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Investigating the effect of ferrous ion on the digestion of diasporic bauxite in the Bayer process

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ABSTRACT

The effect of ferrous ion on the Bayer digestion of diasporic bauxite was studied under different conditions. Results showed that the digestion ratio of diasporic bauxite increased with increasing ferrous ion dosage, temperature, digestion time, and caustic alkali concentration. The product of the reaction between anatase and ferrous ion in synthetic Bayer liquor and the dissolution behavior of anatase in synthetic Bayer liquor in the presence of ferrous ion were further examined to probe the mechanism by which ferrous ion exerts its action. XRD results indicated that anatase reacted with the aluminate solution to form sodium titanate, which dissolved in solution and subsequently reacted with ferrous ion to form Fe_2TiO_4. Fe_2TiO_4 was found to be considerably less soluble than anatase or sodium titanate. Therefore, no re-precipitation of sodium titanate would coat the surface of diasporic bauxite, and the inhibitory effect of anatase on the digestion of diasporic bauxite was eliminated.

1. Introduction

The Bayer process was developed by Karl Bayer in 1888 to leach gibbsitic, boehmitic, or diasporic bauxite to produce aluminum hydroxide (Authier-Martin et al., 2001). Different digestion conditions, especially temperature and caustic alkali concentration, are required to process different types of bauxite. Gibbsitic bauxite requires relatively low temperatures and caustic alkali concentrations (105–150 °C, 120–160 g/L) to process, whereas boehmitic and diasporic bauxite require high temperatures and caustic alkali concentrations (220–280 °C, 180–250 g/L) (Authier-Martin et al., 2001; Zhang et al., 2011; Chen and Peng, 1997). Titanium-containing minerals, which mainly exist in the form of anatase, rutile, or brookite phases in bauxite, have been found to severely inhibit boehmitic and diasporic bauxite digestion but do not affect gibbsitic bauxite digestion (Pawlek et al., 1992; Prakash and Horvath, 1979; Whittington, 1996; Dudek et al., 2009). Such a phenomenon may be attributed to the fact that titanium-containing minerals cannot react in Bayer liquors until approximately 180 °C (Whittington, 1996). During reaction, the titanium-containing mineral phase is important; the anatase phase, not the rutile phase, has been observed to inhibit alumina extraction during high-temperature processing (Loan et al., 2005; Malts, 1992; Malts et al., 1985).

The inhibitory effect of titanium-containing minerals is generally believed to be due to the formation of a dense film of sodium titanate covering the surface of bauxite particles (Whittington, 1996; Loan et al., 2005; Chester et al., 2009; Dudek et al., 2009). Through imaging of elemental distributions within and on the surface of boehmite solids partially dissolved in synthetic Bayer liquors in the presence of anatase minerals by energy-filtered transmission electron microscopy, Ireland et al. (2014) discovered that sodium titanate forms an inhomogeneous layer on the boehmite surface. Thus, a hypothesis stating that dissolved titanates would re-precipitate onto the boehmite surface as sodium titanate and inhibit further dissolution (Ireland et al., 2014) was proposed. Findings obtained by measuring dissolved sodium titanate concentrations in aluminate solutions of different composition at elevated temperatures (Li et al., 2014) demonstrated that dissolved sodium titanate in Bayer liquors could precipitate and form a dense film covering the surface of bauxite particles.

Adding lime to the Bayer process to minimize the impact of titanium-containing minerals has received considerable research attention (Shultze-Rhonhof and Winkhaus, 1972; Malts et al., 1985; Malts, 1992; Whittington, 1996; Croker et al., 2009; Li et al., 2010a,b). The use of lime, however, can result in a series of problems, such as alumina loss, increased red mud amounts, and greater energy consumption and cost (Li et al., 2014). Therefore, developing new additives that both eliminate the inhibitory effect of titanium-containing minerals

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and present no adverse effect to the Bayer process is crucial. Gu et al. (1993) found that certain iron-containing compounds (e.g., $FeSO_4$ and $Fe(OH)_3$) could enhance diasporic bauxite digestion and inferred that iron-containing compounds react with titanium-containing minerals to form several highly insoluble compounds, thereby eliminating the retarding effect of titanium-containing minerals. However, another study found that only ferrous ion could accelerate diasporic bauxite digestion (Chen and Peng, 1997). Interestingly, chamosite, a ferrous alumino-silicate in certain special diasporic bauxites, could improve digestion performance by liberation of ferrous ion to the Bayer liquors and subsequent reaction with titanium-containing minerals (Gu et al., 1993). Therefore, certain diasporic bauxites containing chamosite can be thoroughly digested without lime or other additives (Gu et al., 1993).

However, the mechanism by which ferrous ion enhances diasporic bauxite digestion has not been conclusively determined. Tracing this mechanism mainly involves evaluation of the chemical constituents of the reaction product between titanium-containing minerals and ferrous ion as well as the solubility of the product in the aluminate solution. In this work, the effect of ferrous ion on the Bayer digestion of diasporic bauxite under different conditions (i.e., varying ferrous ion dosages, temperatures, digestion times, and caustic alkali concentrations) was studied. Ferrous sulfate heptahydrate was selected as the ferrous ion source, and the product of the reaction between anatase and ferrous ion in synthetic Bayer liquor was investigated using X-ray diffraction. Finally, the dissolution behavior of anatase in synthetic Bayer liquor in the presence of ferrous ion was examined and the mechanism by which ferrous ion influences diasporic bauxite digestion was discussed.

2. Materials and methods

Diasporic bauxites A and B were respectively sourced from Guangxi and Guizhou Provinces. The bauxites were prepared for 24 h in an oven at 100 °C, ground, and then sieved through a 160-mesh screen. Samples were chemically analyzed using inductively coupled plasma spectroscopy (Intrepid II XSP, USA) as shown in Table 1. Mineralogical analyses of the samples were performed using X-ray diffraction (XRD, TTR-III, Rigaku Corporation, Japan). XRD results in Fig. 1 indicate that the main crystalline phases of the samples are diaspore, kaolinite, hematite and limonite, and anatase. TiO_2 powder and ferrous sulfate heptahydrate were both of analytical grades. XRD phase identification indicated that TiO_2 powder primarily consists of anatase phases with low amounts of rutile phases (Fig. 2). Sodium titanate was prepared as in Li et al. (2014). Sodium aluminate solutions were prepared by dissolving aluminum hydroxide (technical grade) in boiling sodium hydroxide solutions. Caustic alkali and alumina concentrations of synthetic Bayer liquors were determined by titration (Connop, 1996).

Parameters related to the composition of synthetic Bayer liquors used in this paper are as follows:

- Na_2O_k caustic alkali, expressed as grams per liter Na_2O.
- Na_2O_f free alkali $= Na_2O_k - (62 \times Al_2O_3 / 102)$; expressed as grams per liter Na_2O, the free alkali considers the alkali consumed in forming the aluminate ion.
- Al_2O_3 alumina in solution expressed as grams per liter Al_2O_3.
- α_k molar ratio of caustic alkali to alumina $= 102\ Na_2O_k / 62\ Al_2O_3$.

Table 1
Chemical composition of the diasporic bauxites (wt.%).

	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	CaO
Bauxite A	51.46	6.77	3.9	23.92	2.82
Bauxite B	64.19	9.36	2.72	3.32	0.19

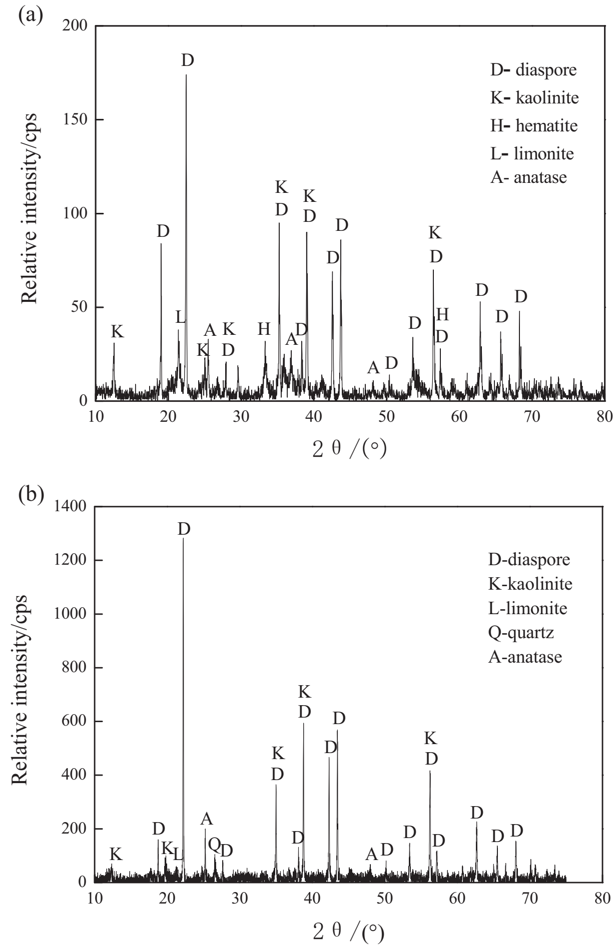

Fig. 1. XRD patterns of two diasporic bauxites from (a) Guangxi Province and (b) Guizhou Province.

The parameter α_k, as a measure of supersaturation, is commonly used in alumina refineries in China. Spent refinery liquors have α_k of ~3.0 while pregnant (green) liquors have α_k of ~1.5.

2.1. Caustic digestion of diasporic bauxite

Digestion experiments were performed in a high-pressure autoclave heated by mixed molten salts of sodium nitrate, potassium nitrate, and

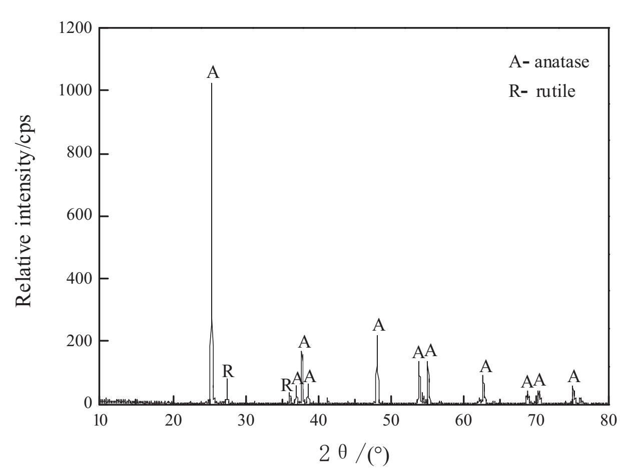

Fig. 2. XRD pattern of TiO_2 powder.