We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,900
Open access books available

185,000
International authors and editors

200M
Downloads

Our authors are among the

154
Countries delivered to

TOP 1%
most cited scientists

12.2%
Contributors from top 500 universities



WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com



Chapter

Melting and Dissolving Fly Ash by NaOH for the Removal of Iron, Calcium, and Other Impurities

Minghua Wang, Hui Zhao, Gulambar Tursun, Jianwang Yang and Long Liu

Abstract

A 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 show the optimum experimental conditions for the dissolution: temperature is 60°C, 15% NaOH solution is used, liquid–solid mass ratio is 11:1, stirring time is 3 h, 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 Fe_2O_3 content of the prepared P-type molecular sieve is only 0.25%, and the CaO content is only 0.066%. The paper provided a viable method to remove Fe, Ca, etc. in mineral thoroughly.

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

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, and 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; and 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.

The 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] have been developed. The domestic and international research on the synthesis of molecular sieve from fly ash is more and more widely and deeply [4].

Yang Liyun et al. recently synthesized zeolite 4A using fly ash fused with synergism of NaOH and Na_2CO_3 [5]. Asifa Iqbal et al. synthesized and characterized pure phase 4A from coal fly ash [6]. Richa Soni and Dericks Praise Shukia synthesized fly ash-based zeolite-reduced graphene oxide composite and evaluated its property as an adsorbent for arsenic removal [7]. A 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 zeolite-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 not only are easy to plug in the channels of the molecular sieve but also 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 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, or alkali dissolving, of fly ash, to remove iron, calcium, and other impurities, was proposed in the paper. Firstly, fly ash and NaOH solid were mixed and 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.

2. Experimental part

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

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

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

The specific steps are as follows. A certain amount of fly ash was weighed, placed in a mortar, and fully ground before putting 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 was added to regulate the ratio of silicon and aluminum for a special molecular type. After that, the mixture was stirred evenly, transferred to an autoclave, and crystallized at a certain temperature for a certain time. The derived solid was just a 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 by Keje company in China.

3. Results and discussion

3.1 Calcination of NaOH and fly ash

SiO_2 and Al_2O_3 existing as quartz and mullite in fly ash have low activity; high-temperature alkali roasting method can greatly increase their activity and improve the efficiency of the fly ash conversion and crystallization synthesis of the molecular sieve. There are commonly two ways to calcine fly ash, one is to add Na_2CO_3 to calcine at 800°C, and the other is to add NaOH to calcine at 600°C. In the experiment, fly ash and NaOH reacted after roasted in a muffle furnace at 600°C for 2 h. **Figure 1** is the contrast diagram of 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 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 releasing 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.

$$3Al_2O_3 \cdot 2SiO_2 + NaOH \rightarrow NaAlO_2 + Na_2SiO_3 + H_2O \quad (1)$$

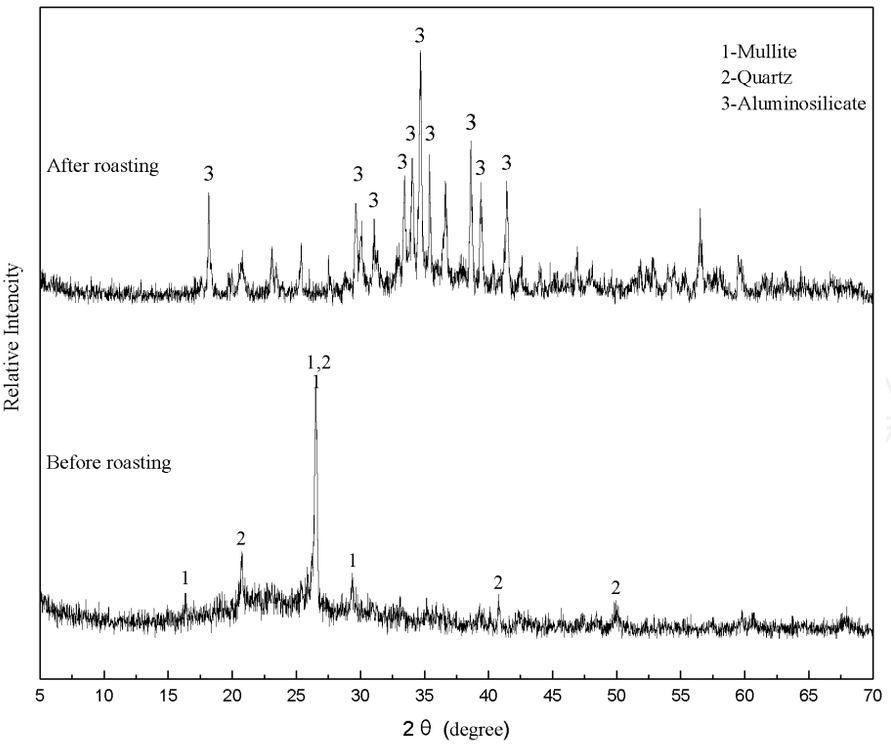


Figure 1.
Effect of alkali melting activation on fly ash structure.

$$SiO_2[\text{quartz}] \rightarrow SiO_2[\text{glass}] \quad (2)$$

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 a 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 Na_2SiO_3 and $NaAl(OH)_4$ derived 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. 100 g of water can dissolve nearly 37 g Na_2SiO_3; however, 56.6% is not high.

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.

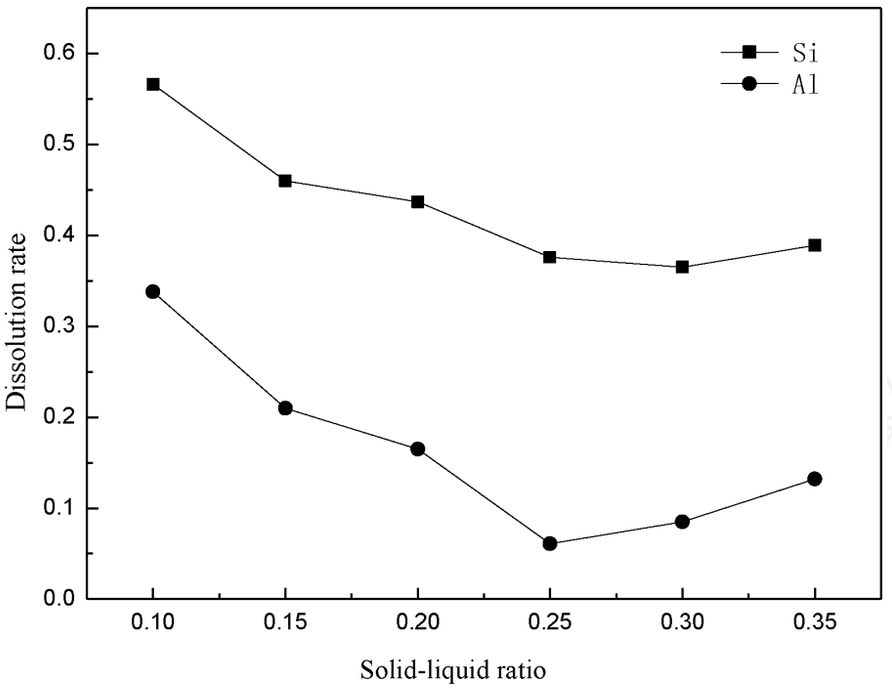


Figure 2.
Effect of mass ratio of solid clinker to alkali solution 15% NaOH, 1 h of stirring time, 60°C.

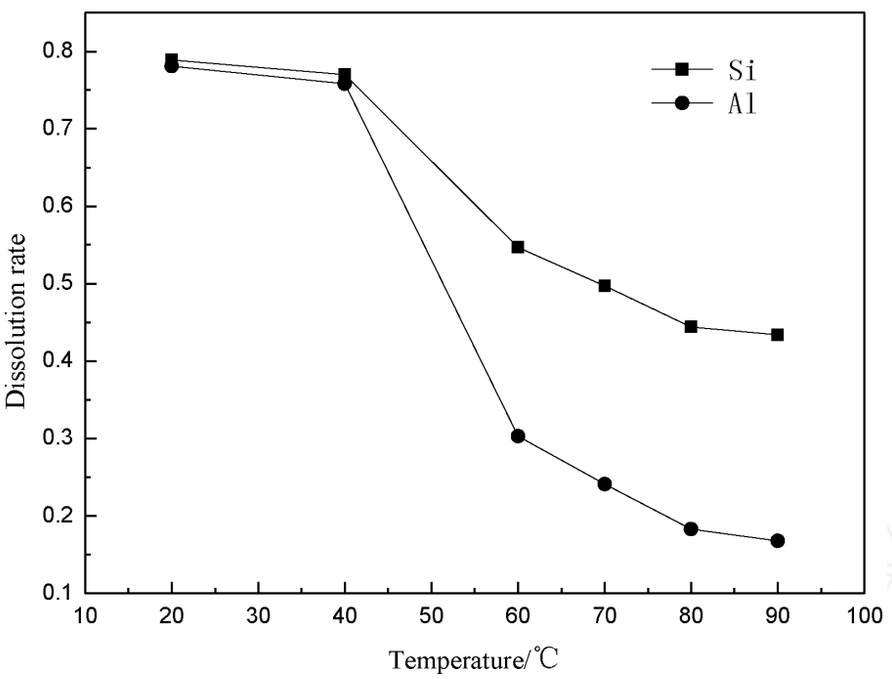


Figure 3.
Effect of temperature on dissolving ratio of Si and Al 15% NaOH, NaOH solution clinker mass ratio of 10:1, 1 h of stirring time.

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 AlO_2^- causes the fluctuation because the AlO_2^- is more soluble than $Al(OH)_4^-$, and the general trend is still rising with the increase of NaOH concentration.

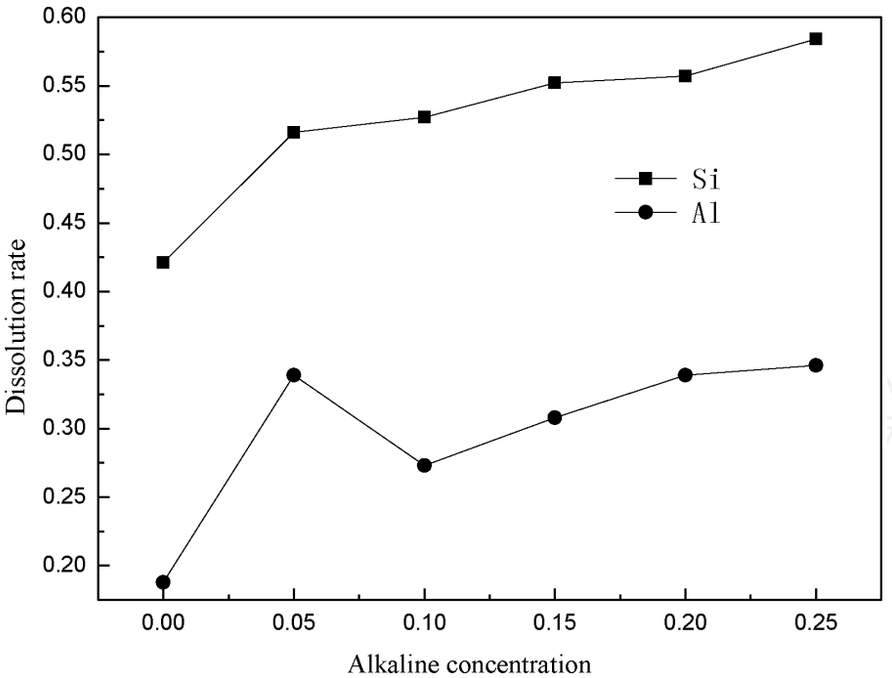


Figure 4.
Effect of mass ratio of NaOH to solution on dissolving ratio of Si and Al 60°C, NaOH solution to clinker mass ratio of 10:1, 1 h of stirring time.

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

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

Thus, insoluble $Na_2O \cdot Al_2O_3 \cdot xSiO_2$ in water dissolved in concentrated NaOH solution. The tendency indicates 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 make the reuse of NaOH solution possible.

Figure 5 shows Na_2O-Al_2O_3-H_2O system phase diagram [16]. The area of OBCO belongs to the dissolving process of Al_2O_3 into the 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, a highly 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 the highest dissolving ratio of Al. 15% NaOH is used, and NaOH is surplus after the roasting process. Overall, the concentration of NaOH is around 20%.

3.5 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 decreases with adding stirring time. The tendency is obvious for Al. The dissolving ratio drops steeply during 2 h or so. The gradual decreasing tendency is due to the 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

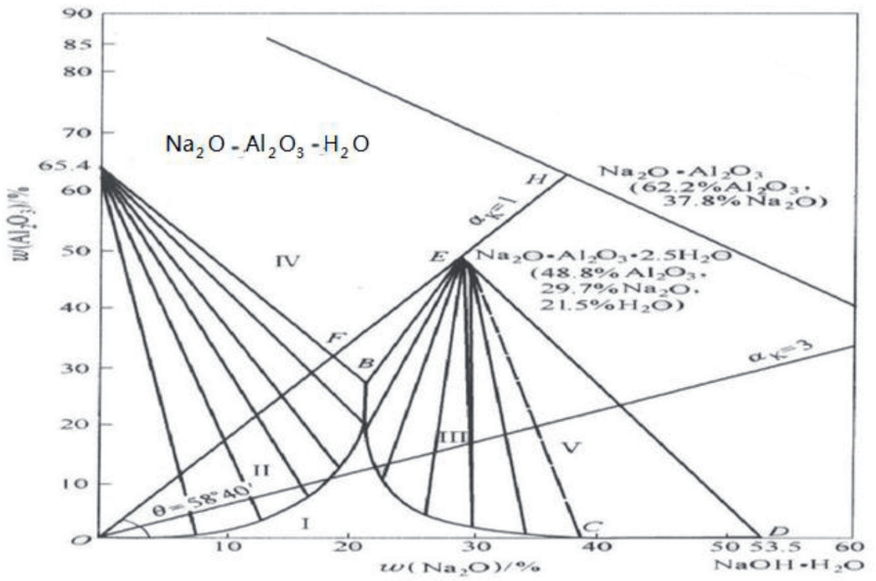


Figure 5.
Na_2O-Al_2O_3-H_2O phase diagram.

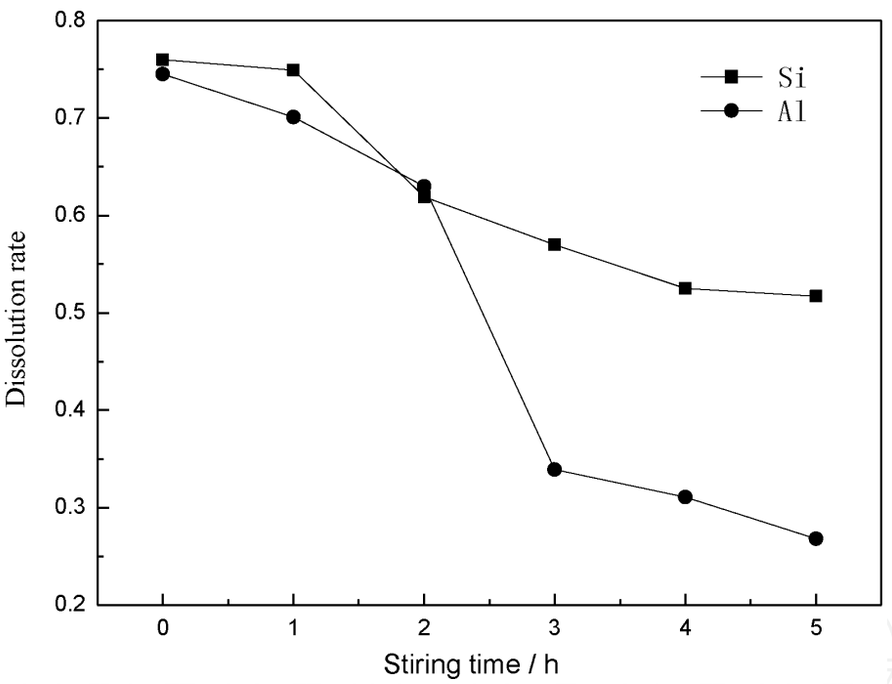


Figure 6.
Effect of stirring time on dissolving ratios of Si and Al 60°C, NaOH solution to clinker mass ratio of 10:1.

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 9 by adding HCl solution. Then, the solution is put in an autoclave after aging for 1 h and taken out after crystallization for 16 h 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.

The Fe_2O_3 content of the prepared molecular sieve drops to 0.25% after the alkali treatment from 2.87% by merely acid leaching of fly ash, while the content of CaO drops to 0.066% from 1.18%. The chemical formula of the P molecular sieve prepared is confirmed as $Na_6Al_6Si_{10}O_{32}{\cdot}12H_2O$ through ICP examination. The purity of the P molecular sieve prepared by the method from coal fly ash



Figure 7.
Residue of insoluble clinker after filtration.

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

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

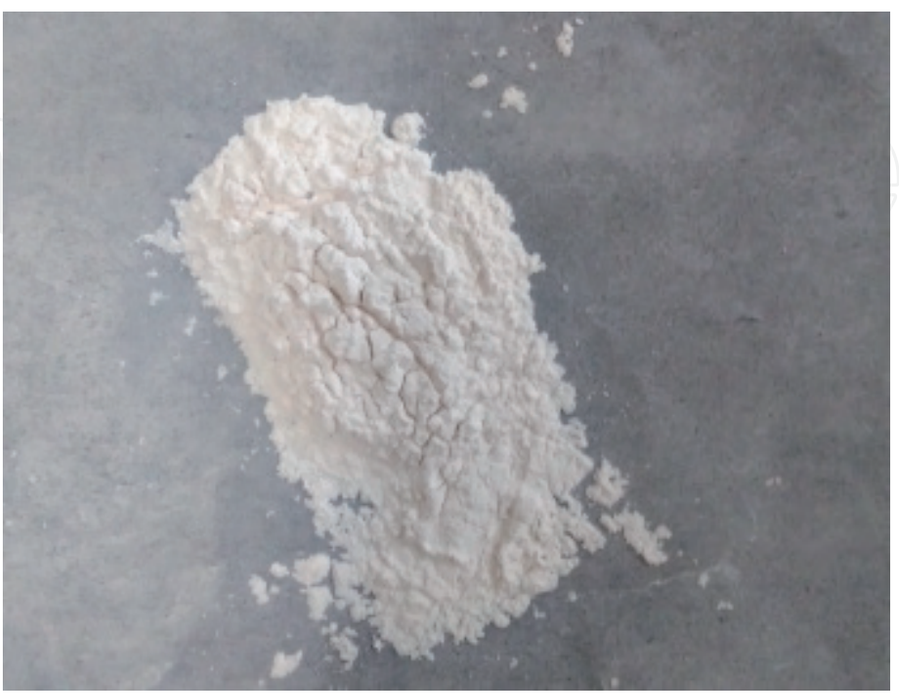


Figure 8.
P molecular sieve prepared by coal fly ash.

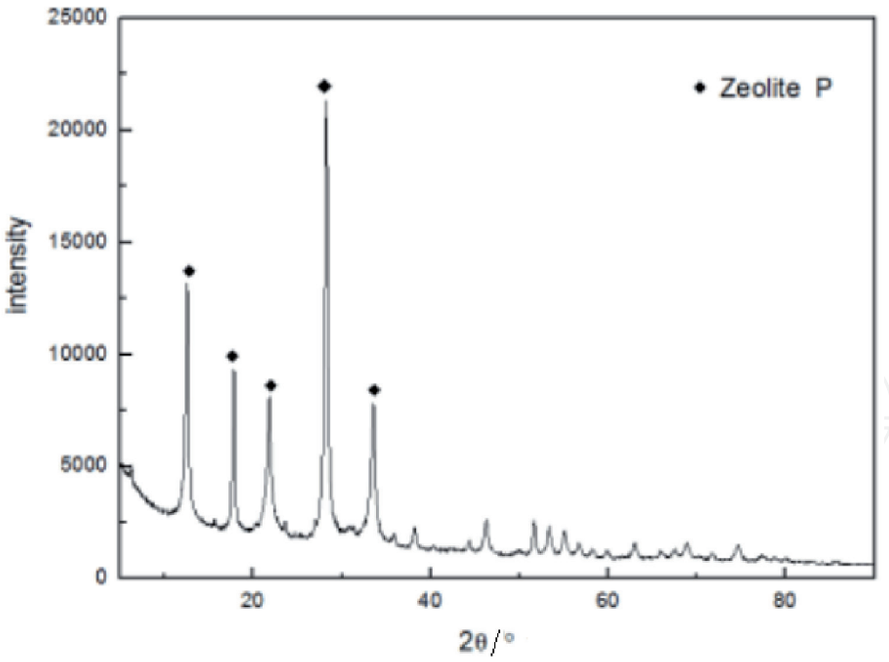


Figure 9.
XRD diagram of P molecular sieve prepared by coal fly ash.

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.

Figure 9 shows XRD diagram of the product; there are five characteristic peaks at 2θ = 12.48°, 17.71°, 21.68°, 28.15°, and 33.37°, respectively, and miscellaneous peaks are few, indicating the product is P molecular sieve (*JCPDS* NO 39-0219). Pure P molecular sieve can be used as petroleum catalyst, support, and detergent additive to soften hard water in washing process.

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 1 h; 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 Fe_2O_3 content of the prepared molecular sieve through actual verification drops to 0.25% after the alkali treatment from 2.87% by merely acid leaching of fly ash, while the content of CaO drops to 0.066% from 1.18%.

IntechOpen

IntechOpen

Author details

Minghua Wang*, Hui Zhao, Gulambar Tursun, Jianwang Yang and Long Liu
School of Metallurgy, Northeastern University, Shenyang, China

*Address all correspondence to: wangmh@smm.neu.edu.cn

IntechOpen

© 2020 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/by/3.0), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. CC BY

References

[1] Wu M. Research progress on modification and application of fly ash. Guangzhou Chemical Industry. 2017;**45**(8):22-24

[2] Lin W, Li G, Wang A, Wang P. Research status of preparation of molecular sieves by fly ash. Anhui Chemical Industry. 2017;**43**(1):9-14

[3] Yan Z, Wang X, Li H, Zhang J. Synthesis and characterization 13X zeolite prepared from desilication solution of high alumina fly ash and coal gangue. Bulletin of Chinese Ceramic Society. 2016;**36**(3):778-784

[4] Fukasawa T, Horigome A, Tsu T, et al. Utilization of incineration fly ash from biomass powder plants for zeolite synthesis from coal fly ash by hydrothermal treatment. Fuel Processing Technology. 2017;**167**:92-98

[5] Yang L, Qian X, Yuan P, Bao B, et al. Green synthesis of zeolite 4A using fly ash fused with synergism of NaOH and Na_2CO_3. Journal of Cleaner Production. 2019;**212**:250-260

[6] Iqbal A, Scattar H, Haider R, et al. Synthesis and characterization of pure phase zeolite 4A from coal fly ash. Journal of Cleaner Production. 2019;**219**:258-267

[7] Soni R, Shukia DP. Synthesis of fly ash based zeolite-reduced graphene oxide composite and its evaluation as an adsorbent for arsenic removal. Journal of Cleaner Production. 2019;**219**:504-509

[8] De Rossi A, Simao L, Ribeiro MJ, et al. In-situ synthesis of zeolites by geopolymerization of biomass fly ash and metakaolin. Materials Letters. 2019;**236**:644-648

[9] Koshy N, Singh DN. Fly ash zeolites for water treatment applications. Journal of Environmental Chemical Engineering. 2016;**4**(2):1460-1472

[10] Feng W, Wan Z, Daniels J, et al. Synthesis of high quality zeolites from coal fly ash: Mobility of hazardous elements and environmental applications. Journal of Cleaner Production. 2018;**202**:390-400

[11] Tauanov Z, Tsakiridis PE, Mikhaiosky SV, et al. Synthesized coal fly ash-derived zeolites doped with silver nanoparticles for mercury (II) removal from water. Journal of Environmental Management. 2018;**224**:164-171

[12] Lim J, M, Park JY, Park JT, et al. Prepared 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. 2019;**71**:378-386

[13] Wang M, Zhao H, Liu Y, Kong C, Yang A, Li J. Removal of Fe from fly ash by carbon thermal reduction. Microporous & Mesoporous Materials. 2017;**245**:133-137

[14] Kong D, Song S, Wang Q, Lin S. Preparation of P-type molecular sieve from fly ash by alkali melting and hydrothermal method. Bulletin of Chinese Ceramic Society. 2016;**35**(3):922-926

[15] Lu H, Xie G, Yu X-H, et al. Investigation of silicon and aluminium removed mechanism by alkaline leaching from the titania slag in electric furnace. Light Metal. 2010;**7**:53-57

[16] Bi S. Production of Alumina by Bayer Process. Beijing: Metallurgical Industry Press; 2007. p. 7