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Synthesis of Zeolites, Merlinoite Minerals of Damavand's Natural Clinoptiloite Zeolites Mineral in Hydrothermal Conditions, under the Influence of Alkaline Mediums

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Abstract

In the present research synthesis of zeolites, merlinoite minerals of natural clinoptiloite mineral in the presence of alkaline mediums, was investigated. The analyzed variants are a result of a concentration of Na+ and K+ ions, temperature and time. Phase transition of clinoptiloite was conducted in the presence of an 8 molar potash solution (KOH) and a 4 molar soda solution (NaOH). Results indicated that merlinoite phase occurs at a temperature of 200 degrees centigrade and the presence of highly concentrated ions of Na+. With the passage of reaction time, the concentration of the synthesized merlinoite is increased accordingly. XRD studies suggest orthorhombic synchrony with the dimensions of c = 9.45 Aº, a = 14/12 Aº, d = 2/19 Aº, n = 1/494 Aº for merlinoite.

Keywords: *Clinoptiloite, Alkaline Solution, Merilonite, Orthoromebic.*

1. Introduction

Zeolites are a group of hydro-aluminosilicates with a scaffolding structure and are a variant of Tectosilicates [1]. Structurally, the plexus of these minerals contains holes and channels through which cations and molecules of water flow. One of the significant characteristics of zeolites is their ability to absorb and reabsorb water and cations present in their holes and channels without causing outstanding changes to their structure [2]. Formation of the row materials, fluid formation, temperature, pressure and the pH of the environment are some of the influential factors in the formation of zeolites.

Clinoptiloite with a $(Na,K)_6\ AL_6Si_3O_{72}\ .\ 20H_2O$ structural formula is the most prevalent natural zeolite. This zeolite can be found mainly in the holes and seams of volcanic stones or sedimentary stones with volcanic origins that have been influenced by hydrothermal processes. Most of the Clinoptiloite crystals have monoclinic synchrony and are box-like in shape [3]. Because Clinoptiloite has catalytic properties, a base molecular structure and cation transition properties, it has many applications in industry. Merilonite with a $K_5Ca_2\ (Al_9\ Si_{23}\ O_{64}.\ 23H_2O)$ chemical formula, is a synthesized zeolite. The crystallization system of this mineral is Orthorombic or glassy polish. It has white and colorless forms with 4/5 petrification and a density of 2.2 $gr/cm^{3.}$ The fundamental elements of Merilonite are L, Ca, H, K, O and Si. Zeolites, divided into two form, natural and artificial, have various applications in industry.

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As well as the naturally synthesized form, more than 150 kinds of artificial zeolites have been produced so far. Iran has numerous mines of zeolites. The aim of this research is to investigate the structural changes of zeolites and the syntheses of merilonite zeolite mineral of clinoptiloite (natural zeolite) with the assistance of fluids containing alkaline and soil-alkaline cations.

2. The Geology of the Area

The significant zeolite zones in Iran are the Eosen zones involving Eastern Azerbayjan (Mianeh), the Semnan Zone and the Tehran Province Zone (Damavand) (Figure 1). For this research, the Tehran Province zeolite Zone was investigated. This zone includes morphologic units such as, the Damavand Volcano, central Alborz Mountain chains, the Aiineh Varzan and Delichay anticline and illuviation plioquartz areas. The studied area is located 140 kilometers east of Tehran, the median strip of Damavand among the areas of Hesarbon and Zarin Dasht and on the constructing tuff and tuffits of Karaj.

The analyzed area is located at $35^o 33' 58''$ latitude and 55° 32′ 52″ to 52° 22′14″ longitude. Generally, eoson magma activity in the Alborz causes significant variation and devastation.

Karaj's green tuff and tuffits with their volcanic mid-layers, devastate a large area [4]. These units have been transformed into zeolites and clayey minerals in the Haserbon and Zarrin Dasht areas [5,6]. Desert investigations illustrate that the green formative tuffits of Karaj have been transformed irregularly, and through this transition, converted to zeolite with benotonit [7].

The sedimentary basin of this formative is possibly a deposited environment related to traction phases after mountain building during the Cretaceous Paleocene period.

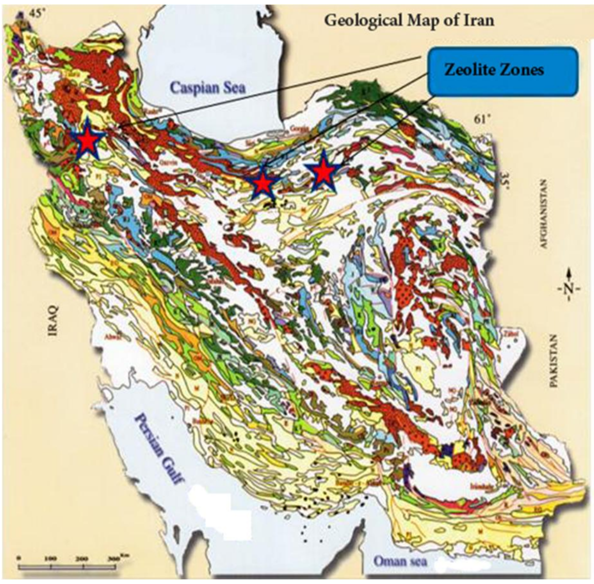

Fig.1. The location of Zeolite zones on geology map [4].

3. Methodology

After analysis and desert sampling, 20 samples from the Damavand zeolites zone were selected for microscopic investigations. After this, the samples were sent to the Center of Investigation and Production of Mineral Materials for XRD ،XRF and SEM studies. In this research, SPSS software was used for drawing comparative diagrams of the elements.

4. The Argument

Synthesis of Merlinoite of Natural Clinoptiloite

Before conducting the necessary actions, 4 samples from Hesarbon and 3 samples from Zarrin Dasht were analyzed with XRF in order to determine the zeolite kind for the region (Table 1). The acquired data was processed and drawn on diagrams using SPSS software (Fig.2). The weight percentage amounts of constructing elements from the Damavand Mine were determined using an electron microscope equipped with EDXray scan. Based on this, the resulting percentages of Na, Al, K, Si, Ca elements are shown in table 2 and Figure 3. According to the acquired results, the amount of Si is calculated as being 52 percent more than all other analyzed elements. Considering the percentage of Si and Al (10), the ratio of Si/Al is 5/2. Therefore, according to the results and also based on Boles theory [8] it can be claimed that Damavand's natural zeolite is of the Clinoptiloite kind. After determining the zeolite kind for the region, 10 grams of clinoptiloite sample were washed with 25 percent Chloridric acid. The sample was mixed in a beaker with 8 molar KOH, 4 molar NaOH and 50 milliliters of ammoniac using a magnetic mixer. The sample was poured into an autoclave and 80 milliliters of distilled water were added. It was then put into an oven at 200 degrees centigrade for 120 hours (in an autoclave, clinoptiloite will be influenced by the concentration of Na^+ and K^+ ions in order to disintegrate its structure and to form new synthesized compounds). After this, the ingredients of the autoclave were washed with distilled water and dried. Then, 2 grams of the synthesized ingredient were ground in a mortar till it reached 300 mesh. Without grinding, some of the microlithic synthesized crystals were fixated on a SEM special stand of a scanning electron microscope using carbon paste containing electricity. Indication of the resulting phases was conducted using X-Ray Diffraction (XRD). Accordingly, the sample possessed electricity using carbon coating. Next, it was analyzed elementally by EDXray revelation in order to find the Bolhera, kind and form of the crystal and spot analysis. Consequently, in hydrothermal conditions and in the presence of an alkaline 8 molar potash solution (KOH) , a 4 molar soda solution (NaOH), 50 milliliters of ammoniac and a 25 percent chloridric acid wash, clinoptiloite changed phase. Analysis of the synthesized sample of the x-ray powder diffractometer illustrated that the primordial clinoptiloite changed phase. According to figure 4, the resulting phase includes merlinoite, natrolite and haloist. The observed peaks in figure 4 are in accordance with XRD model for merlinoite, natrolite and haloist minerals.

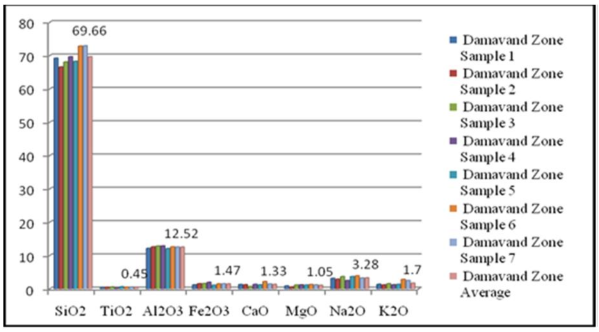

Fig.2. The comparison of the samples of Hesarbon and Zarrin Dasht in Damavand.

Generally, in this research the simultaneous influence of Na^+ and K^+ in the construction of merlinoite in an alkaline environment was investigated. The influence of the variations in the fluid compound and environment temperature on the construction of merlinoite are the investigated parameters. Study of the XRD models of the samples, when exposed to temperatures of 200 degrees centigrade, indicated a reduction in the amount of clinoptiloite.

Table 1. The results of XRF analysis for the studied samples of the region (Hesarbon and Zarrin Dasht).

	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Sample 7	Average
SiO_2	69.22	66.6	68.1	69.65	68.29	72.85	72.95	69.66
TiO_2	0.354	0.43	0.56	0.26	0.62	0.48	0.51	0.45
Al_2O_3	12.14	12.6	12.85	12.88	12.09	12.6	12.54	12.52
Fe_2O_3	1.19	1.53	1.59	1.96	1.06	1.48	1.51	1.47
CaO	1.29	1.21	0.67	1.35	1.2	2.18	1.44	1.33
MgO	0.88	0.56	1.13	1.2	1.13	1.29	1.17	1.05
Na_2O	3.16	2.89	3.67	2.5	3.67	3.89	3.23	3.28
K_2O	1.36	1.17	1.53	1.22	1.34	2.82	2.5	1.70

At a fixed temperature, the increase of the concentration of Na^+ and K^+ ions and pH, resulted in an increase in intensity of disintegration of the clinoptiloite. XRD models of the samples exposed to a temperature of 200 degrees centigrade demonstrated merlinoite peaks. The SEM figures of this sample confirm the formation of merlinoite phase in the same way. In models in which the synthesized merlinoite has a higher ratio of Na^+/ K^+ , increase of this ratio along with a simultaneous increase in disintegration of the clinoptiloite, resulted in an increase of the synthesized amount of merlinoite. The dimensions of the unit cell based on the XRD data and application of "Least Square" calculation method were estimated as being c= 9.45 Aº, a= 14/12 Aº, d= 2/19 Aº, n = 1/494 Aº. According to microscopic figures, the topologic synchrony of the merlinoite crystals is pseudocubic. On the other hand, the XRD investigations suggest an orthorhombic synchrony for merlinoite cells.

Table 2. The weight percentage amount of the of zeolite constructing elements of Damavand Mine, determined by electron microscope equipped with ED X ray scan.

Element	Line	Intensity (C/S)	CONC
Na	Ka	1.02	8.52wt%
Al	Ka	1.84	10.00wt%
Si	Ka	6.19	52.98w%
K	Ka	1.72	14.50wt%
Ca	Ka	1.76	14.86wt%
Total			100.00wt%

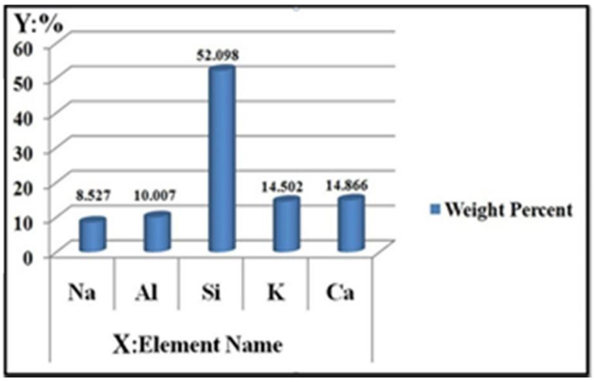

Fig.3. The comparison of SEM element analysis of Damavand zeolite.

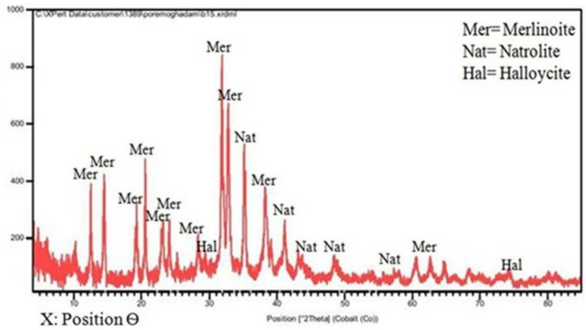

Fig.4. The existence of Mer: merlinoite, Nat: nartroloite, and Hal: halovist on XRD model.

Table 3. The Characteristics of Merlinoite.

	Merlinoite
Chemical Formula	$(K,Na)_5(Ca,Ba)_2Al_9Si_{23}O_{64}.23H_2O$
Crystallization System	Orthorhombic
Color	Colorless, White
Polish	Glassy
Petrification	4.5
Density	2.2 gr/cm^3
Fundamental	Al, Ca, H, K, O, Si

Molecular weight: 2626 grams in each molecule

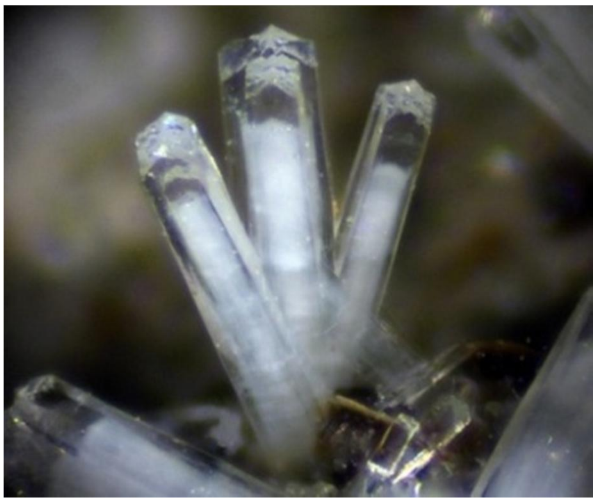

Fig.5. The SEM electron microscope image of merlinoite crystals.

The results of the elemental analysis of the synthesized merlinoite compound are presented in table 4. According to spot analysis and indication of the percentage weight, the ratio of Si to Al in this mineral is calculated as being approximately 2/47.

Table 4. The formative elements of the synthesized merlinoite in the presence of Na^+ and K^+ ions.

Element	Line	Intensity (C/S)	CONC
Na	Ka	0.13	3.71
Al	Ka	0.77	21.21
Si	Ka	1.96	52.40
K	Ka	0.54	16.39
Ca	Ka	0.22	6.27
Total			100.00wt%

5. Significant Points

Ammonium ions that enter water as cations, can cause various physiologic disorders in living things as time goes on and their numbers increase. In order to resolve the problem of absorbing the hysteresis, attempts to apply inexpensive, high efficiency absorbents is not suggested. This research was mainly conducted using inexpensive absorbents such as zeolite, petiolate and merlinoite. Investigation of the characteristics of most of the zeolites indicates that the selectivity of the cations follow this general order:

$$K^+ > NH_4^+ > Na^+ > Ca^{2+} > Mg^{2+}$$

The most significant feature of zeolite that justifies its application in breeding aquatics is its cation interchange quality that can be refined to make it more beneficial in application. Merlinoite zeolites are applied as an absorbent of ammoniac nitrogen to the surface of polluted factory waters leading to fish and shrimp breeding pools. These zeolites have a considerable capacity for absorbing the heavy metals in sewage. The results of the experiments illustrate that zeolites can absorb metals such as Lead, Zinc, Chrome, Cadmium, Arsenic and Mercury and resolve the dangers of their existence. Therefore the selectivity of the aforementioned is as follows:

$$Pb^{2+} > Cd^{2+} > Zn^{2+} > Cr^{3+} > Cr^{6+} > As^{4+} > Mg^{2+}$$

According to this, various zeolites have variable cation interchange capacities. Consequently, the mentioned zeolite (Merlinoite) can eliminate acunism ions from aquatic living environments. Ammonium is one of the most poisonous ions in water environments; a concentration of a few ppm can be highly dangerous. Zeolite is also able to provide needed oxygen for fish life.

6. Conclusion

According to the conducted investigations and the results of the research, it can be claimed that compared to other zeolite zones, Damavand's zeolites have more SiO_2 ‹Al_2O_3 and TiO_2. Also, an increase in the amount of TiO_2 in zeolite, results in augmentation of its hydrophilic feature. The results of the experiments of Damavand zeolites illustrate magnificent absorption characteristics and a high quality. Phase transition of clinoptiloite was conducted in the presence of an 8 molar potash solution (KOH) and a 4 molar soda solution (NaOH). Results indicated that merlinoite phase occurs at a temperature of 200 degrees centigrade and the presence of highly concentrated ions of Na^+. With the passage of, the reaction time, the concentration of the synthesized merlinoite is increased accordingly. The fundamental elements of Merilonite are L, Ca, H, K, O and Si. The dimensions of the unit cell based on the XRD data and application of "Least Square" calculation method were estimated as c= 9.45 Aº, a= 14/12 Aº, d= 2/19 Aº, n = 1/494 Aº. The topologic synchrony of the merlinoite crystals is pseudocubic according to microscopic figures. On the other hand, the XRD investigations suggest an orthorhombic synchrony for merlinoite cells.

In zeolites, a higher ratio of Si/Al results in a lower cation interchange capacity and vice versa. According to this, a petiloit has a low cation interchange capacity. Consequently, the interchange of the synthesized zeolite minerals is as follows:

Ratio of Si/Al in renyayt synthesized kans is 0/96
Ratio of Si/Al in anasim synthesized kans is 1/32
Ratio of Si/Al in merlinoite synthesized kans is 2/47
Based on this, the ion interchange capacity in synthesized zeolites is as follows:
Cans denyat> anasim>monioit>yeknotpiolite
Yektotpmiolite
As the ratio of Si/Al was 4 for all other cases and 2/47 for merlinoite, the ion interchange capacity of Clinoptiloite is lower than molinoite.

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