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REVIEW ARTICLE

Physicochemical evaluation of oxidation of diabase aggregates with sulfide minerals: influence of particle size, pH of the medium and pyrite concentration

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Abstract Large constructions, such as concrete dams, commonly use aggregates extracted from rock masses near the implantation sites, which may contain sulfide minerals in its composition. These aggregates, inside the concrete, may oxidize, forming sulfate ions (SO_4^{2-}), which can cause the internal sulfate attack. Therefore, in order to study aggregates for concrete dosages of these structures, aimed to evaluate on this paper the oxidation process of aggregate containing sulfide minerals in amounts of up to 5.0 %, by way of studies into the effects of particle size and pH of the medium (Study 1) and the pyrite content (Study 2). In Study 1, diabase aggregates containing pyrite (FeS_2) were separated into three particle sizes (sand, coarse aggregate 0 and coarse aggregate 2). Samples were analyzed in two groups and immersed in solutions of distilled water and calcium hydroxide, with pH and electric potential measurements. In Study 2, diabase sand from the same origin of Study 1, but in smaller particle size, and natural aggregates (sand) with the addition of pyrite in four levels (0, 0.5, 1.0 and 5.0 %) were immersed in distilled water, with measurements of pH, electric conductivity and total dissolved solids. The results of the tests, under constant oxygenation, showed that the reduced grain size and alkaline medium accelerate the oxidation reactions, in contrast to aggregates immersed in neutral solutions. Comparing the results by ANOVA test indicates the presence of around 0.5 % of sulfide mineral in the diabase aggregates, with better results from monitoring of electric conductivity and dissolved solids in contrast to pH readings.

Keywords Sulfide mineral · Internal sulfate attack · Oxidation reactions · Pyrite

1 Introduction

In large scale constructions, such as concrete dams of hydroelectric power plants, the consumption of aggregates is quite high due to the high volume of concrete used, as in the construction of the Governador José Richa Hydroelectric Power Plant dam (Salto Caxias), with installed capacity of 1240 MW, where about 912,000 m^3 of roller compacted concrete was produced, with cement and aggregate consumption in the order of 100 and 1260 kg/m^3, respectively, reaching a consumption of about 1,150,000 tons of aggregates distributed in various grain sizes [1].

Thus, due to the large distances and material transport costs from producing centers, usually far away from these construction projects, it is impractical to use selected aggregates from these centers, restricting the extraction of quarries located near the project [2–4].

In most cases, the aggregates extracted from these quarries are considered satisfactory for the production of concrete, but the presence of certain minerals in the composition can cause damage when in contact with the Portland cement hydration products, such as the sulfide

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minerals, as pyrite, which contain sulfur in its composition. The products of pyrite oxidation react with the hydrated composites in Portland cement and result in the internal sulfate attack, causing expansion and cracking of the paste.

Pyrite (FeS_2) is one of the most identified sulfide mineral in rocks, with a cubic structure, composed of 46.6 % Fe (iron) and 53.4 % of S (sulfur), ranging from golden yellow to a polished brass yellow. It is found in sedimentary, metamorphic, igneous (such as diabase) rocks and mineral coal sources. Its hardness is between 6 and 6.5 on the Mohs scale, changing into sulfate ions (SO_4^{2-}) during its oxidation process [5, 6]. In Fig. 1 are illustrated aggregates containing pyrite.

One of the ways to identify pyrite is by the appearance of brown rust stains on hard rock formations and formation of white film adhered to the aggregates, which are characteristic in the formation of compounds such as iron hydroxide and hydrated iron sulfate, products generated by the oxidation of pyrite [5].

Some cases have been reported on the occurrence of internal sulfate attack in concrete dams. In Spain, following anomalous behaviors detected by instrumentation systems of concrete dams in Torán, Graus and Tavascán with a growing trend of expansion of the structure downstream to upstream, there was the presence of sulfide minerals in aggregates [9], causing surface cracks and structural displacements. Still in Spain, other cases [6] were recorded in the dams of Paso Nuevo and Rumedo, and all these structures are near the same geological formation. In Brazil, we can mention the Rio Descoberto dam, executed with mass concrete with the use of aggregates containing pyrite, resulting in leakage points in the dam's downstream face and inside the gallery, a few years after filling the reservoir [7].

Pyrite, in the presence of water (moisture) is initially oxidized by oxygen (O_2) dissolved in water to produce ferrous (Fe^{2+}), sulfates (Eq. 1) and ferric ions (Fe^{3+}) (Eq. 2). The ferric ions released, act as powerful catalysts for further pyrite reactions, being reduced to ferrous ions, releasing sulfate ions again, thereby maintaining a cycle of reactions until the consumption of the whole mineral (Eq. 3). This latter reaction has hydrogen ion (H^+) as a byproduct, which tends to reduce the alkalinity of the system [10, 11]:

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

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

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \tag{3}$$

From the viewpoint of thermodynamic equilibrium of the reactions, it is considered that the iron hydroxide ($Fe(OH)_3$) formed (Eq. 4) is the most stable product of the oxidation of sulfides when they occur in alkaline media ($pH > 7.0$), such as inside the concrete [2, 12]

$$4Fe^{2+} + 10H_2O + O_2 \rightarrow 4Fe(OH)_3 + 8H^+ \tag{4}$$

The iron hydroxide can cause a variation in volume of 3.05 cm^3 per mol of oxidized sulfide mineral, which is considered small compared to the volume generated by the formation of sulfate reaction byproducts with cement hydrates, such as gypsum, monosulfoaluminate or ettringite, which may cause a volume increase of up to 182.89 cm^3/mol of sulfate in the cement matrix [2]. Other compounds may also be formed, such as goethite (α-$FeO(OH)$), by dehydration of iron hydroxide, hematite (Fe_2O_3) and melanterite ($FeSO_4 \cdot 7H_2O$) [2, 7, 12].

In the alteration process of sulfide minerals, some factors may contribute to the development and acceleration of oxidation, such as oxygen concentration, temperature and humidity, pH, specific surface area of the particles, iron content, the presence of bacteria and morphology [3, 6, 12].

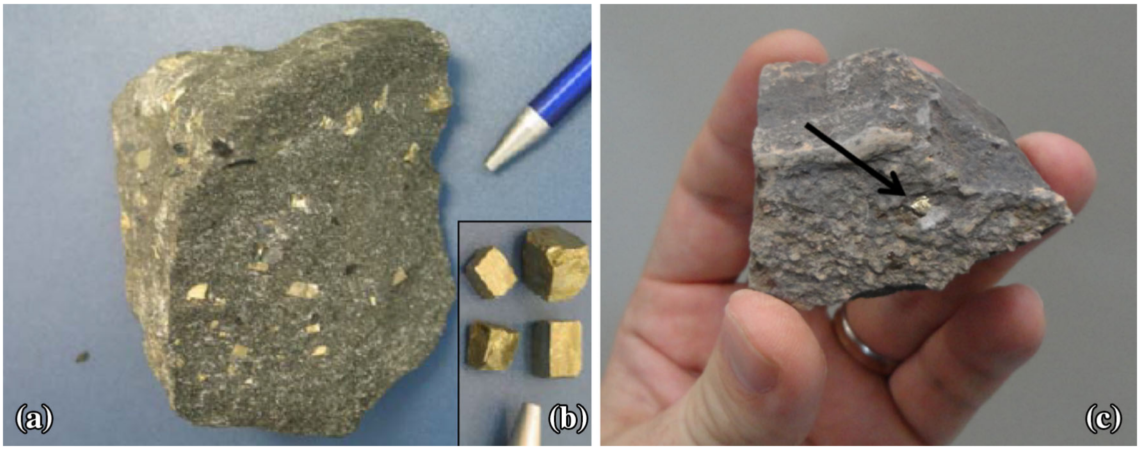


Fig. 1 Rock mass containing sulfides in the form of pyrite (detail **a** and **b**) [7]. Aggregate from a quarry near the area of the Tibagi river in Paraná (detail **c**) [8]

The alkalinity of the medium is the predominant factor in determining what will be the oxidizing agent [5]. For Casanova et al. [12], no sulfide mineral is stable at pH values above 10, whereas, at pH values between 7.5 and 8.5, the reaction rate does not depend on the alkalinity of the medium, but on the availability of oxygen and grain size.

In environments with pH values below 4.0, ferric ion is the main responsible for the initiation of the reactions, whereas in an alkaline media, such as concrete, where the pH is between 12.5 and 13.5, the oxidizing agent is oxygen [6]. Even under alkaline conditions, such as in the concrete, the pyrite oxidation reactions tend to turn the medium more acidic due to the release of hydrogen ions in the solution, according to Eq. 1 [2].

The development of expansive reactions is determined by the change in the surface area of the reagents, thus depending on the original size of the sulfide grains in the aggregate [2]. In research conducted by Casanova et al. [12] with sulfide grains sized between 100 and 200 µm and by Oliveira [6], using grains sized between 4–5 mm and 40–50 mm, the authors analyzed the influence of grain size variation on the oxidation reactions of sulfide minerals present in aggregates, verifying that the evolution rate of these reactions and the formation of ettringite in concrete is higher for smaller grains.

Thus, the first expansion mechanism inside the concrete begins with pyrite oxidation reactions mainly forming iron hydroxide (Eqs. 1–4) [2, 10–12]. In a second stage, the release of sulfate ions from the reaction of this sulfide's alteration and its combination with cement compounds, cause the internal sulfate attack.

The hydrogen and sulfate ions resulting from the oxidation of pyrite and dissolved in the aqueous solution of concrete pores, react with their hydrated compounds, mainly calcium hydroxide ($Ca(OH)_2$ or CH) and tricalcium aluminate ($CaO\cdot Al_2O_312H_2O$ or C_3A), forming new expansive products, such as gypsum ($CaSO_4\cdot 2H_2O$ or $C\overline{S}H_2$) (Eq. 5), monosulfoaluminate ($CaO\cdot Al_2O_3CaSO_4\text{-}18H_2O$ or $C_4A\overline{S}H_{12}$) (Eq. 6) and ettringite ($CaO\cdot Al_2O_33\text{-}CaSO_4\cdot 32H_2O$ or $C_6A\overline{S}_3H_{32}$) (Eq. 7) [2]:

$$CH + \overline{S} + 2H \rightarrow C\overline{S}H_2 \quad (5)$$

$$CH + C_3A + \overline{S} + 11H \rightarrow C_4A\overline{S}H_{12} \quad (6)$$

$$3CH + C_3A + 3\overline{S} + 29H \rightarrow C_6A\overline{S}_3H_{32} \quad (7)$$

These products begin forming in voids, pores and cracks in the concrete, especially in the interface zone between the aggregate and the cement paste. If the reactions have continuity, the volumes generated can cause excessive stresses and microcracks [10]. The solids volumes generated for the formation of gypsum, monosulfoaluminate and ettringite are, respectively 41.63; 182.89 and 172.19 cm^3/mol of sulfate, being therefore more expansive than the products generated in the oxidation of pyrite, such as ferrihydrite (3.05 cm^3/mol of sulfide) [2].

The symptoms which show a concrete contaminated with sulfide mineral are: rust spots, mapped cracking, disaggregation and swelling of the pores, white film on the aggregates, white efflorescence and, eventually, structural displacements beyond the project limits [5].

On the standardized requirements for aggregates to be used in the production of Portland cement concrete, the Brazilian standard NBR 7211/2009, item 5.3.2, recommends that the sulfate content must not exceed the 0.1 % limit on the aggregate mass. Also according to the NBR 7211/2009, the aggregates that exceed this limit may be used in the concrete only when the total content from the other constituent materials does not exceed the value of 0.2 %, or the use of Portland cement resistant to sulfates is proven, as by NBR 5737/1992 [13].

Thus, this study aims to evaluate the mineral pyrite oxidation processes, at levels up to 5.0 %, found in aggregates, through immersion in neutral and alkaline aqueous solutions, subjected to constant oxygenation, by pH, electrical potential, total dissolved solids (TDS) and electrical conductivity monitoring, for their use for the production of concrete.

2 Materials and methods

2.1 Materials

The presence of sulfide minerals in aggregates used in concrete may result in the formation of expansive products, such as ettringite, when in contact with hydrated cement compounds. The evaluation of these sulfides oxidation reactions must be held to decide on its use as an input in the production of concrete.

Thus, a natural aggregate was used (sand) from the São Luiz do Purunã region, and diabase aggregate from a quarry located in Telemaco Borba, close to the region in the middle section of the Tibagi River, referred to on this work as "Crushed aggregate", both in the state of Paraná, Brazil. The natural aggregates, free of pyrite content were considered as reference in this study. The Crushed aggregates were used for having a history of pyrite in its composition, being studied in related studies [4, 14] and citing their results in this study, for their use for the construction of large constructions such as concrete dams.

To fill up the glass beakers, where the tested aggregates were placed, distilled water and an aqueous solution of calcium hydroxide ($Ca(OH)_2$) in concentration of 20 g/L was used, obtaining neutral (pH ≈ 7.0) and alkaline (pH ≈ 12.5) solutions, respectively.

Through transmitted optical light microscopy, the petrographic analyzes were performed on thin sections from the aggregate samples, obtaining a semiquantitative percentage by visual estimation, while an optical microscope with reflected light was used to identify the opaque minerals (Table 1) [4].

Thus, the petrographic analysis carried out in the contaminated aggregates from the quarry in the study showed a greater amount of andesite/labradorite (plagioclase) and augite (pyroxene) in its composition, thus being rocks of igneous nature, classified as diabase.

Through an optical reflected light microscopy, the qualitative analysis found the presence of the following sulfides: pyrite (FeS_2), chalcopyrite ($CuFeS_2$), pyrrhotite ($Fe_{(1-x)}S$) and sphalerite (ZnS). Through the semiquantitative analysis by visual estimation, sulfides contents were detected less than 0.5 %, with low change rate of pyrrhotite into limonite [4].

For the chemical characterization the semiquantitative test of X-ray fluorescence (XRF) was performed, using compressed powder pellets [14]. The results indicated a greater amount of silicon and iron oxides, and 0.3 % sulfur oxides (Table 2).

2.2 Test procedure

The oxidation potential of aggregates containing sulfide minerals was evaluated from the insertion of the same in an aqueous medium, dividing the research into two studies: 1—investigation of the effects of particle size and alkalinity of the medium; 2—study of the effect of pyrite content in aggregates.

2.2.1 *Study 1: effect of particle size and pH of the medium*

This part of the experiment was developed to evaluate the performance of the Crushed aggregate in different particle sizes in a humid environment (water presence) and aerated (O_2 diffusion) being separated by sieving into three different particle sizes: sample 01 (2.36 mm < Ø < 4.75 mm), sample 02 (6.3 mm < Ø < 9.5 mm) and sample 03 (19 mm < Ø < 37,5 mm). The samples were weighed, totaling approximately 610 g of material per particle size range. Prior to use, the aggregates were washed in running water from the local distribution system for removal of dust and excess organic material, being dried in the laboratory room temperature of (24 ± 2) °C.

After preparing the aggregates for the test, the samples were separated into two groups with the three previously mentioned particle sizes and placed individually in glass beakers. Subsequently, a set had its containers filled with distilled water, seeking to maintain a neutral pH environment (≈7,0), while the other set was filled with an alkaline solution of distilled water and calcium hydroxide in concentration of 20 g/L greater than that adopted by [5] in their study, to ensure its saturation. All the beakers were filled with the solution until the total volume of 500 ml. The reason to use a series with the aqueous solution of calcium hydroxide is that it provides a medium with high pH, characteristic of the inside of the concrete environment, in an environment closer to the service conditions under which these aggregates stay in real conditions.

Soon after, the aggregate samples immersed in the solutions were subjected to constant air bubbling through an air compressor with a pressure of 100 mbar, connected to the beakers through 4.0 mm diameter silicone hoses and air diffusers (Fig. 2), for a period of 30 days without

Table 1 Petrographic analysis of the diabase (crushed aggregates) [4]

	Characteristics	
Sample type	Color	Dark grey
	Structure	Massive
Mineralogical composition	Andesine/Labradorite (Na, Ca)(Si, Al)$_4$O$_8$ (%)	55–60
	Augite (Ca, Na)(Mg, Fe, Al)(Si, Al)$_2$O$_6$ (%)	30–35
	Opaque minerals (%)	5
	Apatite ($Ca_5(PO_4)_3$(F,OH,Cl)(%)	<1
	Alkali feldspar (%)	<1
	Clay mineral (%)	1–2
	Microgranular quartz (%)	<1
Rock classification	Type of rock	Igneous
	Name	Micro-gabbro—diabase
Alkali-aggregate reactivity potential	Reactive potential	Potentially reactive

Table 2 Analysis by X-ray fluorescence (XRF) [14]

Sample	SiO_2 (%)	Fe_2O_3 (%)	Al_2O_3 (%)	CaO (%)	TiO_2 (%)	MgO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	SO_3 (%)	P.F. (%)
Aggregate	47.10	18.30	13.00	9.10	3.20	2.80	2.50	1.50	0.80	0.30	0.81

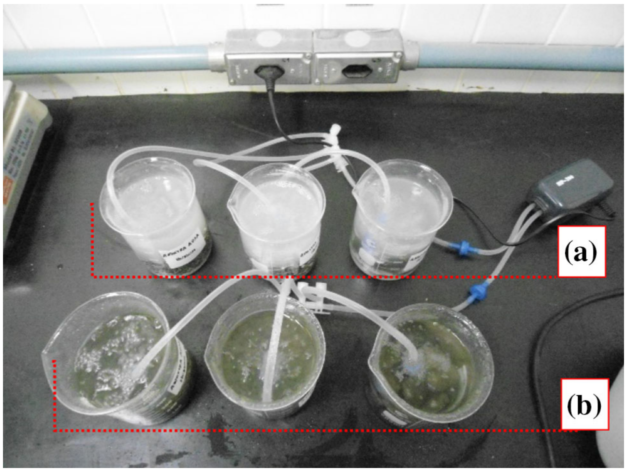


Fig. 2 Assembly of the test system with the aggregates of different particle sizes immersed in an alkaline (**a**) and a neutral (**b**) solution

interruption. During this time periodic pH readings, electrical potential (Eh) and temperature of the solution were obtained using the bench pH meter 210 mPA from MS Tecnopon with a pH measurement ranging between −2.0 and 20.0 and Eh between −1999.9 and +1999.9 mV, with an individual stainless steel thermometer with automatic temperature compensation.

According to the separation of the aggregates in the two solutions for the development of the oxidation test, the samples were divided into the "$Ca(OH)_2$" series (alkaline solution), and the "H_2O" series (distilled water), in an increasing order of particle sizes, as shown in Table 3.

2.2.2 Study 2: effect of the pyrite content

In this part of the study the natural aggregate was evaluated (region of São Luiz do Purunã, Paraná, Brazil) with the addition of pyrite in four different levels of SO_3 (theorical value calculated): reference (0 %); 0.5 %; 1.0 % and 5.0 %, in mass, based on levels found in the studied and reported aggregates by [3–7, 9, 11, 15]. In addition, crushed sand from the same rock mass of Crushed aggregate used in Study 1 was evaluated, with similar particle size to the natural sand previously cited. This material was included in Study 2 due to its history of unknown pyrite content, detected in the same region of Study 1. For each level, 300.0 g samples of aggregate were separated and weighed, subsequently packed in five glass beakers and filled with distilled water. Table 4 shows the details of the tested series.

As in Study 1, the solutions were subjected to a constant bubbling of air through an air compressor with a pressure of 100 mbar. The measured test parameters were: pH, temperature, electrical conductivity and total dissolved solids (TDS), which were monitored daily for 30 days.

3 Results and discussions

3.1 Study 1: effect of particle size and pH of the medium

In Figs. 3 and 4 are shown, respectively, the results obtained from the readings of pH and electric potential during the period of 30 days with constant aeration (bubbling). Throughout the test, the average temperature of the solutions was maintained at (24 ± 2) °C.

As can be seen in Fig. 3, the pH behavior indicated a delay in the reduction of values during the aggregates test for neutral solutions (H_2O-lower, H_2O-average and H_2O-greater) indicating that the predominance of andesine/labradorite (plagioclase) and augite (pyroxene), which have silicon and calcium in its composition, may have acted as buffers in the solution. The presence of some silicates in rocks, such as pyroxene and feldspar, may contribute, through hydrolysis reactions, to neutralize the acidity of the

Table 3 Samples used for conducting the oxidation test of diabase aggregates with sulfide mineral

Sample	Ø (mm)	Solution	Mass (g)
$Ca(OH)_2$—lower	2.36 < Ø < 4.75	Distilled water + calcium hydroxide	305.70
$Ca(OH)_2$—average	6.3 < Ø < 9.5	Distilled water + calcium hydroxide	304.65
$Ca(OH)_2$—greater	19.0 < Ø < 37.5	Distilled water + calcium hydroxide	307.32
H_2O—lower	2.36 < Ø < 4.75	Distilled water	303.05
H_2O—average	6.3 < Ø < 9.5	Distilled water	303.49
H_2O—greater	19.0 < Ø < 37.5	Distilled water	302.82

Table 4 Distribution of samples evaluated with different pyrite contamination levels

Sample	SO_3 content (%)	Total mass of aggregate (g)	Total mass of pyrite (g)	Total sample mass (g)
Reference—0 %	0	300.0	0.0	300.0
SO_3—0.5 %	0.5	298.5	1.5	300.0
SO_3—1.0 %	1.0	297.0	3.0	300.0
SO_3—5.0 %	5.0	285.0	15.0	300.0
Crushed	Unknown	300.0	Unknown	300.0

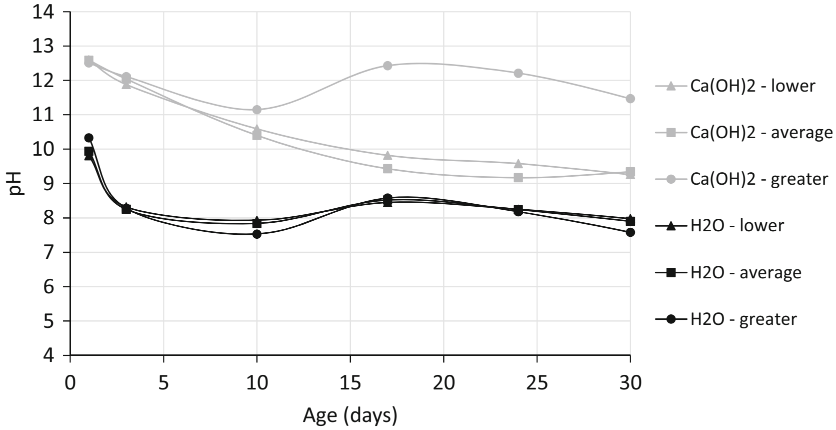


Fig. 3 pH variation values measured for different solutions and samples with particle sizes of 2.36 mm < Ø < 4.75 mm, 6.3 mm < Ø < 9.5 mm and 19 mm < Ø < 37.5 mm

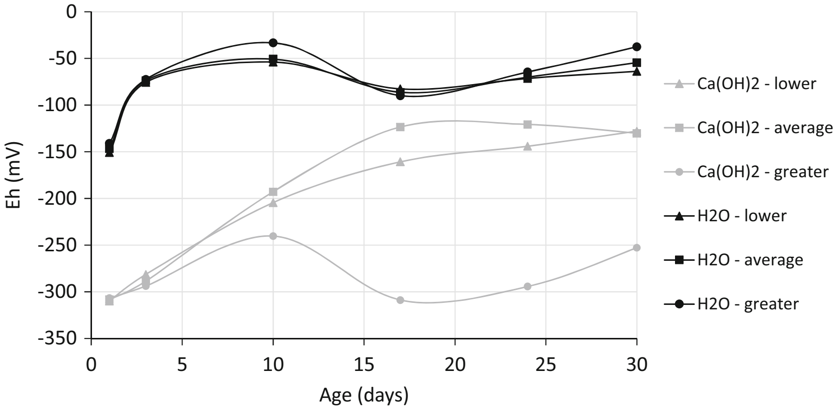


Fig. 4 Electric potential for different solutions and samples with particle sizes of 2.36 mm < Ø < 4.75 mm, 6.3 mm < Ø < 9.5 mm and 19 mm < Ø < 37.5 mm

system, maintaining the high alkalinity [15]. The same behavior was also observed by Pereira [14] while performing pH NAG tests with the aggregates used in this study. This explains the fact that the containers filled with distilled water reached at the beginning of the test a pH of 10, indicating that some aggregate component immediately dissolved in water, raising the pH.

During the oxidation reactions of sulfide minerals, occurs the release of hydrogen into the medium in solution, causing a reduction of pH in the two series, with distilled water and the solution of $Ca(OH)_2$, according to Eqs. 1 and 3. This was more visible in the solution of $Ca(OH)_2$ ($Ca(OH)_2$-lower, $Ca(OH)_2$-average and $Ca(OH)_2$-greater), in which the high initial alkalinity (pH > 12.5) and the instability of the sulfide mineral to pH ≈ 10 values contributed to demonstrate significant reductions in hydrogen concentration over the test. Similar behavior was also observed in the work of Casanova et al. [2] and Oliveira [6].

The profile of the pH curves in the solutions indicated a reduction of the same for the smallest particle sizes in alkaline solutions, an indication that a given aggregate with sulfide mineral the more finely it is ground, the more potent are the effect in terms of internal sulfate attack due to their higher specific surface area ($Ca(OH)_2$-lower, $Ca(OH)_2$-average and $Ca(OH)_2$-greater).

Fig. 5 Aggregate in the initial oxidation process in the region with greater contact with the bubbling oxygen during the 30 days of the study

In neutral environments (pH $\approx$ 7), the reaction rate of oxidation of the sulfide mineral has a higher relation with the amount of dissolved oxygen available to act as an oxidizing agent [2]. For pH values above 10, the influence of the alkalinity of the medium is higher in relation to the presence of oxygen, in which the sulfides become unstable, unlike what occurs when the pH values are close to 7.0, increasing its relation with the dissolved oxygen. When the solution has high alkalinity ($12.5 < \text{pH} < 13.7$), the oxidation rate is increased [12], which may have contributed to the initial phase of the reactions for aggregates of greater specific surface area ($Ca(OH)_2$-lower and $Ca(OH)_2$-average).

For samples in the neutral solution of distilled water (H_2O-lower, H_2O-average and H_2O-greater) after the initial rise in pH and instability of the sulfide mineral, there was a reduction in pH values and a tendency to a constant pH $\approx$ 8.0 in subsequent ages. Sulfide contents found in diabase [4, 14] may not have contributed sufficiently to change the pH of the solutions during the test period.

The variability in sulfide concentrations in the aggregates may also have interfered in their behavior during the test. In the same rock mass there can be different points with varying levels of sulfide minerals, therefore, without uniformity in the results, which could compromise the correct decision on their use for the production of concrete.

Regarding the electrical potential values, shown in Fig. 4, both solutions presented electronegative values throughout the test. Similarly to the pH monitoring, the more alkaline solutions, with $Ca(OH)_2$, showed the greatest change in the electric potential over the time this study was conducted. This trend was observed only for the two smaller particle sizes, as well as in the monitoring of pH.

As shown in Fig. 5, even with the sulfide content in the samples, for some granulometric ranges it was found that the initial surfacing of an orange color efflorescence, similar to iron oxide of the goethite kind, on the surface of the aggregates, mainly the ones with smaller diameters ($2.36\text{ mm} < Ø < 4.75\text{ mm}$ and $6.3\text{ mm} < Ø < 9.5\text{ mm}$). This occurred both for the solution of $Ca(OH)_2$ as for the series with distilled water (Fig. 5). As for the larger aggregates ($19\text{ mm} < Ø < 37.5\text{ mm}$), there was no surface change, which may be related to the higher reactivity of aggregates with greater specific surface area for oxidation reactions.

3.2 Study 2: effect of pyrite content

Figure 6 shows the stabilized pH values at the end of the test (30 days) in solutions with different contamination levels. It is noted that the aggregates contaminated with 0.5, 1.0 and 5.0 %, in mass, theorical, of SO_3 presented acid pH ranging between 3 and 4. The aggregate with 0 % contamination and crushed sand, showed pH above 7.0, indicating that the used crushed sand sample has a SO_3 content lower than 0.5 %, causing a small reduction of pH in the solution, with values close to the pH of the solution with a content of SO_3 0 %.

In Fig. 7 is shown the variation of the electrical conductivity of the water in contact with the aggregate systems tested in the experiment. The results indicated an increase of the value of the property until approximately day 20, at which time stabilization readings were noted. The trend of the data of each series was of an increase in electrical conductivity over time of interaction between the contaminated aggregate and the aqueous medium. It was also noted that the higher the SO_3 content, the higher the conductivity throughout the test. The crushed sand was ranked next to the aggregate with 0.5 % SO_3 content, demonstrating, by ANOVA test ($F_{\text{calculated}} = 0.01 < F_{0.05} = 4.08$), that both have similar amounts of ions in solution, such as Fe^{2+} and Fe^{3+} metals, presenting results consistent with what was disclosed in the optical light microscopy reflected by semiquantitative visual analysis.

In Fig. 8 are shown the results of TDS related to the interaction between the aggregate systems and the water

Fig. 6 pH of the water in contact with aggregates with different contamination levels of pyrite at 30 days of the test

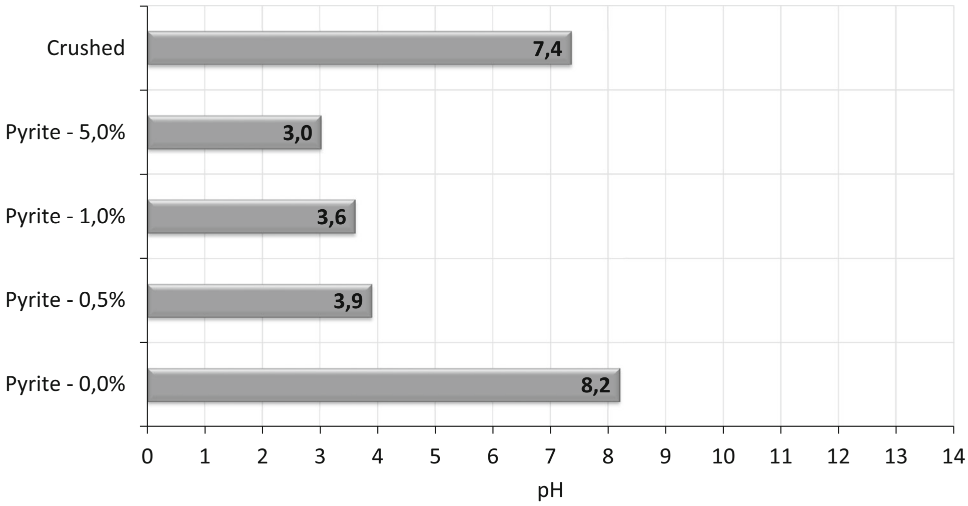


Fig. 7 Electrical conductivity along the water exposure time with aggregates having different contamination levels of pyrite

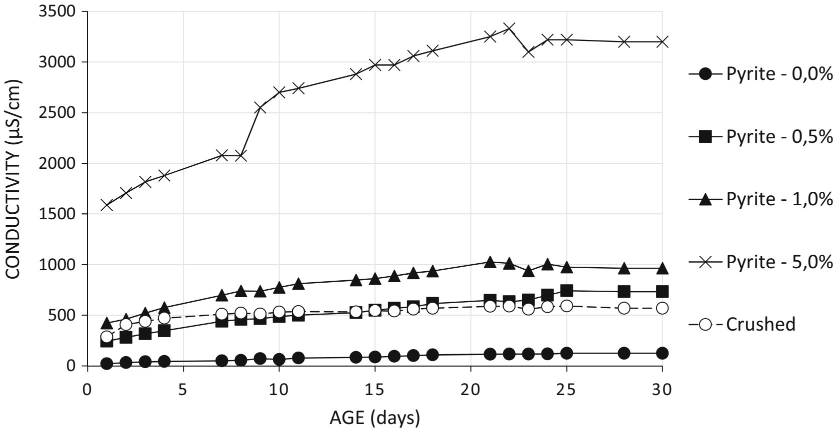
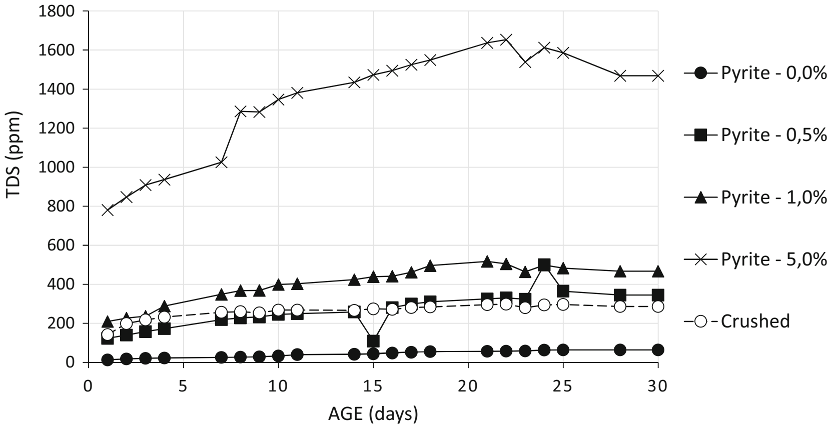


Fig. 8 Variation in the total dissolved solids (TDS) along the water exposure time with aggregates having different contamination levels of pyrite



placed in each beaker. The TDS behavior was similar to what happened during the monitoring of the electrical conductivity, indicating that the interaction of the aggregate with the aqueous medium may have caused the dissolution of ions, which increased the system conductivity. The data allowed distinguishing the pyrite levels present in the natural aggregate and crushed sand, which again showed results close to 0.5 % of content, confirmed by ANOVA test ($F_{calculated} = 0.08 < F_{0.05} = 4.08$).

In both Figs. 7 and 8 it's shown that the 5.0 % of SO_3 content significantly excelled compared to other levels added.

In Figs. 9, 10, 11, 12 and 13 is shown the correlation study between the electrical conductivity data and TDS, indicating a degree of correlation with R^2 values above 0.95, except in the case of 0.50 % SO_3 contamination, which presented R^2 above 0.70. In TDS measurements of 0.5 % of SO_3, a variation can be observed in the results obtained at 15 and 24 days of trial, but the electrical conductivity in these same days did not suffer variation, maybe signaling only one assay variability, since other points correlated.

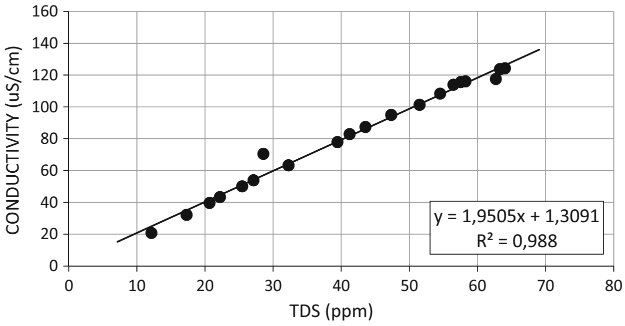


Fig. 9 Relationship between the electric conductivity data and the total dissolved solids (TDS) over time of exposure of water to 0.0 % pyrite content (natural aggregate)

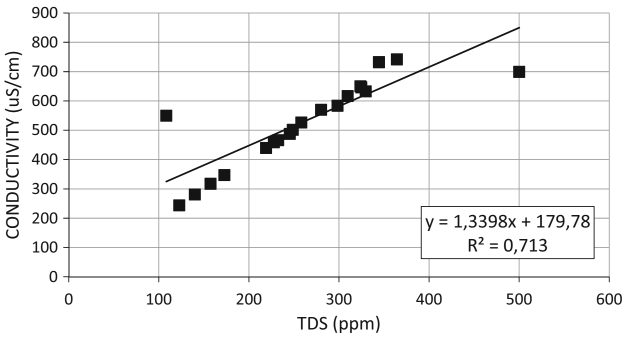


Fig. 10 Data relation between electrical conductivity and total dissolved solids (TDS) over the exposure time of water to 0.5 % pyrite content

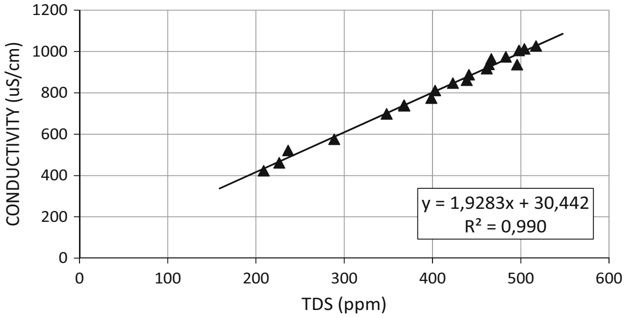


Fig. 11 Data relation between electrical conductivity and total dissolved solids (TDS) over the exposure time of water to 1.0 % pyrite content

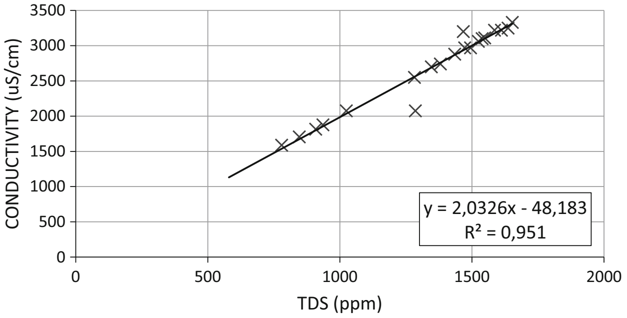


Fig. 12 Data relation between electrical conductivity and total dissolved solids (TDS) over the exposure time of water to 5.0 % pyrite content

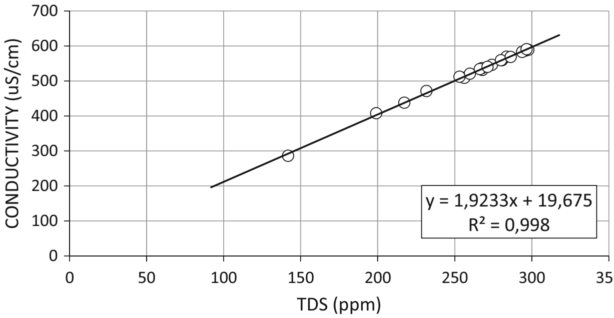


Fig. 13 Data Relation between electrical conductivity and concentration of total dissolved solids (TDS) over the exposure time of water to the crushed aggregate (unknown content)

The electrical conductivity, which quantifies the ease with which an element conducts electrical current, reflecting the presence of ions in the solution, such as metals (iron), proved to be more precise to check the variability of these ions in solution compared to the measurement of pH or H+ ions in solution, as shown in the results of this study. The TDS, which according to Oliveira [6] is closely related to the kinetics of oxidation of the sulfide mineral, whereas the reactions involved in this process can release solid particles that dissolve in water, confirmed the results obtained with electrical conductivity, ratified also by the obtained R^2 correlations.

4 Conclusions

As seen in the measurements of pH and electric potential of Study 1, the pyrite oxidation rate depends more on the alkalinity of the medium in solutions with $pH > 10$. During the reactions, with the release of hydrogen by the formation of ferrous, sulfate and ferric ions, the pH tends to decrease.

Regarding the grain size variation of the aggregates, it was found that in an alkaline medium, it was more influential to the oxidation reactions when compared to the aggregates in a neutral solution in which was observed the same behavior regardless of particle size. This is due to the larger specific surface area formed by reducing the grain size and the instability of the sulfides in alkaline environments (pH > 10), accelerating the reactions in contrast to the aggregates immersed in a neutral solution (pH $\approx$ 8.0).

The initial formation of superficial brown spots on the smaller particle size aggregates showed that the presence of dissolved oxygen, in both alkaline solution and in neutral solution, caused an increase in the sulfide oxidation rates. In the case of neutral solution, the presence of pyroxene and feldspar may have contributed to the initial neutralization in the acidity of the system, but did not avoid the subsequent oxidation of the sulfide mineral.

In Study 2, the crushed sand presented pH readings similar to the reference aggregate (0 %), indicating the presence of a low content of this sulfide mineral. The same results (pH $\approx$ 8.0) were obtained for the aggregates immersed in distilled water from Study 1, irrespective of particle size distribution. Since there was a pH variation of the aggregates in alkaline solutions from Study 1, it showed that the use of pH readings to monitor the oxidation reactions of sulfide minerals did not provide adequate precision for its evaluation with low pyrite content and aeration in neutral solutions for periods up to 30 days of test.

In neutral solutions (distilled water), the results indicated that the monitoring of electrical conductivity and dissolved solids from the interaction of the added sample aggregate with water was suitable to detect the aggregate pyrite contamination rate, even at low levels in a period of 30 days.

It might be said that the crushed rock aggregates (from Telemaco Borba) had equivalent behavior in both trials, with similar characteristics to the aggregate with 0.5 % of pyrite content, confirmed by ANOVA test. In the experiment, it was still possible to distinguish the different levels of pyrite addition.

A correlation was proven for R^2 above 0.95, except for 0.5 % pyrite content that presented R^2 correlation above 0.70, between the electrical conductivity and total dissolved solids, being an indication that the water in contact with the aggregate sulfide minerals dissolved ions in the aqueous system, resulting in increased electrical conductivity.

According to Brazilian standard NBR 7211/2009, the Crushed aggregates, with about 0.5 % pyrite content, may be considered reactive to be used in the Portland cement concrete, exceeding the limit of 0.1 % of sulfate content on the aggregate mass.

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References

1. Krempel AF, Oliveira LFP, Pereira MAC (1997) Controle de qualidade da compactação do CCR na barragem da U.H. de Salto Caxias. XXII Seminário Nacional de Grandes Barragens. São Paulo
2. Casanova I, Agulló L, Aguado A (1996) Aggregate expansivity due to sulfide oxidation—I. Reaction system and rate model. Cem Concr Res 26(7):993–998
3. Gomides MJ, Hasparyk NP, Andrade MAS, Bittencourt RM (2005) Investigação de agregados contendo sulfetos para utilização em estruturas de concreto. XXVI Seminário nacional de grandes barragens. Goiânia
4. Oliveira IC (2013) Análise de dados para elaboração de diretrizes visando à detecção de sulfetos e sulfatos na composição do CCR. Dissertação (Mestrado—Programa de Pós-Graduação em Engenharia de Construção Civil). Universidade Federal do Paraná. Curitiba
5. Hasparyk NP, Muniz FC, Armelin JL, Nascimento JFF, Santos MC, Bittencourt RM, Andrade WP, Carasek H, Cascudo O, Minicucci LA (2002) Contribuição ao estudo da influência de sulfetos presentes no agregado nas propriedades e durabilidade do concreto. In: 44° Congresso Brasileiro do Concreto. Anais. Belo Horizonte. IBRACON
6. Oliveira I (2011) Reacción sulfática interna en presas de hormigón: cinética del comportamiento. Tesis Doctoral. Universitat Politècnica de Catalunya. Barcelona
7. Gomides MJ (2009) Investigação de agregados contendo sulfetos e seus efeitos sobre a durabilidade do concreto. Tese (Doutorado—Programa de Pós-Graduação em Engenharia Civil. Universidade Federal do Rio Grande do Sul). Porto Alegre
8. Capraro APB (2015) Mudanças nas propriedades microestruturais e mecânicas de pastas, argamassas e concretos dosados com diferentes teores de contaminação por sulfetos. 2015. Exame de qualificação para obtenção do titulo de Mestre—Programa de Pós-graduação em Engenharia de Construção Civil, Universidade Federal do Paraná, Curitiba, Paraná
9. Araújo GS, Chinchón S, Aguado A (2008) Evaluation of the behavior of concrete gravity dams suffering from internal sufalte attack. Revista Ibracon de Estruturas e Materiais 1(1):84–112
10. Chinchón-Payá S, Aguado A, Chinchón S (2011) A comparative investigation of the degradation of pyrite and pyrrhotite under simulated laboratory conditions. Eng Geol 127:75–80
11. Czerewko MA, Cripps JC, Reid JM, Duffell CG (2003) Sulfur species in geological materials—sources and quantification. Cem Concr Compos 25:657–671
12. Casanova I, Agulló L, Aguado A (1997) Aggregate expansivity due to sulfide oxidation—II. Physico-chemical modeling of sulfate attack. Cem Concr Res 27(11):1627–1632
13. Associação Brasileira de Normas Técnicas (2009) NBR 7211—Agregados para concreto: especificação. Rio de Janeiro
14. Pereira E (2015) Investigação e monitoramento do ataque por sulfatos de origem interna em concretos nas primeiras idades. Tese (Doutorado—Programa de Pós-Graduação em Engenharia e Ciência dos Materiais). Universidade Federal do Paraná. Curitiba
15. Lima ALC (2009) A influência da presença de sulfetos na implantação da UHE Irapé—Vale do Jequitinhonha—Minas Gerais. Dissertação (Mestrado—Programa de Pós-Graduação em Engenharia Geotécnica. Universidade Federal de Ouro Preto). Ouro Preto