IRON CONTAINING MINERALS IN THE BIOX PROCESS

Nurmurodov To'lkin Isomurodovich
Navoi State Mining and Technology University
Professor

Saidova Nodira Urol kizi
Navoi State Mining and Technology University
2nd year Master's degree student

ABSTRACT

As a result of biooxidation, iron-containing minerals are formed, including jarosite, iron arsenate, goethite and other minerals. Jarosite is a relatively rare iron hydroxosulfate mineral. Interest in jarosite mineral has been growing in recent years. Jarosite plays an important role in acid mine drainage (AMD) pollution. AMD pollution, that is, the release of toxic metals into the environment, occurs as a result of any mining process.

Key words: bacterial oxidation, cyanidation, Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans, jarosite.

The use of bacterial oxidation process in the treatment of sulphide ores has been recognized as environmentally safe and economical. This process allows for the elimination of SO_2 and As_2O_3 gases as present in the roasting process. Again due to the low operating temperatures of 35 - 45 °C, the operating cost of bacterial oxidation is relatively lower. The formation of jarosites causes problems in cyanidation processes for gold recoveries, by causing kinetic barrier between the particles and the dissolving agents. These problems could impact the economics of the process. Jarosites are stable under acidic conditions (pH 1-7) but break down at higher pH (>10.5). Therefore, under the basic conditions required to leach gold, the jarosites break down, reacting with lime to form undesirable ferric hydroxide [1].

$Fe(OH)SO_4 + Ca(OH)_2 \rightarrow Fe(OH)_3 + CaSO_4$

The BIOX process is a biohydrometallurgical process, which was developed for precyanidation treatment of refractory gold ores or concentrates. The bacterial culture consists of a mixed culture of Acidithiobacillus ferrooxidans, Acidithiobacillus thiooxidans and Leptospirillum ferrooxidans.[2,3,4]

In order to attain the highest rate of sulphide oxidation, the number of bacterial cells and their activity is optimised under controlled plant conditions. The bacteria require a very acidic environment (pH 1.0 to 4.0), a temperature of between 30 and 45 °C, and a steady supply of oxygen and carbon dioxide for optimum growth and activity. The reactions that occur in the process are oxidation and hydrolysis [5]. The oxidation reactions are:

$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$

$4FeSO_4 + 2H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$

$4FeS_2 + 15O_2 + 2H_2O \rightarrow 2Fe_2(SO_4)_3 + 2H_2SO_4$

$4FeAsS + 11O_2 + 2H_2O \rightarrow 4HAsO_2 + 4FeSO_4$

$HAsO_2 + 2FeSO_4 + H_2SO_4 + O_2 \rightarrow Fe_2(SO_4)_3 + H_3AsO_4$

$4FeAsS + 13O_2 + 2H_2SO_4 + 2H_2O \rightarrow 2\ Fe_2(SO_4)_3 + 2H_3AsO_4 + 2HAsO_2$

The main end-product of the oxidation reaction is ferric sulphate. The ferric sulphate formed, hydrolyses in aqueous solutions. The extent of the ferric iron hydrolysis is dependent on the pH; in general, ferric iron has an extremely low solubility at a pH of > 2.5. A complete reaction for the hydrolysis is the formation of basic ferric sulphates which have the general formula $XFe_3(SO_4)_2(OH)_6$, where $X=K^+$(potassium jarosite), Na^+ (natrojarosite), NH_4^+ (ammoniojarosite), or H_3O^+ (hydroniumjarosite).

The hydrolysis reactions include [6]:

$Fe_2(SO_4)_3 + 3H_2O \rightarrow Fe_2O_3 + 3H_2SO_4$

The overall reaction is given by the combination of reactions:

$4FeS_2 + 15O_2 + 8H_2O \rightarrow 2Fe_2O_3 + 8H_2SO_4$

Further reactions lead to the formation of jarosites.

$Fe_2(SO_4)_3 + 2H_2O \rightarrow Fe(OH)SO_4 + H_2SO_4$

$3Fe_2(SO_4)_3 + 14H_2O \rightarrow 2H_3OFe_3(SO4)_2(OH)_6$

$3Fe_2(SO_4)_3 + M_2SO_4 + 12H_2O \rightarrow 2MFe_3(SO_4)_2(OH)_6 + 6H_2SO_4$

$(M = Ag^+, NH_4^+, K^+, 1/2Pb^{2+})$

Complexing Characteristics of iron in gold processing

In complexes iron has an electronic configuration of $(Ar)4s^2 3d^6$. The most common oxidation states for iron are +2 and +3. Moreover, the oxidation states +6, 0, -1 and - 2 are of importance. In contrast to osmium, iron never reaches its potential full oxidation state of +8 as a group VIII element. In air, most iron (II) compounds are readily oxidised to their iron (III) analogs, which represent the most stable and widespread iron species. For iron (II) complexes ($[Ar]4s^0 3d^6$) a coordination number of six with an octahedral ligand sphere is preferred. Iron (III) ($[Ar]4s^0 3d^5$) can coordinate three to eight ligands and often exhibits an octahedral coordination. Iron (III) generally is a harder Lewis acid than iron (II) and thus binds to hard Lewis bases. Iron (0) mostly coordinates five or six ligands with trigonal bipyramidal and octahedral geometry. Iron (–II) is tetrahedrally coordinated. Iron in low oxidation states is most interesting for organometallic chemistry and in particular for iron catalysed reactions because they can form more reactive complexes than their iron (II) and iron (III) counterparts. Therefore, iron (0) and iron (–II) compounds are favoured for iron catalysis. Iron carbonyl complexes are of special interest due to their high stability with an iron (0) centre capable of coordinating complex organic ligands, which represents the basis for organoiron chemistry [7].

The jarosite family of compounds, $AFe_3(SO_4)_2(OH)_6$, consists of compounds where A is: H_3O^+, Na^+, K^+, Rb^+, Ag^+, NH_4^+, T^+, Pb^{2+} or Hg^{2+} [8]. Most natural jarosites can be considered as solid solutions of jarosite [$KFe_3(SO_4)_2(OH)_6$], natrojarosite [$NaFe_3(SO_4)_2(OH)_6$] and hydronium jarosite [$H_3OFe_3(SO_4)_2(OH)_6$] [9]. Synthetic jarosite are readily precipitated from sulphate rich solutions containing 0.025 to 3.0 M

Fe(III)[10]. The lower limit of Fe(III) for jarosite precipitation is near 0.001 M. If there are excess alkali metal ions available, the fraction of iron that is precipitated is independent of the iron concentration in solution[11]. Consequently, the total amount of jarosite formed is directionally proportional to the concentration of Fe(III) in solution.

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