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# THERMOMECHANICAL ANALYSIS AND X-RAY HEATING STUDIES OF (Ca,Na)-A ZEOLITES

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## ABSTRACT

Dimensional changes of (Ca,Na)-A zeolites at thermal desorption of water are measured by TMA on packed beds of powder and on discs and by a programmed heating Guinier-Lennè camera. The results of the different methods are compared and explanations for the contraction-expansion steps are given.

## INTRODUCTION

Water desorption of zeolites at programmed heating and also under isothermal conditions is connected with dimensional changes of the zeolite matrix. Thermomechanical analysis of packed beds of zeolite powder has shown a successive expansion-contraction-expansion sequence for NaA [1] and the absence of the second expansion for KA, RbA and CsA zeolites [2]. This was explained with differences in the repulsion forces between the cations which have different site occupancies for the single cation form, when water is removed. Also with X-ray methods could be shown, that zeolites undergo shrinkage or expansion depending on the water content [3].

This paper decribes TMA studies on different forms (packed beds of powder and pressed discs) of (Ca,Na)-A zeolites. The obtained results are compared with those of the X-ray heating method.

## EXPERIMENTAL

TMA investigations were carried out on a DuPont 941 Thermomechanical Analyzer at heating rates of 5 and 10 K $min^{-1}$ in static air. The samples were prepared as follows. For the packed beds zeolite powder was carefully tamped into a glass cup of 3.5 mm Ø and 5 mm hight and for the discs 30-80 mg of powder were pressed at 100 MPa.

The X-ray measurements were performed on a Guinier-Lennè camera of Enraf-Nonius at a heating rate of 0.66 K $min^{-1}$ between 300 and 670 K.

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## RESULTS AND DISCUSSIONS

Examples of TMA curves of packed beds of the zeolite powders obtained between 293-623 K are presented in Fig.1. Introduction of calcium ions into NaA zeolite by ion exchange causes some changes in TMA profile creating new expansions especially for samples of higher $Ca^{2+}$ content. All zeolites show contraction in the temperature range of 323-438 K which is due to water loss from

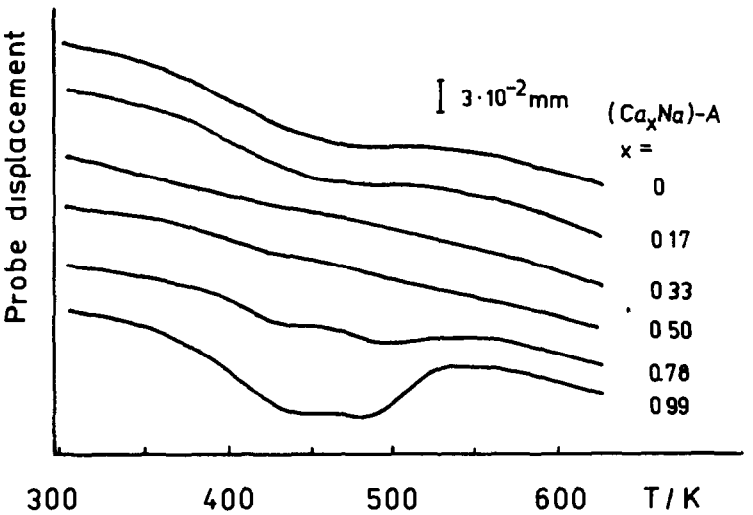



Fig. 1.: TMA curves of packed beds of (Ca,Na)-A zeolites

$\alpha$-cages of the zeolites. A similar effect was observed in TMA of other cation forms of A, X and Y zeolites [2]. After the initial shrinkage for the NaA sample a smaller expansion than noted in earlier papers [1,2] is observed. This hints at the problems of TMA on packed beds of powders. It is difficult to get reproducible density of the packing and moreover the diffusion of desorbed water could be hindered. Therefore discs of 0.8-1.8 mm thickness were prepared and measured. In the first measurement the discs gave an unnormal large contraction (Fig.2). This is probably caused by tensions in the pellet generated during the pressing process. After the first heating and rehydration the discs show reproducible dimensional changes in the following dehydration-rehydration cycles. Zeolite pellets industrially made with clay as binder have a normal thermoanalytical analysis profile already at the first heating.

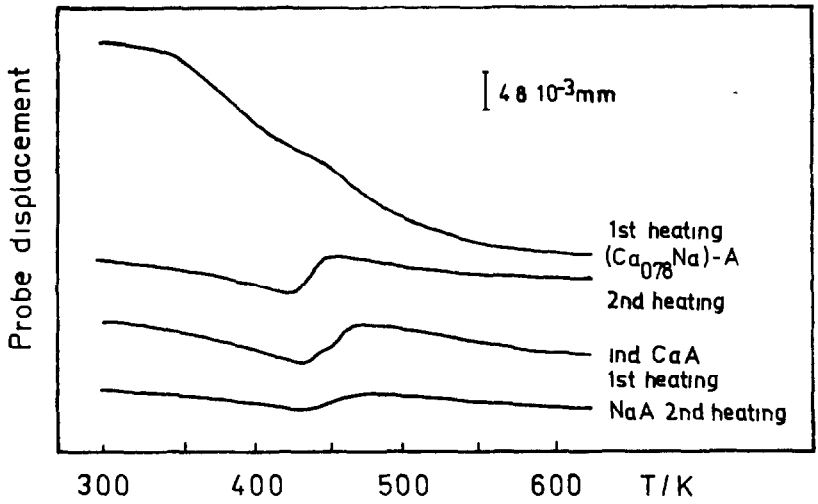
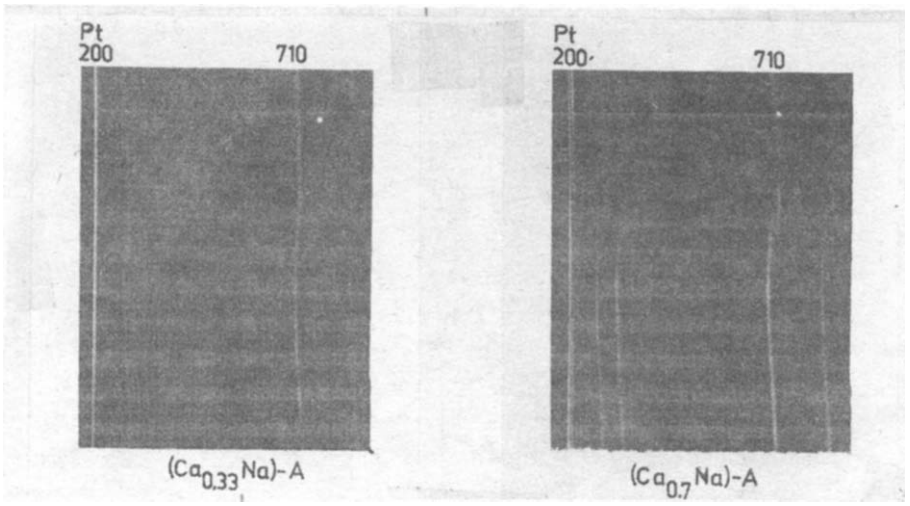



Fig. 2: TMA curves of discs of (Ca,Na)-A zeolites

The contraction-expansion sequence and the influence of increasing calcium ion content on this process is also well characterized by the temperature depending shift of the d-lines for the zeolites in comparison to the d-lines of continous expanding platinum (the zeolite powder is mounted on platinum net as sample support).




Fif. 3: Enlarged detail of Guinier-Lenné-patterns

For zeolites up to calcium contents of about 66 % the expansion step at 430 K is connected with a continous shift of the d-lines to lower values whereas an increasing jump in the d-lines is observed for samples of higher calcium content ( > 66 %). The values of the total dimensional change at heating up to 670 K and of the expansion between 420 and 470 K summarized in Table 1 reveal a good correlation between the TMA results of the discs and of the X-ray heating measurements. The expansion step for NaA should be effected by repulsion forces of the sodium ions after loss of coordinated water. The expansion of calcium containing A zeolites is explicable in similar manner. In the samples with low $Ca^{2+}$ content the expansion is not clearly changed. The loss in cation density is probably compensated by the larger charge of the calcium ion. The marked expansion in the samples with high $Ca^{2+}$ content is caused by the presence of nearly all $Ca^{2+}$ ions in the 6-0 rings. X-ray structural investigations have evidenced, that in CaA 4/5 of the $Ca^{2+}$ are in 6-0 ring positions [4]. In contrast to the calcium containing zeolites (Mg,Na)-A samples show a continous contraction. In the Guinier-Lennè pattern of the zeolites with $Mg^{2+}$ contents > 50 % a jump to higher values in the d-lines is visible. Because of the higher ionic strength of the magnesium ions the interaction with framework oxygen is more intensive, producing a shrinkage of the zeolite.

| Zeolites | TMA on discs $(\Delta l/l)x10^3$ | | progr. heating X-ray $(\Delta d/d)x10^3$ | |
|---|---|---|---|---|
| | 300-670 K | 420-470 K | 300-670 K | 420-470 K |
| $(Ca_{0,17}Na)$-A | 3,3 | 2,9 | 3,1 | 2,6 |
| $(Ca_{0,33}Na)$-A | 3,1 | 2,6 | 3,0 | 2,5 |
| $(Ca_{0,5}Na)$-A | 2,9 | 2,5 | 2,9 | 2,5 |
| $(Ca_{0,78}Na)$-A | 2,3 | 4,7 | 0,1 | 4,5 |
| $(Ca_{0,99}Na)$-A | 1,9 | 8,1 | 0,1 | 9,5 |

Table 1.: Dimensional changes of (Ca,Na)-A zeolites

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