

Evaluation of Jordanian faujasite tuff by comparison with other natural and synthetic zeolites

Khalil M. Ibrahim

Abstract The evaluation of the Jordanian faujasite tuff in wastewater treatment is investigated by comparison with synthetic faujasite (13X) and clinoptilolite-rich tuff. The material used (JORD-FAUJ) is concentrated by mineral processing techniques. It has a faujasite content of 57% and philipsite content of 35%. Thorough characterization of the JORD-FAUJ revealed the high suitability of the product for use in column operation. It either compares closely or gives better thermal stability, attrition resistance, acid resistance, cation exchange capacity (CEC) and water absorption capacity, when compared with products already recommended in column operation. The study has also revealed that the JORD-FAUJ competes efficiently in ammonium removal with the synthetic faujasite 13X and clinoptilolite-rich tuff and gives similar performance. JORD-FAUJ gave a very high performance in removing Pb, Cr, Cu, Zn, and Ni from wastewater, equivalent to 83–100% of that of faujasite 13X and much higher than the clinoptilolite-rich tuff.

Keywords Faujasite · Industrial zeolites · Ion exchange · Jordan

Introduction

Zeolites have found practical applications as ion exchangers in the protection of the environment. The first attempts at purifying waters, using naturally occurring materials containing zeolites, was performed in the 19th

century (Breck 1974). A major factor that has been taken into consideration to choose zeolites is the cost advantage of zeolites over other ion exchangers, their very high selectivity for certain cations such as NH_4^+ (Townsend 1984), and their efficiency in the presence of interfering cations (Ibrahim 1996; Pansini 1996). Currently, several large-scale municipal plant installations are successfully operating in the USA (Lopez and Liberti 1991) and Italy (Amecarelli and Liberti 1991).

In Jordan, uncontrolled pollution causes stress on the fragile environment and aggravates competition for increasingly expensive water resources. Without fundamentally new approaches, the government's commitment to provide sustainable water and environmental sanitation systems for all people may be jeopardized. A major problem of industrial development is the quantity and diversity of wastes generated. Therefore, the need to present solutions to reduce the effect of water pollution assumes a high priority.

Geological setting

The Cenozoic continental plateau lava of northeast Jordan (northern Badia) are part of a major volcanic province that erupts out continuously from Syria across Jordan, and into Saudi Arabia. In northern Badia, ~11,415 km² of lava, defined as Harrat Ash-Shaam Basaltic Super-Group (HASB), is exposed (Ibrahim 1993). It consists of alkali basalt, hawaiite and basanites (Ibrahim 1993), with an age ranging from 26 to <0.5 Ma (Ibrahim and others 1999). The HASB is subdivided into groups and formations of Oligocene to Quaternary age, of which the Aritayn Volcano-clastic Formation (Pliocene–Quaternary) contains authigenic zeolites that act as cement to the volcanic clasts. Recently, faujasite-rich volcano-clastic deposits have been discovered in the formation in three localities in northern Badia (Ibrahim and Hall 1995). The best locality of the three is Jabal Hannoun with an average faujasite content of ~30% and total zeolite of 47%. A product referred to as JORD-FAUJ was selected for the purpose of this study. It was obtained from Jabal Hannoun lapilli tuff by simple mineral processing techniques (Ibrahim and Inglethorpe 1996). JORD-FAUJ contains ~92% zeolite.

Received: 13 April 2000 · Accepted: 1 August 2000

K.M. Ibrahim
Department of Earth and Environmental Sciences,
Institute of Lands, Water and Environment,
Hashemite University, P.O. Box 150549, Zarqa 13115, Jordan
e-mail: ibrahim@hu.edu.jo
Tel.: +962-5-3826600 ext. 4332
Fax: +962-5-3826823

Experimental work

The objectives of this work were a full appraisal of JORD-FAUJ in ion exchange applications, including the removal of ammonia and toxic ions from simulated wastewater of municipal and industrial effluents by comparison with other known zeolites. For this purpose the JORD-FAUJ was compared with other known zeolites. Among the products selected for comparison were synthetic faujasite (molecular sieve type 13X), a product of UOP/Union Carbide and clinoptilolite-rich tuff (CT) from Chalk Hills Formation, Castle Creek, Idaho (Stop 2, Zeolite '93 field trip, Sheppard 1993). Because of the nature of product 13X and the fact that both the 13X and CT samples are only available in small quantities, investigations were conducted using batch-contact experiments. In this mode of experiment, a portion of the sample was in contact with the simulated solution for different times. The solution was then separated by centrifugation for analysis. Sample weight, solution concentration and volume were kept constant throughout the experiment, with only one variable, which was contact time. The results were plotted as concentration versus time.

Samples CT and JORD-FAUJ were first powdered and converted to their Na-form by soaking in 1 M NaCl at 80 °C for 2 weeks with continuous stirring. Each sample of 0.4 g was used throughout the experiments. The samples were placed in covered test tubes, brought into contact with 12 ml of the solution and subjected to continuous shaking. Two sets of experiments were conducted as follows:

1. Removal of heavy metals, where two tests were conducted using the cations Pb, Cr, Cu, Zn, and Ni, one each at 10 ppm and a second batch at 20 ppm.
2. Removal of ammonia, here two other tests were carried out, one at 25 ppm NH_4^+ and the second at 50 ppm NH_4^+ .

Description of the products

JORD-FAUJ

Mineralogy and chemistry

X-ray diffraction analyses indicate that JORD-FAUJ contains ~57% faujasite, 35% phillipsite, 7% calcite and traces of other constituents of volcanic clasts. The chemical composition is given in Table 1. The major oxides, such as SiO_2 , Al_2O_3 , Na_2O , CaO , K_2O and sometimes MgO , were incorporated within the zeolite structure. Other oxides, such as Fe_2O_3 , TiO_2 , P_2O_5 and MnO , correspond to the presence of non-zeolite accessory phases. The high content of CaO is attributed to the presence of calcite.

Grain size and morphology

The JORD-FAUJ consists of particles that vary in grain size between -0.25 and +0.125 mm (equivalent to -60

Table 1
Chemical composition of the studied materials. *LOI* Loss on ignition

	JORD-FAUJ	13X	CT
SiO_2	40.01	40.49	62.72
TiO_2	0.21	0.02	0.16
Al_2O_3	15.13	25.30	12.02
Fe_2O_3	1.06	0.05	0.92
MnO	0.09	0.00	0.04
MgO	0.79	0.02	1.22
CaO	10.18	0.05	0.70
Na_2O	4.91	12.54	3.14
K_2O	0.92	0.02	1.27
P_2O_5	0.33	0.02	0.04
LOI	26.58	21.41	15.80
Total	100.21	99.90	98.02

and +120 mesh). The particles have different shapes, including spherical, irregular angular and subangular, and elongated rod-like particles. The spherical, ball-like particles represent amygdals composed of one or more of the authigenic phases formed within the vesicles of the vitric clasts, the center of which is usually hollow. Other particles may represent single crystals, or monomineralic aggregates of crystals of zeolites and/or calcite. In a few cases, the particles have relicts of a vitric phase attached to a crystal or group of crystals.

Cation exchange capacity (CEC)

Selected technological parameters for the JORD-FAUJ are given in Table 2. The JORD-FAUJ is characterized by high CEC values when compared with the CEC of the Neapolitan phillipsite tuff, which is 2.20 meq/g (de'Gennaro and others 1983). In an attempt to determine the selectivity of Na^+ and NH_4^+ in the JORD-FAUJ, pure phillipsite and faujasite converted to the Na-form were subjected to isotherm experiments by Ibrahim (1996). The isotherms show the preference of phillipsite ($a = 4.88$) and faujasite ($a = 4.26$) for NH_4^+ over Na^+ . This indicates that both minerals in their Na-form have the ability to remove the NH_4^+ from solutions, and emphasizes the higher selectivity of phillipsite towards NH_4^+ compared with faujasite.

Attrition resistance

Most ion exchange applications require the use of a fixed bed or column of sized zeolite. An important property of

Table 2
Selected technological parameters of the studied materials

Sample	JORD-FAUJ	13X	CT
Color	Light brown	White	Off-white-light brownish gray
Water adsorption capacity %	17	26	-
CEC meq/g	3.24	3.6	2.46

Table 3

Wet attrition resistance of products recommended for column operation

Sample	Attrition resistance (wtloss%)
JORD-FAUJ	5.3
Neapolitan phillipsite tuff ^a	9.8
New Mexico clinoptilolite ^b	13
Hector clinoptilolite ^b	7.5
Zeolon 900 ^b	3
Pelletized chabazite ^b	7.6

^a Data from de’Gennaro and others (1983)

^b Data from Mercer and Ames (1978)

sized zeolites is their resistance to wet attrition. Table 3 lists the attrition resistance of the JORD-FAUJ. The tests were carried out following the procedure of Mercer and Ames (1978). When compared with products already recommended for column operation as shown in Table 3, the JORD-FAUJ is better than the attrition resistance of the Neapolitan phillipsite tuff, the New Mexico clinoptilolite, the Hector clinoptilolite and pelletized chabazite, but it compares closely with Zeolon 900 (a synthetic mor-denite).

Packed-bed density

Packed-bed density is the minimum volume occupied in a glass cylinder by a known amount of sample after a suitable rapping until no further reduction in volume occurs (de’Gennaro and others 1983). Since the specific gravity of packed zeolites varies, packed-bed densities were measured so the volumetric capacity, which is important for sizing ion exchange equipment, could be determined. The wet and dry packed-bed density of the JORD-FAUJ is 1.04 and 1.01 g/cm³, respectively, as compared with the wet and dry packed-bed density of the Neapolitan phillipsite tuff, which is 0.80 and 0.68 g/cm³, respectively (de’Gennaro and others 1983). The results of the packed-bed density indicate that the JORD-FAUJ allows the column experiment to work correctly. Products with higher packed-bed density result in excessive head losses of the column, whereas lower packed-bed density results in good channeling.

Thermal stability and water adsorption capacity

Among the zeolites present in the JORD-FAUJ, phillipsite has a limited thermal stability (Mumpton 1978). Phillipsite structure in the JORD-FAUJ remains undamaged up to about 250 °C and starts to collapse thereafter. Faujasite structure, however, is very stable and did not show any change throughout heating experiments (Fig. 1). The behavior of the JORD-FAUJ, therefore, is intermediate between the stability fields of both zeolite minerals. It shows a residual crystallinity of ~78% when heated up to 500 °C as it contains considerable amounts of faujasite. The thermogravimetric analysis (TGA) curves for pure phillipsite and faujasite from JORD-FAUJ are shown in

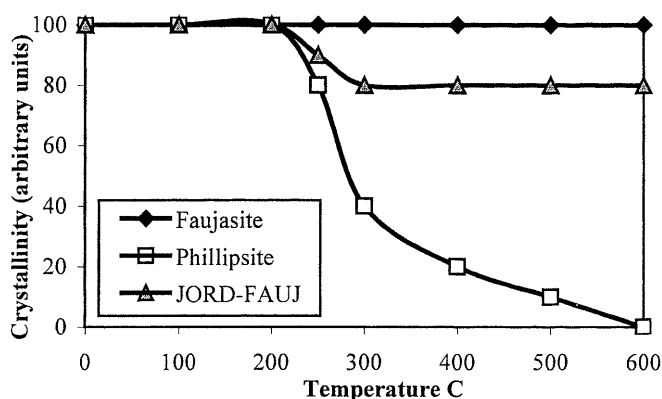


Fig. 1
Thermal stability of purified zeolites and JORD-FAUJ

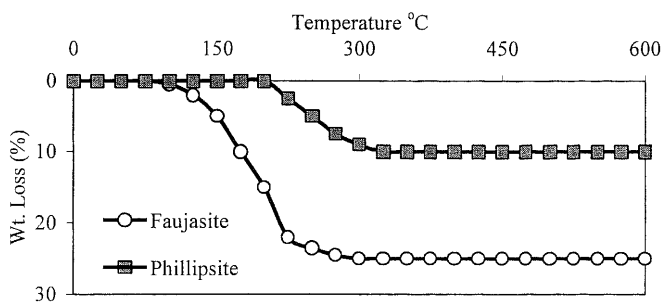


Fig. 2
TGA curves for purified zeolites from JORD-FAUJ

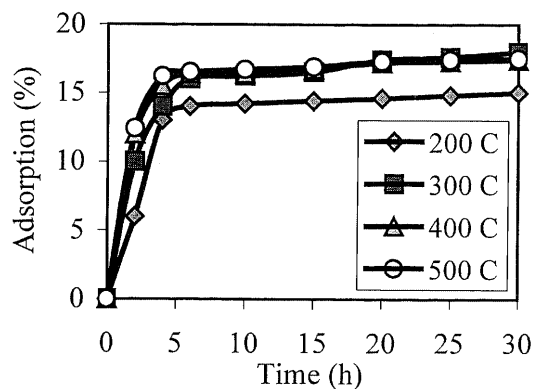


Fig. 3
Adsorption capacity of JORD-FAUJ at different activation temperatures

Fig. 2. They indicate that the maximum loss of phillipsite of ~10% occurs close to 300 °C. Faujasite, however, has a maximum loss of 25% at 300 °C. The maximum percentage of regained water (water adsorption capacity) recorded from JORD-FAUJ is ~17% at the activation temperatures 300, 400 and 500 °C (Fig. 3).

Acid resistance

For the possible use of zeolites in ion exchange applications, it is essential to know their resistance to aggressive environments, which are generally acid solutions. Figure 4 shows the results of acid resistance tests, which indicate that when the JORD-FAUJ is treated with acidic solutions at pH 5 it loses <2% in a contact time of 24 h and <5% in a contact time of 48 h. At pH 3, the JORD-FAUJ resists the acidic attack in the first 4 h, then it starts to lose part of its crystallinity. The residual crystallinity as a result of this reaction after 48 h is ~80%.

Synthetic faujasite 13X

Based on the information sheet provided with the product, the molecular sieve type 13X is a market name for the Na-form of zeolite X, which has a faujasite crystal structure. The chemical formula of the product is $Na_{86}[(AlO_2)_{86}(SiO_2)_{106}] \times (H_2O)$. The material can adsorb molecules with critical diameters up to 10 Å. It is used commercially for general gas drying, air plant purification and liquid hydrocarbon and natural gas sweetening. It is a white powder that consists of agglomerates <10 mm made from crystals with an average size of 1.0–4.5 µm. The maximum water absorption capacity of the material is 26% and its cation exchange capacity is 3.6 meq/g. The chemical composition of synthetic faujasite 13X is given in Table 1.

Clinoptilolite-rich tuff (CT)

The CT has the appearance of off-white to light brownish gray, very fine-grained, moderately resistant mudstone. Clinoptilolite is the most abundant constituent (>80% of the rock; Sheppard 1993). Other constituents include smectite and opal-CT. The chemical composition of the CT sample indicates that the clinoptilolite is a sodaic variety (Table 1). The scanning electron microscope investigation indicated that the clinoptilolite forms are platy and tabular, commonly 3–15 µm in length.

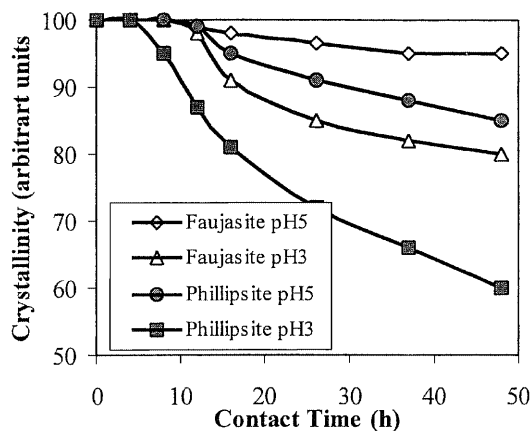


Fig. 4

Acid resistance of pure zeolites and JORD-FAUJ as a function of solution pH

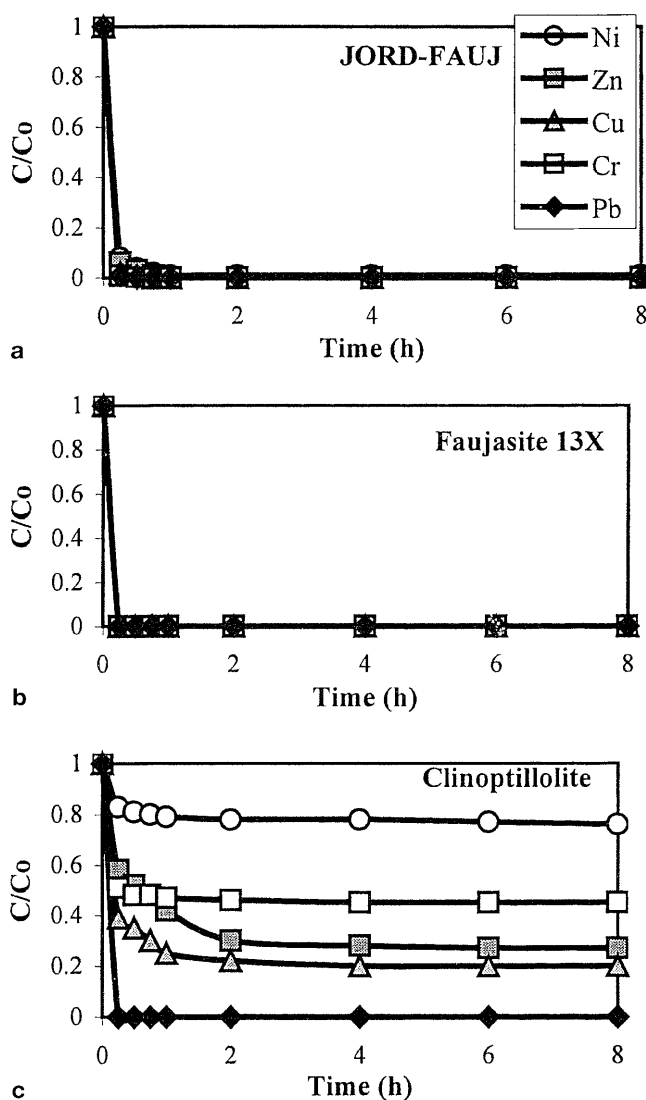


Fig. 5a-c

Combined decay curves for heavy metal cations at 10 ppm concentration

Results and discussion

Figure 5 shows the type of decay curves obtained from the three samples after they were subjected to solutions containing a mixture of heavy metals. The curves give the relationship between the ion exchange as a function of time, and the shape of the curve as an indicative of the affinity for the specific ion. After 15 min of contact time using a solution with 10 ppm of cations, the JORD-FAUJ had removed >99% of both Pb and Cr, ~98% of Cu, 94% of Zn, and 92% of Ni (Fig. 5a). Furthermore, by increasing the concentration of the solution to 20 ppm, the ability of the JORD-FAUJ to remove both Zn and Ni in 3 min was 87 and 83%, respectively (Fig. 6a). However, within 15 min it had removed 90 and 85% of those two elements, and it needed another 15 min to increase these

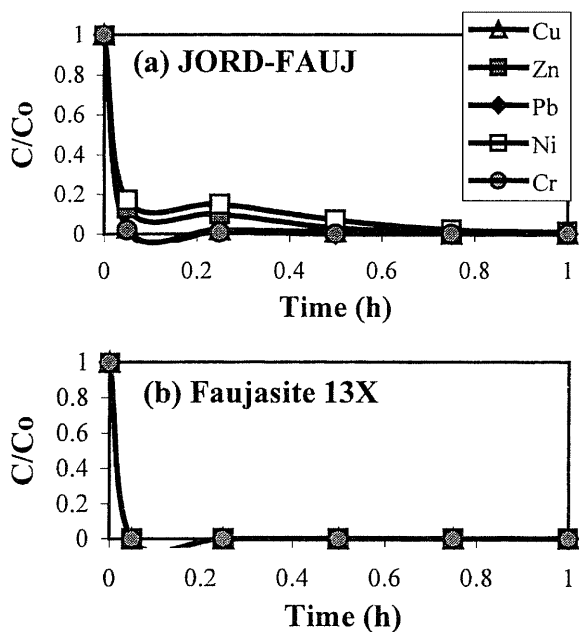


Fig. 6a, b
Combined decay curves for heavy metal cations at 20 ppm concentration

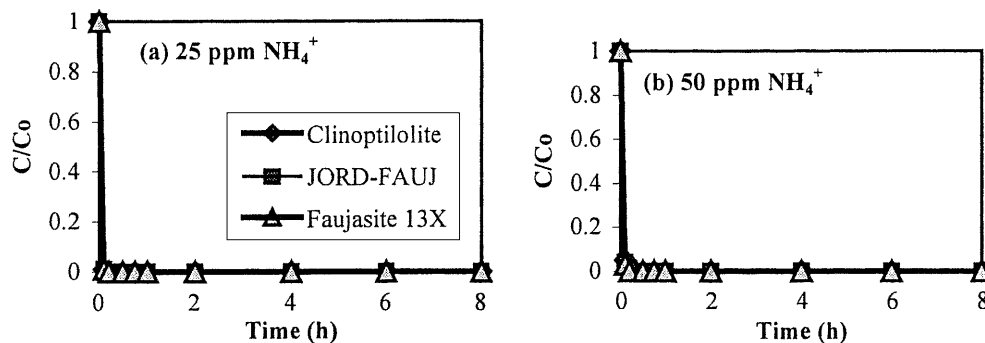


Fig. 7a, b
Combined decay curves for NH₄⁺

values to 97 and 93%, respectively (Fig. 6a). The behavior of Pb, Cr, and Cu remains unchanged, even when using this solution with higher concentration (Fig. 6a). The JORD-FAUJ gives comparable results with the 13X rather than the CT (Figs. 5 and 6). The 13X samples exhibit a very strong ability to remove all of the cations in the solution very rapidly. All cations were removed with 100% efficiency from the 10 and 20 ppm solutions after 15 and 3 min of contact time, respectively (Figs. 5b and 6b). On this basis, it can be concluded that the 13X displays similar efficiency to the JORD-FAUJ in removing Pb, Cr, and Cu, but is more efficient in removing Zn and Ni. The CT samples are characterized by a comparable performance in removing Pb from the 10 ppm solution with that of the 13X and JORD-FAUJ. Nevertheless, its efficiency towards other cations is poor (Fig. 5c). In Figure 7, the results of treating NH₄⁺ solution with the three materials is displayed. Figure 7 emphasizes the sig-

nificant efficiency of JORD-FAUJ compared with the efficiency of the 13X and the CT samples. The three materials have removed the NH₄⁺ from the solution almost completely within 3 min of contact time, even at 50 ppm concentration.

Conclusions

The characterization of the JORD-FAUJ has revealed the high suitability of the product for use in column operation based on its chemical and physical parameters. When JORD-FAUJ is compared with other products already recommended in column operations, it gave better thermal stability, attrition resistance, acid resistance, CEC and water adsorption capacity than the Neapolitan phillipsite tuff of Italy, and better attrition resistance than the New Mexico clinoptilolite and Hector clinoptilolite, but compared well with Zeolon 900. The study has revealed that JORD-FAUJ competes efficiently with synthetic faujasite 13X and clinoptilolite-rich tuff in ammonium removal and gives similar performances. It gave very high performance in removing Pb, Cr, Cu, Zn, and Ni from wastewater, equivalent to 83–100%

of the performance of the synthetic faujasite 13X, but very much higher than the clinoptilolite-rich tuff. The results of the present investigation suggest the positive possibility of employing JORD-FAUJ in ammonium and heavy metal removal from wastewater. The high affinity towards the pollutant in the presence of interfering cations is the main feature that recommends the use of this natural product, along with its low cost and availability in Jordan.

Acknowledgments This work was fully supported by the Higher Council for Science and Technology, the Jordan Badia Research and Development Program through integrated research on the geology of the Azraq basin. The author would like to express his deep gratitude to Professor H. Khoury for critical comments on the manuscript.

References

- AMECARELLI V, LIBERTI L (1991) Zeolite ammonia removal at Manfredonia municipal plant. In: Colella C (ed) Atti Io Convegno Nazionale di Scienza e Tecnologia delle Zioliti, L'Aquila, pp 147–155
- BRECK DW (1974) Zeolite molecular sieves. Wiley, New York
- DE'GENNARO M, COLELLA C, FRANCO E, AIELLO R (1983) Italian zeolites: 1. Mineralogical and technical features of Neapolitan yellow tuff. *Ind Miner* 186:47–53
- IBRAHIM KM (1993) The geological framework for the Harrat Ash-Shaam Basaltic Super-group and its volcanotectonic evolution. Natural Resources Authority, Geological Mapping Division, Amman, Bull 25
- IBRAHIM KM (1996) Geology, mineralogy, chemistry, origin and uses of the zeolites associated with Quaternary tuffs of northeast Jordan. PhD Thesis, University of London
- IBRAHIM KM, HALL A (1995) New occurrences of diagenetic faujasite in the Quaternary tuff of northeast Jordan. *Eur J Mineral* 7:1129–1135
- IBRAHIM KM, INGLETHORPE SDJ (1996) Mineral processing characteristics of natural zeolites from the Aritayn Formation of northeast Jordan. *Miner Deposita* 31:589–596
- IBRAHIM KM, HARLAVAN Y, TARAWNEH K, ILANI S, RABBA I, WEINBERGER R, STEINITZ G (1999) Dating (K–Ar) the Harrat Ash-Shaam Basaltic Super-Group sequence of NE Jordan. Initial results of phase I, Report GSI/21/98, Geological Survey of Israel, Israel
- LOPEZ A, LIBERTI L (1991) Zeolites “closed-loop” regeneration. In: Colella C (ed) Atti Io Convegno Nazionale di Scienza e Tecnologia delle Zioliti, L'Aquila, pp 139–146
- MERCER BW, AMES LL (1978) Zeolite ion exchange in radioactive and municipal wastewater treatment. In: Sand LB, Mumpton FA (eds) Natural zeolites; occurrence, properties, use. Pergamon Press, Oxford, pp 451–462
- MUMPTON FA (1978) Natural zeolites; a new industrial mineral commodity. In: Sand LB, Mumpton FA (eds) Natural zeolites; occurrence, properties, use. Pergamon Press, Oxford, pp 3–27
- PANSINI M (1996) Natural zeolites as cation exchangers for environmental protection. *Miner Deposita* 31:563–575
- SHEPPARD RA (1993) Geology and diagenetic mineralogy of the Castel Creek zeolite deposit and the Ben-Jel bentonite deposit, Chalk Hills Formation, Oreana, Idaho. In: Zeolite '93, 4th International Conference on the Occurrences, properties and utilization of natural zeolites (program and abstract), international committee on natural zeolites, New York, pp 14–24
- TOWNSEND R (1984) Ion exchange in zeolites – basic principles. *Chem Ind* 7:246–251