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Preparation of ammonium jarosite from clinker digestion solution of nickel oxide ore roasted using $(NH_4)_2SO_4$

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Abstract: To obtain the appropriate conditions for eliminating Fe^{3+} from $NiSO_4$ solution, the digestion solution of the clinker was used as raw material, which was obtained from roasting the nickel oxide ore with $(NH_4)_2SO_4$. The ammonium jarosite was successfully synthesized from the solution with analytic grade NH_4HCO_3. The effects of reaction temperature, reaction time, end pH value of reaction on the removal rate of iron were investigated, and the effect of the initial concentration of Fe^{3+} was also discussed. All of those factors had significant effects on the removal rate of Fe^{3+}, among which the reaction temperature was the most prominent. The appropriate reaction conditions were concluded as follows: reaction temperature 95 °C, reaction time 3.5 h, end pH value of reaction 2.5 at initial concentration of Fe^{3+} 19.36 g/L. The physical aspect of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ was cluster figure composed of sheet or prismatic particles with smooth surface.

Key words: nickel oxide ore; ammonium jarosite; influence factor; digestion solution

1 Introduction

Nickel is an important nonferrous metal which is widely used in stainless steel, electroplating, etc [1−2]. Nowadays, nickel is mostly produced form sulfide ores. Because of the immoderately exploitation, the high grade ore, especially sulfide ore is exhausted gradually. The sulfide ore's insufficient makes the utilization of nickel oxide ore urgent, especially the low grade oxide ore, which is the largest resource containing nickel [3−5]. Nickel is found in oxide/silicate minerals formed through the chemical weathering of nickeliferous peridotite rock under humid climate [6,7]. Both pyrometallurgical and hydrometallurgical routes were used in dealing with the nickel oxide ore; however, the pyrometallurgical methods were inadvisable because of high consumption of energy, as well as heavy pollution of gas and waste residue, and the pyrometallurgical route is only suitable to treat the mineral with high grade nickel [8−10]. Commonly, the hydrometallurgical routes consist of reduction roasting followed by ammonia leaching, sulfuric acid leaching and high pressure sulfuric acid leaching, among which the sulfuric acid leaching is the most development prospect process [11,12]. In acid leaching process using H_2SO_4, silica gel is unavoidably generated, which makes the filtration difficulty [13,14]. A new technology, which roasts laterite nickel ore using $(NH_4)_2SO_4$ and by which the obtained clinker is then digested in water, is presented. After filtration, the filtrate is gained, including the valuable metal ions, such as Ni^{2+}, Mg^{2+}, Fe^{3+}/Fe^{2+} and Al^{3+}. The application of roasting nickel oxide ore using $(NH_4)_2SO_4$ can guarantee that Fe^{3+} and Al^{3+} are extracted at a lower efficiency, but they still must be removed. The main impurities in solution are iron and aluminum, as well as trace elements of chromium, cobalt, etc.

Precipitation of iron in the chemical form of jarosite is widely adopted in hydrometallurgy, especially in zinc producing [15,16]. This process shows remarkable liquid−solid separation properties, and the minimum loss of valuable metals [17,18]. In this work, the digestion solution of the clinker obtained from roasting the nickel oxide ore using $(NH_4)_2SO_4$ was used as raw material. The analytic grade NH_4HCO_3 was used to remove iron in solution through synthesizing ammonium jarosite. The influence factors including reaction temperature, reaction time, end pH value of reaction, as well as the initial

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concentration of iron ion on the removal of Fe^{3+} were investigated.

2 Experimental

2.1 Materials

The low-grade nickel oxide ore was dried in a drying oven, and then was crushed and grinded using a medicine grinder until the size of the ore powder was about 75 μm. The ore powder was mixed uniformly with the industrial grade $(NH_4)_2SO_4$, and then was put into a roasting furnace equipped with a temperature controller with a display screen. The material was roasted under a desired temperature schedule. After that, the roasting clinker was added into water at a certain liquid to solid ratio. The digestion solution and residue were obtained after filtration. The residue was washed and dried. The as-obtained solution was used as raw material. The analytic grade ammonium bicarbonate was used as reagent to make ammonium jarosite. Distilled water was also used to wash the filter cake after each experiment.

2.2 Procedure

The experiments were conducted in a 2 L Bunsen beaker, which was fixed in a thermostat water bath. The solution was agitated using a double-leaf agitating controlled by a variable speed motor. Each 1.5 L digestion solution with the pH value proximity to 2.0 was consumed and H_2O_2 was needed to transfer Fe^{2+} into Fe^{3+}. At the desired temperature, the NH_4HCO_3 was slowly added into the solution agitated at a speed of 450 r/min in the whole experiment, the pH value was monitored both by an acidity meter and short range pH paper. Distilled water was added into the solution to keep the liquid quantity consistent. The solution was turned from red color into yellow color 1 h later, and the pH value was lowered during the test and was adjusted in the needed range. After the process of making ammonium jarosite, the solution was adjusted to a certain pH value. At the end of each experiment, the slurry was vacuum-filtered, and the filter residue was washed three times with distilled water and then dried. Both the residue and the solution were determined for the iron content to calculate the removal rate of iron ion.

2.3 Fundamental

The formula of jarosite can be presented as $A_2Fe_6(SO_4)_4(OH)_{12}$, where A represents monovalent cation, such as K^+, Na^+ and NH_4^+ [19]. The relationship between the formation of jarosite and temperature and pH value was studied by BABCAN, as shown in Fig. 1, in which the shadow area is the stable region of jarosite. We can conclude that when the pH value is lower, the high temperature is needed for the formation of jarosite. The lower the pH value is, the higher the temperature needed is. The formation of jarosite needs several factors as follows: attendance of Fe^{3+}, existence of monovalent cation, existence of sulphate ion at pH value lower than 2. The jarosite has the advantages of stability, good sedimentation and excellent filtering performance, and its solubility in water is very low, which is very important in hydrometallurgy. The formation process is complex, but can be simply described using following chemical equations [20].

$$3Fe_2(SO_4)_3+6H_2O=\!=6Fe(OH)SO_4+3H_2SO_4 \tag{1}$$

$$4Fe(OH)SO_4+4H_2O=\!=2Fe_2(OH)_4SO_4+2H_2SO_4 \tag{2}$$

$$2Fe(OH)SO_4+2Fe_2(OH)_4SO_4+2AOH=\!=A_2Fe_6(SO_4)_4(OH)_{12} \tag{3}$$

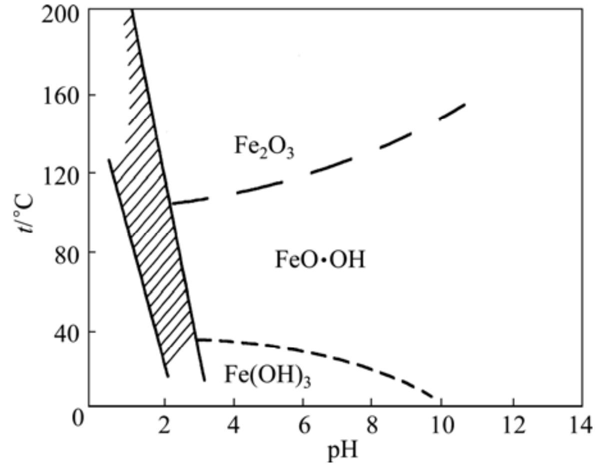

Fig. 1 Relationship between formation of jarosite and temperature and pH value

3 Results and discussion

3.1 Compositions of clinker digestion solution

The compositions of clinker digestion solution are shown in Table 1. The concentration of Ni^{2+} is only 1.49 g/L, far below that of Fe^{3+}/Fe^{2+} as well as Al^{3+}. The Fe^{3+} and Al^{3+} as impurities must be removed to prepare the high-quality nickel products. At this point, it is similar with the zinc metallurgy, but the challenge is much great. This is because the concentration of Ni^{2+} is very low and the concentration of Fe^{3+}/Fe^{2+} is high compared with Zn^{2+} and Fe^{3+}/Fe^{2+} in the solution. In order to get high-quality nickel products, both the impurities of Fe^{3+}/Fe^{2+} and Al^{3+} must be removed by preparing $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ and $Al(OH)_3$. In this work the main research purpose was the removal of iron and synthesizing ammonium jarosite. But several experiments of synthesizing $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ and $Al(OH)_3$ by hydrolysis in one step were carried out to examine the impurities removal efficiency.

Table 1 Compositions of clinker digestion solution

$\rho(\mathrm{Ni}^{2+})$/ $(\mathrm{g{\cdot}L^{-1}})$	$\rho(\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+})$/ $(\mathrm{g{\cdot}L^{-1}})$	$\rho(\mathrm{MgO})$/ $(\mathrm{g{\cdot}L^{-1}})$	$\rho(\mathrm{Al}^{3+})$/ $(\mathrm{g{\cdot}L^{-1}})$
1.49	19.36	30.72	4.25

3.2 Influence of reaction temperature

Under the conditions of reaction time 4 h, end pH value of reaction 2.5, initial concentration of Fe^{3+} 19.36 g/L, the influence of reaction temperature on the removal rate of Fe^{3+} was studied in the range of 70 to 95 °C, as shown in Fig. 2. We could see from Fig. 2 that the higher the reaction temperature is, the higher the removal rate of Fe^{3+} is. The reaction temperature has a significant influence on the Fe^{3+} removal rate, which increases from 23.86% at 70 °C to 98.28% at 95 °C, and the curve is sharp. So, the reaction temperature should be higher than 90 °C in order to remove Fe^{3+}. The reaction temperature 95 °C is selected in the following experiments.

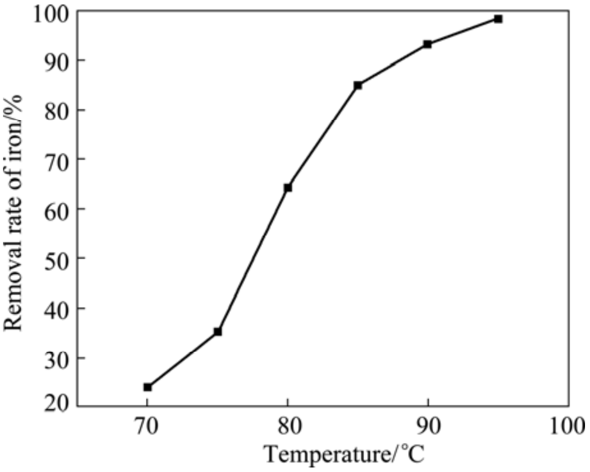

Fig. 2 Influence of reaction temperature on removal rate of iron

3.3 Influence of reaction time

The effect of reaction time on the removal rate of Fe^{3+} was investigated under the conditions of reaction temperature 95 °C, end pH value of reaction 2.5, initial concentration of Fe^{3+} 19.36 g/L. The experimental results were plotted as shown in Fig. 3. It is obvious that the influence of reaction time on the removal rate of Fe^{3+} is pronounced in the range of 2.5−3.5 h, but has no significant effects on the removal rate of Fe^{3+} when the reaction time is longer than 3.5 h. That is to say, the reaction time 3.5 h is enough for synthesizing ammonium jarosite. From the reducing energy consumption and raising productivity, 3.5 h is considered to be suitable.

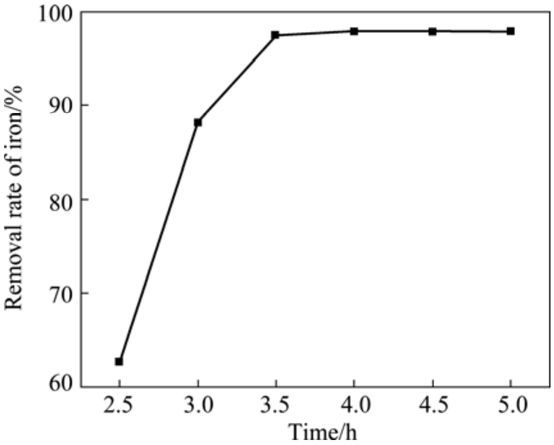

Fig. 3 Influence of reaction time on removal rate of iron

3.4 Influence of end pH value of reaction

The influence of end pH value of reaction on the removal rate of Fe^{3+} was also studied in the experiments with initial Fe^{3+} concentration of 19.36 g/L at 95 °C for 3.5 h. The results are shown in Fig. 4, in which the curve displays a similar trend with the curve in Fig. 3. The removal rate of Fe^{3+} increases along with the end pH value of reaction in the range of 1.5−2.5. When the end pH value of reaction is above 2.5, the removal rate of Fe^{3+} also increases but is very slow. The suitable end pH value of reaction seems to be 2.5 in view of reducing consumption of auxiliary material, nevertheless the Al^{3+} in solution also must be removed to obtain pure $\mathrm{NiSO_4/MgSO_4}$ solution, so the end pH value of reaction is adjustable for different needs.

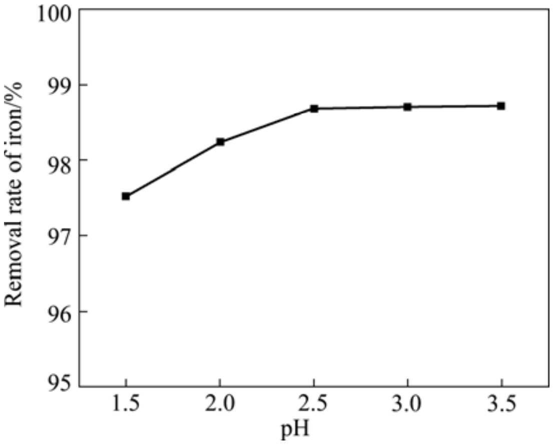

Fig. 4 Influence of pH value of reaction end on removal rate of iron

It is clear that the end pH value of reaction plays a role in removal of iron when the $\mathrm{NH_4HCO_3}$ is enough. That is to say, the dosage of $\mathrm{NH_4HCO_3}$ plays an important role. From the molecular formula $\mathrm{(NH_4)_2Fe_6(SO_4)_4(OH)_{12}}$, the mass ratio of $\mathrm{NH_4HCO_3}$ to Fe^{3+} in solution is about 0.47, but additional $\mathrm{NH_4HCO_3}$ is needed to neutralize the $\mathrm{H_2SO_4}$ yielded during the process of synthesizing $\mathrm{(NH_4)_2Fe_6(SO_4)_4(OH)_{12}}$. The chemical equations are as follows:

$$2NH_4HCO_3+3Fe_2(SO_4)_3+12H_2O \rightarrow (NH_4)_2Fe_6(SO_4)_4(OH)_{12}+5H_2SO_4+2H_2CO_3 \quad (5)$$

$$10NH_4HCO_3+5H_2SO_4 \rightarrow 5(NH_4)_2SO_4+10H_2CO_3 \quad (6)$$

According to the equations, the calculated mass ratio of the dosage of NH_4HCO_3 to Fe^{3+} in solution is about 2.8. So, the experiments were carried out with the mass ratio of the dosage of NH_4HCO_3 to iron ion in solution 1.5 to 3.5. And the experimental results were in agreement with the results of end pH value of reaction.

3.5 Influence of initial concentration of Fe^{3+}

The appropriate conditions for synthesizing ammonium jarosite using NH_4HCO_3 at the initial Fe^{3+} concentration of 19.36 g/L are reaction temperature 95 °C, reaction time 3.5h and end pH value of reaction 2.5. Since the components in laterite nickel ore and theirs contents usually are variable, it is necessary to examine the influence of the concentration of iron ion in solution. Based on the experimental data, the initial concentration of Fe^{3+} was also investigated, and the result is shown in Fig. 5. It is obvious that the removal rate of Fe^{3+} increases along with the initial concentration of Fe^{3+} increasing. The removal rate of Fe^{3+} increases from 83.72% at initial Fe^{3+} concentration 4.97 g/L to 98.36% at initial Fe^{3+} concentration 23.97 g/L. The variation of removal rate of Fe^{3+} is slight when the initial Fe^{3+} concentration is in the range of 23.97−45.22 g/L. Although the initial concentration of Fe^{3+} varies from 4.97 g/L to 45.22 g/L, the residual Fe^{3+} in solution is about 0.3 g/L after each test, which can be removed during the removal of Al^{3+}. If both the Fe^{3+} and Al^{3+} are removed in one step consisting of synthesizing $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ and making $Al(OH)_3$ by hydrolysis, the concentration of Fe^{3+} could be lowered to 0.01 g/L or even less.

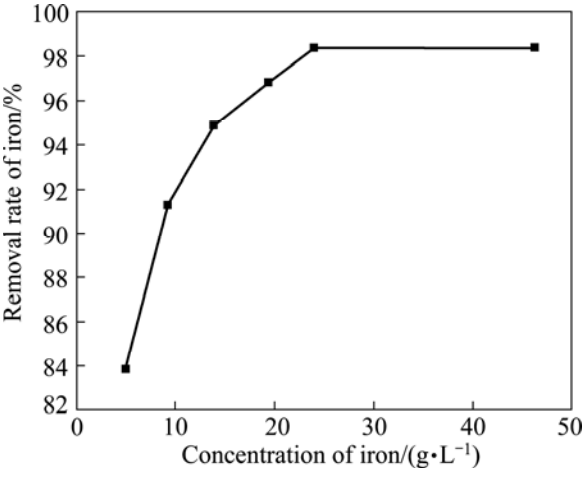

Fig. 5 Influence of initial concentration of Fe^{3+} on removal rate of iron

3.6 Characterization of as-synthesized ammonium jarosite

The XRD pattern and SEM image of ammonium jarosite are displayed in Fig. 6, which was prepared at the conditions of reaction temperature 95 °C, reaction time 3.5 h, end pH value of reaction 2.5 at initial concentration of Fe^{3+} 19.36 g/L. The diffraction data are in good agreement with the standard diffraction peaks and intensity of the $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$. No other phases are detected and the diffraction peaks are sharp. The morphology of ammonium jarosite could be seen clearly in SEM image. The physical aspect of the sample presents cluster figure comprising of many small particles or crystals, which displays a sheet or prismatic morphology with smooth surface. The average particle size of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ is about 15 μm.

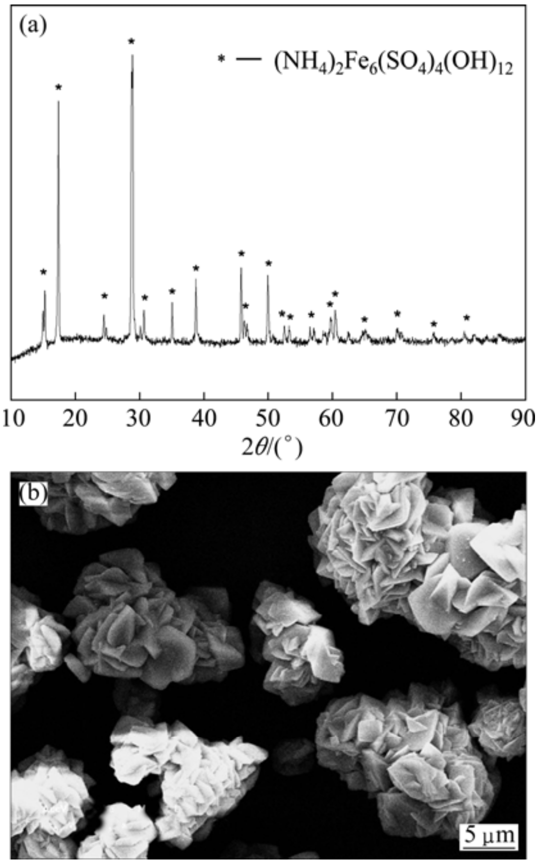

Fig. 6 XRD pattern (a) and SEM image (b) of as-synthesized ammonium jarosite

The main chemical components of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ that was washed three times with distilled water and dried for 12 h in an oven are shown in Table 2. The contents of Fe_2O_3 and SO_3 are 48.86% and 31.95%, respectively. According to the formula of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$, the contents of Fe_2O_3 and SO_3 are 50% and 33.33%, respectively, which are slightly higher than the determined data. There are two reasons for that. On one hand, a small amount of metal ions such as Al^{3+} in solution are precipitated during the process of synthesizing $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ because of high local pH value when NH_4HCO_3 is added into the solution, which were mingled in $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$. On the other hand, when the local pH value of the solution during the experiments is high, $Fe(OH)_3$ is almost certainly generated, which could be transferred into ammonium jarosite but needed a very long time. The presences of $Fe(OH)_3$ and other metal ion's precipitations play a role in chemical components of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ so that the contents of Fe_2O_3 and SO_3 are slightly lower than the theoretical data.

Table 2 Main components of ammonium jarosite

$w(Fe_2O_3)$/%	$w(SO_3)$/%	$w(MgO)$/%	$w(Al_2O_3)$/%	$w(NiO)$/%
48.86	31.95	0.04	0.08	0.016

From Table 2, we also found the existence of NiO. That is to say the valuable metal Ni is lost more or less in the process of synthesizing ammonium jarosite. From the results of quantitative analysis of the jarosite residue, the calculated loss rate of Ni is less than 0.6%, which is acceptable.

4 Conclusions

1) In the synthesizing process of $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ using digestion solution of roasting nickel oxide ore clinker and NH_4HCO_3, the factors consisting of reaction temperature, reaction time, end pH value of reaction have significant effects on the removal rate of Fe^{3+}, among which the reaction temperature is the most prominent. The initial concentration of Fe^{3+} in solution also has effect on the removal rate. At the end of each experiment, the residual Fe^{3+} in solution is about 0.3 g/L. The loss rate of Ni is less than 0.6%.

2) The appropriate reaction conditions are concluded as follows: reaction temperature 95 °C, reaction time 3.5 h, end pH value of reaction 2.5 at the initial concentration of Fe^{3+} 19.36 g/L.

3) The $(NH_4)_2Fe_6(SO_4)_4(OH)_{12}$ shows cluster figure comsisting of sheet or prismatic particles with smooth surface.

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硫酸铵焙烧红土镍矿的溶出液制备黄铵铁矾

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摘　要：为得到硫酸镍溶液除铁的合适工艺条件，以硫酸铵焙烧红土镍矿的熟料溶出液为原料，采用 NH_4HCO_3 合成黄铵铁矾。考查了反应温度、反应时间、反应终点 pH 以及 Fe^{3+}初始浓度对除铁率的影响。以上因素均对 Fe^{3+} 的去除率有显著影响，其中反应温度的影响最为显著。合适的反应条件为：Fe^{3+}初始浓度 19.36 g/L、反应温度 95 °C、反应时间 3.5 h、反应终点 pH2.5。在此条件下所得到的黄铵铁矾为包含片状或棱形颗粒的花簇结构。

关键词：红土镍矿；黄铵铁矾；影响因素；溶出液

(Edited by Hua YANG)