MME SEE CONGRESS 2023

5th Metallurgical & Materials Engineering Congress of South-East Europe
Trebinje, Bosnia and Herzegovina
7-10th June 2023

CONGRESS PROCEEDINGS

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CONGRESS PROCEEDINGS - MME SEE 2023
5th Metallurgical & Materials Engineering Congress of South-East Europe

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Published and printed by:
Association of Metallurgical Engineers of Serbia (AMES)
Kneza Miloša 9/IV,
11000 Belgrade
Serbia

For the publisher:

AMES president Dr. Miroslav Sokić

Circulation:

120 copies

ISBN 978-86-87183-32-2

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PREFACE

On behalf of the Scientific and Organizing Committee, it is a great honor and pleasure to wish all the participants a warm welcome to the Fifth Metallurgical & Materials Engineering Congress of South-East Europe (MME SEE 2023) which is being held in Trebinje, Bosnia and Hercegovina, 07 - 10 June 2023.

The MME SEE 2023 is a biannual meeting of scientists, professionals, and specialists working in the fields of metallurgical and materials engineering. The aim of the Congress is to present current research results related to processing/structure/property relationships, advances in processing, characterization, and applications of modern materials. Congress encompasses a wide range of related topics and presents the current views from both academia and industry: Future of metals/materials industry in South-East European countries; Raw materials; New industrial achievements, developments and trends in metals/materials; Ferrous and nonferrous metals production; Metal forming, casting, refractories and powder metallurgy; New and advanced ceramics, polymers, and composites; Characterization and structure of materials; Recycling and waste minimization; Corrosion, coating, and protection of materials; Process control and modeling; Nanotechnology; Sustainable development; Welding; Environmental protection; Education; Accreditation & certification.

The editors hope that Congress will stimulate new ideas and improve knowledge in the field of metallurgical and materials engineering. The Congress has been organized by the Association of Metallurgical Engineers of Serbia, with the co-organization of the Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia, Faculty of Technology and Metallurgy, University of Belgrade, Serbia, Faculty of Technology, University of Banja Luka, Bosnia and Herzegovina; the Faculty of Metallurgy, University of Zagreb, Sisak, Croatia; the Faculty of Natural Sciences and Engineering, University of Ljubljana, Slovenia; and the Faculty of Metallurgy and technology, University of Podgorica, Montenegro.

Financial support from the Ministry of Science, Technological Development and Innovation of the Republic of Serbia to researchers from Serbia for attending the congress is gratefully acknowledged. The support of the sponsors and their willingness to cooperate have been of great importance for the success of MME SEE 2023. The Organizing Committee would like to extend their appreciation and gratitude to all sponsors and friends of the conference for their donations and support.

We would like to thank all the authors who have contributed to this book of abstracts and also the members of the scientific and organizing committees, reviewers, speakers, chairpersons, and all the conference participants for their support of MME SEE 2023. Sincere thanks to all the people who have contributed to the successful organization of MME SEE 2023.

On behalf of the 5th MME SEE Scientific and Organizing Committee

Miroslav Sokić, PhD

Table of Contents

MECHANOCHEMICAL SYNTHESIS AND CHARACTERIZATION OF THE ADSORBENTS BASED ON NATURAL ZEOLITE AND HYDROXYAPATITE

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Natural zeolite is a good sorbent for many cations due to its specific porous structure. The degree of sorption efficiency depends on the cation type and the availability of exchange positions in the zeolite lattice. The aim of this work is to examine the synthesis possibility of a new adsorbent based on natural zeolite and hydroxyapatite. The adsorbent was prepared mechanochemically by using clinoptilolite-rich zeolite tuff from the Slanci deposit (Serbia) and hydroxyapatite obtained by the hydrothermal process. The milling process was performed in a ball mill and optimized regarding contact time and milling speed. For the synthesis of zeolite/hydroxyapatite adsorbent (ZHAp), optimal values for these two parameters were 10 min and 250 rpm, respectively. The resulting sample ZHAp was characterized by X-ray powder diffraction, thermal analysis and scanning electron microscopy. Diffraction analysis of the ZHAp confirmed the presence of the most abundant mineral in zeolite tuff - clinoptilolite and hydroxyapatite. Needle-like crystals of hydroxyapatite on the clinoptilolite surface are observed in SEM images. Zeolite/hydroxyapatite sample is thermally stable at 800 °C. Adsorption properties of ZHAp were examined for nickel and chromium ions, towards which natural zeolite shows a low affinity. The presence of hydroxyapatite on the zeolite surface led to an increase in the adsorption capacity more than two times for both tested ions compared to the initial zeolite tuff.

Keywords: mechanochemical synthesis, natural zeolite, hydroxyapatite, adsorption.

Introduction

Considering the development of industry and increasing amounts of wastewater, the issue of water treatment is extremely important. Heavy metals are one of the most toxic pollutants in industrial wastewater and can cause human health consequences even at low concentrations [1]. Zeolites are aluminosilicate crystalline minerals that show good results in removing harmful substances from water, including heavy metals [2]. The adsorption properties of zeolites depend on the structure of the crystal lattice, the size of the voids and the size of the metal ions. Therefore, zeolites are not universal adsorbents [3]. The adsorption capacity of natural zeolite clinoptilolite towards metal cations decreases in the order: $Pb^{2+}>Ag^{+}>Cd^{2+}>Zn^{2+}>Cu^{2+}>Ni^{2+}>Mn^{2+}>Cr^{3+}$ [2]. Natural zeolite heulandite from a deposit in Australia has a maximum adsorption capacity of 5.03 mg g^{-1} for Cr^{3+} ions [4], while zeolite from a deposit in Iran has a maximum adsorption capacity of 3.4 mg g^{-1} for Ni^{2+} ions [5]. Due to the low removal efficiency of Ni and Cr ions from aqueous solutions, natural zeolites cannot be successfully used as their adsorbents. On the other hand, calcium hydroxyapatite (HAP), synthesized by hydrothermal procedure, shows a significantly higher adsorption capacity for nickel ions (309.4 mg g^{-1}) compared to natural zeolite [6]. HAP was successfully synthesized on the surface of zeolite by a hydrothermal process and zeolite lattice remained unchanged [7]. In this way, a new composite with improved adsorption properties compared to natural zeolite was obtained. The aim of this work is to examine the possibilities of mechanochemical synthesis of adsorbents based on natural zeolite and hydroxyapatite and their application for the removal of chromium and nickel ions from aqueous solutions. By applying the mechanochemical method of modification, the imperfections of classic hydrothermal methods are overcome and the amount of liquid waste is reduced [8]. By this rout, use of elevated temperature is not required. The method is environmentally friendly and applicable in industrial scale.

Materials and methods

In this research, two adsorbents were used. They were based on natural zeolite (Slanci, Serbia) and calcium hydroxyapatite obtained by mechanochemical activation. A fraction of natural zeolite clinoptilolite (NZ) with a particle size between 63 μm and 125 μm was used. Calcium hydroxyapatite (HAp) was synthesized hydrothermally in stainless steel autoclaves under autogenous pressure at 160 °C for 4 h. The molar ratio of Ca/P in the reaction mixture was 1.67, and the pH value was adjusted to 9 with sodium hydroxide solution (Aldrich). Calcium chloride (Merck) was used as a source of calcium ions, and phosphate ions were introduced into the reaction mixture through a solution of ammonium hydrogen phosphate (Merck). In addition, urea and sodium ethylenediaminetetraacetate were added to the reaction mixture. After hydrothermal synthesis, the obtained HAp was exposed to sonication for 6 minutes in 3 cycles (Sonopuls, Bandelin mini20), then separated by vacuum filtration, washed with distilled water and dried overnight at 105 °C. Two adsorbents based on NZ and HAP were obtained through mechanochemical synthesis: ZHAp1 which has 10 wt.% of HAp and ZHAp2 which has 20 wt.% of HAp in the composite. The milling was performed in a planetary mill Retsch PM100 **using milling parameters:** speed 250 rpm, milling time 15 min and mass ratio of reactants and balls was 1:15.

The adsorption properties of the obtained samples were examined towards Ni^{2+} and Cr^{3+} ions. In the adsorption experiments, the liquid/solid phase ratio was 200:1. The initial concentrations of metal ions in monocomponent aqueous solutions were 80 and 150 mg dm^{-3}. Suspensions were shaken in a thermostatic water bath (Memmert, WNB 22) at 105 rpm during 48 h. After 24 h aliquots were taken. The suspensions were separated by filtration and the concentrations of Ni^{2+} and Cr^{3+} ions before and after adsorption were measured using atomic absorption spectroscopy (SpectrAA 55B, Varian).

X-ray powder diffraction analysis was used to determine and monitor the phase composition of the adsorbents. The intensities of diffracted X-ray radiation were measured at room temperature in the range from 2θ 5 ° to 45 ° using an Ital Structure APD2000 diffractometer. The thermal properties were examined by thermogravimetric analysis by heating in a stream of synthetic air at a flow rate of 100 cm^3 min^{-1}, at a speed of 20 °C min^{-1} up to a temperature of 800 °C using the SDT Q600 instrument (TA Instruments). Scanning electron microscopy was used to examine the morphology of the obtained samples and the size of the resulting crystals using the Jeol JSM-6610LV electron microscope. Before analysis, the samples were dried overnight at 105 °C, after which a thin layer of gold was applied to the surface of the sample. The concentrations of chromium and nickel ions in the solution were determined using a Varian Spectra AA 55B atomic adsorption spectrophotometer.

Results and discussion

Diffractograms of both synthesized samples are shown in Figure 1. The most abundant mineral is clinoptilolite in both composites. In this research, natural zeolite was used, so different impurities are present in the sample: quartz, clay, feldspar and carbonates. Peaks at 2Θ (°) 9.9, 11.2, 17.4 and 22.4 originate from clinoptilolite, while peaks at 2Θ (°) 25.8, 28.9 and 32.6 to 34 ° correspond to calcium hydroxyapatite (HAp). The larger area under the peaks between 32.4 ° and 34 ° in the diffractogram of ZHAp2 indicates that a higher amount of HAp is present in ZHAp2 compared to the ZHAp1. Structural analysis shows that the zeolite structure remained unchanged after mechanochemical synthesis.

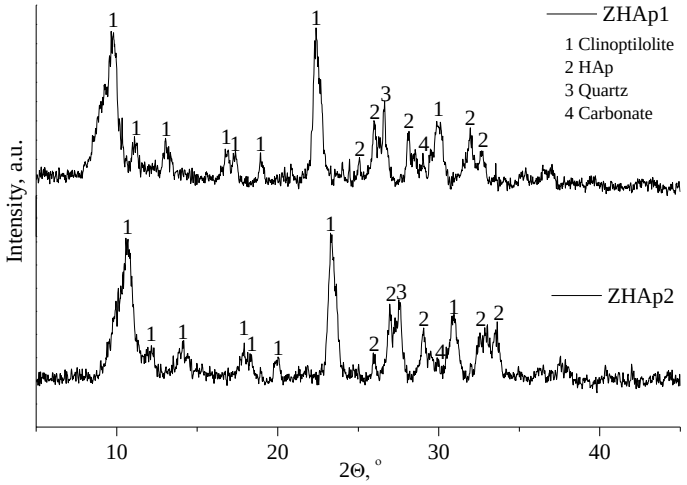

Figure 1 Difractograms of ZHAp1 and ZHAp2

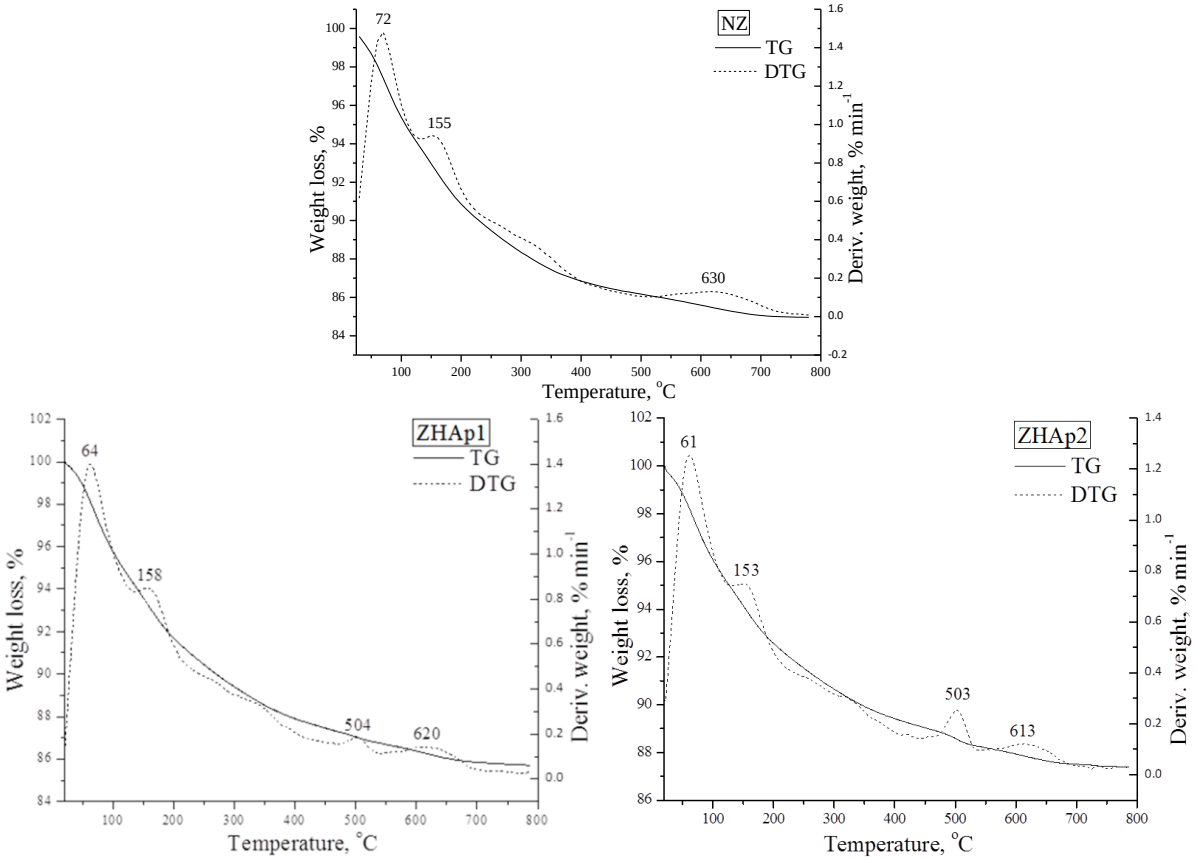

Figure 2 TG and DTG curves of NZ, ZHAp1 and ZHAp2

Figure 3 shows SEM images of ZHAP1 and ZHAp2. Needle-like crystals of calcium hydroxyapatite are observed on the surface of the zeolite in both adsorbents. The morphology of clinoptilolite remained unchanged.

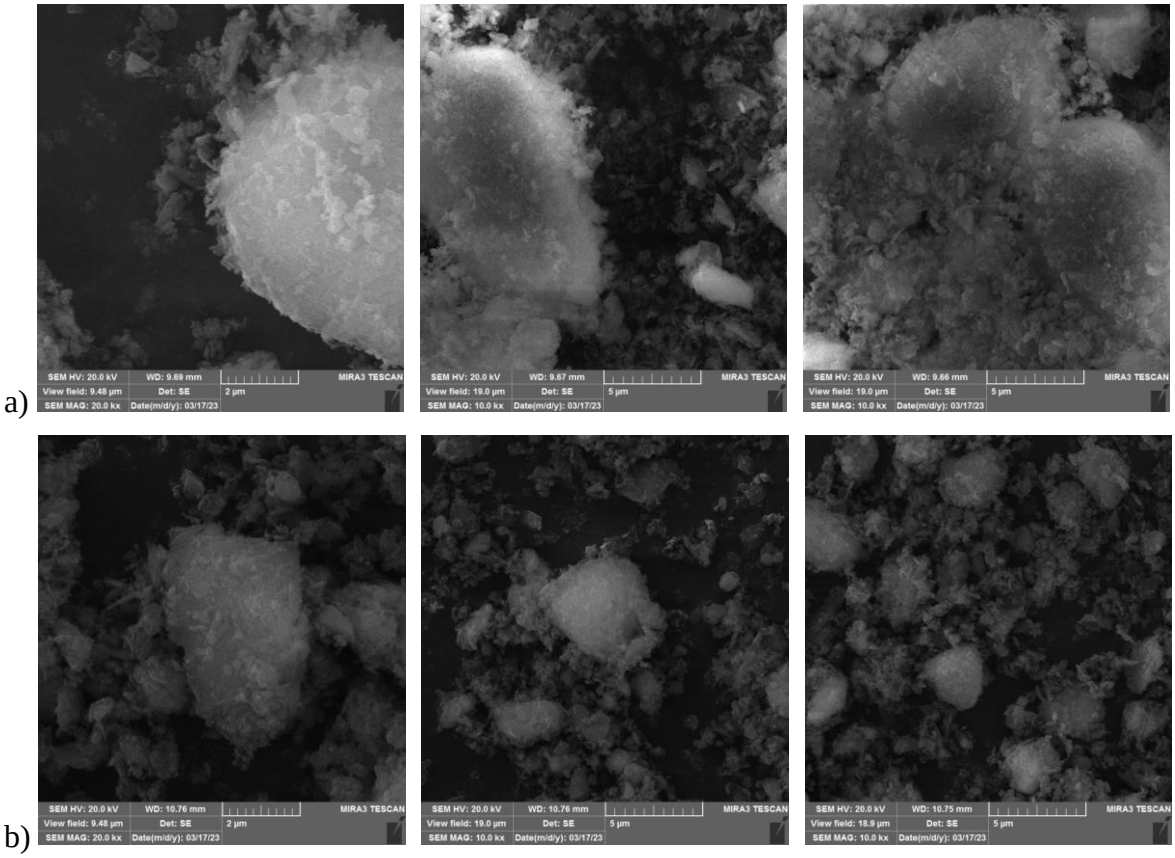

Figure 3 Morphology of the samples a) ZHAp1 and b) ZHAp2

The results show that during the adsorption of chromium ions, the highest value of the adsorption capacity was achieved using the ZHAp2 composite in a solution with an initial concentration of 150 mg dm^{-3} and it has the value of 13.8 mg g^{-1}. The ZHAp2 adsorbent shows a higher maximum adsorption capacity compared to ZHAp1 adsorbent in both solutions with different initial concentrations. This is consistent with the structural and thermal analysis results which showed that the ZHAp2 composite has a higher amount of HAp compared to ZHAp1. Therefore, the increase in the amount of HAp in the composite affects the increase in the adsorption capacity for chromium ions. The differences between the amount of adsorbed ions after 24 h and 48 h are small, which means that the highest percentage of removed ions is in the first 24 h.

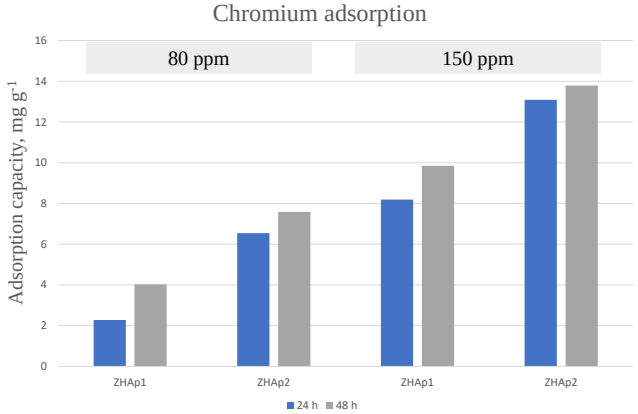

Figure 4 Adsorption capacities for chromium ions

When examining the adsorption of nickel ions, both adsorbents showed similar results. The initial concentration of the solution did not significantly affect the value of the maximum adsorption capacity.

For nickel ions, the differences in adsorption between 24 h and 48 h are greater than for the adsorption of chromium ions, which means that a longer time is needed to establish the equilibrium state. The highest adsorption capacity was achieved by the adsorbent ZHAp1 in a solution with an initial concentration of 150 mg dm^{-3}. Both composites showed better results in the adsorption of chromium ions than in the adsorption of nickel ions.

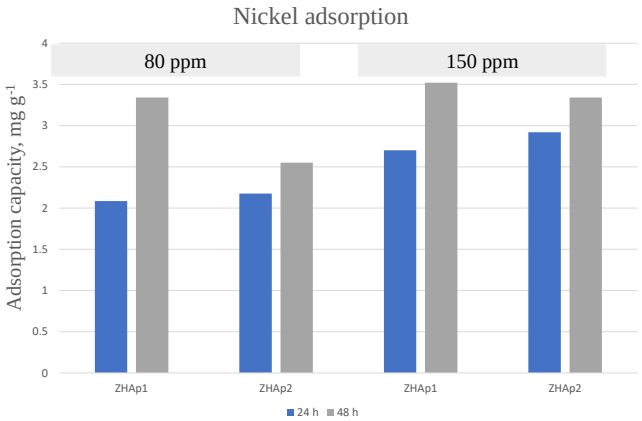

Figure 5 Adsorption capacities for nickel ions

Figure 6 shows the values of chromium and nickel adsorption efficiency for composites. Both adsorbents show higher removal efficiency for chromium ions than for nickel ions. In the adsorption of chromium ions, the highest efficiency of 46.3 % was achieved by adsorbent ZHAp2, while in the adsorption of nickel ions, the highest efficiency was achieved by adsorbent ZHAp1.

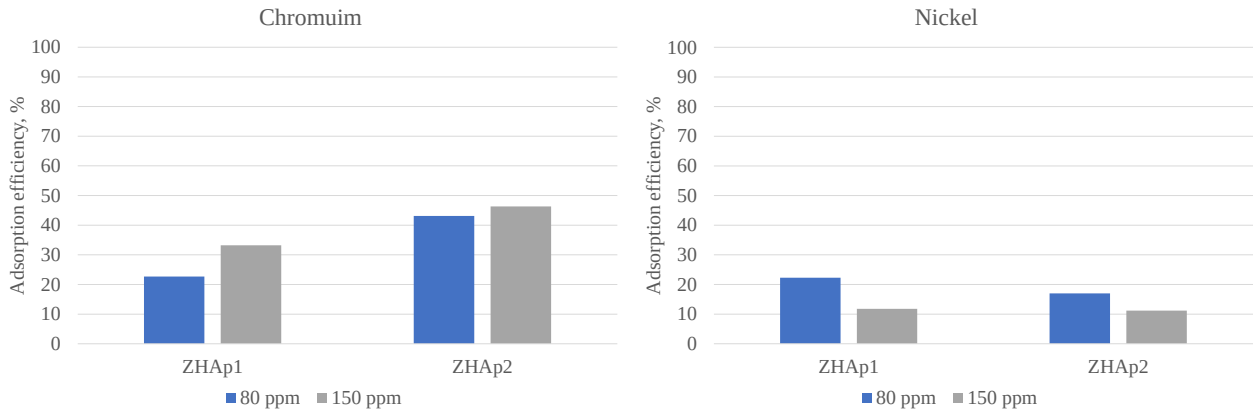

Figure 6 Adsorption efficiency of ZHAp1 and ZHAp2

Conclusion

The aim of this work was to investigate the possibility of mechanochemical synthesis of adsorbents based on natural zeolite and calcium hydroxyapatite (HAp). X-ray powder diffraction showed that the crystallinity of the zeolite did not change in the sample after treatment in the mill, and that the HAp content was higher in the ZHAp2 sample. Scanning electron microscopy showed needle-like crystals of HAp on the surface of the zeolite. The samples are stable up to 800 °C and the total mass loss comes from dehydration. In the adsorption of chromium ions, adsorbent ZHAp2 shows better results, which indicates that the larger amounts of HAp present in this sample influenced the increase in adsorption capacity.

The maximum adsorption capacity for chromium ions is 13.8 mg g^{-1} for ZHAp2, and 9.9 mg g^{-1} for ZHAp1. During the adsorption of nickel, both adsorbents showed similar results and the amount of HAp present in the composite did not affect the adsorption properties. Both used adsorbents show better results in the adsorption of chromium than in the adsorption of nickel.

The maximum efficiency in ion adsorption was achieved for chromium ions using ZHAp2, where 46,3 % of ions were removed from a solution with an initial concentration of 150 mg dm^{-3}.

Acknowledgment

This work was supported by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-47/2023-01/200135 and 451-03-47/2023-01/200287).

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CIP - Каталогизација у публикацији
Народна библиотека Србије, Београд

669(082)(0.034.2)
66.017/.018(082)(0.034.2)
621.7/.9(082)(0.034.2)

METALLURGICAL & Materials Engineering Congress of South-East Europe (5 ; 2023 ; Beograd)

Congress Proceedings [Електронски извор] / 5th Metallurgical & Materials Engineering Congress of South-East Europe MME SEE Congress 2023, Trebinje, Bosnia and Herzegovina 7-10th June 2023 ; [[organized by] The Association of Matallurgical Engineers of Serbia [AMES] ... [et al.]] ; [editors Miroslav Sokić, Branislav Marković, Vaso Manojlović]. - Belgrade : Association of Metallurgical Engineers of Serbia (AMES), 2023 (Belgrade : Association of Metallurgical Engineers of Serbia (AMES)). - 1 USB fleš memorija ; 1 x 6 x 9 cm

Sistemski zahtevi: Nisu navedeni. - Nasl. sa naslovne strane dokumenta. - Tiraž 120. - Preface / Miroslav Sokić. - Bibliografija uz svaki rad.

ISBN 978-86-87183-32-2

а) Металургија -- Апстракти б) Технички материјали -- Зборници в) Наука о материјалима -- Зборници г) Металопрерађивачка индустрија -- Зборници

COBISS.SR-ID 117307657

ISBN 978-86-87183-32-2