Evaluation of Jordanian Phillipsite Tuff in Removal of Ammonia from Wastewater: Experimental Study

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ABSTRACT

The possibility of using Jordanian phillipsie tuffs in the process of ammonium removal from wastewaters containing other competing ions is evaluated. The chemical and physical features and ammonium cation exchange properties of this phillipsite-rich tuff has been determined in comparison with clinoptilolite from Ratka mine in Hungary. The phiilpsite tuff and the Hungarian zeolites in their sodium form were exchanged by solutions containing NH_4^+, Ca^{++}, Mg^{++}, Na^+ and K^+ ions. Results from equilibrium (batch) and column tests showed that the ammonium uptake of both zeolites are comparable, but phillipsite has higher selectivity than clinoptilolite. The data obtained indicates that the Jordanian phillipsite tuff is an excellent candidate and a competitive with clinoptilolite for the removal of ammonia from wastewaters.

ملخص

تبحث هذه الورقة في تقييم التف البركاني الاردني الغني بمعدن الفلبسايت في عمليات التخلص من الأمونيا من المياه العادمة والحاوية على أيونات أخرى منافسة للأمونيا ان الخواص الكيميائية، الفيزيائية واستبدال الأمونيا لهذه المادة قد قيمت بالمقارنة بمعدن زيولايت تجاري آخر ويستعمل لهذا الغرض وهو معدن Clin optilolite (من منجم راتكا Ratka في هنجاريا). كلا المادتين (الفلبسايت الاردني والكلينويتولايت)، عولجا بالصوديوم مسبقاً قبل استبدالها بمحاليل تحتوي على أيونات كل من + K , + Na , 2 + Mg , ++ Ca , 4 NH وقد دلت النتائج من التجارب التي أجريت باستعمال Column و Batch أن استخلاص الأمونيا من المحاليل كانت متقاربة لكلا النوعين من الزيولايت. ولكن وجد أن الفلبسايت له قدرة أعلى على انتقاء (Selectevity) الأمونيا من المحاليل من Clinoptilolite .

كما بينت النتائج أن الفلبسايت الاردني يعتبر بديل ممتاز للكلينوبتولايت لاستخلاص الأمونيا من المياه العادمة.

INTRODUCTION:

The serious and harmful effects to the aquatic life and soils due to the presence of ammonia in waters is well known. Its discharge with wastewaters from municipal and industrial effluents leads to abnormal algal growth, toxicity, and soil corrosion[1]. Therefore, these effluent water must be treated before discharge or reusing. Among the various methods and processes proposed to reduce ammonia concentrations in wastewaters, selective cation exchange was found to be the most competitive one in both laboratory scale and commercial plants[2,3]

Clinoptilolite, a natural zeolite was widely studied and used as ion exchanger in wastewaters ammonium removal installations. Its use was recommeded because of its good selectivity for NH_4^+ and low cost[4]. At present, there are many large sewage plants which are constructed to treat wastewaters by natural clionptilolite, at Upper Occoquan Sewage Authority, Virginia with a capacity of 22.5 MGD, Tahoe - Trucker, California with capacity of 6 MGD, and Denever, Colorado with capacity of 1 MGD[5].

Zeolite manufacturers have developed new synthetic zeolites more effective in selective ammonium removal than natural clinoptilolite. For example, Lind F and W are synthetic zeolites developed by Union Carbide[6] to replace clinoptilolite, but it seems their cost is too high.

Investigators[7-9] have reported that natural phillipsite is more effective in removal of ammonium in the presence of divalent ions than clinoptilolite.

Jordanian phillipsite is the product of alteration of alkaline basaltic tuffs widespread in the northeastern basaltic plateau[10]. Many tuff cones are located within

(1) Merecer, BW, Ames, LL, Touhill, CJ, Van Slyke, WJ and Dean, RB, J. **Water Pollution Control Federation,** 1970: 42, R95.
(2) Koon, JH and Kaufman, WJ, J. **WPCF** 1975: 47, 448.
(3) Sherman, JD, **AIChE Symp. Ser.,** 1978: 74, No. 179, 98.
(4) Ames, LL, Jr. **Proc. 13th Pacific Northwest Indus. Waste Conf.,** Washington State Univ., Pullman, 1967.
(5) Sherman, JD, **NATO ASISer. Ser.** E 1984: 80, 151.
(6) Ames, LL, Jr. **Am. Mineral.,** 1960: 45, 689.
(7) Ciambelli, p., Corbo, p., Porcelli, C. and Rimoli, A. **Zeolites,** 1985: 5,eration, 1970: 42, R95.
(8) Sherman, JD, **op. cit.**
(9) Ciambelli, p., Corbo, P., Lumare, F. and Porcelli, C., In: Pond, WG and Mumpton, FA, eds., **Zeo-Agriculture: Use of Natural Zeolites in Agriculture and Aquaculture, Boulder:** Westview Press, 1984, p. 245.
(10) Dwairi, IM, **A Chemical Study of the Palagonitic Tuffs of The Aritain Area of Jordan With Special Reference to Nature, Origin and Industrial Potential of the Associated Zeolite Deposits, 1987, Ph. D Thesis, Hull University, U.K.**

this plateau which could be a very large source of phillipsite in Jordan.

The Aritain[11] and Tal Ermah cones are examples of these tuff with phillipsite minerals. These phillipsite tuffs could represent a considerable source of zeolite to be used in processes for nitrogen removal from wastewaters.

The present study gives some results on the investigation related to the potential use of the Jordanian phillipsite tuffs in ammonia removal processes from simulated wastewater.

MATERIALS AND METHODS:

The phillipsite tuff used in this study was obtained from Tal Ermah in northeast Jordan (Fig.1) The material exhibit different shades of colours ranging from greenisn yellow to deep brown were the alteration of the original green tuff material is more advanced. The highly altered material contains brown palagonite (residual altered glass), phillipsite, calcite, minor amounts of clays and phenocrysts of olivine and pyroxens. It is easily crushed by hand due to its porosity and friablity.

The morphology of the zeolite crystals was examined by scanning electron microscope, using Cambridge Instrument S600 scanning electron microscope.

Chemial analysis for major elements of the phillipsite crystals, palagonite and fresh glass were carried out by microprobe spot analysis using Cambridge Instrument Geoscan with link system model 290 2Kv energy dispersive spectrometer.

Major elements of phillipsite tuff and fresh tuff were carried out by lithium borate fused discs using Pillips PW 1212 X-ray fluorescence set.

X-ray and thermal analysis using DTA were used to characterize the zeolite.

The ion-exchange experiments were carried out on 25 X 35 mesh fraction, which was obtained by crushing and sieving the highly altered tuff. The total ammonium exchange capacities were determined by contacting tuff samples (2g) with 200 ml 1 M NH_4Cl solution for 48 h on a shaker. The total exchange capacity tests were performed on original phillipsite and sodium exchanged tuff (tests were carried out using a shaker for 48 h).

Continuous ion exchange experiments were carried out in glass columns (0.8 cm i.d.) containing 15 cm of 25X35 mesh size tuff. The original tuff samples used in the column operation were first exchanged to sodium form by feeding 1 M NaCl for 3h, then washing the sample free of Cl ion. The tests were conducted by feeding solution (downflow) at flow rate of 80 bed volume/h. The concentration of ions in the effluent were measured at different volumes of solution passed

(11) **Dwairi, I. M. op. cit.**

through the column. Ammonia was determined by Nessler's method, while Na, K, Mg, Ca were determined by atomic absorption (AA).

The feeding solutions used in the continuous ion exchange tests were: solutions containing ammonia only but at different concentrations and solutions containing ammonia with other cations at concentration simulating tertiary municipal effluents.

The sample was regenerated by 1M NaCl after the exchange cycle was carried out to saturation. All activation, exhausting and regenerating solutions were fed down-flow at a flow rate of 80 bed volumes per hour.

RESULTS AND DISCUSSION:

Phillipsite tuff characterization:

Prismatic phillipsite crystals are well developed in intergranular spaces and growing radiantly at the outer edges of palagonite granules. In addition, smaller intragranular phillipsite is developed in vesicles and on the expense of palagonite within the granules. These features are shown by scanning electron micrographs in Plate (1) where phillipsite crystals from 0.05 to 0.16 mm can be noted.

The chemical composition of the Hungarian clinoptilolite and Jordanian phillipsite - rich tuff (25X35 mesh fraction) is shown in Table 1.

The X-ray diffraction pattern of the phillipsite-rich tuff appears in Figure (2). Differential thermal analysis appears in Figure (3).

Ion exchange experiments:

Total ammonium exchange capacity of the phillipsite tuff, which was determined by batch system containing 1 M NH_4Cl is 1.6 meq/g. The total ammonium exchange capacity under the same conditions of pure phillipsite separated from the tuff is 3.2 meq/g. This gives a phillipsite content in the tuff (by comparison with pure phillipsite) to be about 50%.

The column exchange tests for the solutions containing only ammonium ions with different concentrations (no other competing cations) are presented as breakthrough curves in Figure (4). It gives the exhaustion history of ammonia in three inlet solutions at 120 ppm, 60 ppm and 20 ppm concentrations as a function of the volume treated expressed in bed volume (BV). The Figure shows the column capacities at different percentages breakthrough, at 10% breakthrough it ranges from 80 BV for 120 ppm concentration to 420 BV for 20 ppm ammonia in the solution.

The effect of loading/ regeneration cycles on the capacity of phillipsite was investigated. This was carried out by repeating these cycles several times, in each

loading cycle the tuff bed in the column was fed by a 120 ammonia ppm solution at known flow rate (80 BV/h) till saturation, and the regeneration cycles were carried out by 130 BV of 1 M NaCl solutions.

The results of the ammonia uptake of four loading cycles and three regeneration cycles are presented in Figure (5). The integrated curves of this figure show that ammonia uptake in the first cycle was lower than the others. This increase in the phillpsite exchange capacity after the first cycle was due to its activation during exhaustion and regeneration cycles. Breakthrough curves of the exhaustion/ regeneration cycles (not presented) has shown that K and Ca in the phillipsite were exchanged by ammonia in the loading cycles and by sodium in the regeneration cycles. In the last loading cycle a complete removal of exchanged K^+ and Ca^{++} was accomplished, and only sodium and ammonia exchange process was noted:

$$NH_4^+ + Na^+ = NH_4^+ + Na^+$$
$$\text{(sol)} \quad \text{(zeo)} \quad \text{(zeo)} \quad \text{(sol)}$$
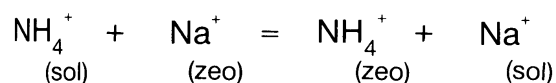
The selectivity of the Jordanian phillipsite tuff for ammonia in the presence of other ions was investigated, this was carried out on synthetic effluent water[12] of the following composition:

NH_4^+ 17 ppm; Ca^{++} 34 ppm; Mg^{++} 9 ppm; Na^+ 56 ppm; K^+ 12 ppm.

The performances of both phillipsite tuff from Jordan and clinoptilolite from Ratka mine, Hungary were investigated. The two zeolites were loaded in two separate columns and were fed in parallel under the same conditions. The uptake of each cation as a function of bed volume (BV) for phillipsite tuff are presented in Figure (6), and that for clinoptilolite is reported in Figure (7).. Comparison of the two figures shows the main difference in the behavior of the zeolitic tuffs: the selectivity of the phillipsite tuff from Jordan for ammonia in respect to Ca^{++} and Mg^{++} is higher than clinoptilolite. The ratio of ammonia to calcium + magnesium uptake is 0.69 for the Hungarian clinoptilolite and 1.19 for the Jordanian tuff. The Na ion exchange by NH for both zeolites is favoured in respect to Ca^{++} and Mg^{++}. The difference with repect to K^+ is not relevant. This suggests that the presence of competing ions such as Ca^{++} and Mg^{++} would not decrease the ammonia uptake by phillipsite, but it would decrease the ammonia uptake by clinoptiolite.

CONCLUSIONS:

Phillipsite tuff of Jordan have shown acceptable cation exchange properties

(12) Ciambelli, p., Corbo, p., Porcelli, C. and Rimoli, A. **Zeolites,** 1985: 5, 184-187.

for ammonia, and demonstrated acceptable features in respect to practical uses in processes for ammonia removal from wastewater, although the selection of the experimental conditions were not dictated for only this objective.

In addition, its exchange capacity and selectivity for ammonium ion in the presence of other competing ions was found to be comparable to the corresponding properties of a commercial clinoptilolite. This aspect is under investigated now for utilization of this and other phillipsite tuffs from Jordan for local municipal wastewater treatments.

Table (1)
Composition of Jordanian phillipsite tuff, pure phillipsite separated from the tuff and Hungarian clinoptilolite tuff.

Oxide%	Jordanian[1] Phillipsite Tuff	Jordanian[2] Pure phillipsite	Hangarian Clinoptilolite Tuff
SiO_2	45.01	53.51	71.48
Al_2O_3	16.16	20.43	10.84
TiO_2	0.47	n.d	0.15
Fe_2O_3	3.79	n.d	0.89
MnO	n.d	n.d	n.d
MgO	3.25	n.d	1.01
CaO	6.56	4.60	2.45
Na_2O	2.99	2.12	0.60
K_2O	4.42	6.02	4.08
LOI	17.02	13.12	8.32
Total	**99.66**	**99.80**	**99.82**

(1) Phillipsite tuff after sieving and crushing.
(2) Microprobe spot analyses, (averge of 10 spots).
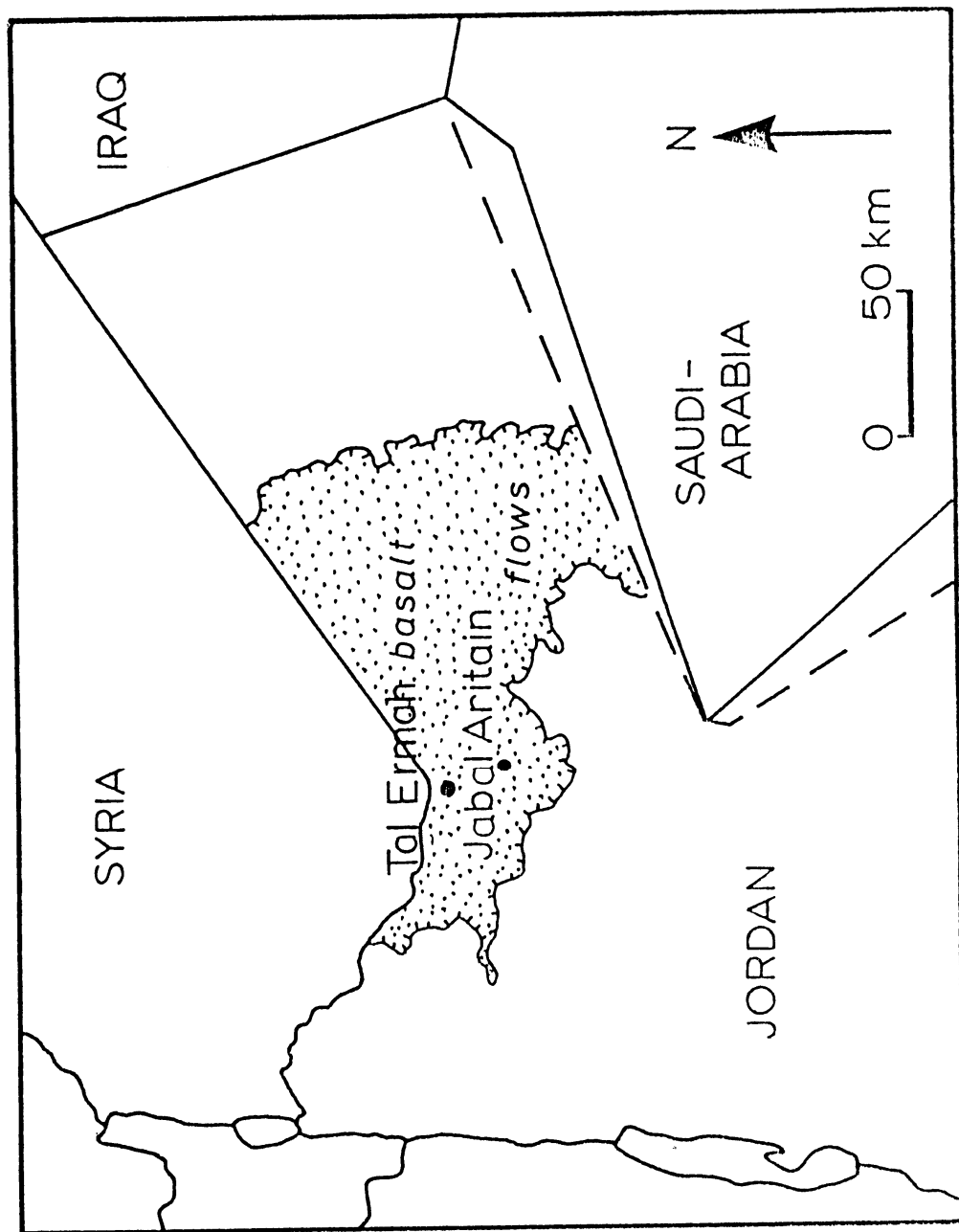
Fig. 1. Cation uptake curves for clinoptilolite from Hungary (same as figure 6).
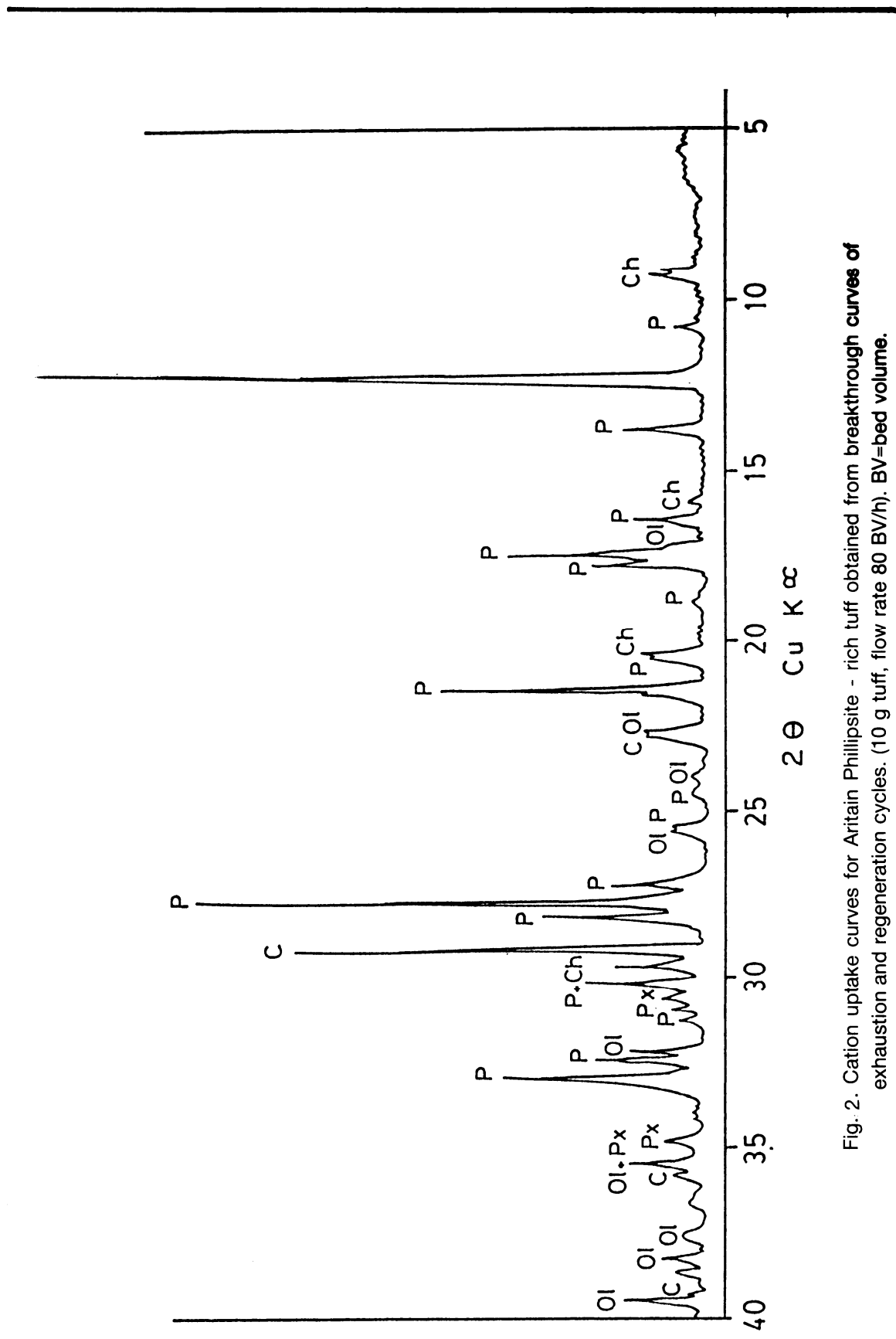
Fig. 2. Cation uptake curves for Aritain Phillipsite - rich tuff obtained from breakthrough curves of exhaustion and regeneration cycles. (10 g tuff, flow rate 80 BV/h). BV=bed volume.
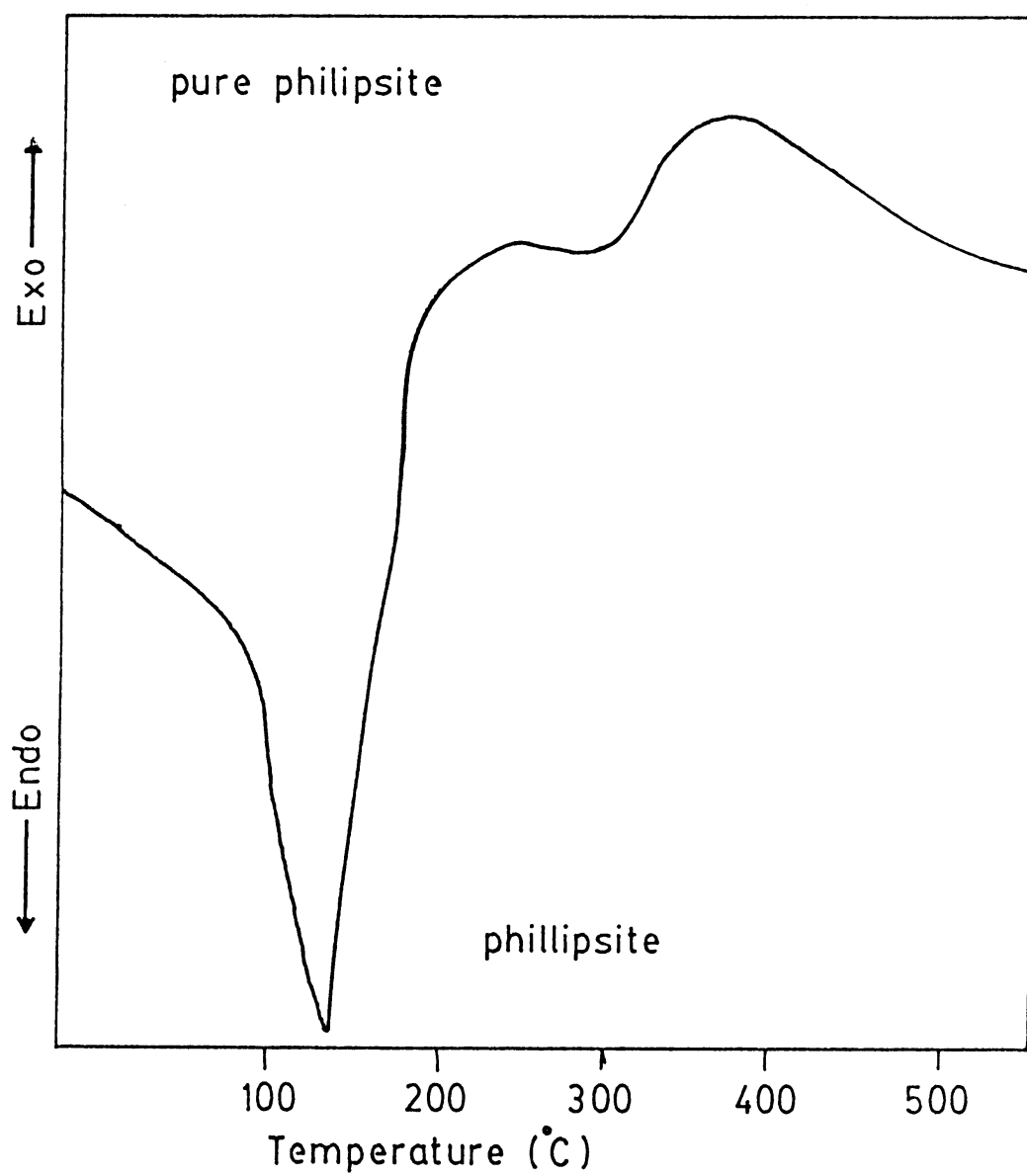
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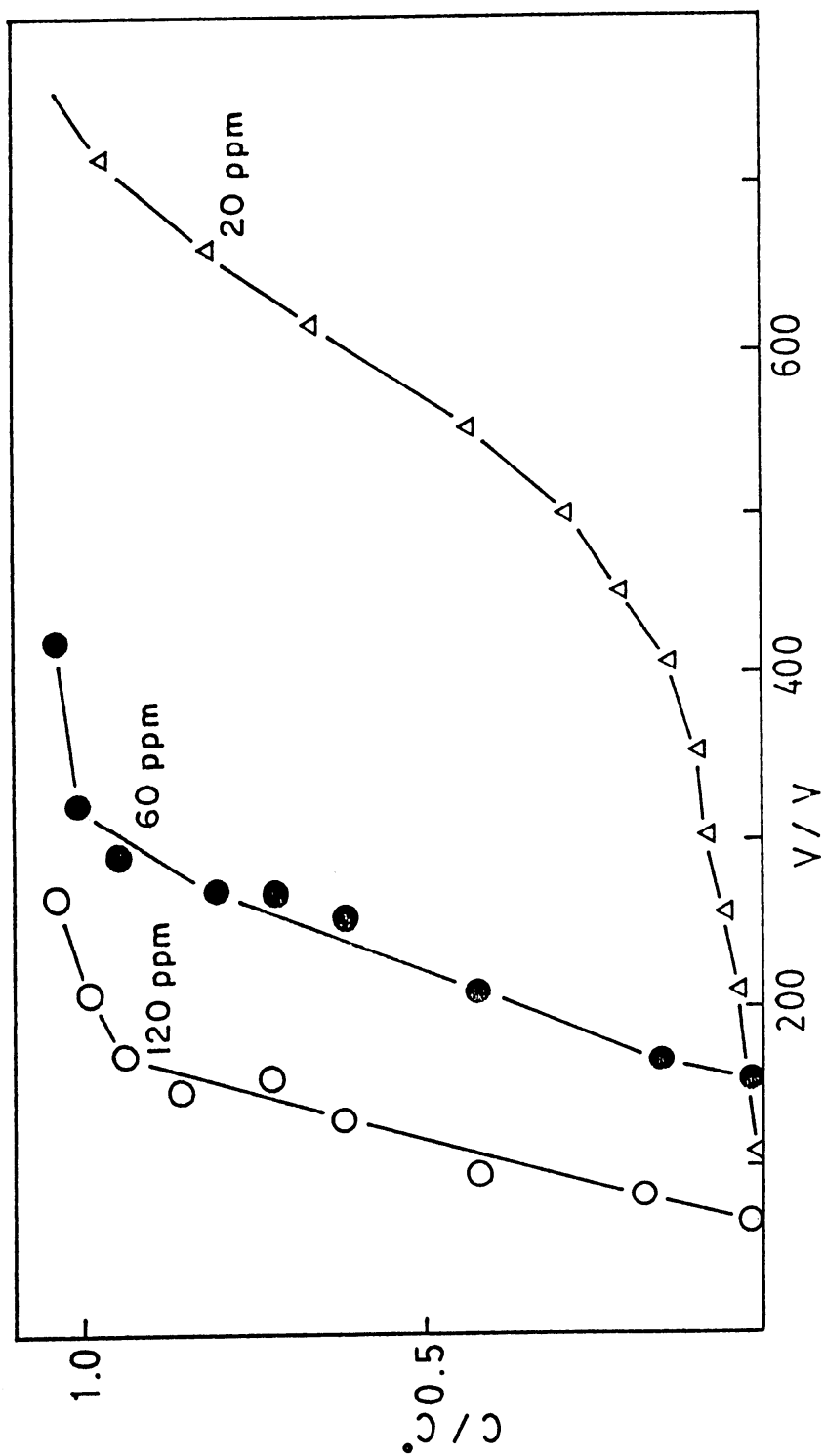Fig. 3. Ammonium uptake in exhausion cycles. (NH$_4$=130; 10 g of tuff; flow rate 80 BV/h). BV=bed volume.

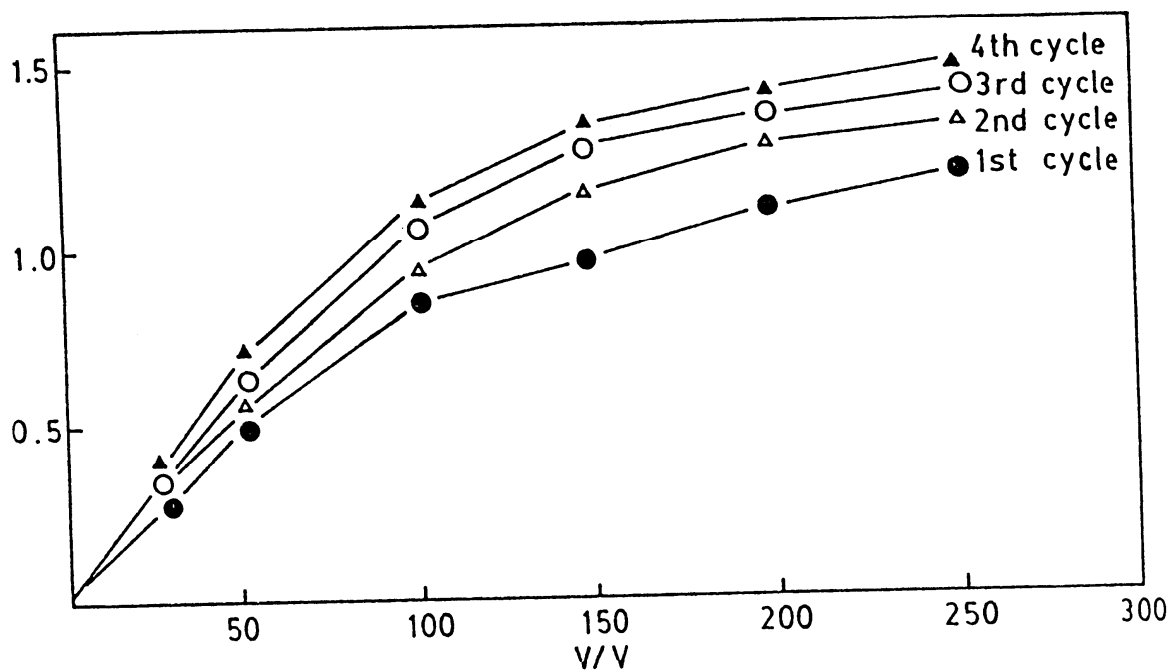Fig. 4. Ammonium ion breakthrough curves as a function of volume of solution passed. (10 g of tuff; flow rate, 80 BV/h). BV=bed volume.

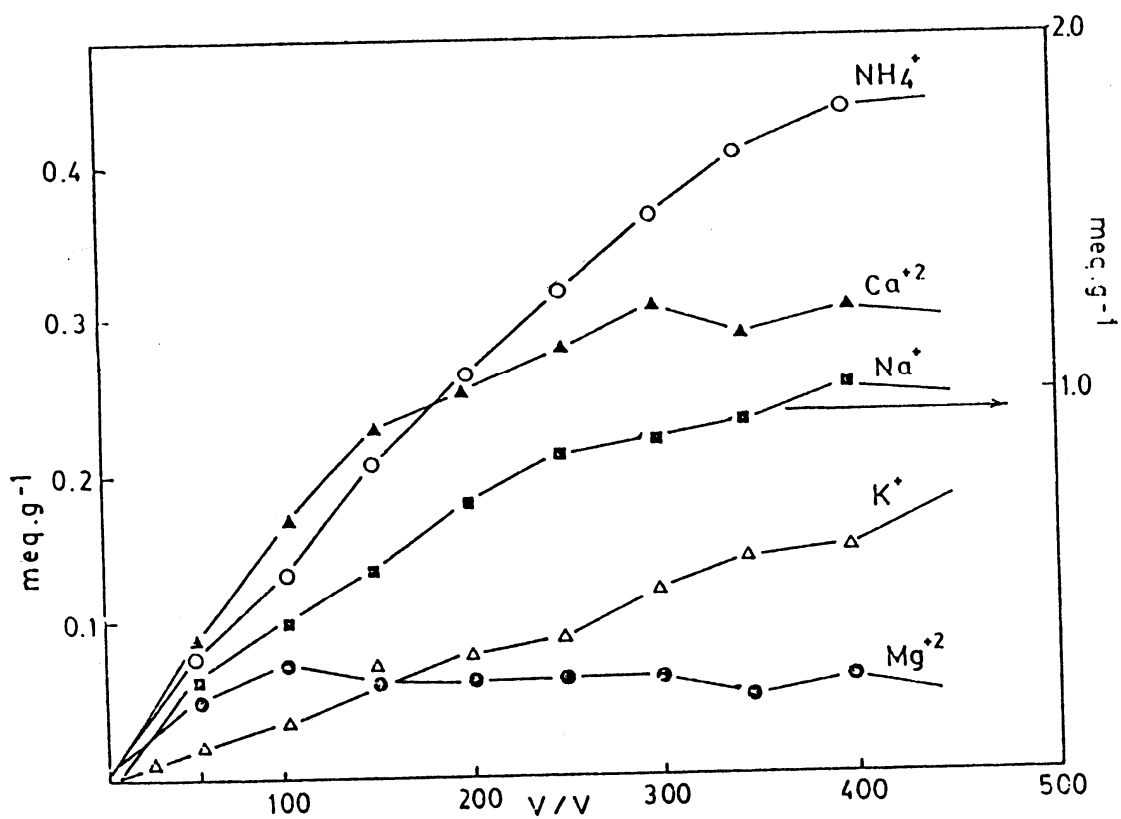Fig. 5. DTA of the phillipsite separated from the tuff.

Fig. 6. -ray powder diffraction trace of phillipsite rich tuff. P=Phillipsite Fo=Forsterite C=Calcite F=Fauja-
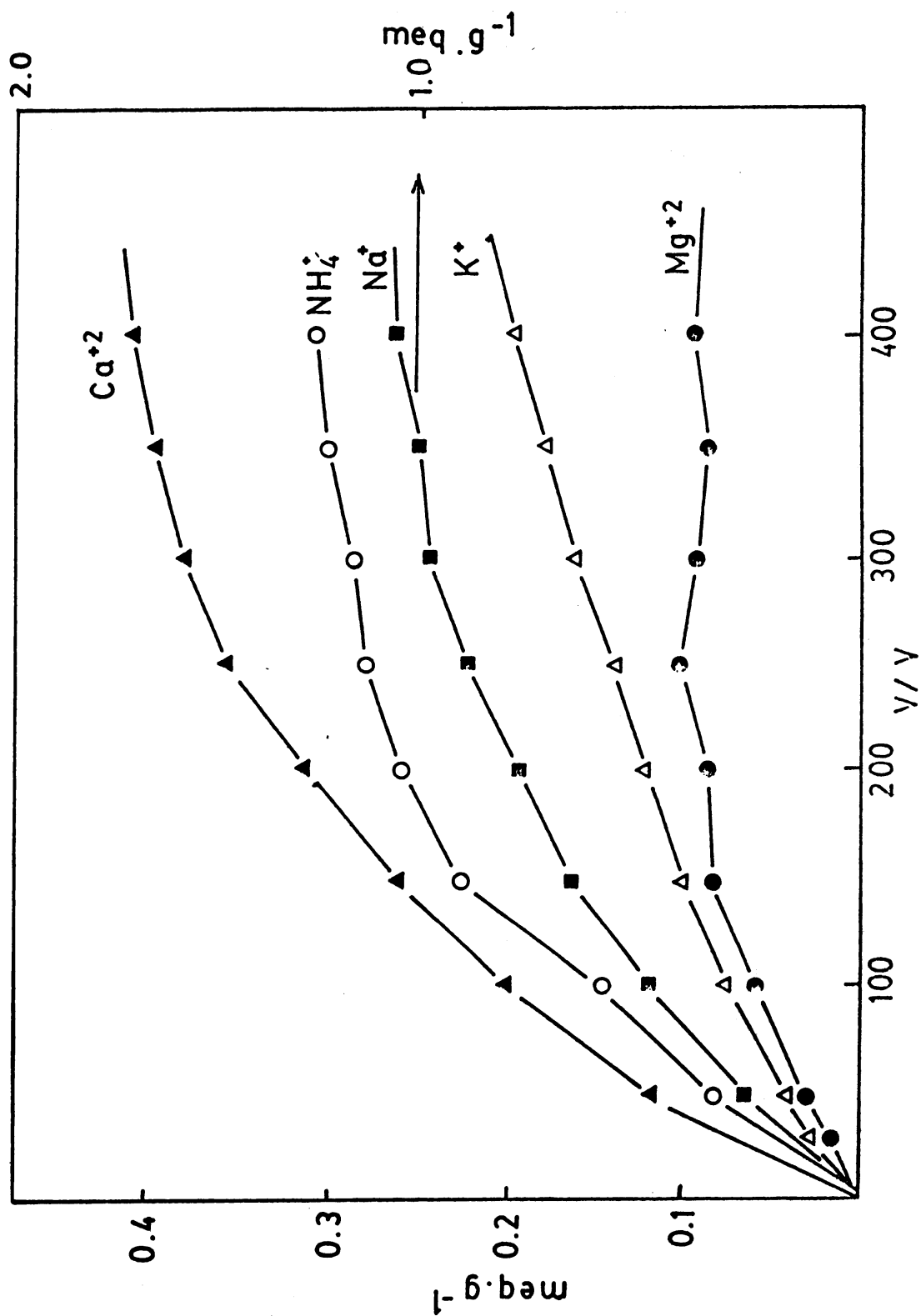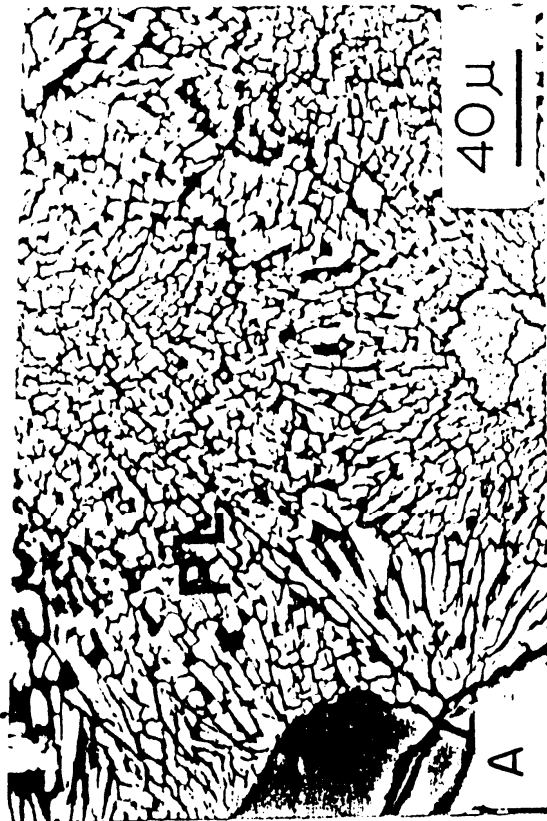site Px=Pyroxene Ch=Chabazite Sm=Smectite.

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Fig-7 Boundaries of Plateau within limits of NE Jordan and Location of Tal Ermah and Aritain Area.

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Pl: 1