

## Physicochemical and structural characteristics of HEU-type zeolitic tuff treated by hydrochloric acid

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**Abstract:** Samples of natural HEU-type zeolites – clinoptilolite-Ca, from the Novakovici deposit (near Prijedor, Bosnia and Herzegovina) were treated with the hydrochloric acid of various concentrations (from 10<sup>-3</sup> M to 2 M). Zeolitic tuffs before and after the acid treatment were examined using IR, XRPD, and chemical analyses. The changes in the crystal structure of acid treated samples showed a significant reduction in the crystallinity of zeolitic tuffs (60–70 %), which were effected by hydrochloric acid with concentrations of 1 M and above.

**Keywords:** HEU-type zeolite, acid modification, X-ray analysis, Novakovici.

### INTRODUCTION

A zeolite mineral is a crystalline substance with a structure characterized by a framework of linked tetrahedra, each consisting of four O atoms surrounding a cation. This framework contains open cavities in the form of channels and cages. These are usually occupied by H<sub>2</sub>O molecules and extra-framework cations that are commonly exchangeable. The channels are large enough to allow the passage of guest species. In the hydrated phases, dehydration occurs at temperatures mostly below about 400 °C and is largely reversible. The framework may be interrupted by (OH, F) groups; these occupy a tetrahedron apex that is not shared with adjacent tetrahedra.<sup>1</sup>

Minerals of the clinoptilolite series are the most common rock forming minerals of sedimentary rocks of volcanic origin. These rocks present mineral deposits of natural zeolites. Clinoptilolite-heulandite tuffs are of the greatest economic interest.

Clinoptilolite series structurally belong to HEU-type zeolites, with common HEU framework topology, and with an approximate chemical formula – [(Na, K, C, Sr, Ba,

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$\text{Mg})_6 \text{Al}_6 \text{Si}_{30} \text{O}_{72}] \cdot n \text{H}_2\text{O}$ .<sup>2</sup> The crystal structure of the HEU-type zeolites is characterized by a three-dimensional aluminosilicate framework consisting fundamentally of secondary building units (SBUs) of the 4-4-1 types, formed by (Si, Al) $\text{O}_4$ -tetrahedral primary building units (PBUs). The primary structural shape of clinoptilolite is presented by four channels. Three of them are formed of eight-membered tetrahedral rings ( $0.46 \times 0.36$  nm), and one ten-membered tetrahedral ring ( $0.75 \times 0.31$  nm). The ten-membered tetrahedral ring (**A**), and one of the eight-membered tetrahedral ring (**B**) are parallel to the *c*-axis, the second eight-membered tetrahedral ring (**C**) is parallel to the *a*-axis. The third channel is positioned at an angle of under  $50^\circ$  relative to the *a*-axis. The fourth channel is parallel to the *a*-axis.<sup>3,4</sup>

Modified forms of HEU-type zeolites are obtained by ion exchange either with  $\text{NH}_4^+$  or by leaching with inorganic acids (H-forms of zeolite are obtained in this way). With these modifications, high Brönsted acidities are reached. It was believed that the extra-framework cations are replaced by  $\text{H}_3\text{O}^+$  and the tetrahedral framework is altered by loss of  $\text{Al}^{3+}$ . According to Misaelides,<sup>5</sup> when natural heulandite are treated with various concentrations of HCl acid (from  $10^{-3}$  M to 2 M), it was noticed that partial surface amorphization and reduction of Al concentrations in the internal space had occurred in samples treated with 1 M and 2 M hydrochloric acid. Yamamoto<sup>6</sup> using atomic force microscopy at the (010) surface of heulandite leached with 0.2 M  $\text{H}_2\text{SO}_4$  found pits caused by layer-to-layer dissolution. In addition, heulandite treated with 1 M HCl acid loses significant amounts of Al (framework cation) and extra-framework cations of the channels whereby only a negligible amount of Si was extracted. Subsequent X-ray single-crystal structure analysis indicated partial rearrangement of the framework Al to hydrated extra-framework Al, where the Al preferred octahedral coordination. Thus, not only  $\text{H}_3\text{O}^+$  cations but also  $\text{Al}^{3+}$  appeared as extra-framework cations.<sup>7</sup>

The acidity of the solution, the time and temperature of leaching, the crystal size, the origin of a crystal, the solid/liquid content, as well as structure and composition have strong influences on the modified structure. Variation of any of these parameters may cause changes in the structural state and in the associated catalytic behavior of the leached material.<sup>8</sup> This phenomenon is the most important in many adsorption and catalytic functions of zeolites. These modified materials can be used for radioactive waste treatment, or for the removal of heavy metals from industrial wastewaters.<sup>9</sup>

The aim of this work was to determine the structural properties and acid stability of zeolitic tuffs from the Novakovici sedimentary deposit in Bosnia and Herzegovina.

## EXPERIMENTAL

The raw material was milled and wet classified to 100 % < 63  $\mu\text{m}$  (sample mark is Z). The wet chemical analysis was done according to the following procedure: silica oxide content, aluminium

oxide content and loss on ignition at 1000 °C (LOI) were determined gravimetrically; alkaline content was determined flamephotometrically; the contents of other elements were determined by AAS method using a Perkin-Elmer M-703 instrument.

The acid treatment of zeolite tuff was performed by mixing 2 g of each sample with 100 ml of HCl acid, for 2 h. Various concentrations of HCl in the range from  $10^{-3}$  M to 2 M were used (sample marks are: ZH1 –  $10^{-3}$  M; ZH2 –  $10^{-2}$  M; ZH3  $10^{-1}$  M; ZH4 – 1 M; ZH5 – 2 M). After the reaction time, the samples were left in contact with the acid for 24 h at room temperature and then centrifuged, washed, and dried (without shaking). The concentrations of inorganic cations released from the zeolitic tuffs and the dissolved aluminium were determined in the supernatants. The total content of exchangeable inorganic cations (CEC) in raw and treated samples was determined by the method of Ming and Dixon.<sup>10</sup>

XRPD analyses of raw zeolitic tuffs and acid treated samples were performed using a Philips PW-1710 diffractometer with monochromatic Cu-K $\alpha$  radiation, in the  $2\theta$  range of 4–35°. Monoclinic crystal system (space group C2/m – 12) was used for the determination of unit-cell parameters ( $a$ ,  $b$ ,  $c$ ,  $V$  and  $\beta$ );<sup>3</sup> using the crystallographic program “LSUCRIPC”.<sup>11</sup> The values of the unit cell parameters were calculated from the characteristic diffraction reflections of clinoptilolite: [020]; [200]; [–311]; [111]; [131]; [400]; [330]; [151]. The microstructural parameters were determined using the crystallographic program “BREDTH”.<sup>12</sup>

The IR-spectra of the raw zeolitic tuffs, and acid treated samples were obtained using a Hewlett Packard IR spectrometer, in the range 4000–400  $\text{cm}^{-1}$  (as KBr pellets).

## RESULTS AND DISCUSSION

### *Effects of acid concentration related to the changes of chemical composition*

Raw zeolitic tuff from the Novakovici deposit has the following mineralogical semi quantitative composition (in wt.%): clinoptilolite  $\approx$  87, and  $\approx$  13 volcanic glass.<sup>13</sup>

The chemical composition of raw zeolitic tuff is given in Table I.

TABLE I. The chemical composition of raw zeolitic tuff from the Novakovici deposit

Oxides	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	LOI
Wt.%	63.64	12.40	0.92	4.93	1.02	0.20	1.80	15.40

Based on the results of the chemical analysis, the crystal-chemical formula of raw zeolitic tuff is:  $(\text{Ca}_{3.6} \text{Mg}_{0.10} \text{Na}_{0.52} \text{K}_{2.64}) (\text{Al}_{6.6} \text{Si}_{29.2} \text{O}_{72}) \cdot 23.6 \text{H}_2\text{O}$  (on the basis of 72 atom of O). The Si/Al ratio is 4.42, and this sample is a high silica content mineral – clinoptilolite-Ca. The content of exchangeable inorganic cations in the raw zeolitic tuff was (in mmol M<sup>+</sup>/100 g): Ca<sup>2+</sup> 138.0; Mg<sup>2+</sup> 3.0; Na<sup>+</sup> 7.9; K<sup>+</sup> 39.0. While the total content of these cations in the raw zeolitic tuff, calculated from chemical analysis was (in mmol M<sup>+</sup>/100 g): Ca<sup>2+</sup> 176.0; Mg<sup>2+</sup> 51.0; Na<sup>+</sup> 6.5; K<sup>+</sup> 40.0.

During the acid treatment, dealumination of the zeolitic tuff appears to be related to increases of the aluminum content in the supernatants. The results of the content of aluminum released from the zeolitic tuff suggested that, at acid concentration above  $10^{-1}$  M, framework attack had taken place and dealumination had occurred. Compared to raw zeolitic tuff (Z), in which the total content of aluminum was 6.5 % (Table I), at acid concentration of 2 M (ZH5), 5.08 % aluminum was leached out from the zeolitic tuff. The results of the content of leached inorganic

cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ) and aluminum released during the acid treatment as a function of ratio  $\text{H}^+/\text{Al}^{3+}$  are presented in Fig. 1. The ratio  $\text{H}^+/\text{Al}^{3+}$  was calculated by dividing the amount of  $\text{H}^+$  ion in exchangeable position by the amount of  $\text{Al}^{3+}$  released from the zeolitic framework, and represents the ratio between the ion exchange process and the dealumination processes.

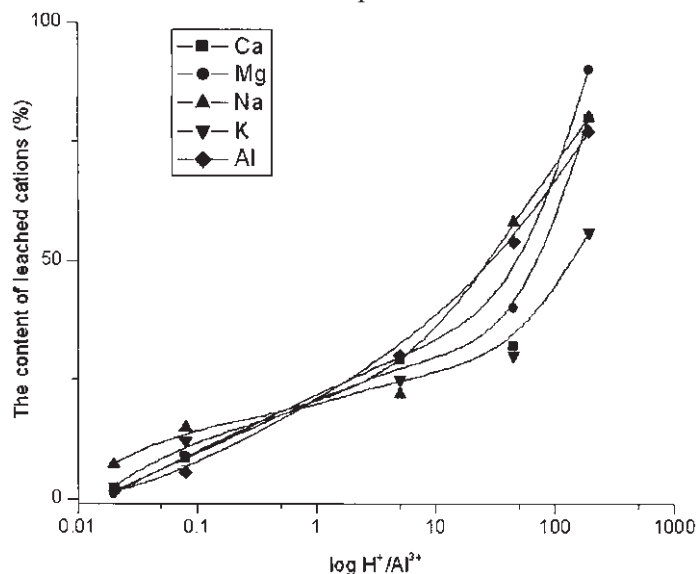


Fig. 1. The content of leached cations after acid treatment as a function of the  $\text{H}^+/\text{Al}^{3+}$  ratio.

Inorganic alkali and alkali-earth cations, released from the zeolitic tuff showed that these cations were progressively leached out as the concentration of acid increased (Fig. 1). The different removal rate of the cations can probably be related to the location of the cations in the channels and their coordination in the zeolite framework.<sup>14</sup> The content of inorganic cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ) in acid treated samples and the amount of leached inorganic cations, calculated in  $\text{mmol M}^+/\text{100 g}$ , are presented in Table II.

TABLE II. Content of exchangeable and leached cations

Mark	Content of exchangeable cations; after acid treatment ( $\text{mmol M}^+/\text{100 g}$ )				Content of leached cations ( $\text{mmol M}^+/\text{100 g}$ )			
	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+$	$\text{K}^+$
Z	138.0	3.0	7.9	39.00				
ZH1	92.0	1.3	6.2	33.30	2.76	0.5	0.43	1.00
ZH2	82.2	0.2	5.7	29.20	15.00	4.2	0.87	1.92
ZH3	50.1	–	3.2	20.00	51.00	15.0	1.30	9.50
ZH4	32.2	–	1.1	14.60	55.00	20.0	3.48	10.50
ZH5	20.2	–	0.3	6.90	115.00	41.6	4.80	15.60

From Table II, it can be seen that the content of calcium in exchangeable position in raw zeolitic tuff (Z) was 138 mmol  $M^+$ /100 g. The content of leached calcium at acid concentration 2 M, in mmol  $M^+$ /100 g, was 115 mmol  $M^+$ /100 g. Based on these results it can be concluded that the calcium leached out originated mainly from exchangeable positions. The exchangeable cations  $Na^+$  and  $K^+$  demonstrated similar behavior during the acid treatment. The higher amount of leached  $Mg^{2+}$  appears partially from the volcanic glass.

#### *X-Ray powder diffraction*

The XRPD pattern in Fig. 2 shows the low crystallinity of the raw zeolitic tuff. Significant structural modification of the zeolitic tuff samples occurs during acid treatment which can also be seen in Fig. 2.

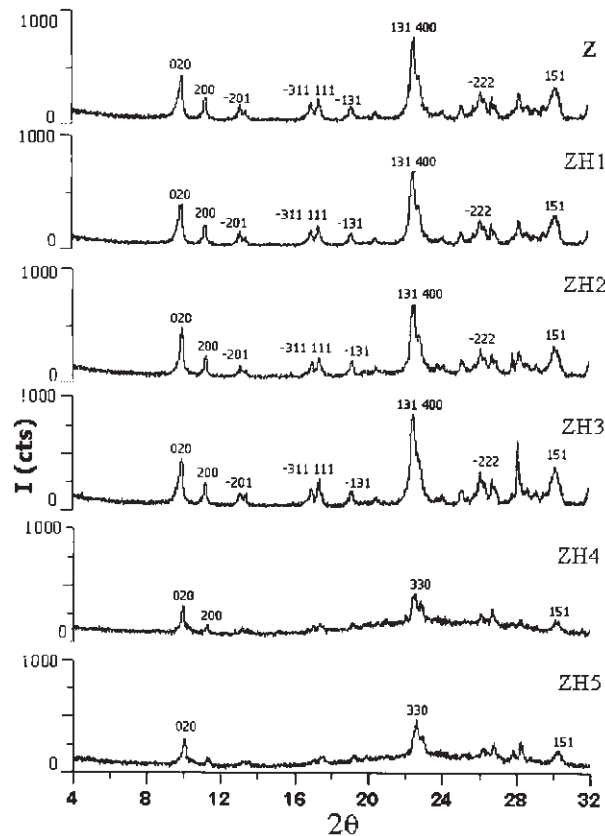


Fig. 2. X-Ray diffraction patterns of clinoptilolite-Ca and acid modified zeolitic samples.

The acid treatment using concentrations between  $10^{-3}$  M and  $10^{-1}$  M does not have any effect on the crystallinity, samples ZH1, ZH2 and ZH3. However, samples treated with higher acid concentrations (1 M to 2 M), showed a decrease in the intensity of the lines. The broad low baseline indicates transformation of the

HEU-type zeolite into an amorphous phase. After the acid treatment with 2 M acid (ZH5), the clinoptilolite lines ( $d_{020}$ ,  $d_{200}$ ,  $d_{330}$ ) were still present but their intensities were very weak (Fig. 2).

The unit-cell parameters of raw zeolitic tuff and the acid treated zeolitic tuffs are presented in Table III.

TABLE III. The unit-cell parameters of clinoptilolite-Ca and acid modified zeolitic samples

Samples	$a/\text{nm}$	$b/\text{nm}$	$c/\text{nm}$	$\beta/^\circ$	$V/\text{nm}^3$
Z	1.76674(4)	1.79046(4)	0.74263(4)	116.48(6)	2.101
ZH1	1.76772(4)	1.79224(4)	0.74245(5)	116.46(6)	2.105
ZH2	1.76748(3)	1.79158(3)	0.74204(3)	116.44(5)	2.103
ZH3	1.76486(4)	1.78775(4)	0.74335(4)	116.46(5)	2.095
ZH4	1.76005(4)	1.78536(3)	0.74058(4)	116.58(3)	2.081
ZH5	1.75712(3)	1.77661(3)	0.74212(4)	116.34(3)	2.075

The calculated unit-cell parameters of the ZH1, ZH2, and ZH3 samples do not show significant changes in comparison with the unit-cell parameters of raw zeolitic tuff (Z). With increasing acid concentration (1 M to 2 M), changes of the unit-cell parameters were significant and the values of parameters  $a$ , and  $b$  decreased. The changes of the unit-cell parameters of these samples (ZH4 and ZH5) point to a tension in the clinoptilolite framework (movement of the tetrahedral coordinated aluminum in the clinoptilolite framework<sup>15</sup>). It may be concluded that extraction of lattice aluminum and eventually its partial replacement by silicon probably occurred since the unit-cell contraction is related to the shorter length of Si–O–Si bonds with respect to those of O–Al–O.

The microstructural parameters (crystallite size) determined by X-ray powder diffraction analysis for all the acid modified samples are presented in Table IV.

TABLE IV. Micro-structural parameters of the acid treated samples

Samples	$D_s/\text{nm}$	$D_v/\text{nm}$
ZH1	80.1	72.3
ZH2	69.0	72.0
ZH3	17.8	15.6
ZH4	5.0	9.9
ZH5	5.8	11.9

Note:  $D_s$  – crystallite sizes obtained from the surface;  $D_v$  – crystallite sizes obtained from the bulk

The results for the microstructural parameters show that the process of amorphization is particularly apparent in the ZH4 and ZH5 acid treated zeolitic samples (Table IV). The crystallinity of these samples decreased by approximately 60 – 70 %.

Dealumination and changes of the structure of the sample treated with 2 M acid can also be discussed using IR-spectroscopy. The IR-spectrum of the acid treated sample ZH5 were compared with the IR-spectrum of raw zeolitic tuff (Z), both spectra are presented in Fig. 3.

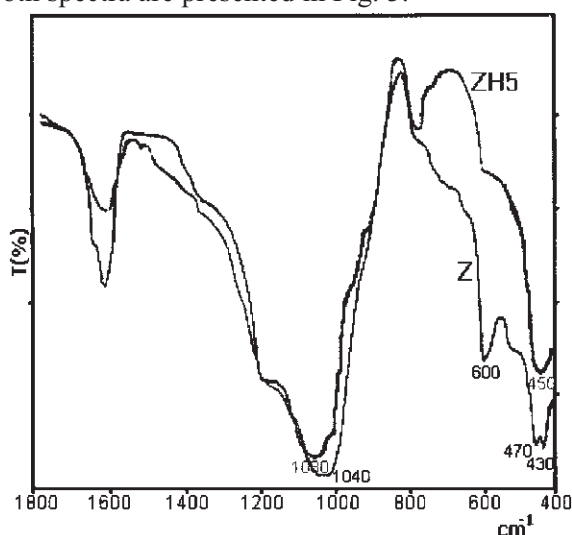


Fig. 3. IR-Spectra of raw zeolitic tuff (Z) and the acid modified zeolitic sample (ZH5).

The IR-spectrum of the acid treated sample (ZH5) showed marked changes of all vibration bands (Fig. 3). The absorption band of the framework vibrations of raw zeolitic tuff (Z) are at approximately  $\approx 1040 \text{ cm}^{-1}$  (asymmetric internal (Si, Al)-O stretching vibrations of the (Al, Si)-O<sub>4</sub> primary tetrahedral building units<sup>16</sup>). This vibrations mode was shifted towards higher frequencies ( $1080 \text{ cm}^{-1}$ ) in the spectrum of the acid treated sample. This results corresponds to a partial structural breakdown, accompanied by the process of dealumination.<sup>5</sup>

The band near  $600 \text{ cm}^{-1}$  disappeared after acid treatment which is also indicative of dealumination and breakage of Al-O bands inside the structure of zeolitic sample. The new absorption bands at approximately  $\approx 870 \text{ cm}^{-1}$  may indicate the presence of a semi-amorphous phase.<sup>5</sup>

#### CONCLUSION

Acid treatment of zeolitic tuff leads to exchange of inorganic cations at lower acid concentrations ( $10^{-3}$  to  $10^{-1}$  M), while at higher concentration this process is accompanied by dealumination of zeolitic tuff.

The intensity of the X-ray diffraction peaks decrease significantly with increasing acid concentration, indicating a loss of crystallinity of the zeolitic tuff. A significant reduction in the crystallinity of the HEU-type zeolite was affected only when the acid concentration was 1 M and higher. The changes of the unit-cell parameters of the samples treated with higher concentrations of acid and indicate tension in the clinoptilolite framework, which can be ascribed to movement of tetrahedral coordi-

nated aluminum. IR-Analysis confirmed the results of X-ray analyses, also indicating an amorphization of the acid treated zeolitic tuff from the Novakovici deposit.

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#### ИЗВОД

### ФИЗИЧКОХЕМИЈСКЕ И СТРУКТУРНЕ ОСОБИНЕ КИСЕЛИНСКИ МОДИФИКОВАНОГ ЗЕОЛИТСКОГ ТУФА (HEU-ТИП ЗЕОЛИТ)

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Узорци природног зеолита (HEU-типа) из лежишта Новаковићи – клиноптилолит-Са (у близини Приједора, Босна и Херцеговина), модификовани су различитим концентрацијама хлороводоничне киселине (од  $10^{-3}$  М до 2 М), а у циљу одређивања њихових физичкохемијских и структурних особина. За праћење структурних промена у киселински модификованим пробама, коришћене су следеће методе: хемијска анализа, рендген-дифракциона анализа праха, инфрацрвена спектроскопска анализа. Утврђено је присуство растворног јона алуминијума, при концентрацијама већим од  $10^{-1}$  М, што указује на процес деалуминације. Резултати добијени рендген-дифракционом анализом праха модификованих проба, указују да при већим концентрацијама од 1 М хлороводоничне киселине, долази до значајних структурних промена и смањења уређености кристалне структуре (60–70 %). Такође, резултати добијени инфрацрвеном спектроскопијом, потврдили су делимичну аморфизацију зеолитског туфа, која се дешава киселинском модификацијом при великим концентрацијама хлороводоничне киселине (> 1 М).

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