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Oxidative Hydrometallurgy of Sulphide Minerals

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1. Introduction

Sulphide minerals are one of the most important sources of value metals, such as gold, silver, copper, zinc, etc. Due to the strong sulphur binding to these minerals, metals are usually extracted by pyrometallurgical route or hydrometallurgy with chemical oxidation. Of these, hydrometallurgy apparently has a lower environmental impact, which has received increased attention in last decades. The main stages of the hydrometallurgical route comprise leaching, extraction and precipitation or electrowinning. For several decades, a number of processes have been developed to leach sulphide ores and concentrates and the conditions are well established. However, there is a renewed interest in hydrometallurgical processes for copper production due to environmental issues and the increasing need to exploit mixed and low grade ores and relatively small isolated deposits.

Processing of these ores and deposits is very slow and requires a significant amount of reagents. Therefore, to make the process profitable, the treatment of large quantities of ore is required. Aqueous oxidation can be conducted under elevated temperature and pressure, but also at ambient conditions, which makes it environmentally and economically attractive. For this reason, studies to optimize aqueous oxidation and to explore more efficient oxidants have been made. However, in mining industry (especially in precious metals extraction), the use of advanced oxidation process or ozone as an oxidant has not been discussed in detail, although lab-scale experiments indicate that ozone may be an alternative to overcome economic and ecological disadvantages of aqueous extraction existing process.

In this Chapter, we will treated the use of ozone and advanced oxidation process, including microwave system, as methods to improve or to help the leaching of different sulphide minerals. For example, it is well known that ozone is a powerful oxidizing with high oxidation potential (2.07 V) compared with hydrogen peroxide (1.77 V) and chlorine (1.4 V), making it advantageous to use in several applications. Importantly, ozone can create favorable conditions to oxidize sulphide minerals in aqueous media. In this context, oxidative leaching with ozone is relevant in copper-iron sulphide and gold- and silver-containing sulphides. Moreover, oxidative leaching of coal-containing iron sulphide might also have a positive impact on coal cleaning prior to its use in energy related applications.

The hydrometallurgy of different sulphide minerals will be treated. We will discuss and analyze the lab result that we obtained with these type of minerals. Cyanidation of gold-silver pyritic minerals with ozone pre-treatment, chalcopyrite and sphalerite leaching with

oxidation and microwave as complementary methods, and pyrite dissolution present in coal by oxidants aqueous media, will be treated here. In each case including aspects as chemical reactions, thermodynamics (Pourbaix´s Diagrams), kinetics and analysis of factors with statistical tools are discussed.

Statistical tool, as Factorial and Taguchi experiment´s design and analysis of variance (ANOVA) will receive a particular attention. These methods are now widely used to provide the optimal selection of parametric values based on their intraparametric interactions to accomplish a process and determine the optimum leaching conditions.

2. Fundamentals

Valuable metals are recovering worldwide relevance due to the development of a whole new range of potential applications in electronics, environmental catalysis, material science, biomedicine, among other fields with significant impact in daily life activities.

Sulphide minerals, as pyrite, FeS2, chalcopyrite and CuFeS2, are one of the most important sources of value metals, such as gold, silver, copper, zinc, etc. Due to the strong sulfur binding to these minerals, metals are usually extracted by metallurgical process of chemical oxidation.

In Extractive Metallurgy, process can be divided in Pyrometallurgy and Hydrometallurgy. Particularly, chemical oxidation can be classified generally as roasting and aqueous dissolution. Roasting under oxidizing condition is a very extensive and well established commercial technology. However, roasting has been considered as a high energy consumer technology, with stringent environmental controls on the emission of gases. Hence, aqueous chemical oxidation methods have attracted increasing attention. The aqueous oxidation can be operated under elevated temperatures and pressures or ambient conditions. Definitely, low pressure and temperature are seen as environmentally and economically attractive (Deng, 1992). Aqueous oxidation can be conducted under elevated temperature and pressure, but also at ambient conditions, which makes it environmentally and economically attractive (Deng, 1992). For this reason, studies to optimize aqueous oxidation and to explore more efficient oxidants have been made. However, in mining industry (especially in precious metals extraction), the use of ozone as an oxidant has not been discussed in detail, although lab-scale experiments indicate that ozone may be an alternative to overcome economic and ecological disadvantages of aqueous extraction existing process.

2.1 Thermodynamics of oxidation process

Ozone has a very high oxidation potential (2.07 V) compared with hydrogen peroxide (1.77 V) and chlorine (1.4 V), making it advantageous to use in several applications (Rice, 1997). Importantly, ozone can create favorable conditions to oxidize sulphide minerals in aqueous media. According to the Pourbaix or Eh – pH diagrams shown in Figures 1 and 2, the sulphide species such as pyrite or pyrrhotite (Fig. 1) and chalcopyrite (Fig. 2), can be oxidized to sulfate in presence of an oxidant such as ozone, in a pH range from 2 to 14; the oxidized products could be solids or solutions. At very acid conditions (i.e, pH < 2), it is possible to dissolve metals as Fe and Cu ions. In this context, oxidative leaching with ozone is relevant in copper-iron sulphide and gold- and silver- containing sulphides. Moreover, oxidative leaching of coal-containing iron sulphide might also have a positive impact on coal cleaning prior to its use in energy related applications. In this paper, we show the
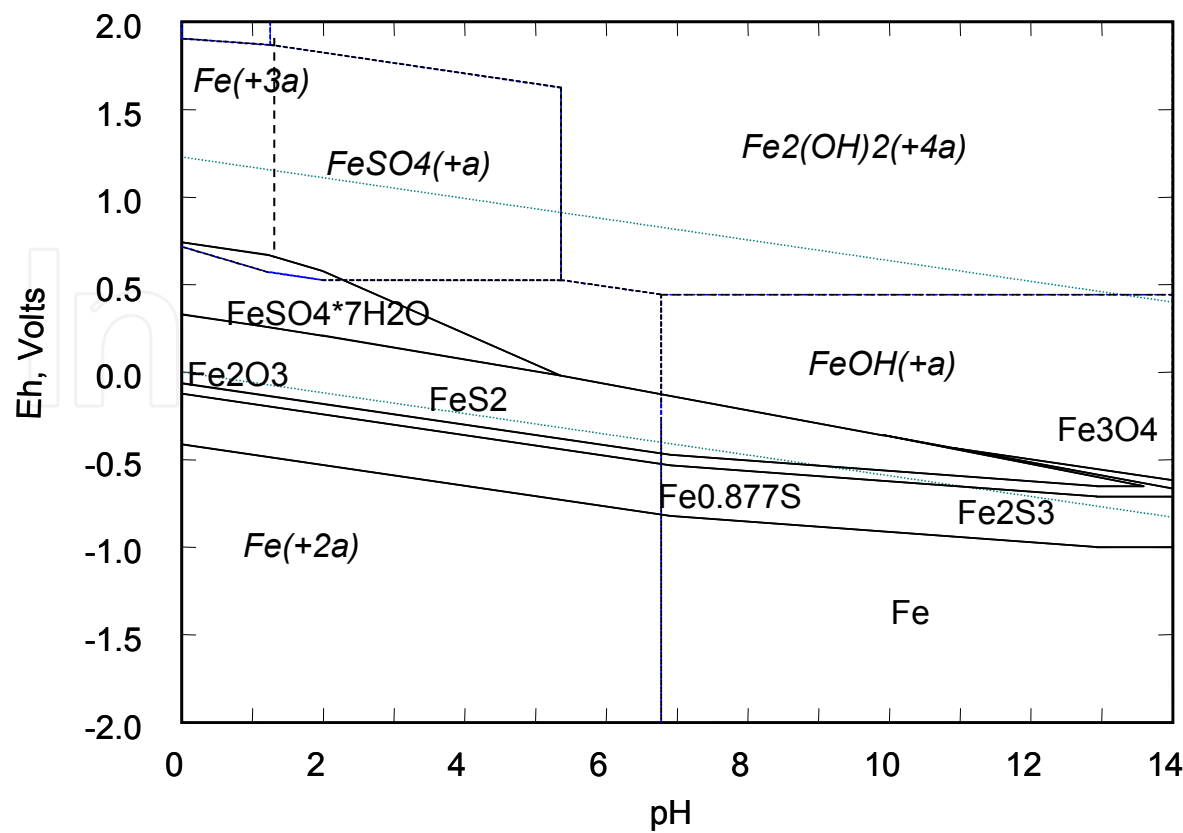
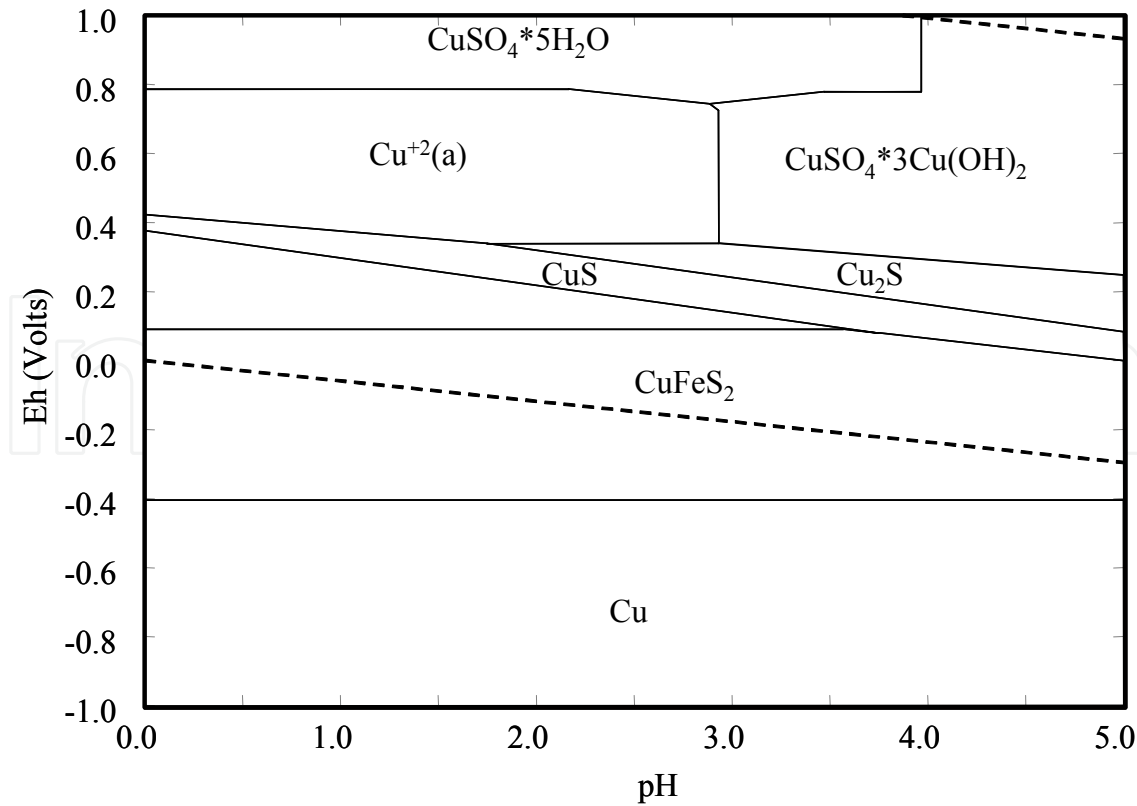Fig. 1. Pourbaix diagram for S-Fe system, at 25 ºC, (Fe) = 1 M; (S) = 1M.

Fig. 2. Pourbaix diagram for Cu-S-Fe system, at 25 ºC, (Fe) = 1 M; (S) = 1M; (Cu = 1M).

beneficial effect of using ozone on process of environmental and commercial importance, and outline the role of ozone layer in process optimization. The practical significance of the study cases is briefly discussed next.

2.2 Chemical reactions

In this context, it should emphasize the process of oxidation of sulfides as exemplified by oxidation of pyrite, one of the most abundant minerals on earth. In general, under oxidant condition and low pH, pyrite oxidation proceeds through two basic steps: In the first step, the dissolution of pyrite to ferrous ions in an acid medium proceeds through the formation of an iron-deficient or a sulfur-rich layer rather than elemental sulfur.

In the second step, further oxidation of this layer occurs, forming sulfides of lower iron content, and eventually are converted to elemental sulfur. In severely oxidizing conditions, the elemental sulfur could be oxidized to oxy-sulfuric species. Anodic reactions, such as pyrite and sulfur oxidations, are sustained by cathodic processes, which could involve oxygen, hydrogen peroxide, or even ozone reduction. The importance of this analysis is based on the fact that, under certain conditions, such as pH, redox potential, temperature, etc., the product layer is protective, thus limiting pyrite oxidation.

Despite the existing discrepancies about the exact composition of the oxidation products, the most well-known general mechanism of pyrite oxidation is described in Eq 1.
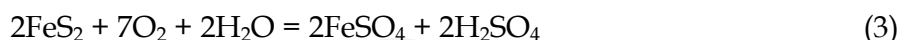
$$FeS_2 = Fe^{2+} + 2S^o + 2e^- \tag{1}$$

Elemental sulfur is stable at low pH and redox potential and could be oxidized to sulfate by molecular oxygen and ferric ions at higher potentials (Eq 2).
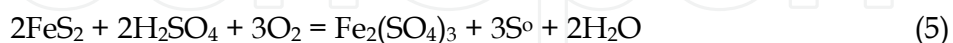
$$FeS_2 + 8H_2O = Fe^{3+} + 2SO_4^{2-} + 16H^+ + 15e^- \tag{2}$$
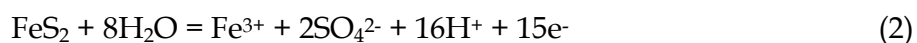
The pyrite dissolution has been characterized in the following media:
i.   in the presence of oxygen at high pressure and temperature

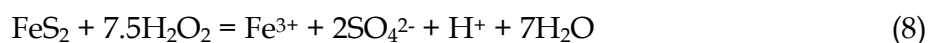$$2FeS_2 + 7O_2 + 2H_2O = 2FeSO_4 + 2H_2SO_4 \tag{3}$$

$$FeS_2 + 2O_2 = FeSO_4 + S^o \tag{4}$$

ii.   in sulfuric acid solutions

$$2FeS_2 + 2H_2SO_4 + 3O_2 = Fe_2(SO_4)_3 + 3S^o + 2H_2O \tag{5}$$

iii.   in nitric acid solutions

$$3FeS_2 + 18HNO_3 = Fe_2(SO_4)_3 + Fe(NO_3)_3 + 3H_2SO_4 + 15NO + 6H_2O \tag{6}$$

$$2FeS_2 + 10HNO_3 = Fe_2(SO_4)_3 + H_2SO_4 + 10NO + 4H_2O \tag{7}$$
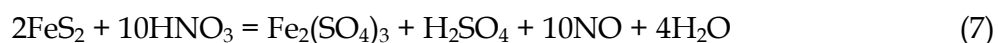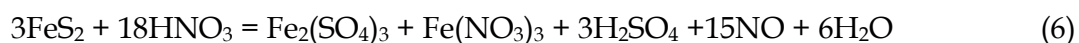
iv.   in hydrogen peroxide solutions

$$FeS_2 + 7.5H_2O_2 = Fe^{3+} + 2SO_4^{2-} + H^+ + 7H_2O \tag{8}$$

v.   in highly acidic solutions

$$FeS_2 + 7.5H_2O_2 + H^+ = Fe^{3+} + 2HSO_4^- + 7H_2O \quad (9)$$

(vi) in presence of ozone
Direct oxidation

$$FeS_2 + O_3 + H_2O + 2\,O_2 = FeSO_4 + H_2SO_4 \quad (10)$$

$$FeS2 + 7/3O_3 + H_2O = FeSO_4 + H_2SO_4 \quad (11)$$

Indirect oxidation

$$2/3O_3(g) = O_2(ac) \quad (12)$$

$$FeS_2 + 7/2\,O_2 + H_2O = FeSO4 + H_2SO_4 \quad (13)$$
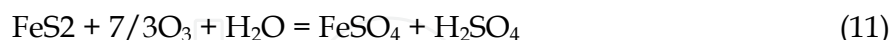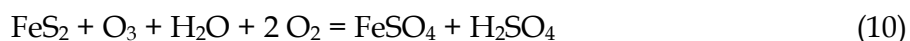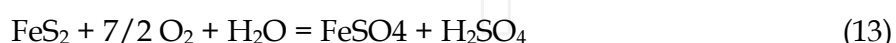
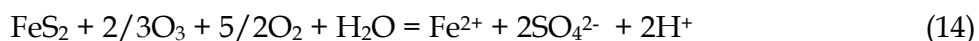The oxidation of sulfide ores by ozone can occur by dissolution of sulfide species and the formation sulfate ion, as suggested by Elorza et al. Then, the global reaction of the pyrite oxidation in the presence of ozone can be described as follows:

$$FeS_2 + 2/3O_3 + 5/2O_2 + H_2O = Fe^{2+} + 2SO_4^{2-} + 2H^+ \quad (14)$$

In the case of chalcopyrite, the acid leaching in presence of Fe occur according to the following reaction:

$$Cu\,FeS_2 + 4Fe^{+3} = Cu^{+1} + 5Fe^{+2} + 2S° \quad (15)$$
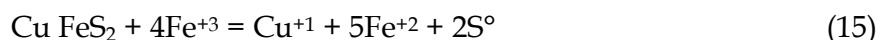
According to Havlik et al. (7, 9), the global reaction of chalcopyrite under the action of O_3 can be represented by:

$$3CuFeS_2 + 8O_3 = 3CuSO_4 + 3FeSO_4 \quad (16)$$

2.3 Kinetics

In hydrometallurgy, most of leaching process follows the kinetic models for heterogeneous solid/liquid reactions, known as shrinking core models (SCM), as showed in Figure 3: the SCM controlled by chemical reaction and the SCM controlled by diffusion trough the solid product layer (Habashi, 1999; Levenspiel, 1999; Sohn and Wadsworth, 1986). A third model, the stochastic model for control by chemical reactions on the non-reacted particle surface (Ciminelli and Osseo-Assare, 1995) is considered.

In the mentioned models, the fraction of iron reacted at any time *t*, can be predicted from the following Equation.

1.   Shrinking core model controlled by the chemical reaction

$$kt = 1 - (1-x)^{1/3} \quad (17)$$

Where, *x* is the fraction of iron reacted and can be calculated from the following relation:
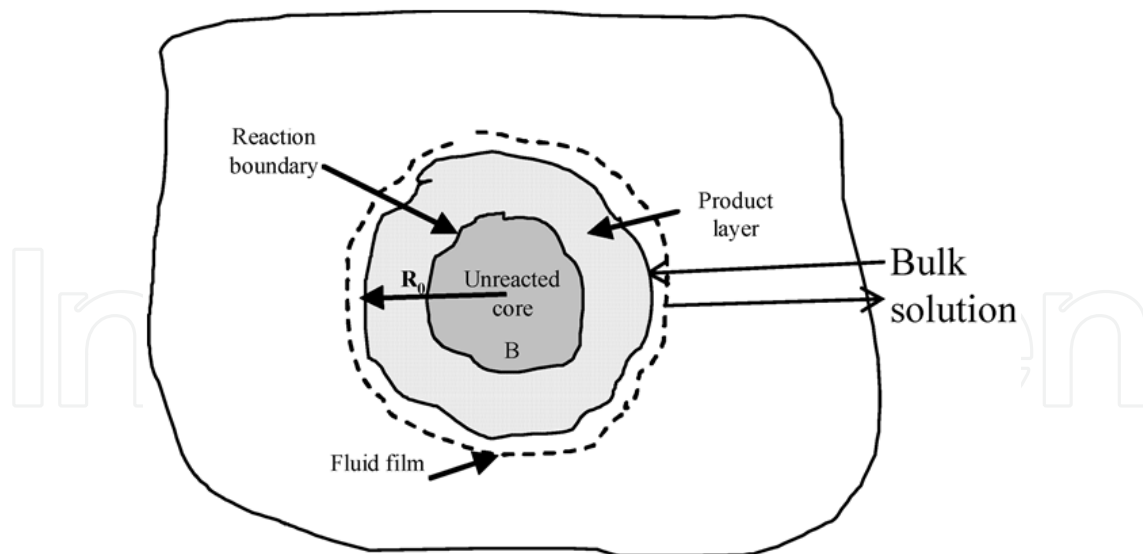
$$x = \frac{C}{C_0} \quad (18)$$

Fig. 3. Squematic diagram of shrinking core model (SCM).

And κ, is the apparent rate constant, and can be calculated from the following relation:

$$k = \frac{k_s C_A}{R_0 \rho} \qquad (19)$$

Where, k_s is the rate constant of the reaction, ρ is the density of the FeS_2 ore, R_0, is the radius of the un-reacted particle, and C_A, is the reactive concentration in the solution. The above equations are applied to mono-sized particles, thus the average size of a narrow fraction of particles can be used in the kinetic model.

2.   Shrinking core model controlled by the diffusion of the reagents or dissolved species through the layer of solid reaction products, the fraction of iron reacted at any time t can be predicted from the following equation.

$$kt = 1 - \frac{2}{3}x - (1-x)^{2/3} \qquad (20)$$

Where κ can be calculated from the following relation:

$$k = \frac{2DC_A}{R_0^2 \rho} \qquad (21)$$

Where, D, is the diffusion coefficient of the iron species.

3.   Stochastic model. It takes into account the heterogeneity of solid minerals by introduction a stochastic distribution for the rate constant. Then, the rate constant, k_s from the shrinking core model is transformed into a variable that changes with time or conversion, according to following relation:

$$k_s(X) = 2 k_0(1-X) \qquad (22)$$

where, $k_s = k_{max}/2$

According to Ciminelli and Osseo-Assare (1995), the resulting equation has the following expression:

$$kt = (1-x)^{-2/3} - 1 \qquad (23)$$

$$k = \frac{4k_s C_A}{\rho R_0} \qquad (24)$$

2.4 Costs

Ozone can be produced by many ways. There are more than 700 patented ways of ozone production. But commercially three most popular methods are being used: a) The UV method of ozone production, b) The plate types Corona ozone production and c) The tube types Corona ozone production (Baratharaj, 2011).

For UV method ozone production, it is therefore necessary to utilize a short wavelength ~185nm. In theory, the yield of O_3 from 185nm UV light is 130g/kWh of light. As lamp efficiencies are so low, ~1%, the production per kWh from the power source is greatly reduced. In practice, with the present state of development, UV lamps can only produce about 20g O_3/kWh of ozone when using oxygen as the feed gas (Smith, 2011).

Ozone production by electrical discharges has been, and remains, the most commercially viable method. Essentially a corona is characterised by a low current electrical discharge across a gas-filled gap at a relatively high voltage gradient. The amount of ozone produced in a given corona ozonator design is relative to the concentration of oxygen in the gas feeding the corona. Basically, the more oxygen in, the more ozone out. In general, ozone concentrations of 1-3% using air, and 3-10% using oxygen can be obtained. The amount of energy applied to the gas gap between the electrodes is critical to the concentration of ozone produced. It is a combination of the voltage and frequency that results in a given energy input. Typically, voltages of between 7 to 30 kV are used with frequencies ranging from mains supply of 50 or 60 Hz, medium up to 1000 Hz, and high up to 4000 Hz. Then, the net effect is that less power is consumed to generate a given quantity of ozone as the oxygen concentration increases: Oxygen ~ 5 to 8kW/kg; Air ~ 15 to 18kW/kg (Smith, 2011).

Although there are no reports on the cost of using ozone in industrial mining applications, Botz et al (2000) reported a pilot scale study for oxidation of cyanide in mining effluents. In this case, the cost of using ozone operation was U.S. $ 0.97 per kg cyanide removed, compared with SO_2/air and chlorination methods, $ 1.35 and $ 1.67, respectively.

Therefore, economical feasibility of the use of ozone in oxidation of sulphide minerals is possible, taking into account the amount of ozone used and the energy cost of production.

3. Cases of study

3.1 Oxidation of sulphide ores-containing gold and silver

Cyanidation is the most aqueous leaching process used to extract gold and silver. However, it has some disadvantages when precious metals are encapsulated in matrixes of iron

sulphide minerals, such as arsenopyrite and pyrite (Shoemaker, 1990). In this case, the minerals receive an oxidation pretreatment (as oxidation roasting, chemical oxidation under pressure or biological oxidation) to facilitate gold and silver extraction by cyanide solution (Weir and Berezowsky, 1986; Chen and Reddy, 1990; Burbank et al., 1990). An alternative to these methods is the use of ozone, which increases the oxidation potential and the oxygen content of solution during cyanidation (Haque, 1992; Roca et al., 2000; Salinas et al., 2004; Elorza et al., 2006; Carrillo et al., 2007). Ozone can create favourable oxidation conditions for sulfide minerals in aqueous mediums. According to the Eh – pH diagram shown in Figure 1 and Eq. 10 to 13, the sulfide species, such as pyrite or pyrrhotite, can be oxidized to sulfate in oxidant conditions and within a pH range from 2 to 14, making it possible to obtain solids or solutions. In both cases, the product formed during the oxidizing reaction of pyrite with ozone permits favorable conditions to the contact of cyanide and oxygen with precious metals containing in the ore, thus increasing the efficiency of the cyanidation process and, on the other hand, the sulfur oxidized to sulfate will no longer react with cyanide to form the thiocyanate ion SCN^-, one of the causes of the increased consumption of cyanide during cyanidation.

Although in the mining industry, especially in the case of extraction of precious metals, the use of ozone has not been much discussed, laboratory experiments indicate that ozone may be a valid alternative for resolving or surmounting the disadvantages of the already mentioned cyanidation process. In the case of refractory minerals, there have been reports of increases in the recovery of gold and silver which vary from 25% to more than 100% for both cases, as well as a significant reduction in the time of cyanidation (Salinas et al. 2004; Elorza et al., 2006). With non-refractory pyritic minerals, the results obtained have shown that pre-treatment with ozone not only permits a greater extraction of gold during cyanidation, but also causes less cyanide consumption.

Table 1 shows gold and silver composition of samples of pyrite containing gold and silver, with a size distribution of 75% -75 µm. The detailed process for experimental tests was previously reported (Carrillo et al., 2007, 2011). Experiment included a pretreatment (before cyanidation) with ozone directly in mineral slurry at pH of 6. Subsequently, solid sample was treated for 48 h under conventional cyanidation conditions. Table displays the amount of metal recovered from the cyanidation process. It is evident that ozone pretreatment increased dissolution of gold in cyanidation, particularly for the sample with the highest gold composition. For samples A and B, dissolution value increased significantly with ozone, and in sample C is interesting to note that it is still possible to recover gold by cyanidation method. Table 1 shows silver dissolved percentage during cyanidation process. When ozone pretreatment is carried out, the amount of silver dissolved increased to 82, 83 and 75 %, respectively. The increase in samples A and B was about 15%, but sample 3 showed a very significant increment in extracted silver. The mineralogy of this metal could explain the difference: the sample was probably in form of argentite, a silver sulfur that is not extracted during cyanidation process. Previous results suggested that ozone introduced in the slurry, chemically reacts with pyrite´s sulfur increasing the oxidation potential of the slurry. In a previous work, we have shown that ozone treatment leads to partial oxidation of sulphide minerals and to sulfate ion formation, specifically in oxidation of sulfur (Carrillo et al., 2007). Improvement in gold and silver recovery from ore with ozone pretreatment indicated that reaction intermediate products promote the conditions for cyanide diffusion to the precious metals in the subsequent cyanidation process.

	Sample A		Sample B		Sample C	
	Au	Ag	Au	Ag	Au	Ag
Initial concentration, g/ton	4.5	435	6.7	326	0.3	34
Extraction, %, Cyanidation without O_3 pre-treatment	84.69	71.51	76.25	71.24	70.20	16.67
Cyanide consumption, kg/ton, without O_3 pre-treatment	5.8		3.12		3.6	
Extraction, %, Cyanidation with O_3 pre-treatment	91.86	81.99	97.39	83.33	61.70	75
Cyanide consumption, kg/ton, with O_3 pre-treatment	1.36		1.2		1.2	

Table 1. Chemical Assay of pyrite samples containing gold and silver, used in dissolution of precious metals by cyanidation (48 h) with and without ozone pre-treatment.

Table 1 also shows the consumption of cyanide during the cyanidation of the samples, with and without pre-treatment. It can be seen that, after pre-oxidation, the consumption of cyanide was high. 5.8, 3.12 and 3.6 kg/ton. For the same samples, the consumption of cyanide decreased considerably with the pre-oxidation, achieving a significant saving compared to untreated samples. According to the results obtained, ozone treatment before cyanidation permits partial oxidation of sulphide minerals, specifically the oxidation of sulphur. The conditions necessary for these reactions would be acidic pH less than 6, and oxidants conditions according to Figure 1. These conditions, pH of 6 in the slurry, can be maintained during the ozone pre-treatment test. The ozone introduced in slurry reacts by chemical reaction with sulfur of pyrite or by ozone decomposition at oxygen, increasing the oxidation potential of the slurry. The fact that recovery of gold and silver improved with oxidation pretreatment of the ore indicates that the obtained product of reaction contributes to creating better conditions for the diffusion of cyanide to the precious metals. However, the low consumption of ozone in the tests permits one to suppose that the principal function of ozone is increase the oxidation potential of slurry, and obtain better conditions for partial pyrite oxidation. In addition, treatment with ozone permits increasing the content of soluble oxygen in the ore slurry, the oxygen that is the product of the decomposition of the ozone during its reaction with the ore. The presence of more oxygen in the slurry permits better conditions for the complexes formation during the cyanidation reaction, since it has been reported already that cyanidation is an electrochemical reaction produced by the cathodic reaction of the oxygen in the surface of the metal, which permits the anodic dissolution of the precious metals in order to achieve the complete cyanidation (Habashi, 1970; Parga et al., 2003). On the other hand, the oxidation of sulfur to sulphate or sulfate ion prevents sulfur species from reacting with cyanide to form thiocyanate, reaction which, as was mentioned above, is the main cause for the consumption of cyanide with this type of sulfide ores. Therefore, the consumption of cyanide decreases, thus increasing the efficiency of the process and decreasing its cost.

3.2 Oxidation of sulphide copper minerals

Sulphide copper minerals, such as chalcopyrite (CuFeS2), are the most abundant copper-bearing minerals, and represent approximately 70 % of the world's known copper reserves

(Davenport et al., 2002). Chalcopyrite is also the most stable of copper minerals due to its structural configuration (face-centered tetragonal lattice) and, consequently, the most refractory for aqueous extraction processing.

Industrially, copper ore leaching is almost always accomplished by diluted sulfuric acid medium and ferric sulphate, which are low-cost reagents and could be regenerated when ores are lixiviated. Several studies have been conducted to optimize the process conditions and to explain the basics of chalcopyrite leaching process. Thus, it has been suggested that a layer of elemental sulfur is formed on the external surface. The type of sulfur layer formed on the surface, according to Eq. 15, depends upon the reagents used, as well as on the process conditions (i.e., temperature and agitation); importantly, this layer inhibits the dissolution of the chalcopyrite, thus reducing the overall leaching rate and the process efficiency. Several approaches have been recommended to accelerate the chalcopyrite dissolution. However, there is an increasing interest in optimizing the aqueous extraction process for copper production due to the negative environmental impact caused by chemical reagents used (Shijie, 2005; Peacey et al, 2003). Although leaching of copper ores is carried out in diluted sulfuric acid medium and ferric sulfate as oxidant (Ukasik and Havlik, 2005; Antonijevic and Bogdanovic, 2004), low-cost reagents, different approaches have been suggested to increase chalcopyrite rate dissolution. The most common is to increase process temperature, but this implies higher energy requirements. Another suggested alternative is the use of strong oxidants such as ozone (Havlik et al., 1999), hydrogen peroxide (Antonijevic et al., 2004) and manganese nodules (Havlik et. al., 2005).

On the other hand, the use of ferric ion (Fe^{+3}) to dissolve copper has an economic constraint and, therefore, Fe^{+3} has to be regenerated. This could be accomplished by oxidizing ferrous ions (Fe^{+2}) with air and oxygen, although this step is usually very slow in acid medium. Pressure oxidation is an alternative for this oxidation process, but it is only applied on concentrated ores . Nevertheless, a thermodynamic point of view, the most effective way to improve the process efficiency is to eliminate the formation of any sulfur layer on the chalcopyrite surface and, at the time, regenerate Fe^{+3}, and this is possible under strong oxidation conditions.

In the leaching of a mixed ore, the high redox potential required in an acidic medium to avoid the sulfur layer formation can be met by using ozone (O_3) as oxidizing agent.

Havlik et al. (9) studied the leaching kinetics of a chalcopyrite concentrate in 0.5 M sulfuric acid ($H2SO4$) solutions, using O_3 as oxidizing agent, in the range of 4 to 75°C. Under the studied conditions, the reaction showed parabolic kinetics. No evidence of the formation of an elemental sulfur layer, or any other product layer, was found. The authors also indicated that the overall reaction rate was controlled by diffusion of O_3 in the interface solid-liquid; in addition, they reported that solubility of ozone decreases as the temperatures rises above 40 °C, thus limiting the beneficial effect of a temperature increase.

Carrillo et al. (2010) mentioned that, according to equation 1, as the reaction takes place, a significant amount of ferrous ion (Fe^{+2}) is formed. The continuous addition of O_3 into the solution favors the oxidation of Fe^{+2} to Fe^{+3}, according to following equation.

$$6Fe^{+2} + O_3 + 6H^+ = 6Fe^{+3} + 3H_2O \tag{25}$$

The occurrence of reaction 24 in preferential conditions such as the reaction rate is enhanced (i.e., large O_3 concentration, low pH) might cause an increase in (Fe^{+3}), which in turn should favor reaction 1 and, in consequence, copper dissolution.

Therefore, a possible mechanism for chalcopyrite dissolution in the presence of Fe^{+3} and O_3 is that Fe^{+3} quickly react with the mineral surface to produce copper ions, Fe^{+2} ions and also an sulfur compounds (sulphate) layer on the surface. Then, Fe^{+3} and Fe^{+2} ions must diffuse through this layer to continue with the dissolution process. In addition, O_3 must diffuse from the gas bulk to the solution and to the interface of chalcopyrite particles and react with chalcopyrite (equation 2) and Fe^{+2} ions (equation 6). This last step takes place in the solution and might be faster, leading to the formation of more Fe^{+3} in the solution.

Figure 4 show copper profiles based on a Taguchi L9 experimental design. The figures show the main effects, as determined with a S/N (Signal/Noise) ratio, which is based on the concept of the "greater-the-better", was used to characterize the response (amount of copper extracted). The S/N ratio was defined as:

$$\text{S/N ratio} = -10\log(\text{MSD}) \tag{26}$$

where, the MSD (mean-square deviation) was calculated by:

$$\text{MSD} = 1/n \sum y_i^2 \tag{27}$$

Where, n was number of tests, and y_i was the value of Cu extracted (%) obtained from the ith test., as a function of the amount of copper extracted. Accordingly, figure shows that
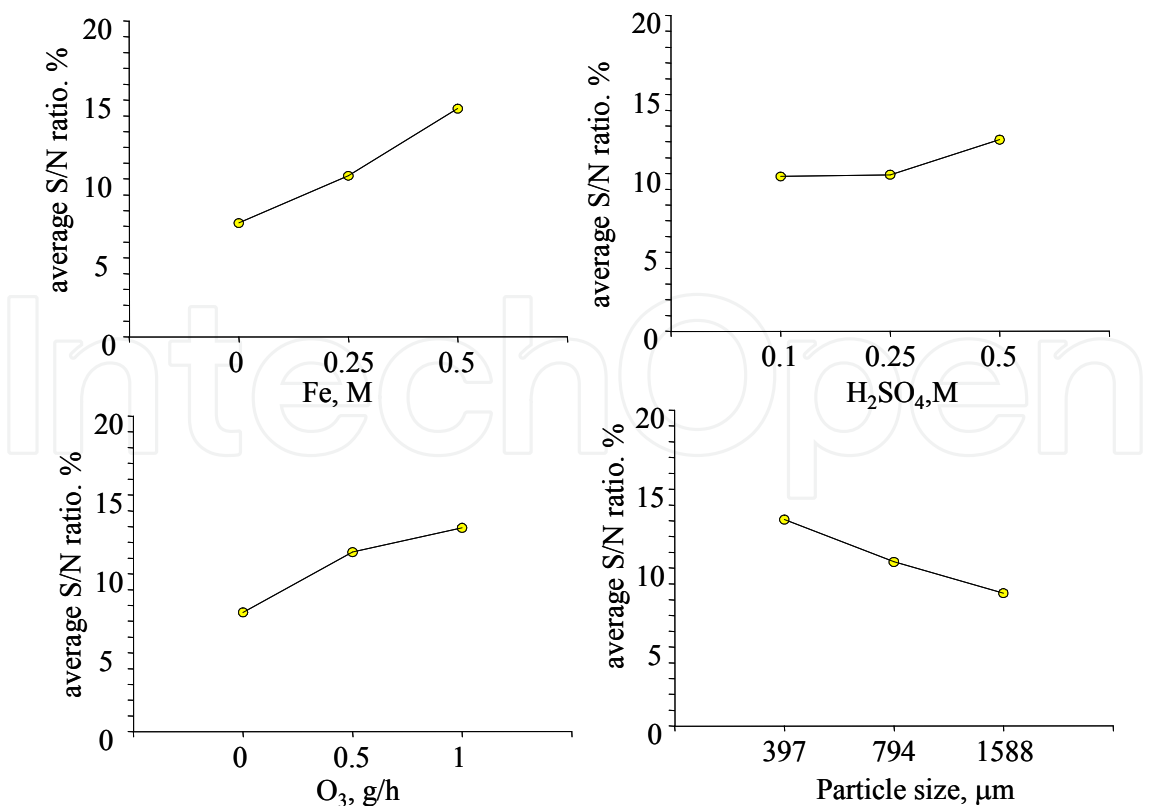

Fig. 4. One factor graphic of the L9 experimental design for the leaching of chalcopyrite.

under the studied conditions, (Fe^{3+}) is the most important factor during the recovery of copper by chemical dissolution of chalcopyrite. Results also indicated that, within the analyzed range, (H_2SO_4) had no effect on the amount of copper extracted. An increase in the levels of (Fe^{3+}) and O_3 concentration from first level to second level, and from second level to third level, resulted in a increase in the amount of copper extracted. Similar results were found for a decrease in the levels of particle size. However, when the levels of (H_2SO_4) were increased, no significant effect was observed in the response.

The results showed in figure suggest that Fe^{+3} react at the interface increasing copper the dissolution. Obviously, reduction of the particle size increases the liberation grade of chalcopyrite and the reaction surface area, thus exposing a larger fraction of the copper mineral, and promoting a better contact between the metal and the chemical agents (Fe^{3+}, O_3 and H_2SO_4) for faster dissolution. In addition, the strong oxidant ion condition is enhanced when O_3 it used. This beneficial effect is found for all (Fe^{+3}) used. Therefore, a possible mechanism for chalcopyrite dissolution in the presence of Fe^{+3} and O_3 is that Fe^{+3} quickly react with the mineral surface to produce copper ions, Fe^{+3} ions and also an sulfur compounds (sulphate) layer on the surface. Then, Fe^{+3} and Fe^{+2} ions must diffuse through this layer to continue with the dissolution process. In addition, O_3 must diffuse from the gas bulk to the solution and to the interface of chalcopyrite particles and react with chalcopyrite and Fe^{+2} ions. This last step takes place in the solution and might be faster, leading to the formation of more Fe^{+3} in the solution. Then, the increased concentration of Fe^{+3} might promote the copper dissolution process, but diffusion of $Fe+3$ ion in sulfur compounds layer could be slower, and thus gradual stop of the overall rate of copper extraction.

Based on results, the effect of adding Fe^{+3} and O_3 is favourable for small particle sizes. For larger particles, only (Fe^{+3}) seemed to affect copper dissolution since an increase in O_3 had no beneficial effect. It has to be considered that for larger particle sizes, there is less chalcopyrite exposed to the reagents and, therefore, the presence of a single oxidant is sufficient to promote copper dissolution. Due to the relatively small liberation of chalcopyrite, the oxidation of Fe^{+2} with O_3 is not a limiting step to promote copper dissolution. Finally, the results obtained here suggest that only minimal quantities of acid in the solution are required for the dissolution of copper, just enough to prevent hydrolysis and precipitation of Fe^{+3} by OH^-.

3.3 Iron sulphide oxidation in coal

Another process is ozone application for iron sulphide oxidation in coal, one of the most important fossil fuels used for energy production. However, due to its nature, coal requires a cleaning stage based on physical methods before its use to meet air pollution regulations (Apenzaller, 2006), but organic sulfur and syngenetic pyrite is removed with low efficiency to the required level (Ozbayoglu, 1998). Previous to the combustion, coal cleaning techniques based in physical methods are extensively used, but are less efficient to remove organic sulfur and syngenetic pyrite ($FeS2$). Syngenetic pyrite is one of the two forms of pyritic sulphur, found as a very fine and highly disseminated mineral in coal, which makes it difficult to separate by conventional cleaning process (Baruah and Khare, 2007; Pysh`yevl et al., 2007; Li and Cho, 2005; Ayha et al., 2005; Baruah et al., 2006).

Many studies have been realized to explore the pyrite dissolution by oxidants aqueous media. For this purpose, various oxidizing agents such as oxygen, hydrogen peroxide, ferric sulfate, ferric chloride, potassium permanganate, perchloric and nitric acids have been used to oxidize pyrite (Elliot, 1978; Bonn and Heijnen, 2001; Borah, 2006; Kawatra and Eisele, 2001; Antonijevic et al., 2003; Karaca et al., 2003; Mukherjee and Srisvastava, 2004). Previous work reported author indicate that hydrogen peroxide, ozone, and combined ozone-hydrogen peroxide in acid medium can to help to the pyrite removal (Davalos et al., 2009; Carrillo et al., 2009).

The oxidation of pyrite in an acid medium has been extensively studied and documented due to its importance in sulfur processing. This anodic process is recognized as a complex method that involves chemical and electrochemical equilibrium. Exactly as Chander et al. have summarized, pyrite oxidation processes have been classified into two mechanisms: (a) the preferential release of iron ions from pyrite and (b) the preferential release of oxysulfuric species. In the first process, the outer reacted layer of pyrite has been identified as elemental sulfur ($S\circ$), "polysulfide," or "metal deficient," which corresponds to the theory proposed by Buckley et al. In the second process, the sulfur in pyrite oxidizes to sulfates or thiosulfates, leaving a reacted layer composed of iron hydroxides.

The use of ozone for pyrite removal in coal and its effect in different conditions were investigated by Dávalos et al. (2009) and Carrillo et al.(2010). The use of ozone and its effect in different conditions were investigated. These works were based on an experimental design with the following parameters and levels: type and concentration of reagents (NaOH, HCl, HNO_3 and H_2SO_4; 0.3, 0.8 and 1.3 M; and distilled water) and presence and concentration of O_3 (0, 0.16 and 0.33 L·g/hr). The main factors affecting the FeS_2 dissolution were determined by analysis of variance (ANOVA). Table 2 shows the main effect ANOVA of the results as a function of the amount of Fe extracted at 90 minutes of treatment. According to the table, ANOVA shows that, under the studied conditions, the type of acid and concentration of O3 employed are the most important factor of the chemical dissolution of pyrite, followed of the reagents concentrations. Test results confirms that the maximum pyrite dissolution is reached when sulphuric acid is used. Increasing the acid concentration (average of the different acids), does not clearly affect the response of these curves. An increase in the levels of factors O_3, results in an increase in the mean value. Based on this, the results indicate a qualitative way to know the behaviour of pyrite dissolution at different combinations of chemicals (aqueous medium, concentration, oxidants).

Source term	DF	Sum of squares	Mean square	F-rato	Prob level	Power ($\alpha = 0.05$)
Reagent type	4	112.83	28.21	0.88	0.5642	0.1122
Reagent concentration	5	235.99	47.20	1.48	0.3979	0.1580
Ozone	2	123.61	61.80	1.93	0.2890	0.1804
S	3	95.99	31.99			
Total (adjusted)	14	1664.24				
Total	15					

Table 2. ANOVA for experimental design used in pyritic removal of coal samples.

In FeS$_2$ dissolution, the previously assumption that the extent of the chemical reaction rate at the interface is similar than that of the diffusion, can be precise. The presence of a strong oxidant conditions prevents the formation of the aforementioned product layer of elemental sulphur due to the high anodic potential achieved, or, at least, the electrochemical conditions influence the layer texture, favouring the formation of a porous cover of product.

The dissolution of pyrite proceeds into a coal matrix, thus the diffusion through the porous in the coal could limit the flux of the reagents and products to or from the reactive layer of pyrite. In addition, to the diffusion, the reagents (alkali and acid) could modify the chemical properties of coal, therefore a consumption of oxidative reagents would occur, thus leading the process to the chemical control. The diffusion and the reagents consumption, could explain the fit of the results to the diffusion and chemical controlling stage. Table 3 shows the kinetics data of pyrite dissolution form coal with the different reagents. This table shows that the SCM for product layer diffusion control, describes well the experimental data with respect to the others. Then, the evidence of kinetics behavior of the experimental data indicates that the reaction can be controlled by diffusion through a layer or film conformed by the surrounding surface coal.

Model	HNO$_3$	HCl	NaOH	H$_2$SO4	H$_2$O
$kt = 1 - (1-x)^{1/3}$	0.91	0.68	0.83	0.78	0.85
$kt = 1 - \frac{2}{3}x - (1-x)^{2/3}$	0.78	0.53	0.52	0.57	0.72
$kt = (1-x)^{-2/3} - 1$	0.81	0.56	0.53	0.63	0.74

Table 3. Correlation coefficient (r2) obtained from the kinetics models for FeS$_2$ dissolution.

In order to compare the results of O$_3$ treatment (leaching) with washability and flotation tests, different coal samples were treated, as shown in Table 4, showing the sulfur content of each product obtained in each test. The O$_3$ treatment was carried out using H$_2$SO$_4$ as aqueous medium solution. The results indicate that sulfur is largely free, so from the first separation in dense medium (washability test), with density 1.3, can get a 27% removal of sulfur. This indicates a ratio of sulfur released that has a higher density than coal. Significantly, the decrease depends on the initial sulfur content in the sample, but the trend continues in the different test.

In subsequent steps of washability separation, sulfur removal rate of 27% is maintained, except the last, which is 18%. Clearly, the washability test is cumulative, so that the sulfur content is relative to the sample proportion remaining in each stage. In the flotation to recover fine coal used, it is possible to obtain low sulfur content, although the removal with respect to the original sample is on average 11%. Although a smaller particle size (100% - 600 mesh Tyler), and therefore possibly a greater release of sulfur, it is also possible that a proportion of pyrite released to interact with the collector or pyrite fines being swept by the foam. On the other hand, it is interesting to note that the sulfur content obtained by the O$_3$ treatment of sample M1-CAO (sample obtained of coal mixed samples, named coal all-in-one) is similar to the first separate density 1.3 (25% removal) and a sample washed coal and may further reduce the sulfur content of such leaching, reaching up to 8% sulfur removal.

Sample	Initial Sulfur content, %	Washability tests at different density medium					Flotation test
		d= 1,3	d=1,4	d=1,5	d=1,6	bottom 1,6	
Block VII	1.35	0.86	0.76	0.88	1.16	1.15	1.11
Block VI	1.17	0.96	0.98	1.07	1.11	1.72	1.1
Mine 6	1.22	0.79	0.75	0.75	0.95	0.9	1.05
Mine 5	1.09	0.79	0.79	0.79	0.75	0.97	1
Mine 3	1.02	0.87	0.79	0.77	0.79	1.24	0.95
Muestras	M1	After O_3 treatment					
M1-CAO	1.17	0.88					
M1-washed	0.87	0.78					

Table 4. Total sulfur, %, for the diferent removal sulfur test.

To confirm the previous results in industrial sample, CAO (labeled M2) samples were obtained from different steps (P) of industrial washing plant. These samples were treated with oxidant leaching tests, which were repeated 4 times. The objective of this procedure was to determine the reduction of sulfur, also determine the degree of repeatability and reproducibility (R) of the tests.

Figure 5 shows the initial sulfur content in each sample (hollows circles), as well as the average, minimum and maximum sulfur analysis obtained for each sample treatment. The error bar indicates the range of results from 4 trials (repetitions) performed on each sample.
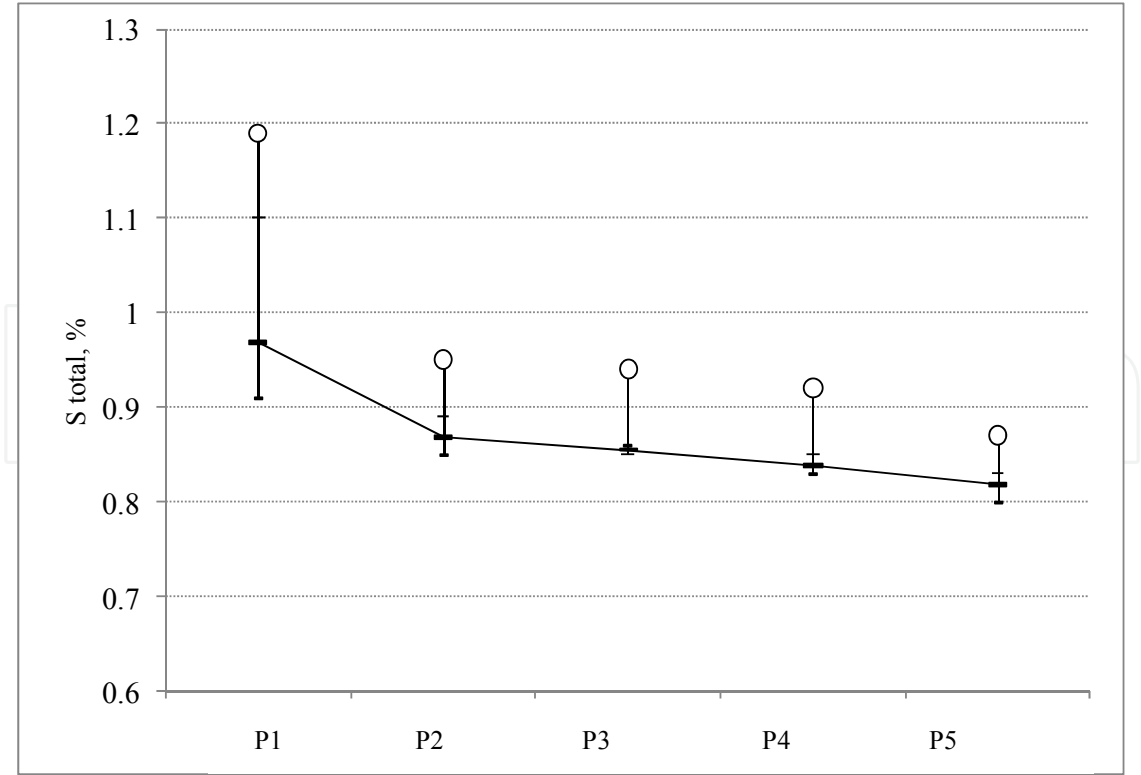

Fig. 5. Total sulfur content (%) in samples obtained from different washing steps (P1 – P5), treated by O_3 leaching. Initial sulfur content in original sample = 1.19 %.

Results indicate that removal of sulfur is greater if the initial sulfur content is higher, although the variability obtained is also high. For example, with P1 step coal, an average 18 % sulfur removal was obtained. When the initial sulfur is lower, it also reduces the variability in treatment result, but the removal percentage is lower, between 8 and 9%. This may be due to the particle size distribution that exists in the wash steps, which consists of steps processes using cell dense media (box Daniels), hydro-cyclones and spirals. The particle size is related to the degree of liberation of sulfur (pyrite). Then, a narrower size distribution, the variability is lower.

The results indicate that ozone is the stronger oxidant to remove the pyrite and its dissolution is enhanced by sulphuric acid medium. The analysis of the results with O_3 as oxidising agent using ANOVA and multiple lab-test, was applied in order to support that diffusion of oxidant agents is the rate controlling step of the overall process: O_3 diffusion from the gas bulk to the dissolution to react with pyrite and diffusion of Fe^{3+} through the layer formed in the boundary surface pyrite and coal particles. The results clearly showed that ozone contributed to the use of lower concentrations of H_2SO_4, with the consequently economical savings.

4. Conclusion

Sulfur is the element that, in copper, gold and silver cases, inhibits metal dissolution present in minerals. On the other hand, the removal of sulfur is greatly needed in case of coal, due to emissions of SO_2 gas during coal fire-combustion. In this Chapter, oxidative hydrometallurgy of different sulphide minerals using ozone has been analyzed. Results show that the treatment with ozone increases sulfur oxidation in the different cases.

Pyrite containing gold and silver results suggests that the treatment with ozone before cyanidation process improves the recovery of gold and silver and reduces the consumption of cyanide. The results obtained from low metal value content sample indicate that is still possible to recover more than half of the gold and silver content by means of cyanidation. The results indicate a significant reduction in the consumption of cyanide which permits the recovery of these metals with less cost. But, the determination of the cost of ozone consumption in order to evaluate its use is very important.

In the case of chalcopyrite, the approach suggested in this work using experimental design with Taguchi L9 design matrix and statistical analysis to study the acid leaching of chalcopyrite with ozone and ferric ions was helpful to optimize the experimental conditions and to rationalize the results. This approach may be used to decrease development costs and ultimately operational costs of copper extraction from low-grade chalcopyrite.

For sub-bituminous coal, the dissolution of pyrite from in different medium using ozone was studied. The results, using ANOVA, indicate that ozone is the stronger oxidant to remove the pyrite and its dissolution is enhanced by sulphuric acid medium, the results support that diffusion of oxidant agents is the rate-controlling step of the overall process: O_3 diffusion from the gas bulk to dissolution to react with pyrite and diffusion of Fe^{3+} through the layer formed in the boundary surface pyrite and coal particles.

Thus, the use of ozone can be a promising auxiliary agent in the actual process of obtaining metals and coal with the following advantages: 1) decreasing operational costs of low-grade

chalcopyrite leaching, 2) increasing gold and silver recovery in cyanidation and decrease cyanide consumption, 3) decreasing the sulfur-containing coal since coal cleaning plants, to be used as clean in energy generation and iron and steelmaking.

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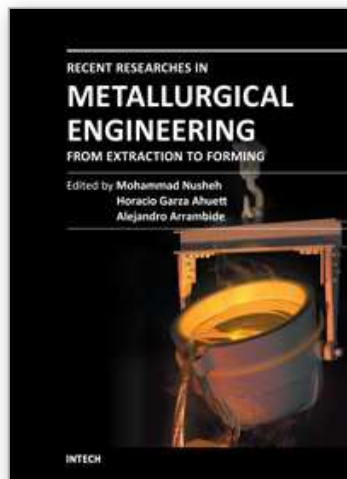
Recent Researches in Metallurgical Engineering - From Extraction to Forming

Edited by Dr Mohammad Nusheh

Metallurgical Engineering is the science and technology of producing, processing and giving proper shape to metals and alloys and other Engineering Materials having desired properties through economically viable process. Metallurgical Engineering has played a crucial role in the development of human civilization beginning with bronze-age some 3000 years ago when tools and weapons were mostly produced from the metals and alloys. This science has matured over millennia and still plays crucial role by supplying materials having suitable properties. As the title, "Recent Researches in Metallurgical Engineering, From Extraction to Forming" implies, this text blends new theories with practices covering a broad field that deals with all sorts of metal-related areas including mineral processing, extractive metallurgy, heat treatment and casting.

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