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Production of low-sulfur hematite by hydrothermal oxydrolysis of ferrous sulfate

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A R T I C L E I N F O

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A B S T R A C T

Hematite produced by the zinc industry exhibits a high sulfur content, being mainly contaminated by jarosite as the main sulfur-containing phase, and is thus of limited use for the steelmaking industry. Herein, we investigate the effects of parameters such as temperature (170–200 °C) and initial concentrations of sulfuric acid (0–19.6 g/L), sodium sulfate (0–35.5 g/L), hematite seeds (0–30 g/L), and Zn^{2+} (80–120 g/L) on the formation and conversion of jarosite during hematite precipitation from a ferrous sulfate solution, obtaining high-quality hematite with a low sulfur content.

We reveal that increased temperature not only benefits jarosite conversion but also reduces the sulfur content of precipitates and enriches them in iron. Sulfuric acid concentrations of 4.9–19.6 g/L greatly decrease the fraction of precipitated iron and produce sulfur-rich precipitates containing significant amounts of both hematite and jarosite, whereas sodium sulfate increases the iron removal efficiency and the sodium content in hematite precipitates. Hematite seeds prompt the precipitation of hematite and affect the composition of the obtained precipitates, promoting the precipitation of hematite in preference to jarosite at relatively low temperatures. Finally, zinc sulfate concentrations of 80–120 g/L have a positive effect on iron removal as hematite.

1. Introduction

The global electrolytic production of Zn amounts to roughly six million tonnes per annum (over 80% of the total Zn production) and utilizes an equivalent of around one million tonnes of Fe per annum (Cheng, 2002). During hydrometallurgical Zn production, Fe is removed from zinc sulfate solutions by precipitating three main phases, namely jarosite ($MFe_3(SO_4)_2(OH)_6$, M = K, Na, NH_4, H_3O), goethite (α-FeOOH), and hematite (α-Fe_2O_3). Among these processes, the precipitation of jarosite is one of the most economical and widely used techniques in the Zn industry, and large quantities of this by-product are consequently released. The jarosite contains toxic substances such as Zn, Pb, Cd, and other metal and non-metal oxides, which negatively impact the environment and/or human health when not properly controlled, and is universally categorized as hazardous waste (Asokan et al., 2006a; Asokan et al., 2006b; Casas et al., 2007; Erdem and Özverdi, 2011; Li et al., 2012a; Özverdi and Erdem, 2010). Although the obtained iron residue can be used to produce construction and ceramic materials (Ju et al., 2011), this approach suffers from potential valuable metal loss and the associated pollution risk. The recovery of valuable metals such as Zn, Pb, In, and Ag from jarosite has also been attempted using pyro- and hydrometallurgical processes (Alizadeh et al., 2010; Asokan et al., 2010; Hoang et al., 2009; Li et al., 2012b; Liu et al., 2009; Rashchi et al., 2005; Rusen et al., 2008), which, however, exhibit the shortcomings of high fixed investment, high operation cost, and air pollution during fuming, with similar observations being also applicable to the goethite process.

Recently, the hematite process has enjoyed renewed attention due to exhibiting distinct advantages despite its high operation cost (Yang et al., 2014a; Yang et al., 2014b; Li et al., 2015), e.g., affording a more environmentally friendly product due to the stability and compactness of hematite, which can be used as a reagent in the cement, pigment, and, potentially, steelmaking industries. However, the use of hematite in steelmaking is still limited by its high sulfur content of 2–4 wt% (Ruiz et al., 2007), which is attributed to the presence of residual sulfate. Hematite is produced by oxydrolysis of ferrous sulfate, which affords jarosite as the main sulfate-containing phase (Dutrizac and Sunyer, 2012), with the remaining sulfate content ascribed to the presence of basic ferric sulfate and chemisorption of sulfate ions.

The hematite process involves the oxydrolysis of ferrous sulfate at temperatures of 170–200 °C and oxygen partial pressures of 150–1000 kPa:

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$$2Fe^{2+} + 0.5O_{2(g)} + 2H_2O = Fe_2O_{3(s)} + 4H^+ \tag{1}$$

The oxydrolysis reaction is a sum of two reaction steps (Cheng and Demopoulos, 2004):

(i) oxidation of ferrous sulfate to ferric sulfate:

$$2Fe^{2+} + 0.5O_{2(g)} + 2H^+ = 2Fe^{3+} + H_2O \tag{2}$$

and (ii) hydrolysis of ferric sulfate to produce hematite:

$$2Fe^{3+} + 3H_2O = Fe_2O_{3(s)} + 6H^+ \tag{3}$$

Alternatively to reaction 3, the complicated hydrolysis of ferric, produced by oxidation of ferrous ions in reaction 2, at elevated temperatures may lead to the formation of undesirable ferric oxide hydrate ($Fe_2O_3{\cdot}H_2O$), basic ferric sulfate ($Fe(OH)SO_4$), and hydronium jarosite ($(H_3O)Fe_3(OH)_6(SO_4)_2$), depending on the solution acidity.

(i) At low acidity up to 110 °C(Cheng and Demopoulos, 2004):

$$2Fe^{3+} + 4H_2O = Fe_2O_3{\cdot}H_2O_{(s)} + 6H^+ \tag{4}$$

At temperatures of ≥200 °C, Fe_2O_3 is the main Fe-containing precipitate.

(ii) At moderate acidity:

$$3Fe^{3+} + 2SO_4{}^{2-} + 7H_2O = (H_3O)Fe_3(SO_4)_2(OH)_{6\,(s)} + 5H^+ \tag{5}$$

The H_3O^+ ion in Eq. (5) can be replaced by Na^+, K^+, or $NH_4{}^+$ to form jarosite. Jiang and Lawson (2006) found that the direct single-step formation of ammonium jarosite from its constituent ions is statistically unlikely, implying that jarosite is probably produced by gradual solid-state conversion of basic ferric sulfates/hydroxides.

(iii) At high acidity:

$$Fe^{3+} + SO_4{}^{2-} + H_2O = Fe(OH)SO_4 + H^+ \tag{6}$$

According to Cheng (2002), roughly 50% of the sulfur content in hematite produced by the Akita Zinc Company is due to the presence of jarosite, especially Na jarosite and K jarosite. The conversion of jarosite to hematite is illustrated by eq. (7) (Kuand and Veltman, 1979; Dutrizac, 1990):

$$2NaFe_3(SO_4)_2(OH)_6 = 3Fe_2O_3 + 2Na^+ + 4SO_4{}^{2-} + 6H^+ + 3H_2O \tag{7}$$

Dutrizac (1990) found that sodium jarosite is readily converted into hematite by hydrothermal reaction. The conversion reaction (7) is unaffected by modest concentrations of $ZnSO_4$, $FeSO_4$ or Na_2SO_4 and hematite seeding is desirable to promote the reaction and to stabilize the reaction system. Based on the above analysis, two most important goals are the prevention of jarosite formation and precipitation of high-quality low-sulfur-content hematite for subsequent utilization in the steelmaking industry. To address these goals, we have performed a series of small-scale laboratory studies, focusing on the effects of operating conditions (reaction time, temperature, and initial concentrations of sulfuric acid, sodium sulfate, Zn^{2+}, and hematite seeds) on the formation and conversion of jarosite during hematite precipitation to obtain high-quality hematite.

2. Experimental

Analytical grade $FeSO_4{\cdot}7H_2O$, anhydrous Na_2SO_4, $ZnSO_4{\cdot}7H_2O$, and concentrated H_2SO_4 (98%) were used to prepare initial solutions. Precipitation was performed in a 2-L titanium Parr autoclave equipped with a heating mantle, PID temperature controller, variable speed stirrer, and an internally mounted cooling coil.

The autoclave was charged with 1.5 L of a solution containing the desired amounts of ferrous sulfate, sodium sulfate, sulfuric acid, and zinc sulfate, sealed, and purged with nitrogen to remove residual oxygen. Subsequently, the autoclave was heated to the set temperature, with no agitation applied during warm-up. When the temperature reached the set value, the partial pressure of oxygen was fixed at the desired level and maintained throughout the experiment, and the system was agitated at 500 rpm. Samples were withdrawn at regular times and immediately filtered through a Buchner vacuum filter. In the end of the test, the autoclave was cooled in 5 min by circulating cold water, the product slurry was filtered, and precipitates were thoroughly washed with water and dried at 80 °C before analysis.

The concentration of Fe^{2+} was determined by titration with potassium dichromate using sodium diphenylamine-4-sulfonate as an indicator, and the total iron concentration was determined in a similar way after reducing Fe^{3+} with stannous chloride prior to the above titration. The solids were chemically analyzed to determine their Fe, Na, S, and Zn contents. Some precipitates were characterized by X-ray diffraction (CuKα radiation, $\lambda = 1.541838$ Å, graphite monochromator filter) and X-ray photoelectron spectroscopy (XPS) to identify their phases and possible impurities. Scanning electron microscopy (SEM) was used to analyze the distribution of major elements (Fe, Na, S and O), and Fourier transform infrared (FT-IR) spectroscopy was used to confirm the existence of sulfate ions. Additionally, particle size distributions were determined using a Laser Diffraction Size Analyzer.

3. Results and discussion

3.1. Effect of temperature

The effect of temperature on hematite precipitation was studied in the range of 170–200 °C for a solution initially containing 30 g/L ferrous ions, 21.3 g/L sodium sulfate, and 1.57×10^{-2} g/L H_2SO_4, with the partial pressure of oxygen equaling 400 kPa, and the reaction time varied from 30 to 180 min. The obtained results (Fig. 1) indicated that the fraction of precipitated iron slightly increased with increasing temperature and time.

Precipitates obtained at different temperatures (170–220 °C) and times were characterized by XRD. The obtained results revealed that precipitates formed at 170–180 °C mainly comprised jarosite with minor amounts of hematite, whereas those produced at 190 °C contained hematite as the major component and jarosite as the minor one. Finally, only hematite was detected in precipitates formed at 200 °C after 180 min. During the oxidation of ferrous ions by pressurized oxygen, the acid generated in reaction 3 is consumed by reaction 2, and thus, it is present at a stably low concentration. Under these conditions, the precipitation of jarosite is likely to be much faster than that of hematite at low temperature. After the complete oxidation of ferrous ions, the progressing precipitation of hematite increases the concentration of acid and decreases that of ferric ions, making jarosite thermodynamically unstable and favoring its dissolution. Thus, jarosite initially formed at 200 °C was converted into the progressively

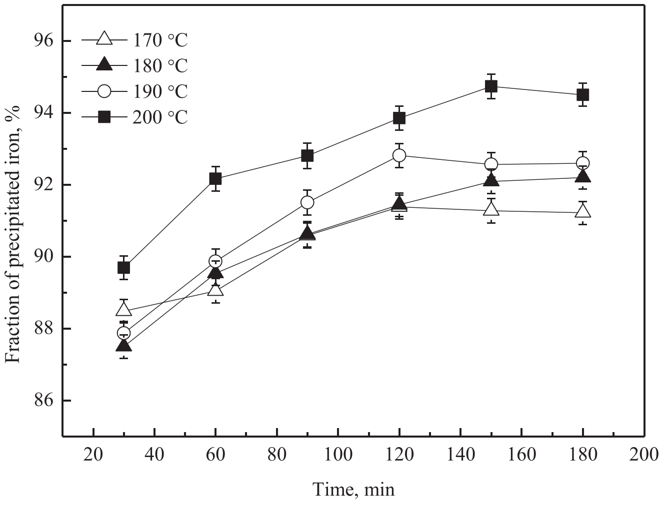

Fig. 1. Effect of reaction temperature on the fraction of precipitated iron.