

## Thermodynamics study on leaching process of gibbsitic bauxite by hydrochloric acid

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**Abstract:** For the low-grade gibbsitic bauxite, the leaching rate of alumina is very low during the Bayer process. The acid leaching method is attracting more attention, and the hydrochloric acid leaching was developed rapidly. The mineral composition and chemical composition were investigated by X-ray diffraction analysis and semi-quantitative analysis. The thermodynamics of leaching process was analyzed. The results show that the major minerals in the bauxite are gibbsite, secondly goethite and quartz, anatase and so on. The acid leaching reactions of the bauxite would be thermodynamically easy and completed. Under the conditions that ore granularity is less than  $-55\ \mu\text{m}$ , the L/S ratio is 100:7, and the leaching temperature is 373–383 K, the leaching time is 120 min and the concentration of HCl is 10%, both the leaching rates of Al and Fe are over 95%. The main composition of leaching slag is  $\text{SiO}_2$  which is easy for comprehensive utilization.

**Key words:** alumina; bauxite; gibbsitic bauxite; acid leaching; thermodynamics

### 1 Introduction

Bauxite is the main raw material for producing alumina [1–6]. With the rapid development of both alumina industry and the other bauxite-required industries, the shortage supplement of high-quality bauxite resources is more serious in recent years. Researchers have done a lot of studies on the development and utilization of all kinds of middle and low grade bauxite and achieved some progresses. The Bayer process is the main method of producing alumina [7–9]. The dressing-Bayer process [10] and Bayer process after roasting pretreatment for desulphurization [11–13] are separately developed according to the refractory low grade diasporic bauxite and the high sulfur bauxite. To the middle-low grade gibbsitic bauxite, desiliconizing is treated by washing bauxite or the floatation firstly, then the Bayer process is used for leaching alumina.

The acid process for alumina production has been

given great attention in recent years, and some achievements have been reached [14–16]. However, the thermodynamics study on the extraction of alumina from the bauxite in the acid system has not been reported.

The gibbsite is also named as the water aluminite or aluminium-oxygen, with  $\text{Al}(\text{OH})_3$  as its structural formula and with  $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$  as its molecular formula. It belongs to monoclinic crystal system, which has complete crystallization of hexagonal plates. The hydroxide ion with a hexagonal close-packing array displays octahedral coordination with the aluminum ion which is filled in 2/3 of octahedral interstices of the two layers adjacent of hydroxide ions. It has ionic bond between layers and molecular bond of interlayer structure. Gibbsite is associated with kaolinite, goethite, hematite and illite.

Low-grade gibbsitic bauxite with high content of iron oxide was used as raw material by hydrochloric acid leaching. The thermodynamics reactions of the main valuable metals were studied in the acid leaching process and verified by the experimental results.

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## 2 Experimental

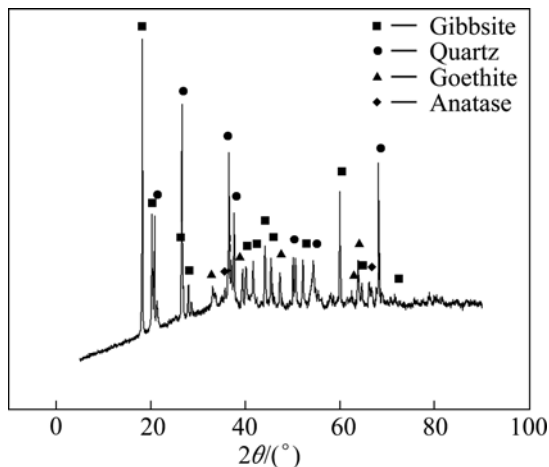
The applied raw material of gibbsite was from Australia. The chemical composition and mineral composition of the gibbsite samples are listed in Tables 1 and 2. The XRD pattern is shown in Fig. 1.

**Table 1** Chemical composition of gibbsite sample (mass fraction, %)

| Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | Fe <sub>2</sub> O <sub>3</sub> | TiO <sub>2</sub> | CaO  | MgO  | LOI   |
|--------------------------------|------------------|--------------------------------|------------------|------|------|-------|
| 38.51                          | 18.58            | 19.26                          | 1.09             | 0.05 | 0.08 | 22.20 |

**Table 2** Mineralogical composition of gibbsite sample (in mass fraction, %)

| Gibbsite | Quartz | Goethite | Anatase | Others |
|----------|--------|----------|---------|--------|
| 58.90    | 18.58  | 21.43    | 1.09    | 0.31   |



**Fig. 1** XRD pattern of gibbsite sample

As shown in Table 2, the bauxite sample mainly exists in the forms of gibbsite, secondly goethite and quartz, anatase and so on. The mineral features with the low content of aluminum, the relatively low aluminum–silicon ratio and the high content of iron indicated that it is a kind of typical refractory ore. The absolute dissolution rate of alumina could only reach 51.75% if the Bayer process for alumina digestion is used. The ore is more suitable as the raw material of bauxite for acid leaching.

## 3 Thermodynamic analysis

Table 2 demonstrates that the Australia gibbsite ores are mainly composed of gibbsite, secondly goethite and quartz, anatase and so on. Based on the thermodynamics analysis, the leaching process of Australia gibbsite ore is relatively complex. The minerals don't only contain gibbsite and goethite and so on. Meanwhile, the reacted

unconventional medium solution is a kind of strong electrolyte solution. Thus it forms a complex multiphase system. Only when the main mineral dissolves, aluminum which is encapsulated and filled could be extracted.

For convenience of the study, it is assumed that the ore only contains the two kinds of minerals named gibbsite and goethite. By the thermodynamic data of Al(OH)<sub>3</sub> and FeO(OH), calculations of the related reactions are carried out. The thermodynamic calculations and analysis are the qualitative analysis and quantitative estimations which still have the certain reference value on the study of leaching process. According to the principles of chemical thermodynamics [17], the calculation formulas are as follows:

$$\sum v_i A_i = 0 \quad (1)$$

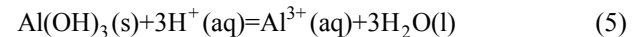
$$\Delta G_T^\ominus = \sum v_i G_{f,T,i}^\ominus \quad (2)$$

$$\lg K_T^\ominus = -\Delta G_T^\ominus / (2.303RT) \quad (3)$$

$$\begin{aligned} \Delta G_T &= \Delta G_T^\ominus + 2.303RT \lg Q_T \\ &= -2.303RT \lg K_T^\ominus + 2.303RT \lg Q_T \\ &= -2.303RT \lg (K_T^\ominus / Q_T) \end{aligned} \quad (4)$$

where  $A_i$  is reactants or products;  $v_i$  is measuring coefficient and it is negative for reactants and it is positive for products;  $T$  is the thermodynamic temperature;  $Q_T$  is reaction quotient at temperature  $T$ ;  $\sum v_i G_{f,T,i}^\ominus$  is standard molar Gibbs free energy at temperature  $T$  for reactants or products;  $\Delta G_T^\ominus$  is standard molar Gibbs free energy change in the chemical-reaction at temperature  $T$ ;  $K_T^\ominus$  is standard equilibrium constant of chemical reactions at temperature  $T$ ;  $R$  is mole gas constant, 8.314 J/(K·mol).

1) The chemical reaction formula of gibbsite and hydrochloric acid is shown as follows:



The Gibbs free energy values of each substance at different temperatures are cited from Ref. [18] and the calculation results are listed in Table 3.

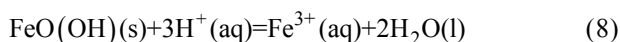
The results show that the free energy change in the chemical-reaction of gibbsite and hydrochloric acid decreases gradually as the temperature rises from 298 K to 423 K. It is explained that increasing temperature is in favor of acid leaching reaction of gibbsite. At the same time, the value of  $\Delta G_T^\ominus$  is far less than 0 and the calculated value of  $K_T^\ominus$  is great (all are over  $10^{30}$  orders of magnitude). So the reaction happens thoroughly. Standard equilibrium constants of  $K_T^\ominus$  and  $Q_T$  are both dimensionless. For the above reaction of gibbsite and hydrochloric acid, the formula is as follows:

$$K_T^\ominus = [(c_{\text{Al}^{3+}}/c^\ominus)/(c_{\text{H}^+}/c^\ominus)^3]_{\text{eq}} \quad (6)$$

$$Q_T = (c_{\text{Al}^{3+}}/c^\ominus)/(c_{\text{H}^+}/c^\ominus)^3 \quad (7)$$

where  $c$  is volume molar concentration of related substances;  $c^\ominus$  is standard concentration; eq is the abbreviation of equilibrium. According to the thermodynamic criterion, the forward reaction can proceed spontaneously until reaching equilibrium (in another word  $Q_T = K_T^\ominus$ ) when  $Q_T$  is less than  $K_T^\ominus$ . The calculation results show that  $K_T^\ominus$  of acid leaching reaction of gibbsite is very large and decreases with increasing temperature. Therefore, with about 2.74% diluted hydrochloric acid (about 1 mol/L),  $\text{Al}^{3+}$  concentration must reach  $5.69 \times 10^{24}$  mol/L ( $T=423$  K, the result is shown in Table 3) when  $c_{\text{H}^+}$  in the leaching system is reduced to  $1 \times 10^{-2}$  mol/L (pH=2, the highest pH of leaching process in experimental study) and  $Q_T = K_T^\ominus$ . But even all of aluminum in the gibbsite is leached,  $\text{Al}^{3+}$  concentration is not likely to reach such a high value. From the theoretical point of view, aluminum in the gibbsite could be digested with about 2.74% diluted hydrochloric acid thoroughly.

2) The chemical reaction equation of goethite with the diluted acid can be expressed as



$$K_T^\ominus = [(c_{\text{Fe}^{3+}}/c^\ominus)/(c_{\text{H}^+}/c^\ominus)^3]_{\text{eq}} \quad (9)$$

$$Q_T = (c_{\text{Fe}^{3+}}/c^\ominus)/(c_{\text{H}^+}/c^\ominus)^3 \quad (10)$$

It is obtained from Table 4 that  $K_T^\ominus$  of acid leaching reaction of goethite is very large and decreases with the rise of temperature. But when the temperature rises to 423 K,  $K_T^\ominus$  is over the order of magnitude of  $10^7$ . This hints that the reaction of goethite and the diluted acid happens easily.  $\text{Fe}^{3+}$  concentration must reach 26.1 mol/L ( $T=423$  K, the result is shown in Table 4) when pH of the leaching system is 2 and  $Q_T = K_T^\ominus$ . But even all of the iron in the gibbsite is digested,  $\text{Fe}^{3+}$  concentration is impossible to achieve such a high value. This suggests that the above reaction could not reach balance. In other words, iron in the gibbsite could be digested with the very diluted hydrochloric acid thoroughly.

## 4 Results and discussion

The leaching experiment was carried out in a high pressure reactor of WHFS-2L. The effects of leaching temperature on the leaching performance were studied at 373–413 K, liquid–solid ratio 100:7, leaching time 2 h, ore granularity less than 55  $\mu\text{m}$ , ore mass 14 g, concentration of hydrochloric acid 10% and volume of hydrochloric acid 200 mL. The results are summarized in Table 5.

The calculation formulas of leaching rate are

**Table 3** Thermodynamic calculation for reaction of  $\text{Al(OH)}_3$  with diluted acid

| $T/\text{K}$ | $G_T^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$ |                          |                              |                          | $\Delta G_T^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$ | $K_T^\ominus$         | $c_{\text{Al}^{3+}}^{\text{aq}} / (\text{mol} \cdot \text{L}^{-1}) (\text{pH}=2)$ |
|--------------|---|--------------------------|------------------------------|--------------------------|--|-----------------------|---|
|              | $\text{Al(OH)}_3 (s)$                             | $\text{H}^+ (\text{aq})$ | $\text{Al}^{3+} (\text{aq})$ | $\text{H}_2\text{O} (l)$ |  |                       |   |
| 298          | -1154.96  | 6.24                     | -416.73                      | -306.68                  | -200.53  | $1.42 \times 10^{35}$ | $1.42 \times 10^{29}$   |
| 323          | -1143.36  | 6.64                     | -407.49                      | -308.50                  | -209.54  | $7.71 \times 10^{33}$ | $7.71 \times 10^{27}$   |
| 348          | -1131.75  | 6.80                     | -398.99                      | -310.42                  | -218.89  | $7.20 \times 10^{32}$ | $7.20 \times 10^{26}$   |
| 373          | -1120.15  | 6.71                     | -391.24                      | -312.47                  | -228.61  | $1.04 \times 10^{32}$ | $1.04 \times 10^{26}$   |
| 398          | -1108.55  | 6.37                     | -384.24                      | -314.62                  | -238.66  | $2.10 \times 10^{31}$ | $2.10 \times 10^{25}$   |
| 423          | -1096.94  | 5.80                     | -377.98                      | -316.88                  | -249.05  | $5.69 \times 10^{30}$ | $5.69 \times 10^{24}$   |

**Table 4** Thermodynamic calculation for reaction of  $\text{FeO(OH)}$  with diluted acid

| $T/\text{K}$ | $G_T^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$ |                          |                              |                         | $\Delta G_T^\ominus / (\text{kJ} \cdot \text{mol}^{-1})$ | $K_T^\ominus$         | $c_{\text{Fe}^{3+}}^{\text{aq}} / (\text{mol} \cdot \text{L}^{-1}) (\text{pH}=2)$ |
|--------------|---|--------------------------|------------------------------|-------------------------|--|-----------------------|---|
|              | $\text{FeO(OH)} (s)$                              | $\text{H}^+ (\text{aq})$ | $\text{Fe}^{3+} (\text{aq})$ | $\text{H}_2\text{O}(l)$ |  |                       |   |
| 298          | -488.60   | 6.24                     | 64.36                        | -306.68                 | -79.12   | $7.38 \times 10^{13}$ | $7.38 \times 10^7$  |
| 323          | -488.60   | 6.64                     | 73.46                        | -308.50                 | -74.85   | $1.27 \times 10^{12}$ | $1.27 \times 10^6$  |
| 348          | -488.60   | 6.80                     | 81.82                        | -310.42                 | -70.81   | $4.26 \times 10^{10}$ | $4.26 \times 10^4$  |
| 373          | -488.60   | 6.71                     | 89.44                        | -312.47                 | -67.01   | $2.42 \times 10^9$    | $2.42 \times 10^3$  |
| 398          | -488.60   | 6.37                     | 96.33                        | -314.62                 | -63.42   | $2.11 \times 10^8$    | $2.11 \times 10^2$  |
| 423          | -488.60   | 5.80                     | 102.48                       | -316.88                 | -60.06   | $2.61 \times 10^7$    | 26.1  |

Because the standard molar Gibbs free energies of solid substances for different temperatures differ little, the standard molar Gibbs free energies of goethite at different temperatures are replaced by 298 K from literature.

**Table 5** Effects of leaching temperature on leaching performance

| Leaching temperature/K | Slag mass/g | Content of slag /%             |                                |                  | Leaching rate of Al <sub>2</sub> O <sub>3</sub> /% | Leaching rate of Fe <sub>2</sub> O <sub>3</sub> /% |
|------------------------|-------------|--------------------------------|--------------------------------|------------------|--|--|
|                        |             | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> |  |  |
| 373–383                | 2.361       | 10.30                          | 3.75                           | 71.71            | 95.49  | 96.72  |
| 393                    | 2.221       | 9.21                           | 2.98                           | 74.26            | 96.21  | 97.55  |
| 403                    | 2.215       | 7.44                           | 2.92                           | 75.42            | 96.94  | 97.60  |
| 413                    | 2.268       | 6.94                           | 2.64                           | 75.74            | 97.08  | 97.78  |

$$\eta(\text{Al}_2\text{O}_3) = 1 - \frac{m_s w_A}{38.51 m_B} \quad (11)$$

$$\eta(\text{Fe}_2\text{O}_3) = 1 - \frac{m_s w_F}{19.26 m_B} \quad (12)$$

where  $\eta(\text{Al}_2\text{O}_3)$  is the leaching rate of alumina;  $\eta(\text{Fe}_2\text{O}_3)$  is the leaching rate of iron oxide;  $m_s$  is the dried solid mass after solid–liquid separation;  $m_B$  is the experimental ore mass;  $w_A$  is the content of alumina in the leaching slag, %;  $w_F$  is the content of iron oxide in the leaching slag; 38.51 is the content of alumina in the raw ore in %; 19.26 is the content of iron oxide in the raw ore in %.

From Table 5, the results are found that increasing the temperature is beneficial to the acid leaching reactions of gibbsite and goethite and the reactions tend to be more complete and agree well with the thermodynamic calculations.

## 5 Conclusions

From the thermodynamic calculations, the values of  $\Delta G_T^\ominus$  of the main minerals gibbsite and goethite in the bauxite by diluted acid leaching are far less than 0 and all of the values of calculated  $K_T^\ominus$  are large. So the reactions can proceed very thoroughly. With a liquid–solid ratio 100:7, leaching time 2 h, ore granularity less than 55  $\mu\text{m}$ , concentration of hydrochloric acid 10% and leaching temperature 373–383 K, both the leaching rates of Fe and Al are over 95% and the main composition of leaching slag is SiO<sub>2</sub> which is easy for comprehensive utilization.

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## 三水型铝土矿盐酸浸出过程的热力学研究

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**摘 要:** 针对低品位三水型铝土矿使用拜耳法提取氧化铝存在溶出率低的情况, 采用盐酸法浸出, 利用 X 衍射分析和半定量分析手段研究铝土矿的矿物组成和化学组成, 并对矿石中主要有价金属的浸出反应进行热力学分析。结果表明: 铝土矿的主要成分为三水铝石, 其次是针铁矿和石英, 以及锐钛矿等, 其主要矿物三水铝石和针铁矿的酸浸反应很容易进行, 在配矿液固比 100:7、浸出时间 2 h、矿石粒度小于 55  $\mu\text{m}$ 、盐酸浓度 10%、浸出温度 373~383 K 的条件下矿物中铁和铝的浸出率均在 95%以上, 浸出渣主要成分为  $\text{SiO}_2$ , 易于综合利用。

**关键词:** 铝土矿; 氧化铝; 三水型铝土矿; 酸浸; 热力学

(Edited by Hua YANG)