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Dissolution behavior of sodium titanate in sodium aluminate solutions at elevated temperatures

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ABSTRACT

A mini-autoclave was used for on-line sampling and solid–liquid separation at elevated temperatures. The concentration of sodium titanate dissolved in sodium hydroxide and sodium aluminate solutions at elevated temperatures was measured. Results show that sodium titanate dissolved quickly in hydroxide and aluminate solutions at elevated temperatures. Sodium titanate concentration in sodium hydroxide solutions increased with increasing alkali concentration and temperature. The dissolution behavior of sodium titanate in sodium aluminate solutions was dependent on temperature and solution composition. Furthermore, sodium titanate concentration in sodium aluminate solutions was primarily dependent on the free alkali concentration and was also affected by alumina concentration.

1. Introduction

Approximately 2% to 4% of minerals contain titanium and are mainly in the form of anatase, rutile, or brookite in diasporic bauxite (Chen and Peng, 1997). Titanium-containing minerals are known to severely inhibit the digestion of diasporic bauxite (Pawlek et al., 1992; Prakash and Horvath, 1979). Lime is frequently introduced in diasporic bauxite digestion process (Malts, 1992; Whittington, 1996; Whittington and Cardile, 1996). However, the use of lime may lead to a series of problems, such as alumina loss, increased red mud amounts, and greater energy consumption and cost. Several studies have analyzed the effect of titanium-containing minerals on the production of alumina, particularly in three aspects.

First is the interaction between titanium-containing minerals and sodium aluminate solutions. The reaction between titanium-containing minerals and sodium aluminate solutions depends on temperature, reaction time, and the free alkali concentration (Bi et al., 1996; Prakash and Horvath, 1979). Moreover, the aluminate anion can enhance the reaction of anatase in sodium aluminate solutions (Li et al., 2010a, b). Second, several studies on the mechanism of the effect of titanium-containing minerals on the digestion of bauxite have been performed. It is generally believed that the inhibiting effect of titanium-containing minerals is due to the formation of a dense film of sodium titanate covering on the surface of bauxite particles (Chester et al., 2009; Dudek et al., 2009). Lastly, methods for removing of the impact of titanium-containing minerals have been proposed. Studies mainly consider the use of lime (Whittington, 1996; Whittington and Cardile, 1996). Other additives have also been reported because of the adverse effects of lime (Gu et al., 1993).

The effect of titanium-containing minerals on the digestion of diasporic bauxite has been considered, but no significant technical advances that counter the negative influence of lime have been reported. Further studies on the reaction behavior and mechanism of titanium-containing minerals in sodium aluminate solutions are required. Only a few studies have examined the dissolution behavior of titanium-containing minerals. Chester et al. (2009) systematically studied the dissolution behavior of various titanium oxide phases (anatase, rutile, sodium titanate and calcium titanate) in synthetic Bayer liquors at 90 °C. The concentration of the different dissolved titanium oxide phases was found to be proportional to the free alkali concentration and generally <10 mg/L [Ti]. Nevertheless, the difficulty in collecting dissolution data at higher temperatures involved the removal of excess solids without significant cooling and subsequent reprecipitation. Few studies have been conducted on the dissolution behavior of titanium-containing minerals at elevated temperatures. Dissolution data for anatase and rutile in sodium aluminate solutions at temperatures ranging from 150 °C to 250 °C in literature are available (Chen and Peng, 1997). However, results are inconsistent, and the approach to the problem is unsystematic.

A systematic approach to the dissolution behavior of sodium titanate in sodium aluminate solutions at elevated temperatures was undertaken in this study. A mini-autoclave with a sampling system was used to

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perform on-line separation of solids from liquids at elevated temperatures. The use of a suitable sample preparation approach could minimize the difficulties in collecting reliable dissolution data at elevated temperatures

2. Materials and methods

2.1. Sodium titanate preparation

Anatase and sodium hydroxide (both analytical grade) were mixed with a mass ratio of 1:10 (anatase:hydroxide), and calcined in nickel crucibles in a muffle furnace at 720 °C for 1 h. The mixture was air-cooled and then washed with deionized water to remove excess sodium hydroxide to obtain powdered sodium titanate. The powder was dried in an oven at 90 °C to 100 °C, followed by sieving using a 160 mesh sieve, with a pore diameter of 98 μm. The powder on the sieve, with particle diameter >98 μm was used as sodium titanate sample. The sample was characterized using X-ray diffraction (XRD, TTR-III, Rigaku Corporation, Japan) and scanning electron microscopy (SEM, JSM-6360LV, JEOL, Japan). XRD analysis indicated that the sample has a poor crystalline structure (Fig. 1). A representative SEM image of the sample is shown in Fig. 2. The chemical composition of the sample was analyzed using inductively coupled plasma spectroscopy (ICP, Intrepid II XSP, USA) after dissolution in hydrochloric acid (prepared as 1:1 analytical grade hydrochloric acid and deionized water). Results showed that the sample contains 66.98% [TiO_2] and 11.93% [Na_2O].

2.2. Dissolution experiments

Sodium hydroxide solutions were prepared by dissolving sodium hydroxide (analytical grade) in deionized water. Sodium aluminate solutions were prepared by dissolving aluminum hydroxide (technical grade) in boiling sodium hydroxide solutions. Sodium titanate samples (0.3 g) and sodium hydroxide or aluminate solutions (120 mL) of certain concentrations were added into the tank of a mini-autoclave (Büchi eco075, Switzerland) and sealed. The mini-autoclave was then heated to the target temperature in 30 min to 90 min with stirring (400 r/min). The samples were obtained from the sampling system. Liquid samples containing sodium titanate particles were passed through a stainless steel powder sintered filter with a pore size of 0.5 μm (Swagelok SS-2F-05, USA) under high pressure. Separation of solids and liquids occurred because the diameter of a sodium titanate particle was significantly larger than the pore size of the filter. Excess hydrochloric acid (1:1) was added to the liquid samples before ICP analysis of Na, Al, and Ti contents. Reprecipitation of sodium titanate was inevitable because the samples were subjected to an abrupt temperature drop. Thus, hydrochloric acid was crucial to overcome this problem because sodium titanate, in either liquid or solid form, can be dissolved in hydrochloric acid. The concentrations of sodium titanate dissolved in sodium hydroxide or aluminate solutions (labeled as [TiO_2]) were obtained from calculations using Na_2O or Al_2O_3 as internal standards. This step was performed to correct for any deviation of sample volume caused by the vapor generated in the process of sampling. The equations are listed as follows:

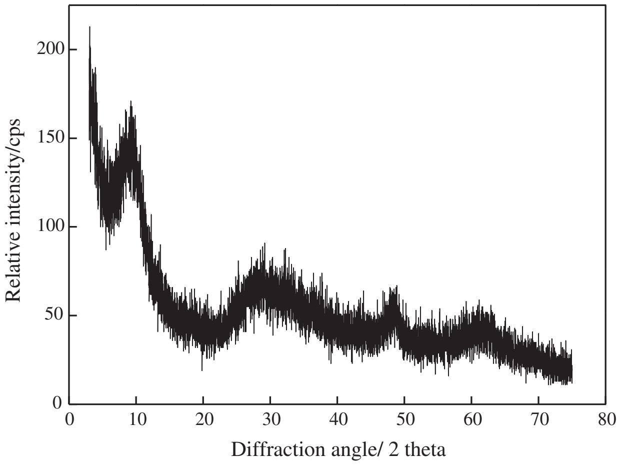

Fig. 1. XRD pattern of the sodium titanate sample.

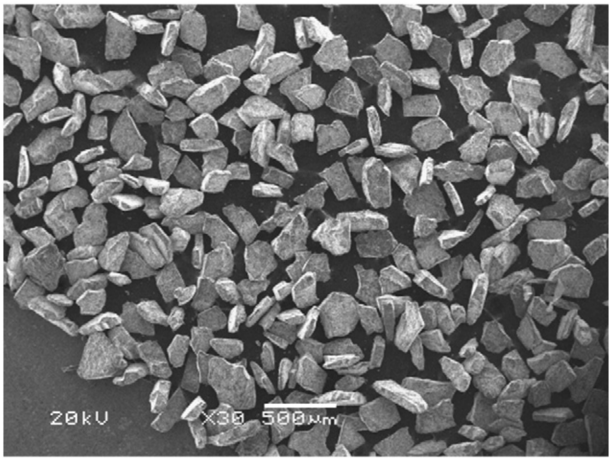

Fig. 2. SEM image of the sodium titanate sample.

$$C(TiO_2) = 1000 \times C(Na_2O)/C_{ICP}(Na_2O) \times C_{ICP}(TiO_2) \tag{1}$$

$$C(TiO_2) = 1000 \times C(Al_2O_3)/C_{ICP}(Al_2O_3) \times C_{ICP}(TiO_2) \tag{2}$$

In both equations, $C(TiO_2)$ is the concentration of sodium titanate dissolved in sodium hydroxide or aluminate solution and expressed as milligram per liter [TiO_2]. $C(Na_2O)$ and $C(Al_2O_3)$ represent alkali concentration in the sodium hydroxide solution and alumina concentration in the aluminate solution, expressed as gram per liter for [Na_2O] and [Al_2O_3], respectively. $C_{ICP}(Na_2O)$ and $C_{ICP}(Al_2O_3)$ refer to the sodium and aluminum concentrations in the HCl solution measured by ICP, expressed as milligram per liter for [Na_2O] and [Al_2O_3], respectively. $C_{ICP}(TiO_2)$ signifies titanium concentration in the HCl solution measured by ICP, expressed as milligram per liter [TiO_2]. The concentration of sodium titanate dissolved in the sodium hydroxide solution and sodium aluminate solution was calculated using Eqs. (1) and (2), respectively. The concentration of Na_2O or Al_2O_3 in sodium hydroxide or aluminate solutions was determined by titration (Connop, 1996).

Other parameters used in this paper are listed as follows:

Na_2Ok	caustic alkali, expressed as gram per liter Na_2O
Na_2Of	free alkali = $Na_2Ok - (62 \times Al_2O_3/102)$; expressed in gram per liter Na_2O, the free alkali considers the alkali consumed in forming the aluminate ion
αk	the mole ratio of caustic alkali to alumina = $102\ Na_2Ok/62\ Al_2O_3$

The reliability of the sampling system was verified. Sodium titanate sample (0.3 g) and 120 mL of sodium chloride (0.1 g/L) were added into the mini-autoclave tank and heated to 200 °C with stirring. Sodium chloride was used as internal standard. After holding for 2 h, the liquid sample was taken using the sampling system. Results indicate that the concentration of sodium titanate dissolved in extremely dilute sodium chloride solution was only 1.56 mg/L, confirming that the sampling system effectively separated solids and liquids. Sodium titanate has also been suggested to be almost insoluble in water at elevated temperatures.