

Available online at www.sciencedirect.com



Transactions of Nonferrous Metals Society of China

www.tnmsc.cn



Trans. Nonferrous Met. Soc. China 25(2015) 3467–3474

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

Xiao-bin LI¹, Nan LIU¹, Tian-gui QI^{1,2}, Yi-lin WANG¹, Qiu-sheng ZHOU¹, Zhi-hong PENG¹, Gui-hua LIU¹

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;

2. Zhongzhou Aluminum Corporation Limited of Aluminum Corporation of China (CHALCO), Jiaozuo 454000, China

Received 15 July 2014; accepted 24 August 2015

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 Fe_3O_4 can be formed by the conversion of Fe_2O_3 at proper redox potentials in alkaline solution. The experimental results show that the formation ratio of Fe_3O_4 either through the reaction of Fe and Fe_2O_3 or through the reaction of Fe and H_2O in alkaline aqueous solution increases remarkably with raising the temperature and alkali concentration, suggesting that $Fe(OH)_3^-$ and $Fe(OH)_4^-$ form by dissolving Fe and Fe_2O_3 , respectively, in alkaline aqueous solution and further react to form Fe_3O_4 . Moreover, aluminate ions have little influence on the hydrothermal reduction of Fe_2O_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 Al_2O_3 and Fe_2O_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 seperated 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 $(T_{\rm Fe})$ 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

Foundation item: Project (51374239) supported by the National Natural Science Foundation of China Corresponding author: Tian-gui QI; Tel: +86-731-88830453; E-mail: qtg_csu@163.com DOI: 10.1016/S1003-6326(15)63984-X

3468

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 Kemiou 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 Branch of CHALCO. The Guangxi chemical composition of the bauxite is as follows: 51.46% Al₂O₃, 23.93% Fe₂O₃, 6.77% SiO₂ and 3.9% TiO₂ (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 ± 1 °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 ± 5) K to obtain the residue for analysis.

The contents of metallic Fe, Fe^{2+} and T_{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.

$$\eta(\text{Fe}) = \frac{m(\text{Fe}) - w(\text{Fe})m_{\text{res}}}{m(\text{Fe})} \times 100\%$$
(1)
$$\eta(\text{Fe}_2\text{O}_3) = [m(\text{Fe}_2\text{O}_3) - (w(\text{Fe})_{\text{T}} - w(\text{Fe}) - 3w(\text{Fe}^{2+}))m_{\text{res}} \times 160/112]/m(\text{Fe}_2\text{O}_3) \times 100\%$$
(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(Fe), $m(\text{Fe}_2\text{O}_3)$ and m_{res} are the mass of iron powder, ferric oxide added in solution and the obtained residue, respectively. $w(\text{Fe})_{\text{T}}$, w(Fe), $w(\text{Fe}^{2+})$ are the mass fractions of total of Fe, metallic Fe and Fe²⁺ 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 Fe^{3+} into 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 ($<10^{-6}$ mol/L) at various temperatures have been published [16], the Pourbaix diagrams of the Bayer digestion solution system with concentrated alkali concentration (>200 g/L Na₂O) corresponding to relatively high equilibrium concentration of dissolved iron species ($>10^{-4}$ mol/L) are still absence form 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 (FeOOH) [17] and ferric hydroxide (Fe(OH)₃) will transform into hematite (Fe₂O₃) under high temperature digestion conditions, while ferrous hydroxide (Fe(OH)₂) is not stable in the alkaline aqueous solution at temperature of above 85 °C [16,18], three iron-containing solid substances of Fe, Fe₂O₃ and Fe₃O₄ are considered in the thermodynamic calculation process. In addition, iron ions like Fe²⁺, Fe³⁺, Fe(OH)₃⁻, Fe(OH)₄²⁻, Fe(OH)₂⁺ and Fe(OH)²⁺ may exist in solution, but Fe(OH)₃⁻ and Fe(OH)₄⁻ mainly exist in strong alkaline aqueous solution with pH value greater than 10 according to Peter's study [16].

The thermodynamic data of $Fe(OH)_3^-$ and $Fe(OH)_4^$ are obtained from Refs. [16] and [18], and those of the rest substances are obtained from Ref. [19]. According to the thermodynamic equilibrium principle of chemical reaction, the variation of standard reaction Gibbs free energy ($\Delta_r G_T^{\Theta}$) of each reaction in Table 1 can be calculated at 373 and 553 K, respectively, based on Eq. (3)

$$\Delta_{\rm r} G_T^{\Theta} = \sum G_{T-\rm products} - \sum G_{T-\rm reactants} \tag{3}$$

The relationship between redox potential (φ) and activities of various ions (a_i) in the investigated alkaline aqueous solution can be described by Eq. (4):

For non-redox reaction

$$\Delta_{\mathbf{r}}G_T = \Delta_{\mathbf{r}}G_T^{\Theta} + 2.303RT \lg \frac{\prod_i (a_i^{v_i})}{\prod_j (a_j^{v_j})} = 0$$
(4a)

For redox reaction

$$\Delta_{\mathbf{r}}G_T = \Delta_{\mathbf{r}}G_T^{\Theta} + 2.303RT \lg \frac{\prod_i (a_i^{v_i})}{\prod_j (a_j^{v_j})} = -nF\varphi \qquad (4b)$$

where $\Delta_{\mathbf{r}}G_T$ is the variation of Gibbs free energy of reaction at temperature of *T*, a_i and a_j are the activity or fugacity of reactant *i* and product *j*, respectively, v_i and v_j are the stoichiometric numbers of reactant *i* and product *j*, respectively, *F* is the Faraday constant and *n* is the number of electrons involved in the electrochemical reaction.

For the digestion system of Bayer process, the molalities of species in solution were adopted instead of the unobtainable activity in concentrated solution. The relationship between redox potential (φ) and the concentration of alkali (ρ (Na₂O)) can be established shown in Fig. 1, according to the data involved in Table 1.

Figure 1 shows that the stable region of Fe_2O_3 and Fe_3O_4 partly overlapped with the stable region of water



Fig. 1 Thermodynamic equilibrium of iron compounds in alkaline system at 373 K (a) and 553 K (b)

No.	Reaction	$\Delta_{\rm r} G_{\rm 373K}^{\Theta} / ({\rm kJ} \cdot {\rm mol}^{-1})$	$\Delta_{\rm r} G^{\Theta}_{553{\rm K}}/({\rm kJ}{\cdot}{\rm mol}^{-1})$	
1	$2H_2O+2e=H_2+2OH^-$	174.57	232.25	
2	$4OH^{-}=2H_2O+O_2+4e$	100.86	-69.82	
3	$Fe+3OH^- = Fe(OH)_3^+ + 2e$	-173.01	-240.86	
4	3Fe(OH) ₃ ⁻ =Fe ₃ O ₄ +4H ₂ O+OH ⁻ +2e	-268.78	-347.226	
5	$3Fe+8OH$ = $Fe_3O_4+4H_2O+8e$	-787.81	-1069.81	
6	$3Fe_2O_3+H_2O+2e=2Fe_3O_4+2OH^-$	135.08	194.97	
7	$Fe_2O_3+2OH^-+3H_2O=2Fe(OH)_4^-$	65.07	76.54	
8	3Fe(OH) ₄ ⁻ +e=Fe ₃ O ₄ +4OH ⁻ +4H ₂ O	-30.06	-17.32	
9	$Fe(OH)_4^+e = Fe(OH)_3^++OH^-$	79.57	109.97	

Table 1 Possible reactions in Fe–OH[–]-H₂O system and $\Delta_r G_T^{\Theta}$

3469

(the redox potential region between O_2 equilibrium line and H_2 equilibrium line) at each temperature, suggesting that Fe_2O_3 and Fe_3O_4 may be stable in alkali system with proper redox potential. The stable region of Fe is beneath the region of water, implying that Fe is unstable in alkali aqueous solution thermodynamically, probably reacting with water to form Fe_3O_4 or $Fe(OH)_3^-$. According to the stable region of Fe_2O_3 , Fe_3O_4 and Fe shown in Fig. 1, the stable iron-containing phase in the alkaline hydrothermal system depends on the redox potential, which means that the conversion of Fe_2O_3 to Fe_3O_4 can be achieved by reducing the redox potential of the solution system.

Figure 1 also indicates that the equilibrium concentrations of Fe(OH)₄⁻ and Fe(OH)₃⁻ in solution strongly depend on the temperature and alkali concentration. The equilibrium concentration of each iron-containing ion becomes higher with increasing either the temperature or the alkali concentration. At fixed temperature and alkali concentration, the concentration of iron-containing ion in the solution relies on the redox potential of the solution. $Fe(OH)_3^{-1}$ is the main iron ion in solution with low redox potential, having relatively high equilibrium concentration and keeping solubility equilibrium with Fe or Fe₃O₄ in solution. Fe(OH)4, the main iron-containing ion, has relatively low equilibrium concentration and keeps solubility equilibrium with Fe₂O₃ in solution with high redox potential. While the redox potential locates in the stable region of Fe₃O₄ which keeps equilibrium with $Fe(OH)_4^-$, $Fe(OH)_3^-$ and Fe_2O_3 , the equilibrium concentration of iron-containing ion is the lowest. Based on the discussion above, it can be concluded that Fe₃O₄ can be formed by the reactions of $Fe(OH)_4^-$ and $Fe(OH)_3^-$ because Fe_3O_4 has the lowest solubility. Whereas $Fe(OH)_4^{-}$ and $Fe(OH)_3^{-}$ may be generated accordingly by dissolving Fe₂O₃ and Fe.

4 Results and discussion

4.1 XRD patterns of residues

In order to clarify the conversion behaviors of iron oxide in bauxite in Bayer digestion process with iron powder as the reductant, the phase conversion of ferric oxide, iron and their mixture reacting in sodium hydroxide solution with the alkali concentration (ρ (Na₂O)) of 280 g/L was studied. The XRD patterns of the residues are shown in Fig. 2.

It can be seen from Fig. 2 that, in obtained residues, there is no visible change observed for the Fe_2O_3 powder (Fig. 2(b)), while there exist both Fe and Fe_3O_4 for the Fe powder (Fig. 2(a)) and only Fe_3O_4 for the mixture of Fe and Fe_2O_3 powder (Fig. 2(c)). Therefore, in the alkaline aqueous solution at elevated temperature, the conversion

Fig. 2 XRD patterns of residues obtained by treating various iron-containing materials in sodium hydroxide solution at 553 K for 60 min: (a) 20 g/L Fe; (b) 100 g/L Fe₂O₃; (c) 20 g/L Fe and 100 g/L Fe₂O₃

reaction of Fe₂O₃ into Fe₃O₄ cannot take place but can occur in the presence of Fe powder, while Fe can be converted into Fe₃O₄. The results are consistent with the thermodynamic calculation. In addition, the characteristic diffraction peak of Fe still appears in Fig. 2(a) but disappears in Fig. 2(c), meaning that Fe₂O₃ can accelerate the transformation reaction of Fe into Fe₃O₄ in alkaline system at elevated temperature as the same amount of Fe powder was added for the two samples.

According to the results shown in Figs. 1 and 2, the overall chemical reaction of the process that Fe reduces Fe_2O_3 at elevated temperature can be described by Eq. (5) in terms of the charge balance:

$$Fe+4Fe_2O_3 = 3Fe_3O_4 \tag{5}$$

Theoretically, Fe_2O_3 the in system can be converted into Fe_3O_4 completely by adding Fe with only 8.75% Fe_2O_3 (mass fraction). That is to say, a small amount of Fe powder can make Fe_2O_3 transform into Fe_3O_4 completely in alkaline aqueous solution.

4.2 Influence of alkali concentration on hydrothermal reduction of ferric oxide

In order to clarify the influence of alkali concentration on the reduction of ferric oxide by iron powder, experiments were conducted to study their reaction behaviors at different concentrations of sodium hydroxide, and the results are shown in Fig. 3.

Figure 3 shows that the alkali concentration has a significant influence on the conversion ratios of Fe and Fe_2O_3 , and the reaction ratios increase with increasing the alkali concentration. However, according to the thermodynamics analysis in Fig. 1, the iron-containing equilibrium solid phase in alkaline aqueous solution

system depends on the redox potential. In the case of enough addition of Fe, the redox potential is determined by the hydrogen evolution potential with the thermodynamic equilibrium solid phase of Fe₃O₄, which means that Fe₂O₃ and Fe can be completely converted into Fe₃O₄ ultimately under the reaction condition in Fig. 3. Therefore, the influence of alkali concentration on the reaction ratios of Fe and Fe₂O₃ in Fig. 3 is not caused by the change of thermodynamic equilibrium but by the dynamics factors related to the formation mechanism of Fe₃O₄ in alkaline aqueous solution.



Fig. 3 Relationship between conversion ratios of Fe and Fe_2O_3 and alkali concentration with 10 g/L Fe and 100 g/L Fe_2O_3 reacting at 553 K for 60 min

The thermodynamic stability diagram in Fig. 1 demonstrates that there are at least two pathways for the transformation of Fe into Fe_3O_4 in alkaline aqueous solution. One pathway is that Fe directly reacts with H₂O to form Fe_3O_4 and H₂ according to Reaction (6):

$$3Fe+4H_2O = Fe_3O_4 + 4H_2 \tag{6}$$

The other path way is that Fe first reacts with alkaline aqueous solution to form $Fe(OH)_3^-$ which further changes to Fe_3O_4 as follows:

$$Fe+OH^{-}+2H_2O = Fe(OH)_3^{-}+H_2$$
(7)

$$3Fe(OH)_3 = Fe_3O_4 + 3OH + 2H_2O + H_2$$
 (8)

If the reaction of Fe in alkaline aqueous solution follows Eq. (6), the Fe conversion process will be independent of the alkali concentration. This does not agree with the fact illustrated in Fig. 3. As for the second pathway, $Fe(OH)_3^-$ is an intermediate whose equilibrium concentration increases with increasing the alkali concentration, and thus concentrated alkaline aqueous solution favors Reaction (7). Moreover, it is believed that Fe_3O_4 is readily formed by $Fe(OH)_3^-$ through Reaction (8). This explanation is consistent with the experimental results in Fig. 3. So, the conversion of Fe in alkaline aqueous solution may obey the later mechanism. Similarly, the reaction of Fe_2O_3 and Fe to form Fe_3O_4 is likely to undergo the reactions of Fe_2O_3 and/or Fe with alkaline aqueous solution, because the reaction ratios of both Fe_2O_3 and Fe strongly depend on the alkali concentration.

In summary, maybe the important intermediates in the hydrothermal reduction process of Fe_2O_3 are to form Fe_3O_4 . The appropriate alkali concentration is required for accelerating the formation of $Fe(OH)_3^-$ and $Fe(OH)_4^-$, thus intensifying the formation of the magnetite.

4.3 Influence of temperature on hydrothermal reduction of ferric oxide

As discussed in Section 3, thermodynamically, ferric oxide can be reduced into magnetite by iron in alkaline aqueous solution even at 373 K, and raising the temperature can increase the concentrations of $Fe(OH)_{4}^{-}$ and thus affect the formation of magnetite. So, it is necessary to further investigate the influence of temperature on the reduction of ferric oxide. The variations of reaction ratios of Fe and Fe₂O₃ with temperature are depicted in Fig. 4.



Fig. 4 Dependence of reaction ratios of Fe and Fe_2O_3 on temperature with 10 g/L Fe and 100 g/L Fe_2O_3 reacting for 60 min

As seen in Fig. 4, temperature has an obviously positive effect on the reaction ratios of Fe and Fe_2O_3 in alkaline aqueous solution, suggesting that raising temperature can accelerate the formation of Fe_3O_4 . This may be attributed to two aspects, i.e., the acceleration of reaction kinetically and the increment of equilibrium concentrations of iron-containing ions thermodynamically.

4.4 Influence of duration on hydrothermal reduction of ferric oxide

Determining the relationship between the reaction ratio and duration is extremely important for understanding the reduction mechanism of ferric oxide in alkaline aqueous solution. Therefore, the influence of duration on the reaction of Fe_2O_3 and Fe at 533 K and 553 K were experimentally studied, and the results are shown in Figs. 5 and 6.



Fig. 5 Relationship between reaction ratios of Fe and Fe_2O_3 and duration with 10 g/L Fe, 100 g/L Fe_2O_3 and 220 g/L Na_2O



Fig. 6 XRD patterns of residues obtained by reaction of Fe_2O_3 and Fe in alkaline aqueous solution at 533 K and various durations with 10 g/L Fe, 100 g/L Fe_2O_3 and 220 g/L Na_2O

In Fig. 5, the reaction ratios of both Fe_2O_3 and Fe increase with increasing the time. The reaction ratio of Fe increases rapidly and only about 20 min is required for approaching the complete conversion of Fe. While the reaction ratio of Fe_2O_3 increases gradually with increasing the time and about 60 min is required for finishing the conversion of Fe_2O_3 at 553 K. This reaction tendency is also confirmed by the XRD patterns of residues, as shown in Fig. 6.

The fact that the reaction of Fe is much faster than that of Fe₂O₃ shows that the conversion reactions of Fe₂O₃ and Fe develop asynchronously, which means that the formation of Fe₃O₄ is not through Reaction (5) directly. The possible mechanism for the formation of Fe₃O₄ by the reaction of Fe₂O₃ with Fe in alkaline aqueous solution could be described as follows: Fe(OH)₃⁻ and Fe(OH)₄⁻ form firstly by dissolving Fe and Fe_2O_3 , respectively, in alkaline aqueous solution, and then Fe_3O_4 forms by the reaction between $Fe(OH)_3^-$ and $Fe(OH)_4^-$ according to Reaction (9).

$$Fe(OH)_{3}^{+}+2Fe(OH)_{4}^{-}=Fe_{3}O_{4}+3OH^{+}+4H_{2}O$$
 (9)

This mechanism can be supported by some other factors. Concentrated alkali concentration and elevated temperature are beneficial to the reactions of either Fe or Fe_2O_3 with alkaline aqueous solution to form $Fe(OH)_3^-$ and $Fe(OH)_4^-$ thermodynamically (Fig. 1). Meanwhile, as discussed in the previous section, the reaction ratios of Fe and Fe_2O_3 increase with increasing the temperature and alkali concentration.

In addition, H_2 as a reductant may reduce Fe^{3+} to Fe_3O_4 thermodynamically. However, considering the extremely low solubility of H_2 in the alkaline aqueous solution especially at elevated temperature, whether H_2 participates the formation reaction of Fe_3O_4 is uncertain and remains to be investigated.

4.5 Influence of sodium aluminate on hydrothermal reduction of ferric oxide

In the previous study, pure sodium hydroxide aqueous solution was employed, while the Bayer solution for digestion consists of aluminate ions. In order to understand the conversion behavior of Fe_2O_3 in Bayer digestion process, the hydrothermal reduction of Fe_2O_3 by Fe in simulated Bayer solution was further studied experimentally, as shown in Table 2.

The reaction ratios of Fe_2O_3 and Fe increase with increasing the time, and almost all the Fe_2O_3 can be converted under the typical Bayer digestion conditions for diasporic bauxite. This provides a possibility for converting hematite to magnetite in the Bayer digestion process.

The experimental results in Table 2 also demonstrate that the free alkali concentration (ρ_r) remarkably affects the reaction rates of Fe₂O₃ and Fe in sodium alumina solution with the fixed caustic alkali concentration (ρ_k), and the higher the free alkali concentration is, the faster the reaction rate is. This conversion character in sodium aluminate solution is similar to that in sodium hydroxide solution. Although aluminate ion seems to slightly retard the conversion process in the early period, the conversion ratios for the two solution systems are almost the same for the duration of 60 min.

For determining the applicability of hydrothermal reduction for iron minerals in bauxite in Bayer digestion process, the digestion experiments of Guangxi high-iron diasporic bauxite were preliminarily conducted with or without the reductant of Fe powder and the XRD patterns of red muds are shown in Fig. 7. The magnetite is the major iron mineral in the red mud with adding Fe

Xiao-bin LI, et al/Trans. Nonferrous Met. Soc. China 25(2015) 3467-3474

Duration/min	$\rho_{\rm k}$ =220 g/L, $\rho_{\rm f}$ =62 g/L		$ ho_{\rm k}$ =220 g/L, $ ho_{\rm f}$ =145 g/L		$\rho_k = \rho_f = 220 \text{ g/L}$		$\rho_{\rm k} = \rho_{\rm f} = 145 \text{ g/L}$				
	η(Fe)/%	η(Fe ₂ O ₃)/%	η(Fe)/%	η(Fe ₂ O ₃)/%	η(Fe)/%	$\eta(\mathrm{Fe_2O_3})/\%$	η(Fe)/%	η(Fe ₂ O ₃)/%			
5	53.10	20.01	50.52	31.55	53.58	38.71	52.81	36.27			
10	46.93	29.59	63.01	34.35	83.61	50.55	79.30	48.25			
20	87.26	49.21	94.11	57.17	97.31	72.07	95.47	70.13			
30	90.71	54.49	98.54	69.91	98.58	80.18	96.73	79.16			
40	92.96	65.03	98.72	87.99	99.10	86.23	98.65	83.21			
60	94.27	76.37	98.09	96.02	99.57	96.76	99.03	95.53			

Table 2 Reaction ratio of ferric oxide in sodium aluminate solution at 533 K with 10 g/L Fe and 100 g/L Fe₂O₃

 ρ_k is caustic alkali concentration; ρ_f is free alkali concentration of sodium aluminate solution and denotes concentration of caustic alkali uncombined with aluminate, $\rho_f = (\rho_k - \rho(Al_2O_3))/102 \times 62$.



Fig. 7 XRD patterns of red muds obtained by digesting Guangxi diasporic bauxite with (a) and without (b) adding 10 g/L Fe powder at 533 K for 60 min (bauxite dosage: 250 g/L; lime dosage: 25 g/L; spent liquor compositions: $\rho(Na_2O)=$ 220 g/L, $\rho(Al_2O_3)=120$ g/L)

powder while no magnetite is detected in the red mud without adding iron powder, proving that iron powder as the reductant is able to convert the iron minerals in bauxite to magnetite in the Bayer digestion process. Further investigation on the formation of magnetite in the Bayer digestion process for treating diasporic bauxite is being conducted.

5 Conclusions

1) The hydrothermal reduction of Fe_2O_3 to Fe_3O_4 is possible at appropriate redox potentials in alkaline aqueous solution thermodynamically. Concentrated alkali concentration and elevated temperature can increase the equilibrium concentrations of $Fe(OH)_3^-$ and $Fe(OH)_4^-$.

2) The hydrothermal reduction of Fe_2O_3 to Fe_3O_4 in alkaline aqueous solution may undergo two steps: $Fe(OH)_3^-$ and $Fe(OH)_4^-$ form firstly by dissolving Fe and Fe_2O_3 , respectively, and then Fe_3O_4 forms by the reaction between $Fe(OH)_3^-$ and $Fe(OH)_4^-$.

3) There is no obvious difference in the hydrothermal reduction of ferric oxide in sodium

hydroxide solution and sodium aluminate solution. Meanwhile, it is feasible to reduce iron minerals to magnetite in the Bayer digestion process of diasporic bauxite.

References

- YUAN Zhi-tao, ZHANG Song, LI Li-xia, YU Fu-jia. Research status on ferrous and aluminum separation of high-Fe bauxite in China [J]. Metal Mine, 2013, 9: 100–103. (in Chinese)
- [2] ZHANG Xiu-feng, TAN Xiu-min, ZHANG Li-zheng, HU Si-chuan. Review of current research status on comprehensive utilization technology of high iron bauxite in China [J]. China Mining Magazine, 2011, 20(7): 110–113. (in Chinese)
- [3] KHAITAN S, DZOMBAK D A, LOWRY G V. Chemistry of the acid neutralization capacity of bauxite residue [J]. Environmental Engineering Science, 2009, 26(5): 873–881.
- [4] GRAFE M, POWER G, KLAUBER C. Bauxite residue issues: III. Alkalinity and associated chemistry [J]. Hydrometallurgy, 2011, 108(1-2): 60-79.
- [5] BHIMA R R, BESRA L, REDDY B R, BANERJEE G N. The effect of pretreatment on magnetic separation of ferruginous minerals in bauxite [J]. Magnetic and Electrical Separation, 1997, 8(2): 115–123.
- [6] PICKLES C A, LU T, CHAMBERS B, FORSTER F. A study of reduction and magnetic separation of iron from high iron bauxite ore [J]. Canadian Metallurgical Quarterly, 2012, 51(4): 424–433.
- [7] SADLER L Y, VENKATARAMAN C. A process for enhanced removal of iron from bauxite ores [J]. International Journal of Mineral Processing, 1991, 31(3–4): 233–246.
- [8] JAMIESON E, JONES A, COOLING D, STOCKTON N. Magnetic separation of red sand to produce value [J]. Minerals Engineering, 2006, 19(15): 1603–1605.
- [9] ZHU De-qing, CHUN Tie-jun, PAN Jian, HE Zhen. Recovery of iron from high-iron red mud by reduction roasting with adding sodium salt [J]. Journal of Iron and Steel Research, 2012, 19(8): 1–5.
- [10] LI Xiao-bin, XIAO Wei, LIU Wei, LIU Gui-hua, PENG Zhi-hong, ZHOU Qiu-sheng, QI Tian-gui. Recovery of alumina and ferric oxide from Bayer red mud rich in iron by reduction sintering [J]. Transactions of Nonferrous Metals Society of China, 2009, 19(5): 1342–1347.
- [11] LI Yi-ran, WANG Jun, WANG Xiao-jun, WANG Bao-qiang, LUAN Zhao-kun. Feasibility study of iron mineral separation from red mud by high gradient superconducting magnetic separation [J]. Physica C, 2011, 471: 91–96.
- [12] LIU Y J, NAIDU R. Hidden values in bauxite residue (red mud): Recovery of metals [J]. Waste Management, 2014, 34(12): 2662–2673.

3474

- [13] NI Xiao-min, SU Xiao-bo, ZHENG Hua-gui, ZHANG Dong-gen, YANG Dan-dan, ZHAO Qing-bao. Studies on the one-step preparation of iron nanoparticles in solution [J]. Journal of Crystal Growth, 2005, 275(3): 548–553.
- [14] GLAVEE G N, KLABUNDE K J, SORENSEN C M, HADJIPANAYLS G C. Chemistry of borohydride reduction of iron (II) and iron (III) ions in aqueous and non-aqueous media: Formation of nanoscale Fe, FeB, and Fe₂B powders [J]. Inorganic Chemistry, 1995, 34(1): 28–35.
- [15] LI Feng-gui, ZHANG Xi-chun. Inspection technology for iron ore
 [M]. Beijing: Standards Press of China, 2005: 392–400. (in Chinese)
- [16] TREMAINE P R, LEBLANC J C. The solubility of magnetite and

the hydrolysis and oxidation of Fe^{2+} in water to 300 °C [J]. Journal of Solution Chemistry, 1980, 9(6): 415–442.

- [17] MURRAY J, KIRWAN L, LOAN M, HODNET B K. In-situ synchrotron diffraction study of the hydrothermal transformation of goethite to hematite in sodium aluminate solutions [J]. Hydrometallurgy, 2009, 95(3): 239–246.
- [18] BEVERSKOG B, PUIGDOMENECH I. Revised Pourbaix diagrams for iron at 25–300 °C [J]. Corrosion Science, 1996, 38(12): 2121–2135.
- [19] YANG Xian-wan, HE Ai-pin, YUAN Bao-zhou. Hand book of thermodynamic data of high temperature aqueous solution [M]. Beijing: Metallurgical Industry Press, 1983: 207–227. (in Chinese)

拜耳法溶出过程中氧化铁水热还原转化为磁铁矿

李小斌1,刘楠1,齐天贵1,2,王一霖1,周秋生1,彭志宏1,刘桂华1

1. 中南大学 冶金与环境学院,长沙 410083;
 2. 中铝中州铝业有限公司,焦作 454000

摘 要: 在铝土矿拜耳法溶出的同时使赤铁矿转化为磁铁矿对高铁铝土矿的经济高效利用至关重要。在热力学计 算的基础上,实验研究氧化铁在碱溶液中的水热还原行为。热力学计算结果表明: 在适当的氧化还原电位条件下, 氧化铁在碱性溶液体系中可转化为磁铁矿。实验结果表明: 铁粉与氧化铁粉或者铁粉与水在碱性水溶液中反应形 成四氧化三铁,反应转化率均随温度和碱浓度的升高而显著升高,这说明四氧化三铁的形成过程可能经历铁粉和 氧化铁粉溶解分别形成含铁离子 Fe(OH)₃⁻和 Fe(OH)₄⁻,Fe(OH)₃⁻和 Fe(OH)₄⁻进一步反应生成四氧化三铁两个过程。 同时,铝酸根对氧化铁在碱溶液中的水热还原没有显著影响,在其拜耳法溶出过程中一水硬铝石中的铁矿物可以 转化为磁铁矿。

关键词:拜耳法;溶出;水热还原;氧化铁;四氧化三铁

(Edited by Mu-lan QIN)