ESTIMATION OF THE ZEOLITE CONTENTS OF TUFFACEOUS SAMPLES FROM THE BIGADIÇ CLINOPTILOLITE DEPOSIT, WESTERN TURKEY

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Abstract—Variation of the NH_4^+-exchange and CO_2-adsorption capacities with zeolite content was investigated in detail to assess the potential use of these capacities for the estimation of the zeolite contents of the samples taken from the Bigadiç clinoptilolite deposit in western Anatolia, as an alternative to the widely used semi-quantitative X-ray diffraction (XRD) technique. Samples with known clinoptilolite contents taken from 2 different zones with fine- and coarse-grained tuffs of the Bigadiç deposit were used for this purpose. Na-enriched forms of the samples were prepared by repeated ion-exchange with NaCl solutions, and NH_4^+-forms by repeated Na exchange followed by NH_4^+ exchange with NH_4Cl solutions, which in turn were calcined to obtain the H-forms. NH_4^+-exchange capacities by Kjeldahl analyses of the NH_4^+-forms and CO_2 adsorption isotherms in the 0 to 100 kPa range of Na- and H-forms of the samples were determined. Dubinin-Astakhov model parameters were calculated from the isotherm data.

A strong relationship exists between the experimental CO_2-adsorption capacities at 100 kPa of the Na-forms and the zeolite contents of the samples. Although the Dubinin-Astakhov model represented the isotherm data quite well, the relationships between the amounts of adsorbate at saturation pressure, calculated from the model, and the zeolite contents of the samples were weaker. The strength of the relationship between NH_4^+ exchange capacities and zeolite contents was seen to vary with the zone of origin. There is a very strong relationship between the adsorption and ion-exchange capacities of the samples in their Na-forms taken from the fine-grained zone, indicating that either ion-exchange or adsorption capacity measurements can be used to estimate the zeolite contents of the samples taken from this zone, whereas, significant diffusion hindrance was observed against ion-exchange of hydrated cations from aqueous solutions for some samples from the coarse-grained zone. Inspection of the data pointed to systematic errors in the zeolite contents determined by a semi-quantitative XRD technique. When both zones are considered together, CO_2-adsorption capacities at 100 kPa of the samples in their Na-forms can be used as a reliable measure of the zeolite content, which in turn is an important index to predict the performance of natural samples in various applications.

Key Words—Clinoptilolite, CO_2 Adsorption, Dubinin-Astakhov Isotherm Model, Natural Zeolites, NH_4^+-Exchange, Zeolite Content.

INTRODUCTION

Zeolites, especially the synthetic ones, have obtained widespread applications in industry as adsorbents, catalysts and ion exchangers. Although several zeolite minerals, such as clinoptilolite, mordenite and phillipsite, are available in mineable deposits having relatively high purity, extensive application of natural deposits has not yet been achieved. Some of the reasons that natural zeolites have not competed with synthetics in industrial applications are variation of the zeolite content and the cationic composition of the zeolite with location and the lack of practical test methods to estimate the zeolite content of the samples taken from a deposit.

Determination of the zeolite content of natural samples is important as an index to predict their performance in various applications (Mumpton 1988). Semi-quantitative XRD, for which the calibration curve has to be prepared with a purified zeolite sample, is the most commonly applied technique for this purpose. Making use of the relationships between ion exchange or adsorption performances and zeolite content have been proposed (Johnson 1978; Valyon et al. 1981; Sheppard and Gude 1982; Kallo et al. 1982; Sersale

1985) as alternatives to the time-consuming, cumbersome and sometimes inaccurate X-ray procedures.

The N_2-adsorption capacity measurements that have been used to estimate the zeolite content of synthetic materials (Johnson 1978) are not suitable for natural samples containing zeolites such as clinoptilolite because of the small pore openings in the crystal structure.

Valyon et al. (1981) have proposed to use the amount of the adsorbate at saturation pressure, calculated from the Dubinin-Astakhov model applied to CO_2 adsorption isotherms of the natural samples in their H-forms, as an estimate of the zeolite content. The characteristic energy of CO_2-adsorption on the H-forms of the 4 mordenite and 3 clinoptilolite-containing rocks were seen to vary in a narrow range by these researchers, and this was taken to indicate that adsorption took place mainly in the zeolite pores (Valyon et al. 1981; Kallo et al. 1982). Adsorption on the outer surfaces and on accompanying minerals was neglected, and the estimation of zeolite content was based on only 1 reference sample for each zeolite type.

The relationship between the ion-exchange performance and the zeolite content was weak in some cases

(Lieu et al. 1988a) and deviated considerably for clinoptilolites from the results determined by other methods (Valyon et al. 1981; Kallo et al. 1982). Conversely, the strength of the relationship is known to depend on the pretreatments and experimental procedures applied (Erdem-Şenatalar et al. 1993).

A cation-exchange capacity (CEC) method based on ion-sieving properties of the zeolites was proposed (Ming and Dixon 1987), where t-butylammonium ion was used to differentiate the non-zeolitic ion-exchange capacity of clinoptilolite-containing soils from total exchange capacity determined by Na exchange. This procedure also has drawbacks such as the possibility of limited diffusion of t-butylammonium ion in non-zeolitic phases.

For a performance test based, for example, on an adsorption (or ion-exchange) capacity to be used to estimate the zeolite content of natural samples, exclusion of either the zeolitic or non-zeolitic components should not be necessary. To demonstrate this, let us denote the capacities (mmoles/g) of pure zeolitic components by q_Z and non-zeolitic components by q_{NZ}, and the weight fraction of the zeolite in a sample by x. The total capacity of the sample, q, can then be written as in Equation [1] as the sum of the capacities of 2 components:

$$q = q_Z \cdot x + q_{NZ} \cdot (1 - x) \qquad [1]$$

The above equation, when rearranged, yields the following linear relationship between capacity and zeolite content:

$$q = (q_Z - q_{NZ})x + q_{NZ} \qquad [2]$$

It then follows that as long as the non-zeolitic components show uniform capacity for the specific gas (or ion) throughout a deposit and this capacity is different in magnitude from that of the zeolite component, a linear calibration curve for the deposit, between the capacity and zeolite content, given by Equation [2], should be possible to establish experimentally. Prior to such a study, the zeolite, of course, should be converted into a near-homoionic form to eliminate as much as possible the well-known effects on capacity of the variation of the cationic composition with location (Ackley and Yang 1992; Sirkecioğlu et al. 1995). CO_2-adsorption and NH_4^+-exchange capacity measurements are suitable to be used in this respect to estimate the zeolite content for a clinoptilolite deposit. Clinoptilolite is known to have a high capacity and a high selectivity for the small and polar gases (Flanigen and Mumpton 1981) such as CO_2, which has a high quadrupolar moment (Barrer and Murphy 1970) and also for the NH_4^+ ion (Ames 1960). Both capacities are significantly higher for clinoptilolite than for any of the probable accompanying minerals (Worrall 1986). Additionally, Na- and H-forms of clinoptilolite

are known to give the highest adsorption capacities for CO_2 (Yücel and Culfaz 1988).

Zeolite-bearing mineral assemblages in pyroclastic deposits of the nonmarine Neogene basins are widespread in western Anatolia (Ataman 1977). The most important occurrence, having a large reserve of approximately 2 billion tons and a high clinoptilolite content, is in the Neogene Bigadiç basin, which extends for 300 km² (Baysal et al. 1986). The lacustrine zeolitic tuffs, about 250 m thick, are rhyolitic in composition and are mainly coarse-grained (2 to 4 mm) and vitric in the lower part of the unit and fine-grained (less than 0.25 mm) and vitric in the upper part. Localizations containing finer grains and altered zones of coarser particles were also seen to be present in the coarse- and fine-grained zones, respectively (Sirkecioğlu et al. 1990).

Zeolites in the tuffs were classified as Ca-rich clinoptilolites, based on their thermal stability and cationic composition (Sirkecioğlu et al. 1990). Common pyrogenic minerals in the tuffs are quartz, K-feldspar, plagioclase and biotite. The major authigenic mineral is clinoptilolite, which coexists with clay minerals, silica minerals, feldspars and carbonates (Etibank 1989).

Samples from the coarse-grained lower part have a higher ratio of alkali to alkaline earth cations in the zeolites and are thermally more stable than those from the fine-grained zone (Sirkecioğlu et al. 1990). The clinoptilolite-rich tuff samples from the 2 visibly different zones in the Bigadiç basin also have differences in their ion-exchange behavior and react differently to pretreatments (Erdem-Şenatalar et al. 1993).

The zeolite contents of the samples taken from 51 localities in the deposit were determined by XRD to be 55% or more, except for one sample from the border region that contained 20% zeolite. Many samples (32 out of 51) contained at least 80% clinoptilolite (Sirkecioğlu et al. 1990). The deposit has a high potential for use in air and natural gas purifications, namely for the adsorptive separation of NO, CO, CO_2, H_2S and SO_2 from N_2 and CH_4 streams (Triebe et al. 1994; Sirkecioğlu et al. 1995).

A detailed investigation of the dependencies of NH_4^+-exchange and CO_2 adsorption capacities on zeolite content for the Bigadiç deposit was carried out in this study using a representative set of samples having known zeolite contents from both zones to assess the potential use of these capacities for the estimation of the zeolite content of bulk tuff. Repeated NaCl treatments were performed to prepare near homoionic forms for adsorption and to determine ion-exchange capacities that are close to the limiting values.

EXPERIMENTAL

Fifteen samples from different locations in the coarse- and fine-grained zones were selected from a larger set of samples previously taken from 4 geolog-

Table 1. NH₄⁺-exchange and CO₂-adsorption capacities of the clinoptilolite-bearing tuffs.

Sample code	Zone†	% Clinoptilolite	Cation exchange capacity meq/q	Adsorption capacity mmol/g	
				H-Form	Na-Form
EIS16/22	C(F)	20	0.81	0.847	0.869
EIS16/3	F	67	1.53	0.949	1.621
K3/15	C(F)	67	1.68	1.865	1.873
K3/26	C(F)	70	1.82	1.511	1.923
EIS2/4	F	73	2.19	2.142	2.581
K2/3	F	77	1.90	2.319	2.206
K3/8	F	80	1.84	1.852	1.995
K1/7	C	82	2.36	1.821	2.178
K1/9	F	87	1.99	2.297	2.395
K1/2	C	88	1.92	2.563	2.413
K1/4	C	90	1.96	2.323	2.473
K3/3	F	93	1.84	2.141	2.113
K1/6	C	93	1.84	2.209	2.006
K3/6	F(C)	100	1.96	2.133	2.855
K2/16	C	100	1.98	1.933	2.698

Key: † F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.

ical cross sections and three drill cores in a 5 km² area of the Bigadiç basin (Etibank 1989). The selection of the sample set was mainly based on the zones of origin (coarse-grained or fine-grained) and the clinoptilolite contents of the samples, which had been previously determined semi-quantitatively by an XRD technique using an internal standard with purified clinoptilolite-glass mixtures (Etibank 1989; Sirkecioğlu et al. 1990; Erdem-Şenatalar et al. 1993). Care was taken to represent the range of zeolite contents in the deposit (20 to 100%) and to include a few samples from the finer and coarser grained localizations of the coarse- and fine-grained zones, respectively.

Samples were crushed and sieved to obtain 90 to 150 μm fractions, which were then washed with hot distilled water for 24 h in a Soxhlet extractor for the removal of water-soluble impurities, approximately 4% of the original samples. Chemical analyses of the samples were reported previously by Erdem-Şenatalar et al. (1993). Na-enriched forms of the samples were prepared by repeated ion exchange with NaCl solutions at 80 °C for 5 hours. 100 ml of exchange solution was used per gram of zeolite. NH₄⁺-exchange of the Na-forms was performed after each NaCl treatment at 80 °C for 5 hours with 1 M NH₄Cl solutions, using the same solution to zeolite ratio. The samples were then washed, dried at 50 °C for 1 day, and brought to moisture equilibrium in a saturated humidity atmosphere at 20 °C for 1 week prior to the determination of their NH₄⁺-exchange capacities by modified Kjeldahl analysis (Lieu et al. 1988b). Treatment with NaCl solutions was continued until constant NH₄⁺-exchange capacities were reached. Five such treatments with NaCl solutions were generally found to be sufficient.

CO₂-adsorption experiments were carried out on the Na-enriched samples prepared by repeated ion-exchange treatments and on H-forms of the samples prepared by calcination of the NH₄⁺-enriched forms. A constant volume adsorption system was used, and CO₂-adsorption isotherms of the samples in the 0 to 100 kPa range were determined. A minimum of 15 minutes at the same pressure was allowed for each equilibrium data point. All samples were heated at a rate of 2 °C/min to 400 °C and were activated at this temperature and at 10^{-5} mbar pressure for 6 h prior to the adsorption experiments. The Dubinin-Astakhov pore filling model (Dubinin 1975) was applied to the isotherm data, and model parameters were calculated.

NH₄⁺-exchange capacities of the samples, CO₂ adsorption capacities at 100 kPa of the Na- and H-forms, and the amounts of adsorbate at saturation pressure calculated from the Dubinin-Astakhov model were correlated with the clinoptilolite contents using statistical methods (Daniel 1976) to search for linear relationships that can be applied for the prediction of zeolite contents of the tuffs from this deposit.

RESULTS AND DISCUSSION

The NH₄⁺-exchange and CO₂-adsorption capacities at 100 kPa of the samples are given in Table 1, together with their zones of origin. Fine-grained zones are represented by the notation F and coarse-grained zones are represented by the notation C. C(F) notation denotes the finer-grained localizations of the coarse-grained zone, and F(C) denotes the altered, coarse-grained regions of the fine-grained zone. The sample codes are also listed in the table, and exact sample localities are in previous reports (Etibank 1989; Sirkecioğlu et al. 1990).

The NH₄⁺-exchange capacities are higher than those obtained previously (Erdem-Şenatalar et al. 1993), without repeated salt treatments, for most of the samples. But, the CO₂ adsorption capacities are generally higher for the Na-forms of the samples.

Ion-exchange and adsorption capacities are plotted against zeolite content in Figures 1 and 2, respectively. The correlation coefficients calculated for the linear regressions between the capacities and zeolite contents are listed in Table 2.

Samples from the coarse- and fine-grained zones were correlated separately, in addition to the total set of samples. The degrees of freedom become quite low when the coarse and fine zones are considered alone, we also combined one or both of the altered zones with coarse- and fine-grained zones, as can be seen from the list of the sample sets in Table 2. Regression lines obtained for the total set of samples are shown in Figures 1 and 2.

The relationship between the NH₄⁺-exchange capacity determined after repeated NaCl treatments and zeolite content for the total sample set of this study is

Table 2. Correlation coefficients of the linear regressions obtained for Bigadiç clinoptilolite samples.

Sample† set	Degrees of freedom	Ion Exc. Cap.–% Clin.	Ads. Cap.–% Clin.				Ion Exc. Cap.–Ads. Cap.			
			H-form		Na-form		H-form		Na-form	
			q‡	q_0§	q	q_0	q	q_0	q	q_0
All samples	13	0.79	0.75	0.59	0.87	0.79	0.70	0.39	0.83	0.78
F + F(C) + C(F)	8	0.86	0.77	0.77	0.88	0.84	0.83	0.58	0.93	0.88
F + C(F)	5	0.88	0.77	0.87	0.62	0.69	0.83	0.40	0.83	0.88
F + F(C)	7	0.29	0.56	0.75	0.85	0.30	0.81	0.66	0.99	0.46
F	4	0.25	0.63	0.76	0.31	0.2	0.81	0.50	0.98	0.45
C + F(C) + C(F)	7	0.86	0.86	0.59	0.95	0.94	0.70	0.42	0.81	0.85
C + C(F)	4	0.87	0.86	−0.03	0.95	0.81	0.70	−0.43	0.85	−0.09
C + F(C)	6	−0.60	−0.06	0.54	0.68	0.94	−0.67	0.40	−0.15	0.89
C	3	−0.64	−0.03	−0.27	0.52	0.73	−0.68	−0.42	−0.11	−0.02

Key: F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.
‡ q = Adsorption capacity, obtained experimentally at 100 kPa.
§ q_0 = Adsorption capacity at saturation pressure, calculated from the Dubinin-Astakhov model.

stronger than any of those tested previously (Erdem-Şenatalar et al. 1993), using different pretreatment and ion-exchange procedures. Contrary to our expectations, the strength of the relationships obtained for the coarse- and fine-zone samples within themselves were not higher than that for the total sample set. However, if Figure 1 is observed more closely, it can be seen that a reasonably strong relationship exists for the fine-grained zone, with the exception of 2 samples, those containing 73% and 93% clinoptilolite. Although that means removal of 2 out of a set of only 6 samples, we believe there is an explanation of their deviating behavior, which will be discussed later in this paper. Addition of the samples from the C(F) zone to the sample sets is seen to increase the strength of the relationships.

Contrary to what had been previously reported in the literature (Valyon et al. 1981; Kallo et al. 1982),
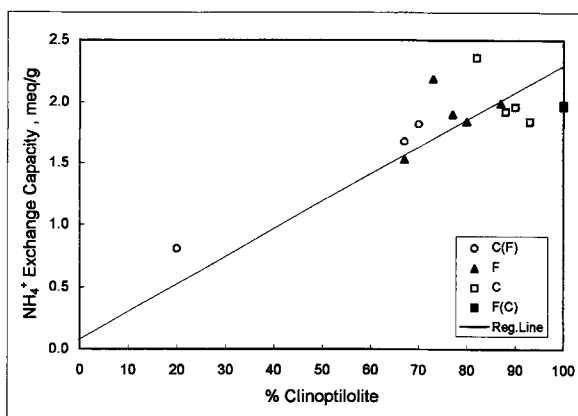

Figure 1. Variation of ammonium exchange capacity with clinoptilolite content. Key: F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.

the relationship between CO_2-adsorption capacity and zeolite content was much stronger for the samples in their Na-forms than for those in their H-forms, as can be seen from Figures 2a and b. When data on H-forms were used, scatter around the regression line increased for all zones, including the altered ones.

The amount of adsorbate at saturation pressure of the natural samples in their H-forms, calculated from the Dubinin-Astakhov isotherm model, had been suggested previously to correlate well with zeolite content. The suggestion was based on the observation that for the H-forms, the characteristic energy seemed to be independent of the zeolite content of the rock (Valyon et al. 1981, Kallo et al. 1982), implying that the adsorption took place only in the zeolitic pores. To test this claim, we also applied the Dubinin-Astakhov model to the isotherm data obtained for the Na- and H-forms. According to this model, which is based on pore filling:

$$q = q_o \exp[-(A/E)^n] \qquad [3]$$

where, q_o is the amount of adsorbate at saturation pressure, E is the characteristic energy of adsorption, n is a geometric constant, and A is the differential molar work of adsorption, which can be written as:

$$A = RT \ln(f_s/P) \qquad [4]$$

where, P is the pressure of the adsorbing gas, and f_s is the fugacity at saturation pressure.

Table 3 lists the best values of E, q_o and n obtained from the solution of the above equations for the isotherm data, together with the E and q_o values calculated, when n was made equal to 3 as in the previous reports (Valyon et al. 1981; Kallo et al. 1982). In the latter case, the correlation coefficients of the solutions were lower, as expected.

The q_o values obtained from the Dubinin-Astakhov model yielded weaker correlations with zeolite content

Figure 2. Variation of CO_2-adsorption capacities of the samples in their a) H- and b) Na-forms, with clinoptilolite content. Key: F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.
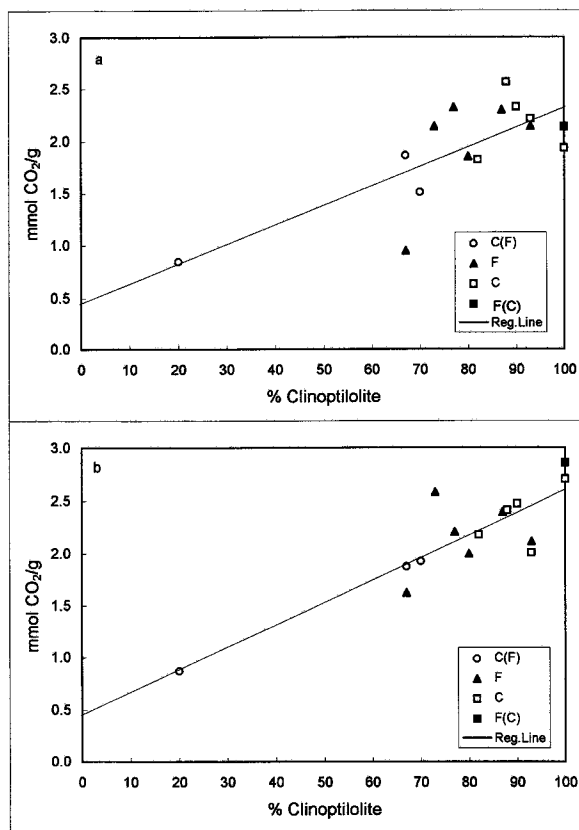
than the experimental adsorption capacities at 100 kPa for the total sample set. The corresponding correlation coefficients are listed in Table 2. The relationships between the q_o values calculated with n = 3 and zeolite contents were much weaker. Therefore, the correlation coefficients of these regressions are not included in the table.

The values of the characteristic energies seem to vary in a relatively wide range for our set of samples in Na- and H-forms, but there is no clear trend of variation with zeolite content. This is also true for both forms, when the geometric factor is forced to three. Thus adsorption cannot be argued to take place only in the zeolitic pores for either ion-form. As was discussed above, this is not necessary either, to develop a relationship between the adsorption capacity and zeolite content. The only condition that needs to be assumed and is likely to hold is that the non-zeolitic components have similar adsorption behavior, which is different from that of the zeolite component, throughout the deposit, for which the correlation is to be developed. One reference sample of high zeolite content as was reported to be used in previous studies (Valyon et al. 1981; Kallo et al. 1982) will not be sufficient then because the regression line will not pass from the origin when extrapolated. There will be some adsorption capacity of the samples even if the zeolite contents are very low due to the adsorption on non-zeolitic components. This argument will also be valid when relating ion-exchange capacity to zeolite content.

The relationship between the experimental CO_2-adsorption capacities at 100 kPa and the clinoptilolite contents of the samples in their Na-forms seems best to estimate the zeolite contents in this study. Samples from the altered zones strengthened the relationship,

Table 3. Dubinin-Astakhov model parameters calculated from the CO_2 isotherm data for the samples in their H- and Na-forms.

| | | Samples in H-Form | | | | | Samples in Na-form | | | | |
| | | | | | n = 3 | | | | | n = 3 | |
Zone[†]	% Clin.	q_0 mmol/g	E kJ/mol	n	q_0 mmol/g	E kJ/mol	q_0 mmol/g	E kJ/mol	n	q_0 mmol/g	E kJ/mol
C(F)	20	1.189	13.02	2.70	1.06	13.68	1.16	17.04	4.60	1.08	15.38
F	67	1.49	11.16	2.30	1.07	12.97	2.01	13.63	3.00	2.01	13.63
C(F)	67	2.92	12.89	1.85	1.94	16.10	2.27	14.13	3.20	2.41	13.77
C(F)	70	1.64	13.31	4.00	2.22	11.81	2.49	11.99	3.45	3.02	11.14
F	73	2.36	13.21	3.70	2.91	12.11	2.67	15.18	5.45	4.29	12.44
F	77	2.90	14.94	2.10	2.29	17.29	3.72	11.09	2.70	3.19	11.78
F	80	2.85	11.30	2.60	2.35	12.26	2.65	12.75	2.85	2.52	13.04
C	82	2.66	11.71	2.50	2.14	12.93	2.46	13.83	3.70	3.79	11.32
F	87	2.72	13.37	3.50	3.18	12.56	2.77	14.85	3.10	2.83	14.69
C	88	5.82	9.40	1.85	2.96	12.95	2.36	16.64	4.15	2.82	15.25
C	90	3.00	13.90	2.50	2.56	15.03	2.60	14.91	4.20	3.46	13.16
F	93	2.99	12.62	2.40	2.40	14.00	2.24	14.46	3.70	2.67	13.35
C	93	3.80	12.12	1.60	2.13	17.07	2.37	14.51	3.10	2.30	12.93
F(C)	100	4.62	9.47	1.80	2.29	13.33	3.36	14.08	3.80	4.33	12.65
C	100	2.18	13.87	2.90	2.75	13.24	3.09	14.96	3.05	3.13	14.86

Key: F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.
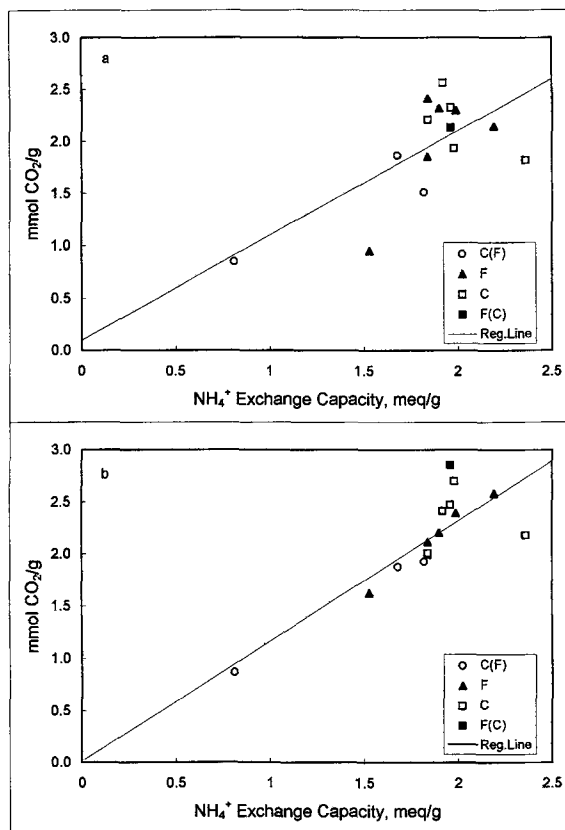
Figure 3. Variation of CO_2-adsorption capacities of the samples in their a) H- and b) Na-forms, with ion-exchange capacity. Key: F = Fine-grained; C = Coarse-grained; C(F) = Fine-grained localization in coarse-grained zone; and F(C) = Coarse-grained localization in fine-grained zone.

as in the case of ion-exchange capacities. The samples from the fine-grained zone that showed the highest deviation from the regression line are the same ones, those with 73 and 93% clinoptilolite contents, that also deviated in similar directions, when ion-exchange capacities were correlated with zeolite contents. When Figure 2b is inspected closely, it is seen that the zeolite contents of the coarse-zone samples can also be predicted with accuracy if the sample containing 93% clinoptilolite is neglected. This sample is also seen from Figure 1 to yield a deviation in the same direction when its ion-exchange capacity is considered. Both the ion-exchange capacity and adsorption capacity of the Na-form are lower than those expected from the zeolite content of this sample, similar to the 93% clinoptilolite containing sample from the fine-grained zone. Conversely, both capacities for the other fine-grained zone sample with 73% clinoptilolite are higher than those expected from its zeolite content. This sample is also the one that yielded the highest ion-exchange capacity at room temperature in a previous study (Erdem-Şenatalar et al. 1993).

The observation that the same samples have deviated considerably in similar directions, when the ion-exchange and adsorption capacities of the Na-forms were correlated with zeolite content, prompted us to question the accuracy of the zeolite contents determined by the semi-quantitative XRD technique. An error of 5%, mainly from the purification procedure, had already been considered in the zeolite content determinations (Erdem-Şenatalar et al. 1993). It is also known that X-ray line intensities may not always be proportional to the zeolite contents (Johnson 1978; Valyon et al. 1981; Ming and Dixon 1987).

When the ion-exchange and adsorption capacities for Na-forms were correlated between themselves, the samples with 73 and 93% clinoptilolite contents indeed were observed to fall on the regression line. Figure 3b shows this relationship. The scatter is again much higher for the samples in their H-forms, as can be seen from Figure 3a. The correlation coefficients of these relationships are listed in Table 2. There is a very strong correlation (r = 0.98) between the ion-exchange and adsorption capacities for samples taken from the fine-grained zone, in their Na-forms, pointing once again to the inaccuracies of the X-ray technique and implying that either ion-exchange or adsorption capacities of Na-forms can be used to estimate zeolite content for this zone.

When the total sample set is considered, the scatter in Figure 3b arises mainly from some coarse-zone samples and from the altered coarser grained sample originating from the fine-grained zone, which gave higher adsorption but lower ion-exchange capacities. For these samples, it is evident that there is more diffusion hindrance for the hydrated cations in aqueous solutions than for gas diffusion. Significantly lower room temperature exchange capacities had been recorded previously (Erdem-Şenatalar et al. 1993) for the coarse-grained zone samples in accordance with this conclusion. As can be seen from Figure 2b, CO_2-adsorption capacity of Na-forms at 100 kPa is a much more reliable measure of zeolite content for samples from this zone.

In previous studies, multi-point BET (Brunauer, Emmett and Teller) surface areas calculated from N_2 adsorption isotherms, which do not include micropore areas, had been observed to vary between 17 and 31 m^2/g for Bigadiç samples (Erdem-Şenatalar et al. 1993). The values seemed to decrease in the coarse-grained zone with increasing zeolite content. A major difference in the meso- and macro-porosity of the samples from 2 zones is the ratio of pore volumes of the pores above 750 Å to those in the range of 100 to 750 Å, which was reflected to the bimodal distribution obtained by Hg-porosimetry (Etibank 1989). This ratio was in the range of 0.1 to 1.1 for samples from the fine zone and about 1.8 for those from the coarse zone.

In spite of the greater macroporosity in the coarse-grained zone, it is interesting to observe higher diffusion hindrance during cation exchange in aqueous solutions for some samples of this zone. The imposed diffusion-limitations for the hydrated cations clearly are due to other specific factors related to the matrix structure and/or texture for samples from the coarse-grained zone.

CONCLUSIONS

Experimental CO_2-adsorption capacities at 100 kPa of the Bigadiç clinoptilolite samples in their Na-forms can be used to estimate zeolite content, as an alternative to the semi-quantitative XRD technique. The X-ray method seems to yield inaccurate results especially for some samples from the fine-grained zone, for which there is a strong linear relationship between the NH_4^+-exchange and CO_2-adsorption capacities of the Na-forms at 100 kPa. Therefore, ion-exchange capacities are also good measures of the zeolite contents for the samples from this zone, whereas significant diffusion hindrance was observed against ion-exchange from aqueous solutions for some coarse-zone samples. Adsorption capacities of the Na-forms are correlated more strongly to the zeolite contents for the samples of this zone. The scatter increases, decreasing the strength of the relationships, when H-forms are used for adsorption capacity determinations. Although the Dubinin-Astakhov model represents the isotherm data well, the relationships between the amounts of adsorbate at saturation pressure, calculated from the model equations, and the zeolite contents of the samples are generally weaker.

ACKNOWLEDGMENTS

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