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# A novel process for synthesis of tobermorite fiber from high-alumina fly ash

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A new two-step process was developed for the synthesis of tobermorite fiber from high alumina fly ash. The results reveal that high alumina extraction efficiency from the fly ash can be achieved in the first step and tobermorite fiber with excellent properties can be produced from the dealumination slag in the second step. FETEM images show that typical single crystal fibers with a length of 5–10 μm and a length-to-diameter ratio of 50–100 have been synthesized successfully. The strength tests after compression molding demonstrate that the compressive and flexural strengths of the products are greater than 0.34 MPa and 0.85 MPa, respectively, with a low bulk density of 218 $kg/m^3$ and a thermal conductivity of 0.059 W/(m·k). It fully complies with China's national standards for calcium silicate insulation materials. Therefore, the fibers production is very promising to be used in the building external wall thermal insulation application.



## 1. Introduction

Fly ash is an ultrafine solid residue generated by combustion of coal in a thermo-electric power plant. It constitutes the greatest amount of industrial solid waste in China. In some regions of China, the alumina content in fly ash reaches 38–50 wt% and this type of fly ash is called "high-alumina fly ash (HAFA)". For example, in Inner Mongolia, which process the biggest coal power industry in China, annual emission of HAFA is about 50 million tons and the cumulative amount over the years has been around 100 million tons [1]. The disposal of such fly ash has become a serious environmental problem [2]. With the diminishing of bauxite resources as well as the increase in alumina demand, the high-value industrial utilization of the HAFA in alumina recovery has attracted extensive attentions in recent years.

In the 2000s, Sun and coworkers [3], for the first time, carried out the extraction of alumina from such HAFA by a sintering process, which has been industrialized successfully. However, the utilization of the alumina tailing still remains a tough task because of the large amounts generation and difficulty in making use of dealumination tailings, in which the alkali content is as high as 4%. Subsequently, a new technology named pressure acid-leaching method [4] was developed. However, the acid media used in this process causes serious corrosion to the reaction equipment and impurities co-leached into the acid solution are hard to be removed. Exploring new alumina extraction processes from HAFA is therefore of great significance. Yang et al. [5] investigated a mild hydro-chemical process to recover alumina from HAFA shown a good application prospect in industry. A high $Al_2O_3$ extraction efficiency of more than 90% has been achieved. However, with each ton of $Al_2O_3$ produced, this process generates 2–2.5 tons of dealumination slag, the leached residue obtained after extracting the alumina Actually, the feature of excessive dealumination slag for mild hydro-chemical process is mainly determined by the property of HAFA instead of the process itself. Generally, the silicon dioxide content in HAFA is almost 50% while in bauxite is only 10–20%. And this means that no matter what kind of technology we take, an excessive slag amount is almost inevitable. In this case, only a well treatment of this silicon slag obtained after extracting the alumina, the process may show good optimistic in industry. What's more,

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based on our mild hydro-chemical process, a demonstration project with an annual output of 10 000 tons $Al_2O_3$ had been built up and put into operation in 2014. And the project has realized a running period of 18 days without shutdown recently. However, as one important follow-up step of the whole process, how to treat this dealumination slag has not been reported at present. $NaCaHSiO_4$ is the main final product of the dealumination slag. $Na_2O$ content reaches 20 wt.% in this slag and has to be dealkalized [5,6]. . It is well known that $NaCaHSiO_4$ can be converted to calcium silicate hydrate in diluted alkaline solution [7]. Some researchers have studied the decomposition of $NaCaHSiO_4$. Zhong et al. investigated sodium removal from red mud using diluted NaOH solution [8]. Zhang et al. investigated the decomposition dynamics of $NaCaHSiO_4$ in diluted NaOH solution [9]. To date, only a few related studies on removing sodium from fly ash dealumination slag are available. And in particular for the praticalization and productization of the dealumination slag, it's currently not reported as well. Tobermorite [$Ca_5Si_6O_{17}\cdot 5H_2O$] is a type of crystalline calcium silicate hydrate synthesized by a hydrothermal reaction in the $CaO-SiO_2-H_2O$ system [10,11]. Many studies have shown that tobermorite-type calcium silicate especially tobermorite fibers exhibits several excellent characteristics such as light weight, flame-retardant and high compressive strength, which makes it very efficient for heat insulating and fire-resistant building material [12,13]. The current method used to synthesize tobermorite-type calcium silicate involves curing a mixture of lime and active silica such as kaolin with steam at 1.5 MPa and ~200 °C for 5–20 h [14]. As well known, both lime and kaolin are natural resources and thus need to be preserved. Moreover, needle-like tobermorite fibers are generally difficult to obtain with such a method and the experimental results are also affected by various factors. Many efforts have been made to synthesize long needle-like tobermorite fibers [15–17].

A new two-step process for the synthesis of tobermorite fiber from HAFA has been proposed in this study. The first step involves the exaction of alumina, which is a comparatively mature technology. Therefore the main focus of this paper is on the second step, which is investigating the preparation of tobermorite fiber material using the solid residue produced in the first step as a raw material. The effects of several key reaction conditions, including reaction temperature, reaction time and the liquid to solid mass ration of reactant slurry, on the phase formation and morphology of the products have been systematically investigated. Mechanical properties of calcium silicate products made from these tobermorite fibers through molded compression have also been studied.

## 2. Experimental

### 2.1. Materials

The primary raw material – HAFA used in this experiment was sampled from a thermoelectric power plant in Inner Mongolia, China. Its chemical compositions are listed in Table 1. The $Al_2O_3$ and $SiO_2$ content of the fly ash are 49.50% and 42.25%, respectively, with a high mass ratio of alumina to silica (A/S) of 1.17. Its XRD patterns, as shown in Fig. 1, show that the main phases comprise mullite and corundum as well as some amorphous material.

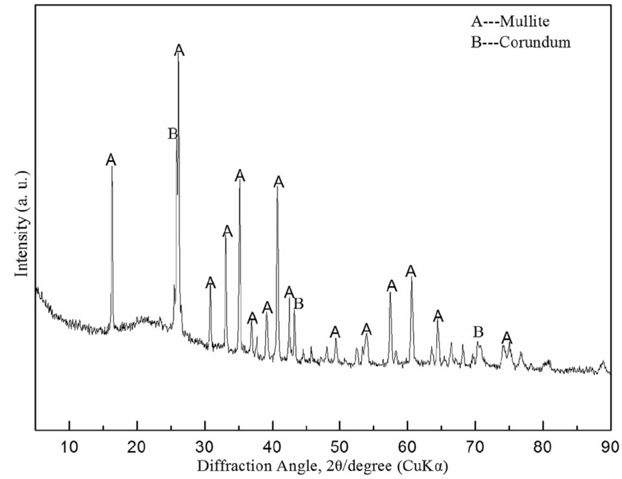


**Fig. 1.** XRD pattern of the HAFA.

The other reagents such as sodium hydroxide, aluminum hydroxide and calcium hydroxide were of reagent grade, obtained from Xilong Chemical Co., Ltd. and were used as received without further purification.

### 2.2. Experimental principles

The technological route for this new two-step process is schematically shown in Fig. 2.

In Step-One, almost all $Al_2O_3$ in HAFA would be dissolved into the solution and $SiO_2$ in HAFA is incorporated into the precipitate in the form of $NaCaHSiO_4$. The chemical equation of this mild hydro-chemical process has been proposed to be

$$3Al_2O_3\bullet SiO_2 + NaOH + Ca(OH)_2 \rightarrow NaCaHSiO_4 + NaAl(OH)_4 \quad (1)$$

After the subsequent liquid–solid separation, the sodium aluminate solution could be used to produce alumina through the mature technology of crystallization.

In Step-Two, the dealumination slag obtained in Step-One is used to synthesize tobermorite fiber according to the following reaction:

$$2NaCaHSiO_4 + nH_2O \rightarrow 2CaO\cdot 2SiO_2\cdot nH_2O\downarrow + 2NaOH \quad (2)$$

Then the hydrolysate $2CaO\cdot 2SiO_2\cdot nH_2O$ continues to react with $Si^{4+}$, $Ca^{2+}$, $Al^{3+}$, and $OH^-$, producing tobermorite fiber under the Step-Two hydrothermal conditions.

### 2.3. Experimental processing

In this study, experiments were carried out in a 1000 mL stainless steel autoclave with a pure nickel protective lining. It was equipped with a mechanical agitator and a temperature-control system to maintain the desired temperature within an error of ±0.5 °C. Firstly, HAFA was treated in concentrated alkaline solution

**Table 1**
Chemical compositions of HAFA, dealumination slag and hydration products.

| Composition | $Al_2O_3$ | $SiO_2$ | $Fe_2O_3$ | $TiO_2$ | CaO | $Na_2O$ | LOI | A/S |
|---|---|---|---|---|---|---|---|---|
| Content of HAFA (wt %) | 49.50 | 42.25 | 2.31 | 1.78 | 1.35 | / | 2.44 | 1.17 |
| Content of dealumination slag (wt %) | 1.89 | 30.67 | 1.03 | 0.86 | 34.91 | 19.22 | / | 0.062 |
| Content of hydration products (wt %) | 1.27 | 32.23 | 1.08 | 0.92 | 36.69 | 0.95 | / | 0.039 |

**Note**: LOI is the loss on ignition; A/S is mass ratio of $Al_2O_3$ to $SiO_2$.