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HYDROTHERMAL SYNTHESIS OF ZEOLITE FROM FLY ASH OF MONGOLIAN COAL

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Have performed experiments for synthesis of pure-form zeolite from fly ash of thermal power station with an additional source of aluminum. Initial fly ash was treated by NaOH solution to dissolve silicon oxide and was added of Al source, to prepare initial gel. Experimental results showed that NaOH concentration and reaction time played an important role in extraction silicon oxide from fly ash. For the extraction of silicon oxide were used following conditions: NaOH with 1.0, 3.0, 5.0, and 7.0 M concentrations; temperature, 80°C; the corresponding dissolving time, 120, 240,360, 480 and 600 min. As aluminum source was used metal Al and dissolved 3M NaOH solution. The hydrothermal syntheses have done in the Teflon lined autoclave at 100°C for 240 minute.
Keywords*:* zeolite, fly ash, synthesis zeolite, autoclave, gel.

I. Introduction

Coal is the most abundant source of energy in Mongolia. About 90% of the electricity generated in Mongolia largely from coal-fired power stations. Three thermal power plants are located in Ulaanbaatar and largest one is 4th thermal power station use coal from Baganuur deposits. Currently, more than 300.000 tons of fly ash is being generated annually in this power station. This ash is disposed of by landfill, which becomes increasingly concern about environmental pollution. The chemical com-

position of fly ash indicates it belongs to class C fly ashes and with a high amount of calcium oxide and lower aluminum oxide.

Fly ashes can be converted into zeolites due to their high contents of silicon and aluminum, which are the structural elements of zeolites [1][2][3].

Zeolites are crystalline hydrated aluminosilicates with a framework structure. The framework of zeolites consists of three dimensional networks of SiO_4 and AlO_4 tetrahedra linked to each other via sharing oxygen atoms. This framework contains voids and channels occupied by water molecules and cations to balance the charge of whole framework. Cations in the structure are mobile and may be exchanged by other cations. Zeolites can be naturally occurring or synthetically obtained [4]. Synthetic zeolites are mostly crystallized from amorphous alkali aluminosilicate gels under hydrothermal conditions. Syntheses of zeolites have become important in industry applications and have large volume markets as a detergent builder, petrochemical processing catalysts and a variety of uses as adsorbents.

The aim of this work is to determine possibilities of a pure zeolite preparation from a gel that obtained from coal fly ash as a source of silicon oxide with addition of sodium aluminate with two stages at hydrothermal condition.

II. Material and Methods

2.1. *Raw fly ash*

Raw fly ash was obtained from the Mongolian 4th thermal power plant located in Ulaanbaatar city which used electrostatic precipitators. The chemical composition of raw fly ash was determined by x-ray fluorescence (XRF) and is listed in Table 1. The particle size was determined using a laser diffraction particle size analyzer; the specific surface area was measured by a BET analyzer and are listed in Table 2.

Table 1

Chemical composition of raw fly ash, amorphous and crystal phases (inweight %)

Component	SiO_2	Al_2O_3	Fe_2O_3	CaO	K_2O	TiO_2
%	55.20	14.15	10.55	15.00	1.31	0.25
Crystalline phase(%)	24,05	5,08	3,67	0,84	0,57	0,00
Amorphous	31,15	9,07	6,88	14,16	0,74	0,25

phase(%)						
%	**MgO**	**Na_2O**	**P_2O_5**	**SrO**	**BaO**	**LOI**
Crystalline phase(%)	1.56	0.001	0.004	0.25	0.001	1.71
Amorphous phase(%)	0,00	0,00	0,00	0,00	0,00	0,00

Amorphous part of the fly ash was determined in order to evaluate the content of silicon oxide ready dissolvable in the NaOH solution.

Table 2

BET specific surface area and specific pore volume of fly ashes sample

Sample	BET /Specific surface area/ m^2/g	Pore volume/ ml/g ($x10^{-4}$)	Particle size distribution, Median diameter, $d_{50}$by laser analyzer/μm
Baganuur fly ash	2.75	2.12	27.91

The XRD pattern of fly ash is presented in Fig.1. As noted from the X-ray diffraction pattern, the major crystalline phases are quartz (SiO_2) and small amounts of microcline.

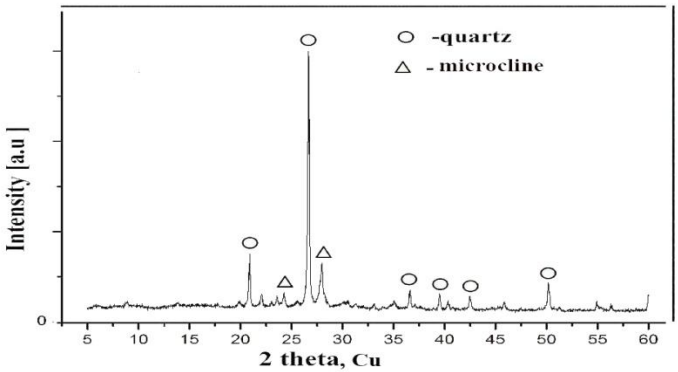

Fig. 1. XRD pattern of the raw fly ash.

2.2. *Two-step synthesis of pure zeolite from coal fly ash*

Preparation of zeolite involves three stages:

1. Fly ash was treated in alkaline solution to obtain silica source.

2. The aluminum solution was prepared from metal Al in alkaline solution

3. The zeolite was synthesized from the silica and aluminum sources in the hydrothermal conditions

6 g of fly ash was mixed with 60 ml of NaOH solutions in a Teflon vessel. Four different NaOH concentrations (1, 3, 5 and 7M) were used. The Teflon vessel was placed in magnetic stirrer and heated at 80°C for 2 hours with stirring constantly (300 rpm). The solution was separated from the mixture by a filtration process. The silicon concentration in the filtrate was measured by gravimetric method and Al_2O_3, CaO, Fe_2O_3 was determination by EDTA complexometric methods. The effect leaching time on silicon oxide dissolution was determined with the following procedure: 6 g fly ash was mixing with 60 ml 3M NaOH solutions in a Teflon vessel and placed in magnetic stirrer and heated at 80°C for 120, 240, 360, 480 and 600 min with constant stirring at 300 rpm. NaOH–$NaAlO_2$ solution was prepared by mixing metal Al of 0.5gr and 20 ml of 3M NaOH solution.

Zeolite synthesis reactions were carried out in 100 mL hydrothermal reaction vessel lined with Teflon at 100°C for 240 min.

III. Results and Discussion

3.1. *Effect of NaOH concentration from fly ash extraction silicon oxide*

The silicon oxide concentration in the filtrate was measured by gravimetric method in represented Fig.2.

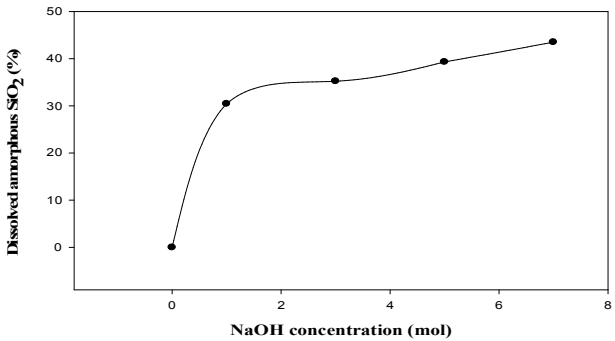

Fig. 2. Effect of NaOH concentration on extraction of silicon oxide from fly ash

The concentration of alkaline solution was changed from 1M to 7M. The silicon oxide concentration in the filtrate was increased with addition of alkaline concentration. The greatest dissolution of amorphous silicon oxide was observed in 7M NaOH (43.5%). But the further experiments revealed that 7 M NaOH is not suitable for the zeolite synthesis because of re-dissolution of the synthesized zeolite. By the trial error method established that 3 M NaOH is more suitable for the zeolite synthesis. Therefore, for amorphous silicon oxide dissolution was chosen the NaOH solution with 3 M concentration, though, the highest dissolution was observed for the 7 M NaOH solution.

3.2. *Effect of leaching time on silicon oxide extraction from fly ash*

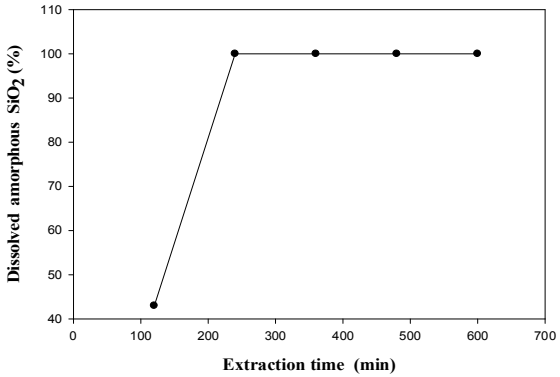

Fig. 3. Effect of leaching time on extraction amorphous silicon oxide

Dissolution time was up to 240 min to completely dissolve amorphous silicon oxide in 3 M NaOH. Further increase of dissolution time was caused dissolution of the crystalline quartz from the fly ash which is undesirable in terms of economical suitability. Therefore for amorphous silicon oxide extraction from fly ash is sufficient to leach for 240 min.

3.3. *Zeolite synthesis*

Fly ash (6 g) was mixed with a 3M 60 mL sodium hydroxide solution in Teflon vessel and placed in magnetic stirrer with heated at 80°C for time 240 min with constant stirring at 300 rpm. The solution was separated from the mixture by filtration process and the volume obtained in the solution was adjusted to about 60 ml. Prepared NaOH–$NaAlO_2$ solution was poured into the silicate solution obtained at first stage to form

initial gel. For the zeolite A synthesis SiO_2/Al_2O_3 ratio in the mixed sources was controlled and kept at 2.4. About 80 ml of obtained initial gel was stirred intensely at 25°C for 30 min. Zeolite synthesis reactions were carried out in 100 mL hydrothermal bomb lined with teflon, placed in electric oven heated at 100^0C for 240 min. The reaction solution was subsequently filtered and the residue dried and analyzed by XRD.

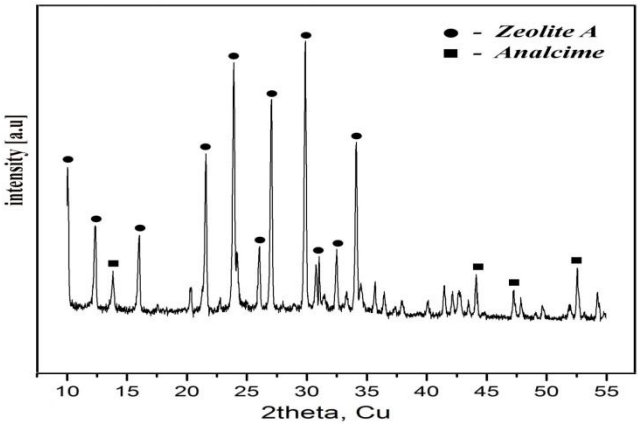

Fig.4. XRD pattern of zeolite sample synthesized from fly ash

Fig. 4 indicates that main crystalline phases of synthesis zeoilte are the Zeolite A ($Na_{96}(H_2O)_{216}$| [$Si_{96}Al_{96}O_{384}$)and analcime. Nowadays, one of the massive usages of zeolite A is in detergent industries as an environmental friendly material to substitute phosphates builders. This synthetic zeolite is also applicable for wastewater treatment plant [5].

IV. Conclusion

The effects of NaOH concentration and leaching time on extraction of amorphous silicon oxide from fly ash have been studied. Results indicated that the amount of dissolved amorphous silicon oxide was increasing while the concentration of NaOH is increased. Mixture containing silicate source from the fly ash with addition of predetermined amount of aluminum source can be used as the source gel for the zeolite synthesis. Hydrothermal synthesis of zeolite A occurs at 100°C for 240 min. We revealed that a simple way of relatively pure zeolite A synthesis is two-step hydrothermal alkaline treatment of fly ash.

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ГИДРОТЕРМИЧЕСКИЙ СИНТЕЗ ЦЕОЛИТА ИЗ ЛЕТУЧИХ ЗОЛЕЙ МОНГОЛЬСКОГО УГЛЯ

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Проведены исследования по получению синтетического цеолита из летучих зол, выходящего от фильтра электростанции и дополнительным источником алюмений. Летучый золь был подвергнут двухстадийной щелочной гидротериальной обработке. К летучему золю добавили концентрированный раствор NaOH. Под действием концентрированного раствор NaOH растворили и выделили оксид кремния, к нему добавили источники алюминия. Таким образом получен первичный гель, который далее подверг-

ся гидротермальному синтезу и был превращен в чистый цеолит А. Результаты исследований показали, что для растворения оксида кремния, очень важную роль играет концентрация NaOH и время проведения реакций. Для получения оксида кремния намиприменены раствор 1; 3;5; 7М NaOH, а реакция проведена при температуре 80^0C, интервалы времен проведеня реакций были 120, 240, 360, 480 и 600 минут. В качестве источника алюминия были использованы металл Al , который обработан 3М раствором NaOH. Гидротермальный синтез проведен в автоклаве из тефлона при температуре 100^0C в течение 240 минут.

Ключевые слова: летучый золь от электрофильтра, синтетический цеолит, гель, автоклав.