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New Insights into the Relation between the Water Content of Zeolites and their Framework and Cation Population

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ABSTRACT

In this work the weight percent water content of various cation-exchanged forms of zeolites X and Y were determined and similar literature data, regarding two samples of natural clinoptilolite and a synthetic analcime, were reported. A simple linear relation was established between the weight percent water content of various cation-exchanged zeolite samples and the quantity $V_{eq\ cat}$ which is the volume of a single hypothetical equivalent cation, representing the cation population of a zeolite. This goal was fulfilled by setting up a simple model of zeolite in which the volume of its cavities and channels is occupied by water molecules and by the cations counterbalancing the negative electrical charge of the zeolite framework itself. Nevertheless the application

of the proposed model evidences the presence of void volume (portion of cavities and channels occupied by nor cations nor water molecules) in the zeolite frameworks, thus allowing also its evaluation. The linear relation found in this work may be used to estimate the water content of various cation exchanged forms of zeolites.

KEYWORDS

zeolitic water, cation population, cavities volume, channels volume, void volume

1. INTRODUCTION

The presence of water bound by interactions of physical nature to the framework of zeolites is well known since a long time. Actually this discovery dates 1756, when Cronsted noted that a mineral zeolite exhibited intumescence if heated in a blowpipe flame. This observation tickled the imagination of this Swedish mineralogist, thus suggesting him the evocative name of zeolite, which in ancient Greek means “boiling stone” [1]. The role played by the water molecules present in the cavities and channels of zeolites appears of crucial importance. Actually the interactions occurring between these water molecules and the framework of zeolites that host them, decidedly contribute to increase their stability.

Moreover, the presence of water physically bound to the zeolite framework may be directly related to one of the earliest technological applications of zeolites. Actually it is well known that zeolites, after dehydration by heating, become very eager for water in order to undergo a prompt re-hydration. On account of this property, thermally dehydrated zeolites are able to extract water molecules from the environment or from other materials, thus justifying their use as desiccants. Since this early discovery, the water contained in zeolites was studied from many points of view, which resulted in the production of many valuable works [2]. In particular a lot of effort has been devoted to the study of the structures that water confined in zeolites framework assumes and the

extent to which such structures affect the adsorption and the various other properties of zeolites [3-8]. Nevertheless, there are aspects of the studies concerning zeolitic water for which marked advances of the knowledge in the field were not recorded. Actually the water content of zeolites was obviously found to depend on the zeolite framework, as the lower its density (intended as the number of tetrahedrally coordinated Si or Al atoms per unit volume), the higher its water content is. Moreover Barrer and co-workers in their fundamental works noted that the cation population of a certain zeolite strongly affects its water content [9-12]. They found that the higher the cationic charge or the lower the cationic radius, the higher the water content.

Nevertheless, these previous considerations that relate the water content of zeolites, on the one hand, to their framework and cation population, on the other, were merely qualitative. What appears, at least a bit, surprising is that this state of the art of the researches on this topic remained unaltered since more than four decades, to the best of our knowledge. Moreover it must be said that quantitatively relating the water content of zeolites to their framework and cation population would possibly fulfil a double goal. On the one hand, it would enlarge the knowledge in this field and could likely help the comprehension of the complicated phenomena, of the same type of those studied in refs. [3-8], related to zeolitic water. On the other, the determination of the water present in zeolites by various, even complicated, techniques is matter of active research because of its effects on the various technological properties of zeolites [13-15]. On the basis of the previous considerations it appears about the time to gain new insights into this field. In particular, this work intends to ascertain if simple mathematical functions may relate the water content of zeolites, on the one hand, to their framework and cation population, on the other. To fulfil this goal, the water content of various cation-exchanged samples of zeolites X and Y was determined. Moreover, data concerning water content of various cation-exchanged samples of two natural clinoptilolites and a synthetic analcime, determined in previous studies, were reported [12, 16-17]. The two groups of data, both the ones produced within the experiments of

this work and the ones of refs. [12, 16-17], were used to elaborate a rationale which quantitatively relates the water content of zeolites, on the one hand, to their framework and cation population, on the other.

2. EXPERIMENTAL

2.1 Materials

Carlo Erba reagent-grade synthetic zeolite 13X ($\text{Na}_{86}\text{Al}_{86}\text{Si}_{106}\text{O}_{384}\cdot 264\text{H}_2\text{O}$, framework type FAU) and Sigma-Aldrich reagent grade zeolite Y ($\text{Na}_{55}\text{Al}_{55}\text{Si}_{137}\text{O}_{384}\cdot 250\text{H}_2\text{O}$, framework type FAU) were used. Carlo Erba reagent grade chemicals and doubly distilled water were used for the ion exchange operations.

2.2 Synthesis

Various cation-exchanged samples of these zeolites were obtained according to the following general procedure. Original zeolites were contacted overnight with warm (60-70) °C aqueous solutions of the relevant cations (usually 0.1 M), at weight solid to liquid ratios (S/L) ranging between 1/20 and 1/50, under continuous stirring. When the cation exchanged by the zeolite was Fe^{2+} , the exchange operations were performed at 7 °C under Ar bubbling to avoid the oxidation to Fe^{3+} [18-19].

Subsequently the solid was separated from the liquid through filtration and, if the case, contacted again with fresh exchange solution. At the end of the exchange operations the zeolites were washed with doubly distilled water. It must be emphasized that these washing operations were iterated the smallest possible number of times so as to bring the concentration of dissolved species in solution to a negligible concentration, without giving raise to hydrolysis and H_3O^+ exchange to an appreciable extent. Finally the exchanged zeolites were dried in a furnace at about 60-70 °C for a day and stored for at least three days in a closed vessel containing a saturated $\text{Ca}(\text{NO}_3)_2$ aqueous solution, which ensures a controlled constant relative humidity of

about 50 %. Some detail more concerning cation exchange operations is reported elsewhere [20-21].

2.3 Characterization

The cation composition of the samples was determined as follows. After calcination, a weighted amount of the dry samples was subjected to digestion, under microwave-induced heating (Perkin-Elmer Multiwave 3000 oven), in a standard solution prepared by mixing 1 cm³ of HCl (37%, w/w), 1 cm³ of HNO₃ (65%, w/w) and 4 cm³ of HF (39.5%, w/w). After addition of 24 cm³ of a 8 M H₃BO₃ solution to attain fluoride complexation, the resulting solution was analyzed by ICP-OES, using a Perkin-Elmer Optima 2100 DV ICP-OES apparatus [22]. The variously cation-exchanged zeolite X and Y samples, obtained as previously described, were subjected to room temperature X-ray diffractometry, using a Philips PW 1730 diffractometer, CuK α 1 radiation, collection of data between 5 and 60 ° 2 θ with a step width of 0.02 2 θ , and 1 s data collection per step.

The weight percent water content (W.C.) of the various cation-exchanged zeolite X and Y samples was determined by subjecting them to thermal treatment carried out using a Netzsch thermoanalyzer model STA 409 Luxx (weight of the sample: 100mg; heating rate: 10°C·min⁻¹; reference material: α -Al₂O₃; atmosphere: N₂), which simultaneously provided both differential thermal analysis (DTA) and thermogravimetry (TG) profiles.

3. RESULTS AND DISCUSSION

The cation composition (expressed as equivalent fraction x) of the various cation-exchanged samples of zeolites X and Y, as well as their weight percent water content (W.C.), were reported in Table 1.

In this same Table the following literature data were reported:

- 1) The cation composition (expressed as equivalent fraction x) and the weight percent water content (W.C.) of a synthetic sodium analcime (framework type ANA, Si/Al = 4.00) and that of its partially and fully potassium-exchanged forms [12].
- 2) The cation composition (expressed as equivalent fraction x) and the weight percent water content (W.C.) of two naturally occurring clinoptilolites (framework type HEU) from North Sardinia (Italy) (samples Lac Ben-4 and 80-3) and that of their various cation-exchanged forms [16-17].

The two different clinoptilolites were labeled as in refs. [16-17], namely sample Lac Ben (Si/Al = 4.71) and sample 80 (Si/Al = 4.60).

The data reported in Table 1 were deliberately arranged as much general as possible, in order to support the validity of the conclusions that will derive from their evaluation.

Actually, the following considerations appear evident from their careful examination:

- 1) The data of Table 1 concern three synthetic zeolites (analcime, X and Y) and two natural zeolites (clinoptilolite Lac Ben and clinoptilolite 80).

- 2) The various samples of the different zeolites contain from one up to five different cations.

- 3) Many largely different cations were considered. In particular various combinations of four alkali (Li^+ , Na^+ , K^+ , Cs^+), three alkaline-earth (Mg^{2+} , Ca^{2+} , Sr^{2+}) and four transition metal (Ni^{2+} , Co^{2+} , Fe^{2+} , Zn^{2+}) cations were present in the zeolite frameworks.

It must be emphasized that the literature data reported in refs. [12, 16-17] refer to alkali and alkaline-earth cations, whereas the results of this work also refer to transition metal cations. This choice was made on purpose to show that the conclusions that will derive from the evaluation of data are not limited to alkali and alkaline-earth cations but are valid also for whatever cation. Nevertheless, there was only one limitation in the selection of the cation-exchanged samples of the various zeolites. Actually, it is reported in literature that there are cations which may develop a disruptive action on some zeolitic framework [9, 23-27]. Thus the exchange operations of such cations may

result in a loss of the zeolite crystallinity. The occurrence of this circumstance largely affects the re-hydration ability of the zeolite after the drying thermal treatment to which they were subjected (one day at 60-70 °C) after the cation exchange operations. This fact, obviously, reflects onto the water content of cation-exchanged zeolite samples in a not predictable manner. To avoid this drawback, the integrity of the framework of the various cation-exchanged samples of zeolites prepared in this work was confirmed by their X-ray diffraction pattern (not reported). As far as literature data are concerned, [12, 16-17] the integrity of the framework of various cation-exchanged samples of zeolites is confirmed in the references themselves [12, 16-17].

The relation existing between the weight percent water content of zeolites (W.C.) and their cation population is based on a rationale which will be explained hereafter. If one bears in mind that density of water at room temperature is about unity, the W.C. of a zeolite numerically represents also the volume of water present in 100 g of this same zeolite, expressed as cm³ per 100 g of zeolite. Let us hypothesize, at a first stage, that the volume of cavities and channels of a zeolite is totally occupied by water molecules and cations. In this case the following relation may be written:

$$\text{W.C.} = V_{\text{cc}} - V_{\text{cat}} \quad (1)$$

where V_{cc} and V_{cat} are the volume of cavities and channels and the volume of the cations expressed as cm³ per 100 g of the zeolite, respectively.

In 100 g of a monocationic zeolite there are CEC/z moles of cation, if CEC is the cation exchange capacity of the zeolite expressed as equivalents per 100 g of zeolite and z is the valence of the cation. Every mole of cations contains an Avogadro number N of cations, whose volume is $\frac{4\pi r^3}{3}$, if r is the cation radius expressed in Å. If these quantities are multiplied among them and by the conversion factor from Å³ to cm³ ($1 \cdot 10^{-24}$), this product represents the volume of the cations expressed as cm³ per 100 g of the zeolite, namely V_{cat} . Thus, it may be written:

$$V_{\text{cat}} = \left(\frac{4\pi r^3}{3z}\right) \cdot N \cdot \text{CEC} \cdot 1 \cdot 10^{-24} \quad (2)$$

If n different cations are present in the zeolite framework, V_{cat} may be written as:

$$V_{\text{cat}} = 1 \cdot 10^{-24} \cdot N \cdot \text{CEC} \cdot \left(\frac{4\pi}{3}\right) \cdot \left[\frac{x_1 r_1^3}{z_1} + \frac{x_2 r_2^3}{z_2} + \dots + \frac{x_n r_n^3}{z_n}\right] \quad (3)$$

where x represents the equivalent fraction of the various cations present in the zeolite framework. In this case the equivalent volume of a single cation becomes:

$$V_{\text{eq cat}} = \left(\frac{4\pi}{3}\right) \cdot \left[\frac{x_1 r_1^3}{z_1} + \frac{x_2 r_2^3}{z_2} + \dots + \frac{x_n r_n^3}{z_n}\right] \quad (4)$$

In practice, if n different cations are present in the zeolite framework, $V_{\text{eq cat}}$ is the volume, expressed in \AA^3 , of a single hypothetic equivalent cation, which represents the cation population of the zeolite. Such hypothetic equivalent cation accounts for the radius and valence of the various cations present in the zeolite framework to an extent which is proportional to their various equivalent fraction. Moreover the volume of such hypothetic equivalent cation ($V_{\text{eq cat}}$), once multiplied by the conversion factor from \AA^3 to cm^3 ($1 \cdot 10^{-24}$), by the Avogadro number N and by the cation exchange capacity CEC (expressed as equivalents per 100 g of zeolite) gives the volume of cations present in 100 g of zeolite (expressed as cm^3 per 100 g of zeolite, see eq. 3).

By substituting equation (3) in equation (1), it becomes:

$$\text{W.C.} = V_{\text{cc}} - 1 \cdot 10^{-24} \cdot N \cdot \text{CEC} \cdot \left(\frac{4\pi}{3}\right) \cdot \left[\frac{x_1 r_1^3}{z_1} + \frac{x_2 r_2^3}{z_2} + \dots + \frac{x_n r_n^3}{z_n}\right] \quad (5)$$

By performing the product $1 \cdot 10^{-24} \cdot N$, equation (5) becomes:

$$\text{W.C.} = V_{\text{cc}} - 0.602 \cdot \text{CEC} \cdot \left(\frac{4\pi}{3}\right) \cdot \left[\frac{x_1 r_1^3}{z_1} + \frac{x_2 r_2^3}{z_2} + \dots + \frac{x_n r_n^3}{z_n}\right] \quad (6)$$

In this expression the cations radii by Shannon may be inserted [28]. It must be said that Shannon found the exact value of the ionic radii to be dependent on ion coordination [28]. As sufficient information concerning the cation coordination in various zeolite framework are not available, the calculations, that will be described hereafter, will be performed by inserting cation radii by Shannon for coordination VI, for coordination VIII and for the highest cation coordination reported for every cation by Shannon [28]. By substituting eq. (4) in eq. (6), it becomes:

$$W.C. = V_{cc} - 0.602 \cdot CEC \cdot V_{eq\ cat} \quad (7)$$

From equation (7) it appears evident that the W.C. of zeolites is a linear function of the sole quantity $V_{eq\ cat}$ defined in equation (4). The value of this quantity can be easily calculated, if the cation composition of the zeolite is known. Moreover the intercept of the straight line on the ordinate axis coincides with V_{cc} , whereas its slope is given by the following expression:

$$\text{slope} = - 0.602 \cdot CEC \quad (8)$$

In practice equation (7) says in symbols that the weight percent water content of a zeolite depends on:

- 1) its framework through V_{cc} , which obviously is a feature of the zeolite itself;
- 2) its Si/Al ratio through CEC, as the positive charge of cations must exactly counterbalance the negative charge of the zeolite framework arising from the isomorphous substitution of Al for Si;
- 3) its cation population through the variable $V_{eq\ cat}$ defined in equation (4).

The cation compositions of the various cation exchanged samples, (see Table 1), were inserted in equation (4), along with the cation radii for coordination VI, VIII and for the highest coordination reported for every cation by Shannon [28] to calculate the values of the quantity $V_{eq\ cat}$. Then the values of W.C., summarized in Table 1, were reported as a function of the relevant values of $V_{eq\ cat}$ and the two groups of data were subjected to linear regression, which allowed to obtain the equation of the straight lines relating $V_{eq\ cat}$ and W.C. . The value of the intercept of these straight lines on the ordinate axis (coinciding with V_{cc}), their slope (the product $- 0.602 \cdot CEC$), their correlation factor (R^2), the values of CEC obtained from equation (8) and the value of CEC calculated from the chemical formula of various zeolites were reported in Table 2. The straight lines relating $V_{eq\ cat}$ and W.C., obtained ascribing coordination VI to cations, were reported in Fig. 1. The careful examination of data of Fig. 1 and Table 2 suggests

some considerations that are reported hereafter. The evaluation of the quantities $V_{eq\ cat}$ and W.C. is subjected to multifarious font of uncertainty such as:

a) instrumental uncertainty in the determinations of W.C. and equivalent fraction of various cations (up to five); b) lack of knowledge of the exact coordination of the various cation, which reflects on the value of cation radius. In spite of such uncertainty, the proposed linear correlation between the quantities $V_{eq\ cat}$ and W.C. appears confirmed for all the five different zeolites tested, when the calculations were performed considering coordination VI or VIII for the various cations. In particular the correlation appears very good in the case of zeolite Y, analcime, clinoptilolite Lac Ben and clinoptilolite 80 (R^2 ranging between 0.980 and 0.998) and good in the case of zeolites X (R^2 ranging between 0.931 and 0.960). When the calculations were performed considering the highest coordination reported for every cation by Shannon [28] the overall agreement was not good (R^2 ranging between 0.845 and 0.987), thus suggesting that the coordination of various cations contained in the framework of zeolites X, Y, analcime and clinoptilolite must be VI or VIII. It must be said that Barrer and Hinds found that W.C. of variously potassium exchanged synthetic sodium analcime to linearly decrease with increasing the weight percent K_2O content of the analcime itself [12]. This finding appears in perfect agreement with the interpretation of experimental data given in this work. Actually both the linear relations of ref. [12] and those reported in this work are established between W.C. and cation population of zeolites. The sole difference is that the linear relation of ref. [12] is valid only for analcime containing exclusively Na^+ and K^+ , whereas the linear relation proposed in this work is valid for whatever zeolite and cation population, provided that cation exchange does not result in structural damage of the zeolite framework. The following positive remarks seem to support the validity of the proposed model:

1) The difference recorded for V_{cc} of zeolites X and Y, which have the same faujasite-type structure but different Si/Al ratio [29] and the difference recorded for V_{cc} of clinoptilolite Lac Ben and 80, which have the same heulandite-type structure but

different Si/Al ratio, are about 2 and 10 % (coordination VI and VIII), respectively. Such differences are fully consistent with the fact that zeolites with the same framework and different Si/Al ratio have cavities and channels of the same shape but their volume may but slightly differ, as it is a function of the Si/Al ratio [1].

2) The values of V_{cc} are about 28, 17 and 14 cm^3 per 100 g of zeolite for faujasite-type zeolites, heulandite type zeolites and analcime, respectively (coordination VI and VIII). These values appear in absolute decidedly likely. Moreover ref. [29] reports for zeolites of the faujasite type, heulandite type and analcime a framework density (intended as the number of Si or Al atom with tetrahedral coordination per nm^3) of 12.7, 17.0 and 18.6, thus denoting that the compactness of the zeolite framework increases in the same order. Obviously it is expected that the more compact is the zeolite, the smaller are their V_{cc} . The values of V_{cc} calculated by the proposed model are fully consistent with this expectation.

3) The slope of the straight lines which relates $V_{eq\ cat}$ and W.C., is equal to the product $-0.602 \cdot \text{CEC}$. Thus, the slope of the straight lines relating $V_{eq\ cat}$ and W.C. for zeolites with similar CEC should be similar as well. This statement is confirmed by clinoptilolites Lac Ben and 80 which exhibit very similar CECs and slopes.

4) Zeolite X and Y exhibit the same faujasite-type structure and differ in the Si/Al ratio (1.23 and 2.48, respectively) and, thus, in the cation exchange capacity (0.473 and 0.315 equivalents per 100 g of zeolite, respectively, as calculated from their chemical formula) [29]. It appears noteworthy that the ratio of their CEC (about 1.50) is very similar to the ratio of the slope of their straight lines (about 1.34) (coordination VI). Nevertheless there is a point in which the proposed model does not seem to properly match reality.

Actually the values of CEC calculated from equation (8) (from this point onward this quantity will be labelled as CEC_{calc}) are far higher than CEC calculated from the chemical formula of zeolites ($\text{CEC}_{chem\ formula}$). This discrepancy decreases going from

coordination VI, to coordination VIII and to the highest coordination reported for every cation by Shannon [28].

A possible explanation for these discrepancies may be found in the following considerations. The value of CEC calculated from eq. (8) (CEC_{calc}) may be written as:

$$CEC_{calc} = CEC_{chem\ formula} + \Delta CEC \quad (9)$$

by substituting eq. (9) in eq. (7) we obtain:

$$W.C. = V_{cc} - 0.602 \cdot (CEC_{chem\ formula} + \Delta CEC) \cdot V_{eq\ cat} \quad (10)$$

and thus:

$$W.C. = V_{cc} - 0.602 \cdot CEC_{chem\ formula} \cdot V_{eq\ cat} - 0.602 \cdot \Delta CEC \cdot V_{eq\ cat} \quad (11)$$

which on rearranging becomes:

$$V_{cc} = W.C. + 0.602 \cdot CEC_{chem\ formula} \cdot V_{eq\ cat} + 0.602 \cdot \Delta CEC \cdot V_{eq\ cat} \quad (12)$$

Eq. (12) says in symbols that the total volume of cavities and channels present in 100 g of zeolite (V_{cc}) is in part occupied by:

- 1) water molecules (W.C.);
- 2) by cations ($0.602 \cdot CEC_{chem\ formula} \cdot V_{eq\ cat}$ represents the real volume occupied by cation as the real value of CEC, calculated from the chemical formula of zeolites, was used);
- 3) by something which is represented by the term ($0.602 \cdot \Delta CEC \cdot V_{eq\ cat}$); this something can be neither water molecules nor cations and, thus, can be only void volume.

This reasoning appears to work as the proposed model was based on a hypothesis (the volume of cavities and channels of a zeolite is totally occupied by water molecules and cations) which proved to be not correct. Nevertheless the model reacted to this not correct hypothesis, on which was based, with the discrepancy in the values of CEC_{calc} and $CEC_{chem\ formula}$. This discrepancy allowed also to calculate the void volume present in a zeolite framework. These considerations are supported by the fact that the void volume decreases going from coordination VI, to coordination VIII and to the highest

coordination reported for every cation by Shannon [28]. Actually the real volume of cations increases in this same sequence.

In practice, if CEC_{calc} is not split in $CEC_{chem\ formula}$ and ΔCEC , the proposed model records the void space present in the zeolite framework as space occupied by cations, thus giving rise to a higher than real cation exchange capacity.

Equation (12) and the $V_{eq\ cat}$ values of all cation exchanged zeolite samples of Table 1 (coordination VI) were used to determine:

- 1) The calculated, and thus slightly different from the experimental value, weight percent water content of various cation-exchanged zeolite samples ($W.C._{calc}$);
- 2) The real volume occupied by cation $V_{real\ cat}$, which is equal to $0.602 \cdot CEC_{chem\ formula} \cdot V_{eq\ cat}$;
- 3) The void volume V_{void} , which is equal to $0.602 \cdot \Delta CEC \cdot V_{eq\ cat}$.

The values of $W.C._{calc}$, $V_{real-cat}$ and V_{void} are reported as a function of $V_{eq\ cat}$ in Fig. 2 and in Table 3, thus denoting that $W.C._{calc}$ steadily decreases and $V_{real-cat}$ and V_{void} steadily increases with increasing $V_{eq\ cat}$. It must be noted that in Fig. 2 the sum of the three quantities reported on the ordinate axis ($W.C._{calc}$, $V_{real-cat}$ and V_{void}) equals V_{cc} , which is represented by the horizontal line crossing the ordinate axis at the related value, for all the $V_{eq\ cat}$ values. Moreover, the careful examination of data of Fig. 2 suggests the following observations:

- 1) $W.C._{calc}$ very slightly differ from $W.C.$ values experimentally determined, as one could expect from the good or very good correlation recorded (see the R^2 in Tab. 2).
- 2) Zeolites X and Y exhibit the same structure but different Si/Al ratios and their V_{void} were calculated in similar range of the $V_{eq\ cat}$ values (1.59-10.81 and 2.76-14.70 \AA^3 , respectively); the reasonable expectation that their V_{void} are similar is fully confirmed as they vary in the range 1.03-6.99 and 1.45-7.48 cm^3 , respectively.
- 3) Clinoptilolite Lac Ben and 80 exhibit the same structure but different Si/Al ratios and their V_{void} were calculated in similar range of the $V_{eq\ cat}$ values (2.14-17.30 and

2.56-16.76 Å³, respectively); the reasonable expectation that their V_{void} are similar is fully confirmed as they vary in the range 0.68-5.53 and 0.77-5.04 cm³, respectively.

On the whole the values of V_{void} calculated appear fully sensible. An other observation deriving from the evaluation of data here proposed is the following. In ref. [16] the thermal stability of various cations forms of clinoptilolite Lac Ben and 80 was determined by measuring their residual crystallinity after 2 h thermal treatments at 450, 600 and 900 °C. What appears interesting is that the thermal stability of various cations forms of these two clinoptilolites increases with increasing $V_{\text{eq cat}}$. Even this consideration appears fully logical as cation forms of zeolites with low values of $V_{\text{eq cat}}$ contains higher amounts of water. It appears obvious that the loss of this higher amount of water upon heating makes such cations forms of clinoptilolite more prone to thermal collapse.

Some final considerations, concerning the use that could be made of the linear relation existing between the weight percent water content of variously cation exchanged zeolites and the quantity $V_{\text{eq cat}}$, which describes its cation population, appear necessary. It is evident that the existence of such relation allows the prediction of the water content of a particular cation-exchanged sample of a certain zeolite. Nevertheless, this same relation would also allow, through the use of the quantity $V_{\text{eq cat}}$, to accomplish the operation that, in a sense, may be considered opposite to the one just described. Actually, if one needs a zeolite sample bearing a certain value of weight percent water content for whatever technological application, this goal could be easily fulfilled by computing the exact value of the quantity $V_{\text{eq cat}}$ from the desired W.C. value. Obviously such value of $V_{\text{eq cat}}$ may be obtained practically in several different ways by inserting, by cation exchange, in the zeolite framework the due combinations of many different cations. In particular this task could be accomplished very easily by inserting by cation exchange only an other cation, in the due amount, so as to attain the value of $V_{\text{eq cat}}$ to which corresponds the required water content.

An other possible use of the linear relation existing between the weight percent water content of variously cation exchanged zeolites and the quantity $V_{eq\ cat}$, which describes its cation population, could be the following. If somebody needs to have an evaluation V_{cc} of a particular zeolite or an evaluation of V_{void} and W.C. of some particular cation exchanged form of a zeolite, it would be sufficient to determine the W.C. of 6-7 different cation exchanged forms of this zeolite and calculate the equation of the straight line which relates $V_{eq\ cat}$ to W.C. . By performing the calculations described in this work, it will be quite easy to determine the quantities previously reported.

4. CONCLUSIONS

In this work a simple linear relation was established between the weight percent water content of various cation-exchanged zeolite samples and a quantity $V_{eq\ cat}$ related to its cation population. This simple linear relation was verified for five different zeolite samples (three synthetic and two natural) and, moreover, largely different cation population were considered within this study.

Obtained results appear at least encouraging and suggest to carry on further investigations in the following directions:

- 1) Verifying the simple linear relation established in this work for other zeolites with still different cation populations;
- 2) Reporting the results of this work, as well as other similar results that could be obtained with other zeolites, to the scale of the unit cell of the various zeolites; this operation could very likely result into a more complete comprehension of the relation between the water content of zeollites and their framework and cation population.
- 3) Relating the conclusions of this work with the results of other studies performed on zeolites and zeolitic water by using different investigative techniques. This type of work could allow to perform some adjustment to the proposed model,

which could possibly extend the field of its validity. In particular, improvements in using this model could result from the knowledge of the exact coordination that the various cations, present in the zeolite framework, exhibit.

ABBREVIATIONS

CEC, cation exchange capacity of the zeolite (expressed in equivalents per 100 g of zeolite);

CEC_{calc} , CEC calculated from equation (8) (expressed in equivalents per 100 g of zeolite);

$CEC_{chem\ formula}$, CEC calculated from the chemical formula of zeolites (expressed in equivalents per 100 g of zeolite);

N, Avogadro number;

r, cation radius (expressed in angstrom);

R^2 , correlation factor of straight lines

V_{cc} , volume of cavities and channels (expressed in cm^3 per 100 g of zeolite);

$V_{eq\ cat}$, volume of an hypothetic equivalent cation, which represents the cation population of the zeolite (see text, expressed in \AA^3);

V_{cat} , volume of the cations (expressed in cm^3 per 100 g of zeolite);

$V_{real-cat}$, real volume occupied by cation (expressed in cm^3 per 100 g of zeolite);

W.C., weight percent water content (expressed in cm^3 per 100 g of zeolite);

$W.C._{calc}$, calculated weight percent water content (expressed in cm^3 per 100 g of zeolite);

x, cation equivalent fraction;

z, valence of cation;

ΔCEC , difference recorded between CEC_{calc} and $CEC_{chem\ formula}$ (expressed in equivalents per 100 g di zeolite).

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Table 1 – Cation composition (expressed as equivalent fraction x), $V_{eq\ cat}$ value (calculated for coordination VI, Å³) and experimental weight percent water content (W. C.) of various cation-exchanged samples of zeolites X and Y, of clinoptilolites Lac Ben and 80 [16-17] and of analcime [12].

Sample	Zeolite X		$V_{eq\ cat}$	W.C.
	cation composition			
X-1	$x_{Na} = 0.420$	$x_{Cs} = 0.580$	10.81	17.2
X-2	$x_{Na} = 0.671$	$x_{Cs} = 0.329$	9.43	18.1
X-3	$x_{Na} = 0.321$	$x_K = 0.679$	8.92	20.2
X-4	$x_{Na} = 0.550$	$x_K = 0.450$	7.37	22.0
X-5	$x_{Na} = 0.310$	$x_{Sr} = 0.690$	3.77	24.4

X-6	$X_{Na} = 0.139$	$X_{Sr} = 0.861$		3.60	24.5		
X-7	$X_{Na} = 0.369$	$X_{Zn} = 0.631$		2.18	25.0		
X-8	$X_{Na} = 0.441$	$X_{Ca} = 0.559$		3.14	25.1		
X-9	$X_{Na} = 0.221$	$X_{Co} = 0.779$		1.63	25.7		
X-10	$X_{Na} = 0.181$	$X_{Fe} = 0.829$		1.59	26.9		
Zeolite Y							
Sample	cation composition			$V_{eq\ cat}$	W.C.		
Y-1	$X_{Na} = 0.321$	$X_{Cs} = 0.679$		14.70	17.4		
Y-2	$X_{Na} = 0.242$	$X_{K} = 0.758$		9.43	21.5		
Y-3	$X_{Na} = 1.000$			4.44	23.9		
Y-4	$X_{Na} = 0.650$	$X_{Zn} = 0.350$		3.18	25.2		
Y-5	$X_{Na} = 0.559$	$X_{Li} = 0.441$		3.31	25.5		
Y-6	$X_{Na} = 0.560$	$X_{Co} = 0.440$		2.85	25.9		
Y-7	$X_{Na} = 0.560$	$X_{Ni} = 0.440$		2.76	26.5		
Clinoptilolite Lac Ben							
Sample	cation composition			$V_{eq\ cat}$	W.C.		
Lac-ben-1	$X_{Ca} = 0.054$	$X_{Cs} = 0.878$	$X_{Mg} = 0.068$	17.30	9.9		
Lac-ben-2	$X_{Ca} = 0.172$	$X_{K} = 0.740$	$X_{Mg} = 0.088$	8.63	14.1		
Lac-ben-3	$X_{Na} = 0.709$	$X_{K} = 0.777$	$X_{Mg} = 0.064$	$X_{Ca} = 0.182$	3.56	16.2	
Lac-ben-4	$X_{Na} = 0.085$	$X_{K} = 0.146$	$X_{Mg} = 0.237$	$X_{Ca} = 0.532$	3.27	16.2	
Lac-ben-5	$X_{Li} = 0.728$	$X_{K} = 0.032$	$X_{Ca} = 0.240$		2.18	16.8	
Lac-ben-6	$X_{Ca} = 0.399$	$X_{Sr} = 0.402$	$X_{Mg} = 0.199$		2.41	16.8	
Lac-ben-7	$X_{Ca} = 0.832$	$X_{K} = 0.036$	$X_{Mg} = 0.132$		2.14	16.9	
Clinoptilolite 80							
Sample	cation composition			$V_{eq\ cat}$	W.C.		
80-1	$X_{Na} = 0.018$	$X_{Mg} = 0.170$	$X_{Cs} = 0.812$		16.76	8.7	
80-2	$X_{Na} = 0.018$	$X_{K} = 0.851$	$X_{Mg} = 0.131$		9.55	11.6	
80-3	$X_{Na} = 0.132$	$X_{K} = 0.221$	$X_{Mg} = 0.288$	$X_{Ca} = 0.359$	4.06	13.9	
80-4	$X_{Na} = 0.846$	$X_{Mg} = 0.154$			3.90	14.0	
80-5	$X_{Na} = 0.066$	$X_{K} = 0.074$	$X_{Mg} = 0.260$	$X_{Ca} = 0.293$	$X_{Sr} = 0.307$	2.68	14.8
80-6	$X_{Na} = 0.026$	$X_{K} = 0.079$	$X_{Mg} = 0.259$	$X_{Ca} = 0.636$		2.56	14.9
Analcime							
Sample	cation composition			$V_{eq\ cat}$	W.C.		
Ana-1	$X_{K} = 1.000$				11.02	0.75	
Ana-2	$X_{Na} = 0.030$	$X_{K} = 0.970$			10.81	1.2	
Ana-3	$X_{Na} = 0.060$	$X_{K} = 0.940$			10.60	1.5	
Ana-4	$X_{Na} = 0.172$	$X_{K} = 0.828$			9.89	2.0	
Ana-5	$X_{Na} = 0.359$	$X_{K} = 0.641$			8.67	2.8	
Ana-6	$X_{Na} = 0.449$	$X_{K} = 0.551$			8.08	3.5	
Ana-7	$X_{Na} = 0.554$	$X_{K} = 0.446$			7.37	4.4	
Ana-8	$X_{Na} = 0.703$	$X_{K} = 0.297$			6.41	6.0	
Ana-9	$X_{Na} = 0.760$	$X_{K} = 0.240$			6.03	6.6	
Ana-10	$X_{Na} = 0.858$	$X_{K} = 0.142$			5.36	7.3	
Ana-11	$X_{Na} = 0.895$	$X_{K} = 0.105$			5.15	7.6	
Ana-12	$X_{Na} = 0.911$	$X_{K} = 0.089$			5.03	7.8	
Ana-13	$X_{Na} = 1.000$				4.44	8.5	

Table 2 - Values of the slope ($-0.602 \cdot \text{CEC}$), of the intercept on the ordinate axis (V_{cc} , expressed in cm^3 per 100 g of zeolite), of the correlation factor (R^2) of the straight lines relating the W.C. to the quantity $V_{\text{eq cat}}$ (eq. 6), of CEC_{calc} (expressed as equivalents per 100 g of zeolite) obtained from eq. 8 and of $\text{CEC}_{\text{chem formula}}$ (expressed as equivalents per 100 g of zeolite) calculated from the chemical formula of various zeolites.

Cations coordination VI					
Zeolite	slope	V_{cc}	R^2	CEC_{calc}	$\text{CEC}_{\text{chem formula}}$
zeolite X	-0.93	27.81	0.960	1.55	0.473
zeolite Y	-0.70	27.77	0.980	1.16	0.314
clinoptilolite Lac Ben	-0.45	17.83	0.998	0.75	0.220 ^a
clinoptilolite 80	-0.44	15.96	0.989	0.73	0.229 ^a
analcime	-1.16	13.45	0.987	1.93	0.454 ^b
Cations coordination VIII					
Zeolite	Slope	V_{cc}	R^2	CEC_{calc}	$\text{CEC}_{\text{chem formula}}$
zeolite X	-0.72	28.11	0.931	1.19	0.473
zeolite Y	-0.64	28.77	0.980	1.06	0.314
clinoptilolite Lac Ben	-0.42	18.31	0.987	0.69	0.220 ^a
clinoptilolite 80	-0.42	16.55	0.993	0.69	0.229 ^a
analcime	-1.01	15.25	0.986	1.68	0.454 ^b
Highest coordination reported for every cation by Shannon [28]					
Zeolite	slope	V_{cc}	R^2	CEC_{calc}	$\text{CEC}_{\text{chem formula}}$
zeolite X	-0.40	27.76	0.845	0.67	0.473
zeolite Y	-0.52	29.71	0.987	0.87	0.314
clinoptilolite Lac Ben	-0.33	18.50	0.963	0.55	0.220 ^a
clinoptilolite 80	-0.34	16.90	0.986	0.57	0.229 ^a
analcime	-1.06	20.19	0.984	1.76	0.454 ^b

^a ref. [16-17]
^b ref. [12]

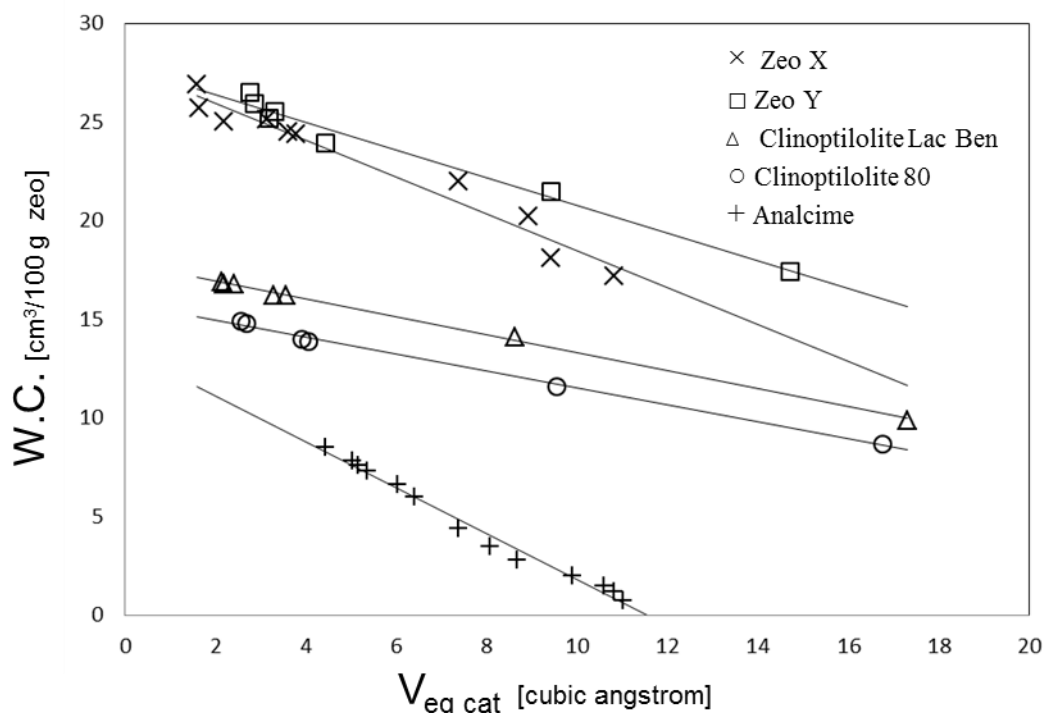


Figure. 1 – Weight percent water content (W.C.) (cm^3 per 100 g of zeolite), of various zeolites as a function of the quantity $V_{\text{eq cat}}$ (\AA^3) defined in eq. (4). The calculation were performed considering coordination VI for the various cations [28].

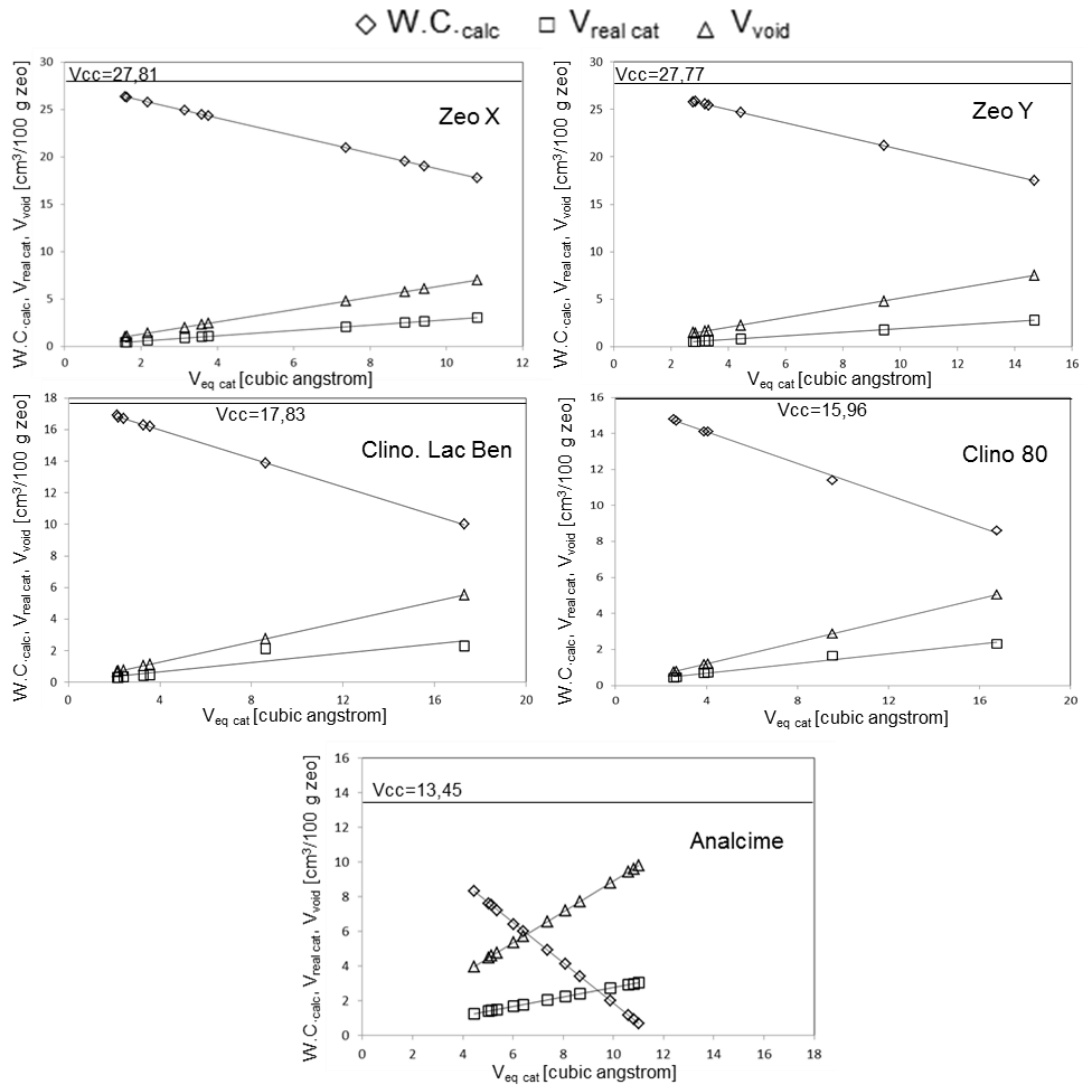


Figure 2 - Values of $W.C. calc$ (cm^3 per 100 g of zeolite, rhombs), $V_{real\ cat}$ (cm^3 per 100 g of zeolite, squares) and V_{void} (cm^3 per 100 g of zeolite, triangles), calculated from eq. (12), as a function of the quantity $V_{eq\ cat}$ (\AA^3) defined in eq. (4). The calculation were performed considering coordination VI for the various cations [28].

Table 3 - Values of $W.C_{calc}$ (cm^3 per 100 g of zeolite), $V_{real-cat}$ (cm^3 per 100 g of zeolite) and V_{void} (cm^3 per 100 g of zeolite), calculated from eq. (12), as a function of the quantity $V_{eq\ cat}$ (\AA^3) defined in eq. (4). The calculation were performed considering coordination VI for the various cations [28].

Zeolite X				
Sample	$V_{eq\ cat}$	$W.C_{calc}$	$V_{real\ cat}$	V_{void}
X-1	10.81	17.75	3.07	6.99
X-2	9.43	19.03	2.68	6.10
X-3	8.92	19.51	2.53	5.77
X-4	7.37	20.95	2.09	4.77
X-5	3.77	24.30	1.07	2.44
X-6	3.60	24.46	1.02	2.33
X-7	2.18	25.78	0.62	1.41
X-8	3.14	24.89	0.89	2.03
X-9	1.63	26.29	0.46	1.06
X-10	1.59	26.33	0.45	1.03
Zeolite Y				
Sample	$V_{eq\ cat}$	$W.C_{calc}$	$V_{real\ cat}$	V_{void}
Y-1	14.70	17.52	2.77	7.48
Y-2	9.43	21.20	1.78	4.79
Y-3	4.44	24.70	0.83	2.26
Y-4	3.18	25.55	0.60	1.62
Y-5	3.31	25.47	0.62	1.68
Y-6	2.85	25.84	0.52	1.41
Y-7	2.76	25.78	0.54	1.45
Clinoptilolite Lac Ben				
Sample	$V_{eq\ cat}$	$W.C_{calc}$	$V_{real\ cat}$	V_{void}
Lac-ben-1	17.30	10.0	2.29	5.53
Lac-ben-2	8.63	13.9	2.14	2.76
Lac-ben-3	3.56	16.2	0.47	1.14
Lac-ben-4	3.27	16.3	0.43	1.05
Lac-ben-5	2.18	16.8	0.29	0.70
Lac-ben-6	2.41	16.7	0.32	0.76
Lac-ben-7	2.14	16.9	0.28	0.68
Clinoptilolite 80				
Sample	$V_{eq\ cat}$	$W.C_{calc}$	$V_{real\ cat}$	V_{void}
80-1	16.76	8.61	2.31	5.04
80-2	9.55	11.40	1.66	2.87
80-3	4.06	14.10	0.70	1.22
80-4	3.90	14.10	0.68	1.17
80-5	2.68	14.70	0.46	0.80
80-6	2.56	14.80	0.44	0.77
Analcime				
Sample	$V_{eq\ cat}$	$W.C_{calc}$	$V_{real\ cat}$	V_{void}
Ana-1	11.02	0.66	3.01	9.78
Ana-2	10.81	0.90	2.95	9.60
Ana-3	10.60	1.15	2.89	9.41
Ana-4	9.89	2.00	2.70	8.78
Ana-5	8.67	3.40	2.37	7.70
Ana-6	8.08	4.10	2.21	7.18
Ana-7	7.37	4.90	2.01	6.54
Ana-8	6.41	6.0	1.75	5.69
Ana-9	6.03	6.4	1.65	5.36
Ana-10	5.36	7.2	1.46	4.76
Ana-11	5.15	7.5	1.41	4.57
Ana-12	5.03	7.6	1.37	4.46
Ana-13	4.44	8.3	1.21	3.94

