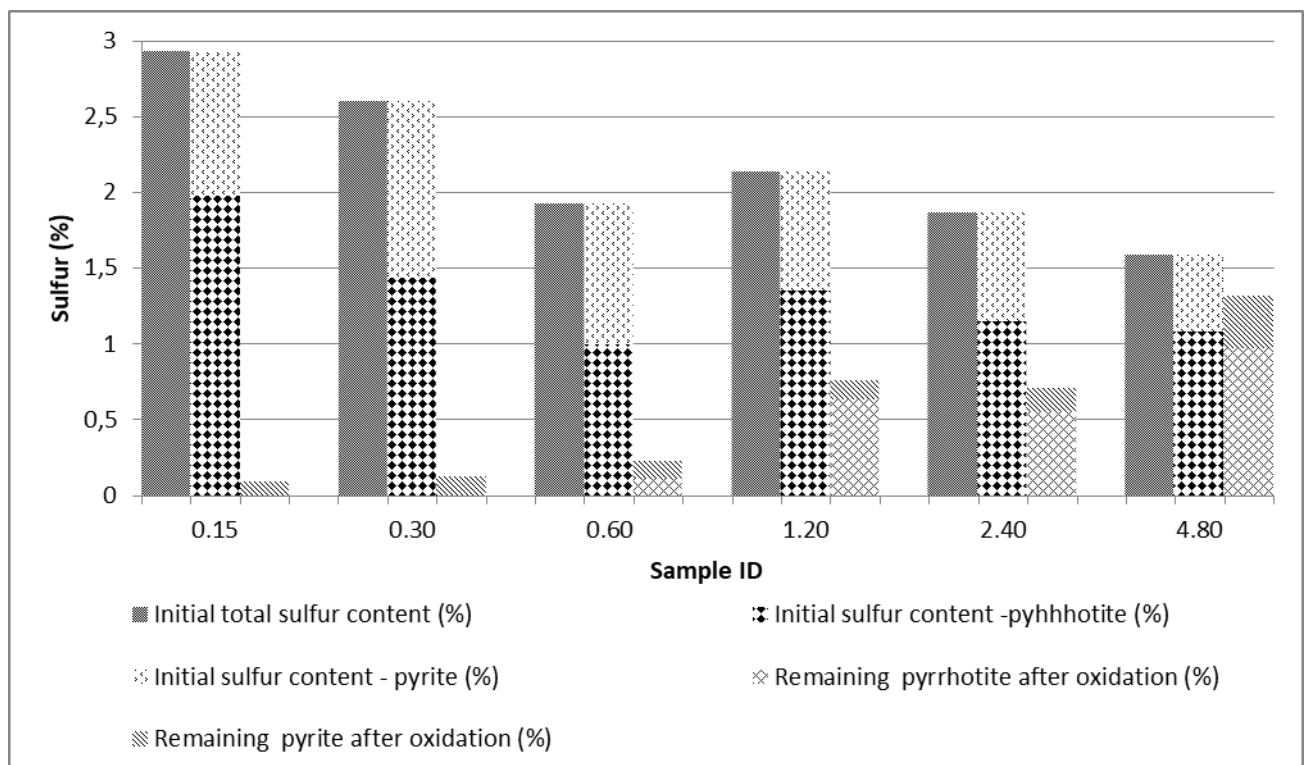


Figure 4. 18: Pyrite and pyrrhotite contents in solid residue after oxidation processes.

Samples of the sulfide-bearing aggregates, after oxidation in an H_2O_2 solution, were evaluated by MLA. The resulting images for 0.15-mm are shown in 4.19 and 4.20.

In Figure 4.19 it was possible to visually observe an expressive reduction in the presence of pyrite and pyrrhotite after oxidation, which demonstrates that the process was efficient. This significant reduction is due to the greater iron sulfides exposed surface for the 0.15-mm aggregate (Figure 4.14).

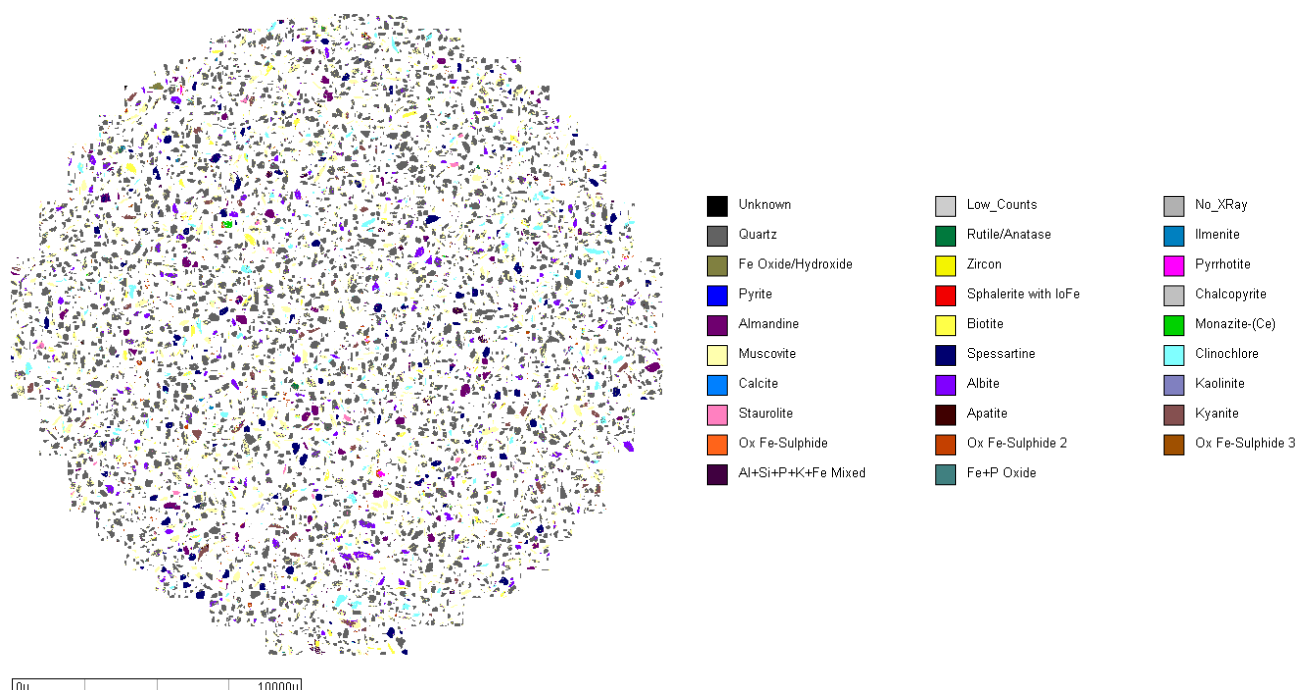


Figure 4. 19: MLA analysis after oxidation– 0.15-mm size particle.

After oxidation, the pyrite and pyrrhotite particles which were not completely disintegrated were very degraded (Figure 4.20). The presence of iron and sulfur oxides after oxidation was observed. They were called Ox Fe-Sulfide (that have about 12% of sulfur and 35% of iron), Ox Fe-Sulfide 2 (that have about 5% of sulfur and 52% of iron) or Ox Fe-Sulfide 3 (that have about 2% of sulfur and 56% of iron). These oxides surround the iron sulfides particles that have not been completely disintegrated by oxidation.

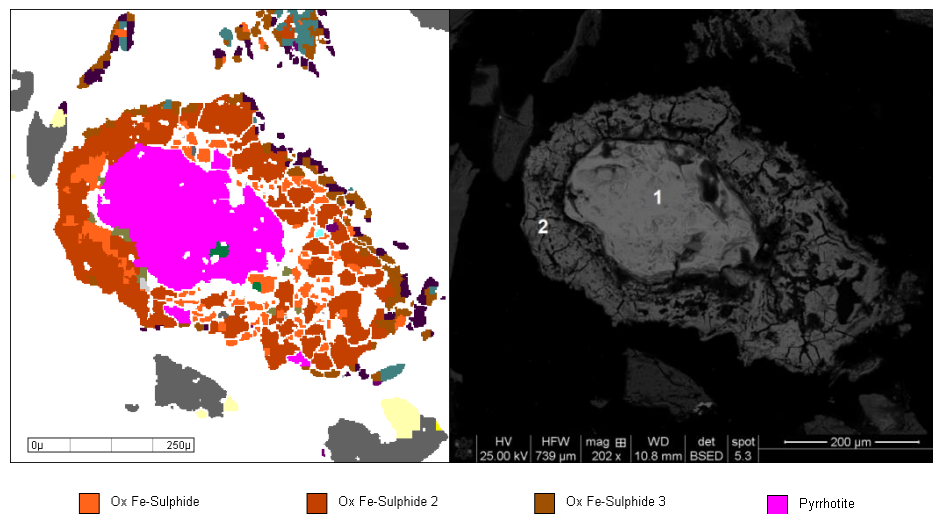


Figure 4. 20: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.15-mm sample: Pyrrhotite grains (1) involved by iron-sulfide (2).

As observed for the 0.15-mm sample, in 0.30-mm particles there is a reduction in the presence of pyrite and pyrrhotite after oxidation (Figure 4. 21). Also for this grain size, the oxides surrounding the iron sulfides were not completely disintegrated by oxidation. The amount of exposed pyrite and pyrrhotite surface is smaller in size 0.3-mm than 0.15-mm, as shown in Figure 4.14 and 4.15. For this reason, several grains after the oxidation had still had preserved sulfides (Figure 4.22).

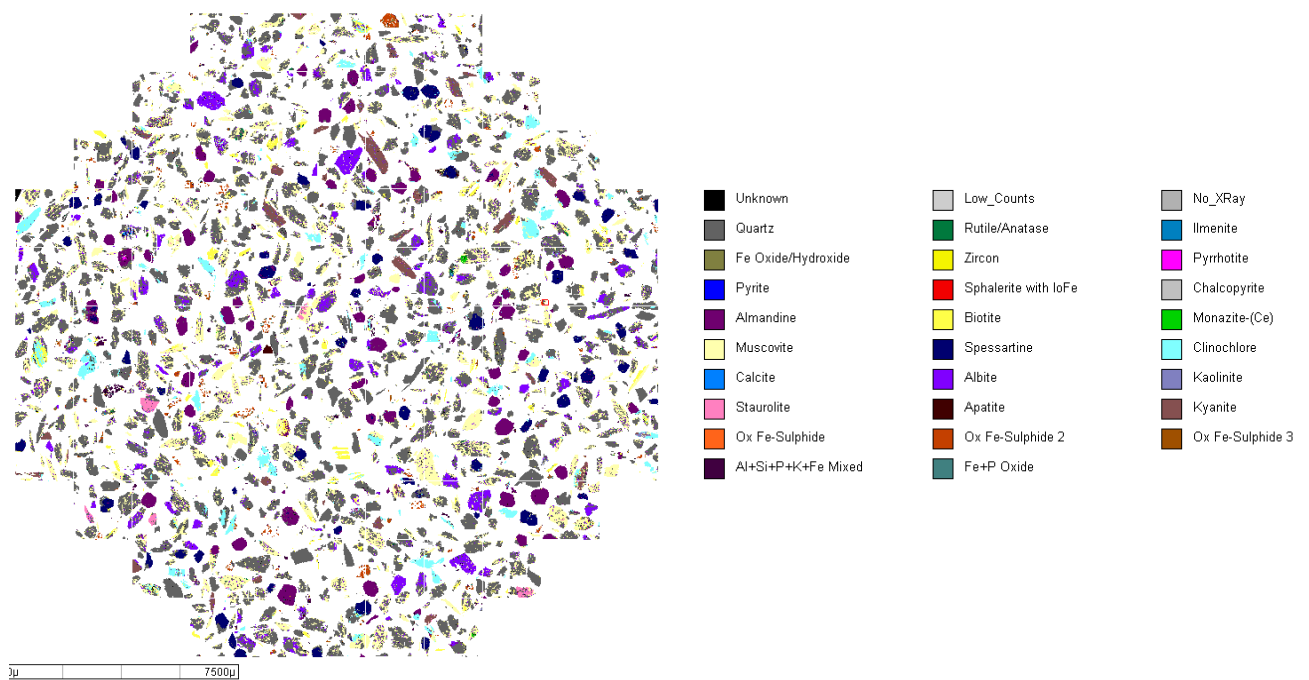


Figure 4. 21: MLA analysis after oxidation – 0.30-mm size particle.

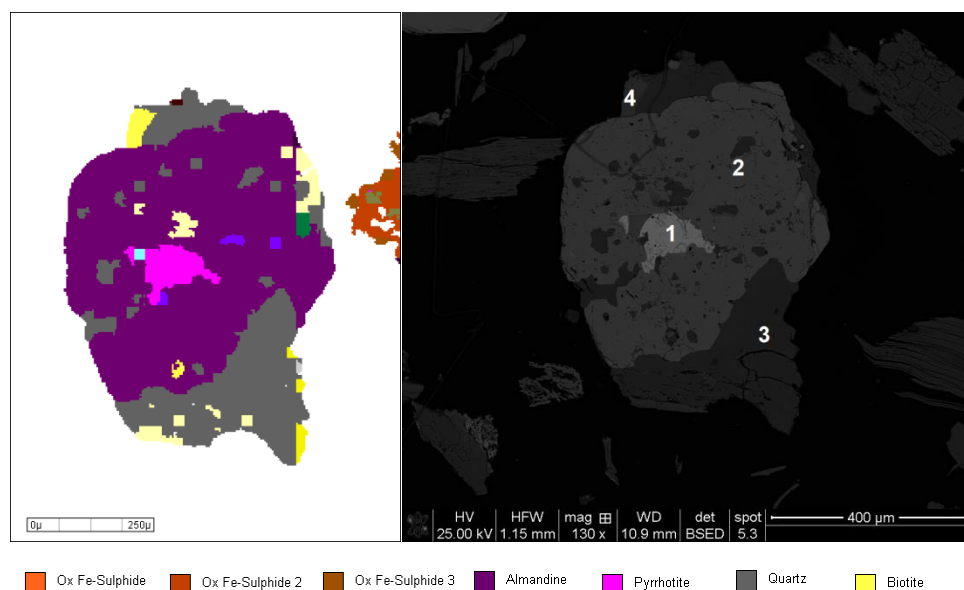


Figure 4. 22: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.30-mm sample: Pyrrhotite grains (1) disseminated in a matrix of Almandine (2), Quartz (3) and Biotite (4). No exposed surface of sulfide and no iron-sulfide oxide.

For 0.60-mm particles, it was also observed a reduction in the presence of pyrite and pyrrhotite after oxidation (Figure 4.23). In this sample, several grains had preserved sulfides after the oxidation because they were inside the particles. In some particles, iron sulfides were not completely disintegrated by oxidation procedures (Figure 4.24).

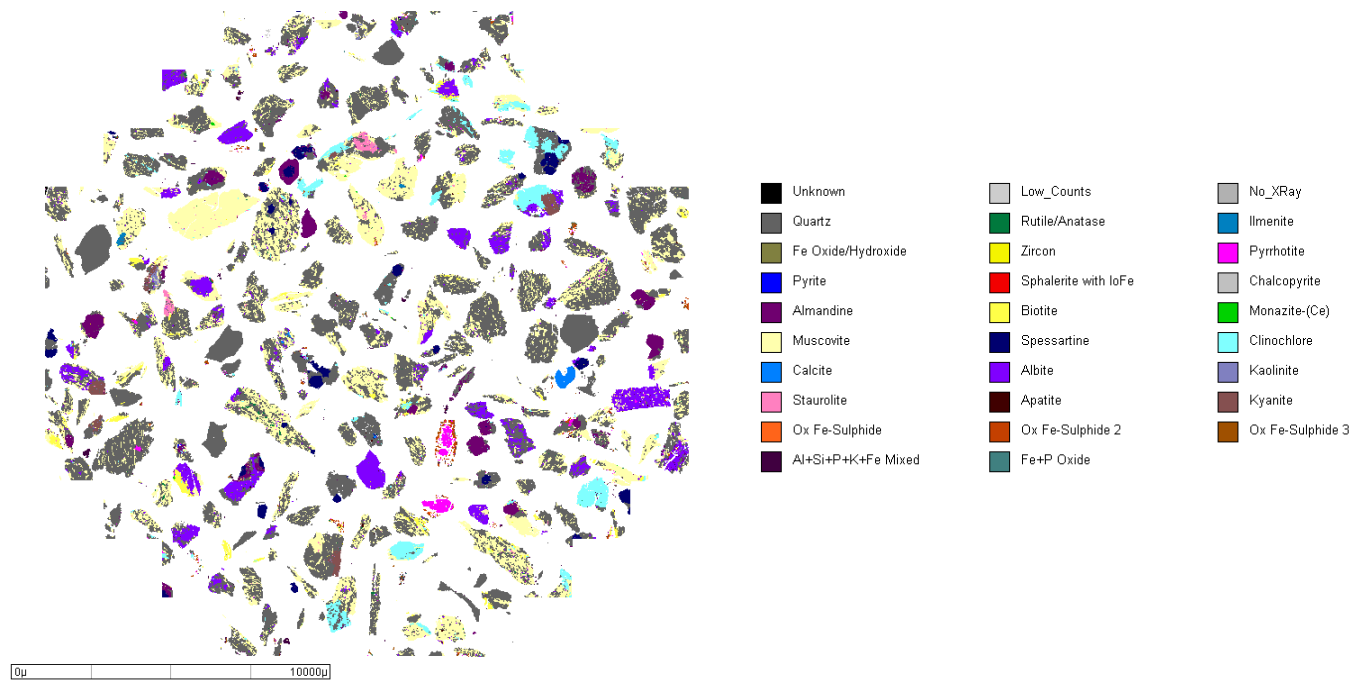


Figure 4. 23: MLA analysis after oxidation – 0.60-mm size particle.

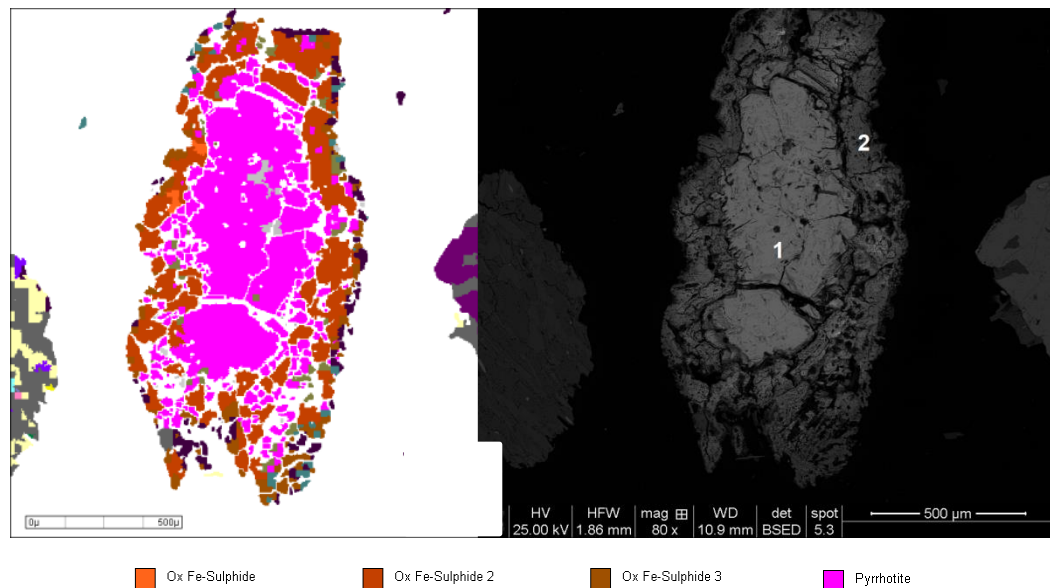


Figure 4. 24: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 0.60-mm sample: Pyrrhotite grains (1) involved by an iron-sulfide oxide (2).

As observed for the 0.60-mm sample, in 1.20-mm particles several grains had preserved sulfides after the oxidation because they were inside the particles. Iron sulfides were not completely disintegrated by oxidation procedures in some particles (Figure 4.25). For example, in Figure 4.26 it is possible to observe that a pyrrhotite grain oxidized only in a small area. This area was exposed at the edge of the aggregate particle. In addition to the protection that the albite and

kyanite matrix provided to the pyrrhotite, it is understood that the oxidation products themselves can serve as protective barriers for the remainder of the sulfide.

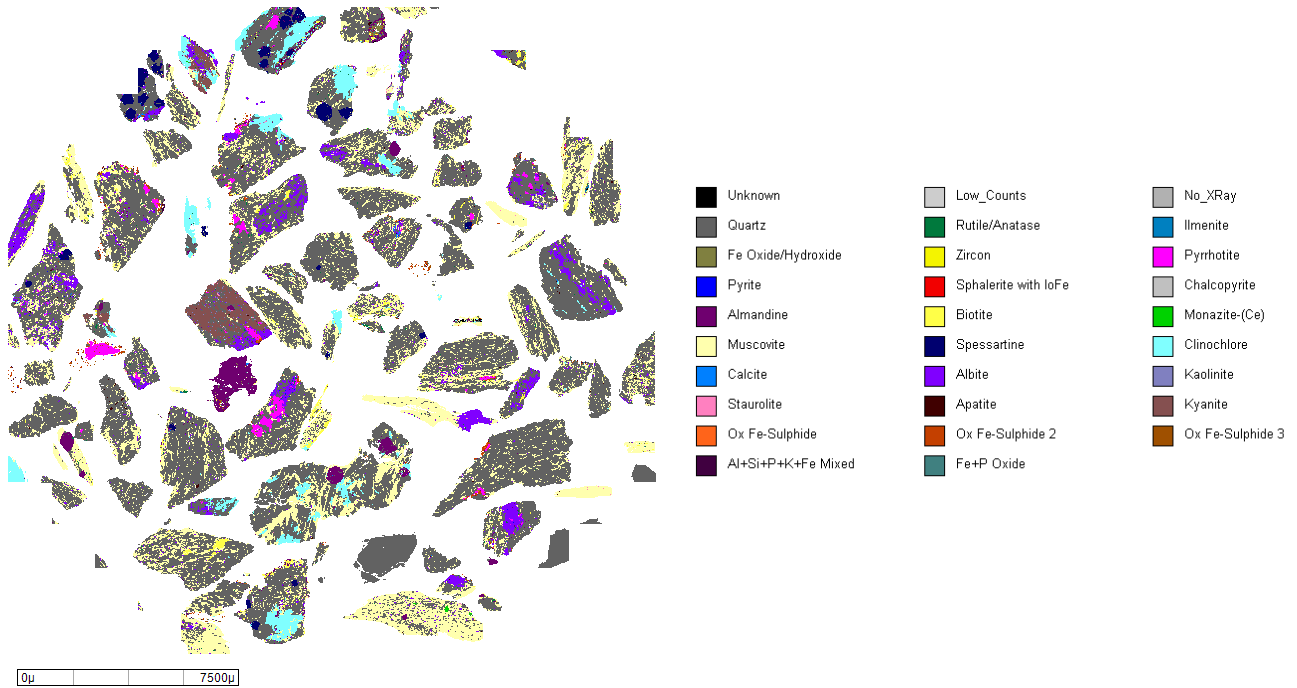


Figure 4. 25: MLA analysis after oxidation – 1.20-mm size particle.

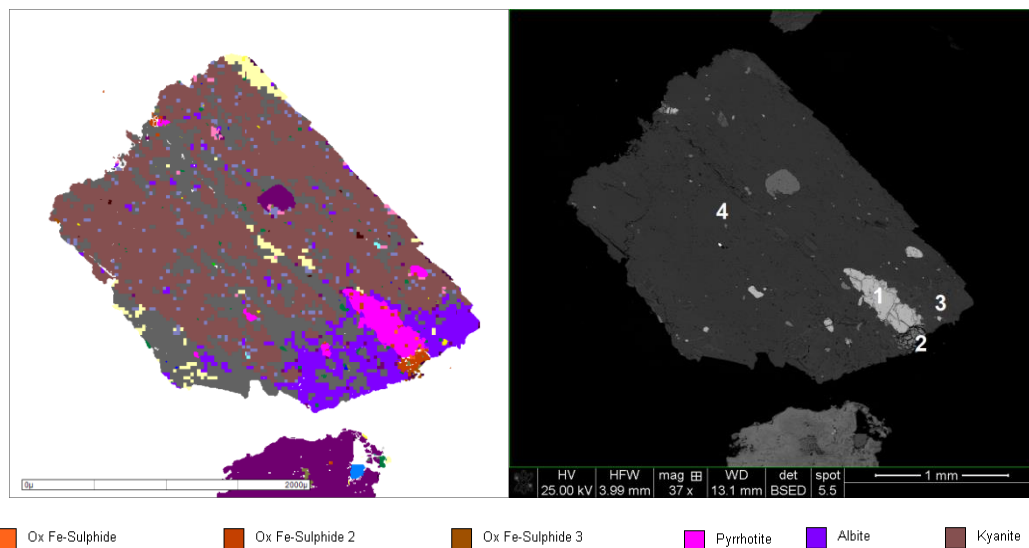


Figure 4. 26: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 1.20-mm sample: Pyrrhotite grains (1) with an iron-sulfide oxide (2) only in edge exposed. Most part of the pyrrhotite is preserved since it is inserted in an Albite (3) and Kyanite (4) matrix.

For 2.40-mm particles, it was also observed preserved sulfides after the oxidation (Figure 4.27). They were inside the particles and with no exposed surface as shown in Figure 4.28. The pyrrhotite grain is completely surrounded by a quartz and muscovite matrix.

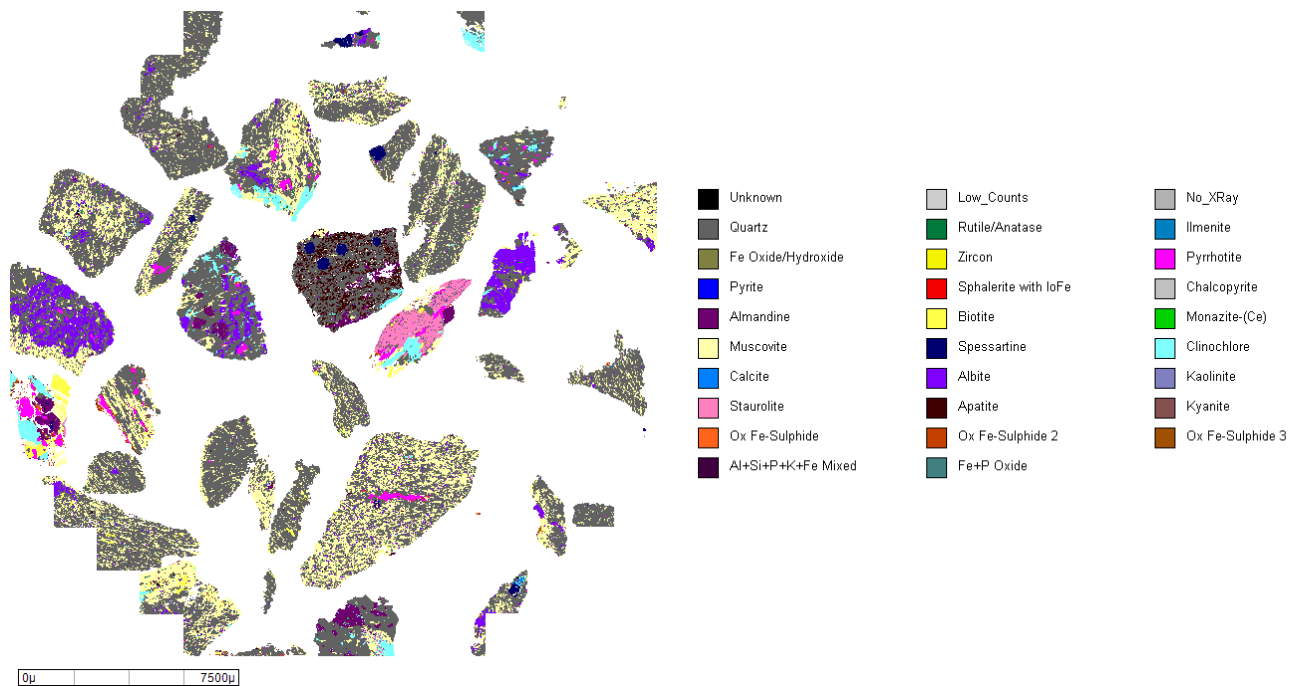


Figure 4. 27: MLA analysis after oxidation – 2.40-mm size particle.

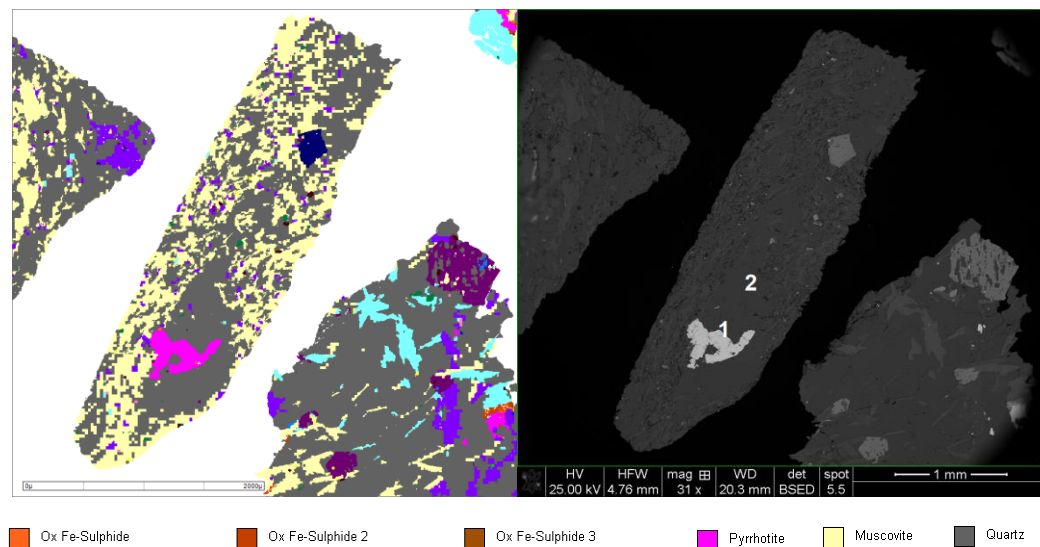


Figure 4. 28: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 2.40-mm sample: Pyrrhotite grains (1) with no iron-sulfide oxide surrounded by a Quartz and Muscovite (3) matrix.

Particles 4.80-mm size show few occurrences of sulfides (Figure 4.29 and 4.30). The reason for this finding may be the fact that the layer exposed after the polishing procedure with abrasive paper is superficial and the sulfides may be more occluded. Therefore the block containing the oxidized sample 4.8 was sawn for exposure of the innermost part of the particles (Figure 4.31).

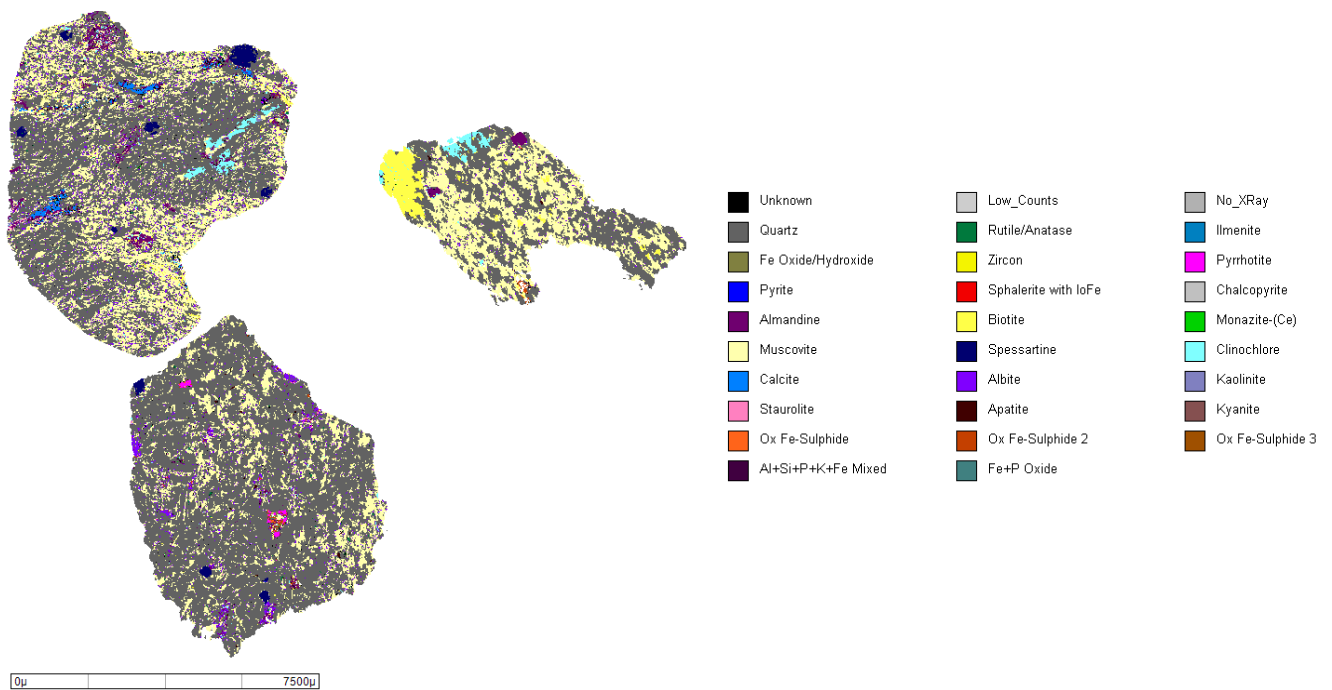


Figure 4.29: MLA analysis after oxidation – 4.80-mm size particle.

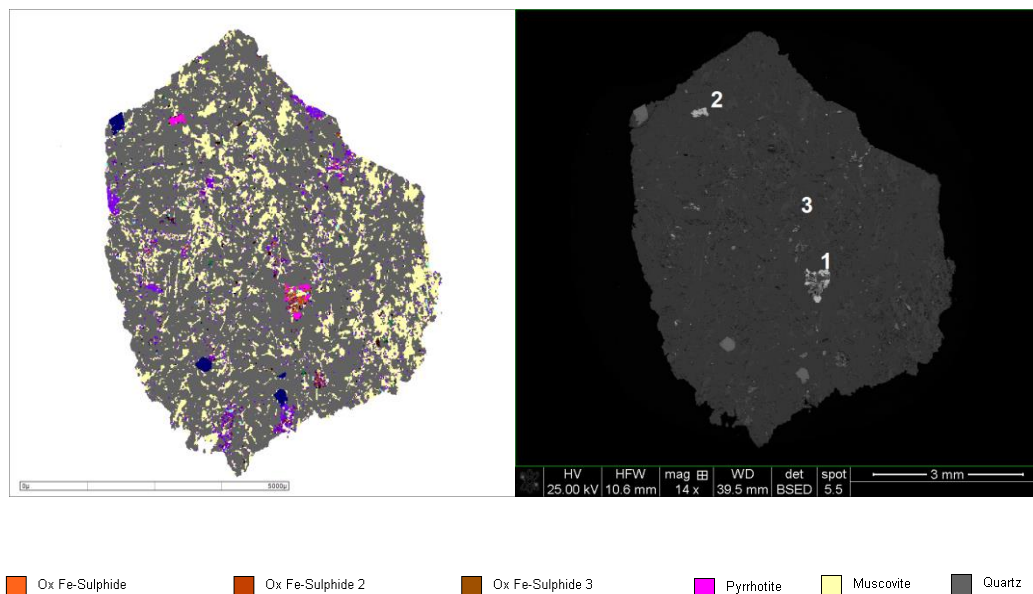


Figure 4.30: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of typical mineralogical phases 4.80-mm sample: Pyrrhotite grains with (1) and without (2) iron-sulfide oxide surrounded by Quartz and Muscovite (3) matrix.



Figure 4.31: Block sawn of sample 4.80 oxidized for MLA analysis.

The pieces were inserted (with the cutting surface facing up) into a round mold with epoxy resin to form another hardened block of 30 mm in diameter; then, and a new MLA analysis was performed. This analysis revealed a large number of pyrrhotite grains in the quartz and muscovite matrix (Figure 4.32). Almost the totality of pyrrhotite grains was preserved, with no sign of oxidation, even after the sample has gone through the oxidation process with an H_2O_2 solution.

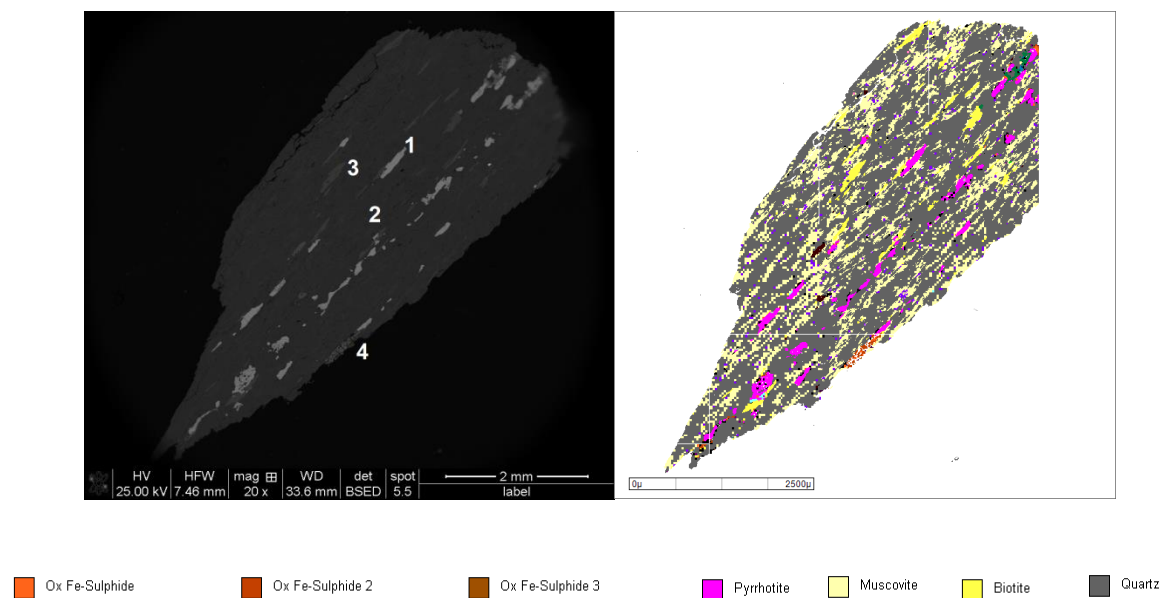


Figure 4.32: Segmented oxidized particles by MLA (left) and backscattered electron (BSE) (right) images of sliced 4.80-mm sample: Pyrrhotite grains (1) with no iron-sulfide oxide disseminated in a Quartz and Muscovite (2) matrix and biotite grains (3). Only at the aggregate edge, there is pyrrhotite with some iron-sulfide oxidation (4).

5

CONCLUSIONS AND SUGGESTIONS

Aggregates can contain minerals that are potentially reactive with the cement hydration products, such as rocks with sulfides in their mineralogical composition. Concrete produced with sulfide-bearing aggregates can degrade due to the appearance of expansive compounds formed inside the hardened concrete and originating from the oxidation of the sulfide minerals. Hence, the technical community has great resistance in the use of sulfide-bearing aggregates. This fact is reinforced by the limited number of standards and specifications that address the problem and the ones that do are extremely conservative. However, it is believed that not every sulfide-bearing aggregate should be discarded and that this behavior may be generating unnecessary environmental and economic liabilities.

In this work, a feasible testing procedure was developed to evaluate how reactive a sulfide-bearing aggregate is to be used in concrete when considering the sulfide type and exposed surface in different aggregate sizes. A contextualization on the sulfide oxidation and the internal sulfate attack on concrete was presented, as well as the state of the art of the research developed worldwide.

Aggregate derived from rocks contained sulfides (pyrite and pyrrhotite) in the order of 5% with least 1.5% of sulfur in their composition was used. The rocks were first crushed and sieved. Particle sizes bigger or equal than 0.15- and smaller than 6.30-mm were selected. The total sulfur amount was determined by direct combustion and the results indicate a significant larger content of total sulfur as well as of pyrite and pyrrhotite in all particle sizes. The results also showed that, in general, the sulfur content decreased with the increasing aggregate size; however for all sizes, the sulfur content was larger than what is commonly acceptable. With

only this information it would not be possible to define the most reactive size. Complementary tests were then performed: the Mineral Liberation Analyzer (MLA) and H_2O_2 solution.

It was possible to quantify the exposed surface of each sulfide by the Mineral Liberation Analyzer (MLA) system. It allows us to evaluate the potential sulfide available for the oxidation reaction. The combination of the MLA and sulfur content indicates that despite all aggregate particle sizes having high amounts of sulfur from the pyrrhotite or pyrite, their exposed surfaces were different. Furthermore, it was observed that the smaller the particle, the larger the sulfide exposed surface was.

The MLA results for the oxidation potential of sulfides (in each particle size) were verified by the test with the H_2O_2 solution. Each size sample was soaked in the H_2O_2 solution to release sulfate (from the sulfide oxidation). Two verifications were done on the solution after the oxidation process: pH measurement and quantification of the released sulfur. The pH values were very close for all particle sizes indicating that the pH is not a suitable parameter to verify the oxidation potential with respect to aggregate size. The sulfate released in solution was determined by spectrophotometry. The total amount of sulfur was calculated using stoichiometry. Particle sizes 0.15- to 0.60-mm released more than 70% of sulfur after H_2O_2 oxidation. The values of released sulfur for aggregate sizes 1.20- and 2.40-mm were slightly smaller: 62% and 55%, respectively. For the 4.8-mm sample, only 12% of the sulfur was released after oxidation. Thus, the quantification of the released sulfur was more adequate to evaluate the reactivity, as it showed significant differences according to the particle sizes.

Samples of the sulfide-bearing aggregates, after oxidation in the H_2O_2 solution, were again evaluated by MLA. It was possible to visually observe in particles sizes 0.15 to 2.40 mm an expressive reduction in the presence of pyrite and pyrrhotite after oxidation, which demonstrates that the H_2O_2 solution procedure was efficient. The exposed pyrite and pyrrhotite were very degraded with Fe-oxides surrounding the iron sulfides. This was abundantly observed in smaller sizes of particles: 0.15- to 0.60-mm. For 1.20- and 2.40-mm, some sulfides were very degraded and other grains oxidized only in a small exposed area at the edge of the aggregate particle. In addition to the protection that the rock matrix provided to the sulfide, it is understood that the oxidation products can themselves serve as mechanical protective barriers for the

remainder of the sulfide. For 4.80-mm particles, the results indicate that most of the sulfides were not oxidized since they were inside the particles and with no exposed surface.

Based on these results, it was concluded that the MLA and H_2O_2 solution procedure complement each other. The results also showed that the smaller the particle size was the more effective was the oxidation procedure with H_2O_2 solution, even when aggregates of different sizes had similar amounts of total sulfur. This corroborates the MLA results: for the investigated rock, smaller size particles have the highest exposed pyrite and pyrrhotite surface and were those that presented higher sulfide degradation after oxidation.

Thus, for the material under scrutiny, smaller size aggregates (2.4- to 0.15-mm) are reactive: thus, it should be discarded for use in concrete. Particle sizes larger than 4.80 mm may not be reactive for the analyzed material; however additional tests will be needed to verify their possible use in concrete.

In this way, limiting the use of the sulfide-bearing aggregate only by the amount of sulfur is a mistake, as it has been observed that the oxidation behavior of these sulfides varies according to their exposed surface as well as the particle size.

5.1 Suggestions for future investigations

Based on the findings of the present study, further investigations should address the following:

- Repeat this protocol in samples of different type of sulfide-bearing aggregates to verify its efficiency;
- Perform mortar/concrete expansion tests with aggregate sizes which showed low levels of sulfide oxidation after H_2O_2 solution procedure;
- If the results from the above tests are satisfactory, establish a threshold value for the amount of oxidation after the H_2O_2 solution procedure.

6

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7

APPENDIX

APPENDIX A: FREE SURFACE (EXPOSED SURFACE)

The free surface result, provided by the MLA, are presented in this appendix. Figures 4.14 and 4.15 were drawn by combining the values of the table first line - Pyrite or Pyrrhotite Free Surface of Particle (%) - and last line - Cumulative Distribution of the Mineral (%). For samples 1.20 to 4.80, the average value from the three tables was used.

Sample 0.15 - pyrite

Data Source: Am 03_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	9,00	16,00	3,00	5,00	7,00	8,00	8,00	8,00	16,00		
Mean Phase ECD (µm)	40,34	32,03	49,62	32,44	39,35	66,16	54,36	59,62	57,12		
Mean Phase Max Span (µm)	71,52	56,61	80,09	49,28	72,79	107,21	96,85	105,58	101,73		
Particle Distribution (%)	0,18	0,27	0,05	0,04	0,06	0,13	0,13	0,08	0,20		
Mean Density	3,41	3,28	3,59	3,42	3,15	3,92	4,38	3,66	4,00		
Distribution of Mineral (%)	0,96	1,12	0,33	0,44	0,80	3,47	3,23	2,04	6,38		
Cum. Distn. of Mineral (%)	99,74	98,78	97,65	97,33	96,88	96,08	92,62	89,39	87,35		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
13,00	13,00	11,00	9,00	16,00	12,00	16,00	19,00	8,00	11,00	6,00	98,00
66,25	54,94	102,30	92,15	75,23	88,08	84,42	79,18	108,96	60,24	146,74	28,56
119,02	85,79	175,81	153,15	141,80	139,28	137,47	120,31	161,46	89,91	221,93	43,47
0,13	0,12	0,23	0,25	0,23	0,16	0,23	0,22	0,14	0,04	0,13	0,07
3,79	4,37	4,25	4,73	4,41	4,77	4,78	4,86	4,96	4,95	5,00	5,01
3,49	4,32	8,48	10,34	9,09	7,03	9,98	9,88	6,68	1,82	6,33	3,54
80,97	77,48	73,16	64,68	54,34	45,26	38,23	28,25	18,37	11,69	9,87	3,54

Sample 0.30 - pyrite

Data Source: Am 04_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	7,00	3,00	3,00	5,00	3,00	5,00	1,00	2,00	1,00		
Mean Phase ECD (µm)	62,02	58,88	60,62	113,43	70,36	80,74	97,26	70,25	70,05		
Mean Phase Max Span (µm)	108,34	86,99	102,78	201,78	109,87	135,83	145,09	109,75	130,28		
Particle Distribution (%)	0,65	0,17	0,36	0,53	0,16	0,15	0,02	0,02	0,01		
Mean Density	2,85	4,46	3,03	3,19	3,37	3,60	4,11	4,75	3,87		
Distribution of Mineral (%)	6,46	0,94	3,52	12,10	3,58	5,27	0,79	0,85	0,41		
Cum. Distn. of Mineral (%)	99,58	93,12	92,18	88,66	76,56	72,98	67,71	66,91	66,06		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
4,00	1,00	1,00	5,00	2,00	2,00	3,00	2,00	2,00	0,00	1,00	9,00
144,80	69,92	145,43	149,10	144,70	67,32	39,23	139,07	120,33	0,00	120,96	42,70
230,54	104,51	276,25	207,60	208,80	111,96	67,55	204,60	193,92	0,00	192,27	59,27
0,37	0,01	0,03	0,31	0,12	0,01	0,01	0,06	0,04	0,00	0,02	0,02
4,61	4,99	4,88	4,89	4,59	4,74	4,65	4,95	4,96	0,00	4,99	5,01
21,53	0,41	1,77	22,54	8,23	0,77	0,39	4,53	2,86	0,00	1,23	1,40
65,65	44,12	43,71	41,94	19,40	11,17	10,40	10,01	5,48	2,62	2,62	1,40

Sample 0.60 - pyrite

Data Source: Am 05_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	2,00	2,00	3,00	1,00	4,00	4,00	4,00	3,00	5,00		
Mean Phase ECD (µm)	93,06	53,63	95,16	41,02	75,79	72,60	103,69	66,07	65,98		
Mean Phase Max Span (µm)	157,94	108,34	162,73	54,31	125,62	116,61	164,66	109,79	122,05		
Particle Distribution (%)	1,39	0,14	0,63	0,01	0,14	0,08	0,46	0,25	0,06		
Mean Density	2,72	3,08	4,13	3,73	3,57	4,29	3,34	3,90	4,50		
Distribution of Mineral (%)	2,07	1,04	31,91	0,20	3,70	2,86	21,71	9,59	2,91		
Cum. Distn. of Mineral (%)	100,00	97,93	96,89	64,98	64,78	61,08	58,22	36,51	26,91		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
1,00	0,00	2,00	3,00	1,00	2,00	4,00	1,00	1,00	1,00	0,00	34,00
59,22	0,00	61,02	102,89	85,37	65,54	62,27	42,51	44,74	37,65	0,00	50,89
73,85	0,00	108,77	156,46	174,42	106,99	85,97	63,85	70,77	63,52	0,00	75,07
0,01	0,00	0,01	0,07	0,04	0,02	0,02	0,00	0,00	0,00	0,00	0,12
4,86	0,00	4,32	4,37	4,74	4,90	4,70	4,62	4,96	4,99	0,00	5,01
0,42	0,00	0,93	4,63	3,25	1,16	1,92	0,22	0,24	0,17	0,00	11,08
24,01	23,59	23,59	22,66	18,03	14,78	13,63	11,71	11,49	11,25	11,08	11,08

[illegible]

Sample 1.20 C - pyrite

Data Source: M1904437_6C_GXMAP

Mineral Groupings: Grupo

Mineral: Pyrite

Liberation Classes: 5% classes

Data Type: Weight%

Filter: Unfiltered

Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%
No. of Particles	20,00	1,00	0,00	0,00	0,00	1,00	0,00	0,00	0,00
Mean Phase ECD (µm)	17,16	48,59	0,00	0,00	0,00	56,23	0,00	0,00	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	28,40	1,56	0,00	0,00	0,00	3,42	0,00	0,00	0,00
Mean Density	2,91	2,85	0,00	0,00	0,00	3,23	0,00	0,00	0,00
Distribution of Mineral (%)	13,28	6,50	0,00	0,00	0,00	76,78	0,00	0,00	0,00
Cum. Distrn. of Mineral (%)	97,60	84,31	77,82	77,82	77,82	77,82	1,04	1,04	1,04

[illegible]

Sample 2.40 A - pyrite

Data Source: Amostra 07_GXMAP

Mineral Groupings: Ungrouped

Mineral: Pyrite

Liberation Classes: 10% classes

Data Type: Weight%

Filter: Unfiltered

Pyrite Free Surface of Particle (%)	0% < x <= 10%	10% < x <= 20%	20% < x <= 30%	30% < x <= 40%	40% < x <= 50%	50% < x <= 60%	60% < x <= 70%	70% < x <= 80%	80% < x <= 90%	90% < x < 100%	100%
No. of Particles	1,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Phase ECD (µm)	33,67	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Phase Max Span (µm)	45,55	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	1,37	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Density	2,75	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Distribution of Mineral (%)	100,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cum. Distrn. of Mineral (%)	100,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00

Sample 2.40 B - pyrite

Data Source: M1904438_7B_GXMAP

Mineral Groupings: Grupo

Mineral: Pyrite

Liberation Classes: 5% classes

Data Type: Weight%

Filter: Unfiltered

Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%
No. of Particles	10,00	1,00	2,00	0,00	0,00	0,00	0,00	1,00	0,00
Mean Phase ECD (µm)	27,12	9,89	56,25	0,00	0,00	0,00	0,00	25,46	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	50,23	0,00	8,72	0,00	0,00	0,00	0,00	0,01	0,00
Mean Density	2,82	2,74	2,81	0,00	0,00	0,00	0,00	3,26	0,00
Distribution of Mineral (%)	38,63	0,01	56,96	0,00	0,00	0,00	0,00	0,18	0,00
Cum. Distrn. of Mineral (%)	98,07	59,44	59,44	2,47	2,47	2,47	2,47	2,47	2,30

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
0,00	0,00	0,00	1,00	0,00	0,00	0,00	1,00	0,00	0,00	0,00	2,00
0,00	0,00	0,00	79,82	0,00	0,00	0,00	63,62	0,00	0,00	0,00	143,40
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,00	0,00	0,00	0,01	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,03
0,00	0,00	0,00	4,19	0,00	0,00	0,00	5,06	0,00	0,00	0,00	5,01
0,00	0,00	0,00	0,25	0,00	0,00	0,00	0,16	0,00	0,00	0,00	1,89
2,30	2,30	2,30	2,30	2,05	2,05	2,05	2,05	1,89	1,89	1,89	1,89

Sample 2.40 C - pyrite

Data Source: M1904439_7C_GXMAP									
Mineral Groupings: Grupo									
Mineral: Pyrite									
Liberation Classes: 5% classes									
Data Type: Weight%									
Filter: Unfiltered									
Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%
No. of Particles	10,00	2,00	0,00	0,00	1,00	0,00	0,00	1,00	0,00
Mean Phase ECD (µm)	21,91	24,22	0,00	0,00	40,38	0,00	0,00	31,86	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	64,90	7,83	0,00	0,00	0,92	0,00	0,00	0,01	0,00
Mean Density	2,87	2,74	0,00	0,00	2,96	0,00	0,00	3,99	0,00
Distribution of Mineral (%)	72,77	16,76	0,00	0,00	10,10	0,00	0,00	0,17	0,00
Cum. Distrn. of Mineral (%)	99,80	27,02	10,27	10,27	10,27	0,17	0,17	0,17	0,00

[illegible]

Sample 4.80 A - pyrite

[illegible]

Sample 4.80 B - pyrite

Data Source: M1904440_8B_GXMAP									
Mineral Groupings: Grupo									
Mineral: Pyrite									
Liberation Classes: 5% classes									
Data Type: Weight%									
Filter: Unfiltered									
Pyrite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%
No. of Particles	7,00	0,00	1,00	0,00	0,00	1,00	0,00	0,00	0,00
Mean Phase ECD (µm)	22,41	0,00	49,60	0,00	0,00	49,49	0,00	0,00	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	62,87	0,00	0,01	0,00	0,00	0,01	0,00	0,00	0,00
Mean Density	2,86	0,00	4,71	0,00	0,00	5,19	0,00	0,00	0,00
Distribution of Mineral (%)	82,11	0,00	0,09	0,00	0,00	0,09	0,00	0,00	0,00
Cum. Distrn. of Mineral (%)	99,24	17,13	17,13	17,04	17,04	17,04	16,95	16,95	16,95

[illegible]

Sample 4.80 C - pyrite

[illegible]

Sample 0.15 - pyrrhotite

Data Source: Am 03_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	41,00	59,00	26,00	15,00	21,00	16,00	12,00	16,00	12,00		
Mean Phase ECD (µm)	33,84	36,77	37,94	33,80	55,64	80,35	50,24	58,59	59,54		
Mean Phase Max Span (µm)	51,87	59,06	66,73	54,95	92,60	134,81	81,79	91,52	91,31		
Particle Distribution (%)	1,20	1,38	0,69	0,14	0,40	0,37	0,10	0,19	0,10		
Mean Density	3,01	3,27	3,86	3,70	3,56	3,36	3,66	4,10	4,14		
Distribution of Mineral (%)	0,43	0,60	0,40	0,14	0,66	0,84	0,27	0,67	0,38		
Cum. Distn. of Mineral (%)	99,80	99,37	98,76	98,36	98,22	97,56	96,72	96,45	95,78		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
14,00	8,00	17,00	22,00	26,00	33,00	37,00	51,00	63,00	97,00	118,00	246,00
73,26	84,53	105,19	116,76	137,16	114,05	145,87	149,07	141,35	171,67	189,12	99,50
118,56	137,25	172,28	180,57	206,22	172,27	218,68	220,86	214,18	253,84	276,70	150,29
0,25	0,17	0,63	0,47	0,73	0,62	1,05	1,29	1,54	3,00	3,81	2,89
4,10	4,25	4,38	4,44	4,37	4,47	4,57	4,58	4,61	4,61	4,62	4,62
0,97	0,76	2,82	2,45	3,78	3,41	5,88	7,39	8,98	17,91	23,21	17,84
95,39	94,42	93,66	90,84	88,39	84,61	81,20	75,32	67,93	58,95	41,04	17,84

Sample 0.30 - pyrrhotite

Data Source: Am 04_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	104,00	28,00	14,00	16,00	7,00	17,00	7,00	7,00	7,00		
Mean Phase ECD (µm)	24,76	46,15	31,24	42,33	32,73	50,73	67,35	35,86	67,65		
Mean Phase Max Span (µm)	37,68	75,36	48,34	67,01	55,92	82,08	117,62	61,32	112,82		
Particle Distribution (%)	10,93	2,51	0,89	1,20	0,33	1,23	0,61	0,25	0,58		
Mean Density	2,95	2,97	3,34	3,32	3,15	3,39	4,03	3,26	3,83		
Distribution of Mineral (%)	3,66	4,82	1,84	2,31	1,39	6,27	2,93	0,95	5,07		
Cum. Distn. of Mineral (%)	98,20	94,54	89,71	87,88	85,56	84,17	77,91	74,97	74,03		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
9,00	4,00	6,00	3,00	2,00	6,00	7,00	4,00	4,00	10,00	5,00	148,00
72,09	80,07	55,24	182,27	87,45	101,74	137,34	112,37	135,68	293,83	303,75	37,45
109,21	125,07	103,49	235,70	140,03	151,32	202,01	183,15	197,04	425,89	476,90	57,35
0,70	0,36	0,20	0,20	0,08	0,76	0,42	0,17	0,15	1,57	0,71	0,53
4,54	4,15	4,43	4,51	4,59	4,40	4,52	4,60	4,61	4,61	4,60	4,62
5,53	3,50	1,96	2,58	0,89	8,40	5,08	1,93	1,86	20,39	9,54	7,30
68,96	63,43	59,93	57,96	55,39	54,50	46,10	41,02	39,09	37,22	16,84	7,30

Sample 0.60 - pyrrhotite

Data Source: Am 05_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	35,00	21,00	8,00	5,00	6,00	7,00	3,00	5,00	3,00		
Mean Phase ECD (µm)	26,84	35,95	62,32	33,37	22,92	58,71	112,34	38,84	42,46		
Mean Phase Max Span (µm)	40,98	58,14	101,02	55,93	36,48	88,78	188,51	62,71	61,10		
Particle Distribution (%)	17,70	4,05	1,80	0,76	0,07	0,43	0,37	0,18	0,02		
Mean Density	2,76	3,08	3,11	3,10	4,35	3,05	3,57	4,10	3,43		
Distribution of Mineral (%)	10,38	11,94	12,93	5,41	0,30	4,21	6,03	2,45	0,38		
Cum. Distn. of Mineral (%)	95,92	85,54	73,59	60,67	55,25	54,95	50,74	44,71	42,26		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
3,00	6,00	9,00	3,00	4,00	3,00	2,00	3,00	2,00	2,00	1,00	172,00
44,27	65,16	80,93	79,31	45,79	28,97	47,97	170,41	95,75	113,67	374,85	26,22
86,22	104,07	141,16	121,88	66,26	42,07	75,08	269,18	163,98	158,32	619,19	38,95
0,02	0,36	0,38	0,12	0,03	0,01	0,01	0,17	0,05	0,03	0,17	0,19
4,31	3,85	4,31	4,51	4,63	4,21	4,17	4,44	4,67	4,58	4,63	4,62
0,28	7,12	10,90	2,77	0,75	0,16	0,18	5,48	1,24	1,05	5,56	6,39
41,88	41,60	34,48	23,58	20,81	20,06	19,90	19,71	14,24	13,00	11,95	6,39

Sample 1.20 A- pyrrhotite

Data Source: Amostra 06_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 10% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 10%	10% < x <= 20%	20% < x <= 30%	30% < x <= 40%	40% < x <= 50%	50% < x <= 60%	60% < x <= 70%	70% < x <= 80%	80% < x <= 90%	90% < x < 100%	100%
No. of Particles	23,00	2,00	2,00	1,00	0,00	0,00	1,00	0,00	0,00	0,00	16,00
Mean Phase ECD (µm)	29,45	47,60	137,70	99,92	0,00	0,00	188,74	0,00	0,00	0,00	21,57
Mean Phase Max Span (µm)	48,39	75,17	245,40	183,62	0,00	0,00	358,37	0,00	0,00	0,00	32,51
Particle Distribution (%)	33,11	7,94	2,99	1,42	0,00	0,00	0,16	0,00	0,00	0,00	0,01
Mean Density	2,78	2,91	3,19	3,18	0,00	0,00	4,02	0,00	0,00	0,00	4,62
Distribution of Mineral (%)	31,01	22,96	22,09	11,32	0,00	0,00	2,58	0,00	0,00	0,00	0,26
Cum. Distrn. of Mineral (%)	90,21	59,20	36,24	14,15	2,83	2,83	2,83	0,26	0,26	0,26	0,26

Sample 1.20 B- pyrrhotite

Data Source: M1904436_6B_GXMAP											
Mineral Groupings: Grupo											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	16,00	7,00	2,00	2,00	1,00	0,00	2,00	0,00	1,00		
Mean Phase ECD (µm)	59,90	114,28	218,52	132,34	132,25	0,00	281,33	0,00	269,43		
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00		
Particle Distribution (%)	22,53	13,67	0,30	0,44	2,80	0,00	0,40	0,00	0,08		
Mean Density	2,91	2,93	3,13	2,94	3,05	0,00	3,77	0,00	3,55		
Distribution of Mineral (%)	8,23	47,01	2,17	2,31	15,80	0,00	6,18	0,00	1,05		
Cum. Distrn. of Mineral (%)	97,69	89,46	42,45	40,28	37,97	22,17	22,17	15,98	15,98		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
1,00	1,00	0,00	0,00	0,00	0,00	0,00	0,00	1,00	2,00	2,00	4,00
195,85	117,75	0,00	0,00	0,00	0,00	0,00	0,00	90,79	224,98	106,57	126,67
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
1,12	0,01	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,07	0,02	0,04
3,36	3,75	0,00	0,00	0,00	0,00	0,00	0,00	4,55	4,59	4,61	4,62
11,76	0,20	0,00	0,00	0,00	0,00	0,00	0,00	0,12	1,50	0,37	0,99
14,93	3,18	2,98	2,98	2,98	2,98	2,98	2,98	2,98	2,86	1,36	0,99

Sample 1.20 C- pyrrhotite

Data Source: M1904437_6C_GXMAP

Mineral Groupings: Grupo

Mineral: Pyrrhotite

Liberation Classes: 5% classes

Data Type: Weight%

Filter: Unfiltered

Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%
No. of Particles	18,00	4,00	4,00	3,00	1,00	0,00	1,00	2,00	0,00
Mean Phase ECD (µm)	71,33	98,26	155,70	110,40	260,32	0,00	129,36	186,30	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	25,72	7,80	5,55	0,71	1,72	0,00	0,03	1,59	0,00
Mean Density	2,86	2,90	3,03	3,06	3,42	0,00	3,29	3,36	0,00
Distribution of Mineral (%)	21,33	21,94	25,32	2,52	14,56	0,00	0,24	11,71	0,00
Cum. Distn. of Mineral (%)	98,59	77,25	55,31	29,99	27,48	12,92	12,92	12,68	0,97

[illegible]

Sample 2.40 A - pyrrhotite

Data Source: Amostra 07_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 10% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 10%	10% < x <= 20%	20% < x <= 30%	30% < x <= 40%	40% < x <= 50%	50% < x <= 60%	60% < x <= 70%	70% < x <= 80%	80% < x <= 90%	90% < x <= 100%	100%
No. of Particles	12,00	2,00	0,00	0,00	1,00	0,00	0,00	1,00	1,00	0,00	0,00
Mean Phase ECD (µm)	48,16	229,28	0,00	0,00	133,39	0,00	0,00	99,34	477,92	0,00	0,00
Mean Phase Max Span (µm)	82,22	442,06	0,00	0,00	305,00	0,00	0,00	127,92	782,01	0,00	0,00
Particle Distribution (%)	61,69	8,32	0,00	0,00	0,67	0,00	0,00	0,09	0,34	0,00	0,00
Mean Density	2,81	2,87	0,00	0,00	3,65	0,00	0,00	4,53	4,47	0,00	0,00
Distribution of Mineral (%)	46,37	31,66	0,00	0,00	11,23	0,00	0,00	1,82	8,54	0,00	0,00
Cum. Distrn. of Mineral (%)	99,64	53,26	21,60	21,60	21,60	10,36	10,36	10,36	8,54	0,00	0,00

Sample 2.40 B - pyrrhotite

Data Source: M1904438_7B_GXMAP											
Mineral Groupings: Grupo											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	12,00	3,00	0,00	2,00	1,00	0,00	0,00	1,00	0,00		
Mean Phase ECD (µm)	69,69	157,74	0,00	74,10	106,58	0,00	0,00	270,52	0,00		
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00		
Particle Distribution (%)	57,28	12,80	0,00	0,05	0,02	0,00	0,00	1,79	0,00		
Mean Density	2,78	2,86	0,00	2,87	3,40	0,00	0,00	3,58	0,00		
Distribution of Mineral (%)	22,36	38,69	0,00	0,17	0,13	0,00	0,00	17,86	0,00		
Cum. Distrn. of Mineral (%)	97,89	75,53	36,84	36,84	36,67	36,54	36,54	36,54	18,68		

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x <= 100%	100%
1,00	1,00	0,00	0,00	0,00	0,00	0,00	0,00	1,00	1,00	2,00	4,00
48,71	742,55	0,00	0,00	0,00	0,00	0,00	0,00	151,48	470,01	639,30	97,77
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,01	0,39	0,00	0,00	0,00	0,00	0,00	0,00	0,01	0,13	0,49	0,02
4,63	4,14	0,00	0,00	0,00	0,00	0,00	0,00	4,58	4,61	4,63	4,62
0,09	6,19	0,00	0,00	0,00	0,00	0,00	0,00	0,26	2,48	9,24	0,44
18,68	18,60	12,41	12,41	12,41	12,41	12,41	12,41	12,41	12,15	9,67	0,44

Sample 2.40 C - pyrrhotite

[illegible]

Sample 4.80 A- pyrrhotite

Data Source: Amostra 08_GXMAP											
Mineral Groupings: Ungrouped											
Mineral: Pyrrhotite											
Liberation Classes: 10% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 10%	10% < x <= 20%	20% < x <= 30%	30% < x <= 40%	40% < x <= 50%	50% < x <= 60%	60% < x <= 70%	70% < x <= 80%	80% < x <= 90%	90% < x < 100%	100%
No. of Particles	7,00	2,00	0,00	0,00	1,00	0,00	0,00	0,00	0,00	0,00	2,00
Mean Phase ECD (µm)	41,10	34,93	0,00	0,00	89,81	0,00	0,00	0,00	0,00	0,00	7,49
Mean Phase Max Span (µm)	66,44	57,57	0,00	0,00	129,63	0,00	0,00	0,00	0,00	0,00	9,60
Particle Distribution (%)	77,78	10,28	0,00	0,00	0,24	0,00	0,00	0,00	0,00	0,00	0,00
Mean Density	2,95	3,46	0,00	0,00	3,42	0,00	0,00	0,00	0,00	0,00	4,62
Distribution of Mineral (%)	81,97	15,33	0,00	0,00	2,33	0,00	0,00	0,00	0,00	0,00	0,00
Cum. Distrn. of Mineral (%)	99,64	17,67	2,34	2,34	2,34	0,00	0,00	0,00	0,00	0,00	0,00

Sample 4.80 B- pyrrhotite

[illegible]

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x < 100%	100%
0,00	0,00	0,00	0,00	1,00	1,00	1,00	0,00	1,00	0,00	1,00	1,00
0,00	0,00	0,00	0,00	122,52	152,08	294,61	0,00	91,53	0,00	87,28	75,89
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,01	0,02	0,07	0,00	0,01	0,00	0,01	0,00
0,00	0,00	0,00	0,00	4,73	4,64	4,64	0,00	4,71	0,00	4,62	4,62
0,00	0,00	0,00	0,00	0,47	0,72	2,70	0,00	0,26	0,00	0,24	0,18
4,56	4,56	4,56	4,56	4,56	4,09	3,37	0,68	0,68	0,42	0,42	0,18

Sample 4.80 C- pyrrhotite

Data Source: M1904441_8C_GXMAP											
Mineral Groupings: Grupo											
Mineral: Pyrrhotite											
Liberation Classes: 5% classes											
Data Type: Weight%											
Filter: Unfiltered											
Pyrrhotite Free Surface of Particle (%)	0% < x <= 5%	5% < x <= 10%	10% < x <= 15%	15% < x <= 20%	20% < x <= 25%	25% < x <= 30%	30% < x <= 35%	35% < x <= 40%	40% < x <= 45%		
No. of Particles	5,00	2,00	0,00	1,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Phase ECD (µm)	80,10	82,36	0,00	45,68	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Phase Max Span (µm)	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Particle Distribution (%)	65,10	23,21	0,00	0,02	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Mean Density	2,78	2,94	0,00	3,04	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Distribution of Mineral (%)	63,74	36,12	0,00	0,07	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Cum. Distrn. of Mineral (%)	100,00	36,26	0,14	0,14	0,07	0,07	0,07	0,07	0,07	0,07	0,07

45% < x <= 50%	50% < x <= 55%	55% < x <= 60%	60% < x <= 65%	65% < x <= 70%	70% < x <= 75%	75% < x <= 80%	80% < x <= 85%	85% < x <= 90%	90% < x <= 95%	95% < x < 100%	100%
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,00	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	63,53	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	4,72	0,00	0,00	0,00
0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,07	0,00	0,00	0,00
0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,07	0,00	0,00	0,00

APPENDIX B: MINERAL ASSOCIATION

The mineral association results, provided by the MLA, are presented in this appendix. The associations referring to pyrite and pyrrhotite are highlighted in the tables. It can be observed that quartz is the main mineral phase associated with these sulfides in the studied material.

Sample 0.15

Mineral	Unknown	Low_Counts	No_XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0.00	0.00	0.00	5.27	0.95	0.00	1.98	0.00	32.06	12.04	0.00	2.96	1.72	0.00	7.35	0.17	0.70	3.84	3.20	0.13	0.04	0.94	0.00
Low_Counts	0.00	0.00	0.00	5.34	0.00	0.40	0.11	0.00	0.31	0.00	0.00	0.00	0.54	0.00	2.30	0.28	0.14	0.00	0.00	0.40	0.00	0.00	0.00
No_XRay	0.00	0.00	0.00	1.45	0.00	0.00	0.00	0.00	1.09	1.45	0.00	0.00	0.00	0.00	0.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.08	0.02	0.00	0.00	0.53	0.09	0.02	0.07	0.70	0.39	0.01	1.06	0.66	0.10	18.23	0.86	0.73	0.12	3.45	0.12	0.26	0.18	0.11
Rutile/Anatase	0.81	0.00	0.00	31.23	0.00	6.35	0.17	0.16	5.56	2.24	0.00	1.53	0.63	0.34	14.16	0.82	2.73	0.17	5.59	0.28	0.53	0.03	1.48
Ilmenite	0.00	0.29	0.00	21.93	24.76	0.00	0.35	0.00	7.21	0.00	0.00	0.45	1.62	0.00	2.61	0.00	3.10	0.00	0.90	0.00	0.16	0.00	0.00
Hematite	1.80	0.02	0.00	1.13	0.19	0.10	0.00	0.01	41.19	1.03	0.00	5.64	0.97	0.00	2.20	0.00	0.12	0.00	0.43	0.02	0.00	0.16	0.00
Zircon	0.00	0.00	0.00	31.14	1.29	0.00	0.04	0.00	1.00	0.00	0.00	2.37	3.95	0.00	26.44	1.12	1.79	0.00	5.36	0.00	1.70	0.00	5.86
Pyrrhotite	2.78	0.01	0.00	4.24	0.57	0.19	3.93	0.01	0.00	1.57	0.01	2.39	1.17	0.00	3.36	0.30	0.34	0.31	1.27	0.03	0.15	0.03	0.00
Pyrite	4.20	0.00	0.02	9.47	0.93	0.00	0.40	0.00	6.34	0.00	0.00	1.21	1.81	0.00	9.01	0.19	1.92	2.15	2.07	0.30	0.41	0.29	0.00
Sphalerite with loFe	0.00	0.00	0.00	31.90	0.00	0.00	0.00	0.00	12.38	0.00	0.00	0.00	0.00	0.00	27.62	0.00	0.00	0.00	12.38	0.00	0.00	0.00	0.00
Almandine	0.51	0.00	0.00	12.69	0.31	0.02	1.06	0.06	4.71	0.59	0.00	0.00	3.97	0.02	5.90	5.12	3.01	0.21	5.55	0.63	1.01	0.39	0.50
Biotite	0.28	0.02	0.00	7.45	0.12	0.08	0.17	0.10	2.16	0.83	0.00	3.72	0.00	0.06	12.92	0.10	4.96	0.06	1.83	0.11	0.37	0.13	0.08
Monazite-(Ce)	0.00	0.00	0.00	57.32	3.28	0.00	0.00	0.00	0.35	0.00	0.00	0.91	2.98	0.00	21.64	0.00	0.00	0.00	3.03	0.00	0.00	0.55	0.00
Muscovite	0.16	0.01	0.00	28.54	0.37	0.02	0.05	0.09	0.87	0.58	0.01	0.77	1.80	0.06	0.00	0.42	0.65	0.11	3.22	0.60	0.49	0.15	0.34
Spessartine	0.05	0.02	0.00	18.09	0.29	0.00	0.00	0.05	1.04	0.16	0.00	8.93	0.18	0.00	5.56	0.00	2.64	1.14	1.30	0.88	0.09	0.20	0.12
Clinocllore	0.09	0.00	0.00	6.62	0.42	0.12	0.02	0.03	0.50	0.72	0.00	2.28	4.02	0.00	3.76	1.15	0.00	0.10	1.83	0.36	0.70	0.33	0.03
Calcite	4.73	0.00	0.00	10.43	0.25	0.00	0.00	0.00	4.36	7.58	0.00	1.48	0.48	0.00	6.15	4.70	0.91	0.00	4.64	0.20	0.00	0.12	0.00
Albite	0.37	0.00	0.00	27.84	0.76	0.03	0.05	0.09	1.69	0.68	0.02	3.73	1.31	0.04	16.63	0.50	1.62	0.43	0.00	0.80	0.76	0.22	0.30
Kaolinite	0.14	0.09	0.00	9.27	0.36	0.00	0.02	0.00	0.34	0.92	0.00	4.01	0.75	0.00	29.15	3.19	2.97	0.18	7.48	0.00	5.41	0.08	13.16
Staurolite	0.03	0.00	0.00	14.57	0.50	0.04	0.00	0.20	1.38	0.93	0.00	4.69	1.84	0.00	17.48	0.23	4.27	0.00	5.29	3.99	0.00	0.07	8.66
Apatite	2.07	0.00	0.00	27.80	0.08	0.00	0.40	0.00	0.65	1.87	0.00	5.10	1.83	0.15	14.60	1.45	5.66	0.22	4.25	0.17	0.19	0.00	0.00
Kyanite	0.00	0.00	0.00	4.31	1.02	0.00	0.00	0.51	0.00	0.00	0.00	1.70	0.28	0.00	8.91	0.24	0.15	0.00	1.49	7.07	6.32	0.00	0.00

Sample 0.30

Mineral	Unknown	Low_Counts	No_XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0.00	0.00	0.00	21.88	2.06	0.00	1.83	0.00	13.62	13.31	0.00	4.71	1.16	0.00	5.82	3.25	0.72	7.88	1.65	0.77	0.00	0.00	0.00
Low_Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No_XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.88	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.13	0.00	0.00	0.00	0.87	0.17	0.32	0.07	1.58	0.36	0.03	2.30	1.76	0.07	35.77	1.34	1.41	0.29	6.51	0.27	0.47	0.23	0.22
Rutile/Anatase	0.47	0.00	0.00	33.59	0.00	1.60	0.21	0.02	3.93	0.53	0.00	2.49	1.51	0.00	27.54	0.56	3.30	0.87	7.16	0.35	0.46	0.07	2.19
Ilmenite	0.00	0.00	0.00	43.93	10.65	0.00	0.09	0.00	1.51	0.00	0.00	1.21	3.50	0.00	18.96	0.00	2.08	0.09	0.64	0.34	0.00	0.91	0.00
Hematite	1.40	0.00	0.00	41.46	0.71	0.05	0.00	0.00	17.36	3.49	0.00	8.54	0.82	0.00	5.08	0.69	0.47	0.02	0.71	0.00	0.00	0.15	0.00
Zircon	0.00	0.00	0.00	29.80	0.25	0.00	0.00	0.00	1.26	0.00	0.00	1.73	2.16	0.00	33.91	0.22	6.53	0.00	5.59	0.29	0.97	0.00	3.79
Pyrrhotite	0.97	0.00	0.00	19.14	1.23	0.07	1.62	0.04	0.00	1.21	0.01	3.51	1.79	0.02	10.44	1.68	1.44	1.82	4.42	0.21	0.18	0.10	0.75
Pyrite	3.71	0.00	0.00	17.32	0.65	0.00	1.27	0.00	4.73	0.00	0.00	2.68	1.06	0.00	10.26	0.18	3.09	0.00	1.34	0.52	0.24	0.18	0.00
Sphalerite with loFe	0.00	0.00	0.00	42.49	0.00	0.00	0.00	0.00	1.16	0.00	0.00	4.91	0.00	3.90	6.36	1.73	1.73	0.00	6.79	1.01	0.00	0.00	0.00
Almandine	0.31	0.00	0.00	25.68	0.72	0.05	0.73	0.05	3.23	0.63	0.03	0.00	2.20	0.13	7.63	6.99	4.08	0.98	6.13	1.23	1.29	0.11	0.25
Biotite	0.07	0.00	0.00	18.12	0.40	0.14	0.06	0.05	1.52	0.23	0.00	2.03	0.00	0.03	21.13	0.62	6.62	0.07	3.64	0.04	0.12	0.51	0.19
Monazite-(Ce)	0.00	0.00	0.00	43.53	0.00	0.00	0.00	0.00	0.92	0.00	1.47	7.24	1.52	0.00	12.13	0.00	4.68	0.00	4.62	0.00	4.08	2.45	0.00
Muscovite	0.04	0.00	0.00	44.07	0.87	0.09	0.05	0.10	1.06	0.27	0.00	0.84	2.53	0.02	0.00	0.50	1.39	0.20	4.01	0.43	0.50	0.22	0.35
Spessartine	0.34	0.00	0.00	23.91	0.26	0.00	0.09	0.01	2.47	0.07	0.02	11.18	1.07	0.00	7.25	0.00	1.75	0.97	2.30	0.71	0.18	0.09	0.00
Clinocllore	0.04	0.00	0.00	13.02	0.78	0.07	0.03	0.15	1.10	0.60	0.01	3.37	5.92	0.07	10.43	0.90	0.00	0.55	1.90	0.75	0.77	0.12	0.69
Calcite	3.11	0.00	0.00	19.19	1.51	0.02	0.01	0.00	10.05	0.00	0.00	5.89	0.46	0.00	10.94	3.65	4.02	0.00	3.99	0.17	0.05	0.00	0.00
Albite	0.06	0.00	0.00	38.91	1.10	0.01	0.03	0.08	2.18	0.17	0.02	3.28	2.11	0.04	19.44	0.77	1.23	0.36	0.00	0.73	0.72	0.20	0.22
Kaolinite	0.28	0.00	0.00	16.54	0.56	0.08	0.00	0.04	1.08	0.68	0.04	6.80	0.25	0.00	21.28	2.43	5.04	0.16	7.52	0.00	4.41	0.10	13.99
Staurolite	0.00	0.00	0.00	24.10	0.62	0.00	0.00	0.12	0.76	0.26	0.00	5.99	0.62	0.34	21.09	0.52	4.35	0.04	6.25	3.72	0.00	0.04	8.42
Apatite	0.00	0.00	0.00	33.90	0.25	0.52	0.17	0.00	1.22	0.58	0.00	1.45	7.28	0.59	26.07	0.78	2.00	0.00	5.01	0.25	0.12	0.00	4.31
Kyanite	0.00	0.00	0.00	6.91	1.78	0.00	0.00	0.29	1.95	0.00	0.00	0.70	0.59	0.00	9.02	0.00	2.37	0.00	1.15	7.17	5.13	0.92	0.00

Sample 0.60

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0,00	0,00	0,00	12,31	2,00	0,04	1,90	0,00	9,63	11,89	0,00	1,32	1,54	0,00	8,61	0,36	0,09	5,93	0,24	0,00	4,06	2,12	0,62
Low Counts	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
No XRay	0,00	0,00	0,00	2,73	0,00	0,00	0,00	0,00	0,30	2,73	0,00	0,00	0,00	0,00	0,91	0,00	1,21	0,00	0,00	0,00	0,00	0,00	0,00
Quartz	0,10	0,00	0,00	0,00	0,92	0,04	0,13	0,09	1,21	0,35	0,01	1,61	2,40	0,03	54,18	1,21	2,13	0,29	6,43	0,21	0,31	0,48	0,26
Rutile/Anatase	0,63	0,00	0,00	34,88	0,00	0,60	0,00	0,02	2,50	0,32	0,00	2,43	0,87	0,00	32,63	0,11	4,57	0,13	8,36	0,26	0,27	0,04	1,48
Ilmenite	0,26	0,00	0,00	31,48	13,17	0,00	0,00	0,00	3,68	0,00	0,00	1,28	0,94	0,00	20,44	0,00	7,36	0,00	0,00	0,00	0,00	0,00	0,00
Hematite	3,43	0,00	0,00	28,47	0,00	0,00	0,00	0,00	15,25	3,48	0,00	14,51	1,35	0,00	7,99	0,74	0,43	12,16	1,14	0,31	1,08	0,00	0,00
Zircon	0,00	0,00	0,00	34,97	0,16	0,00	0,00	0,00	0,00	0,00	0,00	0,68	3,72	0,00	32,49	0,52	6,52	0,00	11,44	0,44	2,16	0,00	0,76
Pyrrhotite	1,58	0,00	0,00	24,06	1,30	0,09	1,39	0,00	0,00	10,14	0,00	5,17	2,23	0,14	11,27	1,95	2,12	1,33	5,63	0,69	0,54	0,63	0,24
Pyrite	3,76	0,00	0,04	13,52	0,32	0,00	0,61	0,00	19,56	0,00	0,00	4,21	1,64	0,00	14,19	0,11	0,10	2,56	1,10	1,03	0,60	0,00	0,00
Sphalerite with loFe	0,00	0,00	0,00	23,74	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	8,56	0,00	61,48	0,00	0,00	0,00	3,89	2,33	0,00	0,00	0,00
Almandine	0,19	0,00	0,00	27,52	1,09	0,03	1,13	0,03	4,45	1,88	0,00	0,00	3,17	0,04	8,01	6,15	4,28	1,71	10,88	1,45	1,38	0,41	0,51
Biotite	0,15	0,00	0,00	28,89	0,27	0,01	0,07	0,11	1,35	0,51	0,03	2,22	0,00	0,01	25,10	0,19	14,81	0,04	4,57	0,10	0,33	0,81	0,35
Monazite-(Ce)	0,00	0,00	0,00	27,54	0,00	0,00	0,00	0,00	7,41	0,00	0,00	2,77	0,55	0,00	29,42	0,00	24,00	0,00	3,32	0,00	0,00	0,00	0,00
Muscovite	0,08	0,00	0,00	62,74	0,99	0,03	0,04	0,10	0,66	0,43	0,02	0,54	2,42	0,03	0,00	0,14	1,71	0,08	5,04	0,31	0,86	0,30	0,44
Spessartine	0,11	0,00	0,00	45,58	0,10	0,00	0,13	0,05	3,68	0,10	0,00	13,52	0,59	0,00	4,65	0,00	4,85	1,59	2,93	1,77	0,52	0,29	0,00
Clinocllore	0,01	0,00	0,00	24,70	1,39	0,10	0,02	0,19	1,24	0,03	0,00	2,90	14,32	0,26	17,20	1,50	0,00	0,05	2,60	0,44	1,37	0,15	1,02
Calcite	4,78	0,00	0,00	28,57	0,33	0,00	5,43	0,00	6,52	0,00	0,00	9,75	0,33	0,00	7,14	4,14	0,42	0,00	3,99	1,52	0,16	0,83	0,00
Albite	0,01	0,00	0,00	39,19	1,34	0,00	0,03	0,18	1,72	0,17	0,01	3,87	2,32	0,02	26,50	0,47	1,36	0,25	0,00	0,86	0,73	0,48	0,25
Kaolinite	0,00	0,00	0,00	16,16	0,53	0,00	0,11	0,09	2,72	2,09	0,05	6,64	0,63	0,00	20,98	3,67	2,97	1,22	11,02	0,00	4,10	0,13	15,97
Staurolite	1,50	0,00	0,00	13,88	0,32	0,00	0,22	0,25	1,21	0,70	0,00	3,61	1,24	0,00	33,37	0,62	5,26	0,07	5,37	2,34	0,00	0,13	2,68
Apatite	1,55	0,00	0,00	42,25	0,10	0,00	0,00	0,00	2,80	0,00	0,00	2,10	5,99	0,00	22,70	0,68	1,11	0,75	7,00	0,15	0,26	0,00	1,15
Kyanite	0,27	0,00	0,00	13,75	2,06	0,00	0,00	0,10	0,64	0,00	0,00	1,58	1,56	0,00	20,30	0,00	4,68	0,00	2,18	10,82	3,18	0,69	0,00

Sample 1.20 A

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Chalcoppyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0,00	0,00	0,00	15,19	0,33	0,00	0,00	0,00	16,82	23,20	0,00	0,00	2,86	0,72	0,00	17,54	0,00	4,64	1,01	6,56	0,25	0,72	1,63	0,00
Low Counts	0,00	0,00	0,00	2,12	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	1,66	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
No XRay	0,00	0,00	0,00	15,12	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	8,14	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Quartz	0,08	0,01	0,00	0,00	1,41	0,12	0,13	0,09	2,65	0,15	0,00	0,00	1,01	2,66	0,09	59,12	1,63	1,88	0,18	7,77	0,26	0,27	0,44	0,40
Rutile/Anatase	0,06	0,00	0,00	52,17	0,00	1,88	0,37	0,01	1,89	0,24	0,00	0,00	0,59	1,63	0,00	24,76	0,00	5,31	0,06	5,26	0,51	0,34	0,22	0,75
Ilmenite	0,00	0,00	0,00	48,80	20,29	0,00	0,00	0,00	0,15	0,00	0,00	0,00	0,65	1,24	0,00	21,67	0,00	1,75	0,00	0,00	0,00	1,45	0,58	0,00
Hematite	0,00	0,00	0,00	10,48	0,83	0,00	0,00	0,00	33,80	0,03	0,00	0,26	13,48	2,70	0,00	28,17	0,00	2,26	0,00	1,39	0,00	0,36	0,17	0,00
Zircon	0,00	0,00	0,00	42,62	0,17	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,66	0,50	0,00	46,02	0,00	3,40	0,00	3,32	0,00	0,50	1,82	0,50
Pyrrhotite	1,16	0,00	0,00	36,43	0,70	0,01	5,61	0,00	0,00	1,38	0,00	0,88	2,84	2,42	0,00	14,76	0,31	2,33	0,28	10,21	0,78	1,23	0,18	0,11
Pyrite	15,91	0,00	0,00	21,00	0,89	0,00	0,05	0,00	13,67	0,00	0,00	0,00	0,27	2,51	0,00	27,12	0,00	2,63	0,00	5,42	0,00	0,00	1,09	0,00
Sphalerite with loFe	0,00	0,00	0,00	100,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00
Chalcoppyrite	0,00	0,00	0,00	1,09	0,00	0,00	3,70	0,00	76,30	0,00	0,00	0,00	1,30	0,00	0,00	7,39	0,00	2,17	2,17	1,74	0,00	0,00	0,00	0,00
Almandine	0,43	0,00	0,00	30,04	0,48	0,05	4,83	0,04	6,13	0,06	0,00	0,03	0,00	5,24	0,14	14,90	2,25	3,23	2,01	18,30	1,63	1,07	0,15	1,31
Biotite	0,04	0,00	0,00	29,66	0,49	0,03	0,36	0,01	1,96	0,21	0,00	0,00	1,97	0,00	0,06	45,00	0,00	5,32	0,02	2,79	0,15	0,58	1,58	0,00
Monazite-(Ce)	0,00	0,00	0,00	48,35	0,00	0,00	0,00	0,00	0,00	0,00	0,00	0,00	2,69	2,89	0,00	35,43	0,00	0,00	0,00	6,30	0,00	0,00	0,00	0,93
Muscovite	0,10	0,01	0,00	67,30	0,76	0,06	0,39	0,11	1,22	0,23	0,00	0,01	0,57	4,59	0,07	0,00	0,02	1,65	0,04	5,11	0,29	0,93	0,71	0,27
Spessartine	0,00	0,00	0,00	70,07	0,00	0,00	0,00	0,00	0,96	0,00	0,00	0,00	3,26	0,00	0,00	0,91	0,00	1,11	1,50	4,42	0,70	0,48	0,00	0,00
Clinocllore	0,38	0,00	0,00	30,70	2,33	0,07	0,44	0,12	2,76	0,31	0,00	0,03	1,78	7,76	0,00	23,68	0,42	0,00	0,00	2,79	0,76	1,66	0,44	1,28
Calcite	0,94	0,00	0,00	33,50	0,30	0,00	0,00	0,00	3,68	0,00	0,00	0,33	12,48	0,37	0,00	5,82	6,43	0,00	0,00	17,44	0,00	0,00	0,33	0,00
Albite	0,20	0,00	0,00	47,36	0,86	0,00	0,10	0,04	4,52	0,24	0,00	0,01	3,76	1,52	0,07	27,32	0,63	1,04	0,58	0,00	0,74	0,59	0,19	0,22
Kaolinite	0,12	0,00	0,00	24,82	1,32	0,00	0,00	0,00	5,42	0,00	0,00	0,00	5,23	1,28	0,00	24,45	1,54	4,42	0,00	11,53	0,00	2,68	0,00	10,51
Staurolite	0,18	0,00	0,00	12,95	0,45	0,18	0,21	0,05	4,38	0,00	0,00	0,00	1,76	2,55	0,00	39,93	0,55	4,98	0,00	4,72	1,38	0,00	0,04	2,26
Apatite	0,61	0,00	0,00	32,71	0,43	0,11	0,15	0,30	0,94	0,59	0,00	0,00	0,36	10,45	0,00	45,85	0,00	2,02	0,13	2,31	0,00	0,05	0,00	0,00
Kyanite	0,00	0,00	0,00	32,40	1,62	0,00	0,00	0,09	0,66	0,00	0,00	0,00	3,55	0,00	0,13	18,84	0,00	6,33	0,00	2,88	8,88	3,73	0,00	0,00

Sample 1.20 B

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinchlore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Ox Fe-Sulphide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown	0.00	0.00	0.00	17.41	0.50	0.00	1.08	0.00	7.08	35.46	0.00	7.00	1.52	0.00	19.51	0.04	0.00	5.80	3.05	0.00	0.00	0.00	0.00
Low Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.06	0.00	0.00	0.00	0.97	0.00	0.08	0.08	1.19	0.50	0.01	2.57	2.32	0.04	65.44	0.47	1.47	0.24	9.50	0.26	0.48	0.38	0.50
Rutile/Anatase	0.09	0.00	0.00	46.54	0.00	0.03	0.00	0.01	3.39	0.63	0.03	0.87	1.51	0.00	28.49	0.06	4.12	0.45	6.90	0.33	0.46	0.10	2.55
Ilmenite	0.00	0.00	0.00	1.34	0.76	0.00	0.00	0.00	0.34	1.26	0.00	0.84	3.52	0.00	45.13	0.00	45.81	0.00	0.00	0.00	0.00	0.00	0.00
Fe Oxide/Hydroxide	0.63	0.00	0.00	13.12	0.00	0.00	0.00	0.00	26.91	1.72	0.61	37.61	0.63	0.00	6.33	0.44	3.25	2.18	2.86	0.45	0.05	0.00	0.00
Zircon	0.00	0.00	0.00	45.69	0.16	0.00	0.00	0.00	1.20	0.00	0.00	2.76	1.16	0.00	34.94	0.00	1.96	0.28	6.51	0.00	1.20	0.00	2.08
Pyrrhotite	0.62	0.00	0.00	28.72	1.71	0.01	4.07	0.05	0.00	6.71	0.82	6.89	2.20	0.00	16.88	0.20	1.31	2.96	5.13	0.42	0.61	0.05	0.67
Pyrite	5.92	0.00	0.00	22.83	0.60	0.05	0.50	0.00	12.73	0.00	0.07	4.96	3.83	0.00	29.89	0.34	0.61	0.71	4.79	0.16	0.30	0.96	0.13
Sphalerite with loFe	0.00	0.00	0.00	57.14	0.00	0.00	0.00	0.00	0.97	0.00	0.00	0.00	11.36	0.00	7.47	0.00	0.00	0.00	23.05	0.00	0.00	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	14.62	0.74	0.00	4.81	0.00	43.20	1.94	0.00	16.28	0.00	0.00	1.85	5.55	0.56	6.75	2.78	0.00	0.00	0.00	0.00
Almandine	0.45	0.00	0.00	45.40	0.32	0.01	4.17	0.09	5.05	1.92	0.23	0.00	2.96	0.20	9.65	1.07	4.36	2.39	12.64	1.14	1.95	0.06	0.16
Biotite	0.07	0.00	0.00	30.65	0.42	0.04	0.05	0.03	1.21	1.11	0.00	2.21	0.00	0.01	42.86	0.04	6.99	0.19	5.71	0.16	0.96	0.10	0.65
Monazite-(Ce)	0.00	0.00	0.00	35.98	0.00	0.00	0.00	0.00	0.00	0.00	0.00	10.06	1.00	0.00	35.44	0.00	3.06	0.00	12.99	0.00	0.00	0.00	1.07
Muscovite	0.08	0.00	0.00	75.89	0.69	0.05	0.05	0.07	0.81	0.76	0.00	0.63	3.76	0.05	0.00	0.11	2.10	0.22	4.78	0.73	0.52	0.35	0.46
Spessartine	0.02	0.00	0.00	48.78	0.13	0.00	0.29	0.00	0.85	0.78	0.45	6.22	0.28	0.00	9.97	0.00	2.94	3.43	9.22	2.37	0.56	0.00	0.00
Clinchlore	0.00	0.00	0.00	25.70	1.50	0.70	0.36	0.06	0.95	0.23	0.01	4.31	9.24	0.06	31.63	0.50	0.00	0.06	4.42	0.41	1.22	0.58	1.07
Calcite	2.27	0.00	0.00	25.98	1.00	0.00	1.47	0.05	13.16	1.67	0.57	14.50	1.54	0.00	20.60	3.56	0.37	0.00	8.11	0.89	0.04	0.16	0.00
Albite	0.06	0.00	0.00	55.23	0.84	0.00	0.10	0.07	1.24	0.61	0.01	4.17	2.52	0.08	23.96	0.52	1.47	0.44	0.00	1.00	0.89	0.24	0.23
Kaolinite	0.00	0.00	0.00	15.34	0.40	0.00	0.17	0.00	1.04	0.21	0.00	3.82	0.73	0.00	36.98	1.36	1.40	0.49	10.11	0.00	3.79	0.13	21.89
Staurolite	0.00	0.00	0.00	30.71	0.62	0.00	0.02	0.14	1.62	0.42	0.00	7.05	4.64	0.00	28.52	0.35	4.45	0.02	9.80	4.09	0.00	0.79	3.94
Apatite	0.00	0.00	0.00	45.54	0.26	0.00	0.00	0.00	0.27	2.55	0.00	0.40	0.88	0.00	36.24	0.00	4.04	0.19	5.05	0.26	1.50	0.00	1.14
Kyanite	0.00	0.00	0.00	28.17	3.03	0.00	0.00	0.22	1.59	0.16	0.00	0.51	2.81	0.07	22.55	0.00	3.50	0.00	2.22	21.07	3.51	0.54	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	0.00	0.00	0.00	2.07	0.00	0.00	11.11	0.00	13.44	0.26	0.00	28.68	1.68	0.00	8.01	0.00	11.63	1.68	2.58	0.00	0.00	0.00	0.00

Sample 1.20 C

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcocopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Ox Fe-Sulphide	0.00	0.00	0.00	5.94	2.94	0.00	8.11	0.00	57.44	7.53	0.00	4.44	2.45	0.00	3.34	0.00	4.16	0.67	0.15	0.00	0.00	0.00	0.00
Unknown	0.00	0.00	0.00	31.90	1.37	0.58	0.18	0.00	5.63	5.69	0.00	3.34	0.74	0.14	13.78	0.20	0.30	28.10	5.68	0.24	0.25	0.53	0.00
Low Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.31	0.00	0.00	0.00	1.01	0.01	0.09	0.09	1.54	0.86	0.01	2.02	1.85	0.02	67.96	0.92	2.05	1.00	8.37	0.17	0.18	0.36	0.11
Rutile/Anatase	0.46	0.00	0.00	34.91	0.00	0.38	0.04	0.07	6.64	2.49	0.00	1.24	1.14	0.00	31.57	0.52	6.55	0.82	8.72	0.20	0.24	0.13	0.37
Ilmenite	2.64	0.00	0.00	5.59	5.17	0.00	0.42	0.00	2.33	0.00	0.00	1.11	4.25	0.00	48.68	0.00	24.95	0.00	0.11	0.00	0.00	0.15	0.00
Fe Oxide/Hydroxide	0.29	0.00	0.00	14.10	0.21	0.14	0.00	0.00	30.77	1.55	0.47	20.27	1.76	0.00	7.58	0.46	7.99	5.26	2.04	0.37	0.00	0.00	0.00
Zircon	0.00	0.00	0.00	31.41	0.67	0.00	0.00	0.00	0.25	2.18	0.00	0.11	2.91	0.00	45.94	0.50	2.58	0.84	10.55	0.00	0.20	0.53	0.00
Pyrrhotite	1.03	0.00	0.00	29.36	3.64	0.09	3.59	0.01	0.00	2.27	0.76	4.71	3.74	0.03	15.47	0.87	3.16	12.06	2.76	0.21	0.21	0.08	0.00
Pyrite	2.38	0.00	0.00	37.28	3.13	0.00	0.41	0.27	5.20	0.00	0.00	4.11	3.28	0.00	19.65	1.53	1.86	1.94	6.06	0.49	0.23	0.23	0.00
Sphalerite with loFe	0.00	0.00	0.00	9.21	0.00	0.00	0.00	0.00	0.00	0.00	0.00	39.47	0.00	0.00	6.58	18.42	0.00	0.00	21.71	0.00	4.61	0.00	0.00
Chalcocopyrite	0.00	0.00	0.00	8.72	0.00	0.00	4.48	0.00	61.52	0.00	0.00	6.97	1.12	0.00	3.74	0.00	0.00	1.74	0.50	0.00	0.00	0.00	0.00
Almandine	0.56	0.00	0.00	35.33	0.62	0.04	2.18	0.01	4.33	1.65	0.08	0.00	3.95	0.13	11.35	2.31	3.87	6.74	16.28	0.96	1.53	0.11	0.25
Biotite	0.11	0.00	0.00	27.70	0.49	0.13	0.16	0.13	2.94	1.13	0.01	3.37	0.00	0.01	36.45	0.15	8.21	1.05	7.53	0.05	0.30	0.34	0.02
Monazite-(Ce)	0.99	0.00	0.00	16.83	0.00	0.00	0.00	0.00	1.10	0.00	0.00	5.46	0.52	0.00	51.54	0.00	0.00	0.00	15.50	0.00	0.00	0.58	4.29
Muscovite	0.15	0.00	0.00	74.71	1.00	0.11	0.05	0.15	0.89	0.50	0.00	0.71	2.68	0.08	0.00	0.22	2.43	0.63	5.80	0.22	0.65	0.42	0.15
Spessartine	0.11	0.00	0.00	54.37	0.88	0.00	0.17	0.09	2.69	2.07	0.00	7.77	0.58	0.00	11.95	0.00	2.09	1.71	3.30	1.25	0.22	0.16	0.00
Clinocllore	0.04	0.00	0.00	27.87	2.57	0.71	0.67	0.10	2.25	0.58	0.00	3.01	7.47	0.00	30.05	0.48	0.00	0.37	1.55	0.07	0.94	0.35	1.27
Calcite	7.86	0.00	0.00	29.06	0.69	0.00	0.94	0.07	18.44	1.30	0.03	11.21	2.05	0.00	16.61	0.84	0.79	0.00	3.83	0.43	0.27	0.49	0.00
Albite	0.31	0.00	0.00	47.42	1.42	0.00	0.07	0.17	0.82	0.79	0.00	5.26	2.85	0.12	29.89	0.32	0.65	0.74	0.00	0.44	0.43	0.85	0.09
Kaolinite	0.35	0.00	0.00	25.63	0.85	0.00	0.34	0.00	1.61	1.67	0.00	8.15	0.50	0.00	29.19	3.17	0.73	2.20	11.57	0.00	4.06	0.11	6.16
Staurolite	0.21	0.00	0.00	15.25	0.61	0.00	0.00	0.05	0.97	0.46	0.00	7.57	1.75	0.00	51.09	0.32	6.00	0.80	6.66	2.36	0.00	0.00	2.93
Apatite	0.50	0.00	0.00	35.36	0.38	0.03	0.00	0.15	0.42	0.51	0.00	0.62	2.25	0.08	37.80	0.27	2.53	1.65	14.77	0.07	0.00	0.00	0.00
Kyanite	0.00	0.00	0.00	22.06	2.22	0.00	0.00	0.00	0.00	0.00	0.00	2.91	0.30	1.24	27.70	0.00	19.35	0.00	3.21	8.57	7.00	0.00	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	0.00	0.00	0.00	11.05	0.00	0.00	8.58	0.00	10.70	0.09	0.00	35.72	2.83	0.00	6.81	0.62	6.19	5.39	1.68	2.12	1.68	0.00	0.00

Sample 2.40 A

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0.00	0.00	0.00	2.91	0.00	0.00	1.32	0.00	9.11	0.00	0.00	0.00	1.32	23.51	0.00	33.95	0.00	1.06	0.00	10.70	0.00	0.00	11.76	0.00
Low Counts	0.00	0.00	0.00	20.83	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	59.38	0.00	0.00	0.00	12.50	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	4.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	68.18	0.00	0.00	0.00	13.64	0.00	0.00	0.00	0.00
Quartz	0.00	0.00	0.00	0.00	0.72	0.00	0.06	0.07	1.97	0.00	0.00	0.01	1.34	4.28	0.03	64.09	0.02	2.26	0.02	10.11	0.06	0.24	0.76	0.08
Rutile/Anatase	0.00	0.00	0.00	31.71	0.00	0.25	0.18	0.00	6.32	0.00	0.00	0.00	2.02	4.42	0.09	34.96	0.00	3.99	0.00	12.10	0.24	0.15	0.58	0.00
Ilmenite	0.00	0.00	0.00	1.89	58.49	0.00	0.00	0.00	18.87	0.00	0.00	0.00	0.00	0.00	0.00	20.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hematite	0.27	0.00	0.00	9.49	0.59	0.00	0.00	0.11	21.95	0.00	0.00	0.48	8.69	29.97	0.00	15.31	0.00	7.79	0.00	0.75	0.00	0.03	0.00	0.00
Zircon	0.00	0.00	0.00	23.15	0.00	0.00	0.23	0.00	0.00	0.00	0.00	0.00	0.00	6.54	0.06	60.28	0.00	1.63	0.00	5.35	0.00	0.28	0.28	0.00
Pyrrhotite	0.24	0.00	0.00	37.97	2.76	0.03	2.86	0.00	0.00	0.07	0.00	2.07	1.31	2.34	0.04	22.61	0.00	1.89	0.17	4.72	0.00	0.17	0.25	0.00
Pyrite	0.00	0.00	0.00	11.36	0.00	0.00	0.00	0.00	47.73	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Sphalerite with loFe	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	6.81	0.00	0.00	2.11	0.00	69.95	0.00	0.00	0.00	8.92	0.00	0.00	2.35	0.00	0.70	0.00	0.94	0.00	0.00	0.00	0.00
Almandine	0.04	0.00	0.00	30.53	1.04	0.00	1.33	0.00	1.54	0.00	0.00	0.31	0.00	11.35	0.38	21.45	4.04	2.85	0.31	14.01	0.16	0.41	2.08	0.00
Biotite	0.16	0.00	0.00	21.40	0.50	0.00	1.01	0.10	0.61	0.00	0.00	0.00	2.50	0.00	0.13	41.34	0.01	20.17	0.08	4.28	0.00	0.41	0.65	0.01
Monazite-(Ce)	0.00	0.00	0.00	12.37	0.82	0.00	0.00	0.07	0.90	0.00	0.00	0.00	6.97	10.72	0.00	53.90	0.00	4.27	0.00	6.37	0.00	0.00	0.00	0.00
Muscovite	0.05	0.01	0.00	68.10	0.84	0.00	0.11	0.20	1.24	0.00	0.00	0.00	1.00	8.78	0.14	0.00	0.01	1.35	0.01	4.52	0.16	0.88	0.30	0.07
Spessartine	0.00	0.00	0.00	8.06	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	58.00	0.41	0.00	3.24	0.00	1.41	0.00	3.76	3.41	0.00	3.00	0.88
Clinocllore	0.02	0.00	0.00	25.66	1.03	0.00	0.60	0.06	1.12	0.00	0.00	0.01	1.42	45.83	0.12	14.48	0.05	0.00	0.52	1.57	0.11	1.57	0.09	0.00
Calcite	0.00	0.00	0.00	18.40	0.00	0.00	0.00	0.00	6.92	0.00	0.00	0.00	10.51	11.76	0.00	8.02	0.00	35.13	0.00	6.92	0.00	0.00	1.94	0.00
Albite	0.08	0.01	0.00	55.75	1.51	0.00	0.03	0.09	1.35	0.00	0.00	0.01	3.40	4.71	0.08	23.49	0.06	0.76	0.05	0.00	0.24	0.51	2.41	0.00
Kaolinite	0.00	0.00	0.00	17.07	1.55	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.01	0.00	0.00	42.70	2.99	2.89	0.00	12.33	0.00	0.83	0.00	6.09
Staurolite	0.00	0.00	0.00	16.52	0.23	0.00	0.01	0.06	0.59	0.00	0.00	0.00	1.24	5.63	0.00	56.92	0.00	9.43	0.00	6.26	0.20	0.00	0.36	0.30
Apatite	0.76	0.00	0.00	36.12	0.63	0.00	0.00	0.04	0.62	0.00	0.00	0.00	4.37	6.19	0.00	13.40	0.44	0.36	0.12	20.87	0.00	0.25	0.00	0.00
Kyanite	0.00	0.00	0.00	42.15	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.99	0.00	38.60	1.48	0.00	0.00	0.00	11.65	2.37	0.00	0.00

Sample 2.40 B

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite	
Ox Fe-Sulphide	0.00	0.00	0.00	10.98	0.72	0.10		8.81	0.00	52.78	5.00	0.00	0.00	2.37	0.00	6.13	0.00	0.00	0.00	0.00	0.00	0.00	1.86	0.00
Unknown	0.00	0.00	0.00	19.36	0.65	0.00		0.71	0.09	8.23	23.17	0.00	1.86	1.63	0.00	24.49	0.00	7.05	5.99	3.25	0.18	0.01	1.32	0.00
Low Counts	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.14	0.00	0.00	0.00	1.11	0.00		0.09	0.10	1.33	0.97	0.00	1.50	2.36	0.03	75.91	0.41	1.37	0.22	6.06	0.21	0.22	0.55	0.00
Rutile/Anatase	0.21	0.00	0.00	48.46	0.00	0.13		0.12	0.04	3.80	0.43	0.14	0.93	0.96	0.02	33.44	0.10	3.96	0.13	5.10	0.28	0.25	0.13	0.00
Ilmenite	0.00	0.00	0.00	9.73	18.14	0.00		0.00	0.00	42.04	0.00	0.00	6.64	0.00	0.00	7.96	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe Oxide/Hydroxide	1.21	0.00	0.00	20.52	0.62	0.00		0.00	0.00	24.85	10.37	0.60	12.20	2.72	0.00	14.71	0.00	1.38	0.10	2.28	0.00	0.00	0.00	0.00
Zircon	0.22	0.00	0.00	35.81	0.32	0.00		0.00	0.00	0.69	0.00	0.00	0.34	3.94	0.00	48.32	0.37	3.84	0.00	3.94	0.00	0.12	0.05	0.00
Pyrrhotite	1.28	0.00	0.00	28.14	1.83	0.14		2.26	0.04	0.00	4.58	1.50	2.07	3.08	0.03	22.34	0.15	2.99	0.86	9.05	0.30	0.33	1.05	0.00
Pyrite	5.37	0.00	0.00	30.75	0.31	0.00		1.41	0.00	6.86	0.00	0.21	1.23	1.09	0.10	22.68	0.71	12.70	4.27	2.87	0.23	0.05	0.06	0.00
Sphalerite with loFe	0.00	0.00	0.00	40.91	0.00	0.00		0.00	0.00	59.09	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	2.38	2.81	0.00		2.26	0.00	61.90	5.80	0.00	4.70	2.75	0.00	5.19	0.00	0.49	0.00	8.36	0.00	0.00	0.00	0.00
Almandine	0.36	0.00	0.00	38.98	0.55	0.03		1.37	0.03	2.56	1.01	0.14	0.00	7.89	0.14	18.39	1.00	4.22	0.37	14.79	0.95	0.41	0.08	0.00
Biotite	0.17	0.00	0.00	33.23	0.31	0.00		0.16	0.16	2.05	0.49	0.04	4.26	0.00	0.00	42.55	0.17	4.59	0.09	5.36	0.07	0.27	0.74	0.00
Monazite-(Ce)	0.00	0.00	0.00	18.39	0.26	0.00		0.00	0.00	0.79	1.97	0.00	3.38	0.00	0.00	60.38	0.00	10.27	0.57	1.67	0.00	0.00	0.83	0.00
Muscovite	0.19	0.00	0.00	78.77	0.79	0.00		0.07	0.14	1.10	0.75	0.01	0.73	3.14	0.10	0.00	0.21	3.18	0.18	3.33	0.30	0.59	0.41	0.02
Spessartine	0.00	0.00	0.00	47.42	0.26	0.00		0.00	0.12	0.81	2.58	0.00	4.41	1.38	0.00	23.08	0.00	2.14	1.13	7.49	1.51	0.93	0.42	0.00
Clinocllore	0.82	0.00	0.00	21.67	1.43	0.00		0.09	0.17	2.23	6.36	0.01	2.56	5.16	0.26	48.41	0.29	0.00	0.56	1.46	0.26	1.87	0.51	0.01
Calcite	6.06	0.00	0.00	29.78	0.40	0.00		0.06	0.00	5.62	18.62	0.00	1.98	0.92	0.13	23.48	1.35	4.89	0.00	3.13	0.23	0.00	0.02	0.00
Albite	0.20	0.00	0.00	50.90	0.98	0.00		0.08	0.09	3.60	0.76	0.08	4.77	3.20	0.02	26.99	0.55	0.78	0.19	0.00	1.22	0.46	0.47	0.01
kaolinite	0.17	0.00	0.00	26.55	0.81	0.00		0.00	0.00	1.85	0.96	0.00	4.72	0.60	0.00	37.70	1.70	2.14	0.22	18.65	0.00	1.67	0.31	0.07
Staurolite	0.01	0.00	0.00	20.75	0.54	0.00		0.00	0.03	1.44	0.16	0.00	1.45	1.81	0.00	52.87	0.76	11.09	0.00	5.16	1.21	0.00	0.10	0.00
Apatite	0.81	0.00	0.00	45.86	0.25	0.00		0.00	0.01	4.16	0.16	0.00	0.25	4.39	0.11	32.70	0.31	2.72	0.01	4.66	0.20	0.09	0.00	0.00
Kyanite	0.00	0.00	0.00	7.32	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	83.23	0.00	2.13	0.00	4.88	2.44	0.00	0.00	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	3.58	0.00	0.00	13.08	0.00	0.00		5.92	0.00	21.18	1.25	0.00	0.00	5.14	0.00	37.38	0.00	3.43	0.00	2.02	0.00	0.00	0.16	0.00

Sample 2.40 C

Mineral	Unknown	Low_Counts	No_XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Ox Fe-Sulphide	0.00	0.00	0.00	9.09	0.00	0.00	7.95	0.00	35.61	19.32	0.00	0.00	0.00	0.00	3.03	0.00	0.00	0.00	6.44	0.00	0.00	0.00	0.00
Unknown	0.00	0.00	0.00	13.92	1.77	0.00	0.00	0.10	3.29	24.22	0.00	5.24	3.94	0.96	27.35	2.57	2.24	4.96	3.98	1.25	0.40	0.63	0.00
Low_Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No_XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.11	0.00	0.00	0.00	1.81	0.09	0.08	0.18	1.30	1.41	0.01	2.93	1.69	0.14	62.73	2.56	3.14	0.43	10.13	0.68	0.34	0.58	1.05
Rutile/Anatase	0.42	0.00	0.00	53.34	0.00	0.69	0.02	0.02	1.54	1.36	0.01	1.19	0.94	0.10	23.15	0.68	3.00	0.12	7.26	0.34	0.17	0.20	4.19
Ilmenite	0.00	0.00	0.00	31.43	8.23	0.00	0.00	0.00	0.64	0.00	0.00	0.41	0.91	0.00	45.61	0.27	0.88	0.17	0.88	0.00	1.08	0.30	0.00
Fe Oxide/Hydroxide	0.00	0.00	0.00	14.55	0.11	0.00	0.00	0.00	10.49	4.45	0.15	39.88	1.98	0.00	8.63	4.44	2.85	3.13	4.42	0.28	0.50	0.07	0.34
Zircon	0.25	0.00	0.00	56.65	0.22	0.00	0.00	0.00	1.23	0.22	0.00	0.15	2.69	0.06	28.68	1.88	0.65	0.00	4.51	0.83	0.25	0.00	1.14
Pyrrhotite	0.82	0.00	0.00	39.93	1.61	0.06	1.68	0.12	0.00	5.84	0.60	4.31	2.91	0.01	17.67	2.14	5.37	0.27	5.78	1.11	1.00	0.26	1.82
Pyrite	5.91	0.00	0.00	42.29	1.40	0.00	0.70	0.02	5.73	0.00	0.39	2.92	1.74	0.01	20.95	2.77	1.99	0.27	5.29	0.22	0.39	0.15	0.27
Sphalerite with loFe	0.00	0.00	0.00	51.91	0.00	0.00	0.00	0.00	3.01	1.09	0.00	11.75	0.00	0.00	13.11	3.28	2.73	0.00	11.48	0.00	0.00	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	16.45	0.43	0.00	1.14	0.00	28.76	19.03	0.00	10.16	2.15	0.00	1.43	4.72	0.00	0.57	14.88	0.00	0.00	0.29	0.00
Almandine	0.58	0.00	0.00	39.82	0.55	0.02	2.83	0.01	1.91	1.32	0.09	0.00	1.99	0.17	8.53	4.85	3.89	4.21	14.66	3.30	3.63	0.41	0.37
Biotite	0.49	0.00	0.00	25.90	0.49	0.04	0.16	0.13	1.45	0.89	0.02	2.25	0.00	0.09	43.88	0.36	13.32	0.15	4.62	0.27	0.56	0.42	0.26
Monazite-(Ce)	3.32	0.00	0.00	60.19	1.49	0.00	0.00	0.08	0.12	0.08	0.00	5.31	2.53	0.00	15.61	0.00	0.50	0.00	6.56	0.25	0.00	1.16	0.83
Muscovite	0.27	0.00	0.00	76.29	0.96	0.16	0.05	0.11	0.70	0.85	0.00	0.76	3.48	0.04	0.00	0.32	1.18	0.16	5.80	0.58	0.70	0.46	0.40
Spessartine	0.48	0.00	0.00	59.08	0.53	0.02	0.53	0.14	1.61	2.13	0.07	8.25	0.54	0.00	6.01	0.00	6.64	2.50	2.80	0.53	0.17	0.29	0.00
Clinocllore	0.25	0.00	0.00	44.07	1.43	0.04	0.21	0.03	2.45	0.93	0.00	4.02	12.19	0.02	13.56	4.03	0.00	0.36	4.16	0.22	1.07	0.15	0.92
Calcite	3.16	0.00	0.00	34.12	0.31	0.04	1.28	0.00	0.68	0.70	0.03	24.38	0.76	0.00	10.59	8.53	2.05	0.00	8.97	1.10	0.37	0.41	0.00
Albite	0.17	0.00	0.00	54.41	1.33	0.01	0.12	0.08	1.01	0.94	0.05	5.79	1.62	0.08	25.61	0.65	1.59	0.61	0.00	1.14	0.47	0.33	0.60
Kaolinite	0.41	0.00	0.00	27.93	0.48	0.00	0.06	0.11	1.48	0.29	0.00	9.90	0.71	0.02	19.39	0.94	0.64	0.57	8.65	0.00	3.81	0.09	23.40
Staurolite	0.20	0.00	0.00	21.13	0.35	0.19	0.16	0.05	2.03	0.80	0.00	16.64	2.29	0.00	35.90	0.46	4.74	0.30	5.49	5.81	0.00	0.06	2.00
Apatite	0.43	0.00	0.00	48.14	0.56	0.07	0.03	0.00	0.71	0.42	0.02	2.51	2.26	0.23	31.39	1.05	0.87	0.43	5.18	0.19	0.08	0.00	4.03
Kyanite	0.00	0.00	0.00	42.36	5.74	0.00	0.07	0.14	2.39	0.37	0.00	1.10	0.69	0.08	13.42	0.00	2.65	0.00	4.48	23.12	1.30	1.95	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	0.00	0.00	0.00	10.15	0.52	0.00	4.44	0.00	1.33	0.00	0.00	57.11	0.89	0.00	7.56	1.93	4.44	0.00	2.22	0.07	0.37	0.00	0.00

Sample 4.80 A

Mineral	Unknown	Low_Counts	No_XRay	Quartz	Rutile/Anatase	Ilmenite	Hematite	Zircon	Pyrrhotite	Pyrite	Sphalerite with loFe	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Unknown	0.00	0.00	0.00	2.23	0.66	0.00	0.38	0.00	21.20	47.65	0.00	0.00	1.51	5.22	0.00	16.61	0.05	0.03	1.78	0.19	0.19	0.02	0.00	0.00
Low_Counts	0.00	0.00	0.00	70.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	30.00	0.00	0.00	0.00	0.00
No_XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.15	0.00	0.00	0.00	1.06	0.01	0.45	0.12	2.73	1.30	0.00	0.00	2.79	1.25	0.09	70.72	0.58	1.06	0.80	5.49	0.37	0.26	0.18	0.12
Rutile/Anatase	1.51	0.00	0.00	35.85	0.00	0.09	0.08	0.14	2.60	4.09	0.00	0.00	2.06	2.78	0.09	43.85	0.00	0.76	0.16	3.22	0.00	0.02	0.06	0.00
Ilmenite	0.00	0.00	0.00	32.81	7.03	0.00	14.84	0.00	14.06	0.00	0.00	0.00	0.00	8.59	0.00	6.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hematite	1.29	0.00	0.00	22.39	0.12	0.28	0.00	0.00	23.36	2.52	0.00	0.00	22.45	9.40	0.04	9.54	0.00	0.10	0.13	0.61	0.22	0.52	0.00	0.00
Zircon	0.00	0.00	0.00	43.05	1.46	0.00	0.00	0.00	0.52	0.00	0.00	0.00	0.00	0.94	3.66	0.00	43.57	0.00	0.00	0.00	6.27	0.00	0.00	0.00
Pyrrhotite	10.59	0.00	0.00	20.05	0.56	0.04	3.48	0.01	0.00	32.89	0.00	0.00	3.49	5.01	0.00	15.07	0.41	0.39	0.07	1.28	0.11	0.13	0.00	0.00
Pyrite	18.42	0.00	0.00	7.37	0.69	0.00	0.29	0.00	25.43	0.00	0.00	0.00	1.49	8.54	0.02	32.06	0.00	0.19	0.17	0.49	1.77	0.86	0.00	0.00
Sphalerite with loFe	0.00	0.00	0.00	75.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Almandine	0.96	0.00	0.00	26.07	0.57	0.00	4.24	0.02	4.44	2.45	0.00	0.00	0.00	17.52	0.00	18.18	0.39	5.68	1.46	1.30	4.58	3.56	0.11	0.18
Biotite	2.63	0.00	0.00	9.25	0.61	0.02	1.41	0.08	5.06	11.14	0.00	0.00	13.92	0.00	0.01	42.51	0.02	1.58	0.21	0.76	0.25	0.31	0.11	0.23
Monazite-(Ce)	0.00	0.00	0.00	62.39	1.92	0.00	0.64	0.00	0.00	2.14	0.00	0.00	0.00	1.07	0.00	29.27	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Muscovite	1.07	0.00	0.00	87.26	1.23	0.00	0.18	0.12	1.95	5.38	0.00	0.00	1.85	5.45	0.04	19.36	0.19	1.99	0.16	3.83	1.23	0.58	0.21	0.08
Spessartine	0.32	0.00	0.00	57.71	0.00	0.00	0.00	0.00	5.46	0.00	0.00	0.00	4.09	0.23	0.00	19.36	0.00	1.57	0.44	2.26	0.00	0.29	0.00	0.00
Clinocllore	0.05	0.00	0.00	23.06	0.49	0.00	0.04	0.00	1.14	0.73	0.00	0.00	13.25	4.64	0.00	45.56	0.35	0.00	0.00	1.27	4.04	2.58	0.00	0.00
Calcite	6.93	0.00	0.00	45.75	0.27	0.00	0.15	0.00	0.57	1.70	0.00	0.00	8.94	1.65	0.00	9.85	0.25	0.00	0.00	6.22	0.50	0.07	0.00	0.00
Albite	0.12	0.02	0.00	50.30	0.87	0.00	0.11	0.16	1.59	0.80	0.00	0.00	1.27	0.94	0.00	36.90	0.21	0.53	1.00	0.00	1.09	0.50	0.07	0.02
Kaolinite	0.41	0.00	0.00	11.78	0.00	0.00	0.14	0.00	0.48	9.86	0.00	0.00	15.54	1.05	0.00	41.03	0.00	5.86	0.28	3.76	0.00	6.10	0.00	1.16
Staurolite	0.08	0.00	0.00	14.06	0.03	0.00	0.57	0.00	0.94	8.08	0.00	0.00	20.45	2.25	0.00	32.56	0.16	6.36	0.06	2.91	10.33	0.00	0.00	0.27
Apatite	0.00	0.00	0.00	41.79	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	2.60	3.47	0.00	49.93	0.00	0.00	0.00	1.80	0.00	0.00	0.00	0.00
Kyanite	0.00	0.00	0.00	38.25	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.90	9.59	0.00	27.93	0.00	0.00	0.00	0.74	11.52	1.57	0.00	0.00

Sample 4.80 B

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinchlore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Ox Fe-Sulphide	0.00	0.00	0.00	2.50	0.00	0.00	22.64	0.00	29.09	10.96	0.81	11.52	0.08	0.00	0.40	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Unknown	0.00	0.00	0.00	6.90	0.48	0.00	0.32	0.12	2.67	48.56	0.00	2.28	2.63	0.00	26.09	1.18	0.25	3.79	2.00	0.27	0.22	0.21	0.00
Low Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.07	0.00	0.00	0.00	0.00	1.52	0.00	0.16	1.77	0.95	0.01	4.89	2.13	0.06	65.42	2.27	3.08	0.14	8.30	1.96	0.48	0.82	0.14
Rutile/Anatase	0.17	0.00	0.00	56.16	0.00	0.04	0.03	0.14	1.25	0.56	0.00	1.61	0.72	0.02	25.05	1.14	4.52	0.13	4.79	1.06	0.39	0.43	0.43
Ilmenite	0.00	0.00	0.00	11.03	9.56	0.00	0.00	0.00	7.35	0.00	0.00	16.91	29.41	0.00	0.00	23.53	0.00	0.00	2.21	0.00	0.00	0.00	0.00
Fe Oxide/Hydroxide	0.47	0.00	0.00	24.84	0.14	0.00	0.00	0.00	11.31	4.86	0.10	32.53	3.03	0.00	6.27	1.38	0.69	0.21	1.66	0.43	1.36	0.24	0.10
Zircon	0.48	0.00	0.00	58.94	1.63	0.00	0.00	0.00	0.00	0.32	0.00	1.38	0.80	0.00	21.70	0.51	5.66	0.00	5.09	0.83	0.00	0.38	1.06
Pyrrhotite	0.74	0.00	0.00	49.84	0.96	0.02	2.11	0.00	0.00	4.50	0.51	3.74	0.80	0.05	12.27	3.10	5.64	0.57	4.59	0.24	0.05	0.29	0.00
Pyrite	15.53	0.00	0.00	31.05	0.49	0.00	1.05	0.02	5.20	0.00	0.20	5.81	4.27	0.00	24.33	1.43	1.56	0.18	3.36	0.37	0.18	0.33	0.00
Sphalerite with loFe	0.00	0.00	0.00	47.61	3.41	0.00	0.24	0.00	26.32	2.63	0.50	0.14	0.49	0.00	10.51	0.19	6.27	0.00	0.69	0.00	0.00	0.11	0.37
Chalcopyrite	0.00	0.00	0.00	22.97	0.00	0.00	1.41	0.00	36.88	12.81	0.00	11.25	1.56	0.00	4.38	0.00	0.00	0.00	0.00	0.00	0.00	0.31	0.00
Almandine	0.23	0.00	0.00	49.34	0.44	0.02	2.17	0.03	1.34	1.80	0.06	0.00	5.27	0.11	10.33	8.93	2.08	0.79	5.76	3.81	2.58	0.14	0.46
Biotite	0.52	0.00	0.00	42.63	0.39	0.06	0.40	0.04	0.57	2.61	0.02	10.43	0.00	0.00	23.61	0.94	3.55	0.10	9.79	0.15	0.10	0.18	0.18
Monazite-(Ce)	0.00	0.00	0.00	53.56	0.48	0.00	0.00	0.00	1.66	0.00	0.00	9.48	0.00	0.00	26.30	0.76	2.01	0.00	3.74	0.00	0.69	0.97	0.00
Muscovite	0.32	0.00	0.00	81.79	0.85	0.00	0.05	0.06	0.54	0.93	0.00	1.28	1.48	0.04	0.00	0.56	0.89	0.15	5.22	1.47	0.59	0.35	0.47
Spessartine	0.25	0.00	0.00	48.97	0.67	0.05	0.20	0.03	2.37	0.95	0.00	19.09	1.02	0.02	9.74	0.00	0.00	8.71	0.33	2.02	0.77	0.03	0.45
Clinchlore	0.04	0.00	0.00	56.85	2.26	0.00	0.08	0.25	3.68	0.88	0.00	3.80	3.27	0.04	13.12	7.43	0.00	1.4	1.73	0.32	0.89	0.71	0.31
Calcite	6.52	0.00	0.00	24.13	0.61	0.00	0.24	0.00	3.54	0.95	0.00	13.76	0.90	0.00	21.09	2.71	1.36	0.00	21.21	1.42	0.92	0.00	0.09
Albite	0.13	0.00	0.00	54.27	0.85	0.00	0.07	0.08	1.06	0.67	0.00	3.73	3.20	0.03	27.28	0.61	0.61	0.79	0.00	3.26	0.62	0.31	0.51
Kaolinite	0.06	0.00	0.00	44.29	0.65	0.00	0.06	0.04	0.19	0.25	0.00	8.50	0.17	0.00	26.44	0.81	0.39	0.18	11.24	0.00	4.11	0.25	1.64
Staurolite	0.13	0.00	0.00	29.66	0.65	0.00	0.56	0.00	0.12	0.35	0.00	15.87	0.31	0.05	29.15	0.09	3.00	0.33	5.87	11.33	0.00	0.14	1.71
Apatite	0.16	0.00	0.00	63.16	0.90	0.00	0.12	0.07	0.80	0.77	0.01	1.09	0.70	0.08	21.63	1.59	2.98	0.00	3.64	0.87	0.17	0.00	0.06
Kyanite	0.00	0.00	0.00	19.31	1.61	0.00	0.09	0.35	0.00	0.00	0.00	6.37	1.28	0.00	51.91	0.00	2.34	0.07	1.16	10.06	3.81	0.12	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	0.00	0.00	0.00	16.25	0.22	0.00	12.45	0.00	1.97	5.16	0.00	47.18	3.45	0.00	3.23	0.00	0.48	0.04	0.31	0.00	0.00	0.00	0.00

Sample 4.80 C

Mineral	Unknown	Low Counts	No XRay	Quartz	Rutile/Anatase	Ilmenite	Fe Oxide/Hydroxide	Zircon	Pyrrhotite	Pyrite	Chalcopyrite	Almandine	Biotite	Monazite-(Ce)	Muscovite	Spessartine	Clinocllore	Calcite	Albite	Kaolinite	Staurolite	Apatite	Kyanite
Ox Fe-Sulphide	0.69	0.00	0.00	7.55	0.62	0.30	7.07	0.00	46.64	10.86	0.00	3.40	2.46	0.00	11.61	0.00	0.73	0.00	0.00	0.23	0.00	0.00	0.00
Unknown	0.00	0.00	0.00	15.56	1.04	0.12	2.07	0.00	16.71	21.71	0.00	2.31	5.42	0.00	17.22	0.19	1.39	0.00	1.39	0.00	0.04	0.46	2.67
Low Counts	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
No XRay	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Quartz	0.14	0.00	0.00	0.00	1.12	0.00	0.09	0.12	3.00	1.07	0.01	2.67	5.18	0.06	64.93	0.42	1.31	0.09	10.51	0.37	0.89	1.54	0.4
Rutile/Anatase	0.28	0.00	0.00	34.68	0.00	0.40	0.20	0.00	7.26	0.44	0.00	0.58	1.14	0.02	37.64	0.14	3.10	0.10	8.99	0.23	0.70	0.07	2.09
Ilmenite	2.51	0.00	0.00	4.77	30.90	0.00	0.25	0.00	34.67	0.50	0.00	3.27	0.00	0.00	11.06	0.00	0.00	0.00	0.00	0.00	5.53	0.00	0.00
Fe Oxide/Hydroxide	3.60	0.00	0.00	18.58	1.28	0.02	0.00	0.00	21.54	3.33	0.37	15.28	5.24	0.00	17.10	0.00	0.17	0.10	0.95	0.00	0.29	0.68	0.00
Zircon	0.00	0.00	0.00	37.67	0.00	0.00	0.00	0.00	0.63	0.00	0.00	1.26	0.93	0.00	36.18	0.00	2.12	0.00	15.67	0.00	1.03	0.40	3.48
Pyrrhotite	2.27	0.00	0.00	46.31	3.61	0.22	1.68	0.03	0.00	1.43	2.60	3.75	3.97	0.00	17.28	0.14	1.49	0.25	5.04	0.74	0.20	0.50	0.00
Pyrite	8.58	0.00	0.00	48.15	0.64	0.01	0.76	0.00	4.15	0.00	0.00	1.59	2.84	0.00	16.38	0.81	0.70	0.03	7.21	0.84	0.16	0.03	0.00
Sphalerite with loFe	0.00	0.00	0.00	25.69	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	35.42	0.00	0.00	0.00	24.31	0.00	14.58	0.00	0.00
Chalcopyrite	0.00	0.00	0.00	3.73	0.00	0.00	0.95	0.00	84.38	0.05	0.00	3.00	0.16	0.00	3.10	0.00	0.00	0.42	1.21	1.89	0.00	0.89	0.00
Almandine	0.38	0.00	0.00	50.28	0.35	0.03	1.46	0.08	4.58	0.67	0.11	0.00	0.00	0.10	11.04	5.76	0.81	1.21	11.02	0.28	0.48	1.15	0.80
Biotite	0.48	0.00	0.00	52.43	0.37	0.00	0.27	0.03	2.60	0.64	0.00	2.39	0.00	0.01	23.53	0.22	5.32	0.09	5.23	0.13	0.42	1.45	0.54
Monazite-(Ce)	0.00	0.00	0.00	47.55	0.41	0.00	0.00	0.00	0.00	0.00	0.00	4.01	0.65	0.00	32.41	1.47	0.16	0.00	7.53	0.00	0.82	0.00	0.00
Muscovite	0.18	0.00	0.00	76.90	1.44	0.01	0.10	0.14	1.33	0.43	0.01	0.69	2.75	0.05	0.00	0.21	1.34	0.05	6.58	0.46	1.43	0.71	1.14
Spessartine	0.15	0.00	0.00	37.44	0.39	0.00	0.00	0.00	0.82	1.61	0.00	27.16	1.97	0.17	16.00	0.00	3.31	2.52	5.19	0.72	0.42	0.36	0.00
Clinocllore	0.29	0.00	0.00	30.87	2.35	0.00	0.02	0.16	2.27	0.37	0.00	1.01	12.38	0.00	26.72	0.88	0.00	0.14	7.95	0.10	2.13	0.74	0.64
Calcite	0.00	0.00	0.00	27.53	1.01	0.00	0.17	0.00	5.20	0.23	0.27	20.61	2.99	0.00	12.49	9.06	1.91	0.00	15.54	1.61	0.00	0.97	0.00
Albite	0.06	0.00	0.00	53.09	1.46	0.00	0.02	0.25	1.65	0.81	0.01	2.95	2.61	0.05	28.07	0.30	1.71	0.25	0.00	0.72	1.13	0.96	0.62
Kaolinite	0.00	0.00	0.00	19.76	0.40	0.00	0.00	0.00	2.56	1.00	0.20	0.78	0.66	0.00	20.85	0.43	0.22	0.27	7.61	0.00	4.55	0.09	39.46
Staurolite	0.01	0.00	0.00	31.98	0.81	0.08	0.05	0.12	0.46	0.13	0.00	0.92	1.48	0.04	43.45	0.17	3.26	0.00	8.07	3.06	0.00	0.26	4.50
Apatite	0.15	0.00	0.00	57.65	0.08	0.00	0.13	0.05	1.22	0.02	0.07	2.30	5.36	0.00	22.48	0.15	1.18	0.11	7.12	0.06	0.27	0.00	0.72
Kyanite	0.81	0.00	0.00	13.96	2.34	0.00	0.00	0.38	0.00	0.00	0.00	1.48	1.86	0.00	33.36	0.00	0.93	0.00	4.23	25.68	4.34	0.67	0.00
Al+Si+P+K+Fe Mixed	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe+P Oxide	0.55	0.00	0.00	10.14	1.55	0.00	8.13	0.00	11.60	1.46	0.00	28.68	2.56	0.00	26.39	0.00	3.20	0.00	1.55	0.00	0.00	0.00	0.00

APPENDIX C: PUBLICATIONS



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Evaluation of pyrite and pyrrhotite in concretes

Avaliação de pirita e pirrotita em concretos

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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 $23^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity of 95 to 100%; calcium hydroxide solution diluted in water kept at two different temperatures: room temperature and 50°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 $23^{\circ} \pm 2^{\circ}\text{C}$ 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.

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C.2: ORAL PRESENTATION: 58 CONGRESSO BRASILEIRO DO CONCRETO, OCTOBER/2016



Anais do 58º Congresso Brasileiro do Concreto
CBC2016
Outubro / 2016



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Avaliação dos Teores de Diferentes Compostos de Enxofre em Concretos

Evaluation of Different Sulfur Compound Levels in Concretos

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Resumo

A construção de barragens de concreto para aproveitamento hidrelétrico demanda um elevado volume de material devido ao grande porte que apresenta. Questões ambientais e econômicas praticamente obrigam a utilização das rochas dos arredores da obra para os agregados do concreto, sendo necessário um estudo prévio dos mesmos para a sua possível incorporação. As características dos agregados interferem fortemente nas propriedades do concreto, podendo muitas vezes conter compostos deletérios ao mesmo, como é o caso dos sulfetos e sulfatos. Visando desenvolver uma metodologia que permita investigar a quantidade de enxofre nesse concreto desenvolveu-se uma técnica para quantificação do enxofre em argamassas que permite o acompanhamento da evolução da oxidação de sulfetos presentes no agregado ao longo do tempo. Nesses ensaios, a amostra de argamassa é submetida a um processo de lixiviação adequado, seca em estufa e posteriormente submetida ao ensaio de combustão direta. Foi realizada uma estimativa teórica do teor de enxofre total com base nas análises químicas dos materiais constituintes e na proporção destes materiais na composição das argamassas que validou a técnica desenvolvida. Essa metodologia proposta apresenta grande relevância no objetivo de estudar os diversos teores que possam comprometer o desempenho das estruturas de concreto e contribui para a adoção de medidas preventivas e corretivas nas etapas de implantação e manutenção das obras civis.

Palavra-Chave: Agregados Sulfetados, Concreto, Comportamento, Barragens

Abstract

The construction of hydroelectric dams demands high volumes of concrete. Environmental and economic issues practically impose the use of surrounding rocks for concrete aggregates, which in turn requires previous studies to their possible use. Aggregate characteristics can intensively interfere in concrete behavior especially when sulfates are presented in the aggregates. In this scenario, the goal of this paper is present a methodology that allows monitoring the rates of different sulfur compounds in concrete along the time as oxidation reactions occur. In this methodology, mortar samples were subjected to a proper leaching procedure and kiln-dried; subsequently sulfur content was determined by direct combustion. A theoretical estimate of the total sulfur content based on the chemical analysis of the constituent materials and their proportion in the mortar mix design showed good correlation with the determined experimental value. The proposed methodology has great relevance in studies aiming to set sulfur compound levels that may affect concrete performance in hydroelectric power dams. It can also lead to the adoption of preventive and corrective measures in concrete dams built with aggregates containing iron sulfides.

Keywords: Sulfide Aggregates, Concrete, Behavior, Dams

C.3: ORAL PRESENTATION: 59 CONGRESSO BRASILEIRO DO CONCRETO, OCTOBER/2017



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Caracterização de agregados sulfetados para análise de seu potencial reativo em concretos e argamassas.

Characterization of sulfide aggregates to analyze their reactive potential in concretes and mortars.

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Resumo

É pacífico no meio técnico que as características dos agregados podem interferir intensamente no comportamento do concreto e da argamassa, especialmente quando sulfetos estão presentes na rocha de origem. A utilização de agregados que contenham enxofre na forma de sulfetos é evitada ou mesmo proibida em diversos projetos uma vez que reações do enxofre com elementos provenientes da hidratação do cimento podem gerar produtos expansivos no concreto endurecido, causando fissuras e levando o concreto à degradação. Porém, estudos vêm mostrando que algumas características do agregado podem influenciar na potencialidade de reação do enxofre ou não, dentre eles granulometria, tipo de sulfeto e quantidade desse sulfeto na rocha. Esse trabalho busca, através de ensaios laboratoriais, nortear a caracterização desses agregados visando à possibilidade de se obter padrões diferentes dos atuais quanto à utilização desses agregados em concretos e argamassas, possibilitando o uso de materiais que em um primeiro momento seriam descartados.

Palavra-Chave: Agregados Sulfetados, Concreto, Argamassa, Comportamento

Abstract

It is well known that aggregate characteristics can intensively interfere in concrete and mortar behavior especially when sulfides are presented in the original rock. The use of sulfur-containing aggregates in the form of sulfides is avoided or even prohibited in several projects since sulfur reactions with cement hydration products can generate expansion in the hardened concrete, causing cracks and leading the concrete to degradation. However, studies have shown that some characteristics of the aggregate may influence the sulfur reaction potential or not: among them are size distribution, type of sulfide and amount of sulfide in the rock. The goal of this investigation is guide the characterization of these aggregates through laboratory tests aiming at the possibility of obtaining different standards of the present ones regarding the use of these aggregates in concretes and mortars. This in turn will make possible the use of these materials that at first would be discarded.

Keywords: Sulfide Aggregates, Concrete, Mortar, Behavior

C.4: ORAL PRESENTATION: CITENEL 2017: CONGRESSO DE INOVAÇÃO TECNOLÓGICA EM ENERGIA ELÉTRICA http://www.citenel.gov.br/pages/exporta_trabalhos.aspx



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Pesquisar trabalhos do evento

Pesquisar trabalho

Evento: IX CITENEL e V SEENEL ▼

Módulo: IX CITENEL ▼

Tema: Gestão de bacias e reservatórios ▼

Título do trabalho: AVALIAÇÃO

Empresa proponente:

Código do projeto: PD-4951-0396/2010

Entidade executora:

Situação: Todos ▼

Pesquisar Cancelar

Lista de trabalhos classificados

Ano	Módulo	Tema	Título	Código do projeto	Autores	Empresa proponente	Entidade executora	Situação	Ação
2017	IX CITENEL	Gestão de bacias e reservatórios	Avaliação de Teores Deletérios de Compostos de Enxofre em Argamassas e Concretos	PD-4951-0396/2010	A. Marcelino, J. M. Calixto, A. G. G...	CEMIG Geração e Transmissão S/A	Universidade Federal de Minas Gerais	Aprovado para apresentação com anais	

« « Pagina 1 de 1 » » 10 ▼

Avaliação de Teores Deletérios de Compostos de Enxofre em Argamassas e Concretos

A. P. Marcelino, J. M. Calixto, A. G. Gumieri, M. C. Ferreira, C. L. Caldeira, M. V. Silva

Resumo – As características dos agregados podem interferir intensamente no comportamento do concreto, especialmente quando sulfetos estão neles presentes. A falta de consenso para o valor limite do teor desses compostos de enxofre deletérios em estruturas de concreto tem motivado várias investigações em todo o mundo. Neste cenário, este trabalho propõe o desenvolvimento de uma metodologia para a definição da concentração de compostos de enxofre em concreto para usinas hidrelétricas. Para o estudo, foram utilizadas amostras de rochas da área de usina hidrelétrica do Irapé, em Minas Gerais, construída em um sítio geológico onde a rocha apresentava níveis de sulfeto de pelo menos 3%. Estas amostras foram moídas e depois utilizadas como agregados em argamassas submetidas a três diferentes condições de exposição. Expansão bem como os teores de compostos de enxofre foram os principais parâmetros utilizados para avaliação do comportamento de concreto ao longo do tempo.

Palavras-chave – Agregados Sulfetados, Concreto, Comportamento, Barragens.

I. INTRODUÇÃO

A construção de barragens se dá, geralmente, em locais remotos, o que encarece e dificulta a logística da obra. Utilizar a rocha proveniente das escavações como agregado do concreto empregado na obra representa ganhos econômicos e ambientais. Porém, alguns componentes das rochas são tidos como deletérios para o concreto, o que é o caso do sulfeto.

O enxofre dos sulfetos presentes nos agregados, quando em contato com a pasta de cimento, reage formando produtos expansivos tardios, ou seja, que ocorrem depois do endurecimento do concreto. Uma das consequências dessa expansão é a formação de fissuras que acarretam em danos estruturais pela diminuição da resistência do concreto ou pela exposição da armação no caso de concreto armado.

Por causa disso, há uma grande restrição na utilização de

agregados com enxofre o que é agravada por existirem poucas normas no mundo que tratem desse assunto, e mesmo nas que o tratam o assunto de forma extremamente conservadora, o que pode ser justificado pela falta de pesquisas na área.

Diante disso, surge o questionamento de se avaliar se qualquer tipo de composto enxofre presente no agregado tem potencial deletério ao concreto ou se o tipo desse enxofre pode fazer diferença.

Na natureza há uma enorme variedade litológica. Consequentemente existe uma gama de agregados contendo sulfetos em sua constituição mineralógica, quais sejam: pirita, pirrotita, marcassita, calcopirita, arsenopirita, esfalerita, galena, entre outros. Evidencia-se, portanto, o quanto se torna difícil evitar o emprego desses agregados na preparação de concretos, principalmente em locais em que a disponibilidade de outra fonte de material é economicamente inviável ou inexistente, tornando-se um enorme empecilho para a construção de estruturas, como no caso de barragens, nas quais grandes volumes de agregados são necessários [1], [2].

Durante a implantação da Usina Hidrelétrica de Irapé, no Vale do Jequitinhonha em Minas Gerais, deparou-se com essa questão da utilização de rochas sulfetadas como agregado. A usina foi construída num sítio geológico onde a rocha apresenta em sua composição teores de sulfetos de pelo menos 3% [3]. Estudos preliminares de viabilização do empreendimento mostraram a incompatibilidade das rochas contendo sulfetos com os componentes resultantes da hidratação do cimento, vetando o uso desses agregados na construção da usina. Definiu-se, portanto, a utilização de agregados produzidos nas pedreiras Olhos D'água e Córrego Bonito, localizadas a aproximadamente seis quilômetros do empreendimento. Nessas pedreiras os teores de enxofre não ultrapassavam 0,5%.

A maioria das normas que tratam do assunto não diferencia a origem do enxofre ao determinar um valor limite para o mesmo. Uma exceção é a norma europeia [4], a qual preconiza que, caso seja detectada pirrotita no agregado, o teor total máximo de enxofre não deve ultrapassar 0,1% em massa. Esse valor é 10 vezes menor que o valor usualmente aceito para o teor total de enxofre em agregados contendo sulfatos e sulfetos. De acordo com [5] esses valores são considerados exagerados por muitos engenheiros e podem ter causado o descarte desnecessário de agregados que seriam adequados na fabricação de concretos.

Em face disso, foi realizado o projeto de pesquisa ANEEL CEMIG GT intitulado Metodologia para Definição

Este trabalho foi desenvolvido no âmbito do Programa de Pesquisa e Desenvolvimento Tecnológico do Setor de Energia Elétrica regulado pela ANEEL e consta dos Anais do IX Congresso de Inovação Tecnológica em Energia Elétrica (IX CITENEL).

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C.5: ORAL PRESENTATION: COMITÊ BRASILEIRO DE BARRAGENS 2018, OCTOBER/2018



CBDB
Comitê Brasileiro de Barragens
ÁGUA E ENERGIA PARA A VIDA

Núcleo Regional de Minas Gerais - NRMG

"Caracterização de agregados sulfetados para avaliação de seu potencial reativo em concretos e argamassas."

18/10/2018 | 19:00h | Av. Brasil, 1731 - Auditório da CPRM – Térreo
A partir das 18h 30min haverá um lanche para os participantes

A utilização de agregados que contenham enxofre na forma de sulfetos é evitada ou mesmo proibida em diversos projetos uma vez que reações do enxofre com elementos provenientes da hidratação do cimento podem gerar produtos expansivos no concreto endurecido, causando fissuras e levando o concreto à degradação. Porém, estudos vêm mostrando que algumas características do agregado podem influenciar na potencialidade de reação do enxofre ou não, dentre eles granulometria, tipo de sulfeto e quantidade desse sulfeto na rocha. Nesse P&D foi utilizado agregados produzidos a partir das rochas da UHE de Irapé com concentração média de 2% de enxofre, o que corresponde a aproximadamente 5% de sulfetos (1% de pirita e 4% de pirrotita).

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Long-term behavior of mortars produced with sulfide-bearing aggregates

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ABSTRACT

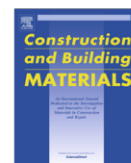
The variety of sulfides (inorganic compounds formed by combining sulfur with a metal element) present in earth crust is not small, which makes it difficult to avoid the use of sulfide-bearing aggregates in the concrete, especially in places where another source of material is non-existent or economically impracticable, as is the case of dams in Brazil. Within this scenario, this work presents an evaluation of the long-term behavior of mortar produced with aggregates containing pyrite and pyrrhotite. 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 1300 days, subjected to three different exposed conditions: 1-temperature of $23^{\circ} \pm 2^{\circ}\text{C}$ and relative humidity of 95 to 100%; 2- submerged in calcium hydroxide solution diluted in water almost 850 days and then kept in water up to 1300 days, both in room temperature; 3- submerged in calcium hydroxide solution diluted in water at 50°C during almost 850 days and then kept in water (50°C) up to 1300 days. 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 calcium hydroxide solution speeds up the expansion just like the temperature. It was also observed 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 only by the total amount of sulfur.

Keywords: sulfide-bearing aggregates, mortar, long-term behavior, dams.

1. INTRODUCTION

On the Earth, the lithological variety is huge and, consequently, aggregates for concrete come from many rocks containing sulfides in their mineralogical constitution. These sulfides are pyrite, pyrrhotite, marcasite, chalcopyrite, arsenopyrite, sphalerite, galena, among others. It can be concluded that it is difficult to avoid the use of these aggregates in the concrete. This is even more difficult in places where the availability of another source of material is economically impracticable or non-existent as in the case of concrete dams where large volumes of aggregates are needed [1,2].

Aggregates containing iron sulfides were used in the Graus and Tavascan 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 concrete degradation problems in the above-mentioned structures mainly related



A feasible evaluation protocol to determine the most reactive sulfide-bearing aggregate for use in concrete



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HIGHLIGHTS

- The iron sulfides (pyrite and pyrrhotite) oxidation in aggregates was investigated.
- Sulfides spatial distribution for different aggregate particle size was evaluated.
- To promote the sulfide oxidation a leaching process was carried out.
- Sulfur from each sulfide in aggregate was determined according to the particle size.
- Total sulfur before and after oxidation was determined according to the particle size.

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ABSTRACT

Internal sulfate attack is one of the most harmful deterioration mechanisms to concrete. A testing procedure was developed to evaluate how reactive is a sulfide-bearing aggregate to use in concrete. The aggregates were produced from iron sulfide rocks that have at least 1.5% of sulfur. Particle sizes between 0.15- and 4.80-mm had the sulfur quantities from sulfide (pyrite and pyrrhotite) determined by direct combustion test. The exposed surface of each sulfide was calculated using a scanning electron microscope (SEM) connected to an automated image analysis system - Mineral Liberation Analyzer (MLA). Samples also were immersed in an H₂O₂ solution and the released sulfate (from the sulfide oxidation) was quantified. The results showed that the larger the sulfide exposed surface and the smaller the particle size are, the more effective is its oxidation and consequently more reactive the aggregate.

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1. Introduction

The use of sulfide-bearing aggregates in concrete production is increasing worldwide since sulfides are present in most rock lithologies. Aggregates containing sulfides cannot always be replaced due to the lack of other available materials and to economic factors. This is even more difficult in places where the availability of another source of material is economically impracticable or non-existent as in the case of concrete dams where large volumes of aggregates are needed [1–3].

Iron sulfides, such as pyrite (FeS₂) and pyrrhotite (Fe_(1-x)S: x = 0–0.17) [4], in the presence of water and oxygen, are oxidized releasing compounds such as sulfuric acid, iron hydroxide and iron sulfate [5]. These compounds can cause internal sulfate attack (ISA) in the concrete with expansive ettringite formation [6–10]. ISA has caused premature concrete deterioration in several parts of the world. Aggregates containing iron sulfides were used in buildings in Maresme in Spain [11] and in the Graus and Tavascán dams in 1992 [5,12], also in Spain, in 1970. These studies reported concrete degradation problems, mainly related to severe cracking, due to the iron sulfide presence in the aggregate used in the above-mentioned structures.

In Switzerland, a dam built in the early 1970s used sulfide-bearing aggregates. Since the early 1980s, the concrete in this dam has been constantly expanding. The dam has been monitored

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