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Technical note

Reductive leaching of manganese from low-grade manganese ore in H_2SO_4 using cane molasses as reductant

Haifeng Su, Yanxuan Wen, Fan Wang, Yingyun Sun, Zhangfa Tong *

School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

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Abstract

Manganese extraction from a low-grade ore was investigated using cane molasses as a reducing agent in dilute sulfuric acid medium. The effects of concentrations of cane molasses and sulfuric acid, leaching temperature as well as reaction time were discussed. The results showed that high manganese recovery with low Fe and Al extraction yield could be obtained by analyzing the leaching efficiencies of Mn, Fe and Al during the leaching process. The optimal leaching condition was determined as 1.9 mol/L H_2SO_4 and 60.0 g/L cane molasses for 120 min at 90 °C while using particles smaller than 0.147 mm. The leaching efficiencies were 97.0% for Mn, whereas 21.5% for Al and 32.4% for Fe, respectively.

Keywords: Manganese ores; Cane molasses; Sulfuric acid leaching; Reductive leaching

1. Introduction

Manganese plays an important role in many fields, such as steel production, preparation of dietary additives, fertilizers, cells and fine chemicals (Sahoo et al., 2001; Hazek et al., 2006). Hence, many efforts have applied recently to develop a commercial hydrometallurgical process to recover manganese from low-grade manganese ores. The ores can be treated by reduction roasting followed by acid leaching (Sahoo and Srinivasa, 1989) or directly by reductive acid leaching using different acidic reducing agents and acids, which includes hydrochloric acid and pyrite (Kanungo, 1999a,b), iron(II) sulphate (Das et al., 1982), aqueous sulfur dioxide (Abbruzzese, 1990; Abbruzzese et al., 1990; Naik et al., 2000), hydrogen peroxide in acidic medium (Jiang et al., 2003, 2004; Hazek et al., 2006), mixed methanol-sulfuric acid solution (Momade and Momade, 1999), an aqueous alcoholic-HCl acid mixture (Jana et al., 1995), sulfuric acid and oxalic acid (Sahoo et al., 2001), non-aqueous dimethyl sulfoxide (Raisoni and Dixit, 1988), mixed sucrose-sulfuric acid solution (Vegliò and Toro, 1994; Beolchini et al., 2001) and glucose in acidic medium (Trifoni et al., 2000, 2001; Vegliò et al., 2000, 2001a,b; Pagnanelli et al., 2004; Furlani et al., 2006).

Cane molasses, a by-product of sugar manufacture, generally contains 25%–35% cane sugar, 15%–25% invert sugar and 9%–11% colloidal materials. It is a low cost rich resource, containing renewable and non-hazardous reducing agents compared to other available raw materials that can be used for manganese leaching under mild acidic conditions. In this paper, the leaching processes of manganese, iron and aluminium from the ores using cane molasses as reducing agent were demonstrated. And the effect of concentrations of cane molasses and acid, leaching temperature and reaction time were investigated.

2. Materials and methods

2.1. Materials

The sample of manganese ore was obtained from Bayi Manganese Mine, Guangxi, China. Both the bulk and sieved samples were characterized by powder X-ray diffraction (XRD, Rigaku model D/max-2500) to define the mineralogical composition. The obtained diffractogram was identical to standard diffraction mineral patterns. From the XRD pattern (Fig. 1), the main metallic minerals include todorokite ($Mn_6O_{12}·4.16H_2O$), hematite (Fe_2O_3) and gangue minerals consisting of quartz (SiO_2) and kaolinite ($Al_2Si_2O_5(OH)_4$). The ore material was also chemically analyzed for its major and minor elements (Table 1).

* Corresponding author. Tel.: +86 771 3233728; fax: +86 771 3233718.
E-mail addresses: bioche@gxu.edu.cn, zhftong@sina.com (Z. Tong).

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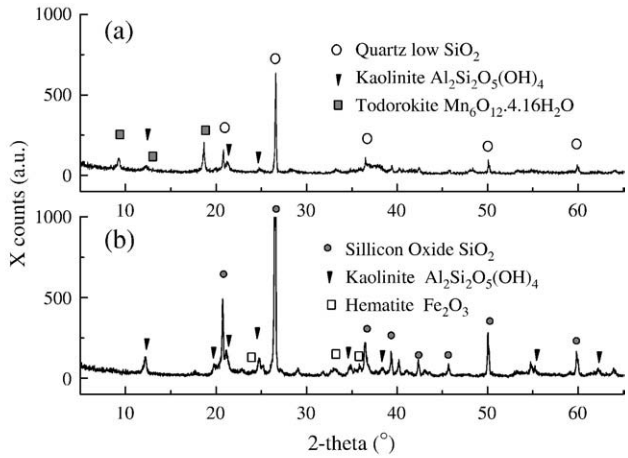

Fig. 1. XRD of manganese ore (a) before and (b) after chemical leaching.

The ore sample was crushed and ground to the required particle size smaller than 0.147 mm (>100 mesh). Cane molasses (Yishan Sugarcane Refinery, Guangxi, China), containing 27.80% cane sugar, 15.35% invert sugar and 9.53% colloidal material, was used in this work. All chemicals were of analytical grade and used without further purification.

2.2. Leaching procedure

The leaching experiments were carried out in a 500 mL three-neck flask immersed in thermostatically controlled water bath with mechanical stirring. In a typical experiment, 10.0 g of sample was first added to 50 mL sulfuric acid solution under stirring (~200 rpm) at 90 °C, keeping the solid:liquid ratio as 200 g/L, and leaching started after cane molasses was added to the solution. The initial concentrations of H_2SO_4 and cane molasses were 1.9 mol/L and 60.0 g/L, respectively. After 120 min, the slurry was filtered and the residue was washed with distilled water. The filtrate was then diluted in HNO_3 solution (pH=2) for analysis. The Mn, Fe, and Al concentrations during the leaching process were measured by an inductively coupled plasma spectrophotometer (ICP, Optima 5300 DV, Perkin Elmer). The leaching efficiency was calculated by referring the amount of leached metal in the liquor to its original input quantity. All the experiments were repeated twice.

3. Results and discussion

3.1. Effect of cane molasses concentration on leaching efficiency

Manganese dioxide ores cannot be leached by the sulfuric acid directly. But its oxidizing ability gets stronger in the acidic medium. In order to obtain high leaching efficiency of manganese, reducing substances must be added in acidic solution. The chemical reactions which take place during the manganese dioxide dissolution by sucrose or glucose can be described by the following reactions (Vegliò and Toro, 1994; Trifoni et al., 2001):

$$24MnO_2 + C_{12}H_{22}O_{11} + 24H_2SO_4 = 24MnSO_4 + 12CO_2\uparrow + 35H_2O \quad (1)$$

$$12MnO_2 + C_6H_{12}O_6 + 12H_2SO_4 = 12MnSO_4 + 6CO_2\uparrow + 18H_2O \quad (2)$$

In order to evaluate the effect of cane molasses, a series of leaching experiments was carried out by varying concentrations of cane molasses from 10.0 to 70.0 g/L while fixing H_2SO_4 concentration at 1.9 mol/L (Fig. 2). From Fig. 2, the leaching efficiencies of Mn increase with the increase of cane molasses concentration but there is little change in Al. However, the increase of cane molasses concentration causes a notable decrease in iron dissolution. Hence, a selective dissolution of Mn is achieved over Fe during digestion in the presence of cane molasses. The reason for such results is not yet understood and is being investigated.

A mineralogical study of the manganese ore has identified hematite as the main iron minerals in the ore. The dissolution of hematite requires a highly acidic medium and is influenced by the crystallinity of the mineral. It also results in the consumption of the H^+ ions (Momade and Momade, 1999). At a given temperature and initial acid concentration, when concentration of the cane molasses increases, the leaching efficiency of Mn increases and causes the H^+ ion concentration and iron dissolution to decrease accordingly. Similarly, Momade and Momade (1999) found that in the leaching of a ferruginous manganese ore in aqueous methanol-sulphuric acid medium, the iron dissolution decreased as the methanol concentration increased.

Table 1
Chemical composition of Bayi Manganese ore material

Component	wt.%
Mn	22.50
Fe	12.35
Si	11.30
Al	6.01
Ca	0.086
Mg	0.072
S	0.005
P	0.078

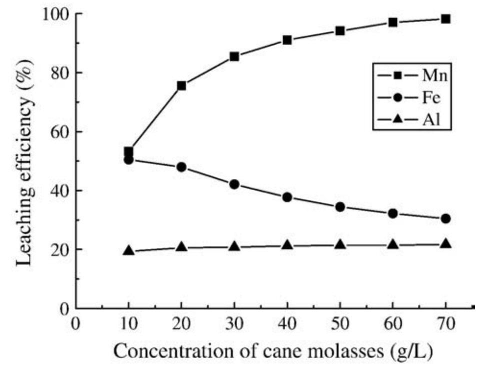

Fig. 2. Effect of cane molasses concentration upon the leaching efficiencies of Mn, Fe and Al.

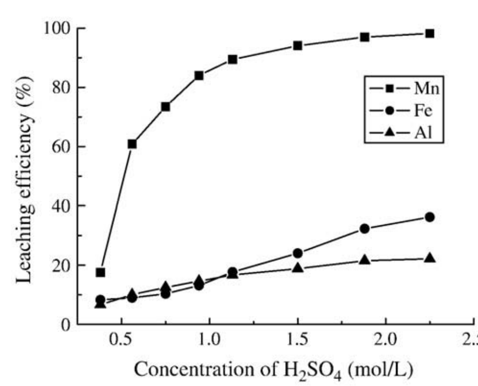

Fig. 3. Effect of H_2SO_4 concentration upon the leaching efficiencies of Mn, Fe and Al.