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ZEOLITE ACID (UN)STABILITY AS MAJOR DISANDVANTAGE FOR ITS HUMAN CONSUMPTION

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ABSTRACT – This study was conducted to examine the potential harmful effects of zeolite consumption in daily supplementation. The research focused on the acid stability of zeolite in HCl solution at pH values ranging from 1.5 to 3, corresponding to gastric pH levels. The initial zeolite sample, as well as the samples subjected to acidic treatment, were characterized using X-ray diffraction (XRD) method, and their chemical composition was analyzed. The results obtained indicate that the crystalline structure of zeolite was not disrupted during the treatment. At a pH of 1.5, up to 2% of aluminum leached into the solution, while at higher pH values, no aluminum leaching was observed. These findings underscore the need for cautious consideration of zeolite supplementation due to potential aluminum release in highly acidic environments.

Keywords: Acidic Stability, Dealumination, Zeolite.

INTRODUCTION

Zeolites are crystalline hydrated aluminosilicates that possess an infinite three-dimensional structure. The fundamental building unit of the crystalline structure of zeolites is the TO_4 tetrahedron (T represents silicon or aluminum) [1,2]. At the center of the TO_4 tetrahedron is either Si^{4+} or Al^{3+}, while at the tetrahedral corners are four oxygen atoms, each shared between two tetrahedra. This connectivity results in a zeolite structure rich in cavities, which contain large cations and water molecules that exhibit significant mobility, allowing for cation exchange and reversible dehydration. Due to the isomorphic substitution of tetravalent Si with trivalent Al, the aluminosilicate framework of zeolites is negatively charged [3,4]. This excess negative charge is balanced by the presence of alkali and alkaline earth metal cations, most commonly Na^+, K^+, Ca^{2+}, and Mg^{2+} which can be exchanged with other cations through ion-exchange reactions [1,3].

The sum of the equivalent positive charges of exchangeable cations equals the negative charge of the framework and is expressed as the cation exchange capacity (CEC)

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in mmol M^+/100g. The CEC depends on the degree of silicon substitution by aluminum, channel dimensions, shape, size, and valency of exchangeable cations [3,4].

Due to their negative charge and porous structure, natural zeolites find widespread applications as cation exchangers and molecular sieves. Their unique structural characteristics enable diverse applications [5-9]:

- Environmental science: Ammonia removal from municipal wastewater [5,6]; Removal of heavy metal ions from contaminated water [7-9]; Water softening [8]; Radioactive waste treatment [10]
- Agriculture: Soil remediation in agriculture [11].
- Healthcare: Medical applications for detoxification [12]; As feed additives for livestock [12]; Zeolites enriched with Cu and Zn micronutrients exhibit antibacterial properties against *Escherichia coli* and *Clostridium* species [13]; Ability to bind carcinogenic substances suggests potential applications in cancer therapy [14]
- Energy and industry: Catalysts and catalyst supports in energy and industrial processes [14].

Treatment of zeolites with mineral acids yields the acidic or H-form of zeolites. Clinoptilolite, characterized by a high Si/Al ratio (> 4), exhibits high acid stability. This enables the formation of H-clinoptilolite with a high ion-exchange capacity while preserving its crystalline structure. However, treatment with concentrated mineral acid solutions (pH = 0) can lead to structural modification or even significant degradation of the crystal lattice. Depending on the acid concentration, dealumination of the crystal framework occurs to varying degrees.

Barrer demonstrated that treatment of clinoptilolite with HCl at concentrations up to 2 mol dm^{-3} results in channel expansion, increased porosity, and enhanced specific surface area. Acid treatment leads to cation exchange with H_3O^+ ions, followed by hydrolysis of Al-O groups, releasing Al into the solution and removing H_3O^+ ions from clinoptilolite channels, ultimately yielding a structure with a large internal surface area. However, at HCl concentrations exceeding 2 mol dm^{-3}, structural degradation becomes significant, with amorphization dominating and specific surface area decreasing.

Despite zeolite extensive industrial use, including applications in water purification, catalysis, and environmental remediation, the incorporation of zeolites into human dietary supplementation remains controversial. A key limitation lies in the presence of aluminum within the zeolite framework, and the potential for its release under acidic conditions-particularly in the human gastrointestinal tract.

Aluminum incorporated in the zeolitic structure is generally considered stable under neutral or mildly acidic conditions; however, exposure to strong acids, may lead to partial degradation of the framework and subsequent aluminum leaching. This phenomenon raises significant safety concerns, especially considering the lack of comprehensive toxicological and clinical studies evaluating the long-term effects of zeolite consumption in humans.

Aluminum is a naturally occurring element found in soil, water, and air. Humans are routinely exposed to small quantities through dietary intake, drinking water, and the use of cosmetic and pharmaceutical products. In recent years, increasing public and scientific

attention has been directed toward reducing aluminum exposure, particularly due to its potential neurotoxic and osteotoxic effects.

Although the human body can eliminate small amounts of aluminum, chronic exposure or accumulation may lead to adverse health outcomes. Aluminum has a high affinity for biological tissues, particularly in the brain and skeletal system. While still under investigation, several studies suggest a possible link between excessive aluminum accumulation and the pathogenesis of Alzheimer's disease and other neurodegenerative conditions [15]. Furthermore, chronic aluminum intake has been shown to interfere with calcium and phosphorus metabolism, potentially leading to bone demineralization and the development of osteomalacia-especially in individuals with impaired renal function [16].

Given these concerns, the aim of this study is to evaluate the stability of the zeolitic framework in acidic gastric conditions and quantify the potential release of aluminum ions under simulated stomach pH conditions (1.5 - 3). Understanding the extent of aluminum leaching from zeolite structures under physiologically relevant conditions is essential for assessing their safety and suitability for human consumption.

EXPERIMENTAL

Raw zeolite, clinoptilolite (Z) from the Igroš deposit in Serbia was used as an absorbent. After crushing and grinding, the sample was sieved to the fractions below 0.043 mm-optimal for the zeolite characterization (XRD, DTA) and investigations of maximum adsorption capacity.

Acid treatment of zeolite was carried out in a batch system. A total of 8 g of zeolite was treated with 200 ml of HCl solution, with initial pH values of 1.5, 2.0, 2.5, and 3.0. After shaking for 24 h on orbital shaker, all suspensions were centrifuged and the concentrations of the Al in supernatants were determined using AAS.

The total CEC of the zeolitic tuff was 135.2 meq/100 g, measured using 1 M NH 4 Cl (Sigma Aldrich, Munich, Germany). Calcium (97.3 meq/100 g) was the dominant exchangeable ion but Na (21 meq/100 g), Mg (16.4 meq/100 g), and K (0.37 meq/ 100 g) were also present in the starting zeolitic tuff.

RESULTS AND DISCUSSION

Due to the large number of figures and limited space, only figures for the zeolite Z and Z 1.5 (treated with HCl on pH 1.5) will be presented.

Qualitative mineralogical composition of the analysed sample is as follows: zeolite minerals of heulandite/clinoptilolite type, plagioclases, quartz, mica and irregular interstratified clays. Among these, zeolite minerals are the most predominant, while all the other minerals are much less represented. Crystallinity degree of zeolite minerals is low. Measured average crystallite size of zeolite minerals is 276 Å. All other crystal phases are below detection limits. Diffractogram of the "Z-Ig" sample is given in the Figure 1.

Qualitative mineralogical composition of the analysed sample is the same as in previous sample. No crystal structure disorder (amorphization) has been determined due to acidic treatment. Diffractogram of the "Z-Ig 1.5" sample is given in the Figure 2.

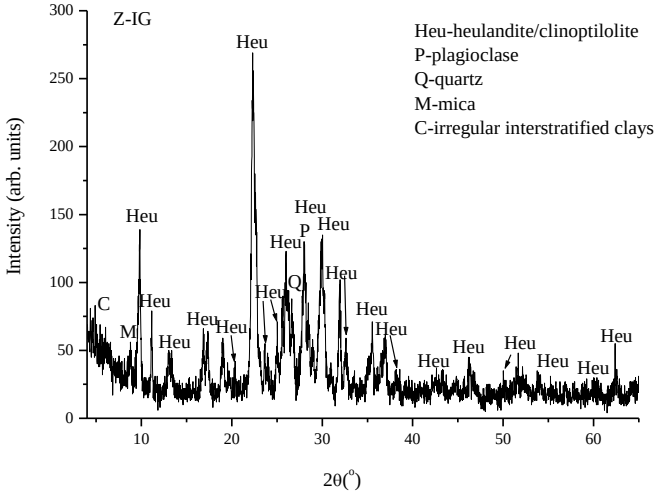

Figure 1 XRD diffractogram of the "Z-Ig" sample.

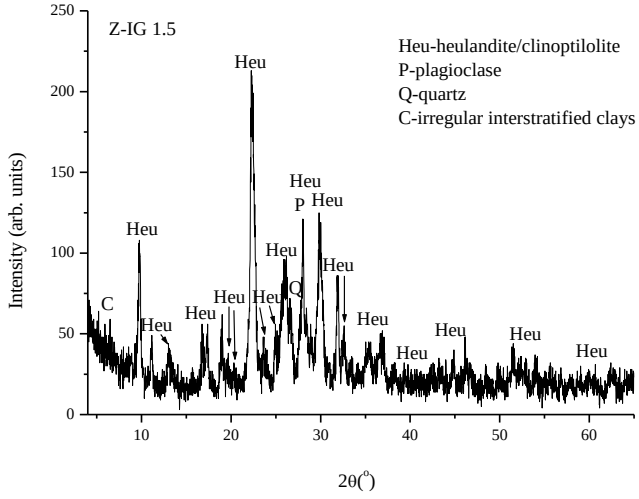

Figure 2 XRD diffractogram of the "Z-Ig 1.5" sample.

Chemical composition of the initial and acidly treated zeolites is presented in Table 1. The obtained results are similar to the XRD one, indicating that there are no significant differences in chemical composition between the samples, indicating that the investigated pH range does not destroy the zeolite structure. Only with the pH 1.5 is noticed the slightly difference in Al content.

Table 1 Chemical composition of the initial and acidly treated zeolites

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	IL
	%							
Z	64.8	15.1	1.47	4.19	1.60	1.16	0.85	10.62
Z 1.5	65.4	14.91	1.53	3.91	1.59	0.91	0.81	10.66
Z 2.0	65.1	15.01	1.50	4.06	1.60	0.96	0.83	10.62
Z 2.5	64.9	15.04	1.45	4.06	1.61	1.06	0.84	10.63
Z 3.0	64.8	15.04	1.44	4.20	1.60	1.10	0.85	10.64

The content of the aluminium is also measured in supernatants and the results are presented in Table 2. The obtained results indicate that at a pH value of 1.5, aluminum leaching did occur. The total amount measured in the solution is 108 mg/L. The initial aluminum content in the zeolite is 15.1%, which implies that its maximum potential leaching amount from 8 g of zeolite could reach 6040 mg/L. Considering this, it can be concluded that less than 2% of aluminum transitioned into the solution, which is why there was no disruption of the crystal lattice of the zeolite.

Table 2 Chemical composition of the supernatants after acid treatment

	Al	Si	Na	K	Ca	Mg	Fe
	mg/L						
F-1.5	108.75	21.6	82.12	4.63	147.5	26.75	3.38
F-2.0	6.1	13.3	47.25	2.08	88.75	12.38	0.13
F-2.5	0.5	10.9	25.12	0.93	27.5	5.06	0.10
F-3.0	2.3	15.6	15.50	0.77	10.0	1.93	0.62

However, it is important to mention that according to joint FAO/WHO Expert Committee on Food Additives, the maximum allowable daily intake of aluminum for humans is 10 mg. This is the amount a healthy individual weighing 70 kg can ingest without the body being unable to effectively eliminate the aluminum. With a daily intake of just 1 g of zeolite through supplementation, an individual would consume 25 - 30% of the maximum permitted aluminum intake, which does not exceed the recommended allowance, but is not negligible-especially if such intake is repeated multiple times a day or combined with other sources of aluminum (diet, medications, etc.).

CONCLUSION

In the conclusion of this study, it has been established that zeolite maintains its acid stability within the pH range characteristic of the stomach, which is between 1.5 and 3, without significant disruption of its crystalline structure. However, at a pH of 1.5, it has been observed that up to 2% of the total aluminum present in zeolite passes into solution. Taking into account a daily intake of just 1 g of zeolite through supplementation, an individual would consume between 25% and 30% of the maximum permitted aluminum intake, which, while not exceeding the recommended limits, represents a significant amount-especially in the context of frequent intake throughout the day or in

combination with other sources of aluminum. At higher pH values, the amount of aluminum leached from zeolite becomes negligible. These results underscore the need for careful consideration of potential aluminum intake when using zeolite as a supplement, particularly in the context of long-term consumption.

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