STUDY ON THE JAROSITE MEDIATED BY BIOLEACHING OF PYRRHOTITE USING *Acidthiobacillus* FERROOXIDANS

ESTUDO SOBRE A JAROSITA MEDIADA PELA BIOLIXIVIAÇÃO DA PIRROTITA USANDO Acidithiobacillus *FERROOXIDANS*

Kaile ZHAO*[1,2]; Guohua GU*[1]; Xiaohui WANG[2]; Wu Yan[2]; Guanzhou QIU[1]

1. School of Minerals Processing and Bio-engineering, Central South University, Changsha-410083, China; 2. Institute of Multipurpose Utilization of Mineral Resources, CAGS, Chengdu-610041, China. guguohua@126.com; zhaokaile0557@sina.com

ABSTRACT: Precipitation of jarosite is a very important phenomenon that is observed in the bioleaching of pyrrhotite by *Acidthiobacillus ferrooxidans* (*A. ferrooxidans*). Jarosite is a major secondary mineral formed in acid supergene environment by oxidation of metal sulphide. The formation of jarosite could decrease leached percentage. The Eh-pH diagram of $FeS_{1.12}$-H_2O showed that the thermodynamic parameters of the jarosite were exists steadily on Eh=360～800, pH=2.8～5, and the results of pH condition test is consonant with the conclusions of thermodynamic analysis. By means of XRD and SEM, it could indicate that full propagation of *A. ferrooxidans* in the solution is beneficial to the formation of jarosite and jarosite mediated by bacterial has a better crystalline form than that synthesized by chemical method. This study indicates that pH value and ferrous/ferric iron concentration are key factors affecting the formation of jarosite. Leached percentage is higher when frequency was set more than 2.0. It is crucial to minimize jarosite formation in order to increase factory's efficiency.

KEYWORDS: Pyrrhotite. Bioleaching. *Acidthiobacillus ferrooxidans.* Jarosite.

INTRODUCTION

Jarosite is a major secondary mineral formed in acid supergene environment by oxidation of metal sulphide. *Acidthiobacillus ferrooxidans* (*A. ferrooxidans*) occurred extensively in metal sulphide ore district that has an important effect on oxidation of metal sulphide and formation of secondary minerals (ZHANG et al., 2013, ZHU et al., 2005). However, the depositing process of jarosite during biological metallurgy of sulfide ore has more harmful impact. Jarosite formation has negative effects on many applications that require the use of *A. ferrooxidans*, especially in the biological process of gas desulphurization and biological metallurgy of sulfide ore (JENSEN et al., 1995). Also, jarosite formation in coal desulfurization results in residual sulfur, which cannot be removed from coal (DAOUD et al., 2006). So it is crucial to minimize jarosite formation in order to increase efficiency and it has enlightenment function to practical industry production.

There are several factors that play a role in rate of oxidation of ferrous ions by *A. ferrooxidans.* These factors include ferrous/ferric iron concentration, cell and oxygen concentrations, pH, temperature and reactor type. Moreover, the pH has significant effects on the formation of jarosite which produced during bioleaching of pyrrhotite (DAOUD et al., 2006, GU et al., 2013, POGLIANI et al., 2000, SONDI et al., 2001).

Several studies have been conducted in order to determine the importance of jarosite formation in bioreactors. But their same method is that studying on the jarosite during cultivation of bacteria (GAO et al., 2007, GU et al., 2013, POGLIANI et al., 2000, ZHENG et al., 2005, ZHU et al., 2005), such as *A. ferrooxidans* and *L. ferrooxidans*. Nevertheless, no experience on the production of jarosite by bio-metallurgy of sulfide ore that has been studied.

The main goal of this study was to investigate jarosite precipitation under different conditions and analyze the formation of thermodynamics condition to mediate precipitation of jarosite, and this results will be very important for determining the environment of ore leaching for minimize jarosite precipitation. Besides, for revealing the role of *A. ferrooxidans* in natural process of jarosite formation more reasonably, this paper was designed for leaching ore experiment, analysis of chemical and biogenic cause on the jarosite, combining with XRD and SEM, and had a further research on the effect of *A. ferrooxidans* on the jarosite formation in natural process. Study on the deposit production in leaching process was more according to practical geochemistry process, and it provides reference for practical production.

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MATERIAL AND METHODS

Jarosite formation

A. ferrooxidans can obtain energy from the oxidation of different inorganic substances, the most common substance is ferrous sulfate. The overall biochemical reaction of the oxidation of ferrous ions is

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{T.f} 4Fe^{3+} + 2H_2O \quad (1)$$

This bioreaction took a great part in practical process (DAOUD et al., 2006).

Since there is consumption of hydrogen ions, the pH of the liquid media initially increased. However, while this pH was increased, counteracted by the hydrolysis of ferric iron. Therefore, it is quite visible that the pH of the system has an effect on the extent of the oxidation and hydrolysis reactions. Furthermore, there is a reaction in competition with the hydrolysis reaction giving products of basic ferric hydroxysulphates with the formula $MFe_3(SO_4)_2(OH)_6$, where M = K^+, Na^+, NH_4^+, Ag^+, or H_3O^+[5,6]. These hydroxysulphate precipitates were known as jarosites. The following is the formula for jarosite precipitation:

$$M^+ + 3Fe^{3+} + 2SO_4^{2-} + 6H_2O \longrightarrow MFe_3(SO_4)_2(OH)_6 + 6H^+ \quad (2)$$

Since the 9K medium or leaching solution contains a high concentration of NH_4^+ ions, the jarosites were produced in ammoniojarosites form with formula $NH_4Fe_3(SO_4)_2(OH)_6$ (WANG et al., 2005, WANG et al., 2006).

Thermodynamics analysis

Eh-pH diagram of $FeS_{1.12}$ -H_2O system and it's analysis

Thermodynamic analysis during the process of bioleaching sulfide minerals is one of the most important theoretical analysis. Through thermodynamic reaction analysis during the leaching process of sulfide minerals, this study is to discuss about the condition of thermodynamic during bioleaching sulfide minerals. The general thermodynamics laws of the process were analyzed by using the Eh-pH diagram of $FeS_{1.12}$-H_2O system (QIN et al., 1999).

The chemical formula of pyrrhotite is $FeS_{1.12}$, all kinds of the iron compounds and sulfur compounds exist in bioleaching of pyrrhotite system. According to the Nernst equation, the possible equilibrium equations of reaction in the $FeS_{1.12}$-H_2O system have been obtained which are showed in the Table 1.

Table 1. The possible chemical equations of pyrrhotite.

NO.	**Reaction Equation**	Potential Equations.
a	2 H^++e= H_2	E=-0.059pH
b	$O_2 + 4H^+ + 4e = 2H_2O$	E=1.229-0.059pH
1	$S + 2H^+ + 2e = H_2S$	E=0.142-0.059pH
2	$HSO_4^- + 7H^+ + 6e = S + 4H_2O$	E=0.338-0.069pH
3	$SO_4^{2-} + 8H^+ + 6e = S + 4H_2O$	E=0.357-0.079pH
4	$SO_4^{2-} + H^+ = HSO_4^-$	pH=1.9
5	$Fe^{3+} + e = Fe^{2+}$	E=0.770
6	$Fe(OH)_3 + 3H^+ = Fe^{3+} + 3H_2O$	pH=1.72
7	$Fe(OH)_3 + 3H^+ + e = Fe^{2+} + 3H_2O$	E=1.02-0.146pH
8	$KFe_3(SO_4)_2(OH)_6 + 8H^+ = K^+ + 3Fe^{3+} + 2HSO_4^- + 6H_2O$	pH=2.80
9	$KFe_3(SO_4)_2(OH)_6 + 8H^+ + 3e = K^+ + 3Fe^{2+} + 2HSO_4^- + 6H_2O$	E=0.672-0.157pH
10	$KFe_3(SO_4)_2(OH)_6 + 6H^+ + 3e = K^+ + 3Fe^{2+} + 2SO_4^{2-} + 6H_2O$	E=0.597-0.118pH
11	$2Fe^{2+} + 1.12SO_4^{2-} + 8.96H^+ + 7.72e = FeS_{1.12} + Fe^{3+} + 4.48H_2O$	E=0.208-0.068pH
12	$2Fe^{2+} + 1.12HSO_4^- + 7.84H^+ + 7.72e = FeS_{1.12} + Fe^{3+} + 4.48H_2O$	E=0.191-0.060pH
13	$Fe(OH)_3 + 1.12SO_4^{2-} + 11.96H^+ + 9.72e = FeS_{1.12} + 7.48H_2O$	E=0.366-0.037pH
14	$Fe(OH)_3 + 1.12HSO_4^{2-} + 10.84H^+ + 9.72e = FeS_{1.12} + 7.48H_2O$	E=0.456- 0.084pH

Calculation was using the parameter which is close to the leaching test system. Activities of aqueous sulphur species and iron species was 1.0mol·L^{-1} and 0.01mol·L^{-1} , respectively. The reaction of bioleaching is usually in response on pH = 1.5 ～4.5, Eh = 300～900mv, so in the Eh-pH diagram, took the pH = 0～5.0, E =- 0.2～1.0V. According to the parameters which we set in the test system based on the Portland's manual data, Fig. 1 showed relations among the equilibrium reaction （ ZHANG, 2007).

The Figure 1 indicates that in the $FeS_{1.12}$-H_2O system, the region which sulfur deposition exists steadily was composed by pH = 0, pH = 5, and 1, 2, 3 phase equilibrium lines. The sulfur mainly exist in the form of H_2S below the region and stable in HSO_4^- or SO_4^- form above it. From the diagram, when the pH is in 1～5 and the Eh is in 400～900mV,the elemental sulfur can not exist steadily. But in the actual extraction process, redox reactions need to overcome a certain barrier, so sulfur maybe exists in this context.

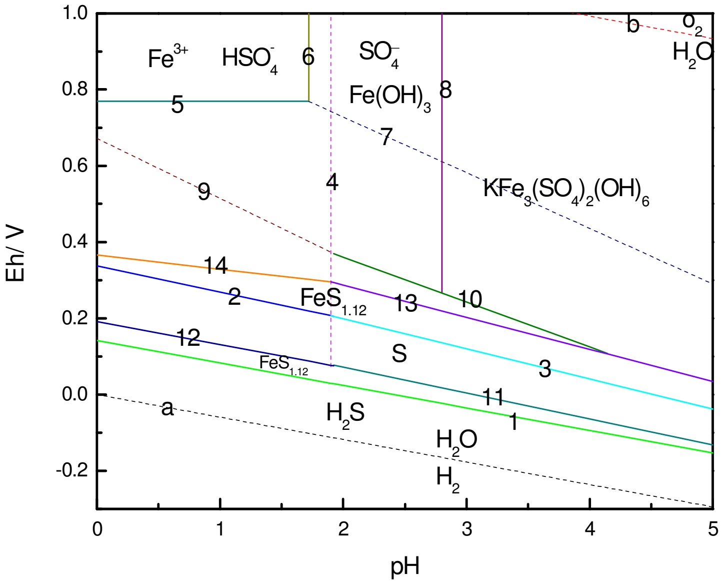

Figure 1. Eh-pH diagram for $FeS_{1.12}$-H_2O system (298K, 1.013×10^{5}Pa).

$$\{\alpha_{Fe^{2+}} = \alpha_{Fe^{3+}} = 0.01 mol \bullet L^{-1}, \quad \alpha_{K^+} = 0.001 mol \bullet L^{-1}, \alpha_{HSO_4^-} = \alpha_{SO_4^{2-}} = \alpha_{H_2S} = 1.0 \mathrm{mol} \bullet \mathrm{L}^{-1}\}$$

The region which Fe^{3+} exists steadily was enclosed by the lines of 5, 6 and the line of pH=0. So we can infer that Fe^{3+} exists steadily when the potential was above 770mv.When the Fe^{3+} reduced, the line 6 move to the right, and the region which Fe^{3+} exists steadily extend to the right. In practical leaching system, when pH is in 2.28～4.0, Eh is in 360～800mv, Fe^{3+} may be mainly exist in the form of precipitates [11].

The Fig. 1 shows that the region which $KFe_3(SO_4)_2(OH)_6$ exists steadily was composed by 8,10,13 phase equilibrium lines and the line of pH=5.The stability region was above 360mv. $KFe_3(SO_4)_2(OH)_6$ generates and exists steadily when the pH is more than 2.80. Thus it is concluded that the thermodynamic parameters of the $Fe_3(SO_4)_2(OH)_6$ exists steadily were at Eh=360～800,pH=2.8～5. This results was also consonant with the the nether experiment of pH condition.

From the diagram, the regions $FeS_{1.12}$ that exists steadily have two parts, one part was composed by the phase equilibrium lines of 2,3,13,14 and the lines of pH=0, pH=5, the other part was composed by the equilibrium lines of 1,11,12 and the lines pH=0, pH=5. The stability region was below 300mv and above the equilibrium line of H_2O/H_2, that can be said to be stable in aqueous solution. From the two-phase equilibrium lines, we can get that the products and the intermediate products were $Fe(OH)_3$,Fe^{2+},S↓,H_2S,HSO_4^- and SO_4^{2-} (OU et al., 2007).

Experimental analysis

Equipment

Based on procedure, the bacteria were grown in 11×250 ml Erlenmeyer flasks with the appropriate medium. The pH of each trial was adjusted using sulfuric acid and monitored using a pH meter (PH METER MODEL PHS-25).The bacteria were allowed to grow in a Rotary flask shaker with speed and temperature adjustment (New Brunswick Scientific Model No. HZD-C). For the ferric and total iron analyses, we used a spectrophotometer (U-Varian 9200) with the appropriate procedure. In order to detect compounds produced during bioleaching of pyrrhotite, at the end of experiment, filter paper with pore size 45μm was used to separate the jarosite produced on the wall of each flask., and air dried for X-ray diffraction(XRD), scanning electron microscopy(SEM) and energy spectrum analysis(EDS).

Chemicals and metallic minerals

All the chemicals used in this study were of analytical grade, including 10% and 20% H_2SO_4, the components of the 9K medium are given in Table 2. *A. ferrooxidans* which we used is supply by School of Minerals Processing & Bioengineering, Central South University. The grade of Fe in the pyrrhotite which used in these experiments is 57.32% and particle size is -0.043mm, the XRD of pyrrhotite is shown in Fig. 2 .It can be seen that except magnetic pyrite, it also has a few extraneous components, such as quartz, metasilicate and so on.

Table 2. Components of the 9K medium

Components	Contents
$(NH_4)_2SO_4$	3.0*g*
$MgSO_4 \cdot 7H_2O$	0.5*g*
$FeSO_4 \cdot 7H_2O$	44.2*g*
K_2HPO_4	0.5*g*
$Ca(NO_3)_2$	0.01*g*
KCl	0.1*g*
5 *mol/l* H_2SO_4	1.0*ml* to pH=1.8
Dist.H_2O	1000*ml*

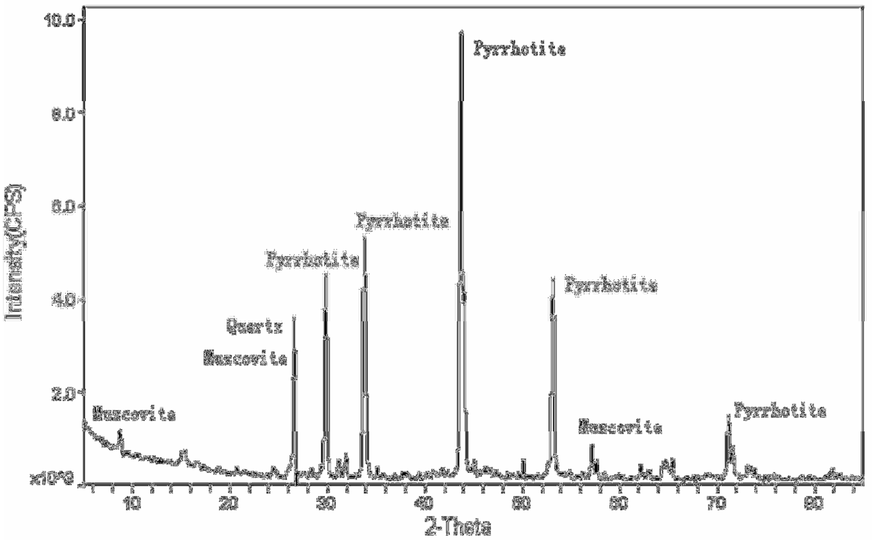

Figure 2. XRD of pyrrhotite which we used in this experimentation

Experimental method

This experiment deals with the effect of pH and the effect of *A. ferrooxidans* on the formation of jarosite. Therefore, the experiment was divided into two sections, dealing with varying pH and effect on the formation of *A. ferrooxidans* .

On this section, we discuss the effect of *A. ferrooxidans* on the formation of jarosite and analyze the different morphology of jarosite-group mediated from biologically and chemically (experiment I and II) condition and the effect of varying pH on jarosite formation (experiment Ⅱand Ⅲ). As shown in Table 3, three 250 ml Erlenmeyer flasks were used, the number for each flask is Ⅰ,Ⅱ and Ⅲ. 150 ml of 9K medium and 5g of pyrrhotite were added into each of 3 flasks. pH adjustment in each flask was obtained by adding 20% H_2SO_4 dropwise, with continuous agitation and pH measurement. Furthermore, 15ml of *A. ferrooxidans* inoculum was added to II and III flasks. The inoculum contained an average of 8×10^7 cells per milliliter. The flasks were then covered with pieces of aluminum foil. Finally, the flasks were placed in the rotary shaker at ambient temperature with 170rpm rotation speed.

Table 3. Experimental conditions in leaching of pyrrhotite

Number	Reactants	T/℃	Original pH	Experimental method
Ⅰ	9K, pyrrhotite	30	2.0	Set solution pH value to 2.0 every two days
Ⅱ	9K, 10ml *A. ferrooxidans*, 5g pyrrhotite	30	2.0	Set solution pH value to 2.0 every two days
Ⅲ	9K, 10ml *A. ferrooxidans*, 5g pyrrhotite	30	2.0	Set solution pH value to 2.0 every three days

RESULTS AND DISCUSSION

This experiment consisted of two parts of analysis, which are the effect of pH and the difference of the jarosite-group precipitates between biologically and chemically jarosite precipitation. For each parameter, we will discuss the data and observations.

Table 2 shows that Experiment Ⅰ and Experiment Ⅱ is a group of comparable parallel experiment. Corresponding to the course of ore leaching, the former is the chemosynthesis producing jarosite, the latter is ore leaching producing jarosite using *A. ferrooxidans* in the same condition (SASAKI et al., 2000, ZHOU et al., 2004). In this experiment, after adding to reaction system the pyrrhotite appeared opaque deposit in the fifth day, and in the tenth day its color became deeper and turned into brownish yellow. They commonly exist in the experiment. The solid substance, that were collected from Experiment Ⅰ and Experiment Ⅱ at last, is mainly jarosite deposit showed by X-ray diffractive and EDS analysis (Fig. 3). By observing the deposit of Experiment Ⅰ and Ⅱ separately with SEM and EDS (Fig. 4) (DING et al., 2007, XIA et al., 2008), we can see that jarosite crystal produced in the course of acid-leaching (Experiment I) developed incompletely, had hollow holes on its surface, and its deposit was irregularly round. It may be amorphous substance; however producing deposit of bioleaching process (Experiment Ⅱ) was comparatively pure jarosite, and its crystal was regular rhombohedron and leveling the crystal face. Therefore, it is different between producing deposit and crystal degree in biological process and chemical process. Compared to the nonsterile with sterile result, we can infer that the Fe^{2+} fast transform by *A. ferrooxidans* and can cause the supply rate of Fe^{3+} increase in mineral surface micro area, and resulted in faster formation of jarosite crystals (GAO et al., 2007). Therefore, we got a further understanding effect of *A. ferrooxidans* on the jarosite formation in natural process.

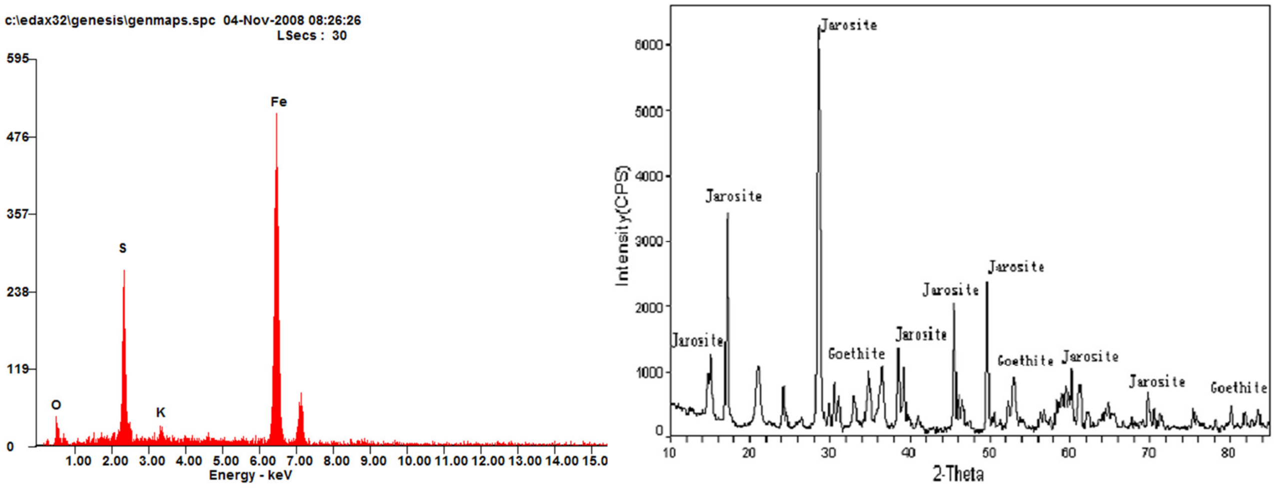

Figure 3. SEM and EDS of the jarosites from experiments Ⅰ and Ⅱ

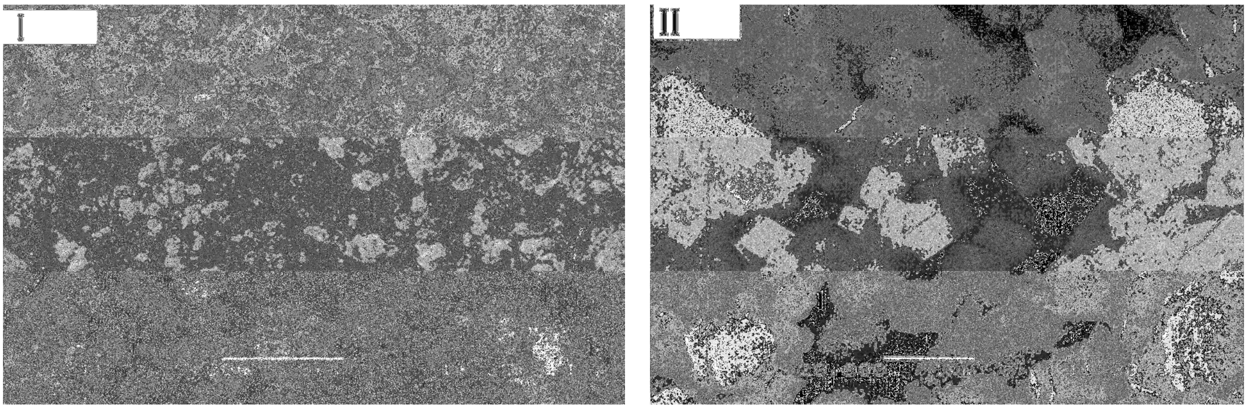

Figure 4. SEM of the jarosites from experiments Ⅰ and Ⅱ

Experiment Ⅱ and Experiment Ⅲ were also group of comparable experiment. The differences is only in regulating frequency of pH condition. Because pH value determines Fe^{3+} hydrolysis process directly, that it is decides whether the precursor of forming jarosite is formed, pH has a significant effect on the deposit forming rate. The research shows that the oxidation of pyrrhotite oxidation was fondness for acidic process, which pH value range from 1.8 to 2.8 the pyrrhotite produce less deposit during the process of leaching. So, when the adjustable frequence of pH value was higher, deposit production will be reduced. Therefore, the deposit produced in the Experiment Ⅱ was less than Experiment Ⅲ, and because of jarosite deposit produced in the oxidation process from Fe^{2+} to Fe^{3+} by *A. ferrooxidans*. Formation of jarosite lost part of Fe^{3+}, because Fe^{3+} involved in jarosite deposit, in the biological oxidation of pyrrhotite, total concentration of Fe^{3+} solution is less than real concentration, seriously affected the leaching rate (JIANG et al., 2007). The total concentration of Fe^{3+} leaching solution from Experiment Ⅱ and Experiment Ⅲ was assayed separately every fourth days, we obtained the change curve of leaching rate, shown on Figure 5 as follow.

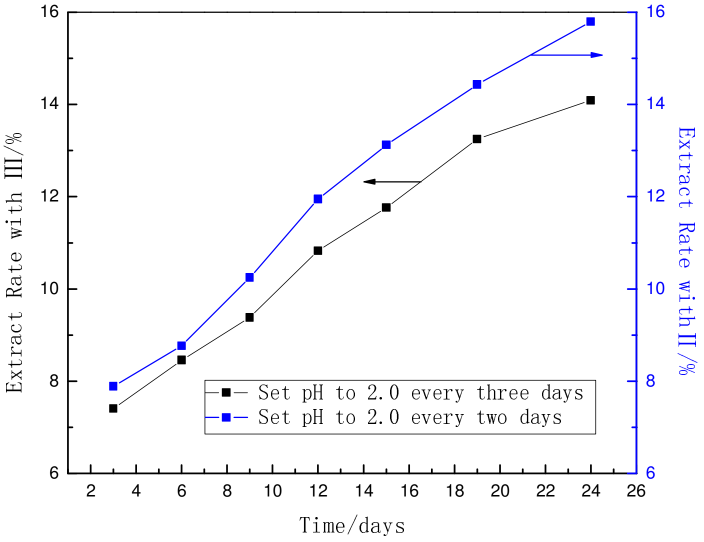

Figure 5. Change of Extract Rate with time in *A. ferrooxidans* leaching pyrrhotite systems

The Figure 5 shows that the leaching rate of the both rised gradually, and the leaching rate of Experiment Ⅱ always larger than Experiment Ⅲ. In the process of leaching pyrrhotite system, lot of jarosite precipitation were produced because of exsiting inorganic nutrient that needed for bacterial growth (such as k^+、 Na^+ NH_4^-), as the leaching process was going, the pH and potential rase, due to Fe^{3+} took part in the reaction and they covered on the surface of mineral, which unfavorable to this leaching process. Therefore, controlling pH value appropriately can reduce the quantity of deposit forming, so as to increase the leaching rate relatively, it has enlightenment function to practical industry production (controlling pH value appropriately), and also to improve the leaching rate and production efficiency.

CONCLUSIONS

From the Eh-pH diagram of $FeS_{1.12}$-H_2O, we can concluded that the conditions of jarosite that given at least Eh<360mv, pH<2.8,and the results of pH condition test was consonant with the conclusions of thermodynamic analysis. So when some factory acts as biological metallurgy of sulfide ore, the frequency is set to pH 1.8, and the leached percentage was higher.

Study on the deposit production in leaching process was more in line to the practical geochemical process, it provides reference for practical production.

This paper also indicates that jarosite mediated by bacteria has a better crystalline form than that synthesized by chemical method. So we got a further understanding on the effect of *A. ferrooxidans* on the jarosite formation in natural process.

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RESUMO: A precipitação de jarosite é um fenômeno muito importante que é observado na biolixiviação da pirrotita por Acidithiobacillus ferrooxidans (A. ferrooxidans). A jarosita é um mineral secundário principal formado no ambiente supergênico ácido pela oxidação do sulfureto do metal. A formação de jarosite pode diminuir a porcentagem de lixiviação. O diagrama de Eh-pH de FeS1.12-H2O mostrou que os parâmetros termodinâmicos da jarosite estavam firmemente presentes em Eh = 360~800, pH = 2.8~5, e os resultados do teste de condição de pH estão em consonância com as conclusões da análise termodinâmica. Por meio de XRD e SEM, pode ser indicado que a propagação completa de A. ferrooxidans na solução é benéfica para a formação de jarosite e jarosite mediada por bactérias tem uma forma cristalina melhor do que a sintetizada por método químico. Este estudo indica que o valor do pH e a concentração de ferro ferroso/férrico são fatores chave que afetam a formação de jarosite. A porcentagem de lixiviação é maior quando a freqüência foi ajustada a mais de 2,0. É crucial para minimizar a formação de jarosite, a fim de aumentar a eficiência da fábrica.

PALAVRAS-CHAVE: Pirrotita. Biolixiviação. Acidithiobacillus ferrooxidans. Jarosite.

REFERENCES

DAOUD J, KARAMANEV D. Formation of jarosite during Fe2+ oxidation by Acidithiobacillus ferrooxidans. Minerals Engineering, v. 19, p. 960–967. 2006. http://www.sciencedirect.com/science/article/pii/S0892687505004139 . https://doi.org/10.1016/j.mineng.2005.10.024

DING JIAN-NAN, GAO JIAN, WU XUE-LING, ZHANG CHENG-GUI, WANG DIA-ZUO, QIU GUAN-ZHOU. Jarosite-type precipitates mediated by YN22, Sulfobacillus thermosulfidooxidans, and their influences on strain. *Transactions of Nonferrous Metals Society of china*, v. 17, p. 1038-1044. 2007. http://d.wanfangdata.com.cn/Periodical/zgysjsxb-e200705029 . https://doi.org/10.1016/S1003-6326(07)60222-2

GAO JIAN, PENG HONG, LI BANG-MEI, WU XUE-LING, DING JIAN-NAN, QIU Guan-zhou. Discrepant analysis of iron precipitate synthesized by two strains of different iron-oxidizing bacteria. *The Chinese Journal of Nonferrous Metals*, v. 3, p. 453-458. 2007. http://lib.cqvip.com/qk/97361X/200703/24092597.html

GU G H, HU K T, ZHANG X, XIONG X X, YANG H S. The step wise dissolution of chalcopyrite bioleached by Leptospirillum ferriphilum. Electrochimica Acta. v. 103, p. 50-57. 2013. http://www.sciencedirect.com/science/article/pii/S0013468613007068 . https://doi.org/10.1016/j.electacta.2013.04.051

GU G H, YANG H S, WANG C Q. Bioleaching of pyrrhotite by moderately and extremely ther mophilic bacteria. Advanced Materials Research. v. 825, p. 274-279. 2013. http://xueshu.baidu.com/s?wd=paperuri:(24cda59ee5a695465c75e75858b7f924)&filter=sc_long_sign&sc_ks_para=q%3D

JENSEN A B, WEBB C. Ferrous sulfate oxidation using Acidthiobacillus ferrooxidans: a review. Process Biochemistry, v. 30 , p. 225-236. 1995. http://www.sciencedirect.com/science/article/pii/003295929585003I . https://doi.org/10.1016/0032-9592(95)85003-1

JIANG LEI, ZHOU HUAI-YANG, PENG XIAO-TONG. Bioleaching of pyrite ,chalcopyrite and pyrrhotite using Acidthiobacillus ferrooxidans. Science Bulletin, v. 52, p. 1802-1813. 2007. https://www.researchgate.net/publication/225615345

OU LE-MING , HE RONG-QUAN , FENG QI-MING. Pyrite Leaching in Germ-free System and Thermodynamic Analysis. *Nonferrous Metals*, v. 59, p.87-90. 2007. http://xueshu.baidu.com/s?wd=paperuri:(c0605ffe6558e802a2033cf712cece35)&filter=sc_long_sign&sc_ks_para=q%3D

POGLIANI C, DONATI E. Immobilisation of Acidthiobacillus ferrooxidans: importance of jarosite precipitation. Process Biochemistry. Process Biochemistry, v. 35, p. 997-1004. 2000. http://xueshu.baidu.com/s?wd=paperuri:(401c26fec3169c75932d27c5ff8c0bad)&filter=sc_long_sign&sc_ks_para=q%3D . https://doi.org/10.1016/S0032-9592(00)00135-7

QI F J, FENG Y L, LI H R. Leaching characteristics and recovery method of nickel from low-grade nickel-pyrrhotite. Journal of University of Science and technology Beijing, v.33, p. 1065-1070. 2011. http://d.wanfangdata.com.cn/Periodical/bjkjdxxb201109005

QIN WEN-QING, QIU GUANZHOU, XU JIN. Electrodepostion and adsorption of dixanthogen on the surface of pyrrhotite electode. *China Mining magazine* , v. 1, p, 73-76. 1999. http://xueshu.baidu.com/s?wd=paperuri:(24847af0cb183fa3a42065ef90c04c1f)&filter=sc_long_sign&sc_ks_para=q%3D

SASAKI K, KONNO H. Morphology of jarosite-group compounds precipitated from biologically and chemically oxidized Fe ions. *Canadian Mineralogist,* v.38, p. 45–56. 2000. http://xueshu.baidu.com/s?wd=paperuri:(12a8da9d2a0c5fc627eaa72f65848960)&filter=sc_long_sign&sc_ks_para=q%3D . https://doi.org/10.2113/gscanmin.38.1.45

SONDI I, SNI S, MATIJEVIC E. Precipitation of monodispersed basic iron(III) sulfate (sodium jarosite) particles. Colloid Polym Sci, v. 279, p. 161-165. 2001. http://xueshu.baidu.com/s?wd=paperuri:(1e8eb034f6836fbf1c0587649652be09)&filter=sc_long_sign&sc_ks_para=q%3D . https://doi.org/10.1007/s003960000401

WANG CHANG-QIU, MA SHENG-FENG, LU AN-HUAI. Experimental study on formation conditions of ammoniojarosite and its environmental significance . Acta Geologica Sinica, v. 80, p. 296–301. 2006. http://xueshu.baidu.com/s?wd=paperuri:(a715c2762612c71ce1f39dd5fd182ea0)&filter=sc_long_sign&sc_ks_para=q%3D

XIA LE-XIAN, LIU JIAN-SHE, XIAO LI, ZENG JIA, LI BAN-MEI, GENG MEI-MEI, QIU GUAN-ZHOU. Single and cooperative bioleaching of sphalerite by two kinds of bacteria-Acidithiobacillus ferriooxidans and Acidithiobacillus thiooxidans. Transactions of Nonferrous Metals Society of china, v. 18, p. 190-195. 2008. http://xueshu.baidu.com/s?wd=paperuri%3A%28c27c13d0b0bd8d59ae0b015ad9e8b009%29&filter . https://doi.org/10.1016/S1003-6326(08)60034-5

ZHENG YU, DI JIN-SHEN, LIU YAN-HUA, LI YING-JIE, HU BIN. Study of precipitation produced during culture of Thiobacillus ferrooxidan. Biotechnology, v. 15, p. 66-69. 2005. http://xueshu.baidu.com/s?wd=paperuri:(e00c831eced09af1f91c1ed84561c3e8)&filter=sc_long_sign&sc_ks_para=q%3D

WANG Chang-qiu, MA Sheng-feng, LU An-huai, ZHOU Jian-gong. The formation conditions of jarosite and its environmental significance. Acta Petrologica Et Mineralogica, v. 24, p. 607−611. 2005. http://en.cnki.com.cn/Article_en/CJFDTotal-YSKW200506021.htm

ZHANG X, GU G H, HU K T, QIU G Z. Differences of Bioleaching of Pyrites from Different Geo-genetic Depositsby Leptospirillum ferriphilum. Advanced Materials Research . v.825, p. 326-330. 2013. http://xueshu.baidu.com/s?wd=paperuri:(24cda59ee5a695465c75e75858b7f924)&filter=sc_long_sign&sc_ks_para=q%3D

ZHANG YAN-SHENG , The bioleaching of low grade copper sulphide ore. Central South University *:Master Graduate Paper*. 2007.

ZHOU SHUN-GUI, ZHOU LI-XIANG. Biosynthesis and characterization of jarosite. Spectroscopy and Spectral Analysis, v. 24, p. 1140−1143. 2004. http://en.cnki.com.cn/Article_en/CJFDTOTAL-GUAN200409032.htm

ZHU CHANG-JIAN, LU JIAN-JUN, LU XIAN-CAI, WANG RU-CHENG, LI QI. SEM study on jarosite mediated by Acidthiobacillus ferrooxidans . Geological Journal of China Universities, v.11, p. 234−238. 2005. http://en.cnki.com.cn/Article_en/CJFDTOTAL-GXDX200502010.htm