

Extraction of edingtonite from a natural zeolite under hydrothermal conditions

F. TUTTI^{1*}, S.M. KAMYAB¹, M.A. BARGHI¹, A. BADIEI²

¹ School of Geology, College of Science, University of Tehran, Tehran, Iran

² School of Chemistry, College of Science, University of Tehran, Tehran, Iran

In the present study, edingtonite has been extracted from natural zeolite clinoptilolite by simulating the natural hydrothermal conditions in the laboratory, under the influence of solutions with different concentrations of Ba^{+2} and Na^{+} , varying from 0.5 to 2.8 mol/L, at 150 °C. In this work, the essential hydrothermal conditions have been provided by hydrothermal autoclaves. The natural and laboratory prepared samples were characterized by XRD, XRF and SEM methods.

Keywords: *clinoptilolite; phase transformation; hydrothermal conditions; edingtonite*

© Wrocław University of Technology.

1. Introduction

Zeolites as a class of crystalline aluminosilicates with rigid anionic frameworks and well-defined channels and cavities, contain alkali-earth and alkaline elements as the exchangeable cations [1] that can absorb and release H_2O molecules to keep ionic balance [2]. Certain natural zeolites such as mordenite and clinoptilolite, (sodium, potassium and calcium bearing aluminosilicates with monoclinic symmetry) [3], can be formed during the hydrothermal process under the influence of hydrothermal fluids passing through the pores of igneous and pyroclastic rocks. These zeolites can also be formed in saline lakes, deep sea sediments, alkaline soil, during the burial diagenesis or low grade metamorphism. Most of them are the products of devitrification of vitric volcanic materials (glassy phases present in tuffs) [3]. The availability of large volumes of internal space is one of the most desirable characteristics of these zeolites for sorbent applications [1]. This property causes high capacity of their ionic exchange also their application as molecular sieves [4, 5]. Edingtonite, as a barium zeolite, can be formed, similar to other zeolites, as the result of the alteration process or phase transition of the natural zeolites, in the pores of igneous rocks, nepheline syenites

and hydrothermal veins, under hydrothermal fluids which change their composition at high temperature. Edingtonite has been found in hydrothermal veins in altered mafic rocks and metasediments, associated with sulfides (pyrite, chalcopyrite, galena, and sphalerite), carbonate (calcite and barytocalcite) hematite, hydroxides (goethite and manganite) and, in one case with analcime and harmotome [6–9]. Edingtonite has a tetragonal structure at low water content or orthorhombic structure when the water content is high [10–13]. Because of its capability of ionic exchange it can be used as a detergent and as an important agent for softening water and removing radioactive residuals.

The experimental studies on zeolites are aimed to improve and understand their ionic exchange ability, the stability field and formation conditions of these minerals. Transformation of clinoptilolite to analcime in alkaline hydrothermal conditions [14] and formation of edingtonite from barium aluminosilicate glasses at 1 kbar and temperatures between 80 to 230 °C [15] are examples of this type of researches. In this study, we investigate the stability of clinoptilolite and the possibility of barium zeolite formation under the effect of barium bearing solutions with various cationic concentrations, at high temperatures. For the above purpose, we have attempted to simulate a variety of hydrothermal conditions on clinoptilolite and found out that it has

*E-mail: tutti@khayam.ut.ac.ir

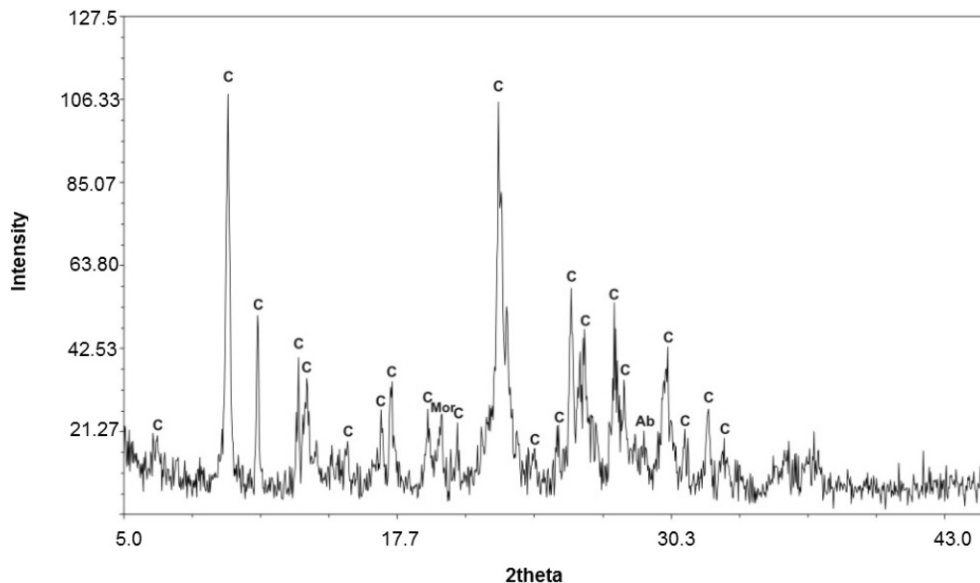


Fig. 1. X-ray powder diffraction pattern of the primary sample. C: clinoptilolite, Mor: mordenite, Ab: albite.

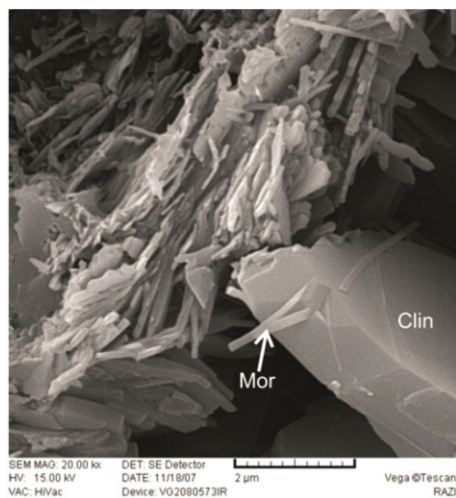


Fig. 2. SEM image of initial material.

Table 1. Chemical composition of primary bulk sample (XRF).

Oxide	Weight %	Mole %
SiO ₂	72.22	61.0444
Al ₂ O ₃	11.53	5.7427
Fe ₂ O ₃	0.42	0.1336
CaO	3.15	2.8525
Na ₂ O	0.97	0.7945
K ₂ O	1.05	0.5673
MgO	0.52	0.6553
TiO ₂	0.180	0.1144
MnO	0.001	0.0007
P ₂ O ₅	0.001	0.0004
H ₂ O	9.958	28.0943

transformed into two new barium zeolites namely edingtonite and harmotome.

2. Experimental

2.1. Materials and methods

The primary sample has been collected from Aftar area, located in the west of Semnan, then powdered and used without purification. The studies performed in this area confirm that the primary sam-

ples had been formed during the transformation process of Eocene dacitic and rhyolitic tuffs, in alkaline environment [16].

The samples were characterized using the standard methods for phase and morphology determination such as X-ray powder diffraction patterns (XRD) (measured with Bruker D8-ADVANCE, equipped with a copper tube and nickel filter, $K\alpha$ Cu, $\lambda = 1.54 \text{ \AA}$), scanning electron microscopic images (SEM) (Zeiss DSM960A) and X-ray fluorescence spectroscopy (XRF) for chemical composition evaluation of bulk sample. Based on the above

Table 2. Variation of total Ba^{+2} content and Na^{+} concentration in 80 mL solution, at 150 °C in the first series of the experiments. Fau: Faujasite, Har: Harmotome, Ana: Analcime, H.S: Hydrosodalite, E: Edingtonite.

The amount of dry $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (g)	Ba^{+2} (mol/L)	The amount of dry NaOH (g)	Na^{+} (mol/L)	Run-products
9.15	0.5	9	2.8	Har Fau, Ana H.S
27.5	1.4	9	2.8	Har Fau, H.S
36.6	1.9	9	2.8	EDI H.S
55	2.8	9	2.8	Har Fau, Ana H.S

Table 3. Variation of total Na^{+} concentration at constant Ba^{+2} content in 80 mL solution, at 150 °C in the second series of experiments. Fau: Faujasite, Har: Harmotome, Ana: Analcime, H.S: Hydrosodalite, E: Edingtonite.

The amount of dry $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (g)	Ba^{+2} (mol/L)	The amount of dry NaOH (g)	Na^{+} (mol/L)	Run-products
55	2.8	1.5	0.5	EDI Ana H.S
55	2.8	4.5	1.4	Har Fau, Ana, H.S
55	2.8	6	1.9	Har Fau, Ana, H.S
36.6	1.9	6	1.9	Har Fau, Ana, H.S

analyses, it was stated that the sample was composed mainly of clinoptilolite with small amounts of albite and mordenite (Figs. 1, 2 and Table 1).

2.2. Procedure of experiment

In this work, clinoptilolite has been treated with the alkaline NaOH solution, as a source of Na^{+} , and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ solution as a source of Ba^{+2} , in a hydrothermal autoclave, at 150 °C, for 96 h. In order to perform the hydrothermal transformation experiments, 5 g of powdered primary sample and proper amounts of dry sodium hydroxide (Tables 2 and 3) were mixed with 30 mL distilled water and stirred with a magnetic stirrer at 300 rpm (Heidolph MR, 3001 K) for 30 min. Secondly, 30 mL solution containing dissolved $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Tables 2 and 3), was added to the previous solution. The final mixture was stirred for 30 min and eventually,

20 mL distilled water was added to the mixture and poured into the autoclave, which was then placed in a temperature-controlled furnace. After 96 h, the produced solid phases were filtered and rinsed with distilled water for several times, then were dried at room temperature.

3. Results and discussion

In two series of experiments performed at high temperature, the barium-bearing solutions were used to investigate phase transition of clinoptilolite to barium zeolite whereas the alkaline solutions were used to provide high content of H^{+} ions and create hydrothermal alkaline conditions to dissolve clinoptilolite.

In the first series of experiments, the Na^{+} concentration was kept constant, at the level of 2.8 mol/L

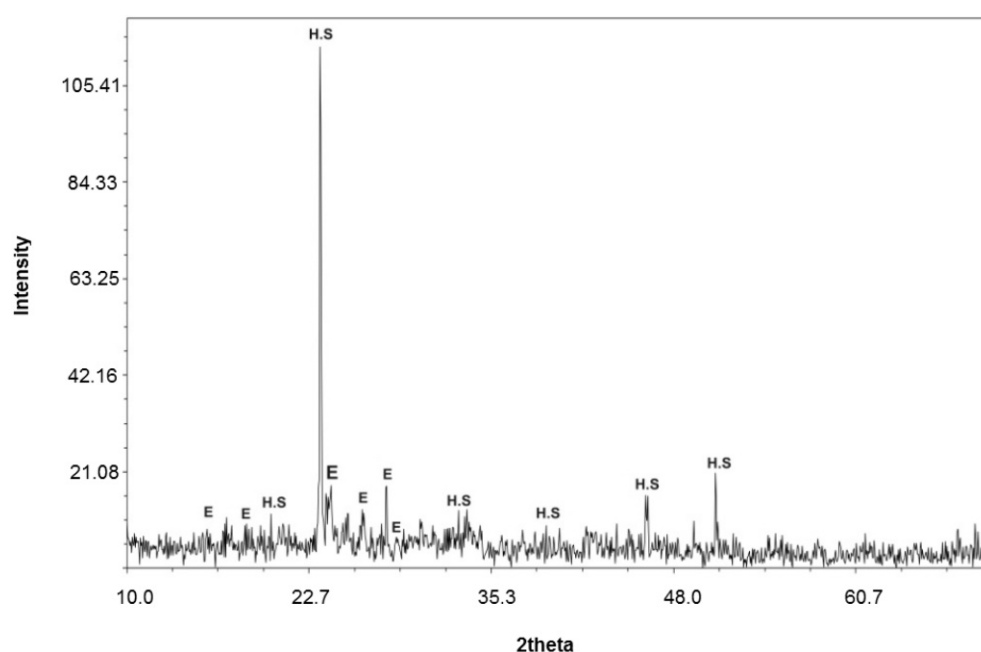


Fig. 3. X-ray diffraction pattern of the sample from the first series of experiments, 1.9 mol/L Ba^{+2} , 2.8 mol/L Na^{+} ; E: Edingtonite, H.S: Hydrosodalite.

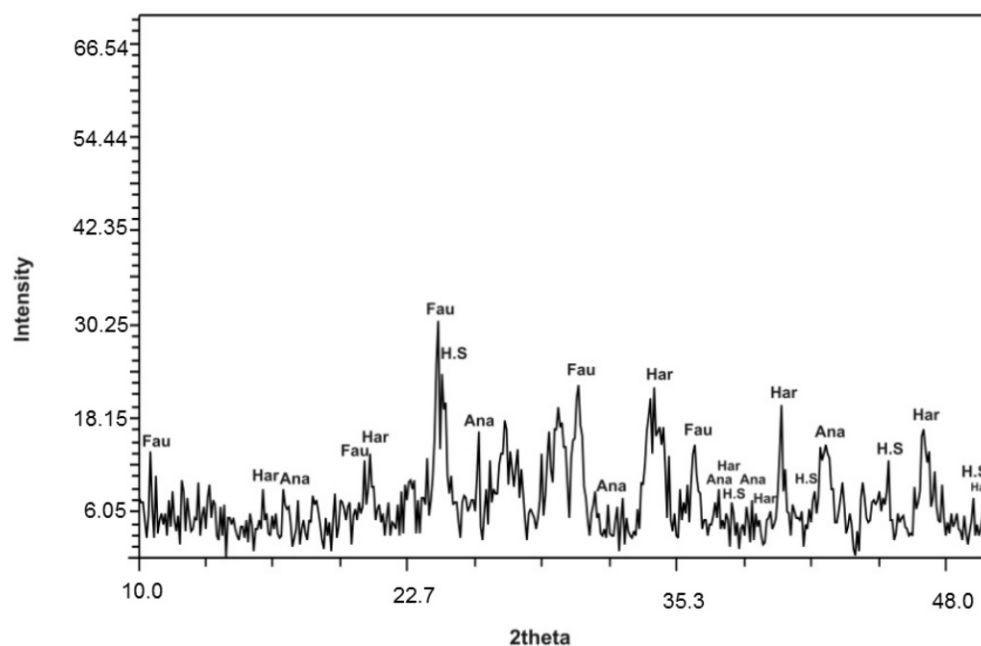


Fig. 4. X-ray diffraction pattern of the sample from the first series of experiments; 1.4 mol/L Ba^{+2} , and 2.8 mol/L Na^{+} ; Fau: Faujasite, Har: Harmotome, Ana: Analcime, H.S: Hydrosodalite.

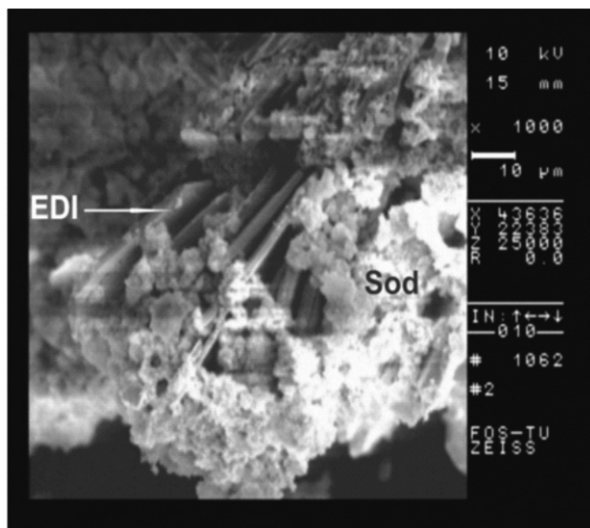


Fig. 5. SEM image of a transformed sample from the first series of experiments containing edingtonite crystals with hydrosodalite: EDI:Edingtonite, Sod: Hydrosodalite.

and Ba^{+2} content was varied from 0.5 to 2.8 mol/L (Table 2). The X-ray diffraction patterns (Figs. 3, 4) and SEM image (Fig. 5), indicate that edingtonite has been formed at the concentration of 1.9 mol/L Ba^{+2} in the barium bearing solution mixed with the solution containing 2.8 mol/L Na^{+} . According to the observations, clinoptilolite was completely dissolved in the alkaline hydrothermal solutions at high temperature and the substitution with Ba^{+2} led to the formation of barium zeolites. During the dissolution process, the structure of clinoptilolite broke down under the influence of NaOH solution at high temperature, which resulted in an increase of Al/Si ratio in the residual material. Consequently, the addition of Ba^{+2} and Na^{+} , present in the solution, to those residuals led to the formation of barium zeolites such as edingtonite and harmotome, along with some sodium bearing minerals such as hydrosodalite, analcime and faujasite.

The second series of experiments was carried out at a high content of Ba^{+2} , kept constant at the level of 2.8 mol/L, which was mixed with different concentrations of Na^{+} , varied from 0.5 to 1.9 mol/L (Table 3). Based on the X-ray diffraction patterns (Figs. 6, 7) and SEM image of the sample obtained at 0.5 mol/L Na^{+} (Fig. 8), it can be stated that the

structure of edingtonite formed in these conditions is not as crystalline as the product obtained in the first series of the experiments. At the low Na^{+} content in the solutions of the second series, only partial dissolution of clinoptilolite took place. Analcime and hydrosodalite as Na^{+} bearing products have also been formed along with the barium zeolite in this series of experiments.

Experimental problems such as temperature gradients and vapor pressure variations inside the autoclaves may have affected the equilibrium conditions of the experiments and as a result may have led to poor crystallization of edingtonite.

Transition of clinoptilolite to edingtonite could have happened through substitution of K^{+} by Ba^{+2} in the widest structural channel of orthorhombic edingtonite (001) located in c direction, where Ba^{+2} cations are surrounded by 6O^{2-} and $4\text{H}_2\text{O}$ molecules. This substitution may take place after a decrease in Si/Al ratio, under the influence of alkaline solution, which is desirable for the formation of minerals with low Si-content such as edingtonite. As it has been observed, Na^{+} bearing minerals, namely analcime and hydrosodalite, have been crystallized in the presence of Si and Na cations. Hydrosodalite is a Na^{+} bearing zeolite with a cubic structure, a synthetic type of natural sodalite [17], and an ionic conductor, in which an anion [18, 19], located at the center of the β cage, has been replaced by H_2O molecules [20–22]. Analcime is another Na^{+} bearing run-product formed in this study that can be found in nature 1) in the pores of plutonic rocks, pegmatite, and volcanic rocks, such as basalt and dolerite 2) as a result of the alteration of volcanic vitreous and primary leucite and nepheline or pyroclastic sediments in marine and terrestrial environment or a low grade metamorphism product 3) as phenocrysts in alkaline igneous rocks [23].

This experimental study can be similarly substantiated in natural geological environment, in which hydrothermal metamorphism as one of the most important features, may lead to the formation of barium zeolite. Naturally, during the alteration process and under the effect of hydrothermal fluids containing Ba^{+2} , primary zeolite located in the pores, cavities or veins of rocks can transform to secondary Ba^{+2} bearing zeolite.

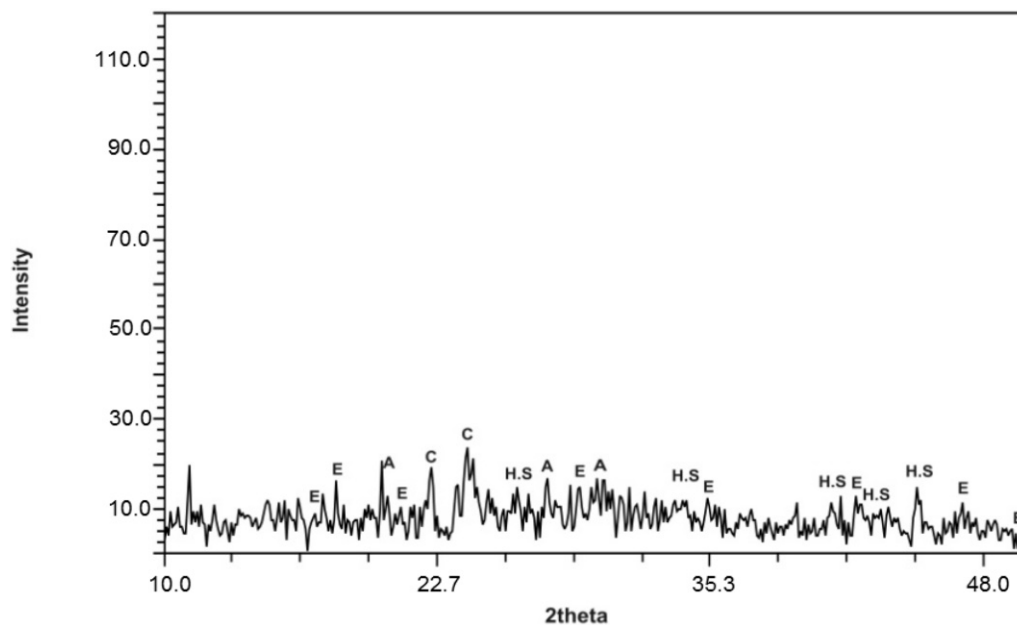


Fig. 6. X-ray diffraction pattern, obtained in the second series of experiments with 2.8 mol/L Ba^{+2} and 0.5 mol/L Na^{+} ; C: Clinoptilolite, E: Edingtonite, A: Analcime, H.S: Hydro-sodalite.

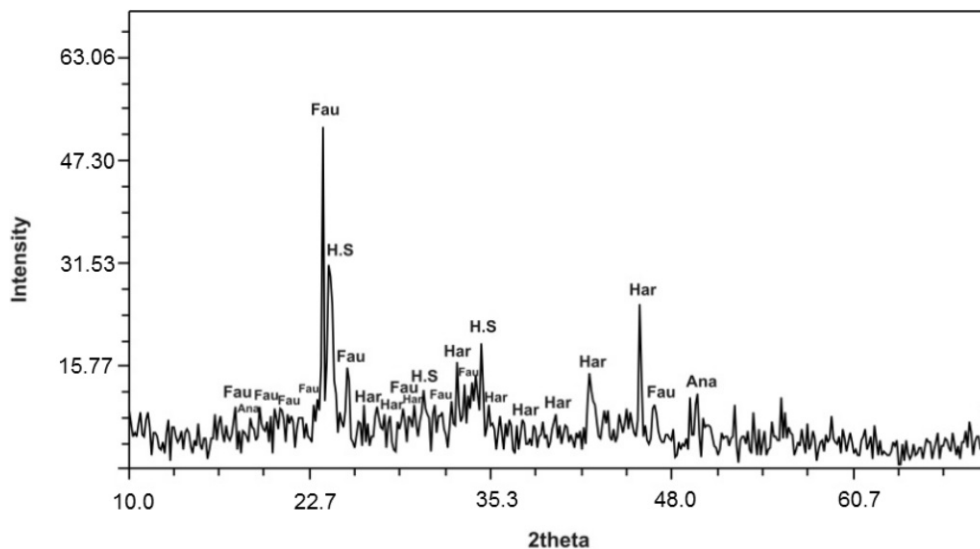


Fig. 7. X-ray diffraction pattern of the samples obtained in the second series of experiments with 2.8 mol/L Ba^{+2} and 1.9 mol/L Na^{+} ; Fau: Faujasite, Har: Harmotome, Ana: Analcime, H.S: Hydrosodalite.

4. Conclusions

Phase transformations of a natural zeolite (clinoptilolite) have been investigated under the influence of barium bearing hydrothermal alkaline

solutions. In order to achieve this aim, two series of experiments were performed with different concentrations of Ba^{+2} and Na^{+} at a temperature of 150 °C. The results revealed that two relatively rare barium zeolites namely edingtonite and harmotome could

