

# Estimation of the Gibbs Free Energy for Calcium Aluminate Sulphate Hydrates Using Iterative Least Squares Regression Method

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**Abstract.** The iterative least squares method was used for the estimation of the Gibbs free energy  $\Delta G$  of calcium aluminate sulphate hydrates the lime desulfurization product in alumina production. By means of the tree diagram theory, the optimal selection of exponential power  $\xi$  in the regression equation is realized. The recursive least square method was used to solve the regression equation, and a regression method for estimating the Gibbs free energy of calcium aluminate sulphate hydrates was obtained. The Gibbs free energies of two kinds of calcium aluminate sulphate hydrates at 343K were estimated by this method. The experimental results were consistent with the estimated Gibbs free energies. It shows that the estimated method is correct and the result is reliable. The Gibbs free energy of calcium aluminate sulphate hydrates at any temperature can be estimated by this means. The study will provide theoretical and experimental basis for the lime desulfurization and synthesis of calcium aluminate sulphate hydrates by process of alumina production.

## 1. Introduction

Calcium aluminate sulphate hydrates is an important compound in the production of alumina.

In the process of alumina production by sintering process, desilication is an essential process in the process of production. Improving the desilication depth of sodium aluminate solution plays a key role in improving the quality of alumina products and the decomposition rate of sodium aluminate solution. Calcium aluminate sulphate hydrates is the most effective desilication agent for calcium compounds. Under the optimum conditions, the desilication of sodium aluminate solution by sintering method was carried out, and the silicon content index of the refining solution was up to 12500. The synthetic conditions and properties of calcium aluminate sulphate hydrates are helpful to the study of desilication mechanism and the improvement of desilication efficiency, thus affecting the quality and yield of alumina produced by sintering process [1-5]. Therefore, it is important to study and optimize the synthesis thermodynamics of calcium aluminate sulphate hydrates for alumina production by sintering process.

The Bayer process of producing alumina, Sulfur pollution is very harmful Sulfur in bauxite mainly exists in the form of pyrite (in China). The pyrite reacts with sodium aluminate and caustic into the solution in the forms of sulfide, thiosulfate and sulfite, and finally transforms into sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) [6-8].so that the alkali consumption is increased; the accumulation of sulfur in the production process reduces the decomposition rate of seed. Sulfide and thiosulfate aggravate the corrosion of steel equipment, resulting in higher concentrations of soluble iron in solution and polluting aluminum hydroxide and so on, therefore, it is important to remove sulfur compounds from the process to control  $\text{Na}_2\text{SO}_4$  content in a harmless range. It is of great significance to reduce the



alkali consumption and stabilize the production process conditions. The researchers have done a lot of research on the desulfurization of alumina production process [9-12].

In the desulfurization process during Bayer alumina production,  $\text{Ca}(\text{OH})_2$  interacts with Sodium aluminate solution ( $\text{Al}_2\text{Na}_2\text{O}_4$ ) containing sulfur to generate calcium aluminate monosulfate and trisulfate hydrates  $3\text{CaOAl}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$  ( $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O}$ ) And  $3\text{Ca}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot n\text{H}_2\text{O}$  ( $\text{Ca}_6\text{Al}_2\text{SO}_{18}\cdot n\text{H}_2\text{O}$ ) respectively under certain conditions, as suggested by some literature reports. Because the number of attached water molecules is different,  $n$  can be 31, 6 and other different figures. Respectively [4, 13-15].

It was noted that the desulfurization efficiency is three times higher when calcium aluminate trisulfate hydrate is generated than when calcium aluminate monosulfate hydrate is produced, leading to a reduction in the loss of  $\text{Al}_2\text{O}_3$ .

In order to study and optimize the synthesis of calcium aluminate sulphate hydrates it is necessary to know the Gibbs free energy generated by calcium aluminate sulphate hydrates. However, the thermodynamic data such as Gibbs free energy of calcium aluminate sulphate hydrates are rarely reported in the literature, which makes it difficult to further study the related problems.

For this reason, we will study the thermodynamic conditions for the formation of calcium aluminate sulphate hydrates. A method for estimating the free energy of calcium aluminate sulphate hydrates Gibbs is proposed. The free energy of Gibbs and the free energy of reaction are calculated to predict the reaction results. The experimental results show that the calculated results are in agreement with the experimental results. The existence and characterization of calcium aluminate trisulfate hydrates  $3\text{Ca}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot n\text{H}_2\text{O}$  ( $\text{Ca}_6\text{Al}_2\text{SO}_{18}\cdot n\text{H}_2\text{O}$ ) were determined, which provided the basis for the thermodynamic study of the synthesis and desulfurization of calcium aluminate sulphate hydrates.

## 2. Estimation of gibbs free energy using iterative least squares regression method

For the determination of Gibbs free energy of Complex oxysalt, the commonly used methods are experimental determination methods (such as calorimetry, hydrofluoric acid dissolution method, etc.) and empirical theory calculation method. For the complex compounds such as calcium aluminate sulphate hydrates, the determination of Gibbs free energy is very difficult, complex and time-consuming.

Karpov *et al.*, [16] Nriagu, [17] Chen [18] and Tardyand *et al.* [19] Proposed empirical formulas for estimating the thermodynamic data of some minerals. It is generally believed that the "regression method", which is first applied to silicate minerals by karpov *et al.*, and further improved by Chen, is a widely used and accurate method.

With the help of regression equation such as

$$\sum \Delta G_f = a \exp(bx_i) + c, \quad (1)$$

Chen estimated standard formation Gibbs free energy of 20 kinds of silicate minerals by using complex multiple regression extrapolations to the limit, and the value is compared with the experiment, the relative error is 1%.

However so far, all literatures using iterative least squares regression method are those to estimate the standard Gibbs free energy of formation of silicate mineral. Due to the complex silicate is various oxide compound [20, 21], the silicate and calcium aluminate sulfate hydrates can decompose into different oxides according to their composition. Such as:

Silicate calcium aluminum:  $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} = 3\text{CaO} + \text{Al}_2\text{O}_3 + 3\text{SiO}_2$ ,

Kaolinite:  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 = \text{Al}_2\text{O}_3 + 2\text{SiO}_2 + 2\text{H}_2\text{O}$ ,

Calcium aluminate monosulfate:  $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O} = \text{CaO} + \text{SO}_3 + 3\text{CaO} + \text{Al}_2\text{O}_3 + 12\text{H}_2\text{O}$ .

They are similar in composition. At the same time oxyacid salts such as silicate at other temperatures have the same structure and composition as that of them in the standard state, but the values of Gibbs free energies of formation of component oxides are different. With the improvement for Chen's method [22], the Gibbs free energy of calcium aluminate sulfate hydrates is estimated by iterative least squares method.

As the literatures [4,13-15] tested that added lime to sodium sulfur aluminum to synthesize  $3\text{CaOAl}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$ , and thinking that the optimum synthesis condition is under about

343K(70°C), but they failed to obtain an exact evidence of generation of calcium aluminate trisulfate hydrates ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ ), and did not give the thermodynamic basis of both existing. So, this paper will use the above method to estimate the Gibbs free energies of the two calcium aluminate sulphate hydrates at the temperature, in order to determine whether they can generate and react in sodium aluminate solution. Because of lack of the corresponding thermodynamic data published as reference. The validity and reliability of the estimation will be experimentally tested here.  $G^\circ$  value of each oxide under standard condition (298K, 25°C) can be found from the thermodynamic data manual. From this,  $G^\circ$  of the calcium aluminate sulphate hydrates under standard condition can be calculated. For the estimation of  $G$  values of calcium aluminate sulphate hydrates under other temperatures, changing  $G^\circ$  value of each oxide under standard condition into the value under the temperature. The thermodynamic data under certain temperature can be found from the thermodynamic data manual or got from calculation by the classical thermodynamic formula,

Table 1 lists  $G^\circ$  of thermodynamic data of each oxide under standard conditions [23] and the thermodynamic data of corresponding substance under 343K (70°C) [24].

**Table 1.** Thermodynamic data of various materials at 25°C and 70°C

Substances	CaO	SO <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	H <sub>2</sub> O	CaSO <sub>4</sub>	3CaO·Al <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>
$G^\circ$ (KJ/mol298K)	-46.15	-472.28	-1690.46	-298.08	-1465.48	-3646.10	
$G$ (KJ/mol343K)	-648.71	-486.83	-1693.98	-308.73	-1472.11	-3659.21	-3512.10

### 2.1. The exponential regression equation setting

According to the composition of complex compounds, the compounds can be expressed as a variety of combination forms. Summing every  $\Delta G_f$  in the combination forms, thus  $\sum \Delta G_{fi}$  ( $i=1, 2, \dots, p$ ) of each combination form can be obtained. Here  $p$  is the number of possible combinations for the mineral. There are  $p=4$  combinations for the two kinds of compounds in this paper. Then the  $\sum \Delta G_f$  are arranged in order from large to small, and shown as in table 2 and 3.

**Table 2.** The possible combination of  $\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18} \cdot 6\text{H}_2\text{O}$  and the sum of Gibbs energy of compounds

The possible combination forms	$y_i = \sum G_{fi}^0$ (kJ/mol)
$6\text{CaO} + \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O}$	-9256.741
$1/2(3\text{CaSO}_4 + \text{Al}_2(\text{SO}_4)_3 + 9\text{CaO} + \text{Al}_2\text{O}_3) + 6\text{H}_2\text{O}$	-9582.81
$3\text{CaO} + \text{Al}_2\text{O}_3 + 3\text{CaSO}_4 + 6\text{H}_2\text{O}$	-9908.88
$\text{Ca}_3 \cdot \text{Al}_2\text{O}_4 + 3\text{CaSO}_4 + 6\text{H}_2\text{O}$	-9927.98

**Table 3.** The possible combination of  $\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18} \cdot 6\text{H}_2\text{O}$  and the sum of Gibbs energy of compounds

The possible combination forms	$y_i = \sum G_{fi}^0$ (kJ/mol)
$4 \text{CaO} + \text{Al}_2(\text{SO}_4)_3 + 12\text{H}_2\text{O}$	-8599.614
$1/2(\text{CaSO}_4 + \text{Al}_2(\text{SO}_4)_3 + 15\text{CaO} + 3\text{Al}_2\text{O}_3) + 12\text{H}_2\text{O}$	-8653.725
$3\text{CaO} + \text{Al}_2\text{O}_3 + \text{CaSO}_4 + 12\text{H}_2\text{O}$	-8817
$4\text{CaO} + 1/3\text{Al}_2(\text{SO}_4)_3 + 2/3\text{Al}_2\text{O}_3 + 12\text{H}_2\text{O}$	-8836.1

The above method, for each  $\sum \Delta G_{fi}$ , selected an integer value  $x_i$ , the  $x_i$  is called the exponent of  $\sum \Delta G_{fi}$ . In this way, a form such as a list of the following functions is constituted:

$$\begin{array}{cccccc} x & x_1 & x_2 & x_3 & \dots & x_p \\ y & y_1 & y_2 & y_3 & \dots & y_p \end{array}$$

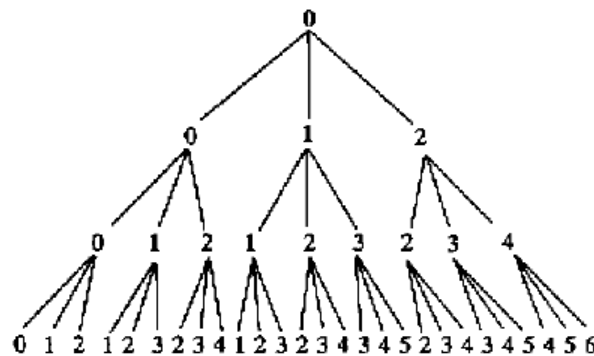
The  $y_i = \sum \Delta G_{fi}$ , noting  $y_i$  as observation value of  $\sum \Delta G_{fi}$ , then fitting curve for the listed functions according to exponential equation, thus a best fitting curve can be obtained. The equation is:

$$\sum \Delta G_{fi} = a \exp(bx_i) + c \quad (2)$$

Where: a, b and c are for the undetermined coefficients; c stands for the  $\Delta G_f$  of the mineral.

### 2.2. The selection of the exponent $x_i$

In equation (2), **exponent**  $x_i$  corresponding  $\sum \Delta G_{fi}$  is selected artificially. How to select  $x_i$  is the key of the regression method. In order to eliminate arbitrariness, according to the nature of exponential curve, the selection of  $x_i$  should combine with tree diagram theory<sup>[25]</sup>. Figure 1 is that when the mineral combination form number  $p=4$ , the combination tree diagram of the corresponding exponent  $x_i$ . In the figure from the straight branch from top 0 down along multi groups of  $x_i$  value can be obtained. It can be known from figure 1 that the combination forms of a group of  $\sum \Delta G_{fi}$  corresponding  $x_i$  are 0012, 0013, 0023, 0024, 0123, 0124, ...



**Figure 1.** When  $p=4$ , a tree diagram of possible combination form corresponding  $x$ .

### 2.3. The iterative least squares method to solve regression equation

In order to determine the values of a, b and c in the best fitting curve equation(2), firstly it was assumed that  $a_0$ ,  $b_0$  and  $c_0$  were the initial values,  $a_1$ ,  $b_1$  and  $c_1$  were the correction values of  $a_0$ ,  $b_0$  and  $c_0$  respectively, that is,  $a = a_0 + a_1$ ,  $b = b_0 + b_1$  and  $c = c_0 + c_1$ . Thus,

$$y' = a_0 \exp(b_0 x_i) + c_0 \quad (3)$$

The difference between the observation value and the best fitting curve value  $a \exp(b x_i) + c$  was  $R_i$ , there were

$$R_i = a \exp(b x_i) + c - y_i \quad (4)$$

Substituting equation (3) into equation (4),

$$R_i = (a_0 + a_1) \exp[(b_0 + b_1) x_i] + c_0 + c_1 - y_i \quad (5)$$

First-order Taylor expanding equation (5) near  $a_1$ ,  $b_1$  and  $c_1$ , it is

$$R_i = y'_i - y_i + a_1 (1 + b_1) \exp(b_0 x_i) + b_1 a_0 x_i \exp(b_0 x_i) + c_1 \quad (6)$$

Equation (6) is a linear combination of  $a_1$ ,  $b_1$  and  $c_1$ , according to the principle of least squares [26]:

the best value of  $a_1$ ,  $b_1$  and  $c_1$  should be the solution of the minimum value of  $\sum_{i=1}^p R_i^2$ . For  $a_0$ ,  $b_0$  and  $c_0$  set, from equation (3) the values of  $a_1$ ,  $b_1$  and  $c_1$  are easily obtained by least square method. And then  $a_0$ ,  $b_0$  and  $c_0$  are modified by equation (3) to get a, b and c, repeating the process of the

iterative least squares until  $a_1$ ,  $b_1$  and  $c_1$  meet the accuracy requirements, and the values of

corresponding  $\sum_{i=1}^p R_i^2$  can be calculated. According to this method, the values of the least squares

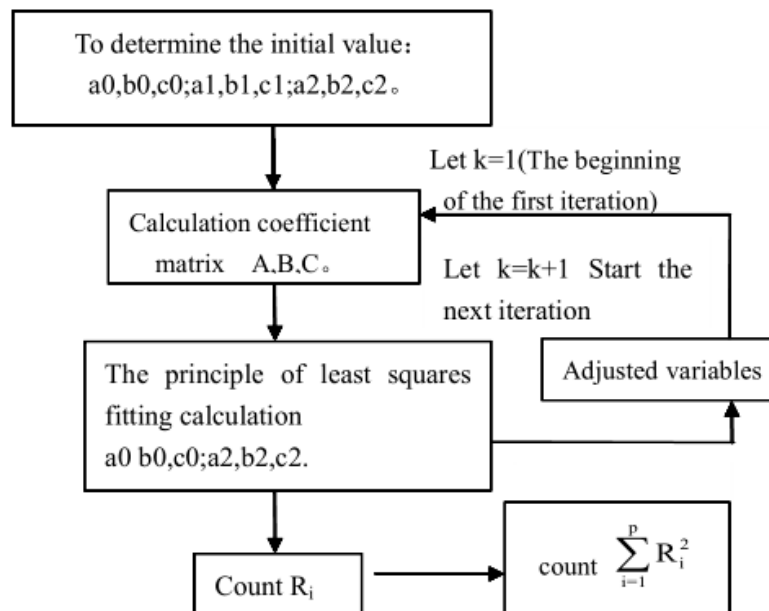
fitting curve and its corresponding  $\sum_{i=1}^p R_i^2$  can be calculated for each  $x$  combination form. Then

selecting the combination of minimum value in  $\sum_{i=1}^p R_i^2$  as a best combination, and its corresponding fitting curve is just the best fitting curve. The  $c$  value is the Gibbs free energy  $\Delta G$  of the compound.

This paper adopts MATLAB programming to calculate [27] (Program omitting). The computational procedure is as Figure 2

### 3. Estimation of the gibbs free energies for two kinds of calcium aluminate sulphate hydrates

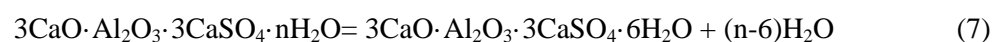
The values of the Gibbs free energies calculated by the tree diagram corresponding  $x_i$  combination for the fitted two compounds, the results are in table 4.



**Figure 2.** Computational procedure.

From the table, when  $x[i] : [0, 0, 1, 3]$  the  $\sum R_i^2$  of the two compounds has a minimum value, then the Gibbs free energies of  $\text{Ca}_4\text{Al}_2\text{SO}_{10}12\text{H}_2\text{O}$  and  $\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18}6\text{H}_2\text{O}$  are -8 894.5 kJ/mol and -9 984.5 kJ/mol respectively.

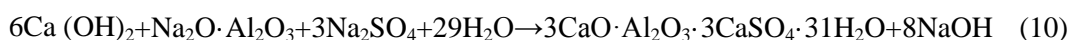
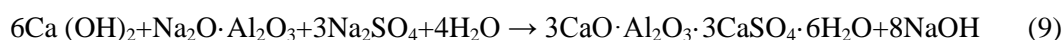
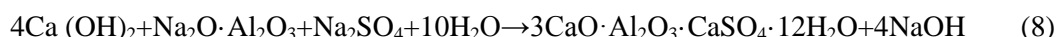
Due to in the  $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ ,  $n$  indicates the number of molecules attached to water. so its Gibbs free energies can be calculated by under formula



**Table 4.** Fitted value of standard Gibbs energy of  $\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O}$  and  $\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18} \cdot 6\text{H}_2\text{O}$ 

X[i]	$\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O}$				$\text{Ca}_6\text{Al}_2\text{S}_3\text{O}_{18} \cdot 6\text{H}_2\text{O}$			
	$\sum R_i^2$	a0	b0	c0	$\sum R_i^2$	A0	b0	c0
[0,0,2,3]	3.5262e-4	85.5906	-1.0041	-8898.6	3.5262e-4	85.5906	-1.0041	-9998.6
[0,0,2,4]	2.5680e-6	82.1721	-1.1601	-8895.2	2.5680e-6	82.1721	-1.1601	-9995.2
[0,0,1,2]	8.2373e-6	82.1746	-2.3203	-8895.2	8.2373e-6	82.1746	-2.3203	-9995.2
[0,0,1,3]	9.5379e-7	81.4389	-2.4066	-8894.5	9.5379e-7	81.4389	-2.4066	-9984.5
[0,1,2,2]	5.6647e-4	371.2362	-0.1353	-9177.7	3.5276	-3.0161	1.6837	-9903.4
[0,1,2,3]	-6.1205	549.1271	-0.0666	-9350.2	-6.1205	549.1271	-0.0666	-1045.0

Adding lime to a sodium aluminate solution to remove sulfur can lead to the formation of calcium aluminate sulfate hydrates according to the following reactions [8-11]:

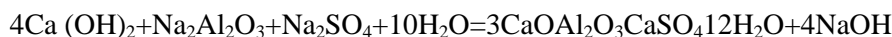


Using the above estimated Gibbs free energies, the directions of reactions (8) - (10) at 343K (70°C) were determined. When calculating the reaction equations (8) and (9), the thermodynamic data for each substance 343K (70°C) are shown in table 5.

**Table 5.** The thermodynamic data at 70°C in reaction equations (1) and (2)

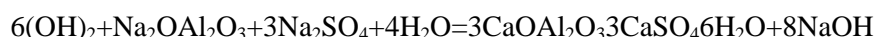
substances	$\text{Ca}(\text{OH})_2$	$\text{NaAlO}_2$	$\text{Na}_2\text{SO}_4$	$\text{NaOH}$	$\text{H}_2\text{O}$
G (KJ/mol,343K)	-937.30	-1158.50	-1441.16	451.28	-308.73

The Gibbs free energy  $\Delta G_8$  of reaction (8) is:



$$\begin{aligned} \Delta G_8 &= G_{3\text{CaOAl}_2\text{O}_3\text{CaSO}_4 \cdot 12\text{H}_2\text{O}} + 4G_{\text{NaOH}} - 4G_{\text{Ca}(\text{OH})_2} - 2G_{\text{NaAlO}_2} - G_{\text{Na}_2\text{SO}_4} - 10G_{\text{H}_2\text{O}} \\ &= -8894.5 + 4 \times (-451.28) - 4 \times (-937.30) - 2 \times (-1158.50) - (-1441.16) - 10 \times (-308.73) \\ &= -104.96 \text{ (KJ/mol)} \end{aligned}$$

The Gibbs free energy of reaction (9) is:



$$\begin{aligned} G_9 &= G_{3\text{CaOAl}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 6\text{H}_2\text{O}} + 8G_{\text{NaOH}} - 6G_{\text{Ca}(\text{OH})_2} - 2G_{\text{NaAlO}_2} - 3G_{\text{Na}_2\text{SO}_4} - 4G_{\text{H}_2\text{O}} \\ &= -9984.5 + 8 \times (-451.28) - 4 \times (-308.73) - 3 \times (-1441.16) - 2 \times (-1158.50) - 6 \times (-937.30) \\ &= -95.54 \text{ (KJ/mol)} \end{aligned}$$

In reaction (7), let  $n=31$  calculate  $G_7$ , and substitute  $G_7$  into reaction (10),  $\Delta G_{10}$  was calculated .result also is  $-95.54 \text{ kJ/mol}$

All the Gibbs free energies calculated for the desulfurization of a sodium aluminate solution were negative ( $\Delta G_8 = -104.96 \text{ kJ/mol}$ ,  $\Delta G_{9,10} = -95.54 \text{ kJ/mol}$ ). These results show that the reactions to form the calcium aluminate monosulfate and trisulfate hydrates are favorable, *i.e.*, two types of calcium aluminate sulfate hydrate should be produced in the sodium aluminate solution. It is impossible to compare and judge whether the thermodynamic calculation mentioned above is reliable because there are no related reports. We use experiments to verify it.

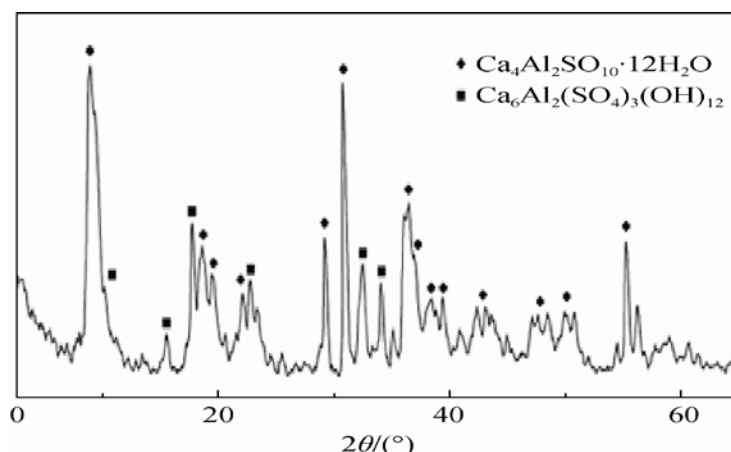
#### 4. Experimental

A sodium aluminate solution was prepared in a high-pressure steel bomb using puriss sodium hydroxide and aluminum hydroxide. Puriss calcium hydroxide was placed in a crucible and calcined at



900°C in a muffle furnace for 2 h. Then, it was cooled in a dryer and sealed under dry conditions for storage.

The sodium aluminate solution was prepared with a molar ratio of 3:1 and then diluted with 4 times as much distilled water. The diluted sodium aluminate solution (500 mL) was placed in a 1 L stainless steel cup, and the  $\text{Na}_2\text{SO}_4$  reagent was then added to it. The experiments were performed in a constant temperature water bath (the temperature was automatically controlled with precision of  $\pm 1^\circ\text{C}$  under stirring by an agitator at a constant speed. A certain amount of calcium oxide was dissolved in water to make lime milk, which was slowly added to the sodium aluminate solution (24 g/L  $\text{Na}_2\text{SO}_4$ ) under stirring for 50 or 120 min at  $70^\circ\text{C}$ . The solution was decompressed and filtered after the reaction, and the filter cake quality was determined. The cakes were washed repeatedly with water and dried with cold wind. The reaction products were analyzed by chemical methods, X-ray diffraction and infrared spectroscopy.



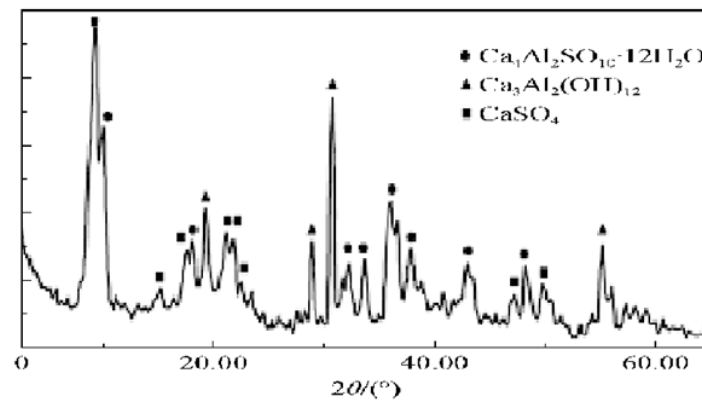
**Figure 3.** XRD pattern of desulfurization product reacted at  $70^\circ\text{C}$  for 50 min.

## 5. Results and Discussion

As shown in the XRD spectrum of the products in Figure 3, both the calcium aluminate monosulfate and trisulfate Hydrates ( $\text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O}$  and  $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$  respectively) were formed when the lime content was 17 g/L, the reaction temperature was  $70^\circ\text{C}$ , and the reaction time was 50 min. Notably, the content of these two compounds reached 96%.

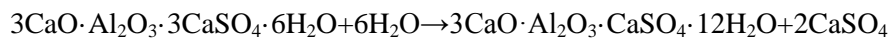
The diffraction peaks of calcium aluminate monosulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ ) were observed in the XRD pattern of the desulfurization product (Figure 3) and had characteristic  $d$  spacings (characteristic values) of 0.890, 0.445, 0.399, 0.287, 0.242, and 0.223 nm. The diffraction peaks of calcium aluminate trisulfate hydrate [ $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ ] were also observed and had  $d$  spacings of 0.980, 0.561, 0.554, 0.491, 0.388, 0.279, and 0.256 nm. The diffraction pattern was important for identifying the compound products, especially calcium aluminate trisulfate hydrate, which was not identified in previous work. These experimental results are consistent with the fact that the calculated  $\Delta G^\circ$  values were significantly less than 0, meaning that the formation of both calcium aluminate sulfate hydrates is favorable and they both should be produced in the sodium aluminate solution. Thus, the estimated Gibbs free energies of the calcium aluminate sulfate hydrates is consistent with the experimental results.

The absence of calcium aluminate trisulfate hydrate ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ ) in previous experiments performed under the same conditions can be explained by the  $\Delta G$  calculations and the experimental results presented here. Figure 4 shows the results of an experiment performed under the same conditions as the experiment in Figure 3, except the reaction time was 120 min. When this longer reaction time was employed, the reaction products were only calcium aluminate monosulfate hydrate and  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ;  $\text{CaSO}_4$  and calcium aluminate trisulfate hydrate ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ ) were not detected



**Figure 4.** XRD pattern of desulfurization product reacted reaction conditions: 70°C for 120 min.

Subtracting reaction (9) from reaction (8) results in the following reaction:



$$\Delta G_{10} = \Delta G_8 - \Delta G_9 = -104.96 - 95.54 = -9.42 \text{ kJ/mol}$$

Because  $\Delta G_{10} < 0$  kJ/mol, calcium aluminate trisulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 6\text{H}_2\text{O}$ ) decomposed into calcium aluminate monosulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ ) and  $\text{CaSO}_4$  at longer reaction times. Subtracting  $\Delta G_8$  from  $\Delta G_7$  also gives. This value corresponds to the following general reaction, which applies to the difference between reactions (7) and (8):



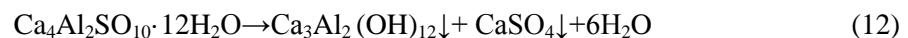
$$\Delta G_{11} = -104.96 - 95.54 = -9.42 \text{ kJ/mol}$$

Therefore, it can be inferred that at longer reaction times, the formed calcium aluminate trisulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ ) decomposes into calcium aluminate monosulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ ) and  $\text{CaSO}_4$  in the sodium aluminate solution.

$$\Delta G = -9.42 \text{ kJ/mol}$$

The results demonstrating this reaction process are shown in Figures 3 and 4.

The presence of calcium aluminate ( $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ ) was observed in Figure 4 because calcium aluminate monosulfate hydrate ( $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaSO}_4 \cdot 12\text{H}_2\text{O}$ ) is also a metastable material and decomposes into calcium aluminate and calcium sulfate after prolonged heating [8-11], shown as by reaction (12):



## 6. Conclusions

1) The Gibbs free energy of complex calcium aluminate sulfate hydrates can be estimated by iterative least squares regression method. This paper estimates the 343K (70°C)

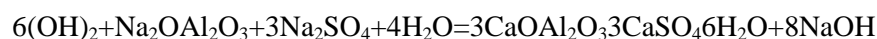
$$G_R, \text{Ca}_4\text{Al}_2\text{SO}_{10} \cdot 12\text{H}_2\text{O} = -8894.5 \text{ (kJ/mol)}$$

$$G_R, \text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12} = -9984.5 \text{ (kJ/mol)}$$

2) The experimental results of calcium aluminate sulfate hydrates are consistent with the Gibbs free energies estimated using the iterative least squares regression method



$$\Delta G = -104.96 \text{ (kJ/mol)}$$



$$\Delta G = -95.54 \text{ (kJ/mol)}$$



And As shown in the XRD spectrum of the products, both the calcium aluminate monosulfate and trisulfate hydrates  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{CaSO}_4\cdot 12\text{H}_2\text{O}$  ( $\text{Ca}_4\text{Al}_2\text{SO}_{10}\cdot 12\text{H}_2\text{O}$ ) and  $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 6\text{H}_2\text{O}$  ( $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$ ), respectively were formed.

3) Adding lime to a sodium aluminate solution to remove sulfur can lead to the formation of calcium aluminate trisulfate hydrate ( $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 3\text{CaSO}_4\cdot 6\text{H}_2\text{O}$ ). The diffraction peaks in the XRD pattern of calcium aluminate trisulfate hydrate were also observed and had  $d$  spacings of 0.980, 0.561, 0.554, 0.491, 0.388, 0.279, and 0.256 nm.

This is an important characterization.

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