University of Belgrade
Technical Faculty in Bor,
Mining and Metallurgy
Institute Bor

54th International October Conference on Mining and Metallurgy

PROCEEDINGS

Editors:
Ljubiša Balanović
Dejan Tanikić

IOC 2023
International October Conference

18-21 October 2023, Bor Lake, Serbia

PROCEEDINGS,
54th INTERNATIONAL OCTOBER CONFERNCE
on Mining and Metallurgy

Editors:
Prof. dr Ljubiša Balanović
Prof. dr Dejan Tanikić
University of Belgrade, Technical Faculty in Bor

Technical Editor:
M. Sc. Miljan Marković
University of Belgrade, Technical Faculty in Bor

Publisher: University of Belgrade, Technical Faculty in Bor
For the publisher: Dean Prof. dr Dejan Tanikić
Circulation: 200 copies

CIP - Каталогизација у публикацији Народна библиотека Србије, Београд

622(082)(0.034.2)
669(082)(0.034.2)

INTERNATIONAL October Conference on Mining and Metallurgy (54 ; 2023 ; Borsko jezero)
Proceedings [Elektronski izvor] / 54th International October Conference on Mining and Metallurgy - IOC 2023, 18-21 October 2023, Bor Lake, Serbia ; [organized by] University of Belgrade, Technical Faculty in Bor and Mining and Metallurgy Institute Bor ; editors Ljubiša Balanović, Dejan Tanikić. - Bor : University of Belgrade, Technical Faculty, 2023 (Niš : Grafika Galeb). - 1 USB fleš memorija ; 1 x 1 x 5 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 200. - Preface / Ljubiša Balanović. - Bibliografija uz svaki rad.

ISBN 978-86-6305-140-9

a) Рударство -- Зборници b) Металургија -- Зборници

COBISS.SR-ID 126659849

Bor Lake, Serbia, October 18-21, 2023

Conference is financially supported by
The Ministry of Science, Technological
Development and Inovation
of the Republic of Serbia

Platinum Donors

ZiJin SERBIA ZIJIN MINING

ZiJin SERBIA ZIJIN COPPER DOO

Sevojno VALJAONICA BAKRA COPPER MILL

Gold Donors

HBIS GROUP HBIS SERBIA

Dundee PRECIOUS METALS AVALA

Silver Donor

trokuttestgroup

Exhibitions

Labtim

Altium

metalurg

MERIS

1969 FMT ZAJEČAR

REFRATEC

Friends of the Conference

DONAU LAB BEOGRAD

DONCAFÉ

LOLA INSTITUT

THE FOUNDATION 'B.SC. ENG. BOŠKO INJAC'

SCIENTIFIC COMMITTEE

ORGANIZING COMMITTEE

PREFACE

On behalf of the Organizing Committee, it is a great honor and pleasure to welcome all esteemed participants of the 54th International October Conference on Mining and Metallurgy (IOC 2023), scheduled to take place at the picturesque Bor Lake, Serbia, from October18th to 21st 2023.

The collaborative efforts of the University of Belgrade, the Technical Faculty in Bor, and the Mining and Metallurgy Institute Bor have meticulously organized this year's IOC. Our focus remains unwavering on showcasing the latest research findings and advancements in geology, mining, metallurgy, materials science, technology, environmental protection, and other engineering disciplines. Our primary objective is to foster a dynamic environment where academics, researchers, and industry professionals can come together to share their knowledge, experiences, and innovative ideas while exploring opportunities for collaborative research endeavors.

Our conference agenda is rich and diverse, encompassing plenary sessions, engaging invited lectures, technical presentations, enlightening oral and poster sessions, informative technical tours, a diverse exhibition, and memorable social gatherings. At the heart of this event lies our strong commitment to sustainable development within the mining and metallurgy sector. We are dedicated to exploring ecologically conscious methodologies, responsible resource extraction practices, and cutting-edge technologies that reduce the industry's environmental impact and enhance the well-being of local communities.

The conference proceedings comprise 129 papers authored by individuals from universities, research institutes, and industries in 22 countries. We are proud to welcome participants from Bosnia and Herzegovina, Bulgaria, Canada, China, Croatia, Germany, Greece, India, Iran, Kazakhstan, Libya, North Macedonia, Montenegro, Morocco, Romania, Russia, Slovakia, South Africa, Spain, Turkey, United States, and, of course, Serbia.

We are excited to host the 8th International Student Conference on Technical Sciences (ISC 2023) as part of IOC 2023. This event offers students from Serbia and the wider region a unique chance to showcase their research and discuss the future of their fields with experts.

We sincerely thank the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia for their generous financial support. In addition, we express our profound gratitude to all our sponsors, exhibitors, and friends of the Conference for their contributions and unwavering support for playing a pivotal role in ensuring the success of IOC 2023.

We would like to express our heartfelt thanks to all authors, committees, reviewers, speakers, and chairpersons for their invaluable contributions in shaping IOC 2023.

We look forward to welcoming you to the 55th International October Conference on Mining and Metallurgy (IOC 2024), which will be held in October 2024.

On behalf of the 54th IOC Organizing Committee,

Prof. dr Ljubiša Balanović

TABLE OF CONTENTS

Plenary Lectures

Invited Lectures

Conference Papers

STUDY OF THERMALLY TREATED ZEOLITIC TUFFS OF SERBIA , DEPOSITS "ZLATOKOP" AND "OPĆIŠTE"-BEOČIN

Vladan Kašić, Ana Radosavljević Mihajlović , Jovica Stojanović , Slavica Mihajlović, Melina Vukadinović, Natasa Djordjević, Ivana Jelić[1]
Institute for Technology of Nuclear and Other Mineral Raw Materials, Franchet d'Esperey 86, Belgrade, Serbia

Abstract

Zeolites are a group of natural and synthetic inorganic compounds. They have specific physicochemical properties suitable for industrial application [1,2]. According to their origin, variety of chemical composition, structural characteristics and application, zeolites form a specific group of minerals within the tectosilicates. In sedimentary formations rich in zeolites, the most characteristic minerals that are present are: clinoptilolite/hailandite, chabazite, mordenite, erionite, phillipsite and analcime. The most widespread zeolite of sedimentary origin is represented by the HEU series (clinoptilolite-heylandite). Its general crystal chemical formula is $(Na,K,Ca)_6Al_6Si_{30}O_{72}nH_2O$.*. Based on chemical and X-ray powder diffraction analysis, it is not possible to separate clinoptilolite and hoylandite . This is due to their isostructural nature. To identify these two isostructural minerals, even today, the simplest so-called Mampton's test [3]. Mumpton [4]. The results of X-ray diffraction analysis of thermally treated clinoptilolitic tuffs from the Zlatokop and Beočin deposits will be presented in this paper. The interplane distance values will be shown in the characteristic temperature range from 400°C to 500°C (when the first polymorphic transition occurs). These values characterize the zeolitic tuffs of our deposits in a certain way.*

Keywords: *zeolitic tuff, X-ray powder analysis, thermal stability*

1. INTRODUCTION

Zeolites are tectro aluminosilicates in which (Si, Al)O^4 tetrahedra build secondary building units (SBU). By connecting with each other, they form characteristic configurations of four-membered, five-membered, six-membered and eight-membered single or double rings. In doing so, they create cavities in which there are cations and water molecules, which have a significant degree of mobility. This allows cation exchange and reversible dehydration. Based on their spatial, chemical and structural characteristics, natural zeolites are systematized into 13 composite series. Within them, 82 minerals have been defined so far [5] In sedimentary formations rich in zeolites, the most characteristic minerals present are clinoptilolite/heylandite, chabazite, mordenite, erionite, phillipsite and analcime.

The main deposits of this raw material are present in all parts of the world. The largest production of this raw material is in the USA, Japan, Jordan, Iran, Korea, Slovakia and Turkey. Demand for this raw material is growing year by year, production is expected to increase by 10% per year. The most important properties of zeolite minerals are absorption capacity, ion exchange processes and catalysis. The very selectivity of the zeolite for the appropriate cations will depend on the basic crystal-chemical and structural properties of each zeolite. It can be defined as a measure of the preference that the exchanger shows for one ion in relation to another. The amount of exchangeable cations or cation exchange capacity depends on the crystal-chemical and structural composition of the zeolite itself (expressed in mmol M+/100g) [5,6].

The deposits of zeolitic tuffs in the area of the former Yugoslavia are spatially related to volcanogenic-sedimentary rocks in the area of the Serbo-Macedonian massif and the outer Dinarides. They were formed in sediments of marine or lake origin, of Senonian and Neogene age. They were created as a product of devitrification of volcanic glass. The lake environment had a great influence on the diagenesis of sediments and the formation of clinoptilolite at the expense of volcanic glass. The most important deposits in the Republic of Serbia are Beočin (Fruškogorsk basin), Zlatokop (Vranje basin), Igroš (Kopaonik slopes), Toponica and the Slanci locality (Danube key, near Belgrade) [2].

2. MATERIAL AND METHODS

For mineralogical and crystallographic tests, tuff samples with a grain size of -63 m were used μ. Quantitative chemical analysis was performed using the silicate analysis method [5]. The content of SiO_2 and LA(loss on annealing at 105 and 1000°C) were determined gravimetrically. Diffractograms of thermally treated zeolite samples were recorded in the angle interval 2θ from 4 to 35°, with a step of 0.02. The morphology of the examined zeolites was analyzed using a scanning electron microscope JEOL 840A (Joel, Japan). Crystallinity tests of zeolitic tuff after annealing were performed in the temperature range from 300 to 750°C, in a time interval of 2 h. The annealed material was examined using the X-ray powder diffraction method on a polycrystalline sample.

Thermal analyzes were performed on the "Netzsch STA 409EP" apparatus. The samples were thermally treated in the range from 25°C to 1000°C. They were tested at a heating rate of 5°C/min, in a static air atmosphere. Al_2O_3 was used as a reference sample . Previously, the samples were first weighed on an analytical balance in 100 mg increments.

3. DTA/DTG ANALYSIS OF ZEOLITIC TUFF

The basic structural motif of the zeolitic network of the minerals clinoptilolite and heylandite is basically identical. That is why it is very difficult to distinguish them from each other. These two minerals are isostructural. They differ in the Si/Al atomic ratio, the arrangement and content of off-lattice cations, and based on thermal stability at certain temperatures. During thermal treatment, clinoptilolite is shown to be a more stable form. The polymorphism of heylandite consists in visible lattice vibrations after minimal heating to 230° C± 10°C [4].

Heylandite is present in two structural forms: Heylandite type 1 at temperatures of about 400°C and above. Then we have a polymorphic transition to phase B. Sometimes this transition is quite slow, and phase B is stable even at room temperature. Another structural form is Heylandite type 2, which represents a polymorphic transition from phase A to phase B at higher temperatures than 400°C. At the same time, phase B is not stable at room temperature and changes to phase A [4]. Based on chemical and X-ray powder diffraction analysis, it is not possible to separate clinoptilolite and hoylandite, due to their isostructural nature. To identify these two isostructural minerals, the simplest is the so-called Mumpton's test [4, 1, 2]. Mampton defines clinoptilolite as a more stable form compared to heylandite, whose structure remains unchanged up to a temperature of 700°C. Polymorphic changes in heylandite begin already at a temperature of 350-400°C. Therefore, an experimental test is introduced to distinguish them. It is performed by X-ray examination and comparison of the powder diagram after heating to a temperature of 350-400°C. If there is no change in the interplane distances of the diffraction line (020), it is clinoptilolite, and on the contrary, hoylandite. Comparative diffractograms of thermally treated zeolitic tuff powder in the temperature range from 300 to 650°C are shown in Figure 1.

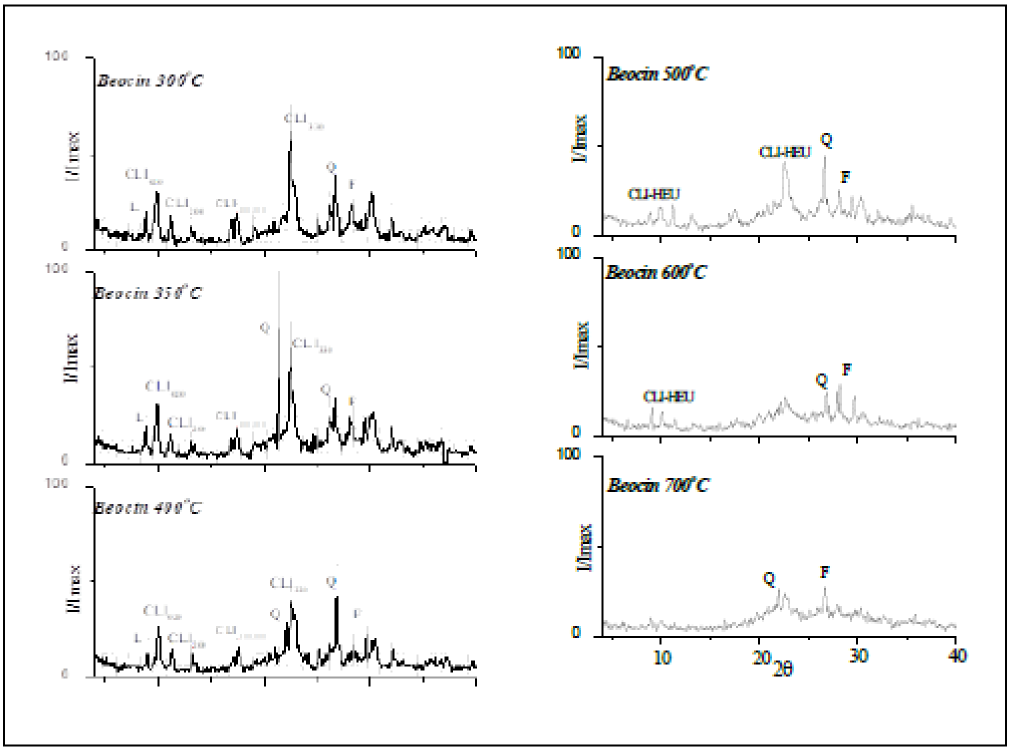

Figure 1 - Comparative X-ray diagrams of the powder of thermally treated clinoptilolite tuff of the Opčište-Beočin deposit (HEU-type zeolites, CLI-clinoptilolite, Q-quartz, F-feldspars).

Structural tests of the thermal stability of zeolitic tuffs were performed by annealing the samples in the temperature range from 300°C to 750°C, in a time interval of 2 hours. The annealed samples were examined by X-ray. The (020) reflection at the 2θ angle of about 9.90 Å was used to determine the thermal stability field. The d-values of the 020 reflection were observed in the characteristic temperature range of 300-500°C. Comparative diagrams of X-ray powder analysis of thermally treated clinoptilolitic tuffs are shown in Figures 1 and 2. [5].

Based on the comparative diagrams (Figures 1 and 2), if the initial and thermally treated samples up to 400°C are observed, the structural stability of both zeolitic tuffs is observed.At these temperatures, dehydration processes are related to the weakest coordinated water, in channel A. At a temperature of 500°C, further dehydration was achieved related to water coordinated by cations in position M2, channel B. It could be said that the structure of the Zlatokop zeolite tuff is still stable . The structure of Beocin zeolite is disturbed. A polymorphic transition to the heylandite structure is present. At temperatures higher than 600°C, the zeolitic tuff of the Zlatokop deposit is more stable. Its structure is still present with appropriate reflections. The zeolite structure of the Beočin deposit is completely destroyed at these temperatures. At higher temperatures, due to the presence of minerals of the tectosilicate group (feldspar and quartz), the formation of feldspathoid structures occurs.

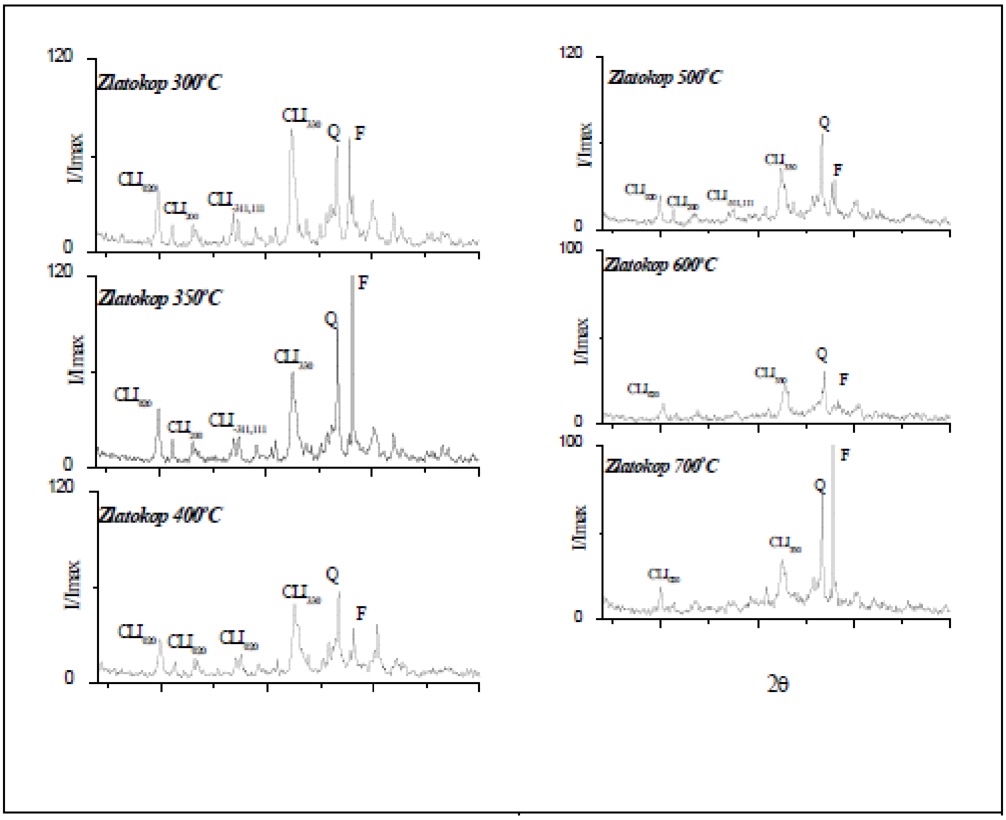

Figure 2 - Comparative X-ray diagrams of the powder of thermally treated clinoptilolitic tuff of the Zlatokop deposit (HEU-type zeolites, CLI-clinoptilolite, Q-quartz, F-feldspars)

The interplane distance values were also observed in the characteristic temperature range from 400ºC to 500ºC. Then the first polymorphic transition occurs. In this temperature interval, the weakest bound water is lost. This loss of water is associated with changes that are most often manifested by changes in the values of interplane distances. Values for interplane distances for both zeolitic tuffs are given in table 1.

Table 1 - Values for interplane distances of thermally treated zeolitic tuffs of the Zlatokop and Općište-Beočin deposits [5]

Treated zeolitic tuffs	Zlatokop d-value (Å)	Beocin d-value (Å)
d- initial	9.91	9.90
d- 400 ° C	9.85	9.83
d-500 ^{about} *C*	9.88	9.78

Based on literature data [7], the following was determined: at temperatures higher than 400ºC, if there is a shift in the value of the interplane distance towards values from 9.90 to 9.80, it is characteristic of clinoptilolite; if the values range from 9.90 to 9.60, then we are talking about the transitional form of clinoptilolite-hoylandite.Values below 9.60 correspond to the hoylandite phase. These values vary depending on both the ratio of network cations and the ratio of off-network cations in the structure of zeolitic tuffs. It is observed that the values of interplane distances in the temperature range from 400ºC to 500ºC, for the tuff of the Zlatokop deposit, range from 9.91Å to 9.88Å. These values are characteristic of the mineral clinoptilolite. The zeolitic tuff Beočin, according to its values of interplane distances from 9.90Å to 9.78Å, corresponds to the transition between the minerals hoylandite and clinoptilolite.

4. CONCLUSION

Based on the above, it can be concluded that there are differences between the minerals of zeolitic tuffs during thermal treatment. They are most likely a function of the chemical and mineral composition, that is, the type and content of both offline and network cations. Based on the results of the Mumpton test (Figures 1 and 2), it can be concluded that the mineral Ca-clinoptilolite is present in the Zlatokop zeolite tuff deposit. The zeolitic tuff of the Općište-Beočin deposit corresponds to the transition between the minerals hoylandite and clinoptilolite.

ACKNOWLEDGEMENT

The authors would like to thank the Ministry of Education, Science and Technological Development of the Republic of Serbia for supporting the research presented in the paper (contract no. 451-03-47/2023-01/200023)

REFERENCES

[1] Kašić V., Simić V., Životić D., Radosavljević-Mihajlović A., Stojanović J. (2017): Mineraloška i kristalohemijska svojstva minerala HEU-tipa i ležišta zeolitskih tufova Srbije, Hemijska Industrija 71 (1), Beograd, 49-60.

[2] Kašić, V., Minerageny of zeolite tuffs of Serbia, Doctoral dissertation, RGF, Beograd, (2017), 168.

[3] Mason B., Sand L. B., (1960): Clinoptilolite from Patagonia, the relation ship between clinoptilolite and heulandite, Am. Mineral. 45, 341-350.

[4] Mumpton F. A., (1960): Clinoptilolite redefined, The American Mineralogist, vol. 45, March-April,Am. Mineral. 45, 351-369.

[5] Radosavljević-Mihajlović, A., (2004): Characterization and stability of dealuminated clinoptilolitic tuffs from different deposits. Master's thesis, Faculty of Physical Chemistry, Belgrade, 123 p.

[6] Radosavljević-Mihajlović, A., Stojanović, J., Kašić, V.,Comparative mineralogical, crystallochemical and thermal properties of deposits of zeolite tuffs of Serbia rich in HEU-type minerals, Geoinstitut papers, Vol.40., (2005), 191 -200.

[7] Treacy, M.M. and Higgins, J.B., (2001): Collection of simulated XRPD patterns for zeolites Structure. Commission of International zeolite Association, ELSEVIER, Amsterdam-London-New York-Oxford-Paris-Shannon-Tokyo, 184-186.