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Thermodynamics and kinetics of the carbothermal reduction of aluminum sulfate

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ABSTRACT

The thermodynamic analysis and kinetics of the carbothermal reduction of aluminum sulfate using anthracite as the reducing agent are reported. The results showed that the reduction reaction was controlled by interfacial chemical reaction when the carbon excess coefficient was 1.15 (aluminum sulfate, anthracite coal particle size, respectively 100 mesh, 180 mesh) and the reaction temperature was in the range of 450–600 °C. The reaction could be represented using the Erofeev equation: $\ln [-\ln (1 - x)] = n \ln t + \ln k$ and the apparent activation energy was 227.50 kJ·mol⁻¹. From the XRD pattern, FTIR spectra and SEM image of the product after reduction was determined at 600 °C for 2 h, it was amorphous alumina and the particle size was small, which provided good conditions for the preparation of metallurgical grade alumina.

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GRAPHICAL ABSTRACT



Introduction

Aluminum compounds such as aluminum sulfate, aluminum oxide, and aluminum nitrate are important chemical raw materials and widely used in flocculants, catalysts, mordants, paper, ceramics, glass, electronics, and other applications.^[1-6] In industrial production, various carbon metal elements are used for smelting and extraction of valuable metal elements to produce metal compounds. The quality and purity of these compounds determine the utilization rate of the raw materials and economic benefits of the entire chemical industry.^[7–13]

Researchers have conducted in-depth studies on carbon thermal reduction,^[14–17] where most have focused on

aspects such as ore size, carbon overdose coefficient, and carbon-oxygen atomic ratio. Chen proposed that the carbothermal reduction barite reaction primarily consists of a gas phase enclosing barite particles. CO reacts with barium sulfate (BaSO₄) on the surface of the particles to form the shell of the BaS product. CO penetrates the product shell, diffuses into the internal reaction interface, reacts with the particles, and CO is then diffused. From the thermodynamics and kinetics, it was concluded that increasing the reaction temperature in the gas phase is conducive to an increased reaction rate, but this assumption has not been studied in depth.^[18] Salem and Osgouei examined the influence of

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 Table 1. Carbothermal reduction of aluminum sulfate series reaction.

Serial number	Chemical reaction equation		
R1	$AI_2(SO_4)_3 + 1.5C(A) = AI_2O_3 + 3SO_2(g) + 1.5CO_2(g)$	24 °C	
R2	$AI_2(SO_4)_3 + 3C(A) = AI_2O_3 + 3SO_2(g) + 3CO(g)$	160 °C	
R3	$C(A) + CO_2(g) = 2CO(g)$	600 °C	
R4	$AI_2(SO_4)_3 + 3CO(g) = AI_2O_3 + 3SO_2(g) + 3CO_2(g)$	-	
R5	$2CO(g) + SO_2(g) = 2CO_2(g) + S$	-	

particle size distribution on the carbothermal reduction barite process and found that when the granularity of barite was reduced from 230 to 400 mesh, its reaction activation energy was reduced by only 5.4 kJ·mol⁻¹.^[19] Liu et al. used microwave and conventional heating to study the carbothermal reduction reaction of manganese ore powder.^[20] Hlabela and Chen used differential scanning calorimetrythermogravimetry (DSC-TG) to study the kinetics of CO reduction of barite. The CO mass fraction was 4.8% between 850 °C and 1000 °C. The CO reduction barite reaction is a primary reaction with an average activation energy of 149 kJ mol^{-1.[21]} Jagtap studied the catalytic effects of Fe(NO₃)₃ and Na₂CO₃ on the carbon thermal reduction of barite.^[22] The studies above differ significantly in terms of ore grades, impurity mass fractions, and reduction conditions. Also, studies on the preparation of alumina via carbon thermal reduction of aluminum sulfate have not been reported, and the reaction mechanism remains unclear.

In addition, the temperature of sulfate decomposition by carbothermal reduction is lower than that of direct calcination and decomposition of sulfate.^[22–27] The reaction activity of alumina in the reduction product is good and the alkali dissolution condition is mild, which provides suitable conditions for the preparation of metallurgical grade alumina in later stages.^[10,18]

The present study used anthracite as a reducing agent. A thermodynamic analysis of the reaction process of the carbothermal reduction of aluminum sulfate revealed limiting factors and a kinetic equation of the reduction reaction rate. These findings should provide theoretical basis for the process of the carbothermal reduction of aluminum sulfate to produce crude alumina and provide conditions for the preparation of metallurgical grade alumina.

Results and discussion

Thermodynamic analysis of the carbothermal reduction of aluminum sulfate

The carbothermal reduction reaction of aluminum sulfate is relatively complicated. Although all the reactants are solid, the reaction system includes a solid reaction and gas-solid reaction. The main potential chemical reactions are listed in Table 1. Using the reaction equation module in the thermo-dynamic software HSC 6.0,^[20,22] thermodynamic analyses of the above chemical reactions were carried out and results were presented in Figure 1.

Table 1 showed that the initial reaction temperature of R1 was 24 °C, R2 was 160 °C, and R3-5 was 600 °C but could occur at any temperature between 0 and 1000 °C. As depicted in Figure 1, reactions at 600–900 °C occurred in



Figure 1. Reactive chemical reaction of Gibbs free energy from R1 to R5.



Figure 2. Effect of reaction temperature on equilibrium composition.

the following order: Type R2 > R1 > R4 > R5 > R3. When the reaction temperature exceeded 600 °C, the order was changed to R2 > R1 > R4 > R3 > R5. All reduction reaction rates increased with temperature.

The relationship between the equilibrium composition of the carbothermal reduction aluminum sulfate reaction system and the reaction temperature was calculated using the equilibrium compositions module in the thermodynamic software HSC 6.0 (Figure 2). Figure 2 showed that the Al_2O_3 system temperature was 150 °C, and its mole balance varied as the temperature rose. The equilibrium tended to remain constant until the temperature reached 400 °C. Theoretically, $Al_2(SO_4)_3$ can be a complete reduction for Al_2O_3 . According to this conclusion, when the reaction temperature reached 500 °C, the four experimental groups were tested using gas chromatography (GC900C) at reaction times of 5 min, 10 min, 25 min, and 30 min of exhaust gas monitoring; the results were shown in Figure 3.

Figure 3 indicated that a large amount of CO and a small amount of CO₂ appeared in the system at the beginning (5 min and 10 min). At this point, the carbon thermal reduction reaction was in the initial stages. CO only reacted with the activation center of $Al_2(SO_4)_3$ with high surface energy to form a new phase crystal nucleus. At this time, the number of activation centers on the surface of aluminum sulfate



Figure 3. Chromatogram at different residence times.

was limited, created difficulties in generating a three-dimensional seed, and the reaction rate was slow. A large amount of CO_2 and a small amount of CO existed in the system at 25 min and 30 min. At this point, with the generation of the three-dimensional crystal nucleus, the two-phase interfacial region gradually increased with the growth of the new crystalline phase. The chemical reaction accelerated with an increase in the boundary area, and the reaction rate reached its maximum.

Overall, when using anthracite as a reducing agent, part of the carbon in the reactant came into close contact with aluminum sulfate particles. At a low temperature, carbon reacted directly with aluminum sulfate to produce a small amount of CO. Due to the presence of O_2 in the system, incomplete combustion of anthracite occurred (partial CO). At temperatures less than 450 °C, CO reacted directly with aluminum sulfate and the solid-solid reaction was given priority, but in the temperature range of 450-600 °C, the gassolid reaction was prioritized. The R2 reaction in Table 1 generated CO. As the temperature increased, the reaction rate increased and a large amount of CO was produced. This stage was primarily formed by the reaction of $Al_2(SO_4)_3$ on the surface of the particle with CO to form Al₂O₃, forming the product shell. CO continued to penetrate the Al₂O₃ product layer to the inside of the particle for reaction. The resulting CO₂ diffused into the gas phase, followed by the reaction of C with $Al_2(SO_4)_3$ to generate CO, and this process was repeated until $Al_2(SO_4)_3$ was completely restored. Therefore, the carbothermal reduction of aluminum sulfate may be controlled by two dynamic reaction regions, namely, diffusion control and interfacial chemical reaction control.

Kinetic analysis of carbon thermal reduction of aluminum sulfate

In theory, the reaction process of the carbothermal reduction of aluminum sulfate can be divided into two kinetic reaction regions: diffusion control and interfacial chemical reaction control. Under diffusion control, the rate of the



Figure 4. Relationship between alumina yield and reaction time at different temperatures.

reaction process shows various rules unique to the mass transfer step. Since the diffusion activation energy of gas is generally only $4-20 \text{ kJ} \cdot \text{mol}^{-1}$, the temperature has little influence on the reaction rate. When controlled by an interfacial chemical reaction, the apparent rate follows various laws inherent in the chemical reaction. The activation energy of the reaction is generally greater than $40 \text{ kJ} \cdot \text{mol}^{-1}$, and the reaction rate can increase significantly as the temperature increases.^[28] Therefore, the limiting step in the reduction process is either the diffusion process or interfacial chemical reaction, where either step can be separated by reaction temperature changes.

The carbon excess coefficient in this experiment was 1.15. As noted earlier, aluminum sulfate and anthracite were passed through 100 mesh and 180 mesh standard sieves, respectively, followed by warming and cooling stages under nitrogen protection (30 mL/min). In the reaction phase, the atmosphere was switched to a mixed gas containing 10% oxygen ($3 \text{ mL } O_2 + 27 \text{ mL } N_2$, a total of 30 mL/min). The effects of reaction temperature and time on the Al₂O₃ yield were investigated. Experimental results are displayed in Figure 4. A kinetic model was applied to analyze the relationship between the yield of Al₂O₃ and reaction time (see Figure 4) to evaluate the control steps of the reduction process.

Kinetic model of the reaction controlled by diffusion step

If the reduction reaction is controlled by the diffusion process, then the diffusion conforms to Fick's Law, and the dynamic equation is expressed by the Fick's Law equation and Ginstling equations, respectively.

$$\left[1 - (1 - x)^{1/3}\right]^2 = kt$$
 (1)

$$1 - 2x/3 - (1 - x)^{2/3} = kt$$
⁽²⁾

where *x* is the yield of Al_2O_3 , *t* is the reaction time, and *k* is the rate constant.

According to Equations (1) and (2), the $\left[1 - (1 - x)^{1/3}\right]^2$ and $1 - 2x/3 - (1 - x)^{2/3}$ curves with respect to time can

Table 2. The rate constant of various temperature sections n and $\ln k$ values at different temperatures.

		<i>Т</i> (°С)				
	450	500	550	600		
N	2.2156	1.8377	1.0885	0.9854		
ln <i>k</i>	-9.2414	-6.9939	-3.5755	-2.8280		

be obtained based on the yield rate of Al_2O_3 at different temperatures (see Figure A1a,b).

The general requirement of the linear fitting correlation coefficient was $R^2 > 0.99$. In Figure A1, when the temperature exceeded 450 °C, the linear relationship of the data was poor and it could be controlled by the diffusion step at lower temperatures. According to standard kinetic laws, the reaction process was controlled by a chemical reaction at low temperatures and diffusion at high temperatures. The above abnormal phenomena preliminarily indicated that the diffusion process; rather, the interfacial chemical reaction was more likely to be the control step.

Kinetic model of the reaction controlled by the interfacial chemical reaction step

The reaction of aluminum sulfate in carbothermal reduction is primarily concentrated at either the interface of two crystalline phases $[Al_2(SO_4)_3 \text{ and } Al_2O_3]$ or in the narrow area near the interface. Such reactions are usually referred to as local chemical reactions or regional chemical reactions. In this case, the kinetic equations describing this situation are the Austin–Rickett, Hulbert–Klawitter, and Erofeev equations.^[29] The expressions are as follows, respectively:

$$\ln\left[x/(1-x)\right] = k\ln t \tag{3}$$

$$\left[-\ln\left(1-x\right)\right]^{2/3} = k\ln t \tag{4}$$

$$\ln \left[-\ln \left(1-x \right) \right] = n \ln t + \ln k \tag{5}$$

where x is the yield of Al_2O_3 , t is the reaction time, k is the rate constant, and n is a constant related to the reaction mechanism.

According to the above equation, the $\ln [x/(1-x)]$, $[-\ln (1-x)]^{2/3}$, and $\ln [-\ln (1-x)]$ curves with respect to $\ln t$ can be obtained, respectively, by using the data relationship between the conversion rate and reaction time at different temperatures. The results were shown in Figure A2.

Figure A2 indicated that only the linear correlation coefficient R^2 of the Erofeev equation was greater than 0.99. Additionally, $\ln \left[-\ln (1-x)\right]$ presented a better linear relationship with $\ln t$, indicating that the process of carbothermal reduction of aluminum sulfate was controlled by the interfacial chemical reaction in this study.

Activation energy calculation

Our analysis revealed that the rate-limiting step was introduced in the carbothermal reduction of the aluminum sulfate reactions the interfacial reaction at a reaction temperature range of 450-600 °C. The rate constants *n* and



Figure 5. The relationship between lnk and 1/T.

lnk at different temperatures were calculated using the data in Figure A2c (as shown in Table 2).

The relationship between the k value of the rate constant and absolute temperature (T) was subjected to the Arrhenius equation, and the rate constant k can be determined as shown in Equation (6):

$$k = A \exp\left(-\frac{E_a}{RT}\right) \tag{6}$$

where *A* is the leading factor (\min^{-1}) ; E_a is the apparent activation energy $(kJ \cdot mol^{-1})$; R is the gas constant $(kJ \cdot mol^{-1} \cdot K^{-1})$; and *T* is the absolute temperature (*K*).

By taking the natural logarithm of both sides of the equation, the equation is shown as:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

If lnk at different temperatures is used to plot 1/T, a line can be obtained by linear fitting, as shown in Figure 5. The linear correlation coefficient $R^2 = 0.9974 > 0.99$, and the expression of k can be obtained through regression analysis as:

$$\ln k = 28.5432 - \frac{27.3632}{T} \tag{8}$$

As the reaction of aluminum sulfate with carbothermal reduction was in the control area of interfacial chemical reaction kinetics, the reduction rate could be effectively improved by appropriately decreasing the particle sizes of the reactants to increase the contact area.

Characterization analysis of reduced products

The XRD pattern of the product after reduction was determined at 600 °C for 2 h presented in Figure 6. According to the phase diagram, the product contained amorphous substances, which may favor the main reaction.^[29–31] Only the "bread" peaks can be seen in the trace shown in Figure 6, and there was no characteristic diffraction peak. From the X-ray diffraction standard spectrum of the amorphous alumina, it can be judged that this is amorphous alumina.^[30]



Figure 6. XRD pattern of the product after reduction.



Figure 7 shows the FTIR spectra of the reduction product, obtained at 600 °C for 2 h. The absorption peak at 3443 cm⁻¹ is the antisymmetric stretching vibration of structural water -OH, and that at 1644 cm⁻¹ is the bending vibration of H-O-H of water. Additionally, the absorption peak at 612 cm^{-1} is due to the stretching vibration of Al-O-Al. However, there is excess anthracite, as indicated by the inplane vibration of carbon-hydrogen bond at 1401 cm⁻¹.^[20,22,25,26] After the carbothermal reduction product was alkali-dissolved, the residual carbon would exist in the form of alkali residue. It can be applied to the production of blast furnace iron-making or iron concentrate according to the content of elements in alkali slag. FTIR results further confirmed that the reduction product determined at 600 °C for 2 h was amorphous alumina.

Figure 8 shows the SEM microphotograph of the reduction product, obtained at 600 °C for 2 h. The surface of the product was smooth and independent, irregular appearance as shown in Figure 8. Meanwhile, the particle size of the product was small, which achieved the requirements of the micron size. The product is easily alkali-soluble. This



Figure 8. SEM image of the product after reduction.

Table 3. Industrial analysis of anthracite.

Composition	M _{ad}	A _{ad}	V _{ad}	Fc_{ad}^*
Anthracite	0.12	0.8	4.56	94.52

provides good conditions for the preparation of metallurgical grade alumina.^[32]

Experimental

Materials

Raw materials in this study consisted of self-made aluminum sulfate $[Al_2(SO_4)_3\cdot 18H_2O]$ and industrial anthracite. To eliminate the influence of ash on anthracite, anthracite was degreased by mixed acid filtration, washed and dried. The anthracite was taken from a coking plant in Yunnan province, China. Industrial analysis was performed using a HKGF-3000 industrial analyzer, as shown in Table 3.

Experimental methods

Preparation of aluminum sulfate

After the bauxite was finely ground and iron-removed, it was reacted with 98% concentrated sulfuric acid at 200 °C for 1 h, and the temperature was lowered to about 100 °C. The solution was filtered with water to obtain an aluminum sulfate solution (aluminum sulfate 18-hydrate, $w[Al_2(SO_4)_3 \cdot 18H_2O] > 99\%$), and the filtrate was crystallized and purified at 110 °C to obtain a high-purity anhydrous aluminum sulfate crystal. The chemical reaction is shown in Equation (9)^[33,34]:

$$\begin{array}{rll} Al_2O_3 \cdot (1 \ {\rm or} \ 3)H_2O \ + \ 14H_2O \ + \ 3H_2SO_4 \\ \\ & \rightarrow Al_2(SO_4)_3 \cdot 18H_2O \end{array} \tag{9}$$

Aluminum sulfate dehydrates

Aluminum sulfate (8 mg) was added to a crucible and then placed into a muffle furnace heated to 500 °C for temperature dehydration in 5 h. The dehydration rate was calculated according to the change in mass before and after aluminum sulfate dehydration.^[32,34]



Figure 9. TG-DSC curves of aluminum sulfate 18-hydrate pyrolysis process.

To investigate the role of $Al_2(SO_4)_3$.18H₂O in the dehydration process, TG-DSC was used to measure changes in energy and mass during dehydration. Throughout the heating process, as the temperature rose, water of crystallization was gradually removed and the quality declined. The energy difference between the sample and the inert reference material varied with temperature. The TG-DSC curve, shown in Figure 9, depicts changes up to 1200 °C in $Al_2(SO_4)_3$.18H₂O throughout the dehydration process.

Anthracite reacts with aluminum and carbon sulfate

Broken, ball-ground anthracite (180 mesh), and aluminum sulfate (100 mesh) were mixed at a carbon excess coefficient of 1.15 and placed in a porcelain boat. Then, it was positioned in a heating device and the heating device used for this experiment was a TCGC-1700 tube furnace.

First, the furnace was programmed for heating, with nitrogen gas (30 mL·min⁻¹) as a shielding gas (eliminate the interference of air in the system). When the temperature reached specified temperature and then maintained at a constant temperature for 30 min. Second, the boat containing reactants was placed in the constant temperature zone of the tube furnace, a mixed gas (27 mL N₂ + 3 mL O₂, a total of 30 mL·min⁻¹) was introduced during the reaction phase and the reaction was started. After the reaction was completed, the boat was naturally cooled to the room temperature under nitrogen protection (60 mL·min⁻¹). The reaction products were weighed and ground and then used for analysis.

Evaluation indices

The content of $Al_2(SO_4)_3$ in residue was analyzed by the BaSO₄ gravimetric method in GB/T22660.1-2008 (China). The Al_2O_3 yield can be calculated as follows:

$$X = \frac{M_0 w_0 - M_1 w_1}{M_0 w_0} \tag{10}$$

where M_0 is the mass of the mixtures before the reaction (g), M_1 is the mass of the mixtures after the reaction (g), w_0 is the mass fraction of the Al₂(SO₄)₃ mixtures before the reaction (%), and w_1 is the mass fraction of the Al₂(SO₄)₃ mixtures after the reaction (%).

Characterization analysis method

Thermogravimetric analysis

Aluminum sulfate dehydration experiments were carried out in a thermogravimetric analyzer (TGA; TGA-STA449F3, NETZSCH, Germany), under nitrogen gas atmosphere, to investigate the dehydration rate of aluminum sulfate. Reactions were performed at $100 \text{ cm}^3 \cdot \text{min}^{-1} \text{ N}_2$ flow, with a heating rate of $10 \,^\circ\text{C} \cdot \text{min}^{-1}$, from room temperature to $1200 \,^\circ\text{C}$. All dehydration experiments were repeated at least with two parallel runs and the relative errors were less than 5%.

Gas chromatography analysis

Monitoring the tail gas of the reaction with GC900C gas chromatography.

XRD analysis

At a scanning voltage of 36 kV and a current of 40 mA, the reaction residue phase was analyzed using a D/max-3B type X-ray diffractometer with a scanning angle ranging from 10° to 80° and a step size of $2^{\circ} \cdot \min^{-1}$.

Scanning electron microscopy

The micromorphology and particle size of the samples were observed using a Quanta-200 scanning electron microscope made by FEI Company (magnification: 30-100000).

Conclusions

Thermodynamics analysis showed a noteworthy effect of the reaction temperature on the reaction rate of the carbothermal reduction of aluminum sulfate. The high-temperature stage (450–600 °C) primarily generated $Al_2(SO_4)_3$ through the reduction reaction of generated CO. The generated CO reacted with $Al_2(SO_4)_3$ and the rapid increase in system temperature was conducive to the reaction of carbon-reducing $Al_2(SO_4)_3$ and generating CO. The reaction kinetics were also improved, and the time required for a complete reaction between carbon and aluminum sulfate was shortened.

Dynamic analysis results showed that at a reaction temperature range of 450–600 °C, the reduction reaction rate was controlled by the interfacial chemical reaction at an apparent activation energy of 227.50 kJ·mol⁻¹. The dynamic equation can be expressed by the Erofeev equation: $\ln [-\ln (1 - x)] = n \ln t + \ln k$.

The XRD pattern, FTIR spectra and SEM image of the product determined at 600 °C for 2 h after reduction showed that it was amorphous alumina and the particle size was small, which provided good conditions for the preparation of metallurgical grade alumina.

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0.5 0.25 **(b) (a)** 450 450 500 0.4 500 0.20 550 550 . 600 600 🗆 $[1-(1-x)^{1/3}]^2$ 0.3 $1-2/3x-(1-x)^{2/3}$ 0.15 0.10 0.1 0.05 0.00 0.0 20 40 50 10 30 60 10 20 30 40 50 60 t/min *t*/min

Appendix A





Figure A2. Relationship between (a) $\ln [x/(1-x)]$, (b) $[-\ln (1-x)]^{2/3}$, (c) $\ln [-\ln (1-x)]$, and $\ln t$ at different temperatures.