FOUNDATIONS OF THERMO-DIELECTRICAL ANALYSIS
Part I. Cationic polarization in zeolites

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The method of thermodielectrical analysis registers in its thermogram a low temperature effect (50-350°) related with the polarization of water or other sorbed phase and cationic polarization, and a high temperature effect (400-900°) which is fundamentally related with cationic conduction. In the present report with the help of the measurement of the dielectrical permittivity of powders of homoionic zeolites was shown the role of cationic polarization in the determination of the intensity of the first thermal effect registered in thermodielectrical analysis.

In the last years, in a series of papers [1-7] published in this journal, we had been reporting the results related with the development and use of the method of Thermo-dielectrical analysis. In these papers was shown that in the samples tested (zeolites, bentonites, caolins, carbonates, quartz [1-8] phosphates [9-10], sulfates, thiosulfates, soil clays (non reported), and other are present two effects: a low temperature one (50-350°) which is related with water (crystallization water, zeolitic water, interlayer water, sorbed water, etc.) or other sorbed phase [4] and with cationic polarization [6] and a high temperature effect (400-900°) which is fundamentally related with cationic conduction [5]. Paralelly with the above described process we had been studying too, the dielectrical properties of zeolites [11-13] with the method of dielectrical spectrometry, using the same principle of measurement developed for the thermodielectrical analyzer [1] but scanning frequency at a constant temperature (in thermodielectrical analysis we scans temperature at constant frequency). Dielectrical spectrometry is by itself an analytical method as was shown [11-13], but the interpretation of the results

of its measurements must shed light in the foundations of thermodielectrical analysis.

Zeolites were used as model material because of the presence of all the effects in its thermal curves i. e.: water polarization, cationic polarization and cationic conduction by cation hopping, the possibility of changing the cation present in the zeolite, the quantity of water or other sorbed phase. moreover zeolite structures are well documented [14, 15], in our laboratory are developed the analytical methods for its study [16-19] and synthesis [8] and its dielectrical properties are not completely unknown, i. e. the dielectrical response of zeolites, is the result of a variety of individual factors which behave differently under the influence of: frequency, temperature, humidity, electric field, etc. Among these factors are: the very rapid electronic polarization, lattice polarization and the slow dipolar response, the last mechanism includes cation hopping [20] in both hydrated and dehydrated zeolites and water polarization [21, 32].

To be definite, and in first approximation in the present paper, we will analyze the cationic polarization, not considering interfacial polarization [33-37] and maintaining constant the water content of the samples to avoid the discussion of water polarization. The model description of cationic polarization used is the following:

During the cationic migration between different structural sites (cationic sites [15]) a change in the polarization due to the disposition of the negatively charged alumino-silicate network of the zeolite in relation with the positively charged cations situated in the zeolite cavities and channels occurs [27], contributing this polarization to the zeolite dielectrical response [37-40].

Experimental

The dielectrical spectrometer which consist in two principal parts: a vacuum system which evacuate a cilindrical capacitor (Fig. 1) and a dielectrical sensor (Fig. 2) was used to measure the dependence between the permittivity of powders of: Na-C3, Na-C4, Ca-C3 and CaC4 {Homoionized natural samples of 70 % HEU phase (C3) and 75 % MOR phase (C4), the other components are: Montmorillonite (2-5 %) quartz (1 to 4 %), calcite (1 to 5 %), feldspars (0 to 2 %) magnetite (0 to 1 %) and volcanic glass (16-19)} and frequency (0.04 to 100 KHz). The samples in the form of powders (0.6 to 1.6 mm of particle diameter) were introduced in the cylindrical capacitor (Fig. 1) and heated (for dehydration) at 573 K by 18
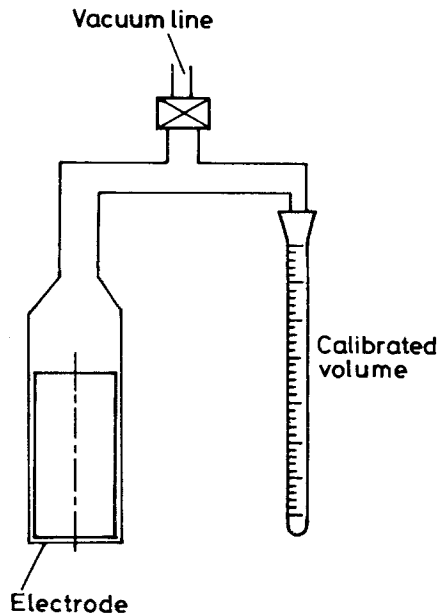
Fig. 1 Cylindrical capacitor coupled with the vacuum system

hours in vacuum (10^{-5} Pa). The dielectrical sensor is a device [11-13] consisting in an operational amplifier (Fig. 2) which compares the capacities of a standard (C_r) and a sample capacitor (C_x), and using the relation between the output (V_{sal}) and input (V_{ent}) voltage of the measuring circuit [1, 4, 12]:

$$C_x/C_r = V_{ent}/V_{sal}$$

is possible to calculate the powder permittivity for different frequencies:

$$\varepsilon(w) = C_x/C_v$$

where C_v: is the capacity of the empty cylindrical capacitor)
Differential dielectrical thermograms of: Na, K, Ca, and Mg HEU (with controlled water content) (Sample of 85 % of HEU phase with: calcite, quartz, felspars and volcanic glass) were obtained in the developed thermodielectrical analyzer [1], the water content was controlled in a volumetric adsorption equipment constructed with pyrex glass in our laboratory [41]. The dispersion spectrum of the samples Na-HEU, K-HEU and Ca-HEU

(with controlled water content) were obtained in the dielectrical spectrometer above described.
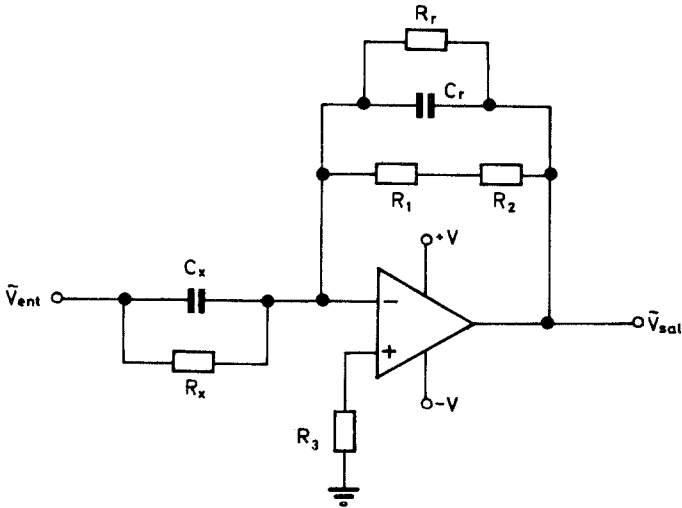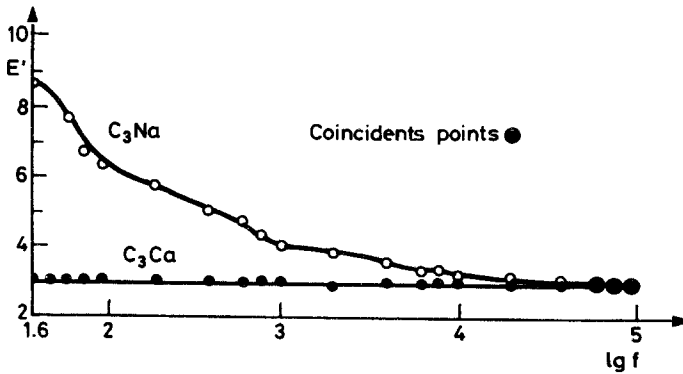

Fig. 2 Dielectrical sensor

Fig. 3 Dispersion spectrums of dehydrated C3-Na and C3-Ca at 300 K

Results and discussion

In Figs 3 and 4 are reported the dispersion spectrums of dehydrated: Na-C3, Ca-C3, Na-C4 and Ca-C4 at room temperature (300 K), in both cases is clearly noted that the polarizability of Ca is less than those for Na, i. e. the mobility of Na is higher than the mobility of Ca; this fact can be explained with the help of the mechanism of polarization proposed in the model description, which relates polarization with cation hopping between sites for compensating charge in the zeolite, where less mobil cation is less polarizable.
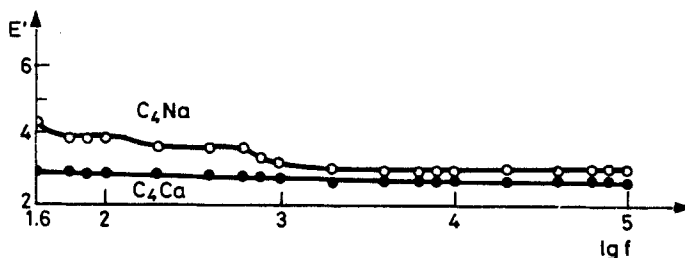

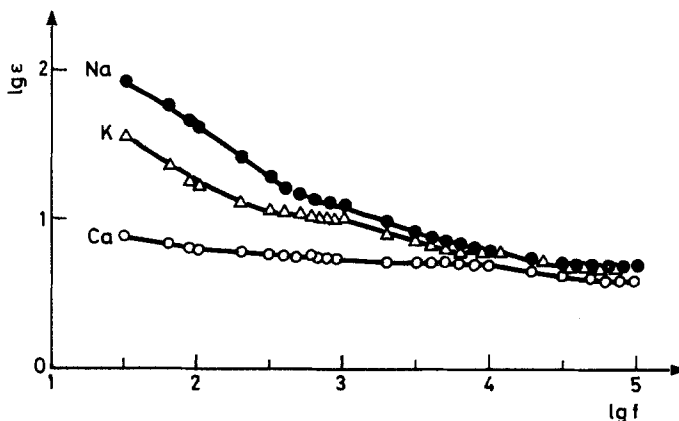Fig. 4 Dispersion spectrums of dehydrated C4-Na and C4-Ca at 300 K

Fig. 5 Dispersion spectrums of Na-HEU, K-HEU and Ca-HEU with 6.2 ±0.05 mmol/g of water adsorbed

The dispersion spectrum (Fig. 5) and dielectrical thermograms (Fig. 6) of samples with controlled water content shows too the role of cationic polarization in the low temperature effect in thermodielectrical analysis, i. e.
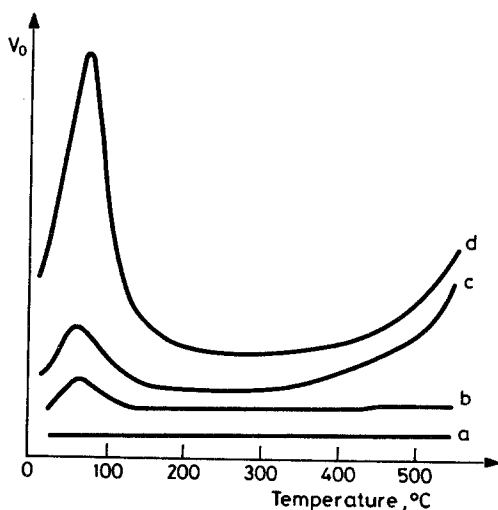
Fig. 6 Dielectrical thermograms of Na-HEU, K-HEU, Mg-HEU and Ca-HEU, d, c, b and a respectively with 6.2 ± 0.05 mmol/g of water adsorbed

both: water and cationic polarization are necessary to be taken into account for the explanation of this effect, but in the present case the water content was maintained constant, and the differencies noted in Figs 5 and 6 can only be explained by a polarizability decrease from: Na, K, Mg to Ca.

Cationic polarization, clearly determines the intensity of the first thermal effect normally registered in thermodielectrical analysis [1-6], and the coincidence between the results of dielectrical spectrometry and thermodielectrical analysis bring us a powerful argument, because of the fact that the dielectrical spectrometer measures the dielectrical permittivity of the powder sample, i. e. a physical parameter with a well specified relation with the polarization mechanism of the substance under test.

In a final comment, is necessary to recognize that cationic polarization is only one of the factors present in the first thermal effect of thermodielectrical analysis, and for a complete explanation (for the substances that at present were tested by the method) is necessary to take into account: water (or other phase sorbed) polarization and interfacial polarization. The analysis of this effect will be the content of the next report about the foundations of thermodielectrical analysis.

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Zusammenfassung — Mittels thermodielektrischer Analyse kann im Thermogramm ein Niedrigtemperatureffekt (50-350°C), verbunden mit der Polarisation des Wassers oder anderer absorbierter Phasen und der kationischen Polarisation, und ein Hochtemperaturef-

fekt (400-900°C) festgehalten werden, welcher grundlegend mit der Kationenleitung in Verbindung gebracht werden kann. In dieser Arbeit wird mittels der Messung der Dielektrizitätskonstante von homoionischen Zeolithpulvern die Rolle der kationischen Polarisierung bei der Bestimmung der Intensität des bei der thermodielektrischen Analyse registrierten ersten thermischen Effektes gezeigt.