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Physical and mineral characterisation of natural zeolites from Taiz, South-western Yemen

N.A.S. Al Muhammadi and A. Hussin*

Geology Program, Faculty of Science and Technology, Universiti Kebangsaan Malaysia, 43600, Bangi, Malaysia

***Corresponding Author Email :** haqqim@ukm.edu.my

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Abstract

Aim: To investigate the physical, minerals and geochemical composition of Taiz natural zeolites.

Methodology: Each zeolite sample were assessed for its characterization via optical microscopy, X-ray Diffraction (XRD) techniques, X-ray Fluorescence Methods (XRF), Inductively Coupled Plasma- Optical Emission Spectrometry (ICP-OES) to examine their mineral composition and geochemistry properties. Further, physical properties like pH, electrical conductivity (EC), plasticity, specific surface area, water content and brightness were estimated by standard methods

Results: Natural zeolite in the studied area occurs within pyroclast of volcanic tuffs. It consists mainly of perlite and rhyolite as lenses grey to light green in color with fine granulation texture. Petrography analysis showed that the Taiz zeolites are mainly classified as clinoptilolite – heulandite and are mixed with various types of others zeolite minerals such as analcime, chabazite and mazzite. Small amounts of impurities like K-.feldspar (orthoclase) and clay mineral such as montmorillonite, kaolinite and illite were also detected. The mean ratio of SiO_2:Al_2O_3 for representative zeolite sample from the study area ranged between of 6.34-6.98.

Interpretation: Zeolites showed fairly medium to high brightness and on comparing with the commercial zeolites, Taiz zeolite showed significant industrial potential to be used as a filler in paper industry.

Key words: Clinoptilolite, Geochemistry, Mineralogy, Taiz, Zeolite

Mineral and physical characterisation of natural zeolites from Taiz, South-western Yemen

12 Representative zeolite samples from Taaiz were tested for
- Physical characterizations (pH, electrical conductivity, brightness, plasticity, specific surface are and water content) and
- Mineral composition (Petrography and XRD analysis)
- Geochemistry (XRF analysis dan ICP-OES)

Physical characterization
- Zeolite from Taiz appear as light - green in colour
- Fine granulation in texture
- Higher brightness
- Low water content

Mineral composition
- Zeolite from Taiz compose of clinoptilolite heulandite as major compositions
- Analcime, Chabazite and mazzite as minor composition
- Impurities<1%

Geochemistry composition
- Slightly alkaline
- Higher content of SiO_2 (71.29%), Al_2O_3 (10.49%), K_2O (1.73%), CaO (3.49%), Na_2O (1.21%) and MgO (0.97%)

Taiz zeolite has significant potential for industrial application such as filler in paper industry.

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Introduction

Zeolite is a natural occurring minerals that are commonly used as commercial ion exchangers, functioning adsorbent and also as a separator in several chemical industries. The unique property of zeolite is that its industrial usage relies on few physico-chemical characteristics such as micro-porous structure, cation mobility and their hydrophilic/ hydrophobic surface (Xu *et al.*, 2007). Historically, zeolite has received its name from the Greek word zeo and lithos meaning "boiling stone" (Mumpton, 1978) and since the discovery of zeolites till this day, the interest in scientific research and use of this profound material has grown immensely (Margeta and Farkas, 2020). Today, deposit of tuffaceous sedimentary rocks containing millions tons of zeolites have been identified in more than 40 countries (Mgbemere *et al*., 2017; Mumpton, 1981). The zeolites structure may, therefore, be divided into three components – the aluminosilicate framework; interconnected void spaces in the framework, containing metal captions, and water molecules present as an occluded phase (Flanigen, 1977).

Theoretically, the possibilities for framework topologies are infinite – around 40 occur in nature and more than 150 synthetic zeolites have been manufactured (Clifton, 1987; Flanigen, 1977; Ma *et al*., 2000). Zeolites have been described as constituting "what is probably the most variable and extensive family of minerals occurring in the earth's crust". Zeolitization involves diffusion-controlled hydration, mainly of volcanic glass and alkali ion exchange procedure (Chmielewská, 2012). The specific type formed depends on the composition of original rock, temperature, pressure, partial pressure of water and activity of certain ions (Hay, 1977). Hay (1977) defined six different geological environments related to zeolites that are saline alkaline lakes, soils and land surfaces, deep-sea sediments, open hydrological systems, zone of hydrothermal alteration and metamorphism deposits.

Significant zeolite deposits are widespread in the Western Yemen in Taiz, Ibb and Dhamar area and are of great interest because of their abundance and potential economic value (Alshameri et al 2014; Veseloy, 1990; Strojexport, 1977). Most of the Yemen zeolites are connected with tertiary and quaternary altered volcanic tuff, which cover more than 60,000 km^2 of the western part. Yemen zeolitic rocks are characterized by light colors (white, grey, green and yellowish) and significantly showed fine grained textures (Grafisk, 2009). The natural composition of zeolites consists of clinoptilolite–heulandites, mordinite, stilbite, laumonotite and natrolite, with percentage varying from 14-85% (Al Hawbani and Maky, 2018; Geomine, 1985). Pumice and perlite fragments are also found in natural zeolite.

Alshameri *et al.* (2019) demonstrated the mineral and chemical composition of natural zeolitic-rich tuff from Yemen (Al-Ahyuq area) and concluded that the natural zeolite of Al- Ahyuq area seems to be more viable for use in environmental applications. They revealed the role of Al-Ahyuq zeolite as an effective adsorbent for ammonium and phosphate removal in water treatment. Their results show that the purities of zeolite minerals from Al Ahyuq ranged between 78 to ~100% and they found that the chemical compositions of Al-Ahyuq zeolitic tuffs are comparable with other zeolites composition of high economic value in the world and potentially viable for other industrial applications.

In view of the above, the aim of the study was to investigate the physical, mineral and geochemical composition of Taiz natural zeolites.

Materials and Methods

For this study, twelve representative samples (1-2 kg each) were collected from the natural zeolite deposits in Wadi Mukasab, Taiz, which is located in the South western part of Yemen .Each sample was quartered into ½ kg specimens for estimating the physical, mineral and also geochemical properties. Physical properties of Taiz zeolites such as pH, electrical conductivity, plasticity, specific surface area, water content and brightness were estimated following the standard methods outlined by Reeuwijk (2002). Mineral composition of zeolites was determined by optical microscopy and X-ray diffraction (XRD) techniques. Geochemical variations of zeolite were evaluated by X-ray fluorescence where composition of minor and trace elements were determined by Inductively Coupled Plasma–Optical Emission Spectrometry (ICP-OES).

Results and Discussion

Natural zeolite present in the study area occurs within the pyroclast of volcanic tuffs. It mainly consists of perlite and rhyolite as lenses, are grey to light green in color with fine granulated

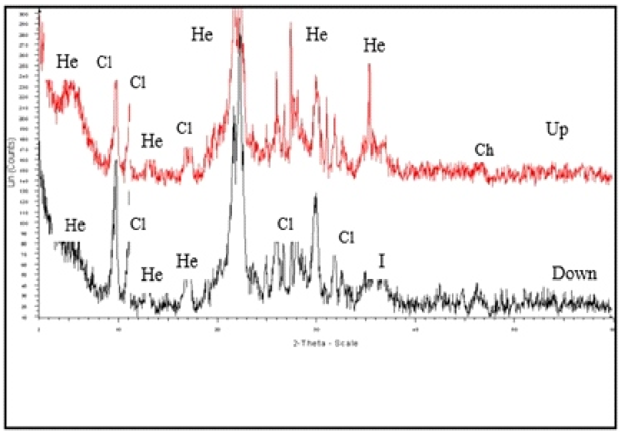

Fig. 1 : X-ray diffraction pattern of Taiz Zeolite (He: heulandite; Cl: clinoptilolite; Ch: chlorite and I: illite)

Table 1 : Physical parameteres of Taiz zeolite

Samples	pH	EC (μ_s)	BR	SSA (m^2g^{-1})	LL	PL	PI	W.C (%)
Z1U	7.9	127.5	91.9	0.21				
Z2U	7.9	113.6	89.9	0.47	1.02	1.0	0.02	6.5
Z3U	7.8	93.2	73.4	0.06				
ZD1	7.1	94.5	89.9	0.02	0.97	0.9	0.7	5.6
ZD2	7.3	103.2	95.8	4.40				
ZD3	7.5	118.1	66.8	5.60				

texture and highly weathered. In field, perlite appeared more lighter in color as compared to rhyolite. Taiz zeolite appeared as decimetric layers making up the banks of 10-20 m thickness with dipping 10-15^0 to the Northwest. The volcanic tuff of this zone was covered with russet tuff of rhyolite and also small beds of volcanic glass (perlite are found between tuff and rhyolite rocks.

The physical properties of zeolite viz pH, electrical conductivity, brightness, plasticity index and water content are presented in Table 1. The perusal of data revealed that Taiz zeolite were mild alkaline in nature, exhibited semiconductor property and were highly bright with low water content. These properties of Taiz zeolite were comparatively at par with the properties of commercial zeolite that are sold with the trade names of "SGW" and "HiZ" (Table 2) . SGW and HiZ commercial zeolite are used as fillers for groundwood and wood-free paper (Hubbe and Gill, 2016).

Fig. 1 shows X-ray diffraction pattern of the representative sample of Taiz zeolites. The mineral composition of Taiz zeolite consists clinoptilolite-heulandites (>50%), with varying amounts of other minerals like mordanite, analcime, montmorrilonite, orthoclase and quartz (Table 3). Montmorillonite, kaolinite, illite, mica, orthoclase, quartz and minor amount of heavy minerals (< 1%) are impurities present in Taiz zeolite.

Table 2 : Selected physical properties of Taiz zeolite as compared to commercial zeolite of SGW and HiZ.

Parameter	Taiz zeolite*	HiZ†	SGW*
Brightness (%)	84.61	84.2	78.5
Water content (%)	6.0	6.9	5.0
pH	7.6	4.5	9.6

*Hubbe and Gill (2016).

Table 3 : Mineral composition (%) of Taiz zeolite as retrieved by XRD and optical microscope evaluation.

Minerals	Composition (%)
Clinoptilolite	55
Mordanite	20
Analcime	10
Montmorrilonite	5
Orthoclase	5
Quartz	5

Results relating to the geochemical properties as revealed by X-ray Fluorescence Methods are given in Table 4. The data is represented an average value from two analysis. The results showed that the zeolite have higher content (wt.%) of SiO_2 and Al_2O_3 compared to other elements. An average geochemical composition of Taiz is 71.29 wt.% SiO_2, 10.49 wt.% Al_2O_3, 1.73 wt.% K_2O, 3.49 wt.% CaO, 1.21 wt.% Na_2O and 0.97 wt.% MgO. The chemical composition of Taiz zeolite reflects considerable difference in the amount of iron, magnesium and titanium oxides. Considerably, those oxides are related to the impurities minerals that associated with zeolite. Iron and titanium oxides have detected to be composed in range of less than 5%. This situation indicates that additional beneficiation treatment with magnetic separator would not be necessary.

Comparatively, the geochemical composition of zeolite in this research were found to be comparable with previous reports (Alshameri *et al.*, 2019; JMayai *et al.,* 2018; Shaban and Abu Khadra, 2017). The mean ratio of SiO_2:Al_2O_3 for representative zeolite sample from the studied area is in the range of 6.34-6.98. This ratio is significantly close to the ratio value of commercial zeolite (4.25-5.25) from various deposits. However, things would be different in case of trace elements variation. The results showed considerable variation in the minor and trace elements of Co, Ni, Cu, Zn, Pb, V, As, Br, Rb, Sr, Zr, Ba and Ce (Table 5). The concentration of these elements can be attributed to variation in activities of the ions in the hydrothermal fluids at the time crystallization of mineral phases and it also reflect a volcanic exhalative origin.

Table 6 shows geochemical composition of Taiz zeolite and some commercial deposits reported by Tsitsishvili *et al.* (1991). Tsitsishvili determined major and minor elements of the commercial deposits through X-Ray Fluorescence technique. These commercial deposits are considered to be among the best types of natural zeolites in the world, and they are used in a

Table 4 : Major elements (%) and loss on ignition of zeolites from Taiz, Yemen

Elements wt.%	Z1U	Z2U	Z3U	Z1D	Z2D	Z3D
SiO_2	70.31	72.31	71.80	71.33	71.59	70.41
TiO_2	0.31	0.03	0.30	0.30	0.30	0.31
Al_2O_3	10.63	10.41	9.87	10.65	10.26	11.11
Fe_2O_3	2.96	2.24	2.19	2.16	3.02	3.17
MnO	0.03	0.05	0.03	0.02	0.03	0.04
MgO	0.88	0.97	0.62	0.76	1.21	1.37
CaO	3.91	2.24	3.23	4.59	3.03	3.98
Na_2O	2.85	0.85	1.16	1.24	0.57	0.58
K_2O	1.35	2.06	2.54	1.3	1.34	1.81
P_2O_5	0.02	0.02	0.02	0.02	0.02	0.02
Total	93.25	91.18	91.76	92.35	91.37	92.8
SiO_2/Al_2O_3	6.61	6.95	7.28	6.69	6.98	6.34
LOI	7.23	9.32	9.03	8.25	9.25	7.77

LOI = Loss on Ignition

Table 5: Minor and trace elements ($\mu g\ l^{-1}$) of Taiz zeolite from Yemen

Elements ($\mu g\ l^{-1}$)	Z1U	Z2U	Z3U	Z1D	Z2D	Z3D
Co	3.67	0.77	1.97	0.79	2.37	0.83
Ni	3.55	2.98	4.03	2.30	3.86	1.90
Cu	30.22	13.34	97.57	20.07	1326.04	22.74
Zn	56.79	69.30	67.42	192.28	200.16	53.18
Pb	17.71	15.42	57.76	15.03	23.51	38.67
V	12.42	11.71	12.47	11.29	14.42	9.89
As	5.22	2.62	6.06	92.03	10.47	4.05
Br	30.87	26.77	15.40	29.38	31.05	32.51
Rb	6.03	6.28	1.23	8.42	8.98	7.23
Sr	45.25	65.15	18.97	30.86	42.44	51.23
Zr	74.34	40.89	3.25	84.71	47.37	42.92
Ba	6.99	7.45	4.85	7.17	7.69	7.615
Ce	70.50	83.80	49.07	67.58	76.82	73.05

Table 6: Geochemical analysis (%) of Taiz zeolite as compared to other commercial zeolite

	1	2	3	4	5	6	7	8	9	10
SiO_2	71.29	69.07	64.70	65.47	62.36	65.90	69.30	64.82	62.02	52.36
Al_2O_3	10.49	10.88	12.43	11.48	13.14	11.72	11.41	11.50	12.07	14.53
Fe_2O_3	2.63	0.08	0.44	0.61	1.63	0.71	0.38	1.19	1.15	4.53
MgO	0.97	0.18	0.34	1.46	0.92	0.88	0.45	1.02	1.17	1.70
CaO	3.49	0.39	1.26	2.04	2.72	3.35	2.70	3.40	4.41	6.71
Na_2O	1.21	4.23	4.32	3.50	3.99	3.10	1.59	0.58	0.36	0.66
K_2O	1.73	2.52	2.28	2.60	1.20	1.25	2.86	1.87	1.49	1.35

1: Taiz, Yemen; 2: Patagonia; 3: California; 4: USSR; 5: Georgia; 6: Azerbaijan; 7: Las Villas, Cuba; 8: China 9: SW, Bulgaria; 10: Camagüey, Cuba

variety of industrial applications such as heavy metal contaminated water treatment, wastewater treatment, gas drying, and a variety of other applications. Zeolites have been thoroughly researched and used as absorbents, ion exchangers, and acid catalysts in petrochemical and chemical companies (Chmielewska, 2012). High safety, low cost, and relative ease of application and operation are just a few of the benefits of using zeolite for environmental applications. Natural zeolite is used to remove ammonia and heavy metals such as cadmium, lead, zinc, copper, and partly chromium ions (Margeta and Farkas, 2020). Clinoptilolite, chabazite, mordenite, erionite, and phillipsite have high ability to absorb hydrogen sulphide, carbon dioxide and ammonia, while providing a deodorising effect (Menzi *et al.,* 2011). Many of these events occur as a result of the use of zeolites, and it is likely that zeolites have the ability to remove toxins such as ammonium, which occurs due to exchange with Na^+ , K^+ , Ca^{2+} , and Mg^{2+} (Ugal, Hassan and Ali, 2010).

In essence, zeolite acts as a molecular sieve, adsorbing, binding and immobilizing solid particles, liquids, and gases in its honeycomb structure. As a result, zeolite protect contaminants and toxins from entering sensitive habitats (Ma *et al*, 2002). Taiz natural zeolites, which are primarily composed of clinoptilolite heulandite have medium to high brightness and are mildly alkaline in nature (pH 7.6). In comparison to some commercial zeolites, Taiz zeolite has significant industrial potential for use as a low cost retention, aid pigment and filler in the paper manufacturing process.

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Add-on Information

Authors' contribution: N.A.S. Al Muhammadi: Designed the study, provided data for all aspects including preparing the manuscripts, **A. Hussin:** Participated in performing the mineral analysis, read and approved the draft.

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