# PREPARATION OF PSEUDO-BOEHMITE BY USING HIGH-ALUMINA COAL FLY ASH

Zhang Xianqi[1,2], Zhang Ting'an[1], Feng Wei[1], Yan Shaoyong[1,2], Sun Junmin[2]✉, Lv Guozhi[1], Yang Huibin[2]
ZHANG Ting-an, Professor, E-mail: zta2000@163.net,Shenyang, Liaoning 110819, China
SUN Junmin, Senior Engineer, E-mail:sunjmdt@163.com,Huhehaota,Neimenggu 010000, China

([1]Key Laboratory of Ecological Utilization of Multi-metal Intergrown Ores of Ministry of Education, Northeastern University, Shenyang 110819, China
[2]High Alumina Coal R&D Center of Datang International Power Generation Co., Ltd.)

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**Abstract**

Fly ash is a very important unconventional aluminum resource in which the alumina content comes up to 40 ~ 60% in part of China. It has great economic and environmental value to exploit the recycling method of fly ash and produce high value-added multi-alumina products. In this paper, preparation of pseudo-boehmite by using Inner Mongolia Datang fly ash sintering clinker has been investigated. After a series of processing under optimized conditions (dissolution at 80℃, 60min, liquid solid ratio 4:1, first stage desilication 120min, 170 ℃, sodium silicon slag 100 g/l, sec-stage desilication 120 min, 90℃, CaO content 15 g/l), the silica ratio of the solution reaches up to 838, which conforms to the requirement of the industry. The pore volume of the seed precipitation product reaches 0.8291cm$^3$/g, which is almost the same with standard sample. The $Na_2O$ content of pseudo-boehmite prepared is below 0.3%, which can meet the sodium content requirements of general catalyst.

## Induction

Coal fly ash, a by-product of coal combustion, it's a kind of solid waste which mainly discharged from power plants. Generally, 250kg coal fly ash is produced for each ton of coal combustion. A latest estimated of worldwide generation of fly ash is 750 million tons each year, and still increase with rapid rate. China, Russia, the United States, India and Germany is the largest country of fly ash emissions [1]. China has vast indigenous reserves of coal, as in recent years, the scale of coal-based thermal power plant continues to expand, resulting in fly ash emissions increased year by year, it has reached 500 million tons in 2013, and the inventory of fly ash reached an estimated 2.5 billion tons. Irregular storage of fly ash lead to its take up vast areas of land, with resultant deteriorate of soil and danger to both human health and environment, therefore, the disposal and utilization of fly ash attracted many countries' attention.

Coal fly ash mainly contain compounds that include $SiO_2$, $Al_2O_3$, carbon, iron, calcium and magnesium ,the oxide of silicon and aluminum are more than 70% and mainly contains mineral that include unburnt carbon, glass microsphere, quartz, mullite, gypsum, magnetite and hematite.

The coal fly ash are produced by coal burning. The percentages of $Al_2O_3$ in the coal fly ash are more than 40%, which is good for recycling and producing $Al_2O_3$. The resources of bauxite are in badly in need of protection with the rapid development in alumina industry, which is a good opportunity for extracting $Al_2O_3$ in the coal fly ash.

Pseudo-boehmite ($\alpha'$-AlOOH) is a subcrystal-line boehmite, the content of crystal water is between 1.25~2. It has characters of large pore volume and specific surface area, strong adhesion, good peptization and thixotropic gel, is the main raw material of the production of a catalyst carrier activated alumina (gamma-$Al_2O_3$) [2]. At present, many methods for the preparation of pseudo-boehmite is reported, of which, mainly neutralization method and the organic alcohol-hydrolysis process can reach the actual industrialization [3]. Neutralization is a method of adopting different aluminum-containing raw materials and corresponding precipitation agent, neutralizing reaction with amorphous aluminum hydroxide product generated under certain conditions, and then by the multi procedure processing to obtain pseudo-boehmite. For example: the reaction of aluminum chloride and sodium hydroxide solution:

$$AlCl_3 + NaOH + aq \rightarrow Al_2O_3 \cdot nH_2O \downarrow + NaCl + aq \quad (1)$$

And as the reaction of aluminum sulfate and sodium aluminate solution:

$$Al_2(SO_4)_3 + NaAlO_2 + aq \rightarrow Al_2O_3 \cdot nH_2O \downarrow + Na_2SO_4 + aq \quad (2)$$

Organic alcohol aluminum hydrolysis method is based on the characteristic of aluminum can generate organic compounds and under certain conditions formating organic aluminium alkoxide $Al(OR)_3$(OR is alkoxy) firstly, and then get pseudo-boehmite by hydrolysis reaction:

$$Al(OR)_3 + aq \rightarrow Al_2O_3 \cdot nH_2O \downarrow + R_3OH + aq \quad (3)$$

Products prepared by the method above have characteristics of high chemical purity, less impurity phase, high crystallinity and good peptization performance, but the price is expensive, only suitable for the high-end products. In this paper, using high alumina fly ash sintered clinker as raw materials, to explore experiment conditions of the carbonation method and seed precipitation method using clinker leaching sodium aluminate solution for preparation of pseudo-boehmite. At the same time, the products of the two methods were characterized and compared.

## 1 Experiment

### 1.1 Material

The main raw material used for preparation of pseudo-boehmite in experiment is high-alumina coal fly ash from China's Inner Mongolia Datang International Togtoh Power Generation Company. The main chemical composition and X-ray diffraction spectra of coal fly ash are shown in Table 1 and Figure 1.

The Table 1 shows that the content of alumina in the coal fly ash is 42.95%, it can reach the general content of low-grade bauxite. And alumina-silica ratio (wt) is 1.03. XRD pattern shows that the phase of the coal fly ash includes mullite ($3Al_2O_3 \cdot 2SiO_2$), quartz and corundum. Because the content of silicon is relatively higher, pre-desilication have be done before sintering by reducing the amount of lime and red mud. The Table 2 shows the chemical composition of coal fly ash sintering clinker.

Table 1 Chemical composition of coal fly ash

| composition | MgO | $Al_2O_3$ | $SiO_2$ | CaO | $Fe_2O_3$ | other |
|---|---|---|---|---|---|---|
| content(%) | 0.48 | 42.95 | 41.90 | 3.66 | 4.00 | 7.01 |

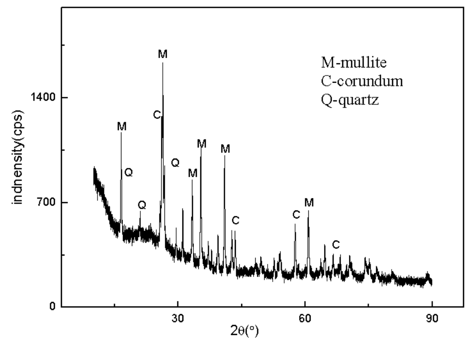



Figure 1 X-ray diffraction of coal fly ash

The Table 2 shows that calcium ratio of the sintering clinker ($CaO/SiO_2$ molar ratio) is 1.73, and alkali ratio ($Na_2O/Al_2O_3$ molar ratio) is 1.06.

In the experiment, NaOH, Al $(OH)_3$ and CaO are analytical reagent; $CO_2$ used for carbonate experiment are bottles for industry, and its concentration needs to preparation by experiment, distilled water is single-distilled water made in laboratory.

1.2 Experiment technology and process

The process was mainly divided into two steps: the first step was the dissolution and desilication process of coal fly ash sintering clinker; the second step was carbonation or seed precipitation of sodium aluminate solution. the second step was highlighted in this paper, and the process is shown in Figure 2.

Firstly a certain concentration and molecular ratio of adjustment liquid was made. The dissolution of coal fly ash sintering clinker and autoclave, deep desilication experiments were done and green liquor was obtained. Green liquor was decomposed into glue, and after a certain time of ageing, the experiment of separation, washing were done. Filter cake was dried at 70℃, and pseudo-boehmite powder was obtained.

Table 2 chemical composition of sintering clinker

| composition | MgO | $Al_2O_3$ | $SiO_2$ | CaO | $Fe_2O_3$ | $Na_2O$ | other |
|---|---|---|---|---|---|---|---|
| content(%) | 1.5 | 29.66 | 16.85 | 27.21 | 1.43 | 19.12 | 4.23 |

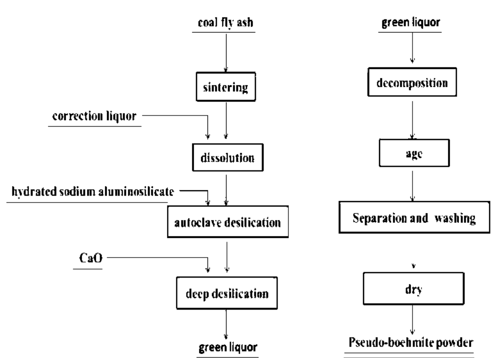



Figure 2 Intended use of fly ash for preparing boehmite process flow diagram

1.3 Design of experiment

Carbonate decomposition of the sodium aluminate solution is an exothermic process. With the deepening of the decomposition reaction, the temperature of decomposition system will rise sharply. That decomposition temperature is exorbitant can result in gibbsite's increasing dramatically. There is a lot of mixed phase in pseudo-boehmite, and finally the quality of pseudo-boehmite will be influenced. Therefore, a constant temperature water bath device is added in decomposition system to prevent the temperature of decomposition system increasing rapidly.

## 2 Results and discussion

In order to get pseudo-boehmite products meeting the requirements of quality, sodium aluminate solution dissolute from coal fly ash sintering clinker was needed removing impurity. Silicon oxide is the most main impurities in sodium aluminate solution. Therefore, the amount of silica ratio ($Al_2O_3/SiO_2$ mass ratio) is an important parameter to measure the quality of sodium aluminate solution. The early stage of the laboratory research has shown that under the condition of the following experiments: the dissolution temperature is 80 °C, dissolution time is 60 min, dissolution liquid-solid ratio is 4; the stripping liquid holding time in autoclave desilication is 120 min, desilication temperature is 170 °C, the additive amount of hydrated sodium aluminosilicate as seed is 100 g/l; deep desilication time is 120 min, desilication temperature is 90 °C, CaO content is 15 g/l, the silica ratio of green liquor can be reached 838, which can reach the requirements of produced pseudo-boehmite.

2.1 Carbonation method

In the carbonation method to prepare pseudo-boehmite, $CO_2$ gas was introduced into the sodium aluminate green liquor, in which process included the reaction of $CO_2$ with sodium aluminate solution and precipitation of alumina hydrate and other physical and chemical processes. This paper explored the impact of carbonation decomposition final pH of decomposition products since the final pH of the product has a greater impact on peptization rate polymorph. The carbonation decomposition conditions were fixed as follows: concentration of carbon dispensing $Al_2O_3$: 40 g/l, a glue temperature: 40 °C, $CO_2$ concentration: 33%. XRD diffraction patterns of different products produced while changing carbonation decomposition final pH from 9.5 to 11.5, are shown in Figure 3.

As can be seen from Figure 3 carbonation that when the decomposition endpoint pH=9.5 ,the product is mainly dawsonite, when pH>11, the product in addition to the pseudo-boehmite also contains gibbsite only when the pH=10.5, the product is mainly pseudo-boehmite.

In the production of carbonated intended boehmite process, $CO_2$ is used to neutralize caustic solution, so the solution ion activity of OH- greatly reduced. With different temperature, time and pH conditions, a variety of products include amorphous aluminum hydroxide, gibbsite, dawsonite, bayerite etc Generated, the reaction the literature [4] is as follows:

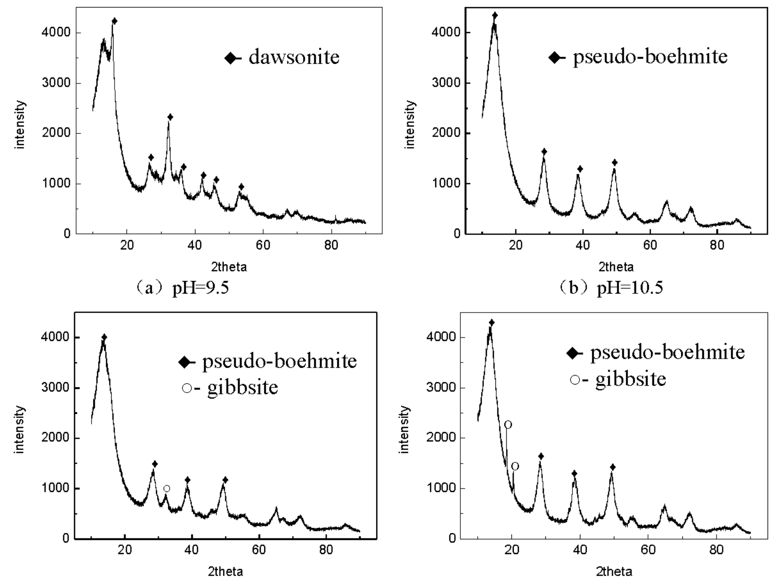
$$2NaOH+CO_2 \rightarrow Na_2CO_3+H_2O \quad (4)$$

$$2NaAl(OH)_4+CO_2 \rightarrow 2Al(OH)_3+Na_2CO_3+H_2O \quad (5)$$

$$NaAl(OH)_4 \rightarrow Al(OH)_3+NaOH \quad (6)$$

$$Na_2CO_3+CO_2+H_2O \rightarrow 2NaHCO_3 \quad (7)$$

$$Al(OH)_3+NaHCO_3 \rightarrow NaAl(CO_3)(OH)_2+H_2O \quad (8)$$




(a) pH=9.5 (b) pH=10.5 (c) pH=11.0 (d) pH=11.5

Figure 3. XRD diffraction images of carbonation end product at different pH values points

The neutralization reaction (4) of the free base was happened firstly when $CO_2$ was untroduced into sodium aluminate solution. With the gradual loss of stability of the solution, occured the precipitation of aluminum hydroxide reaction (5) and spontaneous hydrolysis of sodium aluminate solution (6). $Na_2CO_3$ produced by reaction (4) and (5) reacted with the $CO_2$ and generated $NaHCO_3$,then $NaHCO_3$ and aluminum hydroxide produced basic aluminum carbonate (i.e. dawsonite) by the reaction of (8) (Figure 3a). Meanwhile, the aluminum hydroxide from reaction (5) turned to Pseudo-boehmite after aging under suitable pH and temperature, and the reaction (5) parallel to (6) Generated hydrated alumina below to gibbsite or bayerite (Figure 3c, Figure 3d).

2.2 Seed precipitation

Industrial alkali production of pseudo-boehmite primarily for carbonation method, which was relying boehmite alumina sintering production process, using sintered clinker dissolution intermediates - cheap refined sodium aluminate solution and $CO_2$ as a raw material, preparation of boehmite directly, the process is simple and has a low cost. However, in this method parallel reactions generated two alumina hydrate existed in the gelation process, made it difficult to control the gelation process, and the product pore volume of only 0.30 ~ 0.60 $cm^3$ / g, it is difficult to meet the application needs of large pore volume. In this experiment, macro porous pseudo-boehmite standards from Shandong alumina plant were used for seeds, by seeded decomposition (referred to seed precipitation) supersaturated sodium aluminate solution method for preparing large pore volume, high surface area pseudo-boehmite.

Seed precipitation conditions: decomposition time 1h; 100 ml sodium aluminate solution and seed ratio (the ratio between large aperture standard boehmite added amount and the quality of $Al_2O_3$ in the sodium aluminate solution) 1.0; seed precipitation testing in different decomposition temperature (60 °C, 80 °C, 95 °C). Seed precipitation product was cooled, filtered and washed with deionized water to neutral, then dried 3h at 100 °C. The resulting product was subjected to XRD diffraction analysis, as shown in Figure 4.

As shown in Figure 4, when the decomposition temperature is 60 °C 80 °C, The typical hybrid phase gibbsite phase diffraction peaks appeared when 2θ in 18° and 20°. The reason may be that when the decomposition temperature is low, the pseudo-boehmite phase is not stable enough, there is a pseudo-boehmite to gibbsite transformation. This showed a high decomposition temperature in favor of preparating the pseudo-boehmite.

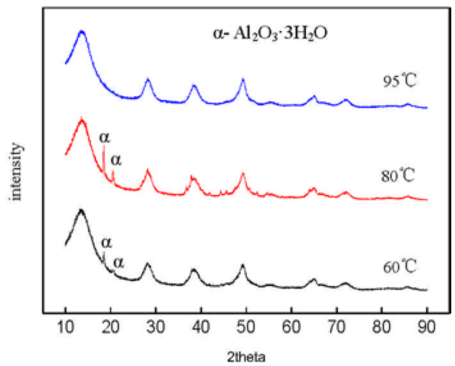
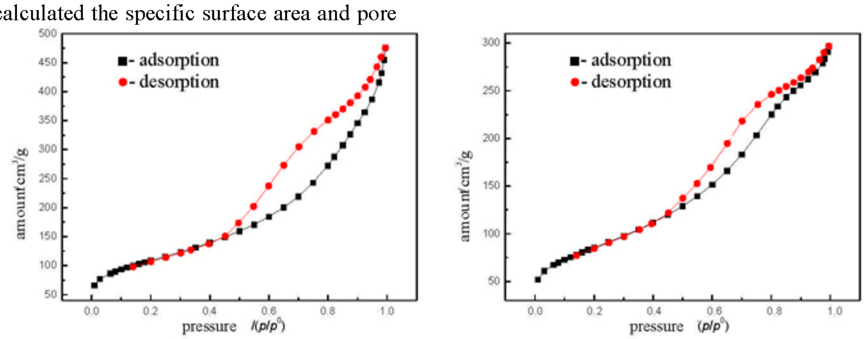



Figure 4. Seed precipitation product under different decomposition temperature

2.3 Characterization and comparison of carbonation-seed precipitation product

At constant temperature, sorption mass corresponds to the pressure, as the solid surface could only acomodate a certain amount of gas adsorption. By measuring a series of relative pressure adsorption quantity accordingly, adsorption isotherm could be obtained. Adsorption isotherm was the basic data of the adsorption phenomenon and to study the solid surface and hole, to study the properties of the surface and hole, calculated the specific surface area and pore size distribution. The pseudo-boehmite by carbon-seed precipitation adsorption-desorption isotherms was shown in Figure 5.

We compared the different pseudo-boehmite products by carbon-seed precipitation experiment, Different products of chemical composition and physical indicators were shown as Table 3. As can be seen from Table 3 the chemical composition of the different pseudo-boehmite products by carbon-seed precipitation ($Na_2O$, $SiO_2$, $Fe_2O_3$) meet the quality requirements of the chemical composition of standard pseudo-boehmite ($Na_2O$ content of less than 0.3%). Carbonation obtained in the experimental mesoporous pseudo-boehmite products, these pore volume could reach 0.6920 $cm^3$/g; Seed precipitation experiment used standard Macroporous pseudo-boehmite as seed, the pore volume of the pseudo-boehmite products could reach 0.8291 $cm^3$/g, Similar to 0.8349 $cm^3$/g of the standard sample pore volume, however, the specific surface area of up to 393.00 $m^2$/g, higher than the standard sample surface area. The pore volume of seed precipitation products was significantly greater than the carbonation products. In seed precipitation, the grain of pseudo-boehmite growth, the degree of crystallinity more complete, increasing the degree of crystallinity, the reaming of mechanism of action could be achieved.



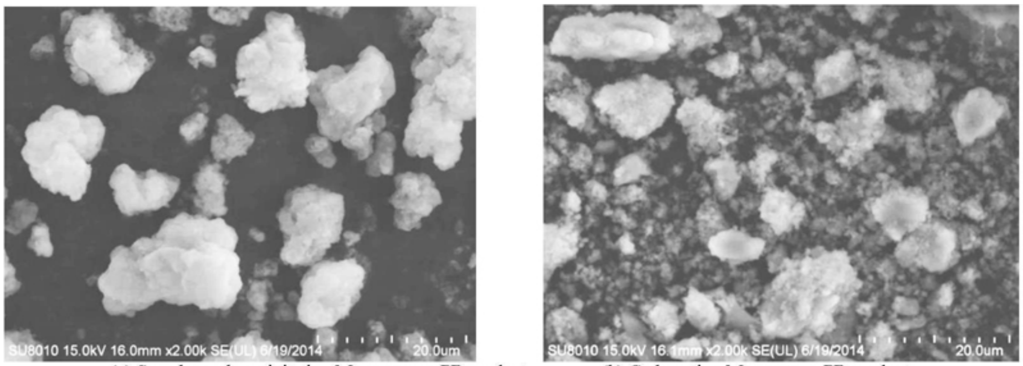

（a） Sample seed precipitation Macroporous PB product （b）Carbonation Mesoporous PB product

Figure 5. Different product isothermal adsorption and desorption curves

Table 3. Different products of chemical composition and physical indicators

| product name | Physical and chemical indicators | | | Chemical composition（%） | | |
|---|---|---|---|---|---|---|
| | BET ($m^2$/g) | BJHl ($cm^3$/g) | BJH (nm) | $Na_2O$ | $SiO_2$ | $Fe_2O_3$ |
| Carbonation PB | 356.46 | 0.6920 | 3.28 | 0.175 | 0.016 | 0.013 |
| Seed precipitation PB | 393.00 | 0.8291 | 7.67 | 0.164 | 0.004 | 0.024 |

Different PB products SEM results were shown as Figure 6. As we could see from Figure 6, both kinds of products: carbonation products or by seed precipitation products, the crystal structure of the product were relatively loose, agglomeration was low intensity, crystal structure was imperfect, the gaps between grains were large, description pseudo-boehmite was a crystalline incomplete from disorder to order, weakly crystalline to crystalline transition products, small crystals with poor crystallinity. Further observation of macroporous product has shown that the product has the crystal structure of platelets with folds. Carbonation products were of significantly smaller size than seed precipitation products. Experiments shown that with the carbonation precipitation, it was difficult to get macroporous pseudo-boehmite product, but experiments with seed precipitation could get macroporous pseudo-boehmite products.




(a) Sample seed precipitation Macroporous PB product (b) Carbonation Mesoporous PB product

Figure 6. Different PB product SEM result

### 3. Conclusion

(1) The following optimum conditions were determined during the study: leaching temperature of sintering clinker 80 °C for 60 min with liquid to solid ratio 4; the autoclave desilication at 170°C for 120 min with DSP seed 100 g/l; deep desilication at 90 °C for 120 min with added 15 g/l CaO. Silica ratio of green liquor reached 838 under these conditions.

(2) When the decomposition endpoint pH was 10.5 for carbonation precipitation, the products were mainly pseudo-boehmite. The suitable seed precipitation decomposition temperature was 95 °C.

(3) The chemical composition of the different pseudo-boehmite products by carbonation and seed precipitation meets the quality requirements of standard pseudo-boehmite. Carbonation and seed precipitation obtained the mesoporous pseudo-boehmite products, with pore volume 0.6920 and 0.8291 $cm^3/g$, respectively. The pore volume of seed precipitation products was significantly greater than the carbonation products.

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