Research on obtaining zeolite from the ash of Erdenet thermal power station

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ABSTRACT
This research work completed the study of obtaining zeolite by hydrothermal method using the ash of Erdenet Thermal Power Plant. According to the results of the study, the ratio of macroelements of ash in the ash pond of Erdenet Thermal Power Plant is less than 1, so it belongs to acid ash. Also, based on the content of oxides, it was determined that the ash of Erdenet Thermal Power Plant is a siliceous type of ash due to the high content of silicon and aluminum oxides, and the low content of iron and calcium oxides. According to the results of the XRD analysis of natural zeolite, it contains $Ca(Si_7Al_2)O_{18}6 \cdot H_2O$-86.94% and SiO_2-13.06%. However, based on the results of XRD analysis of zeolite subjected to heat treatment, $Ca(Si_7Al_2)O_{18}6 \cdot H_2O$ - 47.3%, SiO_2-27.48%, $Al_2Si_2O_8$- 20.64% were formed. Depending on the results of the XRD analysis of the synthesized zeolite, Sodalite ($Na_4Cl(Al_3Si_3O_{12})$-83.72% at 200°C. Optimal reaction conditions for extracting zeolite from ash by hydrothermal method Ash: NaOH ratio 1:6, reaction temperature 80℃, stirring speed 200 rpm, reaction time 3 hours, hydrothermal temperature 200℃, time 4 hours, zeolite yield 83.72% $Na_4Cl(Al_3Si_3O_{12})$ was determined.

Keywords: *Zeolite, Sodium Hydroxide, Radiation, Hydrothermal*

1. INTRODUCTION

In Mongolia, the central regional system consists of II, III,IV stations of Ulaanbaatar city, Darkhan thermal power plant, and Erdenet thermal power plant. The ash composition from these stations varies.

It is considered suitable to extract zeolite from the ash of Erdenet Thermal Power Plant due to the high aluminium and silicon oxide content. We chose this topic because research on extracting zeolites from Erdenet Thermal Power Plant has not yet been conducted in Mongolia.

Since 1987, Erdenet Thermal Power Plant has been operating and producing electricity and heat for 35 years, continuously and reliably providing heat and electricity to the people of Erdenet. Erdenet Thermal Power Plant has 7 furnaces and 3 turbines and is capable of producing 302.5 Giga calories of thermal energy per hour. It produces 154.6 million KWh of electricity and distributes 123.3 million KWh of electricity annually [1, 2]. It is considered appropriate to extract zeolite from the ash of the Erdenet Thermal Power Plant because it has a high content of aluminium and silicon oxide.

There are 4 common ways to synthesize zeolite from ash. From these 4 methods [6, 12], we selected the first or direct synthetic extraction method and completed our experiments and research. This is because we got acquainted with the methodology of similar research projects conducted abroad and domestically, and chose a method that is economical and consumes fewer reagents.

2. RESEARCH METHODOLOGY

2.1. Research Methodology

In this research, we have determined the radioactivity and phase analysis of the ash of Erdenet Thermal Power Plant by XRD method, and the mineral chemical composition by XRF method, respectively. Also, the phase, mineral, and chemical composition of zeolite

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extracted from the ashes of ash ponds by hydrothermal method, zeolite modified by heat treatment of natural zeolite, and zeolite synthesized from pure oxides were determined by XRF and XRD instrumental analysis methods.

The test conditions for zeolite extraction were set including hydrothermal time, temperature, and the reaction time varying among 3, 4, and 5 hours and the temperature was varying among 100ºC, 150ºC, and 200ºC.

There was taken ash and NaOH in a ratio of 1:6 and it was stirred with a magnetic stirrer for 3 hours at T=80℃, 200 rpm [9, 11]. After that, leave it cool for 10 minutes, keep it in a hydrothermal at a certain temperature (100, 150, 200℃) and for a fixed time (3, 4, 5 hours), then cool it again for 1 hour and 30 minutes, filter it with a vacuum filter, and dry it in a drying oven at 105℃ for 1 hour.

2.2. Analytical Methodology

X-ray Diffraction Analysis (XRD)

We performed the structural and phase analysis of the powder crystal sample with an X-ray diffractometer instrument (MAXima XRD-7000) of the Institute of Physical Technology of the Mongolian Academy of Sciences.

X-ray Fluorescence Analysis (XRF)

The X-ray fluorescence method is widely used in the determination of the quality and quantity of elements with a number greater than the 11th (sodium) element of the periodic table [4,10,13]. The mineral chemical composition was determined by an X-ray fluorescence analyzer brand EDX-720.

Radioactivity Analysis

The radioactivity analysis of ash was measured in the accredited laboratory of the "Nuclear Physics Research Center" of the National University of Mongolia.

According to the MNS: 5072:2001 standard, followed in Mongolia, the radiation indicators for building and road materials are shown in Table 1[5].

3. RESULTS

3.1. Ash Radiation Analysis Results

Table 1. shows the results of the radiation analysis of fly ash and slag from the ash pond. The radiation index of ash is not constant at the same level. It largely depends on the coal layer and the characteristics of the deposit [6, 8]. The radium equivalent activity of ash or slag in the ash pond is 363 Bq/kg, which meets the requirements of the "residential and social buildings under construction" category and radium equivalent activity must be below 370 Bq/kg [5].

3.2. Result of XRD Analysis of Ash

Fig. 1 shows the results of the phase composition analysis of the ash from ash pond of Erdenet Thermal Power Plant.

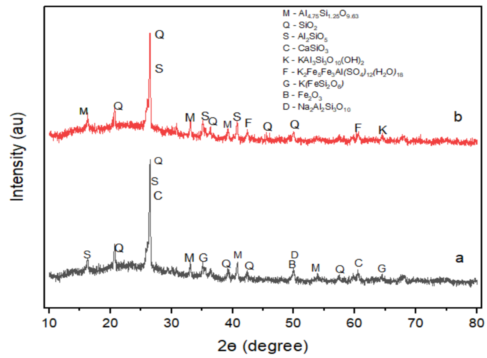

Figure 1 Results of XRD analysis of ash from the ash pond a-current ash pond, b-disused ash pond

Table 2. shows the ash chemical composition from the current ash pond and disused ash pond.

According to the results of the XRD analysis of the ash pond, the currently used ash pond contains quartz (SiO_2) 29.51%, andalusite (Al_2SiO_5) 38.54%, mullite ($Al_{5.65}Si_{0.35}O_{9.175}$) 8.82%, hematite ($Fe_2O_3$) 10.15%, wollastonite ($CaSiO_3$) 4.22%, natrolite ($Na_2(Al_2Si_3O_{10})$) 3.77%, and leucite ($K(K(FeSi_2O_6)$) 5.01%.

But the ash of the disused ash pond mainly contains quartz (SiO_2) 40.45%, aluminum silicate (Al_2SiO_5) 23.76%, mullite ($Al_{5.65}Si_{0.35}O_{9.175}$) 28.83%, voltaite ($K_2Fe_5Fe_3Al\ (SO_4)_{12}(H_2O)_{18}$) 4.75%. , and muscovite ($Kal_3O_{10}(OH)_2$) is present with 2.22%.

3.3. Results of XRF Analysis of Ash

The results of the qualitative and quantitative analysis of the chemical composition of the ash samples from the current ash pond and disused ash pond of Erdenet Thermal Power Plant are summarized in Fig. 2,3 and Table 3.

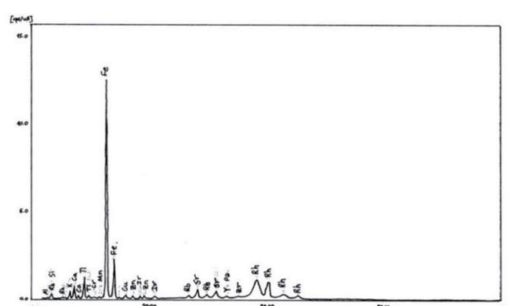

Figure 2 X-ray fluorescence spectra of the ashes of the currently used ash pond

Table 1. Ash radiation analysis results

№	Sample Name	The activity of isotopes, Bq/kg				Element content			The equivalent activity of radium, Bq/kg
		^{226}Ra	^{232}Th	^{40}K	^{137}Cs	U, г/тн	Th, г/тн	K, %	
2	Ash pond	206	73	747	<1.1	16.9	18.0	2.5	363
	The lower limit of detection (with a volume of 0.7 L, when measuring for 1 hour)	1.2	1.3	29.4	1.1	0.1	0.3	0.1	-

Table 2. Mineral composition of ash

№	Chemical formula	Current ash pond		Disused ash pond	
		Nomenclature	Mass percent, %	Nomenclature	Mass percent, %
1	SiO_2	Quartz	29.51	Quartz	40.45
2	Al_2SiO_5	Andalusite	38.54	Andalusite	23.76
3	$Al_{5.65}\,Si_{0.35}\,O_{9.175}$	Mullite	8.82	-	-
4	$Al_{4.75}\,Si_{1.25}\,O_{9.63}$	-	-	Mullite	28.83
5	$CaSiO_3$	wollastonite	4.22	-	-
6	$Na_2(Al_2Si_3O_{10})$	Natrolite	3.77	-	-
7	Fe_2O_3	Hematite	10.15	-	-
8	$K(FeSi_2O_6)$	Leucite	5.01	-	-
9	$K_2Fe_5Fe_3Al(SO_4)_{12}(H_2O)_{18}$	-	-	Voltaite	4.75
10	$Kal_3Si_3O_{10}(OH)_2$	-	-	Muscovite	2.22

Table 3. Chemical composition of ash

Elements	**SiO_2**	**Al_2O_3**	**Fe_2O_3**	K_2O	**CaO**	TiO_2	SO_3	V_2O_5
Ash from current ash pond , (%)	**58.71**	**28.48**	**5.84**	2.55	**2.311**	1.532	0.230	0.095
Ash from disused ash pond, (%)	**51.25**	**36.63**	**5.791**	1.98	**2.511**	1.397	0.184	0.089

Table 4. Natural zeolite mineral composition subjected to heat at 500,600,700℃ for 2 hours

№	Chemical formula	Chemical name	Heat at 500°C	Heat at 600°C	Heat at 700°C
			Mass percentage, %	Mass percentage, %	Mass percentage, %
1	SiO_2	Quartz	19.89	19.38	27.48
2	$CaO_{6.4}Al_{16}Si_{56}O_{142.2}O_{4.6}H_{8.24}$	Stellerite	8.48	-	-
3	$Na_{4.12}Si_{36}O_{72}(H_2O)_{23.12}$	Clinoptilolite	33.32	47.3	40.98

Table 5. Mineral composition of zeolite synthesized at temperatures of 100,150 and 200°C

№	Chemical formula	Chemical Name	Heat at 100°C	Heat at 150°C	Heat at 200°C
			Mass percentage, %	Mass percentage, %	Mass percentage, %
1	SiO_2	Quartz	17.54	-	-
2	$Al_2Si_2O_8$	Andalusite	18.09	-	-
3	$Na_4Cl(Al_3Si_3O_{12})$	Sodalite	20.81	35.57	83.72
4	$Ca_{3.2}(H_{0.6}Si_2O_7)(OH)$	Killalite	17.06	-	-
5	$Na_8Al_6Si_6O_{24}(SO_4)\cdot 2H_2O$	Vishnevit	-	11.32	-

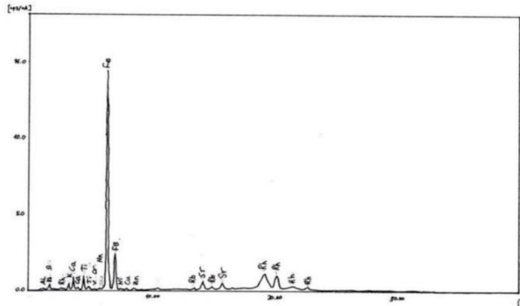

Figure 3 X-ray fluorescence spectra of ash from di sused ash pond

According to the results of the qualitative analysis of the chemical composition of the ashes, spectra of elements such as Si, Fe, Al, K, Ti, Ca, Mn, Zr, Mg, and Sr were formed.

According to the results of the quantitative analysis of the chemical composition of the ash from the current ash pond, the major oxides are SiO_2+Al_2O_3+Fe_2O_3 (58.714%+28.478%+5.844%), while a small amount of CaO+K_2O+TiO_2 oxides (2.311%+ 2.547%+1.532%) are formed. But in the ash from the disused ash pond, SiO_2+Al_2O_3+Fe_2O oxides were formed and the percentage of them is 51.253%+36.628%+5.791%, and in addition, small amounts of CaO+K_2O+TiO_2 were formed and the percentage of them are 2.511%+1.976% +1.397% respectively.

3.4. Experimental Result of Zeolite Obtaining

In this chapter, we include results for natural zeolites and hydrothermally obtained zeolites.

3.4.1. Results of XRD Analysis of Natural Zeolite

The results of the XRD analysis of natural zeolite are shown in Fig. 4.

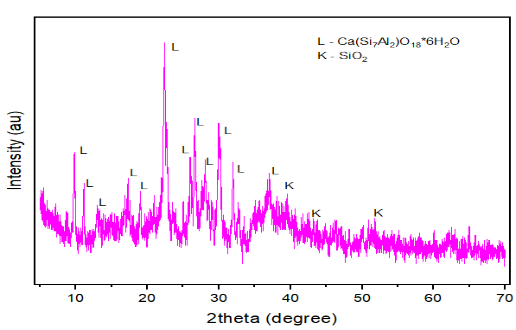

Figure 4. X-ray diffraction spectra of natural zeolite

As seen from the picture above, the zeolite consists 86,4% of $Ca(Si_7Al_2)O_{18}$ $6H_2O$ and 13,06% of SiO_2.

3.4.2. Results of X-ray Diffraction Analysis of Heat-Treated Natural Zeolites

The results of X-ray diffraction analysis of natural zeolite heat treated at 500, 600, and 700°C are shown in Fig. 5.

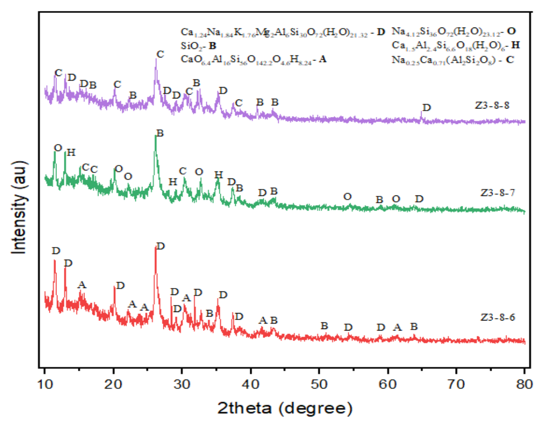

Figure 5 X-ray diffraction spectra of natural zeolite subjected to heat treatment at 500, 600, 700°C for 2 hours. Z3-8-8-700°C, Z3-8-7-600°C, Z3-8-6-500°C

As can be seen from Figure 3.4 and Table 3.4 ab ove, Quartz SiO_2-19.89%, Clinoptilolite $Na_{4.12}Si_{36}O_{72}(H_2O)_{23.12}$-33.32% at 500℃, Quartz SiO_2-19.38%, Clin optilolite $Na_{4.12}Si_{36}O_{72}(H_2O)_{23.12}$-47.3%, Geylandite $Ca_{1.5}Al_{2.4}Si_{6.6}O_{18}(H_2O)_6$-19.97%, Andalusite $Al_2Si_2O_8$-12. 85% at 600℃, Quartz SiO_2-27.48% at 700℃, Clinop tilolite $Na_{4.12}Si_{36}O_{72}(H_2O)_{23.12}$-40.98%, Andalusite $Al_2Si_2O_8$-20.64% are contained respectively.

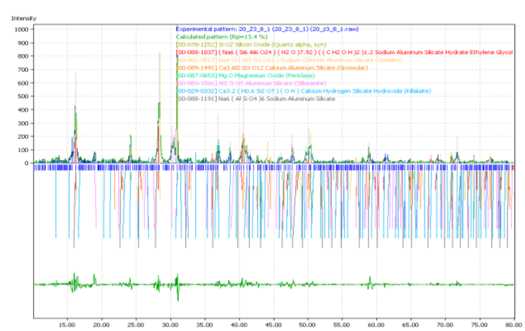

Figure 6 XRD spectra of zeolite synthesized at 100℃

According to the results of X-ray diffraction (XRD) analysis of zeolite synthesized at above 100°C, it contains sodalite($Na_4Cl(Al_3Si_3O_{12})$)-20.81%, quartz SiO_2-17.54%, andalusite Al_2SiO_5-18.09%, and killalite $Ca_{3.2}(H_{0.6}Si_2O_7)$ - 17.06% respectively.

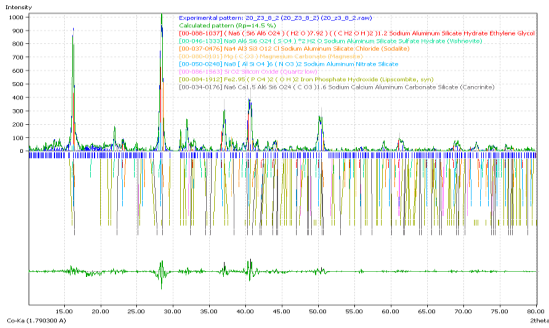

Figure 7 XRD spectra of zeolite synthesized at 150℃

According to the X-ray diffraction (XRD) analysis of the zeolite synthesized at 150 ^{0}C above, it contains sodalite $Na_4Al_3Si_3O_{12}Cl$-35.57% and vishnevite $Na_8Al_6Si_6O_{24}(SO_4)\cdot 2H_2O$-11.32%, respectively.

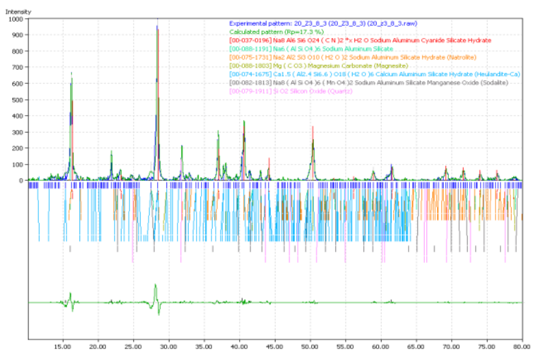

Figure 8 XRD spectra of zeolite synthesized at 200°C

The X-ray diffraction (XRD) analysis of the zeolite synthesized at 200 ºC shows that it contains 83.72% of Sodalite ($Na_4Cl(Al_3Si_3O_{12})$).

As shown in Fig. 6, 7, and 8 above, the analysis results of the zeolite synthesized at 100℃ showed that, it contains sodalite ($Na_4Cl(Al_3Si_3O_{12})$)-20.81%, quartz SiO_2-17.54%, andalusite Al_2SiO_5-18.09%, killalite $Ca_{3.2}(H_{0.6}Si_2\ O_7)(OH)$-17.06%, At 150^{0}C, sodalite $Na_4Al_3Si_3O_{12}Cl$-35.57%, vishnevite $Na_8Al_6Si_6O_{24}(SO_4)\cdot 2H_2O$-11.32% respectively. Sodalite($Na_4Cl(Al_3Si_3O_{12})$)-83.72% is found at 200ºC. It can be seen that at the hydrothermal temperature of 200ºC, sodalite type zeolite has the highest content of 83.72%. According to the analysis results of the zeolite synthesized in the above 3 hours, the zeolite contains 64,34% of sodalite $Na_4Cl(Al_3Si_3O_{12})$.

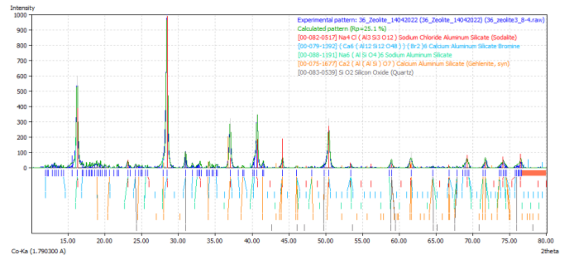

Figure 9 XRD spectra of the zeolite, obtained by synthesizing at a hydrothermal temperature of 200℃ and a time of 3 hours

4. CONCLUSION

In this research work, the following conclusions were reached by carrying out a study on extracting zeolite by hydrothermal method using the ash of Erdenet Thermal Power Plant. It includes:

1. According to the results of XRF analysis, the ratio of macroelements in the ash of Erdenet Thermal Power Plant ash pond is less than 1, so belongs to the acid ash. Also, based on the content of oxides, it was determined that the ash of Erdenet Thermal Power Plant is a siliceous type of ash due to the high content of silicon and aluminum oxides, and the low content of iron and calcium oxides.

2. According to the results of XRD analysis, SiO_2 (quartz)-29.51%, $Al_{5.65}\ Si_{0.35}\ O_{9.175}$ (mullite)-8.82%, and Fe_2O_5 (hematite)-10.15% were formed in the ash of current ash pond of Erdenet Thermal Power Plant, while minerals such as $K(FeSi_2O_6)$, $CaSiO_3$, Al_2SiO_5 (Andalusite) are less. But in the ash of the disused ash pond, mainly SiO_2 (quartz)-40.45%, $Al_{4.75}\ Si_{1.25}\ O_{9.63}$ (mullite)-28.83%, Al_2SiO_5 (Andalusite)-23.76% were formed, while $KAl_3Si_3O_{10}(OH)_2$, $K_2Fe_5Fe_3O_{10}(OH)_2$ elements are formed in smaller amounts.

3. According to the results of the XRD analysis of natural zeolite, it contains $Ca(Si_7A_{12})O_{18}6H_2O$-86.94% and SiO_2-13.06%. However, according to the results of XRD analysis of heat-treated zeolite $Ca(Si_7A_{12})O_{18}6H_2O$-47.3%, SiO_2-27.48%, and $Al_2Si_2O_8$- 20.64% were formed. According to the results of the XRD analysis of the synthesized zeolite, at 200°C, the content of Sodalite ($Na_4Cl(Al_3Si_3O_{12})$) was 83.72%.

4. Results of XRD analysis show that, the ideal conditions for the reaction to obtain zeolite from the ash of Erdenet Thermal Power Plant: ash: NaOH ratio 1:6, reaction temperature 80℃, stirring speed 200 rpm, reaction time 3 hours, hydrothermal temperature 200°C, it was determined that the yield of zeolite was 83.72% ($Na_4Cl(Al_3Si_3O_{12})$) at a time of 4 hours.

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