

BASIC RESEARCH ON CALCIFICATION TRANSFORMATION PROCESS OF LOW GRADE BAUXITE

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Keywords: low grade bauxite; calcification-carbonation; calcification transformation; hydrogarnet

Abstract

Our group put forward a "Calcification-Carbonation" new process use of low grade bauxite to produce alumina based on the problem of bauxite grade are decreasing gradually in china. This paper studies the effect of reaction thermodynamics, kinetics and processing parameters in calcification process. The thermodynamics calculation results show that both calcification reactions of gibbsite and diasporic can proceed within their dissolution temperature range. The study of Non-isothermal kinetics by high-pressure DCS results show that the calcification reaction for gibbsite occur within the temperature range 231.7-248.2°C and 248.2-268.7°C, with an activation energy of 23.7kJ/mol and 18.0kJ/mol respectively; diasporic occur within the temperature range 236.7-255.6°C and 255.6-287.5°C, with an activation energy of 264.9kJ/mol and 118.5kJ/mol respectively. Experimental results show that the appropriate calcification temperature of diasporic and gibbsite are 245°C and 180°C, molar ratio of CaO to SiO₂ is 4.69:1; under these condition, silicon phase in minerals transformed hydrogarnet completely.

Introduction

China's alumina production increased year by year, have more than 30 million tons in 2011. The bauxite resources of China are abundant. However, high-grade bauxite is being exhausted gradually, its service life is less than 10 years. Most bauxite in China is diasporic with the typical character of high aluminum oxide and silica, bauxite with mass ratio of Al₂O₃ to SiO₂ is 4-6 accounted for more than 80% [1].

In China, the way to extract alumina is mainly by sintering processing or a combination of sintering and Bayer process[2]. Sintering processing is extremely energy-intensive and its energy-consuming is 3-4 times of Bayer method's[3]. Bayer process of alumina production by using low-grade bauxite will result in extraction of alumina decreased and caustic alkali loss increased, because solid phase of red mud in Bayer process are mainly Na₂O•Al₂O₃•1.7SiO₂•nH₂O. The mass of Al₂O₃ is just equal to SiO₂ in this matter, which cause 1 kg of SiO₂ in the bauxite will carry 1 kg Al₂O₃ into red mud, thus the loss of alumina and caustic alkali in red mud increased with increasing content of silica in bauxite. Therefore, China is in urgent need of new method use of low grade bauxite to produce alumina.

"Calcification-Carbonation" new process was purposed by Northeastern University for alumina production by using low grade bauxite. The calcification treatment is a key part of the new process. This paper researches on the effect of reaction thermodynamics, kinetics and processing parameters in calcification process and provides theoretical basis for actual application.

Material and Methods

Bauxite

The low grade gibbsite and diasporic used in calcification and kinetics experiment comes from Shandong and Henan respectively, the chemical composition of gibbsite and diasporic are shown as Table 1.

Table 1 Chemical composition of gibbsite and diasporic (mass fraction, %)

Component		Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	L.O.I
Content/%	Gibbsite	49.60	11.36	14.65	0.44	24.37
	Diasporic	60.07	12.92	7.20	2.86	25.45

Thermodynamics Calculation

The product of calcification process is hydrogarnet(3CaO·Al₂O₃·xSiO₂·6-2xH₂O), its thermodynamic data is related to x, saturation coefficient of SiO₂. According to reference [4], their expressions are as follows:

$$\Delta S_{298}^0 = 409.6 - 23.4x \quad (1)$$

$$-\Delta G_{298}^0 = 5670.1 + 345.3x \quad (2)$$

$$C_p^0 = a - 8x + bT \times 10^{-3} \quad (3)$$

where a and b are experience coefficient, their values are 385.0 and 232.88 respectively. The expression of average heat capacity is:

$$C_p^0 \Big|_{298}^T = \frac{1}{T - 298} \int_{298}^T C_p^0 dT \quad (4)$$

The value of standard Gibbs free energy of 3CaO·Al₂O₃·xSiO₂·6-2xH₂O was calculated by the expression[5]:

$$\Delta G_T^0 = \Delta G_{298}^0 - (T - 298)\Delta S_{298}^0 + (T - 298)C_p^0 \Big|_{298}^T - \left(T \ln \frac{T}{298} \right) C_p^0 \Big|_{298}^T \quad (5)$$

Kinetics Experiments

The Non-isothermal kinetics of calcification reaction was studied by high pressure DSC (DSC 204 HP), and detection process was controlled by Proteus software. Samples of certain weight were added to a crucible composed of gold base and stainless steel cover, sealed the crucible, then put the reference and samples crucible on the left and right stands respectively. Opening the pressure reducing valve of high purity argon and setting parameter of temperature range, heating and cooling rate. After the experiment, the DSC curve was analyzed by Proteus Analysis software.

The Non-isothermal kinetics studied the following two systems, shown as Table2.

Table 2 Experimental parameters of DSC

NO.	Sample	Mass ratio	Heating rate	Atmosphere	Gas flow rate	T _{max}
1	Gibbsite+CaO	1: 0.49	10K/min	Ar	20mL/min	300°C
2	Diasporic+CaO	1: 0.51	10K/min	Ar	20mL/min	300°C

The activation energy for calcification reaction has been calculated by Freeman-Carroll Method. kinetics equation:

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} e^{-E/RT} (1-\alpha)^n \quad (6)$$

where α is change rate of reaction

$$\alpha = \frac{\Delta H_t}{\Delta H} = \frac{S'}{S} \quad (7)$$

where ΔH_t is the change of enthalpy at temperature t , ΔH is the change of enthalpy of the complete reaction, S' is peak areas at temperature t , S is peak areas of the complete reaction.

Differential equation:

$$\frac{d\alpha}{dT} = \frac{d}{dT} \left(\frac{S'}{S} \right) = \frac{1}{S} \frac{dS'}{dT} = \frac{1}{S} \frac{d}{dT} \int_0^T \Delta T dT = \frac{\Delta T}{S} \quad (8)$$

The equation (8) substituted into (6) and taken logarithm on both sides, it is changed into:

$$\frac{\Delta \lg \Delta T}{\Delta \lg S''} = -\frac{E}{2.303R} \cdot \frac{\Delta(1/T)}{\Delta \lg S''} + n \quad (9)$$

where E is activation energy, n is reaction order, $S''=S-S'$.

Draw $\Delta \lg \Delta T / \Delta \lg S'' - \Delta(1/T) / \Delta \lg S''$ graph, it should be a line with slope of $-E/2.303R$ and intercept of n .

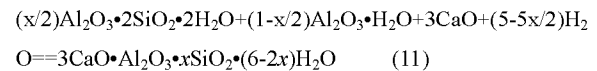
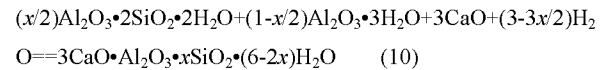
Calcification Experiments

Reaction kettle WHFS-1 was used for calcification experiment, temperature and molar ratio of CaO to SiO₂ have influence on the calcification reaction were studied. Criterion of calcification reaction degree is that content of sodium in the red mud after calcification process and mass ratio of alumina to silica in the red mud after the whole process.

Results and Discussion

Calcification Thermodynamics

Calcification reaction equations of gibbsite and diasporic are shown as equation 10 and 11:



where x is the saturation coefficient of SiO₂ in hydrogarnet(3CaO·Al₂O₃·xSiO₂·(6-2x)H₂O), the value of x is usually from 0.1 to 1. In these two reactions, kaolinite, gibbsite(diasporic), calcium oxide and hydrogarnet are solid

phase, thus the $RT \ln J$ item is far less than ΔG^0 under their real reaction conditions, so it can be ignored. This paper applied ΔG^0 to analyze the thermodynamic conditions for calcification reaction (Figure 1. and Figure 2.).

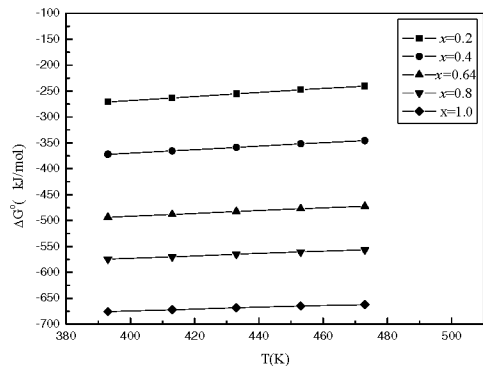


Figure 1.

ΔG^0 of the calcification reactions of gibbsite with different x under different temperatures

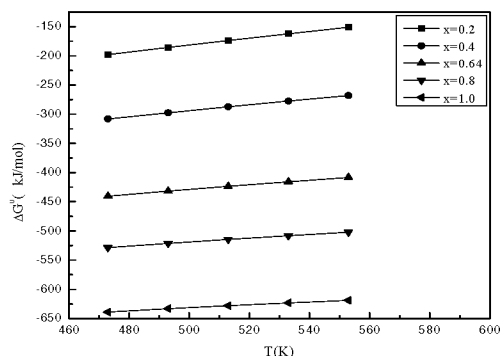


Figure 2. ΔG^0 of the calcification reactions of diasporic with different x under different temperatures

The results shown in Figure 1 and Figure 2 indicate that calcification reactions of gibbsite and diasporic can proceed within their dissolution temperature range. With the temperature and saturation coefficient of SiO_2 in hydrogarnet increases, the ΔG^0 of the two reactions increased too, the thermodynamics conditions of forward reaction get worse, its goes against calcification reaction.

Calcification Kinetics

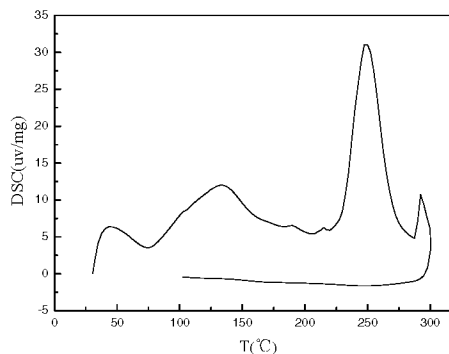


Figure 3. DSC curve of calcifications transformation process of gibbsite

Gibbsite DSC curve of gibbsite calcification transformation process is shown as Figure 3. The results show that there are three endothermic peaks on the DSC curve. The peak under 100°C should be corresponding to gibbsite react with alkali, peak in $100\text{-}200^\circ\text{C}$ corresponding to formation reaction of calcium aluminate hydrate and $225\text{-}290^\circ\text{C}$ to reaction of calcification ($231.7\text{-}248.2^\circ\text{C}$ to upward section and $248.2\text{-}268.7^\circ\text{C}$ to downward section). $\Delta \lg \text{Intensity} / \Delta \log S^* - \Delta(1/T) / \Delta \log S^*$ graphs at different temperature are shown as Figure 4 and Figure 5.

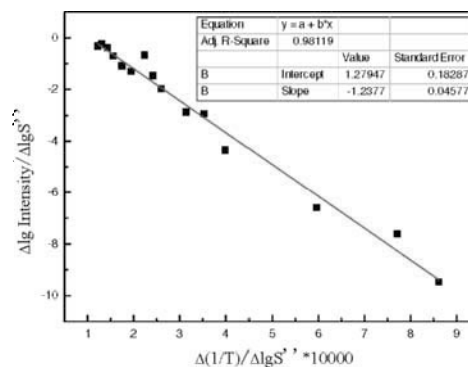


Figure 4. The result of analysis DSC curve of the calcifications process by using gibbsite within $231.7\text{-}248.2^\circ\text{C}$

Figure 4 indicate that reaction order of calcification transformation of gibbsite is 1.28, with an apparent activation energy of 23.7kJ/mol within $231.7\text{-}248.2^\circ\text{C}$, therefore, the reaction belongs to mix control; Figure 5 indicate that reaction order is 1.12 with apparent activation energy of 18.0kJ/mol , it belongs to mix control too, but its apparent activation energy decreased significantly, this shows high

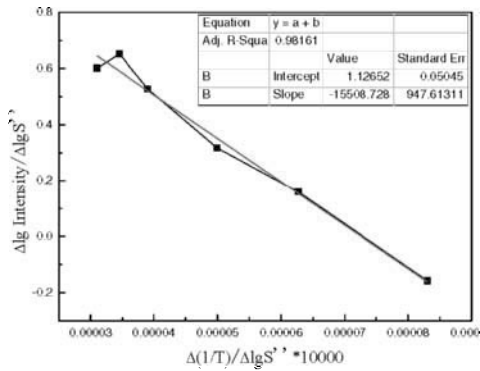


Figure 5. The result of the analysis DSC curve of the calcifications process by using gibbsite within 248.2-268.7°C

temperature conditions is beneficial to calcification reaction. Because of calcification transformation belongs to solid state reaction, it likely to cause delay of the DSC curve, it is well known that the digestion temperature of gibbsite is lower than 200°C, therefore, the real calcification temperature should be lower than DSC analysis.

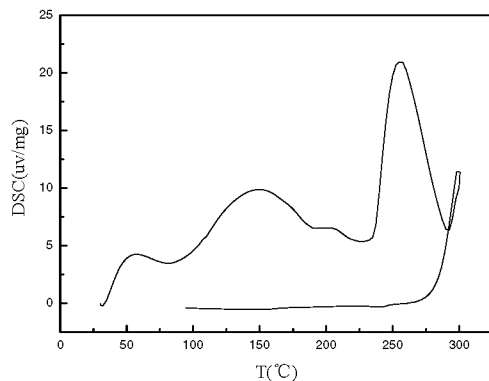
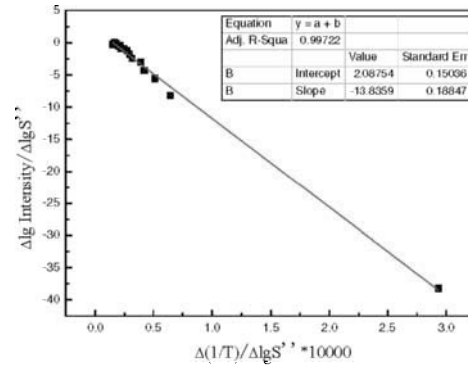


Figure 6. The DSC curve of calcifications process by using diasporic bauxite

Diasporic DSC curve of diasporic calcification transformation is shown as Figure 6. The results show that there are 2 endothermic peaks on the DSC curve, peak in 100-220°C corresponding to formation reaction of calcium aluminate hydrate and 220-300°C to reaction of calcification, calculating the DSC curve and the results are shown as Figure 7 and Figure 8.

Figure 7 and Figure 8 indicate that reaction order of calcification transformation of diasporic are 2.09 and 0.917 with apparent activation energy of 264.9kJ/mol and 118.5 kJ/mol within 236.7-255.6°C and 255.6-287.5°C respectively,



both two

Figure 7. The result of the analysis DSC curve of calcifications process by using diasporic bauxite within 236.7-255.6°C

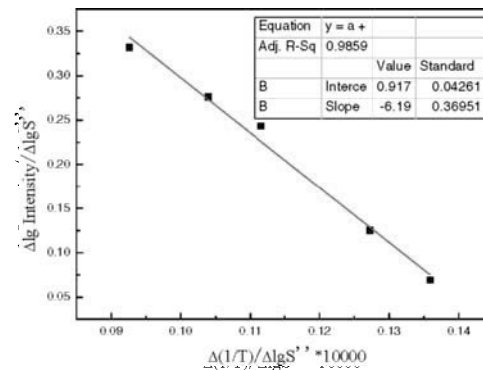


Figure 8. The result of the analysis DSC curve of calcifications process by using diasporic bauxite within 255.6-287.5°C

section belong to chemical reaction control. Likewise, the DSC analysis results show that high temperature condition is beneficial to diasporic calcification reaction. The digestion temperature of diasporic within 240-280°C in most cases, although there is delay phenomenon in DSC curve of diasporic calcification, it is weaker than gibbsite because it needs higher digestion temperature itself.

Calcification Transformation Experiments

Phase Comparison of Calcification and Normal Digestion of Gibbsite As Figure 9 shows, when digestion temperature is 160°C, digestion time is 60min, the main phase composition of the red mud is sodium aluminosilicate hydrate when normal digestion; compared with normal digestion, the main phase is ferrous hydrogarnet by using calcification digestion.

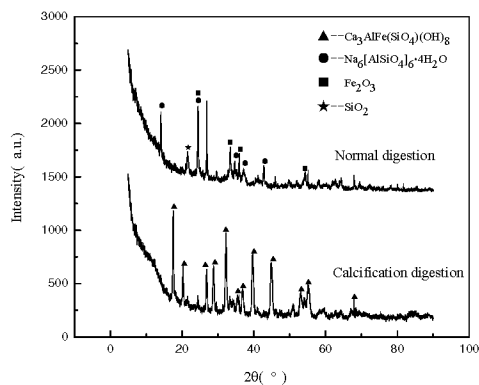


Figure 9. XRD patterns of red mud produced by calcification and normal digestion of gibbsite

The Influence of Temperature on Calcification Transformation of Gibbsite

Influence of temperature on calcification transformation of gibbsite was studied when temperature is 130~200°C, the results are shown as Figure 10, the results indicate that with temperature increased, mass ratio of Na₂O in the calcification red mud decreases and mass ratio of Al₂O₃ to SiO₂ in dissolution red mud decreases

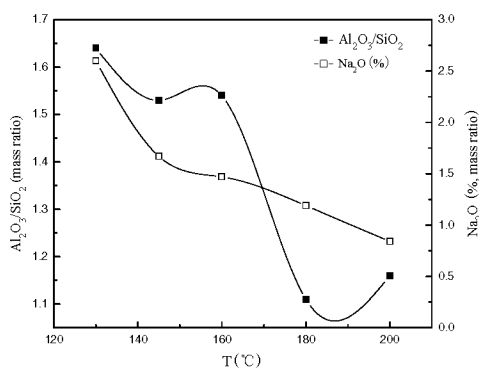


Figure 10. The relationship of sodium content of calcification residue with calcification progress within different temperature

Experiment conditions: molar ratio of CaO to SiO₂ 4.69: 1, temperature 130~200 °C, reaction time 60min, molecular ratio of Na₂O to Al₂O₃ of digestion liquor 3.1, concentration of Na₂O 140g/L. calcification red mud produced under different condition was to carried out parallel experiments of carbonation and dissolution aluminum hydroxide.

initially and then increases, the mass ratio of Al₂O₃ to SiO₂ reached the lowest point at 180°C(1.11), it shows that high temperature conditions is beneficial to calcification reaction and the optimum temperature is 180°C for gibbsite.

The Influence of CaO Addition Amount on Calcification Transformation of Gibbsite.

The results are shown as Figure 11.

it indicates that with CaO addition amount increased, mass ratio of Na₂O in the calcification red mud decreases, when the molar ratio of CaO to SiO₂ is 4.69:1, the content of Na₂O is reduced to a lower level, and continue to increase the amount of CaO will cause consumption of CaO increased, therefore, the optimum molar ratio of CaO to SiO₂ is 4.69:1.

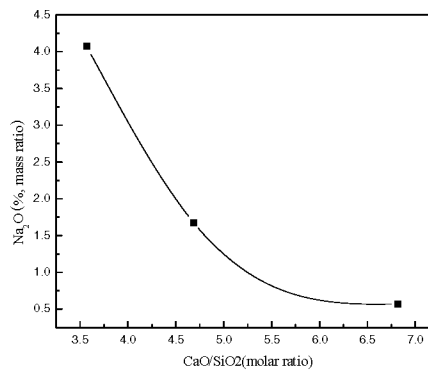


Figure 11. The Relationship of Sodium content of calcified residue with calcification progress dissolved

Experiment conditions: molar ratio of CaO to SiO₂ 3.57: 1, 4.69: 1 and 6.82: 1, temperature 160°C, reaction time 60min, molecular ratio of Na₂O to Al₂O₃ of digestion liquor 3.1, concentration of Na₂O 140g/L.

The influence of temperature on calcification transformation of diasporic

Influence of temperature on calcification transformation of diasporic was studied when temperature is 215~260°C, the results are shown as Figure 12, it indicates that influence of temperature on calcification transformation of diasporic and gibbsite has the approximately same trend, with temperature increased, mass ratio of Na₂O in the calcification red mud decreases, when the temperature is 260°C, the content of Na₂O reduced to 0.08%.

The influence of CaO addition amount on calcification transformation of diasporic

The influence of CaO addition amount on calcification transformation of diasporic was studied when molar ratio of CaO to SiO₂ 3.13:1 to 5.27:1, the results as shown in Figure 13.

From the experiment results that Figure 13 show, with CaO addition amount increased, mass ratio of Na₂O in the calcification red mud decreases. In general, the content of Na₂O in diasporic calcification red mud is lower than gibbsite, it can be explained by calcification temperature of diasporic is much higher than gibbsite.

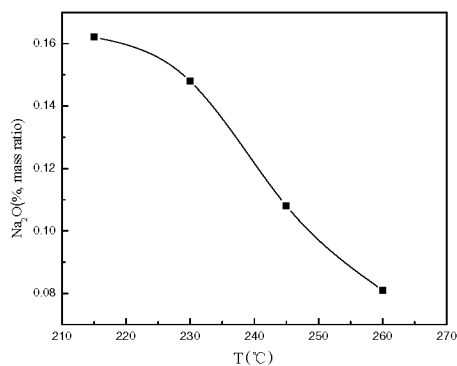


Figure 12. The Relationship of Sodium content of calcified residue with calcification temperature

Experiment conditions: molar ratio of CaO to SiO₂ 4.69: 1, temperature 215~260 °C, reaction time 60min, molecular ratio of Na₂O to Al₂O₃ of digestion liquor 3.1, concentration of Na₂O 240g/L.

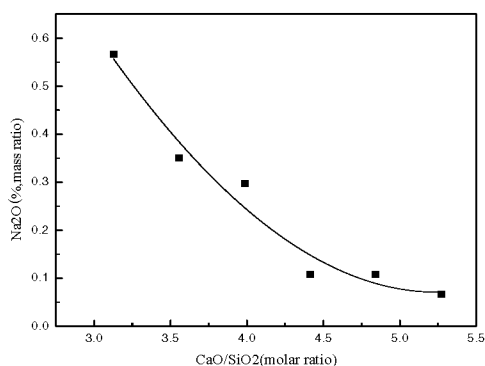


Figure 13.

The effect of C/A on Sodium content of calcified residue

Experiment conditions: molar ratio of CaO to SiO₂ 3.13:1 to 5.27:1, temperature 240 °C, reaction time 60min, molecular ratio of Na₂O to Al₂O₃ of digestion liquor 3.1, concentration of Na₂O 240g/L.

Conclusion

- (1) The thermodynamics calculation results show that calcification reactions of gibbsite and diasporic can proceed within their dissolution temperature range. With the temperature and saturation coefficient of SiO₂ in hydrogarnet increased, the ΔG^0 of the two reactions increases too, the thermodynamic conditions of forward reaction get worse, its goes against calcification reaction.
- (2) High-pressure DCS results indicate that reaction order of calcification transformation of gibbsite is 1.28 and 1.12, with an apparent activation energy of 23.7kJ/mol and 18.0kJ/mol within

231.7-248.2 °C and 248.2-268.7 °C respectively, it belongs to mix control; reaction order of calcification transformation of diasporic is 2.09 and 0.917 with apparent activation energy of 264.9kJ/mol and 118.5 kJ/mol within 236.7-255.6 °C and 255.6-287.5 °C respectively, it belongs to chemical reaction control.

(3) Calcification transformation experiments results show that increasing the temperature and CaO addition amount are beneficial to calcification reaction. The appropriate calcification temperature of diasporic and gibbsite are 245 °C and 180 °C, molar ratio of CaO to SiO₂ is 4.69:1.

Acknowledgements

This research was supported by the National Natural Science Foundation of China (Nos. U1202274, 51004033, 50934005, 50974035, 51204040 and 51074047), National 863 Plan (2010AA03A405 and 2012AA062303) and Operation Expenses for Universities' Basic Scientific Research (N100302005), and The Doctoral Fund of EDU gov (20050145029).

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