ADSORPTION OF NITROGEN OXIDES IN ZEOLITES

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THE ADSORPTION PROPERTIES OF DIFFERENT SYNTHETIC AND HUNGARIAN NATURAL ZEOLITES IN THE ADSORPTION OF NO AND NO_2 WERE INVESTIGATED BY X–RAY DIFFRACTION, DERIVATOGRAPHY, INFRARED SPECTROSCOPY, MASS SPECTROSCOPY AND CLASSICAL ANALYTICAL METHODS. NITRATE ION FORMATION WAS FOUND TO OCCUR IN THE ZEOLITE STRUCTURE DURING THE ADSORPTION OF NITROGEN OXIDES. THE SOLUBILITY OF NITRATE FROM NITRATE/NATURAL ZEOLITE SYSTEMS WAS INVESTIGATED. THE POSSIBILITY OF THE USE OF NATURAL ZEOLITES AS FERTILIZER ADDITIVES IS DISCUSSED.

Introduction

One of the current fundamental environmental problems is acidic rain, in which the main role is played by sulphur oxides and nitrogen oxides. The disadvantage of nitrogen oxides in the atmosphere is that they increase the acidity of rain, but the presence of nitrogen in rain has some advantages for plants (vegetables), too.

Adsorption is one of the possible methods for the removal of nitrogen oxides from waste and industrial flue gases. Zeolites, as excellent adsorbents, have been widely investigated in this process [1–3].

The present work had two aims: to determine the adsorption properties of natural and synthetic zeolites, and to investigate the possible agricultural application of Hungarian natural zeolites, to utilize both the nitrogen content that accumulates during adsorption and the original cations, as useful mineral components.

Experimental

Materials

The zeolites used in experiments were NaX (Union Carbide Co., Linde Div.), Na–mordenite (NaM) (Norton Co.), and natural mordenite (Hegyalja Works, Hungarian Ore and Mineral Mines, Bodrogkeresztúr) (BoM), with 30% mordenite content [4].

The nitrogen oxides were produced by classical preparation methods: NO from the reaction of HNO_3 with metallic copper; and NO_2 by the decomposition of $Pb(NO_3)_2$. N_2O was obtained commercially.

$NaNO_3$, NH_4NO_3 and chemicals for analytical work were REANAL products.

Methods

X–ray diffraction analysis with a DRON–3 diffractometer was carried out to check the crystallinity of the zeolites before and after different treatments.

The decomposition behaviour of nitrate in the zeolite structure was investigated with a MOM–Q derivatograph, usually operating at a heating rate of 10 degree/min.

Two infrared techniques were used: in a vacuum cell, the adsorption of nitrogen oxides was investigated by using self–supporting wafers appr. 10 mg cm^{-2} thick, pressed from zeolite; in other cases, the KBr pellet technique (with 1% zeolite in KBr) was used to determine the NO_3^- ion content under different experimental conditions. A SPECORD–75 IR spectrophotometer was used. The desorbed gas mixture was analysed with an MX–7301 mass spectrometer. In the quantitative determination of NO_2^- and NO_3^- ions in the washing water, classical analytical methods were used.

In the adsorption experiments, two methods were applied: the static method involved volumetric adsorption, while in the dynamic flow method a thermal conductivity detector was used for gas analysis.

Results and discussion

We initially investigated the adsorption of different nitrogen oxides (N_2O, NO, NO_2) on synthetic zeolite NaX by IR spectroscopy. These measurements were connected with our dealumination work with nitrosyl chloride [5].

Figure 1 shows infrared spectra of N_2O adsorbed under different conditions.

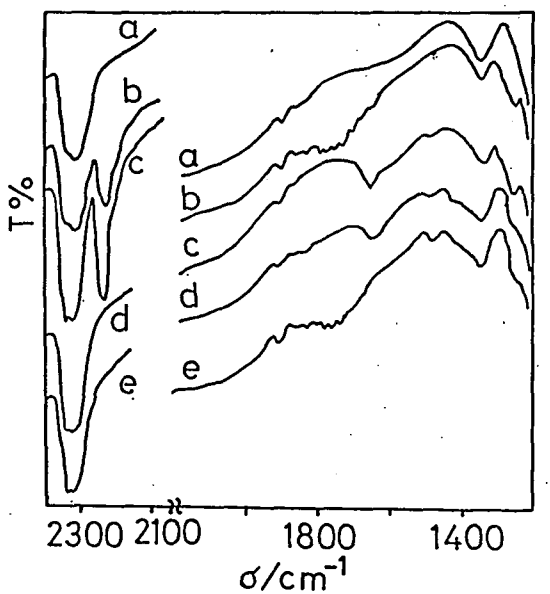


Figure 1: Infrared spectra of adsorbed N_2O

(a) pretreated NaX

(b) adsorption of 400 Pa N_2O at ambient temperature

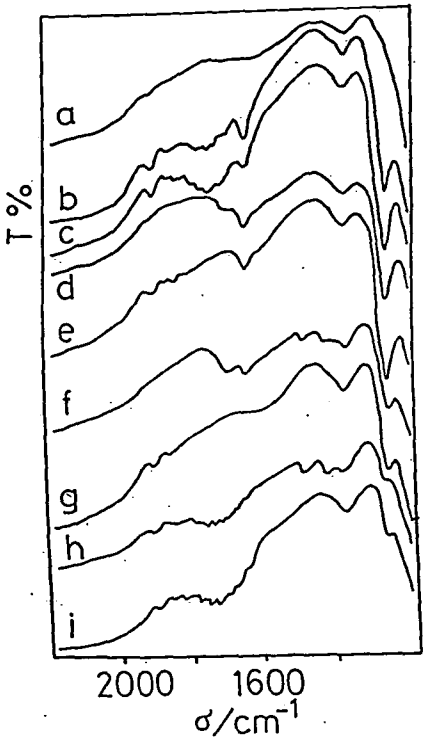
(c) 840 min at 370 K

(d) evacuated for 30 min at 370 K

(e) evacuated for 30 min at 470 K

At room temperature, two adsorption bands were registered: at 2230 cm^{-1} and 1255 cm^{-1} (the vibration of adsorbed N_2O) [6]. After 840 minutes at 370 K, a new band appeared at 1630 cm^{-1}; this practically disappeared upon evacuation for 30 minutes at 470 K and the background spectrum of the zeolite was recorded, proving that N_2O adsorption is reversible under these conditions.

Infrared spectra of adsorbed NO are shown in Figure 2.



(a) pretreated NaX

(b) adsorption of 1000 Pa NO at ambient temperature

(c) 30 min at 370 K

(d) 930 min at 370 K

(e) evacuated for 30 min at 370 K

(f) 960 min at 470 K

(g) evacuated for 30 min at 470 K

(h) 150 min at 570 K

(i) evacuated for 30 min at 570 K

Figure 2: Infrared spectra of adsorbed NO

At room temperature, bands were found at 1630 cm^{-1} (due to adsorbed NO) and at 1240 cm^{-1} (due to NO_2^- ion in the zeolite structure) [7]. It can be clearly seen that with rising temperature the intensity of the band at 1240 cm^{-1} increases, and attaining a maximum decreases.

Heating resulted in two new bands, at 1470 cm^{-1} and 1410 cm^{-1}, but on evacuation for 30 minutes at 570 K the original spectrum was obtained.

Figure 3 shows spectra following the adsorption of NO_2 on NaX zeolite. At room temperature, bands appeared at 1915 and 1370 cm^{-1}, due to adsorbed NO_2 [8] and to NO_3^- ion present in the zeolite structure [9], respectively. A third band appeared in the range of framework vibration, at 810 cm^{-1}. This means that the formation of NO_3^- ion causes changes in the zeolite framework. At higher temperatures two other bands developed at 1690 and 1245 cm^{-1}, while the intensity of the 1370 cm^{-1} band decreased; however, this latter band, due to NO_3^- ion, was present even at 670 K, *i.e.* above the decomposition temperature of $NaNO_3$, proving that NO_3^- ion can be stabilized by salt occlusion in the framework.

In the next step of this work, the adsorption of nitrogen oxides in a Hungarian natural zeolite (BoM) was investigated.

The adsorption isotherms of NO and NO_2 at 423 and 573 K are shown in Figure 4. It can be seen that the adsorbed amounts are always higher in the case of NO_2 than for NO.

Table I gives the results of dynamic adsorption measured in the apparatus was described previously [10], at room temperature (298 K). The adsorbed amounts are in good agreement with literature data [2].

Figure 5 depicts infrared spectra of this zeolite, investigated with the KBr pellet technique, after desorption. It can be concluded that desorption is not complete, even at 570 K, and NO_3^- ion is formed in the zeolite structure from both NO_2 and NO. It is clear

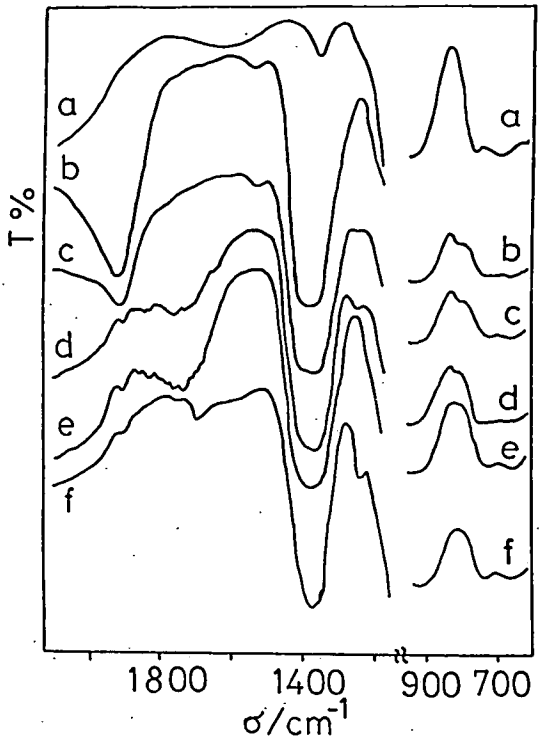


Figure 3: Infrared spectra of adsorbed NO_2

(a) pretreated NaX

(b) adsorption of 400 Pa NO_2 at ambient temperature

(c) evacuated for 30 min at ambient temperature

(d) 30 min at 570 K

(e) evacuated for 30 min at 570 K

(f) 30 min at 670 K

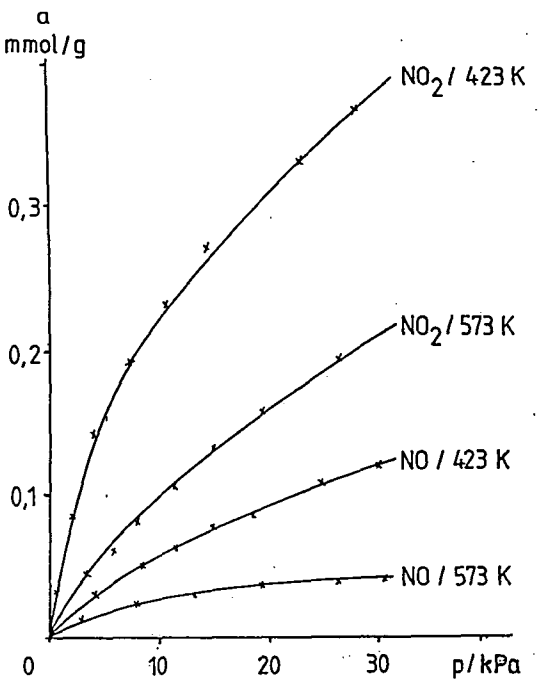


Figure 4: Adsorption isotherms of NO and NO_2 on Hungarian mordenite

that NO_2 yields a more characteristic NO_3^- ion band than NO.

Qualitative experiments were carried out to measure the composition of the desorbed gas mixture by mass spectrometry. In agreement with the infrared data, the composition of the desorbed gas indicated that reactions take place with the zeolite framework to form NO_3^- ion. The desorbed gases contain reduced molecules, for example N_2O and NO from NO_2 (see Fig. 6), and N_2 and N_2O from NO (Fig. 7).

In a further experimental series, we investigated the stabilization of NO_3^- ion in the

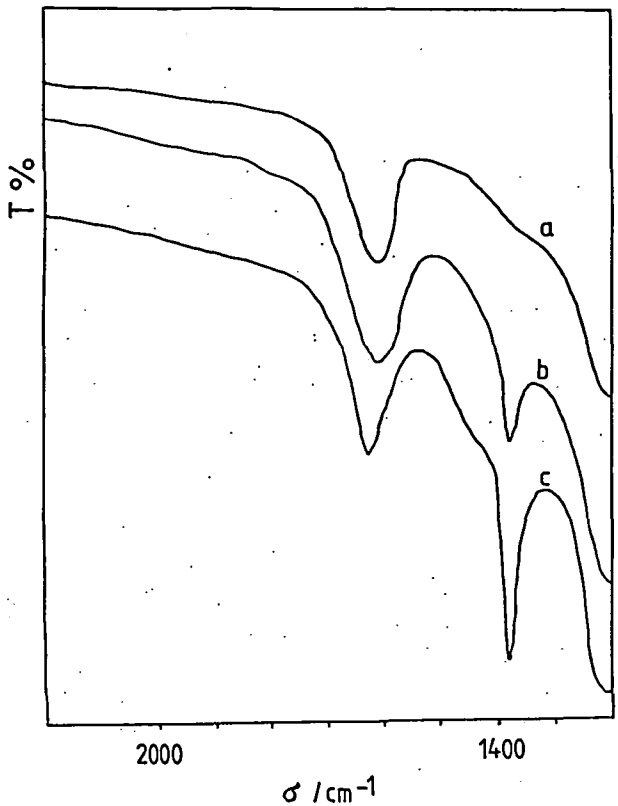


Figure 5: Infrared spectra of Hungarian natural mordenite

(a) original BoM

(b) after NO adsorption

(c) after NO_2 adsorption

mordenite structure. It is well known that inorganic ions can be formed in zeolites by the chemisorption of different gases at elevated temperatures, and guest ions or molecules can be occluded into the pore system of zeolites as well [11]. The occlusion of NO_3^- ion has been investigated in the case of A, X, and Y type synthetic zeolites, but not in the structure of synthetic mordenite and the natural zeolites.

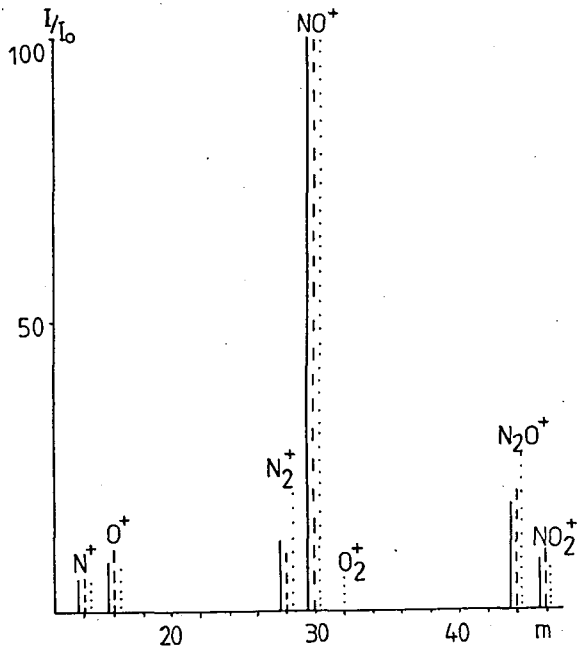


Figure 6: Mass spectra of desorbed NO_2
(—— at 373 K, – – – at 473 K, ... at 573 K)

Na–mordenite was treated with $NaNO_3$ solution and water was evaporated off to yield 5% $NaNO_3$ in Na–mordenite. Samples were treated for 5 hours at different temperatures in a furnace. The effects of heat treatment were investigated by derivatography. The adsorbed water desorbed from pure $NaNO_3$ up to 400 K and the sample melted at 580 K. Decomposition through $NaNO_2$ to Na_2O started at 870 K.

Figure 8 shows TG and DTG curves of heat–treated samples. The first step in the DTG curve relates to water loss, the second one to the decomposition of $NaNO_3$. The DTG curves reflect the decomposition in detail.

Figure 9 shows X–ray diffractograms of different samples. Reflexions of crystalline

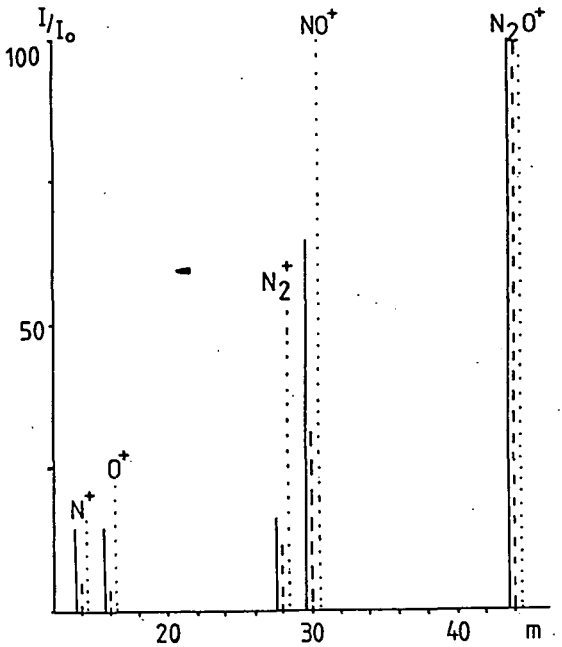


Figure 7: Mass spectra of desorbed NO
(—— at 373 K, – – – at 473 K, ... at 573 K)

$NaNO_3$ can clearly be seen in the diffractogram of the non–heated sample.

The results on the $NaNO_3$/Na–M system revealed that $NaNO_3$ was partially occluded in the pore system of mordenite. The $NaNO_3$ content of the sample obtained by heat treatement at 770 K was the same as originally added, but reflections of crystalline $NaNO_3$ were not detected in the X–ray diffractogram. The samples obtained by heat treatment at elevated temperatures had smaller $NaNO_3$ content, probably because of NO_3^- decomposition. The X–ray diffraction results indicated that the sample heat treated at 870 K had partially lost its crystallinity. It can be concluded that the optimum temperature for

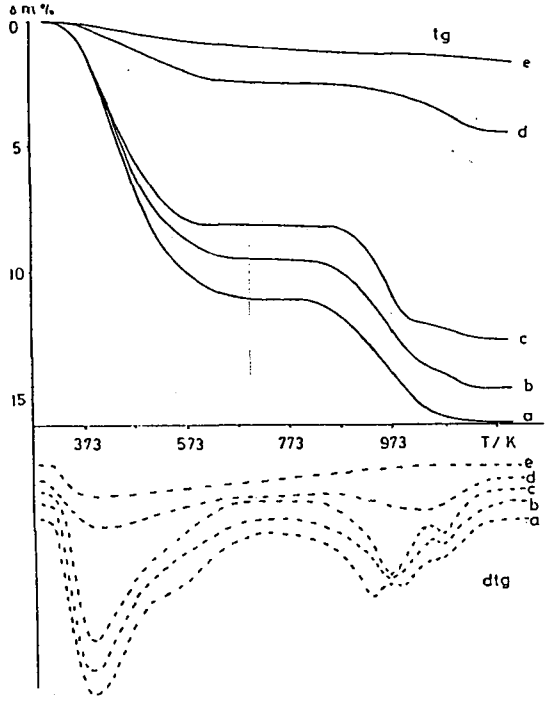


Figure 8: Derivatograms of 5 m% $NaNO_3$/Na–mordenite samples after different heat treatments
(a) at 370 K, (b) at 470 K, (c) at 570 K, (d) at 770 K
and (e) at 870 K

the stabilization of $NaNO_3$ in the mordenite structure is below 770 K.

The solubility of NO_2^- and NO_3^- ions from the zeolite framework was investigated in the case of natural mordenite. After the adsorption of NO and NO_2, 0.5 g BoM was washed with 50 cm^3 distilled water, and NO_2^- and NO_3^- contents of the solution were analysed by

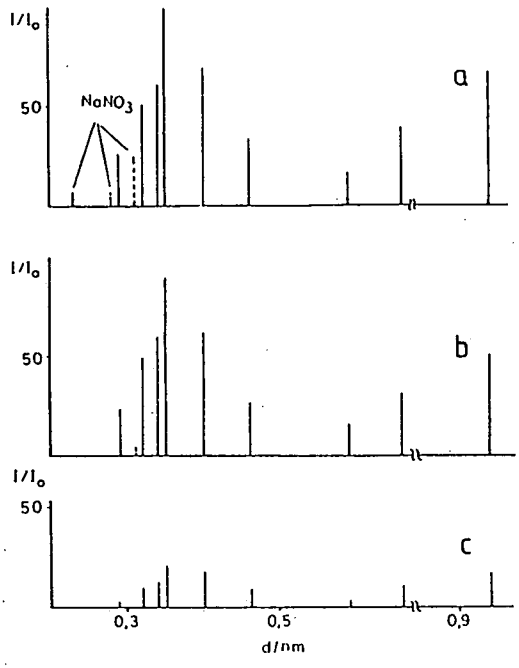


Figure 9: X–ray diffractograms of $NaNO_3$/Na–mordenite samples
(a) after evaporation of the $NaNO_3$ solution
(b) after heat treatment at 470 K
(c) after heat treatment at 870 K

classical methods. Typical results are given in Table II. From these data it can be concluded that the amounts of NO_2^- and NO_3^- ions formed following NO adsorption are of the same order of magnitude, whereas NO_2 adsorption led to a higher amount of NO_3^- ion without NO_2^- ion formation.

In the case of natural mordenite two preparation methods were used. In the first method, BoM powder and NH_4NO_3 powder were mixed to avoid the NH_4^+ ion–exchange, which was impossible in the second method, when the solvent of the NH_4NO_3 solution was

evaporated from the zeolite. The NH_4NO_3 content of the sample was the same in the two cases.

The solubility of NH_4NO_3 from the NH_4NO_3/BoM system was investigated in model experiments [12]. The soil was modelled with sand from the River Maros. The NH_4NO_3/BoM system was mixed with this sand. A glass column was filled with this mixture and distilled water was loaded on the bottom of the column. The conductivity of the outlet solution was measured. Figure 10 shows the results of a typical experiment. It is

Table I

Dynamic adsorption measurements

Reactants	Amount of adsorbent[#] (g)	Cross-section of column (cm^2)	Column volume (cm^3)	V_d:dead volume (cm^3)	w:flow rate (cm^3/min)	c^o:NO_x concn. (vol%)	$\bar{t}$:retention time (min)	Adsorbed* amount (mg/g)
BoM+NO	22 (A)	1.76	22	11	22.5	11	8	1.04
BoM+NO	22 (A)	1.76	22	11	12.5	20	10	1.26
BoM+NO	22 (A)	1.76	22	11	31.6	5	4	0.32
BoM+NO_2	12 (B)	0.50	12.4	6.4	25.3	21	58	47.67
BoM+NO_2	12 (B)	0.50	12.4	6.4	82.0	2.4	65	20.03
NH_4BoM+NO_2	12 (B)	0.50	12.4	6.4	20.5	17	84	45.71
NH_4BoM+NO_2	9.2(B)	0.50	9.5	4.9	40.5	1.2	40	3.97
NH_4BoM+NO_2	9.2(B)	0.50	9.5	4.9	92.6	7.2	30	43.09
BoM+NO_2	12 (A)	0.50	12	6.0	41.0	2.4	130	20.03
BoM+NO_2	10.5(C)	0.50	11.5	6.25	42.6	6.1	180	83.07

[#]Size fraction of adsorbent: A: 0.63–1.1 mm, B: 0.515–0.63 mm, C: 0.125–0.315 mm

*The equation $a = c^o(\bar{t}w - V_d)$ was used to calculate sorbed amounts

Table II

Removable anion content of saturated adsorbent

Reactant	Temperature of adsorption (K)	Washed–out anions (μmol/g zeolite)	
		nitrate	nitrite
NO	423	64	30
	573	38	18
NO_2	423	325	–
	573	272	–

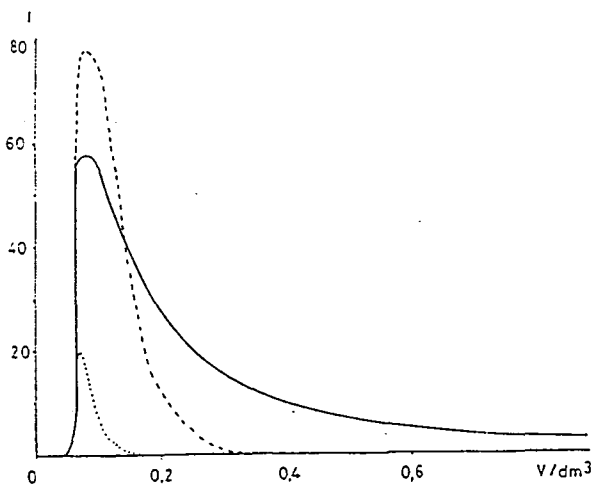


Figure 10: Conductivity of outlet solution vs. volume of solution

(... sand, – – – NH_4NO_3/sand, —— NH_4NO_3/BoM/sand)

clear from the curves that the dissolution of NH_4NO_3 requires more water and a longer time for the NH_4NO_3/BoM/sand system than for the NH_4NO_3/sand system.

Conclusions

–The adsorption of NO and NO_2 resulted in NO_3^- ion formation in the zeolite structure.

–NO_3^- ion was stabilized by salt occlusion in the mordenite framework.

–Natural zeolites can be regarded as possible fertilizer additives due to retardation of the dissolution of nitrates, especially in sandy soil.

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АДЦОРБЦИЯ ОКСИДОВ АЗОТА В ЦЕОЛИТАХ

И.ГАННУШ, Я. ГАЛАС, У. КИРИЧИ, ДЬ. ШЕБЕЛ, ДЬ. ТАШИ и П. ФЕЕШ

Исследованы адсорбционные свойства различных синтетических и венгерских естественных цеолитов к NO и NO_2. Измерения были проведены с помощью рентгеновской диффракции, дериватографии, инфракрасной спектроскопии, масс-спектрометрии и классических аналитических методов. В процессе адсорбции оксидов азота в цеолитных структурах было найдено образование NO_3^- нонов. Изучена растворимость NO_3^- нонов из системы NO_3^-/естественный цеолит в связи с возможностью их применения в качестве компонента удобрений.