

## **MELTING AND DISSOLVING FLY ASH BY NaOH FOR THE REMOVAL OF IRON, CALCIUM AND OTHER IMPURITIES**

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### **Abstract**

Mixture of fly ash and sodium hydroxide was calcined, which converted mullite ( $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), 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  $\text{SiO}_3^{2-}$  and  $\text{AlO}_2^-$ . The insoluble impurities including  $\text{Fe}_2\text{O}_3$ , FeO, CaO, and  $\text{CaSO}_4$  were filtered out. Experimental results show that the optimum experimental conditions for the dissolution: temperature is  $60^\circ\text{C}$ , 15% NaOH solution is used, liquid-solid mass ratio is 11:1, stirring time is 3h, and about 78.9% of silicon and 78.1% of aluminum are dissolved. The obtained pure silicon aluminum solution provides the raw material for preparing high-purity molecular sieves, and  $\text{Fe}_2\text{O}_3$  content of the prepared P type molecular sieve is only 0.25% and the CaO content is only 0.066%.

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Keywords and phrases: melting and dissolving of coal fly ash, removal of Fe, P molecular sieve.

Communicated by Ana Rosa Silva.

Received October 29, 2019; Revised January 13, 2020

## 1. 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. [1]. 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 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 [2]. Since then, more and more molecular sieve types [3] has been developed. The domestic and international research on the synthesis of molecular sieve from fly ash is more and more widely and deeply [4].

Recently Yang et al. synthesized zeolite 4A using fly ash fused with synergism of NaOH and Na<sub>2</sub>CO<sub>3</sub> [5]. Iqbal et al. synthesized and characterized pure phase 4A from coal fly ash [6]. Soni and Shukia synthesized fly ash based zeolite-reduced graphene oxide composite and evaluated its property as an adsorbent for arsenic removal [7]. De Rossi et al. synthesized zeolite by geopolymerization of biomass fly ash and metakaolin [8]. Koshy and Singh described applications of fly ash zeolites for water treatment [9]. Fang et al. synthesized high quality zeolites from coal fly ash and researched mobility of hazardous elements and environmental applications [10]. Tauanov et al. synthesized coal fly ash-derived zeolites doped with silver nanoparticles for mercury (II) removal from water [11]. Lim et al. prepared quasi-solid-state electrolytes using a coal fly ash derived zeolite-X and -A for dye-sensitized solar cells [12]. 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, and reduce the exchange capacity, catalytic performance and cycle performance. The drawbacks has 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 included iron and calcium impurities does not dissolve, this process can only get rid of 60% of iron and calcium, is not complete. We once used carbon reduction - magnetic separation - acid leaching method, although the iron removal

efficiency is high, the process is slightly lengthy [13]. Alkali melting method was used in literature, but the following alkali dissolving was not used. The impurities still exist in prepared molecular sieve [14].

A new method, alkali melting, alkali dissolving, of fly ash, to remove iron, calcium and other impurities was proposed in the paper. 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  $\text{Fe}_2\text{O}_3$ , CaO, and  $\text{CaSO}_4$  insoluble impurities etc., so as to obtain purified  $\text{Na}_2\text{SiO}_3$  and  $\text{NaAlO}_2$  solution. The purified solution can be used for the preparation of high pure molecular sieve to improve the performance and the service life.

## 2. Experimental Part

In this study, the fly ash was got from a power plant in Shandong, the main chemical composition is shown in Table 1.

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

Ingredient	$\text{SiO}_2$	$\text{Al}_2\text{O}_3$	$\text{CaSO}_4$	MgO	$\text{Na}_2\text{O}$	$\text{Fe}_2\text{O}_3$	others
Percent	41.36	30.45	24.75	1.15	0.26	3.70	1.66

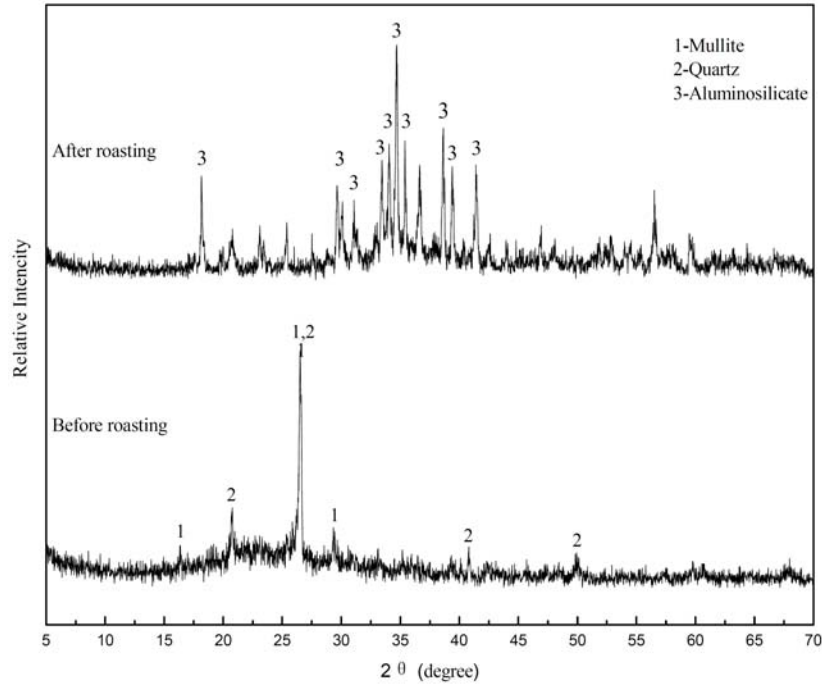
The specific steps are as follows. A certain amount of fly ash was weighed, placed in a mortar, and fully ground before put through a 200 mesh sieve prior to be mixed with NaOH powder with a mass ratio of 1 to 2. The mixture was transferred to a crucible and was roasted at  $600^\circ\text{C}$  in a muffle furnace for 2h. 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  $\text{Na}_2\text{SiO}_3$  solution and the seed crystal directing agent was added to regulate the ratio of silicon and aluminum for special molecular type. After that, the mixture was stirred evenly, transferred to a 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 [14]. Ion concentration is analyzed by 3600A inductively coupled plasma atomic emission spectrometer made Keje company in China.

### 3. Results and Discussion

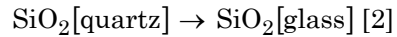
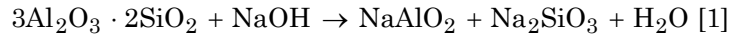
#### 3.1. Calcination of NaOH and fly ash

$\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  existing as quartz and mullite in fly ash have low activity, high temperature alkali roasting method can greatly increase its activity, improve the efficiency of the fly ash conversion and crystallization synthesis of molecular sieve. There are commonly two ways to calcine fly ash, one is to add  $\text{Na}_2\text{CO}_3$  to calcine at  $800^\circ\text{C}$ , the other is to add NaOH to calcine at  $600^\circ\text{C}$ . In the experiment, fly ash and NaOH reacted after roasted in a muffle furnace at  $600^\circ\text{C}$  for 2h. Figure 1 is the contrast diagram of XRD for fly ash before and after calcination with NaOH.



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

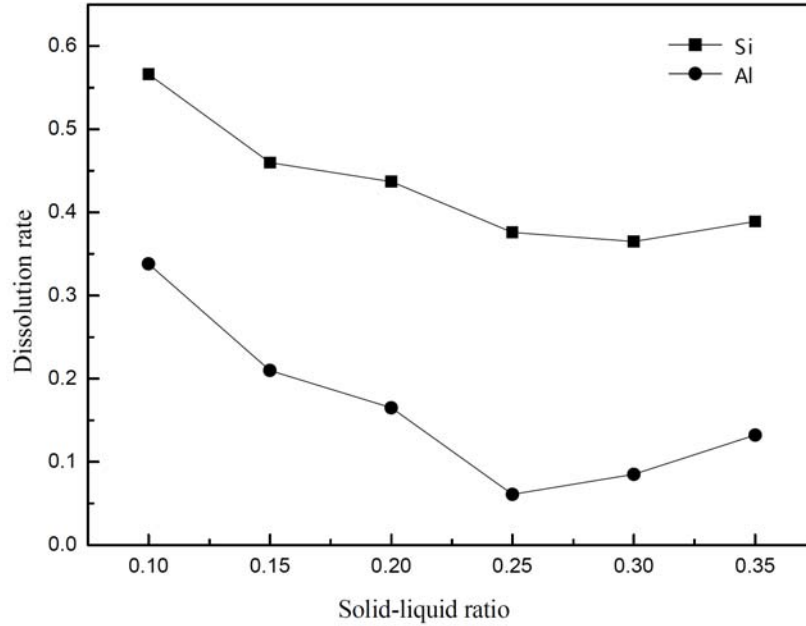
From Figure 1, the diffraction peaks of quartz and mullite are strong before calcination, which show the main minerals are quartz and mullite. Quartz and mullite are difficult to react with NaOH at room temperature due to their low activity. Therefore, calcination of fly ash and NaOH at high temperature 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  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . These substances react with NaOH, and generate amorphous aluminosilicate that is able to participate in the zeolite framework structure.



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 real mass amount of NaOH reacted is equal to the of fly ash according to the experimental result.

### **3.2. Effect of mass ratio of solid clinker to alkali solution**

Figure 2 shows that the NaOH solution can dissolve alkali melting residue, which includes  $\text{Na}_2\text{SiO}_3$  and  $\text{NaAl}(\text{OH})_4$  deriving from mullite, quartz and other silicon aluminum phases of coal fly ash. Dissolving ratios of Si and Al decrease with increasing mass ratio of solid clinker to alkali solution. The maximum dissolving ratio of Si is 56.6% while the maximum dissolving ratio of Al is 33.8% under the experimental condition. 100g water can dissolve nearly 37g  $\text{Na}_2\text{SiO}_3$ , however, 56.6% is not high.

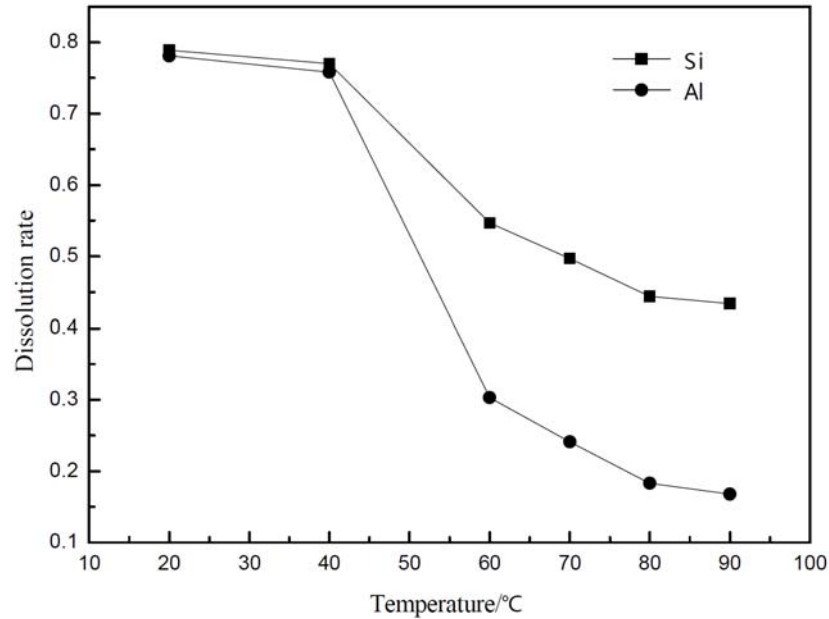


**Figure 2.** Effect of mass ratio of solid clinker to alkali solution 15% NaOH, 1h of stirring time, 60°C.

### 3.3. 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 reach 78.9% and 78.1%, respectively as the leaching temperature is 20°C. Similar research showed dissolution ratio of Si is 75% while dissolution ratio of Al is only 25% during alkali leaching from titania slag [15]. 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 led to the low dissolving ratios.



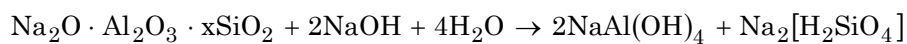


**Figure 3.** Effect of temperature on dissolving ratio of Si and Al, 15% NaOH, NaOH solution clinker mass ratio of 10:1, 1h of stirring time.

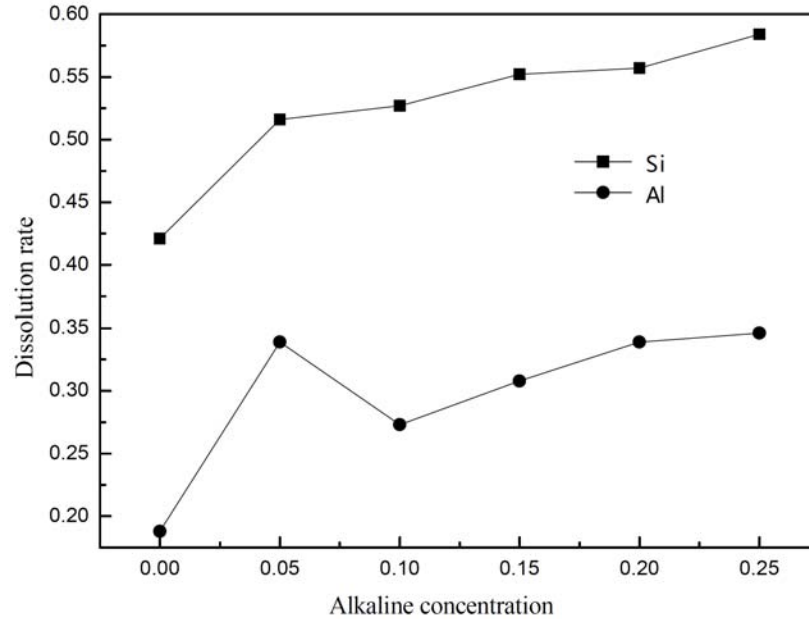
### 3.4. Effect of mass ratio of NaOH to solution on dissolving ratio of Si and Al

Figure 4 shows higher NaOH concentration is more viable in order to dissolve more Si and Al. When the alkali concentration is increased from 5% to 10%, the dissolution rate of aluminum decreases. The leaching rate fluctuated, just like the acid leaching of titanium bearing minerals, at present it is thought that the evolution of  $\text{AlO}_2^-$  causes the fluctuation because the  $\text{AlO}_2^-$  is more soluble than  $\text{Al}(\text{OH})_4^-$ , and the general trend is still rising with the increase of NaOH concentration.

The possible following reaction occurs when NaOH concentration is larger than 10%.



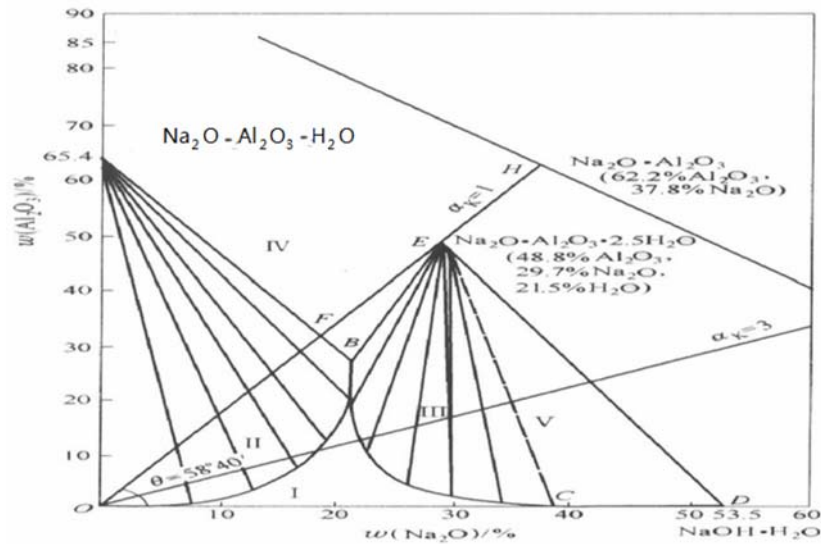
Thus, insoluble  $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x\text{SiO}_2$  in water dissolved in concentrated NaOH solution. The tendency indicates  $\text{OH}^-$  plays an important role during the process, which takes part in the coordination process. The large amount of use of NaOH causes big cost. Reusing the redundant NaOH solution is significant and economical. The condensation and the seed can enable the reuse of NaOH solution possible.



**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, 1h of stirring time.

Figure 5 shows  $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$  system phase diagram. The area of OBCO belongs to dissolving process of  $\text{Al}_2\text{O}_3$  into NaOH solution according to Figure 3. The solubility of  $\text{Al}_2\text{O}_3$  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

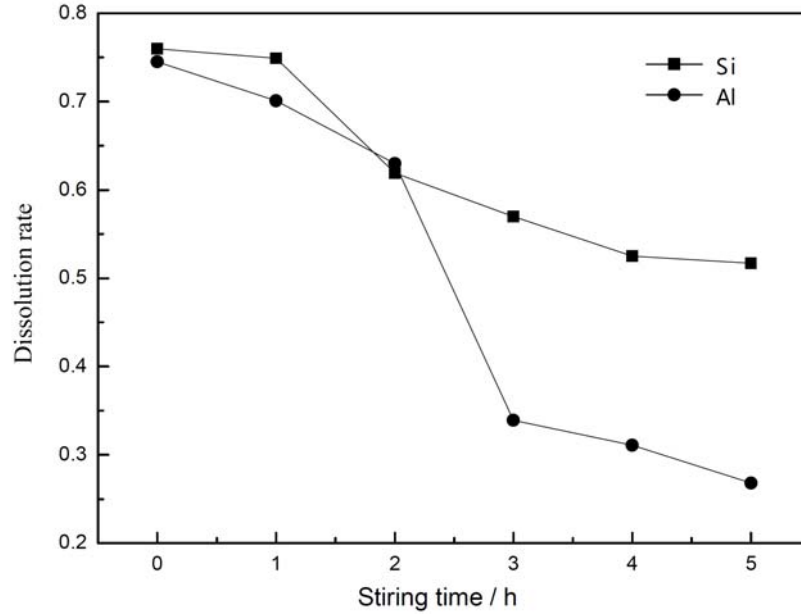
the increasing NaOH concentration [line BC]. Therefore, high efficient NaOH concentration is around 20%, the number is consistent with our experimental result in Figure 4 where 0.20 mass ratio of NaOH made highest dissolving ratio of Al. 15% NaOH is used, NaOH is surplus after the roasting process. Overall, the concentration of NaOH is around 20%.



**Figure 5.**  $\text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{H}_2\text{O}$  phase diagram.

### 3.5. Effect of stirring time on dissolving ratio of Si and Al

Figure 6 indicates too long time is disadvantageous for high dissolving ratio of Si and Al. The dissolving ratio decreases with adding stirring time. The tendency is obvious for Al. The dissolving ratio drops steeply during 2h 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. 1h is enough for the stirring time.



**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.

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 molar ratio of Si to Al in the leach solution is adjusted to 4.6, pH drops to be 9 by adding HCl solution. Then, the solution is put in a autoclave after aging for 1h, and taken out after crystallization for 16h at 100°C. The p-type molecular sieve is obtained after filtration, washing and drying. The cost of raw material and the environmental pollution were reduced because of using fly ash as raw material.



**Figure 7.** Residue of insoluble clinker after filtration.

The  $\text{Fe}_2\text{O}_3$  content of the prepared molecular sieve drops to be 0.25% after the alkali treatment from 2.87% by merely acid leaching of fly ash, while the content of  $\text{CaO}$  drops to be 0.066% from 1.18%. The chemical formula of P molecule sieve prepared is confirmed as  $\text{Na}_6\text{Al}_6\text{Si}_{10}\text{O}_{32} \cdot 12\text{H}_2\text{O}$  through ICP examination. The purity of the P molecular sieve prepared by the method from coal fly ash is 99.06% (seen in Table 2) while the whiteness level is 96 (seen in Figure 8). Both purity and whiteness level of the molecular sieve can meet the standard of market molecular sieve.

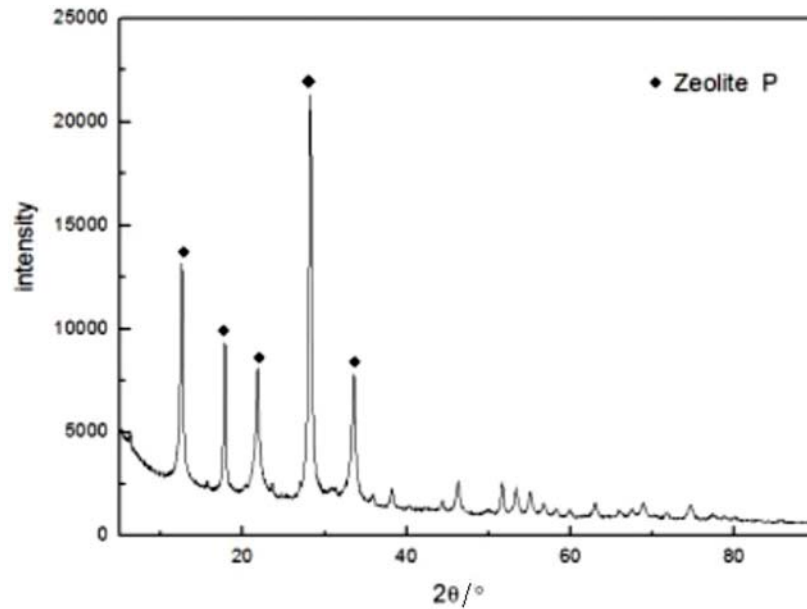
**Table 2.** Chemical composition of P molecule sieve prepared by fly ash (mass fraction, %)

Ingredient	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>
Percent (%)	58.74	25.65	14.67	0.61	0.25	0.066	0.011



**Figure 8.** P molecule sieve prepared by coal fly ash.

Figure 9 shows XRD diagram of the product, there are 5 characteristic peaks at  $2\theta = 12.48^\circ, 17.71^\circ, 21.68^\circ, 28.15^\circ,$  and  $33.37^\circ$ , respectively, and miscellaneous peaks are few, 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.



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

#### 4. 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 is 20°C, using 15% NaOH solution, the liquid solid ratio is 10:1, and the stirring time is less than 1h, the whole dissolution ratio of Silicon reaches 78.9% while that of Al reaches 78.1%. The method provides pure solution for preparing molecular sieves from fly ash. The  $\text{Fe}_2\text{O}_3$  content of the prepared molecular sieve through actual verification drops to be 0.25% after the alkali treatment from 2.87% by merely acid leaching of fly ash, while the content of CaO drops to be 0.066% from 1.18%.

### References

- [1] Meiling Wu, Research progress on modification and application of fly ash, *Guangzhou Chemical Industry* 45(8) (2017), 22-24.
- [2] Wei Lin, Guangxue Li, Anshun Wang and Peigen Wang, Research status of preparation of molecular sieves by fly ash, *Anhui Chemical Industry* 43(1) (2017), 9-14.
- [3] Zhenlei Zuo, Xingrui Wang, Huiquan Li and Jun Zhang, Synthesis and characterization 13X zeolite prepared from desilication solution of high alumina fly ash and coal gangue, *Bulletin of the Chinese Ceramic Society* 36(3) (2017), 778-784.
- [4] Tomonori Fukasawa, Akira Horigome, Takayuki Tsu, Achmad Dwitama Karisma, Norio Maeda, An-Ni Huang and Kunihiro Fukui, Utilization of incineration fly ash from biomass powder plants for zeolite synthesis from coal fly ash by hydrothermal treatment, *Fuel Processing Technology* 167 (2017), 92-98.  
DOI: <https://doi.org/10.1016/j.fuproc.2017.06.023>
- [5] Liyun Yang, Xiaoming Qian, Peng Yuan, Hao Bai, Takahiro Miki, Fanxu Men, Hong Li and Tetsuya Nagasaka, Green synthesis of zeolite 4A using fly ash fused with synergism of NaOH and Na<sub>2</sub>CO<sub>3</sub>, *Journal of Cleaner Production* 212 (2019), 250-260.  
DOI: <https://doi.org/10.1016/j.jclepro.2018.11.259>
- [6] Asifa Iqbal, Hamed Sattar, Rizwan Haider and Shahid Munir, Synthesis and characterization of pure phase zeolite 4A from coal fly ash, *Journal of Cleaner Production* 219 (2019), 258-267.  
DOI: <https://doi.org/10.1016/j.jclepro.2019.02.066>
- [7] Richa Soni and Dericks Praise Shukia, Synthesis of fly ash based zeolite-reduced graphene oxide composite and its evaluation as an adsorbent for arsenic removal, *Chemosphere* 219 (2019), 504-509.  
DOI: <https://doi.org/10.1016/j.chemosphere.2018.11.203>
- [8] A. De Rossi, L. Simao, M. J. Ribeiro, R. M. Novais, J. A. Labrincha, D. Hotza, R. F. P. M. Moreira, In-situ synthesis of zeolites by geopolymerization of biomass fly ash and metakaolin, *Materials Letters* 236 (2019), 644-648.  
DOI: <https://doi.org/10.1016/j.matlet.2018.11.016>
- [9] Nevin Koshy and D. N. Singh, Fly ash zeolites for water treatment applications, *Journal of Environmental Chemical Engineering* 4(2) (2016), 1460-1472.  
DOI: <https://doi.org/10.1016/j.jece.2016.02.002>



- [10] Wei Feng, Zhijian Wan, Jacqueline Daniels, Zhikao Li, Gongkui Xiao, Jialin Yu, Dong Xu, Hua Guo, Dongke Zhang, Eric F. May and Gang (Kevin) Li, Synthesis of high quality zeolites from coal fly ash: Mobility of hazardous elements and environmental applications, *Journal of Cleaner Production* 202 (2018), 390-400.  
DOI: <https://doi.org/10.1016/j.jclepro.2018.08.140>
- [11] Z. Tauanov, P. E. Tsakiridis, S. V. Mikhalovsky and V. J. Inglezakis, Synthetic coal fly ash-derived zeolites doped with silver nanoparticles for mercury (II) removal from water, *Journal of Environmental Management* 224 (2018), 164-171.  
DOI: <https://doi.org/10.1016/j.jenvman.2018.07.049>
- [12] Jeong Min Lim, Jaehyeong Park, Jung Tae Park and Sungjun Bae, Preparation of quasi-solid-state electrolytes using a coal fly ash derived zeolite-X and -A for dye-sensitized solar cells, *Journal of Industrial and Engineering Chemistry* 71 (2019), 378-386.  
DOI: <https://doi.org/10.1016/j.jiec.2018.11.049>
- [13] Minghua Wang, Hui Zhao, Yan Liu, Chuiyu Kong, Amin Yang and Jingyu Li, Removal of Fe from fly ash by carbon thermal reduction, *Microporous and Mesoporous Materials* 245 (2017), 133-137.  
DOI: <https://doi.org/10.1016/j.micromeso.2017.02.068>
- [14] Deshun Kong, Shuojiang Song, Qian Wang and Shilian Lin, Preparation of P-type molecular sieve from fly ash by alkali melting and hydrothermal method, *Bulletin of the Chinese Ceramic Society* 35(3) (2016), 922-926.
- [15] Lu Hui, Xie Gang, Yu Xiao-Hua, Lin Rong-Xing, Fang Ning, Yang Ni and Yao Yun, Investigation of silicon and aluminium removed mechanism by alkaline leaching from the titania slag in electric furnace, *Light Metal* 7 (2010), 53-57.

