SURFACE MODIFICATION OF PYRITE DURING AUTOGENOUS GRINDING

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Abstract

Oxidation and surface modification of pyrite mineral during autogenous grinding in an inert mill (nylamid) were studied by zeta potential measurement and FTIR analysis. They were studied in function of reaction pH and chemical conditions of the aqueous medium. Experimental results show that the pyrite particles are superficially modified during wet grinding due to oxidation of the mineral's iron and surface sulfur, thus forming: iron oxyhydroxide, iron sulfate oxyhydroxide and sulfate complexes coordinated with iron in a mono- or bi-dentate manner respectively. These species were determined by Fourier transform infrared spectroscopy (FTIR). Despite the absence of contact with iron surfaces (grinding steel media), pyrite has a strong tendency to oxidize. Pyrite particles obtained at different grinding times and pH values generally present positive zeta potential values (ζ). However, at certain grinding times and pH values, they invert their magnitude and polarity, while at an acid pH value, the, ζ of pyrite presents negative values.

Keywords: Oxidation, modification, pyrite, grinding, autogenous.

1. INTRODUCTION

The surface reactivity of pyrite in aqueous environments and grinding with steel media has been the object of several studies [1, 2, 3]. These studies indicated that the surface modification of pyrite is given by effect of the indiscriminate adsorption of solid iron hydroxides generated by the association of iron and OH^- ions resulting from the surface decomposition of the pyrite mineral, as well as from the grinding steel media that are present during the mineral process [4, 5, 6]. However, the oxidation and surface of pyrite during autogenous grinding has hardly been studied.

The presence of solid and aqueous species of ferric and ferrous iron in mineral pulps also comes from other iron-bearing sulfides and from the corrosion of the grinding steel media. During the oxidation process of the mineral, sulfur and not the Fe^{2+} contained in the pyrite, is mainly oxidized. However, via the oxidizing conditions of the aqueous medium, Fe^{2+} oxidizes to Fe^{3+}. This ferric ion hydrolyzes and allows for the formation of solid species of ferric iron (oxyhydroxides, hydroxides and III iron hydroxisulfates [6].

The energy involved during the grinding process is another important factor that significantly alters the surface of mineral sulfides. Studies on the alteration of the physicochemical properties of the mineral pulp of pyrite during grinding due to a mechanical activation process have been recently published [4, 7, 8]. Such process is caused by fracture, impact, friction and abrasion mechanisms between the mineral particles, the mill and the grinding steel media. Regarding the autogenous grinding processes without steel media (grinding media are composed of minerals and bigger-size rocks), the applied energy comes mainly from an abrasion mechanism [9]. In autogenous grinding, sulfurous minerals are broken along the particle limit, thus ensuring a complete release and homogeneous particle size distribution [10].

It is known that the presence of solid and aqueous iron species during mill grinding with steel media is inevitable due to the oxidation-release of iron and sulfur atoms from the mineral, as well as Fe^{2+} iron from the grinding media. However, there is no information on the superficial state of the pyrite ore particles obtained from autogenous grinding in an inert mill. Likewise, its electrokinetic behavior and the structural-chemical nature of the meta stable and non-stoichiometric solid phases of iron formed on the surface of pyrite are unknown.

For this reason, this research paper presents a study on the nature of the chemical surface of pyrite by infrared and electrokinetic (zeta potential) analysis of particles obtained during autogenous grinding in an inert mill under a wide range of pH values and grinding times.

2. EXPERIMENTATION

In order to assess the oxidation and surface modification of the pyrite mineral during the grinding process in absence of grinding steel media, autogenous grinding (AG) of pyrite was performed using slightly larger pyrite pieces as grinding media in a 1 L inert nylamid mill that was sealed during the grinding process. On the whole, for these tests we used 200 grams of d_{80} 1.27 cm pyrite ore, 200 grams of d_{80} 0.23 cm particles and 0.25 L solution. It should be pointed out that the aim of these experiments was to study the effect the type of grinding has on the mineral particles' surface, not to simulate the grinding process as such.

Table 1 shows the chemical composition of the used mineral. Oxidation and surface modification of pyrite in grinding was assessed under a wide range of initial pH values: 5, 7, 9, 11, 12, 13. pH was titrated with a solution of NaOH 1 M, and four different grinding times were used: 5, 15, 30 and 45 minutes, which allowed us to vary the pH during the whole grinding process.

Table1. Chemical composition of pyrite mineral

Mineral	Elemental Composition (% w/w)							
	Fe	S	Cu	Pb	Zn	Ca	Na	Si
Pyrite	43.71	54.12	0.138	0.010	0.004	0.003	0.001	0.371
Not characterized 1.64 (% w/w)								

3. EXPERIMENTAL PROCEDURE

Autogenous grinding of pyrite mineral in an inert mill was conducted using the following experimental procedure: The mill, containing pyrite mineral and solution at desired pH was sealed and placed between a series of rollers in order to start the "cascade" drop of the thicker pyrite particles over the smaller mineral particles, and thus complete the particle size decrease. When the first grinding time period had concluded, the total volume of the pulp (mineral + water) was retrieved from the mill. For each grinding time period and reaction pH, fresh pyrite mineral and solution were used; this procedure was repeated for each time period and grinding pH.

The mineral pulp sampled from the grinding process was analyzed by measuring the most important physicochemical variables that participate during the oxidation and surface modification reaction of pyrite, such as: pH, electrical conductivity κ (μS/cm), oxidation-reduction potential ORP (mV) and dissolved oxygen concentration DO ($mg \cdot L^{-1}$). Concentration of iron and sulfur in the solution was also analyzed after the grinding process through Inductively coupled plasma spectrometry (ICP). In addition, ferrous iron in the solution was determined by volumetry with the method described in the literature [11].

Dispersion of pyrite particles contained in the mineral pulp resulting from each grinding time period and for each pH value was analyzed according to its zeta value potential ζ (mV), while the obtained solids were analyzed by XRD, FTIR and SEM-EDS..

4. RESULTS AND DISCUSSION

In some metallurgical plants, grinding with steel media has been replaced with autogenous grinding, where the main goal is to diminish contamination of the surface of mineral particles with the products of iron oxidation coming from steel media. In addition, it has been established that autogenous grinding produces better grades and higher recoveries of the desired species than conventional grinding [10].

PHYSICAL CHEMISTRY OF THE GRINDING PULP

The mineral pulp sample of pyrite obtained in each autogenous grinding time in an inert mill was characterized according to its most significant physicochemical properties, such as pH, electrical conductivity (κ) $\mu S \cdot cm^{-1}$, oxidation-reduction potential (ORP) mV, dissolved oxygen concentration DO $mg \cdot L^{-1}$ and zeta potential (ζ) mV. The obtained results show that, regardless of the galvanic contact between the mineral sulfides and the iron from the grinding media, the physicochemical characteristics of the pulp during the autogenous grinding process are constantly modified as the grinding time increases. The presence and oxidation of iron sulfide in the grinding process have a decisive influence on the final chemical state of the pulp, that is to say, the mineral sulfide is not only superficially modified by itself through the grinding effect, but the physicochemical properties of the pulp are also altered, thus affecting the success of the next stage in the mineral extraction process.

It was found that the hydrogen-ion potential of the pulp obtained in autogenous grinding of pyrite in an inert mill decreases progressively during the grinding process (as observed in Fig. 1), except for the solution with an initial pH value of 5. OH^- ions in the solution are quickly consumed and adsorbed in the surface of the pyrite mineral; this adsorption occurs along with the transfer of electrons in the solid-liquid interface.

We found that, at an initial pH value of 11, the consumption of OH^- ions is higher compared to the other studied pH values. When the grinding time (45 minutes) had concluded, the remaining pulp had a pH value of 10.3. OH^- ions in the solution were quickly consumed by the pyrite surface, thus oxidizing it and forming surface complexes with iron (Fe^{3+}).

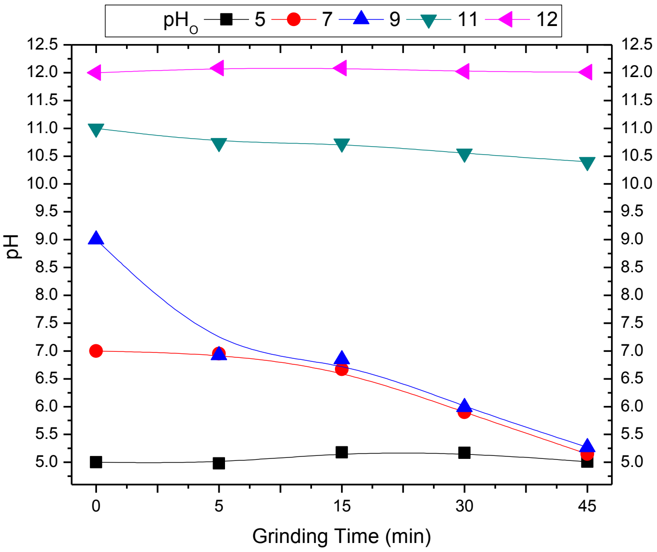


Fig. 1 pH vs. Grinding time of pyrite in inert mill.

The electrical conductivity of the pulp was monitored, and we found that it increases along with the grinding time in the case of initial pH values 5, 7 and 9, while in the case of the pH value that surpasses 11, it decreases. The first case is due to an increase in the concentration of sulfur and ferrous ions in the solution, which is a result of the oxidation of pyrite, as shown in Figure 2. In the second case, although the concentration of ferrous and sulfur ions increases in the solution as observed in Figure 2, the decrease in electrical conductivity is caused by the consumption of hydroxyl ions OH^-, which react with the oxidized iron, forming solid and aqueous complexes, the latter of which can be adsorbed into the surface of the pyrite mineral or remain as an aqueous phase.

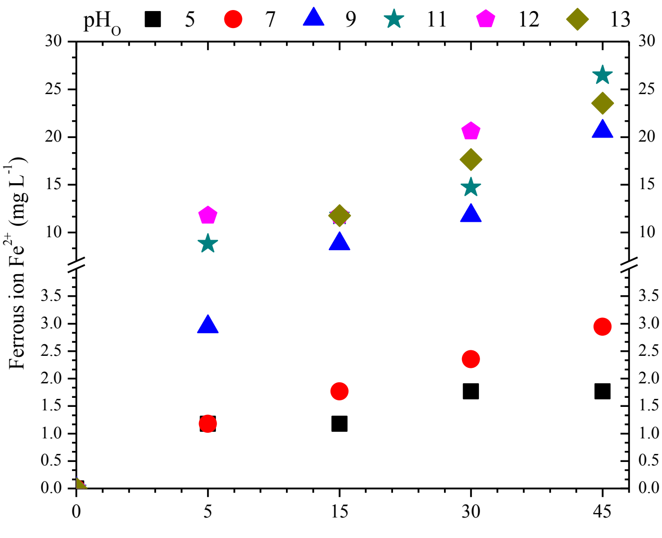


Fig. 2 Concentration of the ferrous ion Fe^{2+} ($mg \cdot L^{-1}$) Vs. Grinding time of pyrite in inert mill

As the grinding time progresses, the oxidation of pyrite releases iron and sulfur into the solution. In addition, the oxidative reaction of pyrite produces electrons, while the cathodic reduction of dissolved oxygen attracts them, thus decreasing the concentration of dissolved oxygen (DO) in the solution, as found in DO concentration measurements in the mineral pulp (Figure 3).

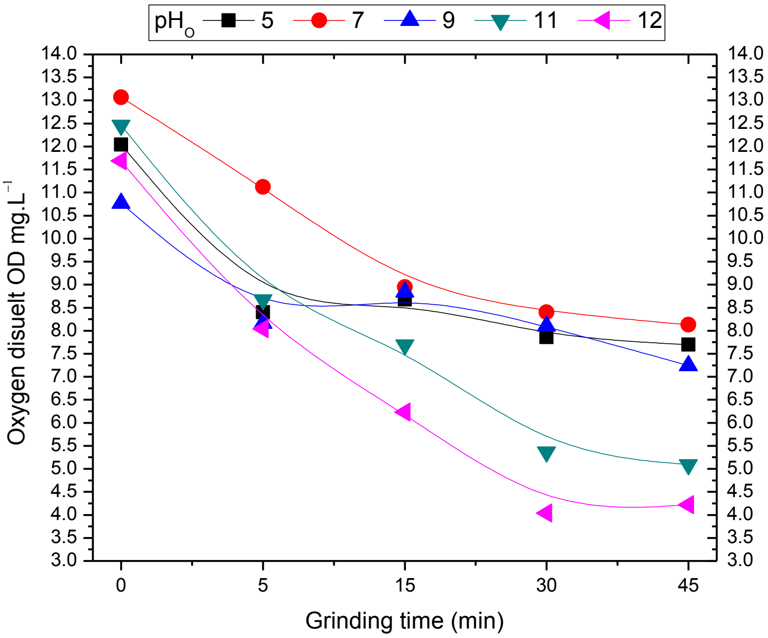


Fig. 3 Dissolved oxygen ($mg \cdot L^{-1}$) Vs. Grinding time, inert mill

Along with this, the constant transfer of electrons between solid and aqueous species formed during the pyrite grinding process leads to a decrease in the positive value of the oxidation-reduction potential (ORP). We also noted that the positive value of ORP decreases during the titration of the initial pH, so there is a less positive ORP value with the increase of pH, except for the grinding pulp obtained at an initial pH value of 9. Fig. 4 shows the ORP variation of the grinding pulp obtained in the autogenous grinding of pyrite in inert mill for the initial pH values 5-12.

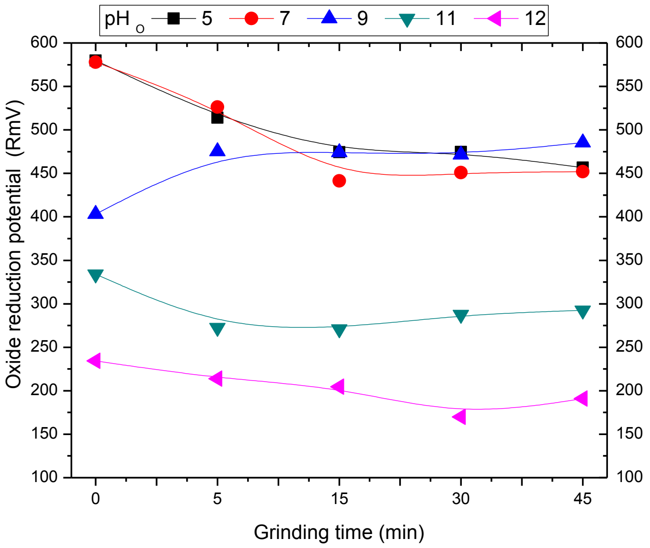
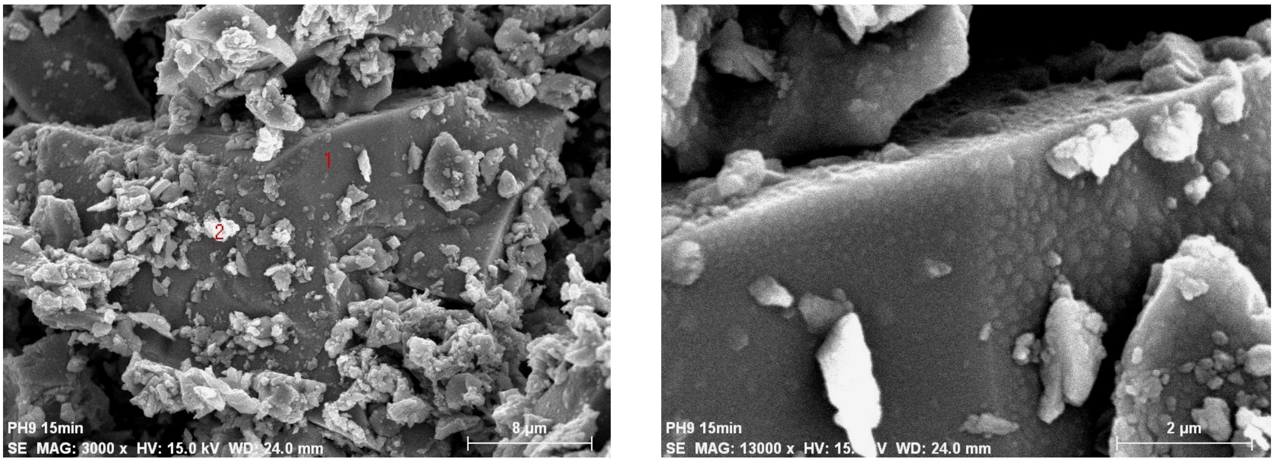


Fig. 4. Oxidation-reduction potential (mg·L^{-1}) Vs. grinding time, inert mill



POINT 1 (%w/w)	Oxygen 18.87; Sulfur 40.85; Iron 40.28
POINT 2 (%w/w)	Oxygen 27.65; Sulfur 32.49; Iron 39.86

Fig. 5. Microphotographs showing pyrite particles obtained during autogenous grinding in inert mill at pH 9 and 15-minute grinding

The particles that were obtained during the autogenous grinding in inert mill were characterized by x-ray diffraction and scanning electron microscopy. Fig. 5 shows the microphotographs of pyrite particles obtained at pH 9 and 15-minute grinding.

These microphotographs show not only the presence of the iron oxidation products adsorbed in the surface, but also the surface alteration of pyrite (right photograph) by effect of the oxidation (release of iron and sulfur into the solution). The change in the superficial state of the pyrite particles at an initial pH value of 9 and 15-minute grinding has also a direct effect on the inversion of the value and magnitude of the zeta potential of pyrite particles, as shown in Fig. 6, which shows the behavior of the zeta potential (ζ) mV in function of pH at different times of autogenous grinding in inert mill. It can be also noticed that the ζ of pyrite generally shows positive ζ values, except for the initial pH value of 5, where for all the grinding times, the particles have a negative ζ.

XRD analyses confirmed the presence of pyrite (as seen on Figure 7). However, it was not possible to detect other present phases with this technique; for this reason, all the pyrite particles obtained for each initial pH and grinding time were characterized by fourier transform infrared spectroscopy (FTIR). Fig. 8 shows the IR spectra of pyrite particles obtained during the autogenous grinding in inert mill at pH 9 and 5, 15, 30 and 45-minute grinding. It is important to remember that, as previously shown in the microscopy analysis, the fact that the pyrite inverts its value and magnitude is due to the oxidation and surface alteration of the pyrite particles (as seen on Fig. 6, pH 9, 15-minute grinding).

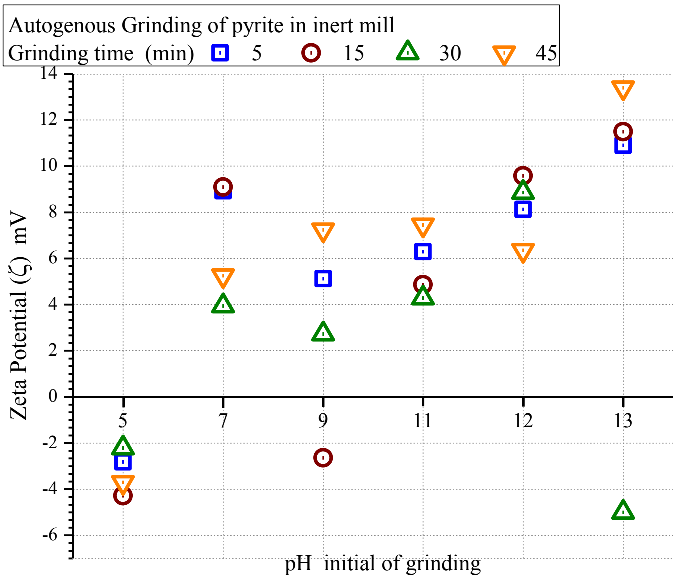


Fig. 6. Zeta potential (ζ) mV Vs. initial grinding pH for different grinding times of pyrite in inert mill.

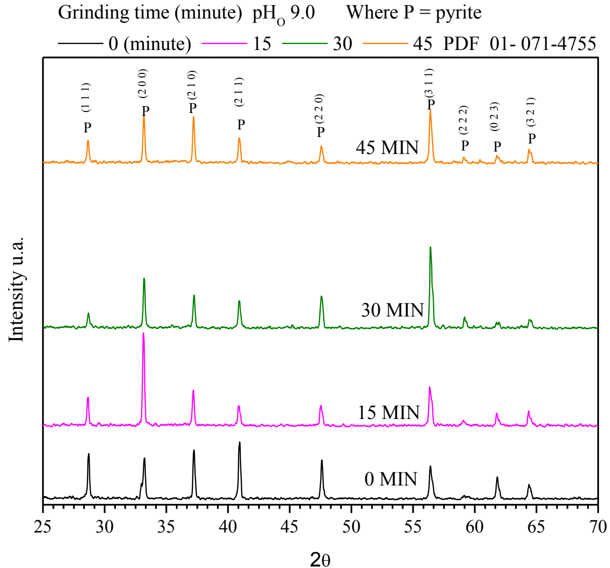


Fig. 7. X-ray diffraction of pyrite particles obtained during autogenous grinding at initial pH 9: 5, 15, 30 and 45-minute time periods

The inversion of the zeta potential of pyrite particles is related to an intensity decrease in the multiple adsorption bands of the IR spectrum at 15 minutes grinding that were found in the spectral section corresponding to the sulfates, around 1030 cm^{-1}, 1109 cm^{-1}, 1179 cm^{-1} and 1239 cm^{-1}. The presence of four adsorption bands is characterized by a bidentate complex with sulfate, which is mainly coordinated with iron.

Fig. 8 also shows that there is a variety of nucleated or well precipitated phases on the pyrite's surface. The weak adsorption peak at 477 cm^{-1} was assigned to the Fe – O group of the solid species lepidocrocite γ – FeOOH [12], while the higher, larger adsorption band at 546 cm^{-1} corresponds to the Fe – O group of akaganeite β – FeOOH. In addition, a high adsorption peak can be observed at 696 cm^{-1} of the Fe – O bond, which is present in iron oxyhydroxide sulfates [12].

Furthermore, the atmospherical reaction of CO_2 with the pulp solution allows for the formation of the bicarbonate ion, which reacts with the pyrite surface forming carbonate-type complexes with adsorption bands at 1447 cm^{-1}, 1492 cm^{-1} and 1506 cm^{-1}. The excision in the main band of the typical molecule of the carbonate ion is characterized by a carboxylate bidentate complex on the surface of the pyrite mineral. The presence of carbonate species is probably influenced by the mill's walls made of polymeric material, which can act as a precursor in the formation of carbonates from atmospherical CO_2.

This complex indicates the coordination of carbonate with iron in compounds like siderite $FeCO_3$, identified in the adsorption band at 755 cm^{-1}. Moreover, the adsorption band at 834 cm^{-1}, which is present only at 30 and 45-minute grinding times, is attributed to the vibration mode of the Fe – O group in the goethite phase $Fe_2O_3.H_2O$. Even the IR spectra of pyrite that were obtained from the autogenous grinding in inert mill show the previously suppressed absorption band v_1 at 914 cm^{-1} of sulfate, indicating that the sulfate symmetry is reduced by its coordination with cations [13, 14]. The absorption band at 1380 cm^{-1} shows the chemisorption of oxygen into superficial sulfur of pyrite S = O, while the band at 1623 cm^{-1}, indicates the presence of water molecules absorbed into the mineral particles.

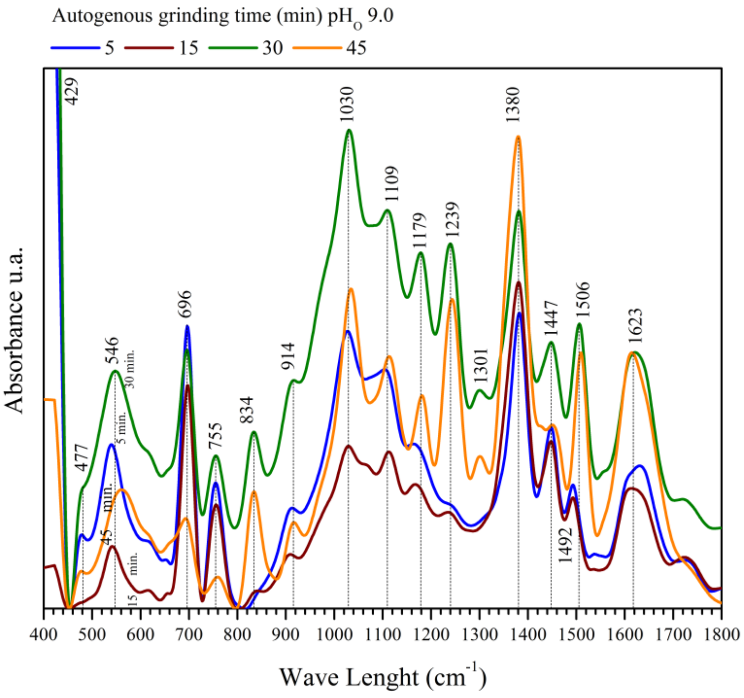


Fig. 7. Infrared spectra (FTIR) of pyrite obtained during autogenous grinding in inert mill at initial pH 9.0.5,15, 30 and 45 minutes.

CONCLUSIONS

The oxidative reaction of pyrite during autogenous grinding in inert mill alters both the physicochemical properties of the pulp and the mineral's surface, causing, for some grinding times, the inversion of the value and magnitude of the zeta potential of pyrite. The presence of iron and sulfur in the mineral pulp's solution is a consequence of the oxidation and release of these species from the surface of the mineral into the pulp's solution. Although galvanic contact during grinding was avoided, the surface of the pyrite mineral was modified by effect of nucleation and growth of the iron oxidation products, resulting in the superficial alteration of the pyrite particles, mainly by nucleation and growth of the iron oxidation products in active or oxidized sites, where a rupture of the surface bonds Fe – S and S –S occurs, thus promoting the growth of iron oxyhydroxides, such as lepidocrocite $\gamma-$ FeOOH, iron oxyhydroxide-sulfates $Fe(OH)SO_4$ and iron complexes coordinated with sulfate in a mono- or bi-dentate manner. These species were identified by infrared spectroscopy.

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