Asian Journal of Chemistry Vol. 18, No. 2 (2006), 1405–1412

Evaluation of Gördes Zeolite Deposit of Turkey for Industrial Uses

AHMET MAHMUT KILIÇ and ÖZEN KILIÇ*
Mining Engineering Department, Faculty of Engineering and Architecture
Cukurova University, 01330, Adana, Turkey
Fax: (90)(322) 3386126; Tel: (90)(322)3386503; E-mail: zenkilic@cu.edu.tr

In this study, the Gördes natural zeolite deposits were characterized and assessed potentially in industrial uses. In the present work, chemical, mineralogical, physical properties (brightness, hardness, abrasive, bulk and dry density, specific gravity, apparent porosity, grain density, water and oil absorption, bleaching capacity of the original material, bleaching capacity of the activated material, specific surface area, pore diameter, void ratio, angle of repose), cation exchange capacity and thermal stability of zeolites were investigated. The sample presented fairly high specific surface area, porosity, adsorption and cation exchange capacity. Overall, it has been understood that the Gördes zeolite could be used for agricultural production, chemical binder, cat litter, animal feed and fertilizer, absorbents for gas purification, building materials, fillers, pool filter media and waste treatment.

Key Words: Natural zeolite, Clinoptilolite, Gördes, Industrial uses.

INTRODUCTION

Zeolite is a naturally occurring mineral that was formed when ash from volcanoes was deposited in alkaline/saline lakes millions of years ago. Over time, the interaction of the volcanic ash with the salts in the lake water altered the ash creating the mineral zeolite[1,2]. Zeolites are crystalline, microporous materials, hydrated alumina silicates of group 1 and 2 elements, a structure type typified by quartz, consisting of SiO_4 and AlO_4 tetrahedra linked by oxygen atoms to compose the framework[3,4]. In the zeolite framework, each aluminium atom introduces one negative charge on the framework which must be balanced by an exchangeable cation (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, etc.). The exchangeable cations located within the framework play a crucial role in adsorption and thermal properties of the zeolites.

Natural zeolites are clinoptilolite type, which are abundant in nature and an important clay mineral in sufficiently high purity in many parts of the world. It has a three-dimensional crystal structure and its typical unit cell formula is given either as $Na_6[(AlO_2)_6(SiO_2)_{30}]·24H_2O$ or $(Na_2, K_2, Ca, Mg)_3$ $[(AlO_2)_6$ $(SiO_2)_{30}]·24H_2O$[4–7]. Zeolite mineral species shall not be distinguished solely on the basis of the framework Si/Al ratio. Clinoptilolite is defined as the series with the same framework topology and Si/Al ≥ 4.0. Its framework structure consists of three channels. The channels A and B, 10-member and 8-member rings, respectively, are parallel to each other while the channel C, 8-member ring, intersects the channels A and B[4, 6]. Zeolites have channel and cage dimensions ranging between 0.2 and 2.0 nm[8]. Zeolite is an amazing crystalline mineral capable of adsorbing and absorbing many different types of gases, moisture, petrochemicals, heavy metals, low-level radioactive elements and a multitude of various solutions. The channels in the zeolite provide large surface areas on which chemical reactions can take place. The cavities and channels within the crystal could occupy up to 50% of its volume.

Only a few of the existing natural zeolites in the world are found in sufficient quantity and purity as required by industry. Within this group, silica-rich heulandite (clinoptiolite) and mordenite are the most important and play a significant role, due to their structural, ion exchange and sorption properties and also many other characteristics[3, 9, 10]. At present clinoptilolite is widely used in many fields of industrial technology, agricultural production, ecology, chemical binder, cat litter, animal feed and fertilizer, absorbents for gas purification, building materials, medicine and pharmacy. Furthermore, the wide availability of these low-cost materials can also favour the exploitation of their chemical properties in new applications[11, 12].

The present study provides the evaluation of characteristic properties of the Gördes zeolite deposit and their suitability for industrial uses. The results of laboratory research of chemical, mineralogical and physical properties of zeolite are presented in this paper.

EXPERIMENTAL

The natural zeolite samples used in the experiments were received from the Rota Mining and Agriculture and Trading Company in the Gördes region (Manisa, Turkey). Natural zeolites are abundant in Turkey; its total zeolite reserve is 4.5 billion tons[13]. The zeolites are of clinoptilolite type, which are abundant and of high purity in the Gördes.

In order to assess the chemical, mineralogical composition and physical properties of representative bulk samples have been studied. Evaluated physical properties are particle size, brightness, hardness, abrasive, bulk density, dry density, specific gravity, apparent porosity, grain density, water and oil absorption, bleaching capacity of the original material, bleaching capacity of the activated material, specific surface area, pore diameter, void ratio, angle of repose) and cation exchange capacity.

- XRF (Siemens SRS 300 X-ray fluoresience Spectrometer) was used to determine the chemical compositions of zeolite samples. The loss on ignition was determined by heating at 1000°C for 2 h.
- Transmitted light microscopy (Nikon, Optiphot-Pol) was carried out in

polished thin sections of zeolite in order to identify the texture, shape and size of the grains.

- X-ray diffraction (XRD) analysis of finely pulverized zeolite samples was measured for the identification of the presented crystalline compounds. The analysis was performed with a Shimadzu XRD-6000. The diffraction interval was between 2θ–20°–60° with a step of 0.02°.
- Mercury intrusion porosimetry (Autopore U 9220) was used to measure the microstructural characteristics of zeolite.
- Adsorption of nitrogen was performed on zeolite in order to evaluate the value of specific surface area, porosity and grain density by physical sorption isotherm data according to the method of Brunauer-Emmet Teller.
- SEM (Scanning Electron Mircoscopy) (JEOL 840 AJXA) was carried out on zeolites.
- EDS (Energy Dispersive Spectrometer) (IXRF-EDS2004) was examined for elemental analysis related energy dispersive (kV, 20.0; takeoff angle, 40°; elapsed live time, 30.0).
- Particle size distribution was determined by sieving.
- Mechanical properties (compressive strength and bending strength) were determined to be contingent with the quality of stone available and stringency of requirement (ASTM-373-56 and TS 699)[14].
- Water absorption values of zeolites were determined by the routine procedure involving boiling a previously prepared and fired briquette in a beaker of water and measuring the amount absorbed.

RESULTS AND DISCUSSION

The zeolite sample is white-beige in colour and cryptocrystalline in size and massive homogeneous in view. It was not any reaction with acid treatment.

Chemical analysis was carried out by XRF and chemical composition of the zeolites used in this study and presented in Table-1. This result showed that with an Si/Al ratio of 5.49 and $(Na + K) \geq Ca$, the zeolite is fine within the composition range of high-silica clinoptilolite.

The sample was homogenized and sieved before characterization and experimentation. The particle size of zeolite sample is 100% below 180 μm. As the fraction of size less than 75 μm is about 4% for the zeolite (Table-2), it was inferred that a reduction of particle size could be advantageous to get better performance. Then, the zeolite was ground to pass completely a 75 μm sieve. The physical properties of natural zeolite were determined and results were given in Table-3. The sample was presented fairly high specific surface area, porosity, adsorption, cation exchange capacity, light weight and good strength.

Thin section of the sample was investigated by petrographic polarizan microscope. The sample determined mainly consists of volcanic glassy material. Glass and rarely pumice fragments have altered secondary fine grained (aproximately 10 μm) crystals (Fig. 1).

TABLE-1
CHEMICAL COMPOSITION OF ZEOLITE

Component	Wt (%)
Loss on ignition	6.90
SiO_2	70.75
Al_2O_3	12.88
CaO	1.85
MgO	1.23
Fe_2O_3	1.81
K_2O	3.62
Na_2O	0.65
SO_3	0.13
TiO_2	0.10
MnO	< 0.01
P_2O_5	0.02
Total	99.95

TABLE-2
PARTICLE SIZE DISTRIBUTION OF ZEOLITE

Size range, μm	Wt (%)
>180	9.7
150–180	5.6
125–150	36.6
106–125	31.3
90–106	9.8
75–90	3.1
63–75	2.4
53–63	0.2
45–53	1.1
< 45	0.2

TABLE-3
PHYSICAL PROPERTIES OF ZEOLITE

Colour	Greyish white
Bulk density	1050 kg m^{-3}
Dry density	890 kg m^{-3}
Specific gravity	1350 kg m^{-3}
Appearence porosity	42.7%
Porosity	31.2%
Grain density	2.16 g/cc
Water absorption (grinding)	98%
Oil absorption	71 cm^3 oil/ 100 g
Whiteness	73%
Bleaching capacity of the original material	2.32 g sample/g tonsil
Bleaching capacity of the activated material	1.99 g sample/g tonsil
Cation exchange capacity	2.1 meq/100 g
Compressive strength	85 kgf cm^{-2}
Bending to strength	15 kgf cm^{-2}
Hardness	3.5 MOHs
Abrasive	20–37 g
Specific surface area	13900 cm^2/g
Pore diameter	4 Å (nm)
Void ratio	1.56
Angle of repose (°)	35
Water absorption as cat litter	50%
pH	7.3

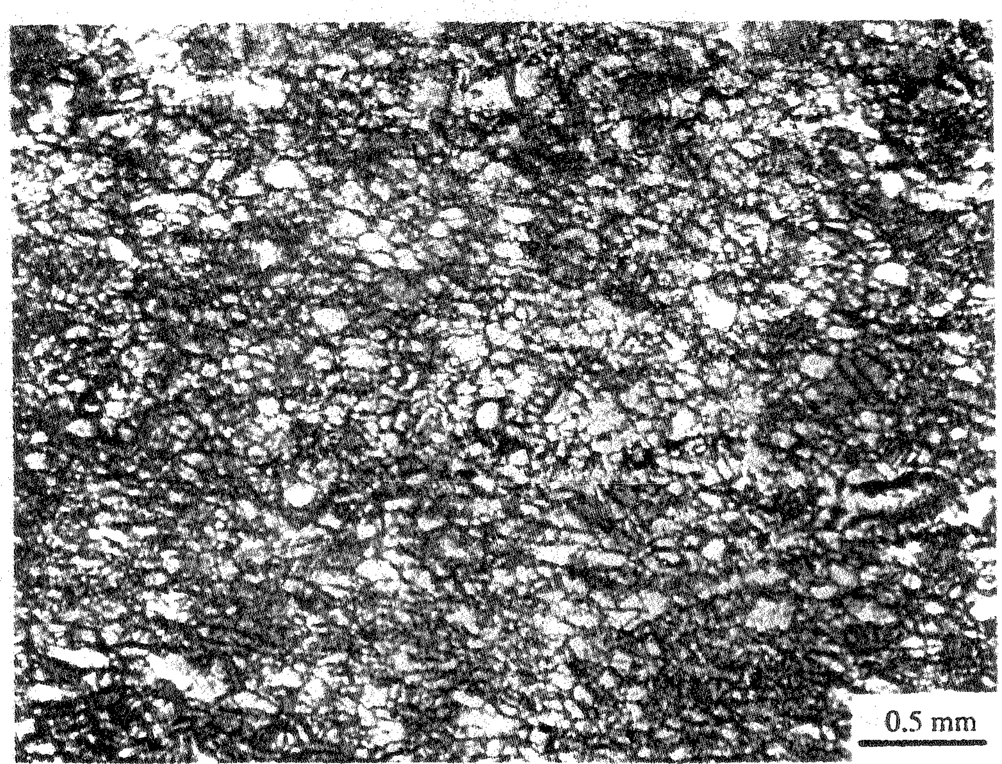


Fig. 1. Microphotographs of the zeolite sample

Mineralogical nature was found by X-ray diffraction analysis. It is seen that quantitative clinoptilolite content (by volume) was determined as 95%, feldspar 0–5% and clay, mica *et al.* 0–5% by volume. SEM of zeolite and X-ray powder diffraction studies indicates that this is almost pure clinoptilolite. In general, the monoclinic nature of clinoptilolite is easily recognized in the scanning electron microscope (Fig. 2). On the other hand, clinoptilolite in this sample is K-and Ca-rich type. This cationic parameter is K + Na > Ca + Mg and thermal stability is high according to spacing of d: 5.10 Å and d: 5.25 Å of this material.

The relationships between phase morphologies of the sample which are

Fig. 2. SEM images of monoclinic nature of clinoptilolite

observed at the SEM indicate that tabular/prismatic, unhedral crystal shapes and very fine (1–5 μm) clinoptilolite crystals are formed by the alteration of volcanic glass and feldspar minerals in the original volcanic rock (tuff, probably a crystal or vitric tuff) (Figs. 3, 4).

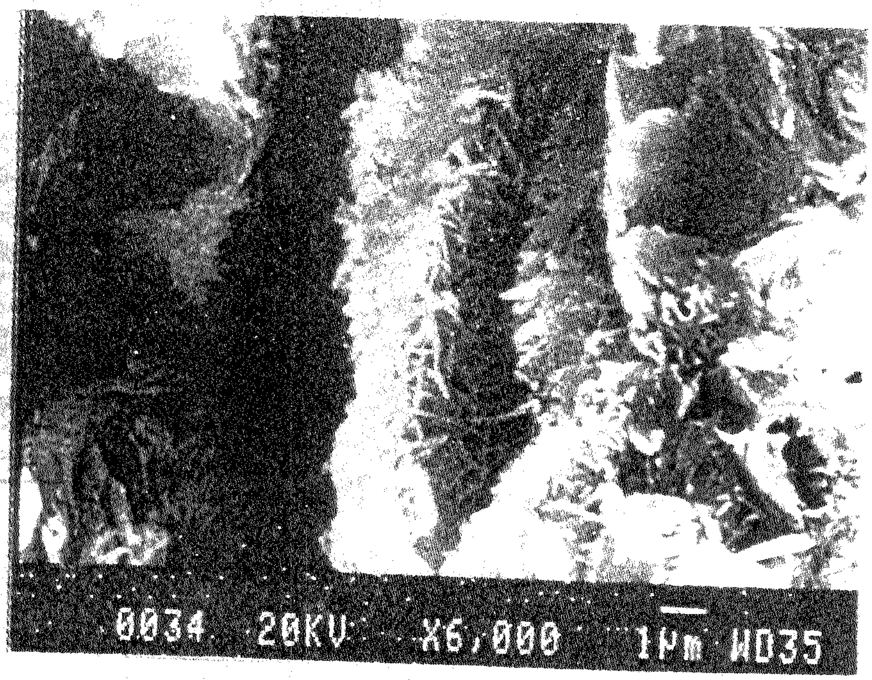


Fig. 3. SEM image of the volcanic glass phases with original framework preserved but totally transformed into small, tabular clinoptilolite type zeolite minerals

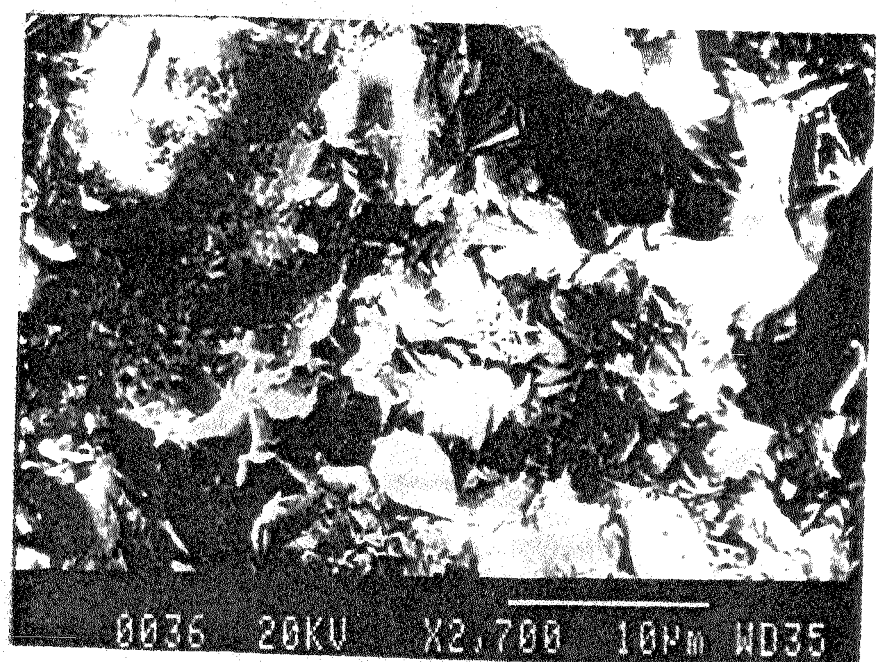
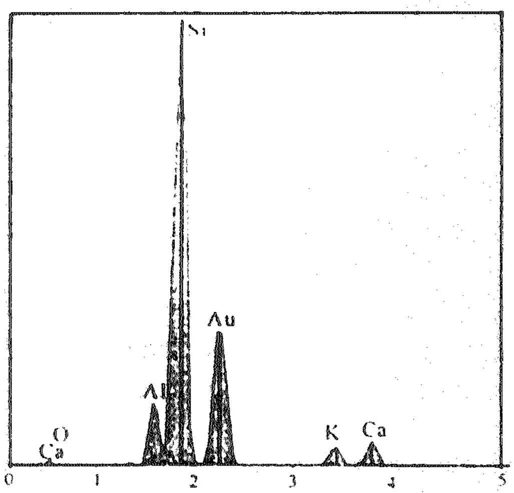


Fig. 4. SEM image of the feldspar mineral phases with original crystal framework preserved but totally transformed into small, tabular clinoptilolite type zeolite minerals

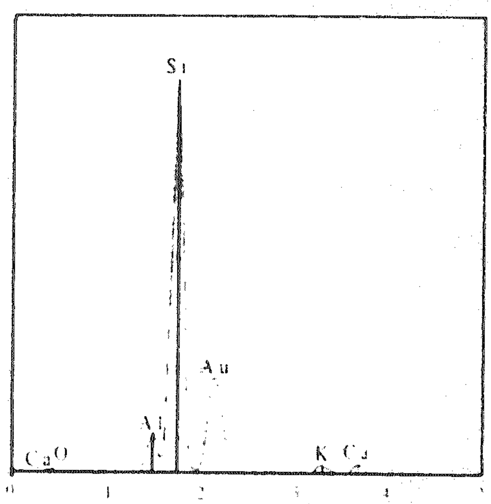
Elemental analyses of the EDS system indicate that clinoptilolite minerals in the sample are composed mainly of silica, aluminum, calcium and potassium (Fig. 5 and Fig. 6). The detected Au peaks at the EDS spectrum come from sample coating material.



Component	Wt%
Al_2O_3	28.80
SiO_2	57.23
K_2O	4.42
CaO	9.54
Total	100.0

Elt.	Line	Intensity (c/s)	Error 2-sig	Wt%
O	Ka	5.16	0.830	47.511
Al	Ka	211.06	5.304	15.243
Si	Ka	1563.13	14.436	26.752
K	Ka	75.70	3.177	3.670
Ca	Ka	89.27	3.450	6.824

Fig. 5. Semi-quantitative microanalysis (EDS) spectrum which is taken from general image area of the clinoptilolite



Component	Wt%
Al_2O_3	28.76
SiO_2	57.64
K_2O	4.23
CaO	9.36
Total	100.0

Elt.	Line	Intensity (c/s)	Error 2-sig	Wt%
O	Ka	5.64	0.867	47.626
Al	Ka	174.98	4.830	15.221
Si	Ka	1644.13	14.807	26.944
K	Ka	43.27	2.402	3.516
Ca	Ka	53.07	2.660	6.692

Fig. 6. Semi-quantitative microanalysis (EDS) spectrum which is taken from a point of the clinoptilolite

Scanning electron micrographs of tuff from Gördes, Manisa and X-ray powder diffraction studies indicate that this is almost pure clinoptilolite.

The cation exchange capacity of zeolite used in this study was calculated as 2.1 meq/100 g. Bleaching capacity of the original material and bleaching capacity of the activated material (at 800°C) were determined 2.32 g sample/g tonsil, 1.99 g sample/g tonsil, respectively.

Conclusion

This work shows the physical, mineralogical and physico-chemical data of a Gördes natural zeolitic-rich tuff sample, composed mainly by clinoptilolite. The sample was presented fairly high specific surface area, porosity, adsorption, cation exchange capacity, light weight and good strength. Due to its structure and properties, zeolite may be used as a slow releasing carrier of agrochemicals of various kinds: fertilizers, pharmaceutically and biochemically effective compounds for veterinary pharmacy and also disinfectants. Natural zeolites are effective in improving soil properties and treatment of contaminated soil. Natural zeolite of the clinoptilolite type is also suitable—in low doses—as a feed additive. It could also be used for agricultural production as a chemical binder, cat litter, animal feed, fertilizer, absorbent for gas purification, building material, filler, pool filter media and for waste treatment.

As the contemporary area of practical uses of zeolites may seem, the search for other application possibilities is still going on. Zeolite is a cheap raw material and its utilization leads to considerable savings in the usage fields.

REFERENCES

1. F.A. Mumpton, in: L.B. Sands and F.A. Mumpton (Eds.), Natural Zeolites: Occurrence, Properties and Uses, Pergamon Press, Oxford, p. 3 (1978).
2. E.R. Allen and D.W. Ming, in: D.W. Ming and F.A. Mumpton (Eds.), Natural Zeolites' 93: Occurrence, Properties, Uses, Int. Comm. Natural Zeolites, Brocport, p. 505 (1995).
3. K.D. Mondale, R.M. Carland and F.F. Aplan, *Minerals Engineering*, **8**, 535 (1995).
4. D.W. Breck, Zeolite Molecular Sieves, Wiley, New York (1974).
5. G.M. Haggerty and R.S. Bowman, *Environ. Sci. Technol.*, **28**, 452 (1994).
6. R.M. Barer, Zeolites and Clay Minerals as Sorbent and Molecular Sieves, Academic Press, New York (1987).
7. S.M. Auebach, K.A. Corrado and P.K. Dutta, Handbook of Zeolite Science and Technology, Marcel-Dekker Book News Inc., Portland, OR, p. 928 (2003).
8. E.C. Moloy, L.P. Davila, J.F. Shackelford and A. Navrotsky, *Microporous and Mesoporous Materials*, **54**, 1 (2002).
9. R.W. Tschemich, Zeolites of the World, Geoscience Press, Phoenix (1992).
10. C. Colella, Application of Natural Zeolites, Handbook of Porous Solids, Vol. 2, pp. 1156–89 (2002).
11. T. Armbruster, Clinoptilolite-heulandite: Applications and Basic Research, in: A. Galarnau, F. Di Renzo, F. Faujula and J. Vedrine, (Eds.), Studies in Surface Science and Catalysis 135, Zeolites and Mesoporous Materials at the Dawn of the 21th Century, Elsevier, New York, pp. 13–27 (2001).
12. A.H. Englert and J. Rubio, *Int. J. Miner. Process.*, **75**, 21 (2005).
13. E. Sabah and M.S. Çelik, Sepiolite: Occurrence, Properties, Uses, Radar Press, Konya (1998) (in Turkish).
14. TS 699, Methods of Testing for Natural Building Stones, TSE, Ankara (1987) (in Turkish).

(*Received*: 17 August 2005; *Accepted*: 31 December 2005) AJC-4583