

## The Hydrothermal Treatment of Aluminium Hydroxide to Improve Alumina Production Efficiency

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### Abstract

In this study, the conversion of gibbsite to boehmite in low alkali media was efficiently achieved with sodium bicarbonate as catalyst material under hydrothermal condition. The aluminium hydroxide conversion was effective at a temperature from 200 to 290 °C and concentrations of NaHCO<sub>3</sub> from 0 to 100 g/L, and the presence of NaHCO<sub>3</sub> had a different effect on the process depending on the temperature. At low temperatures, soda accelerates conversion, while at ambient temperatures the formation of dawsonite is observed, the presence of which disappears at high temperatures. It was found that to reduce the conversion temperature of gibbsite to boehmite, it is possible to use a seed in the form of boehmite obtained under hydrothermal conditions at a temperature above 260 °C. The obtained data allow to reduce energy consumption for the conversion of gibbsite into boehmite, as well as to obtain high purity aluminium hydroxide with low soda content and pseudoboehmite.

**Keywords:** alumina, hydrothermal treatment, gibbsite, boehmite, soda.

### 1. Introduction

With ongoing developments in the industry, a wide range of special qualities of aluminum hydroxide and alumina products have become widespread, which are used as catalysts, flame retardants, sorbents, etc. [1]. To obtain them, a large number of methods are proposed. The most frequently proposed are alkoxide technology, the sol-gel method and hydrothermal treatment [2]. Various aluminum salts or metallic aluminum are used as precursors according to these technologies, which significantly increases the cost of production. In addition, the production processes themselves are quite complex and may result in the release of harmful gaseous products [3].

The idea of obtaining boehmite as a precipitation product from an alkaline-aluminate solution instead of gibbsite has recently become widespread. This approach reduces the cost of subsequent calcination in the production of metallurgical alumina [4]. Several variants of precipitation [5] are proposed. However, in the direct precipitation of boehmite, the degree of alumina recovered from solution is lower than in the precipitation of gibbsite. According to the technology proposed by Li et al. [6] gibbsite is proposed to convert in the second stage in the presence of boehmite seed, but this process is slow and may lead to product contaminated by impurities.

One of the possible solutions to these adverse effects is the the hydrothermal treatment of gibbsite, which has been repeatedly proposed for the production of nanoscale powders of boehmite and alumina [7-9]. However, the data presented in the literature are contradictory with respect to the mechanism and conditions of transformations, which is most likely due to the different method of obtaining the starting material, which significantly affects the path and

conditions of phase transformations. The lowest temperature (achieved in the work [8]), for the conversion of gibbsite into boehmite is 160-170 °C, however, fine powder is used as the feedstock, and the processing time was more than 8 hours.

In this work, a study was conducted to determine the possibility of using the hydrothermal treatment of aluminum hydroxide in the presence of sodium bicarbonate to find conditions that allow production of boehmite for metallurgical and special purposes at lowest cost. Baking soda or sodium bicarbonate (NaHCO<sub>3</sub>) was used because under hydrothermal conditions, it allows transformation of gibbsite into pseudoboehmite – nanosized powder of aluminum hydroxide with a high specific surface area [10].

## 2. Experimental

The industrial aluminum hydroxide from the branch of JSC "RUSAL Ural" in the town of Krasnoturinsk was used as the raw material. The particle size distribution of the initial aluminum hydroxide is given in Table 1. The chemical composition of the initial aluminum hydroxide is shown in Table 2, according to which the main impurity in this hydroxide is sodium oxide. The main phase of the industrial aluminum hydroxide according to Figure 1 is gibbsite. The sodium bicarbonate used in the experiments were of analytical purity. The distilled water was obtained in the distillator GFL 2004.

**Table 1. The particle size distribution of the initial aluminum hydroxide.**

Particle size, $\mu\text{m}$	-5	-10	-20	-30	-40	-45	-56	-63	-71	-90	-100	-125
Content, %	1.2	1.3	2.5	5.5	11.3	15.7	29.2	40.1	52.6	74.3	81.2	91.5

**Table 2. Chemical composition of initial aluminium hydroxide.**

Compound	Al(OH) <sub>3</sub>	Na <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	SO <sub>3</sub>	CaO	K <sub>2</sub> O	ZnO	P <sub>2</sub> O <sub>5</sub>
wt. %	99.40	0.40	0.013	0.0070	0.0135	0.0091	0.018	0.0033	0.0011

Experiments on hydrothermal treatment were carried out in steel bombs with a volume of 100 ml, in which 20 g of the initial aluminum hydroxide, the necessary sodium bicarbonate sample and water were placed. Then the steel bombs were loaded into a thermostated air oven and kept at a predetermined temperature for 1 hour. Mixing was carried out by rotating steel bombs at a speed of 60 rpm. The Liquid: Solid ratio (L:S) in all experiments was 4:1.

The phase composition of the initial aluminum hydroxide and the obtained products was determined using x-ray spectrometry on the Rigaku D/MAX-2200 instrument. The chemical composition of the initial aluminum hydroxide was determined by x-ray fluorescence spectrometry on an XRF-1800 instrument. The Na<sub>2</sub>O content of the products was determined by inductively coupled plasma (ICP) spectrometry on a Perkin Elmer NexION 300S. Specific surface area (BET) was determined by a Sorbi-m gas adsorption analyzer.

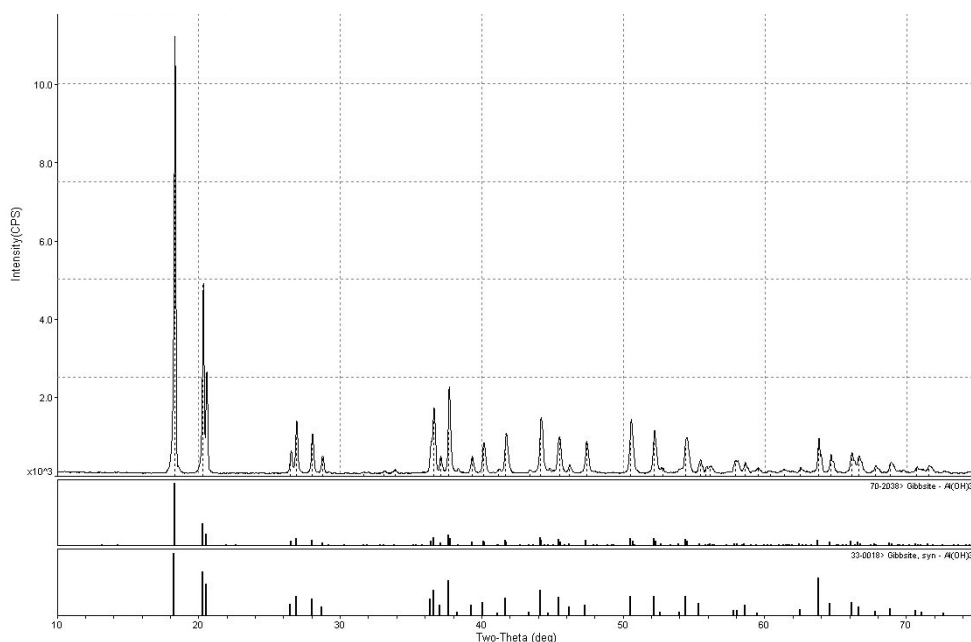


Figure 1. X-ray diffraction pattern of the initial aluminium hydroxide.

### 3. Results and Discussion

To study the effect of temperature and concentration of sodium bicarbonate on the properties of the hydrothermal treatment product (product yield, its phase composition, specific surface area and caustic alkali content), a series of experiments presented in Tables 3-6 was carried out.

Table 3. Effect of sodium bicarbonate concentration on product properties at 200 °C.

№	NaHCO <sub>3</sub> concentration, g/L	Product yield, %	Phase composition	BET, m <sup>2</sup> /g	Na <sub>2</sub> O content, %
1	0	97.0	gibbsite	20.4	0.21
2	25	86.8	pseudoboehmite	245.0	0.31
3	50	87.7	pseudoboehmite	143.0	0.38
4	100	180.0	dawsonite	-*	-*

\* Specific surface area and Na<sub>2</sub>O content for dawsonite were not studied.

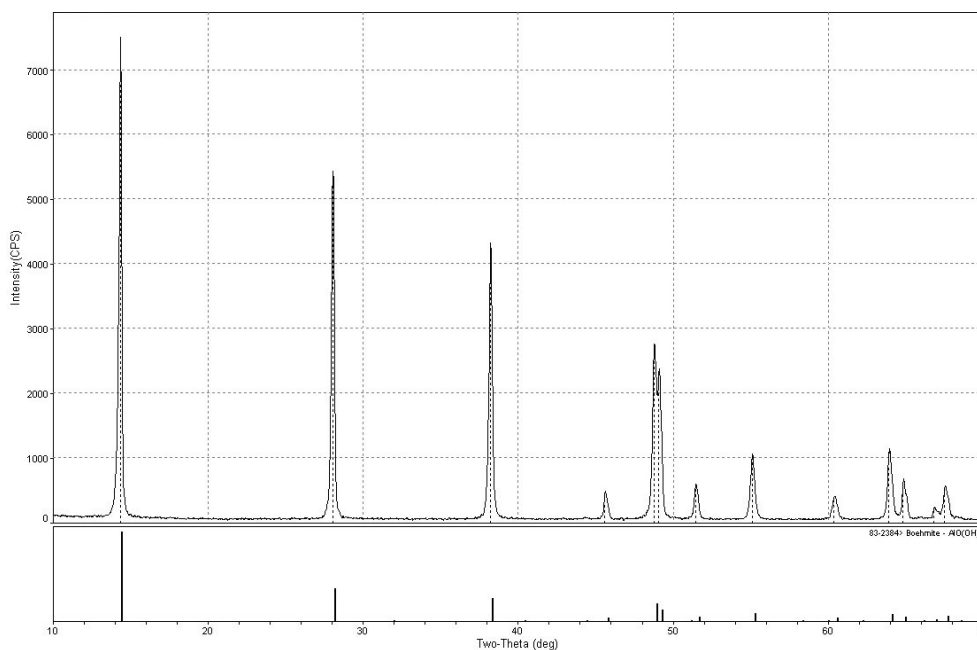
As seen in the results in Table 3, the presence of sodium bicarbonate at low concentrations leads to the formation of pseudoboehmite with a high specific surface area. The presence of the pseudoboehmite phase (not a mixture of boehmite and gibbsite) is confirmed by the X-ray diffraction pattern presented in Figure 2. Thus, a fairly cheap method of obtaining raw materials for non-metallurgical purposes, which does not involve the use of high temperatures or expensive reagents, has been demonstrated.

Increasing the concentration of sodium bicarbonate prevents the production of pseudoboehmite and the formation of dawsonite (NaAl(CO<sub>3</sub>)(OH)<sub>2</sub>), which in turn, under hydrothermal conditions in water also decomposes with the formation of pseudoboehmite [10].

**Table 4. Effect of sodium bicarbonate concentration on product properties at 230 °C.**

№	NaHCO <sub>3</sub> concentration, g/L	Product yield, %	Phase composition	BET, m <sup>2</sup> /g	Na <sub>2</sub> O content, %
1	0	92.5	gibbsite + boehmite	19.5	0.22
2	25	179.3	dawsonite	-*	-*
3	50	180.2	dawsonite	-*	-*
4	100	180.8	dawsonite	-*	-*

\* Specific surface area and Na<sub>2</sub>O content for dawsonite have not been studied.



**Figure 2. X-ray diffraction pattern of product №2 in Table 3.**

When the temperature rises to 230 °C in the absence of sodium bicarbonate (Table 4), boehmite begins to form, but the degree of completion of the conversation process is low, and most of the product solid is untransformed gibbsite. In the presence of sodium bicarbonate, regardless of temperature, dawsonite was formed.

**Table 5. Effect of sodium bicarbonate concentration on product properties at 260 °C.**

№	NaHCO <sub>3</sub> concentration, g/L	Product yield, %	Phase composition	BET, m <sup>2</sup> /g	Na <sub>2</sub> O content, %
1	0	78.5	boehmite	2.53	0.007
2	25	76.7	boehmite	4.23	0.33
3	50	80.1	boehmite	9.70	0.36
4	100	179.8	dawsonite	-*	-*

\* Specific surface area and Na<sub>2</sub>O content for dawsonite were not studied.

According to Table 5, increasing the temperature leads to the completion of the crystallization of boehmite in the absence of sodium bicarbonate. At the same time, there is a significant reduction in the amount of sodium oxide impurities in the product due to the rejection of impurities during

conversion. In addition, an increase in temperature leads to the appearance of the boehmite phase in the presence of sodium bicarbonate. Figure 3 shows an X-ray diffraction pattern of the product obtained at 260 °C and a concentration of 25 g/L NaHCO<sub>3</sub>. Boehmite obtained in a solution of sodium bicarbonate is contaminated with sodium oxide, and with an increase in the concentration of sodium bicarbonate, dawsonite begins to form.

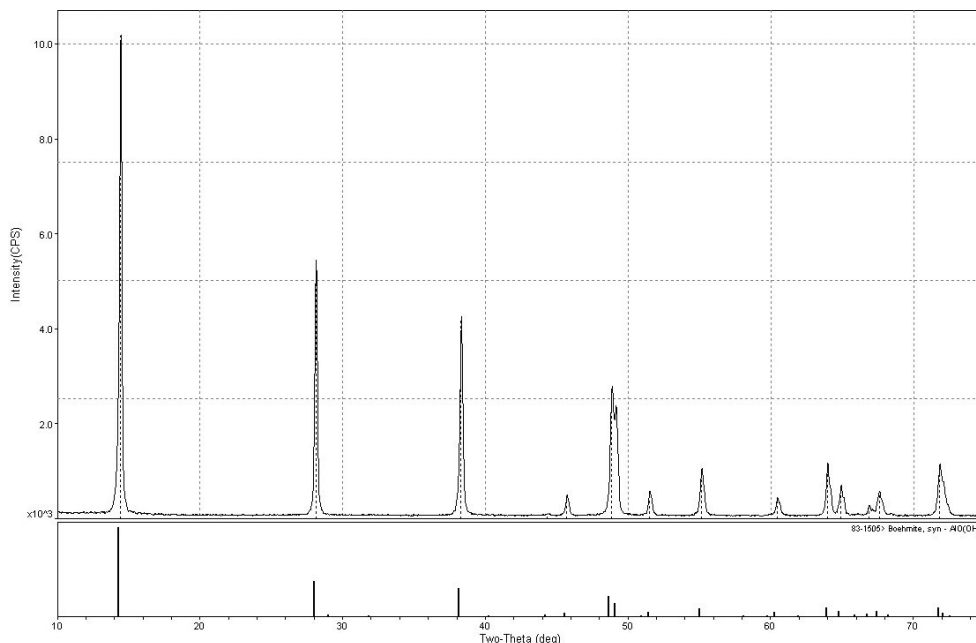


Figure 3. X-ray diffraction pattern of product №2 in Table 5.

Table 6. Effect of sodium bicarbonate concentration on product properties at 290 °C.

№	NaHCO <sub>3</sub> concentration, g/L	Product yield, %	Phase composition	BET, m <sup>2</sup> /g	Na <sub>2</sub> O content, %
1	0	77.0	boehmite	2.30	0.005
2	25	76.7	boehmite	2.33	0.30
3	50	76.5	boehmite	2.50	0.32
4	100	76.5	boehmite	2.50	0.34

Table 6 presents the results of experiments on hydrothermal treatment of the industrial aluminum hydroxide at 290 °C. As the data shows, with a further increase in temperature the stable phase under these conditions is boehmite, regardless of the concentration of sodium bicarbonate. At the same time, due to the greater degree of completion of the conversion process, the boehmite obtained in the absence of bicarbonate contains the least impurities and has the smallest specific surface area. The presence of sodium bicarbonate leads to contamination by caustic alkali product.

According to the data obtained, the conversion of gibbsite to boehmite requires fairly high temperature or long exposure [8]. In work [6] to increase the conversion efficiency of gibbsite to boehmite, use of a boehmite seed is proposed. In the following experiments therefore, boehmite obtained at 260 °C was used as a seed for conversion of the initial aluminum hydroxide at lower temperatures. The results of these experiments are shown in Table 7. The quantity of boehmite seed was 50 wt.% of the sample of industrial aluminum hydroxide.

**Table 7. Results of using of hydrothermal boehmite as a seed.**

Temperature, °C	Product yield, %	Phase composition
170	99.2	gibbsite + boehmite
180	97.0	gibbsite + boehmite
190	80.5	gibbsite + boehmite
200	76.7	boehmite

It is obvious that the presence of the boehmite seed significantly accelerates the conversion of the industrial aluminum hydroxide. To obtain the pure boehmite phase within 1 hour, 200 °C is necessary, which is lower than 260 °C, and reduces the cost of the process. Next, the effect of the amount of seed on conversion efficiency (Table 8) at a temperature of 200 °C was studied.

**Table 8. Results of using different amounts of hydrothermal boehmite as seed.**

Seed amount, %	Product yield, %	Phase composition
5.0	79.6	gibbsite + boehmite
12.5	76.7	boehmite
25.0	76.6	boehmite
50.0	76.6	boehmite

The results in Table 8 indicate that for complete conversion to boehmite at 200 °C within 1 hour, seeding with 12.5 % of the weight of the sample of the industrial aluminum hydroxide is sufficient. At the same time, according to the measurements of particle size distribution, the particle size of boehmite remains the same as that of the original hydroxide.

#### 4. Conclusions

This study demonstrates that the use of sodium bicarbonate in the hydrothermal treatment of industrial aluminum hydroxide precipitated from an alkaline aluminum solution by the Bayer process allows at low temperatures (about 200 °C) to obtain pseudoboehmite with a high specific surface area without the need for complex flowsheets and expensive reagents. When the temperature rises to 230 - 260 °C, the presence of sodium bicarbonate in the solution leads to the formation of dawsonite. With an increase in temperature to 290 °C, regardless of the presence and concentration of sodium bicarbonate, the stable phase in the process is boehmite. It was found that to reduce the conversion temperature of industrial aluminum hydroxide to boehmite, it is possible to seed using boehmite obtained under hydrothermal conditions and at a temperature above 260 °C. When seeded at 12.5 % of the initial sample of the industrial aluminum hydroxide at 200 °C, it is possible to completely transform gibbsite to boehmite. Thus the cost of this process is significantly reduced, making it possible for its industrial application to reduce costs at the subsequent stage of calcination, while reducing the amount of impurities in the final alumina product.

#### 5. References

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