

**Research on the phase transformation and separation performance in calcification - carbonation
method for alumina production**

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Keywords: Bauxite; Calcification-Carbonization Method; phase transformation; settling performance

Abstract

With the rapid development of China's aluminum industry, deficiency of high-quality bauxite reserves has become a bottleneck restricting for the healthy development of China's aluminum industry. According to these issues, "Calcification-Carbonization Method" was purposed by Northeastern University for alumina production by using low grade bauxite. This paper researched on the transformation and separation performance in the new method. The experiment results indicated that: Al, Fe, Si transformed into hydrated garnet at 180°C and 245°C through calcification treatment, and silicon phase changed into $2\text{CaO} \cdot \text{SiO}_2$ through carbonization treatment. The settling performance of calcification slurry by using gibbsite is near to that of bayer process, when the settling performance by using diasporite get worse because of the solid content is higher than that of bayer process. Under the pressure of 0.18MPa, the filter constant of calcinated slurry are $4.18 \times 10^{-5} \text{m}^2/\text{s}$ and $1.15 \times 10^{-4} \text{m}^2/\text{s}$ for diasporite and gibbsite.

Introduction

In recent years, Chinese alumina production scale and technology level have been constantly improved with strong demand of aluminum. However, Chinese bauxite resource, especial high grade bauxite reserves decreases greatly. The majority (>95%) of bauxite resource in China are diasporite bauxite with high contents of aluminum and silica, and the A/S is lower than 7 of most bauxite resource in China (>70%), part of

Chinese alumina production factory use bauxite of A/S=4-5 for alumina production. Such composition combination presents less economic attraction due to the high levels of reactive silica, which require high digestion temperature and usher appreciable amount of caustic soda losses during Bayer processing. Meanwhile, part of Chinese alumina enterprise use gibbsite from import for alumina production.

In the other hand, because the balance solid phase in Bayer red mud is $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 1.7\text{SiO}_2 \cdot x\text{H}_2\text{O}$, so two problems occurred when we use Bayer process for alumina production by using low grade bauxite: (1) the recovery rate of alumina is low, the theoretical yields of alumina is only 75% when the A/S of bauxite is 4, because the A/S is always higher than 1 (about 1.3 of production) in red mud; (2) Na_2O content in Bayer red mud is higher than 4%, the red mud is hard to use in cement industry, and the piling amount of red mud is 2 billion ton in China as well^[1-4].

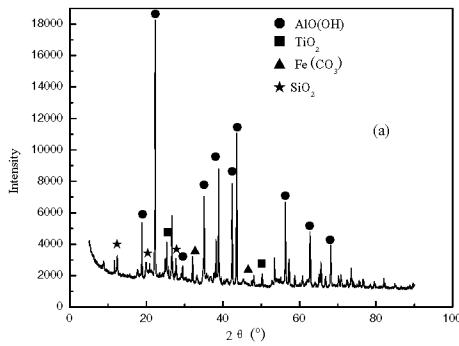
Under this condition, "Calcification-Carbonization Method" was put forward to deal with middle-low grade bauxite and red mud by Northeastern University, the main purpose of this method is to change the balance phase of red mud into $2\text{CaO} \cdot \text{SiO}_2$ and CaCO_3 with hydrometallurgical process. In the new process, the alumina (in bauxite or red mud) phase is transformed into hydrogarnet through calcification process firstly, and then the hydrogarnet phase is changed into $\text{Al}(\text{OH})_3$, $2\text{CaO} \cdot \text{SiO}_2$ and CaCO_3 through carbonization process with CO_2 , the $\text{Al}(\text{OH})_3$ is digested by alkali when the digestion temperature is lower than 100°C, and the main phase of the new type red mud is $2\text{CaO} \cdot \text{SiO}_2$ and CaCO_3 , the new type red mud

could be used in cement industry, so the solid waste problem can be solved by the new method. This paper researched on the transformation and separation performance of calcified slurry in the new method for providing theoretical basis of the new type alumina production method^[5-6].

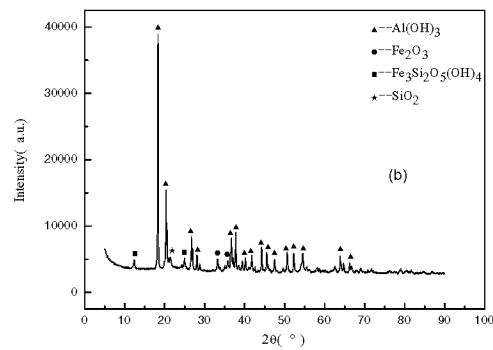
Experimental

Experiment materials

Chemical composition	Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	LOI
Content of diasporic bauxite, %	54.41	16.55	7.20	2.86	25.45
Content of gibbsite, %	49.60	11.36	14.65	0.44	24.37



(a) Diasporic bauxite



(b) Gibbsite

Fig.1 XRD patterns of bauxite

Calcification experiment

The calcification experiment was carried out in a WHFS-1 autoclave, the mother liquid, lime(CaO) and bauxite were put into the autoclave together, the temperature of the



Fig.2 WHFS-1 autoclave

In our research process, pure materials synthesis experiment (pure NaOH, Al(OH)₃ for simulate NaAlO₂ solution, pure CaO, NaSiO₃ for simulate lime and Si phase of bauxite), and transformation experiment by diasporic bauxite and gibbsite were applied.

The chemical and phase analysis results are shown in Table I and Fig.1, respectively. Phase analysis of the initial samples (Fig.1) was performed on a PW3040/60 X-ray diffractometer with scanning angle from 5 to 90 degree.

autoclave was raised to the predetermined value then holding for 30~60 minutes. After digestion, the temperature of autoclave was lowed to below 100°C, the digested slurry was separated into the solution and red mud by filtration.

Carbonation experiment

The carbonation experiment was also carried out in the WHFS-1 autoclave, the calcified slag was mixed with water, the temperature of autoclave was raised to the predetermined value holding for 60~240 minutes. The carbonated slag was digested with alkali solution for Al(OH)₃ recovery. The concentrations of Al₂O₃ and Na₂O_K (concentration of caustic soda) in solution and the content of Al₂O₃ and SiO₂ in the new type red mud were determined by ICP Prodigy xp and chemical titration.

The recovery rate of Al₂O₃ is expressed as:

$$\eta = \frac{(A/S)_o - (A/S)_r}{(A/S)_o} \times 100\% \quad (1)$$

where (A/S)_o and (A/S)_r are the ratio of alumina to silica in raw ore and the new type red mud, respectively.

Separation experiment

The separation performance of calcified slurry was researched as well, directly settlement and pressure filtration performance of calcified slurry were tested, the separation equipment are constant temperature water bath and plate and frame filter press, respectively.

Results and discussion

Calcification process of pure materials synthesis and diasporic bauxite

XRD patterns of calcified slag by pure materials at different calcification temperature are shown in Fig.3. The experiment condition are listed as below: molar ratio of $\text{CaO}:\text{SiO}_2=3:0.64$, calcification time is 60mins, Na_2O concentration of mother liquid is 240g/L, α_k of mother liquid is 3.1. In our research, effect of CaO addition amount and calcification time on calcification effect was also researched, and the optimal CaO addition amount and time is $\text{CaO}:\text{SiO}_2=3:0.64$ and 30mins, respectively.

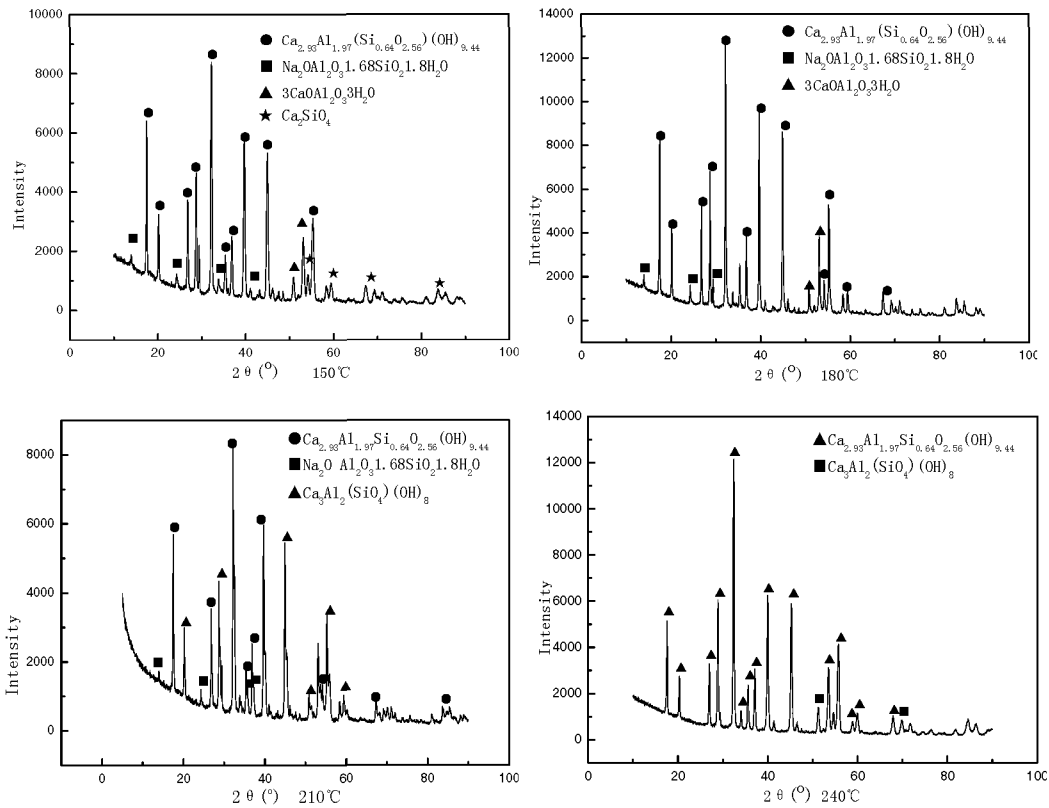


Fig.3 XRD patterns of calcified slag at different temperature

Fig.3 shows that silicon phase changed into hydrogarnet and sodium-silicon residue, and calcium aluminate hydrate phase is existed when calcification temperature is lower than 200 °C. When the calcification temperature get above 200 °C, the calcium aluminate hydrate phase disappeared with the dissolution effect of silicon, and the silicon begin to dissolved in calcium aluminate hydrate phase and change into hydrogarnet. At the calcification temperature of 240 °C, the aluminate hydrate phase disappeared completely, so (>)240 °C is considered as a optimal calcification temperature. The calcification process of

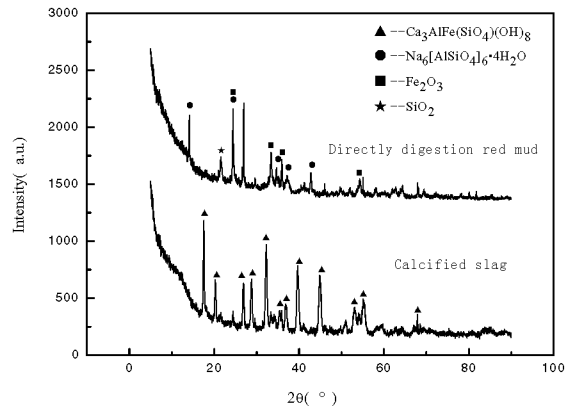


Fig.4 XRD patterns of calcification slag of gibbsite

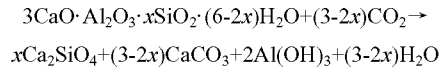
diasporic bauxite is same with the pure materials synthesis experiment.

Calcification process of gibbsite

XRD patterns of calcification slag of gibbsite are shown in Fig.4. The calcification conditions of gibbsite is: molar ratio of CaO:SiO₂=3:0.64, calcification time of 30mins, Na₂O concentration of mother liquid of 140g/L, α_k of mother liquid of 3.1. Fig.4 shows that through calcification treatment, high iron content in gibbsite lead the part of Fe₂O₃ instead Al₂O₃, and the main phase of calcification slag is iron-hydrogarnet. The optimal calcification temperature is 180°C.

Carbonation performance of diasporic bauxite and gibbsite

Through calcification treatment, the calcified slag was treated with carbonation process, the reaction of this process is:



Through carbonation treatment, hydrogarnet phase is changed into Al(OH)₃, 2CaO·SiO₂ and CaCO₃, the Al(OH)₃ is digested by alkali when the digestion temperature is lower than 100°C, and the main phase of the new type red mud is 2CaO·SiO₂ and CaCO₃. We have researched the carbonation conditions such as temperature, CO₂ pressure, time and liquid-solid ratio on the carbonation effects. The result at the optimal conditions is shown in Table 2.

Table 2 A/S and chemical content in new type red mud through calcification-carbonation treatment					
Materials	Carbonation times	Experiment result			
		Al ₂ O ₃ /%	SiO ₂ /%	Na ₂ O/%	A/S in new type red mud
Diasporic bauxite	1	11.09	11.02	—	1.01
	2	4.41	10.02	0.12	0.44
Gibbsite	1	11.27	10.16	0.67	1.11
	2	8.49	10.32	0.57	0.82

Table 2 shows that through calcification-carbonation treatment, the A/S and Na₂O content in new type red mud by using diasporic bauxite lowed to 0.44 and 0.12%, meet the requirements of cement industry. But for gibbsite, although the A/S is lower than 1, but it is also higher than that of diasporic bauxite, the main reason is the optimal carbonation conditions of iron-hydrogarnet is different from hydrogarnet, the effect of carbonation condition on the decomposability of iron-hydrogarnet is in researching step.

Separation performance of calcified slurry

The propose of calcification process is to change the

silicon phase of bauxite into hydrogarnet, so in the new method, lime addition is higher than that of Bayer process (mass of lime addition amount for diasporic bauxite is m(CaO):m(SiO₂)≈1:1, in Bayer process of gibbsite lime addition is 0, but in calcification-carbonation process is n(CaO):n(SiO₂)=3:0.64, m(CaO):m(SiO₂) ≈ 4.375 : 1). So the solid content in calcification slurry is about 2~2.5 times of Bayer digested slurry. In this section, settling performance of calcification slurry is researched firstly, and the settling speed of calcification slurry and Bayer digested slurry by using diasporic bauxite and gibbsite is shown in Fig.5.

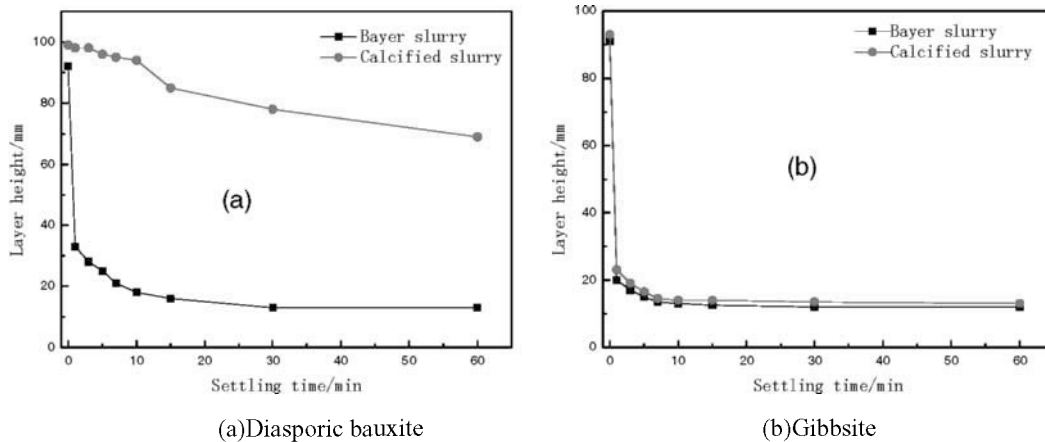


Fig.5 The height of settlement layer go with time under different lime addition

The settling performance experiment results in Fig.5 show that:

(1) For diasporic bauxite, the solid content of calcified slurry effects on the settling performance is great, the settling speed of calcified slurry is much more lower than that of Bayer slurry. The reason is: in Bayer or calcification process for diasporic bauxite, the Na₂O concentration in the mother liquid is higher than that of gibbsite (about 240g/L), the solid content of Bayer slurry is about 120g/L, and in the calcified slurry is higher than 200g/L. High solid content lead the settling slurry change into interference settlement status, and the settling speed decreased greatly.

(2) For gibbsite, although the lime addition is n(CaO):n(SiO₂)=3:0.64 as well, but the Na₂O concentration in the mother liquid is about 140g/L, and the total gibbsite and lime addition amount is lower than that of diasporic bauxite, which lead the solid content of calcified slurry is lower than 200g/L, the interference settlement phenomenon do not happened in settling process. Meanwhile, in the Bayer process of gibbsite, goethite in settling process is easy to change into colloid Fe(OH)₃, which will decrease the settling speed of digested slurry. But in calcified slurry, Fe content changed into iron-hydrogamet, which will not effect the settling performance,

so it is the main reason of settling speed of calcified slurry is the same with Bayer slurry.

For finding the reasonable separation method for the calcified slurry (especial for the calcified slurry of diasporic bauxite), pressure filtration performance of calcified slurry were tested. In this paper, the filter constant K is calculated to represent the filter performance of the calcified slurry. The calculation method for K is:

Constant pressure filtration equation:

$$(q + q_e)^2 = K(\theta + \theta_e) \quad (2)$$

Where q is volume of filtrate of unit area;

q_e is virtual volume of filtrate of unit area;

θ is actual filtration time;

θ_e is virtual filtration time;

K is filter constant.

From equation (2), we get:

$$\frac{d\theta}{dq} = \frac{2}{k} q + \frac{2}{k} q_e \quad (3)$$

So when we get the liner relationship between $\Delta\theta/\Delta q$ and q , the slope is $2K$.

The liner relationship and between $\Delta\theta/\Delta q$ and q for diasporic bauxite and gibbsite at different pressure are shown in Fig.6 and Fig.7.

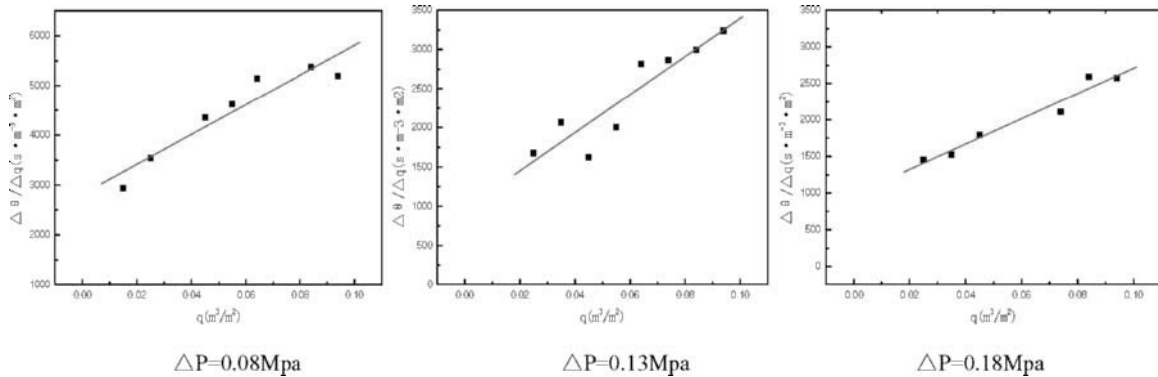


Fig.6 Liner relationship between $\Delta\theta/\Delta q$ and q for diasporic bauxite

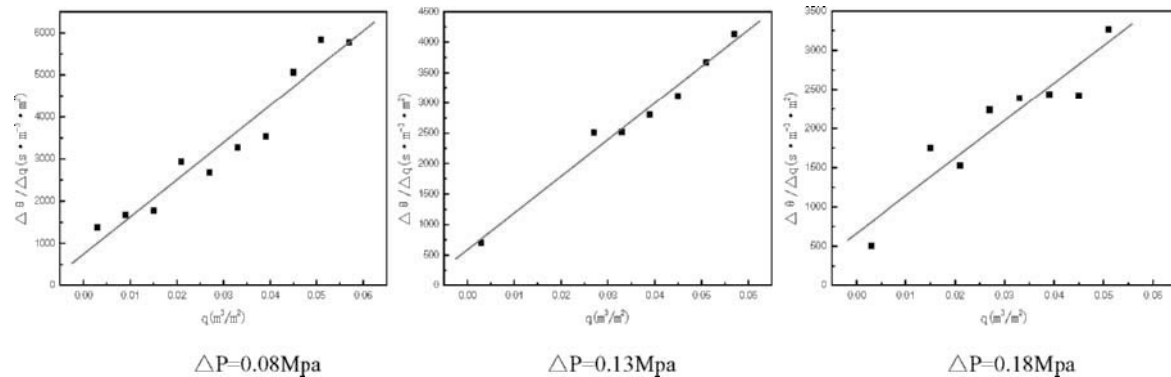


Fig.7 Liner relationship between $\Delta\theta/\Delta q$ and q for gibbsite

The calculation results of K is listed in Table 3.

Bauxite type	$\Delta P/MPa$	Slope	Intercept	$K (m^2/s)$
Diasporic bauxite	0.08	8.83×10^4	214.95	2.26×10^{-5}
	0.13	6.02×10^4	584.23	3.32×10^{-5}
	0.18	4.79×10^4	665.10	4.18×10^{-5}
Gibbsite	0.08	3.00×10^4	2816.30	6.67×10^{-5}
	0.13	2.43×10^4	963.85	8.22×10^{-5}
	0.18	1.73×10^4	976.04	1.15×10^{-4}

The experiment results in Table 3 show that the K of calcified slurry by using diasporic bauxite get 4.18×10^{-5} , and the compression index get 0.4, which is much more lower than that of settling process, so filtration is considered as a reasonable method for separation of the diasporic calcified slurry. For gibbsite, directly settling is fit for the production process.

Conclusion

(1) The optimal calcification condition are molar ratio of $CaO:SiO_2=3:0.64$, calcification time is 30mins, Na_2O concentration of mother liquid is 240g/L, α_k of mother liquid is 3.1 calcification temperature of 240°C for diasporic bauxite, and molar ratio of $CaO:SiO_2=3:0.64$, calcification time is 30mins, Na_2O concentration of mother liquid is 140g/L, α_k of mother liquid is 3.1 calcification temperature of 180°C for gibbsite.

(2) In calcification process, silicon content phase in diasporic bauxite changed into hydrogarnet, and for gibbsite is iron-hydrogarnet.

(3) Filtration is considered as a reasonable method for separation of the diasporic calcified slurry. For gibbsite, directly settling is fit for the production process.

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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