



## Conversion of ferric oxide to magnetite by hydrothermal reduction in Bayer digestion process



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**Abstract:** Digesting aluminum-bearing minerals and converting ferric oxide to magnetite simultaneously in Bayer digestion process is crucially important to deal with high-iron diasporic bauxite economically for alumina production. The reaction behaviors of hydrothermal reduction of ferric oxide in alkali solution were studied by both thermodynamic calculation and experimental investigation. The thermodynamic calculation indicates that  $\text{Fe}_3\text{O}_4$  can be formed by the conversion of  $\text{Fe}_2\text{O}_3$  at proper redox potentials in alkaline solution. The experimental results show that the formation ratio of  $\text{Fe}_3\text{O}_4$  either through the reaction of Fe and  $\text{Fe}_2\text{O}_3$  or through the reaction of Fe and  $\text{H}_2\text{O}$  in alkaline aqueous solution increases remarkably with raising the temperature and alkali concentration, suggesting that  $\text{Fe}(\text{OH})_3^-$  and  $\text{Fe}(\text{OH})_4^-$  form by dissolving Fe and  $\text{Fe}_2\text{O}_3$ , respectively, in alkaline aqueous solution and further react to form  $\text{Fe}_3\text{O}_4$ . Moreover, aluminate ions have little influence on the hydrothermal reduction of  $\text{Fe}_2\text{O}_3$  in alkaline aqueous solution, and converting iron minerals to magnetite can be realized in the Bayer digestion process of diasporic bauxite.

**Key words:** Bayer process; digestion; hydrothermal reduction; ferric oxide; magnetite

### 1 Introduction

The high-iron bauxite ores with prospective storage over 1 billion tons are distributed in many regions in China, especially in Guangxi and Yunnan [1,2]. Although the total mass fraction of  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in such ores is more than 70%, most of them are low A/S (mass ratio of alumina to silica) bauxite and cannot be economically treated by traditional Bayer process aiming to extract alumina only. Even for those with high A/S, the iron cannot be separated and recovered effectively in traditional Bayer process, resulting in the inevitable large mass of red mud and thus great potential danger to the environment [3,4]. Therefore, the comprehensive utilization of iron compounds with low cost has become the key issue for treating high-iron bauxites.

To utilize the iron in the high-iron bauxite, the previous researchers proposed two kinds of methods. One is to recover iron from bauxite directly, the other is from red mud. The former includes gravity concentration, magnetic separation and pre-roasting–magnetic separation, etc. [5–7]. The later involves

reduction roasting–magnetic separation, direct smelting and direct beneficiation, etc. [8–10]. However, the methods mentioned above have some drawbacks hindering their industrial application, such as low iron recovery, relatively complex process, and high energy consumption or high cost.

It should be noted that the direct magnetic separation of iron from red mud is the most competitive in view of the cost. Unfortunately, only 20%–30% iron recovery with iron grade ( $T_{\text{Fe}}$ ) of 56% in content can be obtained in Guangxi alumina refinery with high temperature Bayer digestion process [11,12]. Meanwhile, it is noticed that the magnetic separation of iron compounds from red mud generated by high temperature digestion process is more efficient than that from raw bauxite and even than that from red mud by low temperature digestion process. The fact suggests that iron minerals in bauxite perhaps transform to magnetic compounds somewhat in high temperature Bayer digestion process. Obviously, the sufficient transformation of iron compounds to magnetite in Bayer digestion process may favor the separation of iron from red mud. Therefore, it is necessary to clarify the

transformation mechanism of iron minerals, in order to search the route to enhance the transformation of iron-bearing minerals in Bayer digestion process of bauxite.

Up to now, the researches on the transformation of iron minerals to magnetite in Bayer digestion process have been scarcely reported. Some researchers reported that iron hydroxide colloid or iron oxide can be reduced into nanoscale iron or magnetite by the reductant of hydrazine hydrate or borohydride in hydrothermal alkaline systems [13,14]. As such expensive reductants are inappropriate for alumina refinery, and there exists big difference between the solution system of the mentioned researches and that of the Bayer digestion, it should be studied for iron minerals to convert to magnetite with cheaper reductants in Bayer digestion solution system. So, in this work, based on the thermodynamic analysis of the transformation rule of iron-containing substances in alkaline aqueous solution, the hydrothermal reduction of ferric oxide to magnetite with iron powder as the reductant were experimentally investigated under the Bayer digestion conditions.

## 2 Experimental

Both ferric oxide powder (Sinopharm Chemical Reagent Co., Ltd) and iron powder (Tianjin Kemiu Chemical Reagent Co.) were analytical pure. Sodium hydroxide solutions were prepared by dissolving sodium hydroxide (Xinjiang Tianye Group Co. Ltd, analytical grade) in deionized water. While sodium aluminate solutions were prepared by dissolving aluminum hydroxide (CHALCO, technical grade) in boiling sodium hydroxide solutions. Diasporic bauxite was sourced from Guangxi Branch of CHALCO. The chemical composition of the bauxite is as follows: 51.46%  $\text{Al}_2\text{O}_3$ , 23.93%  $\text{Fe}_2\text{O}_3$ , 6.77%  $\text{SiO}_2$  and 3.9%  $\text{TiO}_2$  (mass fraction). The mineralogical analysis indicated that the main minerals in the bauxite are diasporic, hematite, kaolinite and anatase, etc.

XYF-d44×6 experimental autoclave (made in machinery plant affiliated to Central South University, China) was used for hydrothermal experiments, with temperature control accuracy of  $\pm 1\text{ }^\circ\text{C}$ . 100 mL sodium hydroxide or sodium aluminate solution and certain mass of ferric oxide powder (or bauxite) and iron powder were added into 150 mL sealed rotating steel bomb immersed in mixed nitrate molten salts cell with a preset temperature. Two steel balls with 15 mm in diameter and two steel balls with 8 mm in diameter were added into the bomb in order to strengthen stirring. After a certain duration, the bomb was taken out of the molten salts cell and then placed in cold water to cool to room temperature. The obtained slurry was subsequently

filtered and the filter cake was washed with hot water and then dried at  $(373\pm 5)\text{ K}$  to obtain the residue for analysis.

The contents of metallic Fe,  $\text{Fe}^{2+}$  and  $T_{\text{Fe}}$  in residues were analyzed by titration methods described in Ref. [15]. The XRD patterns of the materials and residues were recorded by a D8 X-ray diffractometer (Bruker, Germany). The reaction ratios of iron and ferric oxide were determined by the composition of residues according to Eqs. (1) and (2), in which the amount of iron-containing compounds in alkaline aqueous solutions was ignored due to very slight solubility compared with that added.

$$\eta(\text{Fe}) = \frac{m(\text{Fe}) - w(\text{Fe})m_{\text{res}}}{m(\text{Fe})} \times 100\% \quad (1)$$

$$\eta(\text{Fe}_2\text{O}_3) = [m(\text{Fe}_2\text{O}_3) - (w(\text{Fe})_T - w(\text{Fe}) - 3w(\text{Fe}^{2+}))m_{\text{res}} \times 160/112] / m(\text{Fe}_2\text{O}_3) \times 100\% \quad (2)$$

where  $\eta(\text{Fe})$  and  $\eta(\text{Fe}_2\text{O}_3)$  are the reaction ratios of iron powder and ferric oxide powder, respectively.  $m(\text{Fe})$ ,  $m(\text{Fe}_2\text{O}_3)$  and  $m_{\text{res}}$  are the mass of iron powder, ferric oxide added in solution and the obtained residue, respectively.  $w(\text{Fe})_T$ ,  $w(\text{Fe})$ ,  $w(\text{Fe}^{2+})$  are the mass fractions of total of Fe, metallic Fe and  $\text{Fe}^{2+}$  in residue, respectively.

## 3 Thermodynamic analysis of iron minerals transformation in alkaline system

It is understandable that magnetic transformation of iron minerals in bauxite can be realized by reducing some  $\text{Fe}^{3+}$  into  $\text{Fe}^{2+}$  and then forming magnetite in Bayer digestion process. The Pourbaix diagram (or potential pH diagram) is well known as an essential and useful tool for analyzing thermodynamic possibilities of redox reactions in solution. Although various Pourbaix diagrams for iron–water system with low alkali concentration corresponding to extremely low concentration of dissolved iron species ( $<10^{-6}\text{ mol/L}$ ) at various temperatures have been published [16], the Pourbaix diagrams of the Bayer digestion solution system with concentrated alkali concentration ( $>200\text{ g/L Na}_2\text{O}$ ) corresponding to relatively high equilibrium concentration of dissolved iron species ( $>10^{-4}\text{ mol/L}$ ) are still absence from literatures. The alkali concentration was found influencing the reaction of iron oxide dramatically in alkaline aqueous solution [13]. In order to better understand the transformation rule of iron mineral in Bayer digestion process, the thermodynamic stability diagrams of alkaline system similar to the Bayer digestion system should be firstly drawn.

Hematite, goethite, magnetite, etc., are the common iron minerals in bauxite. In view of the fact that goethite ( $\text{FeOOH}$ ) [17] and ferric hydroxide ( $\text{Fe}(\text{OH})_3$ ) will

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