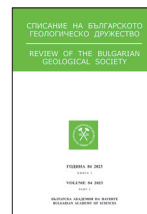




СПИСАНИЕ НА БЪЛГАРСКОТО ГЕОЛОГИЧЕСКО ДРУЖЕСТВО,  
год. 84, кн. 3, 2023, с. 55–58

REVIEW OF THE BULGARIAN GEOLOGICAL SOCIETY,  
vol. 84, part 3, 2023, p. 55–58



Национална конференция с международно участие „ГЕОНАУКИ 2023“  
National Conference with International Participation “GEOSCIENCES 2023”

## Interaction of sodalite and cancrinite with $\text{NH}_4\text{NO}_3$ solution. First case of low-temperature synthesis of buddingtonite

*Tsveta Stanimirova, Georgi Kirov*

University of Sofia “St. Kliment Ohridski”, Faculty of Geology and Geography, Department of Mineralogy, Petrology and Economic Geology, 15 Tzar Osvoboditel Blvd., 1504 Sofia, Bulgaria; E-mail: stanimirova@gea.uni-sofia.bg

## Взаимодействие на содалит и канкринит с $\text{NH}_4\text{NO}_3$ разтвор. Първи случай на нискотемпературен синтез на бъдингтонит

*Цветя Станимирова, Георги Киров*

**Abstract.** Hydroxyl sodalite and sulfate cancrinite were synthesized from fly ash from TPP Varna, Bulgaria. The interaction of the two feldspathoids with  $\text{NH}_4\text{NO}_3$  solution at 90 °C was investigated. Because of the reaction, sodalite is dissolved and ammonium feldspar (buddingtonite) is formed, which is the first case of low-temperature synthesis of this mineral. The interaction of cancrinite with  $\text{NH}_4\text{NO}_3$  induces ion exchange and the formation of cancrinite with composition  $(\text{NH}_4)_{5.4}\text{Na}_{3.6}(\text{NO}_3)_{1.45}(\text{SO}_4)_{0.25}(\text{OH})_{0.05}[\text{Al}_6\text{Si}_6\text{O}_{24}] \cdot 2\text{H}_2\text{O}$ , suggesting potential for the use of this form as a slow-acting fertilizer.

**Keywords:** fly ash, cancrinite, sodalite, ion exchange, buddingtonite.

### Introduction

Fly ash is a residue from the combustion (typically 60–88%) of coal in thermal power plants. One of the most attractive applications of fly ash is its use as a raw material for synthesis of microporous aluminum-silicate minerals – zeolites and feldspathoids (Yaping et al., 2008).

The ion exchange and sorption properties of these microporous natural and synthetic materials are the basis of diverse applications in industry, agriculture, ecology, and life. Through ion exchange of various cations, catalysts for petrochemical and organic synthesis, microbicide substances for medicine, pharmacy, and cosmetics are obtained (Cerri et al., 2004; Linares et al., 2005). Sorbents for toxic anions (arsenate) and colloidal pollutants (heavy metals) were obtained by re-modification.

Through ion exchange and occlusion, the zeolites and feldspathoids can be “charged” with significant amounts of substances that radiate for a long time into the environment (fertilizers, medicines, etc.) (Park, Komarneni, 1997; Park et al., 2001; Stanimirova, Kirov, 2023).

The main goal of the present work is to investigate the possibilities of ion exchange incorporation of  $\text{NH}_4^+$  and  $\text{NO}_3^-$  into feldspathoids (sodalite and cancrinite) obtained from fly ash, with potential agricultural applications as slow-acting fertilizers.

### Materials and methods

The initial sodalite sample was obtained as 1 g of fly ash from the Varna thermal power plant (TPP) dispersed in 30 ml of 1.5 M  $\text{NaAl}(\text{OH})_4$  solution at 70 °C for 24 h. The cancrinite sample was obtained

as 1 g fly ash treated with 30 ml solution of 3.5 M  $\text{NaAl}(\text{OH})_4 + \text{Na}_2\text{SO}_4$  at 70 °C for 24 h.

The ion exchange reactions were carried out as 0.2 g of the cancrinite or sodalite sample was dispersed in 30 ml of 1 M  $\text{NH}_4\text{NO}_3$  solution. The reaction was carried out at 90 °C for 48 h under continuous stirring with a magnetic stirrer. Washing with distilled water and drying at room temperature of the obtained products follows.

The initial samples and the obtained products were characterized by powder X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). The powder XRD patterns were recorded on a Bruker D8 Advance diffractometer. Filtered  $\text{Co-K}\alpha$  radiation was used in the range  $2\Theta$  4–80°, step 0.02°  $2\Theta$ , and exposure time per step 1.5 s. The FTIR spectra in the range of 400–4000  $\text{cm}^{-1}$  were recorded on an FTIR Bruker TENSOR 37 Spectrometer in KBr tablets, at a ratio of the investigated substance to KBr of 1:200. The SEM images are obtained using a JEOL scanning electron microscope – model JSM-6010PLUS/LA.

## Results and discussion

*Initial samples.* The initial fly ash samples consist of glass globules enclosing a small amount of amorphous carbon and 30–35% crystalline phases: quartz, feldspars, mullite, hematite–magnetite and mica (Fig. 1a). The data from XRD and SEM investigation suggest that at the expense of the entire amount of glass from the globules, pure hydroxyl-sodalite and sulfate Na-cancrinite were obtained (Fig. 1a). Sodalite forms aggregates occupying the spherical shape of the glass globes. The conclusion follows that the sodalite crystallized almost simultaneously with the dissolution of the glass. In agreement with the high concentration of  $\text{NaAl}(\text{OH})_4$  and the alkalinity of the solution, cancrinite crystallization has started after the complete dissolution of the glass, manifested by the ubiquitous uniform distribution of cancrinite crystals (Fig. 1a).

*Reaction products.* The powder XRD patterns of the starting sodalite-OH (Fig. 1a) and the product obtained after treatment with  $\text{NH}_4\text{NO}_3$  (Fig. 1b) are different. In the powder XRD pattern of the product, a pronounced halo centered at about 30°  $2\Theta$ , and low intensive but relatively sharp X-ray reflections were registered. The measured d-spacing values show that the rare mineral buddingtonite ( $\text{NH}_4\text{AlSi}_3\text{O}_8$ ) was formed (PDF reference card 45-1428). Obviously, the hydroxyl-sodalite is unstable in the ammonium nitrate solution and dissolves, causing formation of an X-ray amorphous aluminum silicate phase (73%)

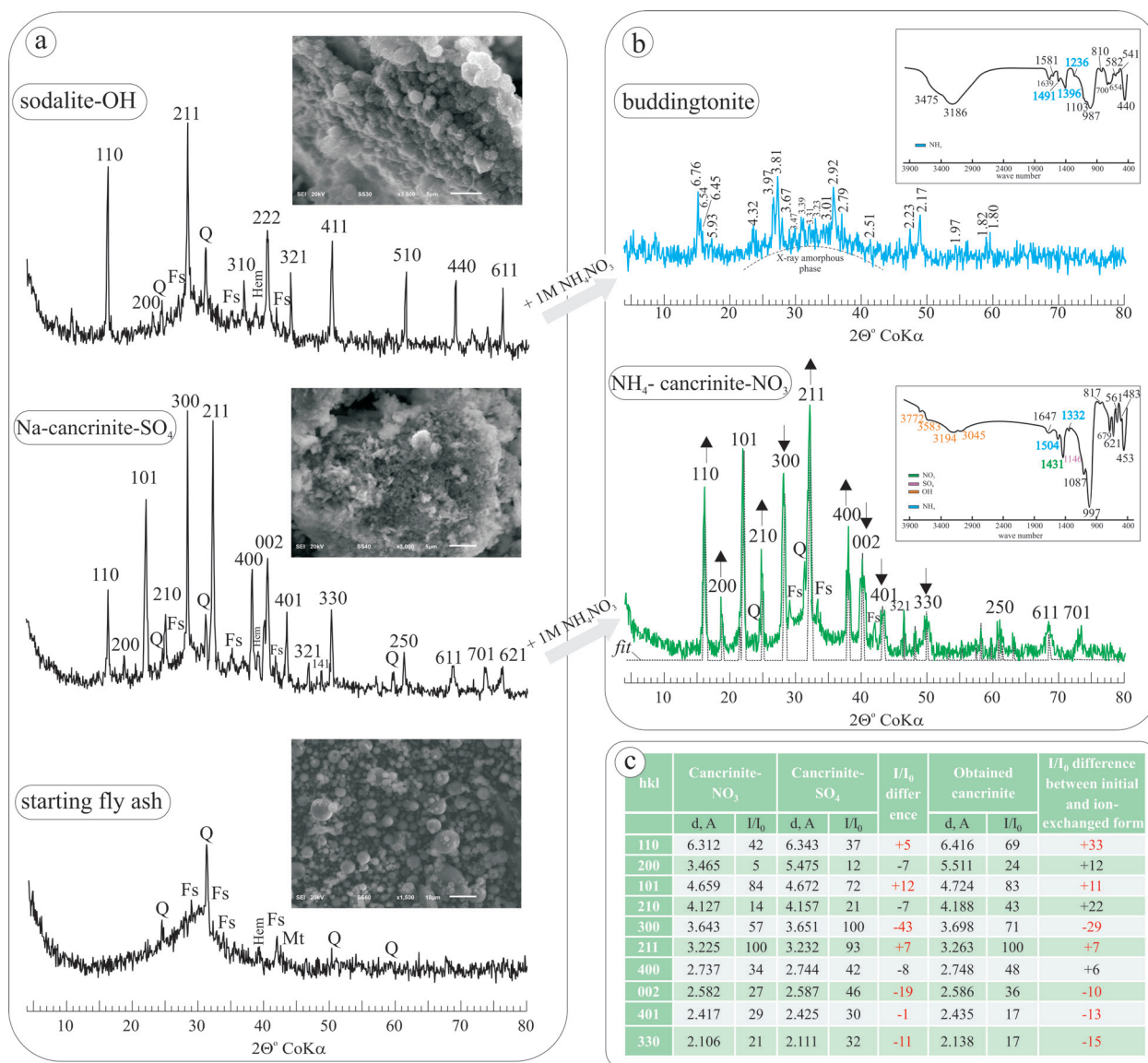
and crystallization of some amount of ammonium feldspar (27%). The FTIR data confirm such an assumption. The recorded absorption bands at 987  $\text{cm}^{-1}$  and 1103  $\text{cm}^{-1}$  are due to the superimposition of the bands of the feldspar framework and the vibrations of the silicate phase with high aluminum content. The absorption bands at 1600  $\text{cm}^{-1}$  and 3200  $\text{cm}^{-1}$  attributed to water molecules indicate that this X-ray amorphous phase is probably an aluminum-silicate gel. The presence of absorption bands at 1396, 1425, and 1491  $\text{cm}^{-1}$  indicates the presence of ammonium ions.

The crystallization of buddingtonite in the low-temperature conditions of the present experiment is an unexpected result since it is a low-temperature hydrothermal mineral, and its synthesis was achieved under high-temperature (600 °C, 2 kbar) conditions (Voncken et al., 1988).

In contrast to sodalite, the measured d-spacing values of the product obtained after the reaction of cancrinite- $\text{SO}_4$  and  $\text{NH}_4\text{NO}_3$  show preservation of the cancrinite structure (Fig. 1b). However, significant changes are visible in the intensities of the X-ray reflections of the planar networks where the exchangeable ions are localized. The comparative analysis of the intensities shows the presence of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  anions (Fig. 1c). In addition, the presence and higher intensity of the reflection 200 reveals that hydroxyl groups are also present in the structure. The presence of several anions in the structure is evidenced by the observed splitting of some (400, 002, 401, 330, etc.) reflections. Using the software programs PowderCell (Kraus, Nolze, 1996) and VESTA (Momma, Izumi, 2011), a good fit has been achieved between the experimentally obtained and simulated powder XRD patterns for exchanged cancrinite with composition  $(\text{NH}_4)_{5.4}\text{Na}_{3.6}(\text{NO}_3)_{1.45}(\text{SO}_4)_{0.25}(\text{OH})_{0.05}[\text{Al}_6\text{Si}_6\text{O}_{24}]\cdot 2\text{H}_2\text{O}$  (Fig. 1b). The FTIR data give evidence for the presence of three anions and the presence of an  $\text{NH}_4^+$  cation. The absorption band around 1146  $\text{cm}^{-1}$  indicates the presence of sulfate anions in the structure. The band at 1431  $\text{cm}^{-1}$  is the  $\nu_3$  absorption band of  $\text{NO}_3^-$  anion. The absorption bands 3773, 3583, and 2874  $\text{cm}^{-1}$  indicate the presence of OH-groups. The registered absorption bands at 1332 and 1504  $\text{cm}^{-1}$  attributed to  $\text{NH}_4^+$  cation reveal the inclusion of the cation in the structure.

## Conclusions

The obtained results show that in the more open cancrinite structure, an ion exchange occurs, which is almost complete in the anionic part and partial in the cationic part. Under the same conditions, the hydroxyl-sodalite structure is unstable, and processes of sodalite dissolution and crystallization of  $\text{NH}_4$ -



**Fig. 1.** *a*, powder XRD patterns and SEM images of starting materials (initial fly ash, synthesized from fly ash hydroxyl-sodalite and sulfate cancrinite); *b*, powder XRD patterns and FTIR spectra of products obtained from the interaction of the synthesized feldspathoids with NH<sub>4</sub>NO<sub>3</sub> solution; *c*, d-spacing and intensities of different cancrinite ionic forms

feldspar (buddingtonite) occurred. For this reason, only the cancrinite samples yield materials with the potential for use as a long-acting fertilizer.

**Acknowledgments:** The authors thank for the financial support and equipment provided by Project BG05M2OP001-1.002-0019: “Clean Technologies for a Sustainable Environment – Water, Waste, Energy for a Circular Economy” (Clean & Circle) for the construction and development of a Competence Center, funded by the Science Operational Program and Smart Growth Education, co-financed by the European Union through the European Structural and Investment Funds.

## References

- Cerri, G., M. de’Gennaro, M. C. Bonferoni, C. Caramella. 2004. Zeolites in biomedical application: Zn-exchanged clinoptilolite-rich rock as active carrier for antibiotics in anti-acne topical therapy. – *Appl. Clay Sci.*, 27, 141–150; <https://doi.org/10.1016/j.clay.2004.04.004>.
- Linares, C. F., S. Sanchez, C. Urbina de Navaro, K. Rodriguez, M. R. Goldwasser. 2005. Study of cancrinite-type zeolites as possible antacid agents. – *Micropor. Mesopor. Mater.*, 77, 215–221; <https://doi.org/10.1016/j.micromeso.2004.08.030>.
- Kraus, W., C. Nolze. 1996. POWDER CELL – a program for the representation and manipulation of crystal structure and calculation of the resulting X-ray powder pattern. – *J. Appl. Crystallogr.*, 29, 301–303; <https://doi.org/10.1107/S0021889895014920>.

- Momma, K., F. Izumi. 2011. VESTA 3 for three-dimensional visualization of crystal, volumetric, and morphology data. – *J. Appl. Crystallogr.*, 44, 1272–1276; <https://doi.org/10.1107/S0021889811038970>.
- Park, M., S. Komarneni. 1997. Occlusion of  $\text{KNO}_3$  and  $\text{NH}_4\text{NO}_3$  in natural zeolites. – *Elsevier Sci. Inc Zeolites*, 18, 171–175; [https://doi.org/10.1016/S0144-2449\(96\)00130-3](https://doi.org/10.1016/S0144-2449(96)00130-3).
- Park, M., C. S. Seung, L. C. Choy, D. H. Lee, W. T. Lim, S. Komarneni, M. C. Kim, J. Choi, N. H. Cheo. 2001. Role of framework on  $\text{NH}_4\text{NO}_3$  occlusion in zeolites pores. – *Micropor. Mesopor. Mater.*, 50, 91–99; [https://doi.org/10.1016/S0144-2449\(96\)00130-3](https://doi.org/10.1016/S0144-2449(96)00130-3).
- Stanimirova, T., G. Kirov. 2023. Modification of zeolite Na-X, sodalite and cancrinite in salt melts. – *Geologica Balc.*, 52, 3, 41–49; <https://doi.org/10.52321/GeolBalc.52.3.41>.
- Voncken, J. H. L., R. J. M. Konings, J. B. H., Jansen, C. F. Woensdregt. 1988. Hydrothermally grown buddingtonite, an anhydrous ammonium feldspar ( $\text{NH}_4\text{AlSi}_3\text{O}_8$ ). – *Phys. Chem. Miner.*, 15, 323–328; <https://doi.org/10.1007/BF00311036>.
- Yaping Y., Z. Xiaoqiang, Q. Weilan, W. Mingwen. 2008. Synthesis of pure zeolites from supersaturated silicon and aluminum alkali extracts from fused coal fly ash – *Fuel*, 87, 10–11, 1880–1886; <https://doi.org/10.1016/j.fuel.2007.12.002>.