A study on the zinc sulfide dissolution kinetics with biological and chemical ferric reagents

Sina Ghassa¹², Mohammad Noaparast³, Sied Ziaedin Shafaei², Hadi Abdollahi²⁴, Mahdi Gharabaghi¹, Zohreh Boroumand²

¹ School of Mining, College of Engineering, University of Tehran, Tehran 1439957131, Iran
² Applied Geological Research Center of Iran, Nano-Bio Earth Lab., Karaj 3174674841, Iran

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ABSTRACT

The leaching kinetics of a sphalerite concentrate containing 38.25% zinc was studied in the presence of biological and chemical ferric reagents. To produce the biological ferric reagent (BFR), a pyrite concentrate sample was oxidized to ferric ions by iron and sulfur oxidizing bacteria, and this pregnant leach solution was then applied as oxidizing reagent in ZnS leaching. This process is commonly referred to as two-step bioleaching. This biological reagent contained 12.75 g/l ferric and its pH was 0.86. The chemical ferric reagents (CFR) were made by dissolution of Fe₂(SO₄)₃ and FeCl₃ salts in deionized water. Leaching experiments were carried out at different temperatures to study the mechanism of ZnS dissolution and its kinetics. The kinetic modeling of ZnS dissolution with BFR followed the interfacial transfer and diffusion across the product layer mechanism within the first minutes (about 60 min) while it changed to the diffusion-control mechanism after passing this initial period. On the other hand, the ZnS dissolution in presence of ferric sulfate was described by a diffusion mechanism. The surface analysis by SEM and FTIR confirmed that sulfur layer formation on the mineral surfaces could prevent the solvent diffusion to the minerals surface, and consequently it controls the dissolution reaction. The highest zinc recoveries were 70%, 99% and 83% in presence of biological ferric reagent, ferric sulfate and ferric chloride at 90 °C after 200 min, respectively. The zinc recovery for one-step bioleaching was 90% and was achieved after 20 days at 35 °C, by iron and sulfur oxidizing bacteria.

1. Introduction

Being employed in > 85% of total world zinc production (Souza et al., 2007a, 2007b), the Roast-Leach-Electrowinning (RLE) process is the most important method of zinc extraction from sulfide ores and concentrates. In this method, as an indirect leaching approach, the zinc sulfide minerals (such as sphalerite) are roasted at a temperature around 925 °C in order to produce zinc calcine (ZnO) (Eq. (1)), prior to subsequent leaching in sulfuric acid media, solution purification and zinc electrolysis (Han et al., 2015).

\[ 2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + \text{SO}_2 + \text{energy} \] (1)

However, there are many environmental and economic problems associated with this method. Large amounts of poisonous gases are produced during roasting process, especially \( \text{SO}_2 \) (Eq. (1)) would seriously affect the future application of RLE in metals extraction industries. Although modern zinc plants that employ the conventional method convert the \( \text{SO}_2 \) produced in the roasting stage to sulfuric acid or \( S^0 \) (Balarini et al., 2008), the need to sell it to an over-supplied market could be an important problem for this industry (Dehghan et al., 2008). This problem is more serious for countries with large oil industries because huge amounts of sulfuric acid and elemental sulfur are produced during crude oil processing, too.

Due to the above mentioned problems, the direct leaching of the sphalerite has received considerable attention in recent decades. In this process, sulfidic sulfur is converted to elemental sulfur, and thus no \( \text{SO}_2 \) is produced (Dehghan et al., 2009).

Three different methods have been proposed for sphalerite direct leaching which are pressure leaching (Veltman and Bolton, 1980), bioleaching (Mehrabani et al., 2013; Ahmadi and Mousavi, 2015), and ferric leaching (Li et al., 2010). Fig. 1 summarizes different hydrometallurgical methods for sphalerite processing. The most important advantage of direct leaching is that there is no \( \text{SO}_2 \) emission in these methods due to elemental sulfur formation during sulfide minerals processing.

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Pressure leaching is carried out in industrial autoclaves at temperatures higher than 100 °C and a pressure in the range of 2500–5000 kPa (Habashi, 1999). Although this method can be employed to extract zinc with high recovery (Li et al., 2010), the high equipment cost and the high operational costs make it an expensive method. On the other hand, the direct atmospheric leaching (including bioleaching and ferric leaching) should be carried out at atmospheric pressure in a simple mixing reactor which can be a suitable alternative method for pressure leaching.

In bioleaching, acidophilic bacteria are used to accelerate the sphalerite dissolution via direct and/or indirect mechanisms (Schippers et al., 2014). In the direct mechanism bacteria attach to the minerals surface and break up the crystal structure, either by sulfur extraction or electrochemical dissolution (Tributsch, 2001; Zeng et al., 2011). In the indirect mechanism, bacteria oxidize ferrous ions to ferric ions in the bulk solution or within a biofilm, and the ferric ions oxidize the sulfur moiety (Eqs. (2) and (3)). In this mechanism, ferric ions act as oxidant by reduction to ferrous ions and increase the sphalerite dissolution kinetics by providing electrons for sulfate oxidation. The ferrous ions which are produced in sphalerite biooxidation, are re-oxidized to ferric by bacteria, and this accordingly makes the bio-dissolution reaction self-sustaining.

\[
2\text{Fe}^{2+} + \frac{1}{2}\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{bacteria}} 2\text{Fe}^{3+} + \text{H}_2\text{O}
\]

\[
\text{ZnS} + \text{Fe}^{3+} \rightarrow \text{Zn}^{2+} + \text{Fe}^{2+} + \text{S}^0
\]

The most important problem associated with this method is its slow kinetics which in turn increases the residence time. Usually bioleaching of sphalerite concentrate with acceptable zinc recovery operates at diluted slurries and requires several days processing, therefore much larger reactors are to be required as compared to pressure leaching plants (Svens et al., 2003; Lahtinen et al., 2005). Additionally, it is impossible to increase temperature, in order to improve the dissolution rate in bioleaching process, because most microorganisms cannot tolerate the high temperatures. Direct ferric leaching with a higher kinetic rate could be suggested for solving this problem. In this method, it is usually possible to recover > 90% of zinc from sphalerite concentrate within few hours (Santos et al., 2010; Lampinen et al., 2015). This method would be applied at higher temperatures without any limitation. The \(\text{ZnS}\) dissolution in solution with high \(\text{Fe}^{3+}\) concentration follows Eq. (3) (Otrizac et al., 2003; Aydogan et al., 2005), which is the main reaction in bioleaching as well. According to this reaction, two ferric ions should be reduced to ferrous in order to oxidize one \(\text{ZnS}\) molecule. This means that a high amount of ferric (usually added in form of ferric sulfate or chloride) is needed for this process, which makes it to be an expensive method. Although the ferrous ions that produced during \(\text{ZnS}\) oxidation can be regenerated by oxygen at elevated temperatures, a large amount of chemicals is yet needed for starting the reaction which is the most important disadvantage of this process.

Pyrite biooxidation can be suggested as a low-cost method for producing ferric ions. Acidophilic bacteria oxidize \(\text{FeS}_2\) to \(\text{Fe}^{2+}\) and \(\text{SO}_4^{2-}\). The ferrous then oxidizes again to ferric and acts as reagent to dissolve more pyrite by reduction \(\text{Fe}^{3+}\) to \(\text{Fe}^{2+}\). The \(\text{Fe}^{2+}\) which is produced in the last reaction re-oxidizes to \(\text{Fe}^{3+}\) and this loop continues until there is no pyrite available for dissolution. In addition, bacteria produce sulfuric acid by oxidizing elemental sulfur (Chandra and Gerson, 2010; Basson et al., 2013). Fig. 2 shows the chemical reactions that control the pyrite biooxidation process. As a gangue mineral, pyrite is an easy-access material in most polymetallic sulfide mining sites (Sheoran and Sheoran, 2006). Most sulfide ores contain high concentrations of pyrite (\(\text{FeS}_2\)), which should be separated from the ore during mineral processing. Therefore, usually mineral processing tailing dumps contain high concentrations of pyrite which can cause formation of acid mine drainage. Acid mine drainage (AMD), or acid rock drainage (ARD), is normally considered as one of the main pollutants of water in many countries that have historic or current
mining activities (Simate and Ndlovu, 2014). AMD occurs by biooxidation of pyrite based on the mentioned reactions. AMD is a strongly acidic wastewater with high concentrations of dissolved ferrous and non-ferrous metals (Macingova and Luptakova, 2012), and if AMD is left untreated, it can contaminate underground and surface watercourses, damaging the health of plants, wildlife, and aquatic species. As Fig. 2 shows, the final product of pyrite biooxidation (or AMD) are ferric ions and sulfuric acid. Thus, AMD or pyrite that biooxidized can be implemented as a Fe$^{3+}$ source for ferric leaching.

The aim of the current research is to solve problems associated with bioleaching (long reaction time) and chemical ferric leaching (high chemical costs) by a combination of these two methods. This method is named “Two-Step Bioleaching (TSB)”. To achieve this goal, the biooxidation method was applied to produce a bioreagent with high ferric concentration from pyrite (FeS$_2$). In this research work, a pyrite concentrate and a screened consortium of acidophilic bacteria have been used to produce ferric ions. This high ferric biological reagent can be implemented as a Fe$^{3+}$ source for ferric leaching.

The X-ray diffraction (XRD) analysis of the concentrate sample shown that pyrite (FeS$_2$) is the main mineral of the sample. Anorthite (Ca(Al$_2$Si$_2$O$_8$)) and jarosite (K(Fe$_3$(SO$_4$)$_2$(OH)$_6$) were also detected as gangue minerals. The XRD pattern of pyrite concentrate is shown in Fig. 3. ICP-OES was used to determine the chemical composition of pyrite concentrate. The sample contained 43.77% of iron. The chemical composition of pyrite concentrate is listed in Table 1.

2. Material and methods
2.1. Material preparation and characterization

A pyrite bearing sample was prepared from Sarcheshmeh Copper Complex, located in Kerman, Iran. The sample was ground down to 80% finer than 100 μm, and a two-step flotation process, including rougher and cleaner stages was then carried out to obtain high grade pyrite concentrate. The X-ray diffraction (XRD) analysis of the concentrate sample shown that pyrite (FeS$_2$) is the main mineral of the sample. Anorthite (Ca(Al$_2$Si$_2$O$_8$)) and jarosite (K(Fe$_3$(SO$_4$)$_2$(OH)$_6$) were also detected as gangue minerals. The XRD pattern of pyrite concentrate is shown in Fig. 3. ICP-OES was used to determine the chemical composition of pyrite concentrate. The sample contained 43.77% of iron. The chemical composition of pyrite concentrate is listed in Table 1.

The sphalerite concentrate sample used in the leaching experiments contained 38.25% of Zn, 2.6% of Pb, and 7.17% of Fe, which was supplied from Koushk Mine, located in Yazd, Iran. 100% of particles were finer than 38 μm. The X-ray diffraction (XRD, Inel EQUINOX3000, USA) technique was employed to determine the main minerals of the sample. The results of the mineralogical studies revealed that the major zinc bearing phase is sphalerite. The concentrate sample also contained jarosite (KFe$_3$(OH)$_6$(SO$_4$)$_2$), pyrite (FeS$_2$), and sanidine (K(AlSi$_3$O$_8$)) as minor minerals. The XRD pattern for sphalerite concentrate is
presented in Fig. 4. The elemental composition of concentrate used in leaching experiments was determined by using inductively coupled plasma optical emission spectroscopy (ICP-OES, Varian 720 ES) (Table 2). The ore sample that used to produce zinc concentrate also contained galena (PbS) (Mehrabani et al., 2013).

2.2. Zn concentrate leaching

To compare the results of one-step and two-step bioleaching, two series of experiments was designed and performed. In one-step bioleaching, bacterial consortia were added to the leaching environment directly, while in two-step bioleaching, bacteria were applied in order to produce an oxidant, which in the second step was used for zinc dissolution.

2.2.1. One-step bioleaching

Shake flask experiments were conducted in 250 ml Erlenmeyer flasks containing 90 ml of 9 K medium and 10 ml of enriched bacteria. This mineral salts medium contained Ca(NO₃)₂ 0.01 g/l, KCl 0.1 g/l, K₂HPO₄ 0.5 g/l, MgSO₄·7H₂O 0.5 g/l and (NH₄)₂SO₄ 3.0 g/l. The media pH was maintained at 1.8 with sulfuric acid. A mesophilic bacterial consortium including Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans which was screened from Angouran Zn-Pb mine's AMD (Ghassa et al., 2015), was used for this experiment. This bacterial consortium was adapted naturally to the high concentration of zinc before being used in the tests. The test was operated at 35 °C and 125 rpm with 10 g/l of pulp density. Elemental sulfur (10 g/l) and ferrous ions (in form of Fe₂SO₄·7H₂O) were added to this test as bacterial energy resources. The Fe²⁺ concentration selected for this test was similar to the ferric concentration in two-step bioleaching. The solution samples were withdrawn at the same time intervals and zinc concentration were determined in the pregnant leach solution. In addition, the pH and oxidation-reduction potential (ORP) changes were measured to determine the biological and chemical reactions changes in this process.

2.2.2. Two-step bioleaching

2.2.2.1. Biological reagent. The biooxidation process for producing high concentration of ferric solution was carried out in Erlenmeyer flasks, using a shaking incubator (Shin Saeng SKIR-601, Korea). Each flask
A mixed culture of mesophilic bacteria, including *A. ferrooxidans*, *A. thiooxidans* and *L. ferrooxidans* which was initially enriched from the Sarchezmeh Copper Mine, was employed for pyrite biooxidation (Seyyed Bagheri and Hassani, 2001). The biooxidation process was performed for 20 days at 35 °C. After biooxidation of pyrite, the solution with high ferric concentration was used in direct leaching of sphalerite concentrate. It should be noted that this process is a laboratory simulation of acid mine drainage production.

2.2.2.2. Chemical reagents. To compare the biological and chemical reagents, the effects of ferric sulfate and ferric chloride solutions on sphalerite leaching were investigated. In these experiments, the solution was prepared using distilled water and analytical grades of HCl and FeCl₃ or H₂SO₄ and Fe₂(SO₄)₃ from Merck Chemicals Co. The concentration of ferric and all other conditions (such as pH) in these tests were completely identical to the concentration and conditions of solution that were obtained from the biooxidation process.

2.3. Leaching apparatus and experimental procedure

Atmospheric direct leaching experiments were carried out in a 1-liter sealed glass reactor (1) immersed in the electrically heated silicon oil bath (2), equipped with the Heidolph mechanical stirrer (HPS-55 model, Germany) having a digital controller unit and a Teflon impeller (3). A magnetic stirrer (Multi stirrer DM-8 Scinics, Japan) was also used as the base of the setup (4). This stirrer keeps the temperature uniform in all parts of oil bath. The reactor temperature was monitored and controlled within ± 0.1 °C by a thermostat (8). The one port to keep losses to a minimum. The reactor temperature was adjusted to the desired temperature, the predetermined amount of sphalerite concentrate was then added to 100 ml of leaching solution. The agitation speed was 900 rpm in all the leaching tests in which all the solid particles become fully suspended in the solution. The experiments were performed at 1% of solid content (10 g/l) at different temperatures. The temperatures selected between 35 and 90 °C for leaching with biological ferric and between 50 and 90 °C for chemical ferric leaching to determine the leaching kinetic by shrinking core model. All other conditions such as agitation speed, initial pH, solid content, reactor conditions were kept completely similar for all tests. A test without any Fe³⁺ also was run at 90 °C and the same pH as the other tests in order to investigate the acid-only leachable sphalerite in sample. Samples were taken during the 200 min reaction period at pre-determined intervals which were filtered, using a syringe filter and analyzed for Zn using ICP-OES technique and consequently Zn recoveries in every stage were accordingly calculated. To calculate the fraction of zinc leached, the Eq. (4) (Demopoulos and Papangelakis, 1998) was used:

\[
X_i = \frac{V_0 - \sum_{i=1}^{i-1} v_i C_i + \sum_{i=1}^{i-1} v_i C_i}{M (C_{i1}/100)}
\]

(4)

where \(X_i\) is the Zn extraction corresponding to sample i, \(V_0\) the initial volume of the leaching solution in the reactor (ml), \(v_i\) the volume of sample i withdrawn from the reactor (ml), \(C_i\) the Zn concentration in sample i (mg/l), \(M\) the initial mass of the sphalerite concentrate in grams added into the reactor and \(C_{i1}\) the Zn percentage in the sphalerite concentrate.

3. Results and discussion

3.1. One-step bioleaching

The one-step biolcalcing test was carried out to compare its results with two stages sphalerite bioleaching. The pH, oxidation-reduction potential (ORP) and zinc extraction changes during 33 days biolcalcing treatment are shown in Fig. 6. The zinc dissolution started from initial days and ended up after about 20 days. On the other hand, the oxidation-reduction potential started to increase after day 12th, and stabilized on its highest level after around day 20th. In most acidic bacterial leaching systems, the oxidation-reduction potential predominantly reflects the Fe³⁺ /Fe²⁺ ratio. In addition, following biochemical reaction (Eq. (5)) shows that how iron-oxidizing bacteria affect the Fe³⁺ /Fe²⁺ ratio.

\[
2\text{Fe}^{2+} + 0.5\text{O}_2 + 2\text{H}^+ \xrightarrow{\text{Bacteria}} 2\text{Fe}^{3+} + \text{H}_2\text{O}
\]

(5)

Therefore, an increase in ORP reflects the increase of iron-oxidizing bacterial activity (Manafi et al., 2013). This means that in the first few days zinc was dissolved due to chemical reactions while it was dissolved due to bacterial activities in the following days. In fact, when bacteria were inoculated into the biolcalcing test, some ferric ions were transformed to the new environment which caused sphalerite dissolution before starting bacterial activity. As Fig. 6B shows, the pH decreased from 1.8 to < 0.9, within 20 days. The pH dropped because both sulfur biooxidation and jarosite precipitation are acid production processes, according to the Eqs. (6) and (7):

\[
\text{S} + 1.5\text{SO}_2 + \text{H}_2\text{O} \xrightarrow{\text{bacteria}} \text{SO}_4^{2-} + 2\text{H}^+
\]

(6)

\[
[\text{K}^+,\text{Na}^+] + 3\text{Fe}^{3+} + 2\text{SO}_4^{2-} + 6\text{H}_2\text{O} \rightarrow [\text{K},\text{Na}]\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6 + 6\text{H}^+
\]

(7)

The zinc extraction was calculated based on Eq. (8). The zinc recovery was about 90% for this test and was achieved after 20 days processing. After 20 days the oxidation-reduction potential and pH became constant which showed the completion of bacterial activity.

\[
R_{\text{Zn}} = \frac{\text{Transferred metal from ore to solution}}{\text{Metal contain dininore}} \times 100
\]

(8)
3.2 Two-step bioleaching

3.2.1 Pyrite biooxidation

As mentioned before, the pyrite biooxidation step was carried out in a shaking incubator using mesophilic bacteria. After 45 days processing, solid-liquid separation was performed by using a vacuum filter with grade 42 filter paper (Whatman, Germany). The flask content was applied as biological ferric reagent (BFR) for the sphalerite leaching kinetic study. The atomic absorption spectroscopy (AAS) analysis of this solution indicated that BFR contained 12.75 g/l iron. The potassium dichromate titration indicated that BFR did not contain any ferrous ions. This means that bacteria oxidized all ferrous ions to ferric and BFR contained 12.75 g/l of Fe\(^{3+}\). Table 3 shows the chemical analysis of biological ferric solution determined with an inductively coupled plasma atomic emission spectroscopic (ICP-AES). In addition to the ferric, the BFR also contained high concentrations of magnesium, manganese, zinc and copper and low concentrations of phosphorous, cobalt, nickel, lead and cadmium. It should be noted that the chemical ferric reagents contained no metals except iron. Also, bacteria decreased pH from 1.8 to 0.86 by producing sulfuric acid.

The oxidation-reduction potential (ORP) and pH changes during 45 days processing are shown in Fig. 7. According to this diagram, both ORP and pH started to change after 15 days of treatment. The counting of bacterial cells under an optical microscope (KRUSS, Germany), using Neubauer counting chamber showed that bacterial count also increased after 15 days of treatment from almost 4 × 10\(^6\) to 2 × 10\(^7\) cells/ml (data not shown). As mentioned, A. ferrooxidans oxidize ferrous ions to the ferric ions (according to the Eq. (2)). Fig. 8 shows the changes in the total iron, ferric and ferrous concentrations in biooxidation environment. This diagram obviously shows that the ferrous ions started to oxidize to the ferric ions after 15 days of processing, which confirms the direct relation between ORP and bacterial count.

Both the bacterial consortium and the pyrite bearing ore were obtained from the same mine, and the bacteria adapted naturally to the pyrite. However, the concentrations of iron and other metals increased dramatically by concentrating pyrite and this caused the increase in the biooxidation time (usually pyrite biooxidation needs 10–15 days). In other words, although bacteria adapted naturally to the pyrite bearing ore, they did not adapt to the pyrite concentrate. Therefore, it is

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**Table 3**

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<thead>
<tr>
<th></th>
<th>Fe (g/l)</th>
<th>Mg (mg/l)</th>
<th>Mn (mg/l)</th>
<th>Zn (mg/l)</th>
<th>Cu (mg/l)</th>
<th>P (mg/l)</th>
<th>Co (mg/l)</th>
<th>Ni (mg/l)</th>
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<td>12.75</td>
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<td>50.5</td>
<td>39.3</td>
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<table>
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<th>Cd (mg/l)</th>
<th>Cr (mg/l)</th>
<th>Ag (mg/l)</th>
<th>Ba (mg/l)</th>
<th>Li (mg/l)</th>
<th>Nb (mg/l)</th>
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<td>&lt; 0.1</td>
<td>&lt; 0.1</td>
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</tbody>
</table>

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Fig. 6. ORP (A), pH (B) and zinc recovery (C) changes during one-step bioleaching.

Fig. 7. ORP (A) and pH (B) changes in pyrite biooxidation.
suggested to adapt bacteria with pyrite concentrate before biooxidation, in cases pyrite concentrate is used as biooxidation feed. This adaptation will reduce the lag phase and accelerate the process.

It should be noted that the sphalerite concentrate contains 7.2% iron in the form of jarosite, and dissolution of this jarosite may release some Fe³⁺. However, the jarosite dissolution rate is very low under acidic condition and this process would need several weeks, as previous researchers reported (Baron and Palmer, 1996; Smith et al., 2006). Therefore ferric production due to jarosite dissolution is likely to be negligible.

In the following parts, the ZnS leaching kinetic in presence of biological ferric reagent and chemical ferric reagents will be comprehensively described.

### 3.2.2. Reaction models

The dissolution of solid particles in liquids can roughly be described by two main processes in series: the escape of solute molecules from the solid surface, and the diffusion of these molecules toward the bulk liquid phase (Hsu et al., 2009). Depending on the operating conditions, the rate of dissolution can be controlled by one of these two steps (Riazi and Faghri, 1985; Bhaskarwar, 1988; Crundwell, 1995). The major models that have been developed for non-catalytic fluid-solid reactions are the 1) shrinking core, 2) shrinking particle, 3) homogeneous and 4) grain models (Ghor and Jia, 2004). Among these models, the shrinking core model, which was developed by Yagi and Kunii (1955) for the first time, has been widely used in the area of hydrometallurgy to model leaching systems. The shrinking core model considers that the leaching process is controlled either by the diffusion of reactant through the solution boundary, or through a solid product layer, or by the surface chemical reaction rate.

The sphalerite leaching in presence of ferric ions (both chemical and biological ferric) occurs based on the Eq. (3).

Assuming that sphalerite particles have a spherical geometry and the surface chemical reaction is the slowest step, the following expression (Eq. (9)) of the shrinking core model can be employed to describe the dissolution kinetics (Levenspiel, 1999):

$$K_t = 1 - (1 - X)^{3/2}$$

Similarly, when the diffusion of ferric ions through the ash layer is the rate controlling step, the shrinking core model as Eq. (10), can be used (Levenspiel, 1999):

$$K_t = 1 - 2X - (1 - X)^{3/2}$$

Some reactions have been controlled by both chemical and diffusion parameters. Different models were proposed to describe these reactions (Vidgorkchik and Shein, 1971; Overhoff et al., 2007; Lan et al., 2009; Theiss et al., 2016; Yang et al., 2016). To determine the kinetics mechanism for sphalerite dissolution, reaction fraction was reacted in different temperatures plotted versus time for different models. Different kinetics models which were proposed for sulfide minerals dissolution are presented in the Table 4, where X is the fraction reacted, $K_t$ the kinetics constant, and t is time.

#### 3.2.3. Kinetics analysis and modeling in presence of biological ferric ion

As mentioned before, the biological ferric reagent was produced by pyrite bio-oxidation by using iron and sulfur oxidizing bacteria. Leaching tests were carried out at temperatures 35, 50, 65, 80, 90 °C, to study on the ZnS dissolution kinetics in presence of BFR. Some tests (both with BFR and CFR) were selected randomly and repeated (data not show); however, results were very close together and errors were negligible. The effect of temperature on sphalerite leaching is given in Fig. 9. The final zinc extraction for these tests were 25.6, 32.6, 51.6, 54.6, and 70.0%, after 200 min.

The test without any external ferric show that only 7.11% of Zn recovered by acid treatment, at 90 °C and pH = 0.86. This acid leached sphalerite was negligible compared to high Zn recoveries in ferric leaching tests. The sphalerite that solvs in acid is obviously less in lower temperatures.

The fraction reacted (X) at different temperatures was drawn versus time for different models (presented in Table 4), to determine the kinetics mechanism in this reaction. The $K_t = \frac{1}{3} \ln(1 - X) + \left[ \frac{1}{3} \ln(1 - X)^2 - 1 \right]$ model was best fitted to the data during first minutes (about 60 min); however the kinetics mechanism was changed to $K_t = 1 - \frac{2}{3}X - (1 - X)^{3/2}$ model after this period. This means that the interfacial transfer and diffusion across the product layer

### Table 4

<table>
<thead>
<tr>
<th>Eq. no.</th>
<th>Model</th>
<th>Mechanism</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$K_t = 1 - (1 - X)^{3/2}$</td>
<td>Chemical reaction control</td>
<td>Levenspiel (1999)</td>
</tr>
<tr>
<td>2</td>
<td>$K_t = 1 - (1 - X)^2$</td>
<td>Mixed model control by shrinking core model</td>
<td>Gao et al. (2009)</td>
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<tr>
<td>3</td>
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<td>Ibiz et al. (2006)</td>
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<td>4</td>
<td>$K_t = 1 - \frac{1}{2}X - (1 - X)^2$</td>
<td>Mixed model control by shrinking core model</td>
<td>Sokic et al. (2009)</td>
</tr>
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<td>5</td>
<td>$K_t = 1 - \frac{1}{2}X - (1 - X)^2$</td>
<td>Mixed model control by shrinking core model</td>
<td>Aydogan et al. (2005)</td>
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<td>6</td>
<td>$K_t = 1 - \frac{1}{2}X - (1 - X)^2$</td>
<td>Mixed model control by shrinking core model</td>
<td>Dickinson and Heal (1999)</td>
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<td>7</td>
<td>$K_t = \frac{1}{3} \ln(1 - X) + \left[ \frac{1}{3} \ln(1 - X)^2 - 1 \right]$</td>
<td>Interfacial transfer and diffusion across the product layer</td>
<td>Dreisinger and Abed (2002)</td>
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<tr>
<td>8</td>
<td>$K_t = 1 - \frac{2}{3}X - (1 - X)^{3/2}$</td>
<td>Diffusion of hydrogen ions through a product layer by shrinking core model</td>
<td>Padilla et al. (2008)</td>
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</table>
mechanism would control the ZnS dissolution within first minutes (Dehghan et al., 2009), while it was changed to the diffusion-control mechanism after passing this period. Table 5 shows the correlation coefficients ($R^2$) for these two mechanisms. The means of correlation coefficients for first and second periods are 0.97 and 0.94 which show accuracy of curve fitting to data. In addition, Fig. 10 presents the $K_t$ diagram versus time for sphalerite dissolution in presence of biological ferric reagent.

To study the surface changes, Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) were used. The FTIR test carried out for feed sample and leaching residuals (at 90 °C) in order to study the surface chemistry and their changes during two-step bioleaching. In Infrared Spectroscopy, IR radiation is used. The FTIR test carried out for feed sample and leaching residuals (at 90 °C) in order to study the surface chemistry and their changes during two-step bioleaching. In Infrared Spectroscopy, IR radiation is passed through a sample and some of the infrared radiation is absorbed by the sample but some of it passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint, no two unique molecular structures could produce the same infrared spectrum. Fig. 11 depicted the FTIR spectrum for two mentioned samples. Peaks in range of 1000 to 1200 (cm$^{-1}$) show the elemental sulfur bands (Shi and Fang, 2004; Varotsis et al., 2014; Panda et al., 2015). According to the FTIR graphs, the feed sample contained no elemental sulfur. However, after processing, an elemental sulfur layer was formed on the particles’ surfaces. In addition, the 3404 (cm$^{-1}$) shows the C–H band. This component and other organic bands were formed in the minerals surface due to bacterial extracellular polymeric substances (EPS) (Govender and Gericke, 2011).

Additionally, the Scanning Electron Microscopic (SEM) analyses were performed to determine the surface properties before and after processing. As Fig. 12 shows, an ash layer covered the minerals surface. In fact, the SEM images confirmed the FTIR result for sulfur formation on minerals surface. This layer of elemental sulfur prevents the solvent diffusion to the minerals surface, and consequently controls the dissolution reaction. Therefore, both Fourier Transform Infrared Spectroscopy (FTIR) and Scanning Electron Microscopy (SEM) confirmed the diffusion-control mechanism for this reaction.

### Table 5

<table>
<thead>
<tr>
<th>Reaction temp. (°C)</th>
<th>First period</th>
<th>Second period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_t = \frac{2}{3} \ln(1 - X) + \left[ (1 - X)^{\frac{2}{3}} - 1 \right]$</td>
<td>$K_t = 1 - \frac{2}{3} X - (1 - X)^{\frac{2}{3}}$</td>
</tr>
<tr>
<td>Interfacial transfer and diffusion model</td>
<td>Diffusion-controlled model</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>0.9538</td>
<td>0.8202</td>
</tr>
<tr>
<td>50</td>
<td>0.9534</td>
<td>0.9533</td>
</tr>
<tr>
<td>65</td>
<td>0.9613</td>
<td>0.9797</td>
</tr>
<tr>
<td>80</td>
<td>0.9981</td>
<td>0.9696</td>
</tr>
<tr>
<td>90</td>
<td>0.9834</td>
<td>0.9962</td>
</tr>
</tbody>
</table>

![Fig. 9. Effect of temperature on zinc extraction ([Fe$^{3+}$]: 12.75 g/l; pulp density: 10 g/l; pH: 0.86).](Image 39x261 to 287x401)

![Fig. 10. Plot of $K_t$ versus time for sphalerite leaching in presence of BFR.](Image 39x261 to 287x401)

#### 3.2.4. Kinetic analysis and modeling in presence of chemical ferric ion

To study on the sphalerite dissolution in presence of $\text{Fe}_2(\text{SO}_4)_3$, leaching experiments were carried out at temperatures of 50, 65, 80, 90 °C. All the leaching conditions were completely identical to the experiments that were carried out with biological ferric reagent. The final zinc extractions for these tests were 38.0, 59.67, 76.4, 99.1% respectively. The zinc extractions for different tests are shown in Fig. 13. The dissolution reaction for sphalerite in acidic ferric sulfate solutions is expressed as following (Eq. (11)):

$$\text{ZnS} + 2\text{Fe}_2(\text{SO}_4)_3 \rightarrow \text{ZnSO}_4 + 2\text{FeSO}_4 + \text{S}^0 \quad (11)$$

One again the fraction reacted in different temperatures were plotted versus time for different models, in order to determine the kinetics. Among mentioned models, two models fitted much better to the data. Table 6 presents the correlation coefficients of the kinetics models at different reaction temperatures for these two models which included reaction-controlled model and diffusion-controlled model. However, the diffusion-controlled model presented a better fit to the kinetic data in almost all of the leaching experiments in comparison to the reaction-controlled model. As mentioned before, this phenomenon occurred due to sulfur formation in ZnS particles surface. Fig. 14 shows the plot of $K = 1 - \frac{2}{3} X - (1 - X)^{\frac{2}{3}}$ versus time for ZnS dissolution for this reaction.

It should be noted that the ZnS leaching with CFR at 35 °C was also conducted; however the fractions reacted for this test were very low (lower than 0.1 at the end of process). By plotting fraction reacted versus time based on the diffusion-controlled model, all calculated $K_t$ obtained were near zero. This shows that ZnS leaching at temperatures lower than 35 follows another kinetic mechanism. Thus more than one temperature is needed to study the kinetic mechanism and calculate activation energy. Therefore, leaching tests with CFR should be done in the lower temperatures (such as 25, 15 °C). However, because the purpose of leaching process is to maximize metals recovery, it is decided to remove the information for leaching test at 35 °C from kinetic modeling.

Comparing the ZnS leaching tests performed in presence of biological and ferric sulfate (Figs. 9 and 13) indicates that the dissolution kinetics with BFR is higher in the first 30 min. However, it decreased drastically after 30 min. The slope of zinc extraction versus time diagram (Fig. 9) is very high for first 30 min and then it decreased. On the other hand, the Zn extraction continued for around 150 min in the presence of ferric sulfate. This means that the sulfur layer is formed faster on minerals surface in the presence of BFR.

In addition, the biological ferric reagent contained different metals ions such as magnesium, manganese, copper, cobalt, phosphorous and nickel while chemical ferric reagent merely contained iron ions. These metals ions were added to the reagent during pyrite biooxidation step.
Electronegativity is a chemical property that describes the tendency of an atom or a functional group to attract electrons toward itself (Jensen, 1996). According to the Eq. (12), the Zn in the solid matrix is substituted by another element with higher electronegativity which causes ZnS dissolution by metathesis.

$$\text{ZnS} + \text{M}^{2+} \rightarrow \text{Zn}^{2+} + \text{MS}$$

These metathesis reactions could cause higher dissolution kinetics for ZnS in presence of BFR in first 30 min compared to CFR. However, after sulfur layer formation on the minerals surface, the ZnS leaching dropped.

The activation energy for mentioned reactions could be calculated by Arrhenius equation (Eq. (13)):

$$K_p = A \exp\left(-\frac{E_a}{RT}\right)$$

The Arrhenius equation is a formula for the temperature dependence of reaction rate. This equation has a vast and important application in determining rate of chemical reactions, and for calculation of activation energy, as well (Naveršnik and Jurečič, 2016). The activation energy is defined as the minimum energy which must be available to a chemical system with potential reactants to result in a chemical reaction. Rate constants for different temperatures were calculated from Figs. 10 and 14. It should be noted that the activation energy for ZnS dissolution with BFR was calculated only for the first mechanism, because as per its definition activation energy is the minimum energy for starting a reaction. The Arrhenius plots of ln $K_p$ versus $T^{-1}$ for ZnS leaching data (both for biological and chemical reagents) are shown in Fig. 15. The rate constants ($K_p$) were calculated from the slopes of each straight line in Figs. 10 and 14. By using the Arrhenius plots, the activation energies of 32 kJ/mol and 60 kJ/mol were calculated for the sphalerite dissolution in presence of biological ferric and sulfate ferric reagents, respectively. Therefore, it could be concluded that ZnS dissolve in presence of BFR easier than CFR, which is due to its lower activation energy. This occurs because of the catalyst effect of dissolved metals in BFR within pyrite biooxidation step.

The activation energy of a diffusion-controlled process was characterized to be from 4.2 to 13 kJ/mol, while for a chemically-controlled process, it is usually $> 42$ kJ/mol (Habashi, 1969). This means that the sphalerite dissolution in presence of biological ferric reagents follow the chemical-control and diffusion-control mechanisms simultaneously as it confirms the kinetic modeling results. However, the effect of chemical-control mechanism is more that diffusion-control mechanism because the activation energy for this reaction is near 42 kJ/mol. While ZnS dissolution with ferric sulfate just follows the chemical-control mechanism. In the other words, as activation energies and kinetics modeling shows, the sphalerite leaching with ferric sulfate starts with chemical parameters while being limited under diffusion parameters.

Apart from previous experiments, one more test was carried out to compare the ZnS leaching in presence of ferric chloride with two other ferric reagents. All the conditions for this test, including ferric...
concentration, pH, pulp density etc., were identical to other tests. This test was performed at 90 °C. Fig. 16 shows the zinc extraction for these three reagents. The final zinc recoveries were 70%, 99% and 83% in presence of biological ferric reagent, ferric sulfate and ferric chloride, respectively. According to this diagram, ZnS dissolved rapidly during first 20 min in presence of FeCl₃; however after this period the sphalerite dissolution stopped completely. Dichromate titration of pregnant leach solution showed that ferrous concentration became constant after around 20 min. This means that although ferric ions (as chemical reagent) were available in the environment, but sulfide minerals leaching stopped. Therefore, it could be concluded that this reaction was control by a diffusion mechanism.

4. Conclusions

ZnS dissolution with biological ferric reagent and ferric sulfate was
studied in this research work. The kinetics modeling of ZnS dissolution in presence of biological ferric reagent showed that this reaction follows the mechanism of interfacial transfer and diffusion across the product layer during first minutes, while the mechanism was changed and re-action was limited by diffusion parameters after about 60 min. On the other hand, the ZnS dissolution with chemical ferric sulfate is best described by diffusion control. The surface studies confirmed that the formation of elemental sulfur on the minerals surface would limit these reactions. The zinc recovery for the one step bioleaching was 90% which was achieved after 20 days of processing by Acidithiobacillus thiooxidans and Acidithiobacillus ferrooxidans. The final zinc recoveries were 70%, 99% and 83% in presence of biological ferric reagent, ferric sulfate and ferric chloride, respectively. These recoveries were achieved after 200 min leaching at 90 °C. Although the zinc recovery with two-step bioleaching was lower than one-step bioleaching, this new method can decrease the process time from few days to a few minutes. For future studies, it is suggested to replace the BFR by acid mine drainage (AMD) which contains high ferric concentration. Using AMD as the leaching lixiviant would be a good strategy to turn an environmental problem to an economic opportunity.

Acknowledgments

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