



## Zn-exchanged clinoptilolite from Beli plast deposit, Eastern Rhodopes, Bulgaria

## Зп-обменен клиноптилолит от находище Бели пласт, Източни Родопи, България

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### Introduction

Ion exchange properties of clinoptilolite are utilized in practice and the study of these processes is progressing. Clinoptilolite displays selectivity towards the metals of the first and second group as well as for  $\text{Al}^{3+}$ ,  $\text{Fe}^{2+}$ , and  $\text{NH}_4^+$ . Ames (1960) found the following selectivity decreasing order:  $\text{Rb}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^+$ ,  $\text{Sr}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Li}^+$ . The big monovalent cations like Cs are preferred by the microporous structure of zeolites (Petrov et al., 1991). For small bi-valent cations the selectivity is low. For Cd, Cu, and Zn it has been established to be in the order  $\text{Cd}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+}$  (Langella et al., 1999). The antibacterial properties of zinc are used in cosmetics and medicine in various preparations for local therapy of skin deceases caused by Propionibacterium acnes or injuries. The system erythromycin – zinc is more effective when during the contact with skin the useful components are released gradually. Clinoptilolite is a suitable for such an effect as it ensures gradual release of zinc in a medium of erythromycin.

The purpose of the present paper is to study in detail the structural changes that take place in clinoptilolite, when undergoing greater  $\text{Zn}^{2+}$  exchange at higher temperatures and durations.

### Materials and Methods

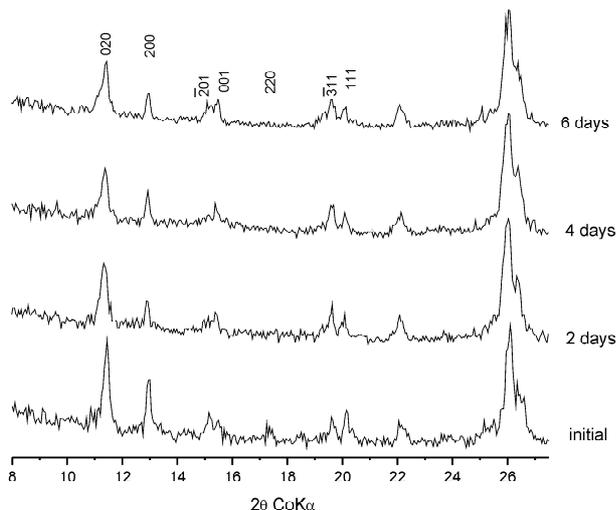
Enriched clinoptilolite fraction was obtained from rock (Beli plast deposit, East Rhodopes, Bulgaria), which was crushed, ground, and fractioned by sedimentation giving fractions 0.160–0.032 mm (sample C1), 0.032–0.016 mm (C2), and 0.016–0.002 mm (C3). The fractions were enriched in clinoptilolite by separation with heavy liquid.  $\text{Zn}^{2+}$  exchanged cli-

noptilolite was obtained for fractions C1, C2, and C3 in the way: The material was placed in teflon-lined autoclaves with 1M solution of  $\text{ZnCl}_2$  at  $100^\circ\text{C}$  for 6 days duration. The solution was renewed on two days intervals with separating material for study. After the 6-th day the samples were decanted, washed with distilled water, and dried at room temperature. The powder XRD experiments were done in the range  $8\text{--}50^\circ 2\theta$  (DRON 3M diffractometer, Fe-filtered  $\text{CoK}\alpha$  radiation). The chemical analyses were done with AAS for the Zn exchanged modifications and with wet chemical analysis of the light fractions after separation.

### Results and Discussion

The material in the fraction below 0.016 mm is proved by XRD phase analysis to contain major clinoptilolite (about 75%) and small amounts opal-C, quartz, plagioclase and mica. The phase composition of the heavy fractions is represented by plagioclase, sanidine, muscovite (illite), quartz, calcite, dolomite, and less potassium feldspar. The light fractions contain mainly clinoptilolite and always traces of opal-C, which is difficult to be removed.

Ion exchange degree with heavy cations can be followed by the intensity changes of the basal reflections 0k0 (Petrov, 1995).  $\text{Zn}^{2+}$  ions after significant exchange also cause intensity variance of the peaks in the clinoptilolite XRD pattern that allows evaluation of the  $\text{Zn}^{2+}$  exchange following the intensity changes of some peaks (Fig. 1). It is seen from the figure that when comparing the diffraction patterns of the initial and the exchanged samples there are apparent changes in some of the peaks. Namely, slight lowering of  $I_{020}$  and more expressed lowering of  $I_{200}$ . Also, the peaks 201 and 111 decrease in intensity



**Fig. 1.** Powder XRD patterns of clinoptilolite sample (fraction 0.032–0.016 mm) from Beli plast deposit (initial) and its  $Zn^{2+}$  exchanged forms for duration of 2, 4, and 6 days

with the exchange while peaks 001 and  $\bar{3}11$  increase. Interestingly, the small peak 220 fully disappears even at the 2nd day of Zn exchange of clinoptilolite. The shown intensity changes in the powder XRD patterns of Zn exchanged clinoptilolite are undoubtedly due to changes in the cationic sub-lattice in the structure of this zeolite.

Additionally, the refinement of the unit cell parameters (program PDI – Macicek, 1989) showed constant increase of the values with the content of exchanged Zn. For the initial clinoptilolite sample we obtained  $a=17.694 \text{ \AA}$ ,  $b=18.045 \text{ \AA}$ ,  $c=7.408 \text{ \AA}$ ,  $\beta=116.28^\circ$ , and  $V=2120 \text{ \AA}^3$ , while the exchanged

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**Table 1.** Content of Zn (wt.%) after ion exchange determined by AAS in different clinoptilolite fractions

Duration of ion exchange	Fraction C1	Fraction C2	Fraction C3
initial	0.002	0.002	0.002
2 days	2.8	3	2.9
4 days	3.4	4.1	3.3
6 days	4.2	4.7	4.3
10 days	–	5.6	–
30 days	–	6.7	–

sample for 30 days has the following parameters:  $a=17.709 \text{ \AA}$ ;  $b=18.114 \text{ \AA}$ ;  $c=7.412 \text{ \AA}$ ;  $\beta=116.09^\circ$ ; and  $V=2135 \text{ \AA}^3$  (0.7% increase).

AAS confirms the XRD data for Zn content in clinoptilolite after ion exchange (Table 1). From the theoretically possible 7.1%  $Zn^{2+}$  ions for the studied clinoptilolite ( $K_{1.8}Ca_{1.7}Na_{0.5}Mg_{0.2}Al_{5.8}Fe_{0.22}Si_{29.94}O_{72} \times 20H_2O$ ) we reached exchange level of 6.8%. Best exchanged is fraction 0.032–0.016 mm (sample C2).

Possible explanation for these results is that this fraction contains less opal-C than C3 (higher clinoptilolite content) and it is finer than C1 (greater exchange surface).

## Conclusion

The performed studies reveal some crystal chemical peculiarities of Zn-exchanged sedimentary clinoptilolite, which are needed background for future more detailed structural investigations to explain the localization of  $Zn^{2+}$  ions in the channels of clinoptilolite and predict the possible desorption processes connected with biological contacts.

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