Appendix 5.

By the decision of the Academic Council of the Faculty of Technology, University of East Sarajevo, number: 342/2025 dated March 18, 2025, a Commission for the evaluation and defense of the completed doctoral dissertation of candidate **Duško Kostić**, entitled "**Innovative Approaches to the Production of Titanium(IV) Oxide Nanopowders from Secondary Raw Materials**" (hereinafter referred to as: the Commission[1]), has been appointed with the following members:

1. **PhD Srećko Stopić**, Private Dozent (Associate Professor), Faculty of Georesources and Materials Engineering, Institute for Process Metallurgy and Metal Recycling, RWTH Aachen University, Rheinische Westfällische Technische Hochschule (RWTH), Germany; Scientific Advisor, Institute of Chemistry, Technology, and Metallurgy, University of Belgrade. Specialized Scientific Area: Metallurgy and Metal Recycling / Other Engineering and Technologies, Chair of the Committee;
2. **PhD Željko Kamberović**, Full Professor, Faculty of Technology and Metallurgy, University of Belgrade. Specialized Scientific Area: Metallurgy / Other Engineering and Technologies, Member;
3. **PhD Antonije Onjia**, Full Professor, Faculty of Technology and Metallurgy, University of Belgrade. Specialized Scientific Area: Chemistry / Analytical Chemistry, Member;
4. **PhD Goran Tadić**, Full Professor, Faculty of Technology, Zvornik. Specialized Scientific Area: Process Engineering, Member;
5. **PhD Radislav Filipović**, Full Professor, Faculty of Technology, Zvornik. Specialized Scientific Area: Process Engineering, Member.

The Commission has reviewed and evaluated the doctoral dissertation and submitted the following report to the Academic Council of the Faculty of Technology, University of East Sarajevo:

REPORT
regarding the evaluation of the completed doctoral dissertation

1. The significance and contribution of the doctoral dissertation from the perspective of the current state in the respective scientific field
The research presented in this doctoral dissertation significantly contributes to the technology of secondary raw material processing, with a particular focus on innovative methods for producing titanium(IV) oxide nanopowders. In light of the growing environmental and economic challenges associated with industrial waste management, this dissertation offers new approaches that enable the utilization of secondary raw materials, such as red mud and tionite. Current trends in materials research highlight the need for sustainable and economically viable methods for obtaining nanomaterials, particularly those based on

[1]The Commission must be appointed in accordance with Article 40 of the Regulation on Third Cycle Studies at the University of East Sarajevo

titanium(IV) oxide, which has widespread applications in photocatalysis, energy-related technologies, and environmental protection. Compared to existing research, this dissertation presents an original approach that combines various reduction, leaching, and ultrasonic spray pyrolysis methods to achieve the synthesis of nanopowders with improved properties.
The contributions of this research are reflected in several aspects:

- Development and optimization of red mud reduction methods to extract iron and enrich slag with other elements, particularly titanium,
- Investigation of leaching parameters to achieve maximum titanium extraction efficiency with minimal energy and reagent consumption,
- Optimization of the titanium(IV) oxide nanopowder synthesis process via ultrasonic spray pyrolysis, including an analysis of the effects of temperature, precursor concentration, and gas flow ratios,
- Proposal of a sustainable industrial waste management model based on circular economy principles, ensuring complete utilization of secondary raw materials without generating new waste streams.

The originality and significance of this work lie in the fact that previous studies have not included such an integrated approach, simultaneously offering solutions for efficient industrial waste management and nanomaterial synthesis. The research findings have the potential for broad applications in metallurgy, the chemical industry, and environmental science.

2. An assessment that the completed doctoral dissertation is the result of the candidate's original scientific work in the relevant scientific field

The doctoral dissertation of candidate MSc Duško Kostić represents the result of original scientific research in the fields of metallurgy, chemical engineering, and nanotechnology. The research was designed and conducted to process secondary raw materials and synthesize nanomaterials.
The scientific originality of the dissertation is reflected in the application and comparison of three different red mud reduction methods for iron extraction and slag enrichment with titanium, the optimization of leaching parameters to achieve maximum titanium extraction efficiency, and the development of a novel approach to synthesizing titanium(IV) oxide nanopowders via ultrasonic spray pyrolysis, with controlled crystal structure, morphology, and product purity.
Through an experimental and analytical approach, employing modern instrumental analytical techniques (XRD, SEM, EDS, ICP), the candidate has demonstrated the ability to independently solve scientific problems and has presented significant scientific findings. Therefore, the candidate's dissertation represents an original contribution to science and meets all the criteria for obtaining the academic title of Doctor of Science.

3. Overview of the candidate's achieved research results in the respective scientific field.

Since enrolling in the third cycle of studies in 2020, the candidate has published, as an author or co-author, several scientific papers in the field of engineering and technology, specifically in metallurgy, chemical engineering, and process engineering. The majority of these papers are referenced in prestigious databases with an impact factor (IF). Additionally, the candidate has participated in multiple scientific conferences.
Papers published in scientific journals:

1. **Kostić, D.**; Stopic, S.; Keutmann, M.; Emil-Kaya, E.; Husovic, T.V.; Perušić, M.; Friedrich, B. Synthesis of Titanium-Based Powders from Titanium Oxy-Sulfate Using Ultrasonic Spray Pyrolysis Method. Materials 2024, 17, doi:10.3390/ma17194779.

2. Stojkić, O., Filipović, R., Janković, M., **Kostić, D.**, Perusic, M., Stopić, S., & Damjanović, V. (2024). Influence of process parameters on the adsorption properties of zeolite 13X. *Journal of Chemists, Technologists and Environmentalists*, *5*(1), 20–31. https://doi.org/10.59919/JCTE05202401005
3. Stopic, S.; **Kostić, D.**; Emil-Kaya, E.; Uysal, E.; Gürmen, S.; Mitrašinović, A.; Perušić, M.; Friedrich, B. High-Pressure and High-Temperature Dissolution of Titanium from Titanium and Aluminum Residues: A Comparative Study. *Surfaces* **2024**, *7*, 1096-1108. https://doi.org/10.3390/surfaces7040072.
4. Stopic, S., **Kostić, D.**, Schneider, R., Sievers, M., Wegmann, F., Emil Kaya, E., Perušić, M., & Friedrich, B. (2024). Recovery of Titanium from Red Mud Using Carbothermic Reduction and High Pressure Leaching of the Slag in an Autoclave. Minerals, 14(11), 1151. https://doi.org/10.3390/MIN14111151
5. Vuković, J., Perušić, M., Stopić, S., **Kostić, D.**, Smiljanić, S., Filipović, R., & Damjanović, V. (2024). A review of the red mud utilization possibilities. Ovidius University Annals of Chemistry, 35(2), 165–173. https://doi.org/10.2478/auoc-2024-0021
6. Vasiljević, N.; Mićić, V.; Perušić, M.; Mitrović, M.; **Kostić, D**. Optimization of Ultrasound-assisted Extraction of (Poly)phenolic Compounds from Blueberry (Vaccinium Myrtillus) Leaves. Chemical Industry and Chemical Engineering Quarterly 2024, 28–28, doi.org/10.2298/CICEQ240207028V.
7. Damjanovic, V.; Filipovic, R.; Obrenovic, Z.; Perusic, M.; **Kostic, D**.; Smiljanic, S.; Stopic, S. Influence of Process Parameters in Three-Stage Purification of Aluminate Solution and Aluminum Hydroxide. Metals (Basel) 2023, 13, doi:10.3390/met13111816.
8. Janković, M.B.; Perušić, M.D.; Damjanović, V.M.; Filipović, R.L.; Obrenović, Z.B.; Tadić, G.S.; **Kostić, D.D**.; Janković, M.B.; Perušić, M.D.; Damjanović, V.M.; et al. Influence of Suspension Heating Rate on Properties of Zeolite 13X. Hem Ind 2023, 77, 275–282, doi:10.2298/HEMIND230418023J.
9. Petričević, S.; Došić, A.; Filipović, R.; Damjanović, V.; Obrenović, Z.; Perušić, M.; Sekulić, V.; Mićić, V.; **Kostić, D.** The Influence of Process Parameters on the Morphological Characteristics of Fine Precipitated Hydrate. Journal of Engineering & Processing Management 2023, 15, 30–37, doi:10.61458/jepm2301030p.
10. Vasiljević, N.; Mićić, V.; Vasiljević, L.; Lazić, D.; Tomić, M.; **Kostić, D.** Influence of Process Parameters on Hawthorn (Crataegus Monogyna Jack.) Extraction. Technologica Acta 2023, 16, 29–37, doi:10.51558/2232-7568.2023.16.1.29.
11. Paprica, N.; Filipović, R.; Perušić, M.; **Kostić, D**.; Pantić, S.; Damjanović, V. Influence of the SiO_2/Al_2O_3 Molar Ratio on the Specific Properties of NaA Zeolite. Chemical Papers 2022, 76, 5421–5428, doi:10.1007/s11696-022-02255-4.

Papers published in scientific conference proceedings:

1. Kostić, D.; Perušić, M.; Balanović, Lj.; Stopić, S.; **Kostić, D.;** Damjanović, V.; Kešelj, D.; Smiljanić, S.; Filipović, R. Analysis and initial qualitative assessment of Red Mud in the Bayer process, Proceedings of the Conference *Contemporary Materials*; Academy of Sciences and Arts of the Republic of Srpska: Banja Luka, September 2024. Novičić, V.; Filipović, R.; Perušić, M.; Obrenović, Z.; **Kostić, D.;** Damjanović, V.; Sekulić, V.; Vasiljević, N. Influence of Process Parameters on the Sorption Characteristics of Aluminum Hydroxide, U zborniku radova Savremeni materijali; Akademija nauka i umjetnosti Republike Srpske: Banja Luka, September 2024.
2. Vasiljević, N.; Mićić, V.; **Kostić, D**.; Jovanović, Z.; Lazić, D.; Perušić, M.; Tadić, G. Influence of Process Parameters on the Extraction of Phenolic Compounds from Black

Elderberry Flowers (Sambucus Nigra l.). In Proceedings of the VIII International Congress "Engineering, Environment and Materials in Process Industry"; 2023.

3. Vasiljević, N.; Mićić, V.; Vasiljević, Lj.; **Kostić, D.;** Perić, J.; Radić, M. Extraction of (poly)phenolic compound from hawthorn (Crataegus Monogyna Jack.) U zborniku radova Savremeni materijali; Akademija nauka i umjetnosti Republike Srpske: Banja Luka, September 2023; pp. 131–141.
4. Rikić, V.; **Kostić, D**.; Mićić, V. Unapređenje energetske efikasnosti izolacionih materijala dodatkom produkata reciklaže polimernog otpada. Proceedings of the Conference *Contemporary Materials*; Academy of Sciences and Arts of the Republic of Srpska: Banja Luka, September 2022; pp. 117–129.

4. Assessment of the scope and quality of the approved topic (by chapters)[2]

1. Subject of Scientific Research

The research thoroughly encompasses all aspects of the development and optimization of the process for obtaining titanium dioxide nanopowders from industrial waste materials. The topic is elaborated in detail through an analysis of key technological steps: reduction, leaching, and ultrasonic spray pyrolysis. Covering the entire technological process, from waste material management to the final nanopowder production, indicates a high level of completeness and quality of the research on the submitted topic.

2. Research Objectives

The objectives are precisely defined and fully cover all phases of the research. Starting from the primary reduction of red mud, through leaching and purification of titanium compounds, to the final synthesis of nanopowders. Additionally, an accent is placed on the potential application of the obtained materials in various industries. The scope and quality of the research fully align with the objectives set during the topic submission.

3. Working Hypotheses

The formulated hypotheses are clear, logical, and directly related to the set objectives. They encompass each phase of the process – from red mud reduction to leaching and nanopowder synthesis. The scientific approach in defining the hypotheses is justified, and their verification through experimental methods ensures high research validity. A comparative thermochemical analysis of the reduction process using hydrogen and carbon was of great significance in testing some hypotheses, intending to examine the potential for reducing carbon dioxide emissions and forming titanium carbide in a novel process.

4. Research Plan and Methods

The research plan is systematic, with clearly defined phases and experimental methods. The selected methods (carbothermal reduction, reduction with hydrogen and hydrogen plasma, sulfuric acid leaching, and ultrasonic spray pyrolysis) are modern and relevant for use under experimental conditions. Additionally, the application of advanced analytical techniques (EDS, XRD, SEM, ICP) ensures precise characterization of the obtained materials. The scope and quality of the research in this field fully meet established standards.

Red Mud Reduction. Three methods of red mud reduction were examined – reduction with hydrogen, hydrogen plasma reduction, and carbothermal reduction. During hydrogen reduction, with an increase in temperature from 700°C to 1000°C, a significant transformation in the composition of red mud was observed. The content of metallic iron increased, while magnetite content decreased, as confirmed by XRD analysis. New phases, such as perovskite and nepheline, appeared, while cancrinite completely transformed into nepheline. Hydrogen plasma reduction demonstrated high efficiency, with a mass loss of up to 57%, primarily due

[2] The compliance of the scope and quality with the approved topic should specifically include: an analytical and systematic approach in evaluating the research subject, objectives, and research tasks; and compliance with the scientific approach in proving claims or assumptions in the hypotheses, including data processing.

to the reduction of oxides into metals and oxygen release. The optimal reduction time was 10 minutes, after which the content of the metallic phase was the highest. XRD analysis confirmed the presence of elemental iron, ilmenite, cristobalite, wüstite, and magnetite, while some elements detected by ICP-OES were in an amorphous form and not visible in the XRD spectrum. Carbothermal reduction, using graphite and CaO as a fluxing agent, was highly effective in iron reduction. The addition of CaO played a crucial role in preventing FeO from reacting with silicon. XRD analysis confirmed that hematite had completely disappeared, with metallic iron, perovskite, and gehlenite dominating the phases.

Leaching Process. The second part of the research focused on optimizing the leaching of carbothermal reduced slag and tionite to extract titanium. Parameters such as acid concentration, temperature, reaction time, and oxygen pressure were adjusted to achieve the best efficiency with minimal energy consumption. Testing under milder conditions did not yield satisfactory results, but increasing the temperature to 180°C revealed that titanium was less soluble at higher temperatures. Further process optimization, by increasing oxygen pressure to 9 bar, achieved a titanium leaching rate of 97.5% with high efficiency for iron and aluminium. Notably, silicon leaching remained low, preventing the problem of silicon gelation, which significantly complicates the filtration process. Leaching of tionite showed low efficiency for titanium, while aluminium and iron were effectively leached. Increasing temperature and pressure were also tested, but the results suggested that the rutile phase of titanium dioxide was too stable. A proposed solution involved roasting with alkalis to convert titanium into easily soluble titanates.

Ultrasonic Spray Pyrolysis with Hydrogen Reduction. The third part of the research focuses on the synthesis of TiO_2 nanopowders through ultrasonic spray pyrolysis (USP) involving hydrogen transformation. The impact of temperature, precursor concentration, and gas ratio on the properties of the obtained powders was analyzed. EDS analysis showed that increasing the temperature reduces sulfur content, yielding purer TiO_2. SEM analysis revealed that higher temperatures lead to the formation of smaller, more uniform, spherical nanoparticles, while XRD showed that temperature influences the crystal structure – lower temperatures favor anatase formation, whereas higher temperatures promote rutile formation. The effect of precursor concentration was also examined, with lower concentrations leading to smaller particles, though excessively low concentrations resulted in incomplete transformation of $TiOSO_4$. Gas ratio analysis determined that hydrogen is essential for successful reduction, and lower gas ratios resulted in longer retention times, improving reduction and yielding smaller particles.

5. Expected Research Results and Their Significance

The research is expected to contribute to the development of technologies for industrial waste recycling and the production of nanomaterials. The potential application of the obtained nanopowders in various industries (energy, chemical industry, or even medicine) indicates significant practical importance. The research also provides a substantial contribution to the field of sustainable development and circular economy, further affirming its scientific and societal relevance.

General Information about the Doctoral Dissertation

The doctoral dissertation of MSc Duško Kostić is technically refined, highly structured, and presented:

List of Abbreviations (p. 148)
List of Figures and Tables (pp. 149–152)
Author's Biography (pp. 153–154)
The dissertation is written in English, consists of 154 A4-format pages, and includes 70 figures, 8 tables, and 148 literature references. At the beginning of the dissertation, key documentation is provided along with an abstract in both Serbian and English.

5. Scientific Results of the Doctoral Dissertation

The research conducted in this doctoral dissertation has led to advancements in metallurgy, industrial waste processing, and the synthesis of titanium dioxide (TiO_2) nanopowders. Optimized methods for red mud reduction, slag leaching, and ultrasonic spray pyrolysis of titanium oxysulfate solutions were developed, enabling the production of high-purity TiO_2 with controlled morphology. Experiments on red mud reduction demonstrated that hydrogen plasma reduction is the most efficient method for extracting metallic iron, causing significant changes in the mineral composition. The carbothermal reduction has been confirmed as a reliable method for iron extraction and the transformation of titanium compounds into forms suitable for further processing.

The leaching process was systematically optimized, revealing that the highest titanium extraction efficiency is achieved by increasing oxygen pressure. It was discovered that the rutile phase of titanium present in tionite is highly stable, indicating the need for additional thermal treatment before leaching.

Ultrasonic spray pyrolysis (USP), as the final stage of nanopowder synthesis, enabled the production of uniformly shaped particles, with a direct correlation established between process temperature, crystal structure, and nanoparticle purity. It was shown that USP conditions significantly influence the crystal structure of the obtained nanopowders, where lower temperatures favor the formation of anatase, while higher temperatures promote the formation of the more stable rutile phase.

6. Applicability and Usefulness of the Results in Theory and Practice[3]

The research results presented in the doctoral dissertation of MSc Duško Kostić have significant applicability and usefulness in both theory and practice, particularly in the context of industrial waste recycling and nanomaterial production. These results not only introduce new technological approaches for obtaining titanium(IV) oxide from secondary raw materials but also represent a substantial advancement in the theoretical foundations of reduction and leaching processes.

From a theoretical perspective, this research contributes to a better understanding of the transformation and reduction of industrial waste materials, as well as the formation of new phases during hydrogen and carbon reduction. Additionally, it expands theoretical knowledge regarding the interaction between various phase transitions of titanium compounds and their behaviour in processes such as leaching and ultrasonic spray pyrolysis. These theoretical contributions serve as a foundation for further research and improvements in nanomaterial synthesis technologies, as well as for exploring the production of titanium metal powders and their alloys from titanium oxides. A particularly noteworthy application is the use of titanium(IV) oxide nanopowders in catalysis, energy processes, and potentially in medical implants.

Compared to existing theoretical and practical solutions, this research introduces innovative approaches based on the utilization of secondary raw materials for the production of high-quality nanomaterials. This overcomes the limitations and shortcomings of current methods,

[3] Emphasize the applicability and usefulness in relation to existing solutions in theory and practice.

such as the high costs associated with obtaining nanomaterials from primary raw materials and their negative environmental impact.

7. Presentation of Research Results to the Scientific Community[4]

The candidate has fulfilled all the required criteria by the Regulations on Third Cycle Studies, successfully passed all exams, and has at least one published paper as the first author in a journal indexed in the SCI list:

1. **Kostić, D.**; Stopic, S.; Keutmann, M.; Emil-Kaya, E.; Husovic, T.V.; Perušić, M.; Friedrich, B. Synthesis of Titanium-Based Powders from Titanium Oxy-Sulfate Using Ultrasonic Spray Pyrolysis Method. Materials 2024, 17, doi:10.3390/ma17194779.
2. Stopic, S.; **Kostić, D.**; Emil-Kaya, E.; Uysal, E.; Gürmen, S.; Mitrašinović, A.; Perušić, M.; Friedrich, B. High-Pressure and High-Temperature Dissolution of Titanium from Titanium and Aluminum Residues: A Comparative Study. *Surfaces* **2024**, *7*, 1096-1108. https://doi.org/10.3390/surfaces7040072.
3. Stopic, S., **Kostić, D.**, Schneider, R., Sievers, M., Wegmann, F., Emil Kaya, E., Perušić, M., & Friedrich, B. (2024). Recovery of Titanium from Red Mud Using Carbothermic Reduction and High Pressure Leaching of the Slag in an Autoclave. Minerals, 14(11), 1151. https://doi.org/10.3390/MIN14111151

8. CONCLUSION AND PROPOSAL[5]

The doctoral dissertation of **MSc Duško Kostić**, titled "**Innovative Approaches to the Production of Titanium(IV) Oxide Nanopowders from Secondary Raw Materials**" represents an exceptionally original study in the fields of metallurgy, chemical engineering, industrial waste recycling, and nanomaterial production. The dissertation thoroughly explores the development and optimization of processes for obtaining titanium dioxide nanopowders from industrial waste materials as the main product, and iron as a byproduct suitable for iron and steel metallurgy.

The candidate clearly defined the research objectives and comprehensively addressed them at all stages of the process, from waste material management to nanopowder production. The hypotheses are logical and directly linked to the research objectives, while the experimental methods are valid, ensuring high research quality.

The research plan is systematic, and the applied methods, such as carbothermal reduction, reduction with hydrogen and hydrogen plasma, high-pressure leaching in a closed reactor (autoclave), and ultrasonic spray pyrolysis, contribute to the successful synthesis and analysis of nanomaterials. The integration of advanced analytical techniques such as EDS, XRD, SEM, and ICP has provided precise characterization of the obtained materials. The prediction of chemical reduction processes was performed using thermochemical analysis with *FactSage* software.

The research results demonstrate a high potential for the application of the obtained nanopowders in various industries. Furthermore, the dissertation makes a significant contribution to the field of sustainable development and circular economy, which is of great importance both scientifically and socially.

The doctoral dissertation is written in English, with a clear presentation of all parts of the study, including the experimental section, results, and discussion. The literature review is extensive and provides a strong scientific foundation for all applied methods and theoretical concepts.

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[4] In accordance with Article 37 of the Regulations on Third Cycle Studies at the University of East Sarajevo.

[5] In the conclusion, among other things, the title of the qualification that the doctoral candidate acquires upon defending the thesis is stated.

Based on the research results and the comprehensive approach applied by the candidate in the preparation of the dissertation, the committee positively evaluates the doctoral dissertation and is pleased to propose to the Academic Council of the Faculty of Technology, University of East Sarajevo, that the doctoral dissertation "Innovative Approaches to the Production of Titanium(IV) Oxide Nanopowders from Secondary Raw Materials" by candidate Mr Duško Kostić be approved and accepted.

Location: Aachen (Germany), Belgrade (Serbia), Zvornik
Date: 11.04.2025.

Commission:

1. **PhD Srećko Stopić**, Private Dozent (Associate Professor), Faculty of Georesources and Materials Engineering, Institute for Process Metallurgy and Metal Recycling, RWTH Aachen University, Rheinische Westfällische Technische Hochschule (RWTH), Germany; Scientific Advisor, Institute of Chemistry, Technology, and Metallurgy, Scientific advisor University of Belgrade. Scientific Area: Engineering and Technology, Specialized Scientific Area: Metallurgy and Metal Recycling / Other Engineering and Technologies, **Chair of the Committee;**

2. **PhD Željko Kamberović**, Full Professor, Faculty of Technology and Metallurgy, University of Belgrade. Scientific Area: Engineering and Technology, Specialized Scientific Area: Metallurgy / Other Engineering and Technologies, **Member**;

3. **PhD Antonije Onjia**, Full Professor, Faculty of Technology and Metallurgy, University of Belgrade. Scientific Area: Natural Sciences, Specialized Scientific Area: Chemistry / Analytical Chemistry, **Member**;

4. **PhD Goran Tadić**, Full Professor, Faculty of Technology, Zvornik, University of East Sarajevo, Scientific Area: Engineering and Technology, Specialized Scientific Area: Process Engineering, **Member**;

PhD Radislav Filipović, Full Professor, Faculty of Technology, Zvornik. University of East Sarajevo, Scientific Area: Engineering and Technology, Specialized Scientific Area: Process Engineering, **Member.**

Dissenting opinion[6]:

1. _____, holding the title of_____ (SA _____, SSA _____, University _____, Faculty_____ in _____, Member of the Commission;

Justification:

_____

[6] Commission members who disagree with the majority opinion are required to include a dissenting opinion in the report, along with a justification of the reasons for their disagreement with the majority opinion. The commission member who provides the dissenting opinion must sign below the statement of the dissenting opinion.