



## Occlusion of $ZnCl_2$ in a clinoptilolite matrix

### Оклюдия на $ZnCl_2$ в клиноптилолит

*Luiza Dimova, Georgi Kirov, Ognyan Petrov, Yana Tzvetanova, Nadejda Lihareva*  
*Луиза Димова, Георги Киров, Огнян Петров, Яна Цветанова, Надежда Лухарева*

Central Laboratory of Mineralogy and Crystallography, BAS, Acad. G. Bonchev Str., Bl. 107, 1113 Sofia;  
 E-mail: anien@abv.bg

**Key words:** clinoptilolite, occlusion, Zn exchange.

The ion exchange properties of natural zeolites are very promising in applications as sorption of harmful compounds from various systems or for their utilization as carriers of useful elements. Insertion of cations and molecules in the channels of zeolites can be realized by mixing salt melt of certain metals with the zeolite carrier (Liquornik, Marcus, 1968). Such studies have been performed by Park et al. (2001) using synthetic zeolites and salt of ammonium nitrate.

The inclusion of desired salts or ions into the zeolite matrix by use of occlusion gives opportunity to intrude, preserve, transport, or extract such salts in specific media. This can result in a series of applications. Some limitations occur when the melting temperature is higher or close to that of the thermal stability of the zeolite. Another point of interest is to describe the way of extraction of the occluded salts or ions for special purposes.

In our study we use clinoptilolite as a matrix for occlusion of zinc salt. Zinc finds application in medicine and cosmetics due to its antibacterial properties and there are papers treating its combined application with erythromycin (Habbema et al., 1989; Holland et al., 1992). In this case clinoptilolite is used as carrier of Zn ions as well as “buffer” for more fluent release of Zn in the drug (Cerri et al., 2004). The mechanism is effective because it ensures stable, supply, of the drug with the needed component.

The studied zeolite is clinoptilolite from Beli plast deposit, Eastern Rhodopes, which was purified by separating the sample with heavy liquid. Opal-cristobalite, which is not separable mechanically, was removed using chemical treatment with NaOH solution. The occlusion was conducted on preliminary  $NH_4^+$  exchanged clinoptilolite (sample C1) and on a clinoptilolite with the natural cation exchange complex (sample C2). We used 2 g of clinoptilolite and 2 g of  $ZnCl_2$ , mixed and heated for 1 hour up to  $380^\circ C$ , then kept the sample at that temperature for 4 h. After the heat treatment the samples were washed with ethyl alcohol and distilled water (Table 1). The obtained sam-

ples were characterized by powder XRD analysis, chemical methods (ICP, AAS) and IR spectroscopy.

The comparison of the XRD patterns between the initial samples and occluded ones displays changes in the intensities of peaks 020 and 200, which in the processed samples have relatively lower intensities than that of the initial sample (Fig. 1). In the case of the ammonium exchanged sample (C1) this tendency is weakly expressed, which can be attributed to certain remainder of ammonium cations in the channel of clinoptilolite. Another feature is the increase of the intensity of peaks 001 and 311 in respect to 201 and 111. Also, it is noticeable that peak 201 emerges and 220 disappears. The observed intensity changes are similar for both samples and are result of the changes in the cationic complex of clinoptilolite after the occlusion treatment.

The AAS data show slightly higher Zn content in sample C1 compared to sample C2 (Table 1). The crystal chemical formula for the initial clinoptilolite according to ICP and DTA-TG data is:  $(K_{1.11}Ca_{1.77}Na_{1.10}Mg_{0.49})Al_{6.39}Fe_{0.13}Si_{29.44}O_{72} \cdot 21H_2O$ . The maximal possible exchange with  $Zn^{2+}$  ions for this structure is 7% per unit cell. It is possible that a part of zinc measured by AAS is not occluded in the channels being present in the form of  $Zn(OH)_2$  outside or inside the pores of the zeolite.

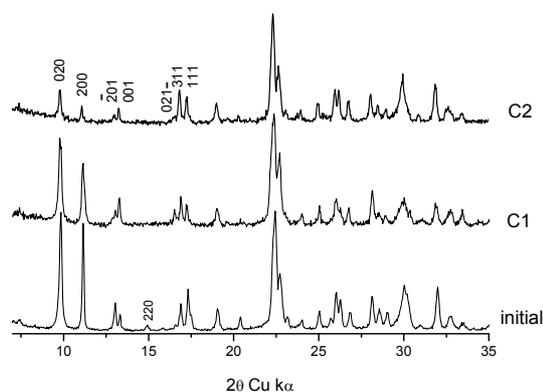


Fig. 1. X-ray patterns of the studied samples

The comparison of the IR spectra of the samples reveals a band in the region of  $1400\text{ cm}^{-1}$ , related to the presence of ammonium ions and this band is better pronounced in the samples exchanged with  $\text{NH}_4\text{NO}_3$  (Fig. 2). ICP data indicate that the original cations in the clinoptilolite structure are strongly reduced in the ammonium exchanged samples (C1, Table 2).

The two treated samples were washed several times to check if zinc easily leaves the structure of clinoptilolite. In the case of typical occlusion of salts in zeolite the process is relatively difficult (Park et al, 2001). Table 1 contains the results of the washing stages and the control was performed by powder XRD and AAS. It is to be noted that the content of zinc lowers to 5% per unit cell even when varying the temperature, pH, and saturation time. Only in the experiment with prolonged soaking for 14 days the result was 3%. The applied washing procedures

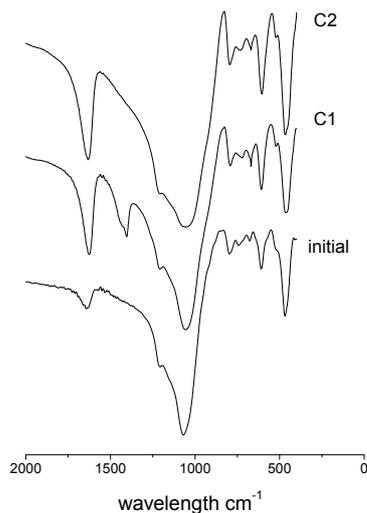


Fig. 2. The comparison of the IR spectra of the samples

Table 1. Washing stages after occlusion and AAS data for Zn content

Washing stages	1) ethyl alcohol 100 ml	2) ethyl alcohol 50 ml	3) ethyl alcohol 100 ml distilled water 150 ml	4) distilled water – 100 ml, 100°C – 40 min
C1 Zn wt. %	7.50	7.20	7.00	5.25
Washing stages	1) ethyl alcohol 100 ml	2) 100 ml distilled water – 20 h	3) distilled water 100 ml 24 h: a) pH 6, b) pH 3.7	4) distilled water 100 ml – 14 days
C2 Zn wt. %	7.00	6.90	a) 6.60 b) 6.40	3.1

Table 2. Chemical composition of the samples C1 and C2

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	MgO	TiO <sub>2</sub>	MnO	Zn	3H	Total
C1	67.94	12.96	0.36	0.46	0.09	0.35	0.24	0.07	0.01	10.13	7.51	100.12
C2	65.40	12.20	0.30	2.98	1.11	0.84	0.66	0.07	0.01	9.46	7.00	100.30

show that after the high temperature exchange with use of melt, the zinc ions release is hampered. The XRD and AAS data and the slow release of Zn during washing indicate that there has been realized a process of occlusion. The presence of absorption band (IR) due to  $\text{NH}_4^+$  groups as well as the residue cations from the initial ion exchange complex indicate that the process of occlusion has not been fully realized.

## References

- Cerri, G., M. de Gennaro, M. C. Bonferoni, C. Carrella. 2004. Zeolites in biomedical application: Zn-exchanged clinoptilolite-rich rock as active carrier for antibiotics in anti-acne topical therapy. – *Applied Clay Sci.*, 27, 141–150.
- Habbena, B. K., H. E. Menke, S. Doornweerd, K. de Boule. 1989. A 4% erythromycin and zink combination (Zinerit) versus 2% erythromycin (eryderm) in acne vulgaris: a randomized, double-blind comparative study. – *British J. of Dermatology*, 121, 497–592.
- Holland, K. T., R. A. Bojar, W. J. Cunliffe, A. G. Cutcliffe, E. A. Eady, L. Farooq. 1992. The effect of zink and erythromycin on the growth of erythromycin-resistant and erythromycin-sensitive isolated of *Propionibacterium acnes*: an in-vitro study. – *British J. of Dermatology*, 126, 505–509.
- Liquornik, M., Y. Marcus. 1968. Ion exchange in molten salts. The ion-exchange properties of sodium zeolite A in molten sodium nitrate. The exchange with calcium and strontium cations. – *J. Phys. Chem.*, 72, 13, 4704–4705.
- Park, M., C. S. Seung, L. C. Choy, H. L. Dong, T. L. Woo, S. Komarneni, C. K. Muir, C. N. H. Jyung. 2001. Role of framework on  $\text{NH}_4\text{NO}_3$  occlusion in zeolite pores. – *Microporous and Mesoporous Materials*, 50, 91–99.