Academia Journal of Scientific Research 7(11): 000-000, November 2019
DOI: 10.15413/ajsr.2019.0712
ISSN 2315-7712

Publishing

Research Paper

Melting and dissolving fly ash by NaOH for the removal of iron, calcium and other impurities

Accepted 8th November, 2019

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ABSTRACT

Mixture of fly ash and sodium hydroxide was calcined, which converted mullite ($3Al_2O_3{\cdot}2SiO_2$), the high-temperature stability phase containing silicon and aluminum oxides, and quartz into activated silica alumina phase, and they were dissolved by concentrated NaOH solution into soluble SiO_3^{2-} and AlO_2^{-}. The insoluble impurities including Fe_2O_3, FeO, CaO and $CaSO_4$ were filtered out. Experiment results showed the optimum experimental conditions for the dissolution: temperature of 60°C, 15% NaOH solution was used, liquid-solid mass ratio was 11:1, stirring time was 3 h, and about 78.9% of silicon and 78.1% of aluminum were dissolved. The obtained pure silicon aluminum solution provided the raw material for preparing high-purity molecular sieves, and Fe_2O_3 content of the prepared P type molecular sieve was only 0.25% and an CaO content was only 0.066%.

Key words: Melting and dissolving of coal fly ash, removal of Fe, P molecular sieve.

INTRODUCTION

Fly ash is a kind of solid waste discharged from power plants and various coal-fired boilers. According to statistics, the amount of fly ash accumulation in China is up to 0.2 billion tons, and it is increasing every year. It is the largest output of ash in industrial waste residue. Fly ash can seriously pollute the environment and cause serious harm to people's lives, animals and plants, and so on. According to local conditions, timely and effective treatment of fly ash and comprehensive utilization of fly ash have far-reaching significance. It not only saves water, saves soil, turns waste into treasure, but also protects the environment.

At present, fly ash is mainly used as building material. It is used in thermal insulation board, slag cement, wall tile, floor brick etc. (Meiling, 2017). The utilization ratio of fly ash is large, reaching 67%, but the added value of products is not high. The main representative components of fly ash are silica and alumina, which account for as high as 70%, while the silicon and aluminum are also the main ingredients of expensive molecular sieve. Preparing high price molecular sieve with cheap fly ash is an important way to promote the use of additional value. The application of molecular sieve is very wide, can be used for gas or liquid dehydration, drying, separation and purification, can also be used as adsorbent, catalyst and ion exchange agent for various types of reactions in the field of petroleum chemical industry, fine chemical industry, agriculture and environmental protection. The preparation of molecular sieve with fly ash can not only save raw materials, but also can simplify the process and equipment, and provide the conditions for large-scale production and wide application of molecular sieves.

Study on the synthesis of molecular sieves with fly ash began from 1985 by Holler and Wrisching. Since then, more and more molecular sieve types (Zhenlei et al., 2016) has been developed. The domestic and international research on the synthesis of molecular sieve from fly ash is on the increase (Tomonori et al., 2017).

Liyun et al. (2019) recently synthesized zeolite 4A using fly ash fused with synergism of NaOH and Na_2CO_3. Asifa et al. (2019) synthesized and characterized pure phase 4A from coal fly ash]. Richa et al. (2019) synthesized fly ash based zeolite-reduced graphene oxide composite and

Table 1: Representative components of the fly ash (mass fraction, %).

Ingredient	SiO_2	Al_2O_3	$CaSO_4$	MgO	Na_2O	Fe_2O_3	Others
Percent	41.36	30.45	24.75	1.15	0.26	3.70	1.66

evaluated its property as an adsorbent for arsenic removal. De Rossi et al. (2019) synthesized zeolite by geopolymerization of biomass fly ash and metakaolin. Nevin and Singh (2016) described applications of fly ash zeolites for water treatment. Wei et al. (2018) synthesized high quality zeolites from coal fly ash and researched mobility of hazardous elements and environmental applications. Tauanov et al. (2018) synthesized coal fly ash-derived zeolites doped with silver nanoparticles for mercury (II) removal from water. Jeong min et al. (2019) prepared quasi-solid-state electrolytes using a coal fly ash derived zeolite-X and -A for dye-sensitized solar cells. Collectively, researches on zeolites derived from fly ash focus on applications gradually.

However, fly ash is not pure aluminum silicate. In addition to containing valuable elements of silicon and aluminum, fly ash also contains a considerable part of the iron and calcium and other impurities, leading to impure molecular sieve. The impurities are not only easy to plug the channels of molecular sieve, but reduce the exchange capacity, catalytic performance and cycle performance. The drawbacks have not drawn enough attentions so far. Therefore, it is necessary to pretreat fly ash to remove the impurities such as iron, calcium and so on before preparing the molecular sieve with fly ash.

Acid leaching of fly ash to remove iron and calcium used to be employed by previous patent literature, as the reaction temperature is below 100°C, the process can not destroy the high-temperature phase such as mullite and quartz, so the high temperature phase, which includes iron and calcium impurities, does not dissolve, this process can only get rid of 60% of iron and calcium, and is not complete. Carbon reduction - magnetic separation - acid leaching method has previously been used, although the iron removal efficiency is high, the process is slightly lengthy (Minghua et al., 2017). Alkali melting method was used in literature, but the following alkali dissolving was not used. The impurities still exist in prepared molecular sieve (Deshun et al., 2016).

A new method, involving alkali melting and alkali dissolving of fly ash to remove iron, calcium and other impurities was proposed in the study. Firstly, fly ash and NaOH solid was mixed, roasted to convert the mullite and quartz into glass phases. The roasted clinker was leached by NaOH solution to dissolve silicon and aluminum components, and to filter out Fe_2O_3, CaO and $CaSO_4$ insoluble impurities etc., so as to obtain purified Na_2SiO_3 and $NaAlO_2$ solution. The purified solution can be used for the preparation of high pure molecular sieve to improve the performance and the service life.

EXPERIMENTAL PART

In this study, the fly ash was obtained from a power plant in Shandong, and the main chemical compositions are shown in Table 1.

The specific steps are as follows: A certain amount of fly ash was weighed, placed in a mortar, and fully ground before put through a 200 mesh sieve prior to be mixed with NaOH powder with a mass ratio of 1 to 2. The mixture was transferred to a crucible and was roasted at 600°C in a muffle furnace for 2 h. The clinker was then leached with a high concentration of NaOH solution to dissolve the silicon aluminum phase, and the impurities such as iron and calcium are filtered out to obtain a pure solution containing the silicon aluminum phase merely. The contents of Si and Al in the filtrate were analyzed by ICP analyzer, and the dissolution ratios of silicon and aluminum were calculated according to the total amounts. At the same time, the dissolution ratio of fly ash in clinker was also measured. The filtrate was added with hydrochloric acid and the alkalinity (OH/Si) was controlled. A certain proportion of Na_2SiO_3 solution and the seed crystal directing agent were added to regulate the ratio of silicon and aluminum for special molecular type. Thereafter, the mixture was stirred evenly, transferred to an autoclave, crystallized at a certain temperature for a certain time. The derived solid was just molecular sieve, and was filtered and dried, measured by SHIMADZU X ray diffractometer XRD-6000. Zeolite P was synthesized according to the document (Deshun et al., 2016). Ion concentration was analyzed by 3600A inductively coupled plasma atomic emission spectrometer made by Keje Company in China.

RESULTS AND DISCUSSION

Calcination of NaOH and fly ash

SiO_2 and Al_2O_3 existing as quartz and mullite in fly ash have low activity, and high temperature alkali roasting method can greatly increase its activity, improve the efficiency of the fly ash conversion and crystallization synthesis of molecular sieve. In the experiment, fly ash and NaOH reacted after roasted in a muffle furnace at 600°C for 2 h. Figure 1 shows the XRD for fly ash before and after calcination with NaOH.

From Figure 1, the diffraction peaks of quartz and mullite are strong before calcination, which show the main minerals are quartz and mullite. Quartz and mullite are difficult to react with NaOH at room temperature due to their low activity. Therefore, calcination of fly ash and NaOH

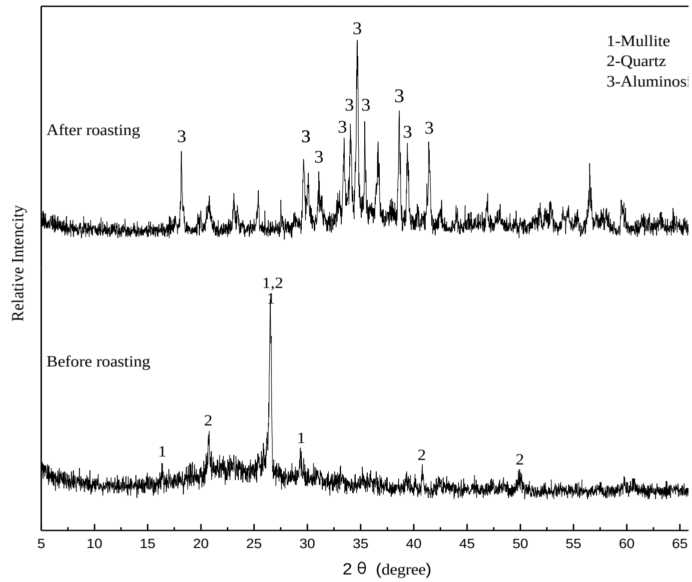

Figure 1: Effect of alkali melting activation on fly ash structure.

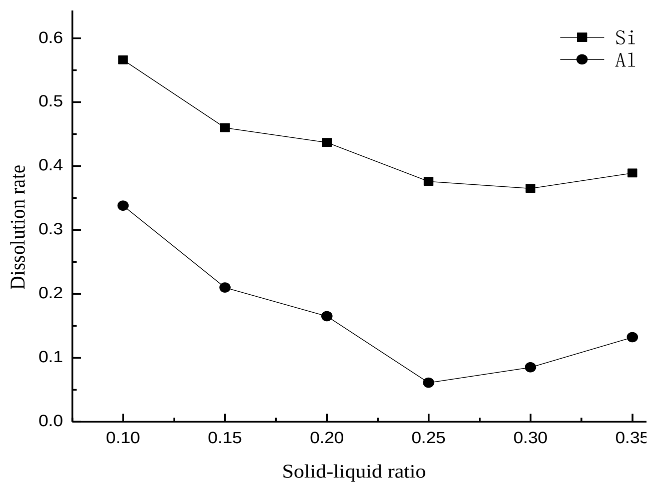

Figure 2: Effect of mass ratio of solid clinker to alkali solution 15% NaOH, 1h of stirring time, 60°C.

at high temperature is necessary and can stimulate its activity. The diffraction pattern of calcined fly ash and NaOH shows that the form of the material is mainly aluminosilicate when calcined at high temperature. At this time, there are few quartz and mullite, and the diffraction peak almost disappeared. This is because as the reaction proceeded, high temperature roasting destroyed crystal structure, thus released the active SiO_2 and Al_2O_3. These substances react with NaOH, and generate amorphous aluminosilicate that is able to participate in the zeolite framework structure:

$3Al_2O_3 \cdot 2SiO_2 + NaOH \rightarrow NaAlO_2 + Na_2SiO_3 + H_2O$ [1]

$SiO_2[quartz] \rightarrow SiO_2[glass]$ [2]

What is more, high temperature roasting can get rid of the organic impurities in fly ash and amorphous carbon, thereby improving the purity of raw materials. In addition, alkali melting of fly ash provided large amount of NaOH for the following leaching process since the real mass amount of NaOH that reacted is equal to the of fly ash according to the experimental result.

Effect of mass ratio of solid clinker to alkali solution

Figure 2 shows that the NaOH solution can dissolve alkali melting residue, which includes Na_2SiO_3 and $NaAl(OH)_4$ derived from mullite, quartz and other silicon aluminum

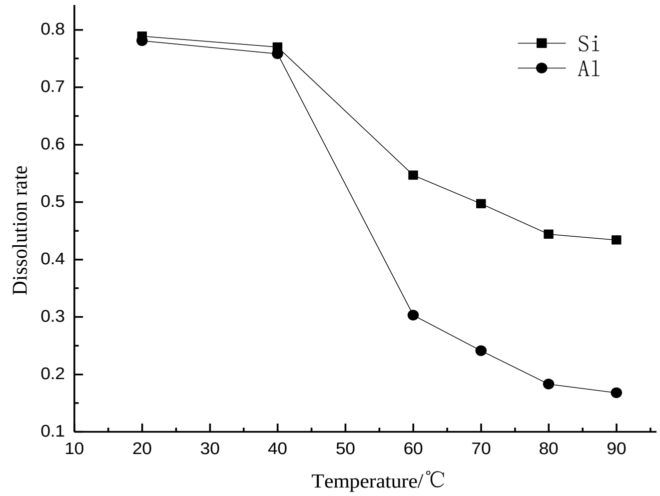

Figure 3: Effect of temperature on dissolving ratio of Si and Al 15% NaOH, NaOH solution clinker mass ratio of 10:1, 1h of stirring time.

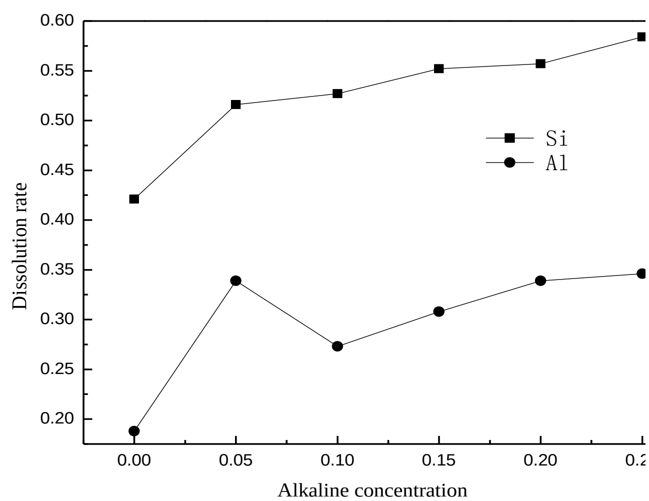

Figure 4: Effect of mass ratio of NaOH to solution on dissolving ratio of Si and Al 60°C, NaOH solution to clinker mass ratio of 10 to 1, 1 h of stirring time.

phases of coal fly ash. Dissolving ratios of Si and Al decreased with increasing mass ratio of solid clinker to alkali solution. The maximum dissolving ratio of Si was 56.6%, while the maximum dissolving ratio of Al was 33.8% under the experimental condition. 100 g water can dissolve nearly 37 g Na_2SiO_3, however, 56.6% is not high.

Effect of temperature on dissolving ratio of Si and Al

From Figure 3, low leaching temperature is beneficial to high dissolving ratio of Si and Al. Dissolving ratios of Si and Al reached 78.9 and 78.1%, respectively as the leaching temperature is 20°. Similar research showed that the dissolution ratio of Si was 75%, while the dissolution ratio of Al was only 25% during alkali leaching from titania slag (Lu et al., 2010). Both the dissolving ratios dropped sharply with increasing leaching temperatures because hydrolysis reaction occurred at higher temperatures. H_4SiO_4 and $Al(OH)_3$ precipitates stayed in solid residues, which resulted in low dissolving ratios.

Effect of mass ratio of NaOH to solution on dissolving ratio of Si and Al

Figure 4 shows that higher NaOH concentration is more viable in order to dissolve more Si and Al. The possible following reaction occurs:

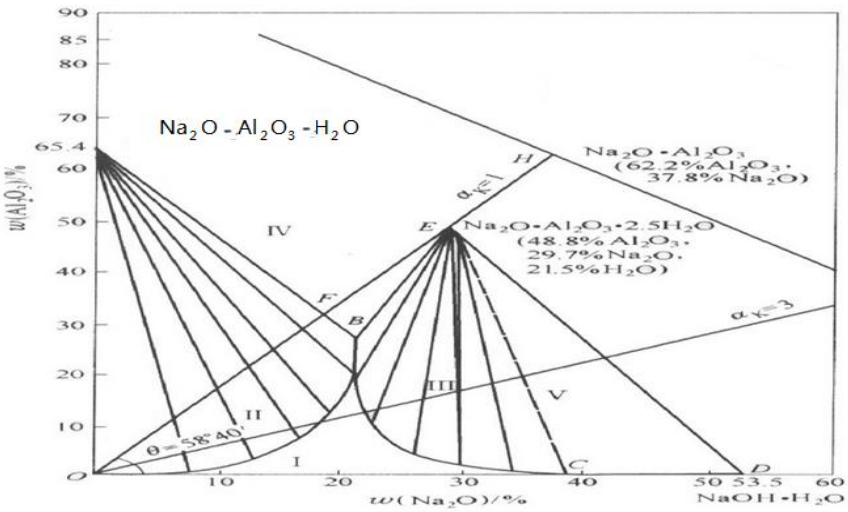

Figure 5: Na_2O-Al_2O_3-H_2O phase diagram.

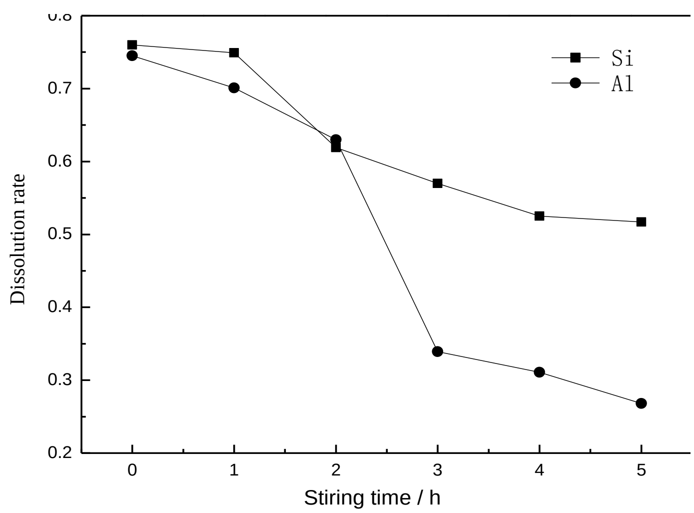

Figure 6: Effect of stirring time on dissolving ratios of Si and Al 60°C, NaOH solution to clinker mass ratio of 10 to 1.

$Na_2O{\cdot}Al_2O_3{\cdot}xSiO_2 + 2NaOH + 4H_2O \rightarrow 2NaAl(OH)_4 + Na_2[H_2SiO_4]$

Thus, insoluble $Na_2O{\cdot}Al_2O_3{\cdot}xSiO_2$ in water dissolved in concentrated NaOH solution. The tendency indicates that OH- plays an important role during the process, which takes part in the coordination process. The use of large amount of NaOH is not cost effective. Reusing the redundant NaOH solution is significant and economical. The condensation and the seed can enable the reuse of NaOH solution possible.

Figure 5 shows the Na_2O-Al_2O_3-H_2O system phase diagram. The area of OBCO belongs to dissolving process of Al_2O_3 into NaOH solution according to Figure 3. The solubility of Al_2O_3 in NaOH solution is increasing along the NaOH concentration until 20% (line OB), after the summit of 20% of the solubility, the dissolving ability decreases with the increasing NaOH concentration [line BC]. Therefore, high efficient NaOH concentration is about 20%, the number is in line with our experimental result shown in Figure 4, where 0.20 mass ratio of NaOH obtained highest dissolving ratio of Al. When 15% NaOH was used, NaOH was surplus after the roasting process. Overall, the concentration of NaOH was about 20%.

Effect of stirring time on dissolving ratios of Si and Al

Figure 6 indicates too long time is disadvantageous for high dissolving ratio of Si and Al. The dissolving ratio decreased

Figure 7: Residue of insoluble clinker after filtration.

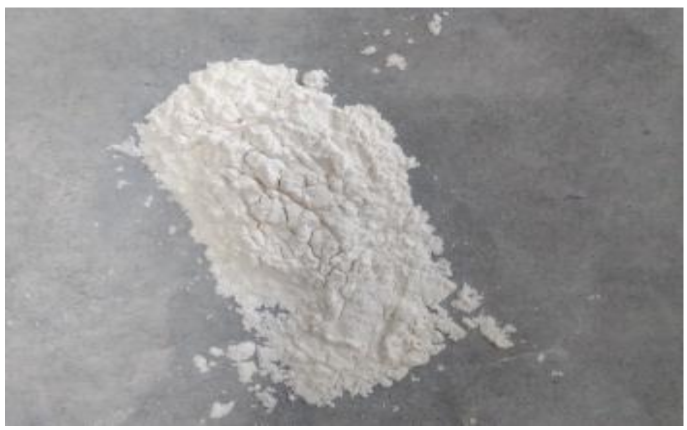

Figure 8: P molecular sieve prepared by coal fly ash.

Table 2: Chemical composition of P molecule sieve prepared by fly ash (mass fraction, %).

Ingredient	SiO_2	Al_2O_3	Na_2O	K_2O	Fe_2O_3	CaO	SO_3
Percent (%)	58.74	25.65	14.67	0.61	0.25	0.066	0.011

with increasing stirring time. The tendency is obvious for Al. The dissolving ratio decreased steeply during 2 h or so. The gradual decreasing tendency is due to precipitate of Si and Al. Reducing stirring time is essential so as to get high dissolving ratios of Si and Al. 1 h is enough for the stirring time.

Figure 7 shows the filtration of slag after alkaline solution filtration. The color of the slag is red, which proves that the slag contains iron oxide, which can be used for carbon reduction to obtain sponge iron for steel-making. The filtered solution can be used for the preparation of the molecular sieve, the Fe_2O_3 content of the prepared molecular sieve decreased to 0.25% after the alkali treatment from 2.87% by mere acid leaching of fly ash, while the content of CaO decreased to 0.066% after alkali treatment from 1.18% by mere acid leaching of fly ash. The chemical formula of P molecule sieve prepared was confirmed as $Na_6Al_6Si_{10}O_{32}{\cdot}12H_2O$ through ICP examination. The purity of the P molecular sieve prepared using the method from coal fly ash was 99.06% (Table 2), while the whiteness level was 96 (Figure 8). Both purity and whiteness level of the molecular sieve can meet the standard of market molecular sieve.

Figure 9 shows XRD diagram of the product, there are 5 characteristic peaks at 2θ = 12.48°, 17.71°, 21.68°, 28.15° and 33.37°, respectively and miscellaneous peaks are few,

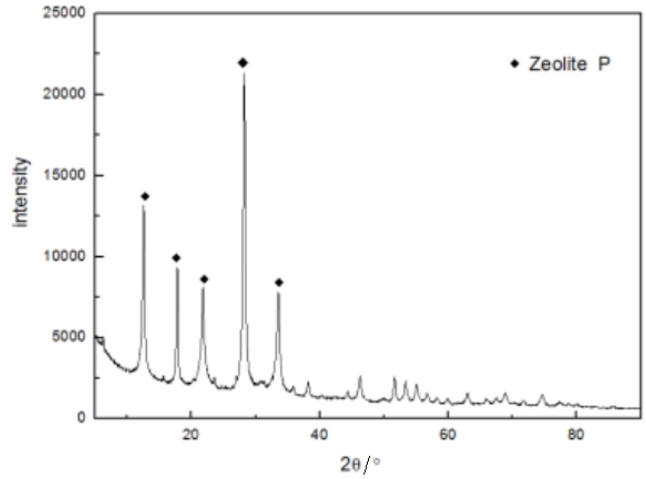

Figure 9: XRD diagram of P molecule sieve prepared by coal fly ash.

indicating the product is P molecule sieve. Pure P molecule sieve can be used as petroleum catalyst, support and detergent additive to soften hard water in washing process.

Conclusion

At 600°C, the alkali melting activated quartz and mullite in the fly ash into the aluminosilicate glass phase, which can be dissolved in the alkali solution. The optimum conditions of alkali dissolving of clinker were obtained by optimizing experiments, that is, the reaction temperature was 20°C, using 15% NaOH solution, the liquid solid ratio was 10:1, and the stirring time was less than 1 h, the whole dissolution ratio of Silicon reached 78.9% while that of Al reached 78.1%. The method provided pure solution for preparing molecular sieves from fly ash. The Fe_2O_3 content of the prepared molecular sieve through actual verification decreased to 0.25% after the alkali treatment from 2.87% by merely acid leaching of fly ash, while the content of CaO decreased to 0.066% after alkali treatment from 1.18% by merely acid leaching of fly ash.

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