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Recenzja rozprawy doktorskiej
Mr. Nelson Kiprono Rotich, M.Sc.
Titled "The Role of Radiation and Conventional Techniques in the Development of Hydrometallurgical Processes for the Recovery of the Critical and Strategic Metals"

Doctoral dissertation by Mr. Nelson Kiprono Rotich, M.Sc. was done under the supervision of: Professor Dr. ing. Andrzej G. Chmielewski D.Sc. in Institute of Nuclear Chemistry and Technology in Warsaw – Poland. This dissertation is concerned on the application of radiation and conventional techniques in the analysis of strategic and critical metals in Ti, Zn-Pb ores and Cu wastes and the development of hydrometallurgical methods for the extraction of selected metals.

In a modern economy, where growth is an obligation, the requirements for its sustainability, economy, low emission and competitiveness must be met at the same time. At present, practically all elements, including metals, have applications in modern technologies for the production of elements necessary for the functioning of devices operating in them. Countries rich in minerals use their resources to restructure their economy towards sustainable growth. Each region has its own types of metals that have been identified as essential and of strategic value for the economies present there, most of which face a serious challenge due to the potential shortage of critical resources. One of the sources is the extraction of these important metals as by-products during the main process of obtaining the main component from them. Such an example is Ti ore, the deposits of which contain other important metals. Another example is the Cu and Zn-Pb mining industry, particularly important in Poland, generating large amounts of waste containing other important metals. These wastes, which constitute over 90% of the processed ore, contain critical and strategic metals. Also, the recovery of additional metals from mining waste can increase economic profits, reduce the impact on the environment and improve the security of supply of valuable metals. Such an approach is consistent with sustainable mining practices and promotes innovation in mining technologies. The solution to such problems is the creation of improved or new hydrometallurgical techniques for the extraction of metals from by-products of industrial waste. In the dissertation, the Author emphasizes that ores and mining wastes should be well studied in order to improve mining processes. The obtained results also justify the use of advanced spectroscopic techniques providing high sensitivity and accuracy using radiation to determine the concentration of metals in solutions and solids. The research conducted in this study also addresses several important problems in hydrometallurgy, especially in relation to the selective recovery and separation of critical and strategic metals from complex ore deposits and wastes. The research in the dissertation showed how the rate of these processes is influenced by factors such as pH, temperature, ligand concentration and mixing. and how these factors affect the extraction efficiency of various metals from Ti, Zn-Pb ore and Cu waste. The correct selection of these variables can lead to increased metal recovery

rates. In addition, the research in the thesis covers the issue of real-time (online) monitoring of extraction processes. Radiotracers enable monitoring of metal ions throughout the extraction process, and feedback on the system's performance is provided continuously during the process. This possibility is of primary importance for both safety and process efficiency.

In connection with the above, the doctoral dissertation submitted to me for review is important for both cognitive and practical reasons. The topics discussed in this dissertation are current and should be continued.

The main objective of the doctoral dissertation submitted to me for review is the application of radiation, radionuclides and conventional techniques in the analysis of strategic and critical metals in Ti, Zn-Pb and Cu waste ores and the development of hydrometallurgical methods for the extraction of selected metals. In detail, the research is to concern:

1. Application of radiation and conventional methods to study solid and liquid samples using techniques such as: TXRF, EDXRF, XRD, SEM, ICP-MS, WDXRF and EDXRF.

2. Preparation and use of radiotracers for hydrometallurgical research involving the use of Ti ore and Zn-Pb, Cu waste to obtain Zn-65, activated in nuclear reactor, and for online studies of the Zn leaching process and the use of the aqueous phase of Ti ore and Zn-Pb, Cu waste to produce Mn-56 using a D-T neutron generator for "offline" studies of the Mn leaching process.

3. Application of $^{181}HfOCl_2$ as an external radiotracer for online monitoring of the Hf extraction process by D2EHPA from Ti ore. Use of the same radioisotope to determine the residence time (RTD) in the mixer-settler system.

4. Application of ICP-MS to study the recovery of selected strategic and critical metals from Ti ore and Zn-Pb waste using different ligands.

The integration of hydrometallurgical methods with ICP-MS analysis and radiation-based methods leads to obtain detailed information on strategic and critical metals contained in Ti ore and Cu and Zn-Pb mine wastes. The use of labeled atoms should improve and provide an "online" method for monitoring the leaching processes. ICP-MS analysis also provided the possibility of creating more efficient extraction methods for various metals. This technique also provides the necessary parameters for the selected radiotracer in order to optimize the extraction, thus improving the efficiency of metal recovery.

The dissertation was submitted in the form of a printed book, written in English, consisting of 214 pages, 88 figures and 10 tables. The bibliography contains 220 items consisting mainly of scientific articles. Doctoral thesis by Mr. Nelson Kiprono Rotich, M.Sc. consists of summaries in English and Polish (4 pages), introduction (6 pages), theoretical and literature part (31 pages), experimental part and discussion of obtained results (130 pages), final conclusions (4 pages), appendices (5 pages) and list of literature (25 pages). The list of publications and presentations of the author at scientific conferences was attached to the dissertation.

Chapters 1-2 contain the so-called literature part and are an introduction and preparation of the reader for the problems of the dissertation, which is raised by the PhD student in chapters related to the experiment and interpretation of results.

Chapter 1 presents an introduction, hypotheses and research objectives

Chapter 2 is concerned with literature review about hydrometallurgical processes. A number of challenges were identified research related to leaching and extraction. Also the use of radiation and conventional techniques to analyze of strategic and critical metals in Ti ore, tailings from the processing of Zn-Pb and Cu ores and the development of hydrometallurgical methods for the extraction of metals from these materials were described.

In my opinion the theoretical part of the dissertation was developed very well by the Author. Based on the competently presented material, it is clear that Mr. Nelson Kiprono Rotich, M.Sc. is strongly involved in the subject presented in the doctoral dissertation. The wide range of literature cited by the author, including the latest items, should be noticed.

In the summary of this of the dissertation part, I state that the information collected and the summaries and analyses carried out are necessary to describe the results and conduct discussions in the next stages of the work, and therefore constitute an integral part of the dissertation.

Chapter 3 presents the materials and methods used in the laboratory tests, with a detailed overview of the equipment, reagents and analytical techniques used in the experimental procedures.

Chapter 4 contains the full results of instrumental analyses of Ti ore and tailings post-process ores from the front of Zn-Pb and Cu ores. The following techniques were used: TXRF, WDXRF, ICP-MS, portable EDXRF, XRD and SEM, to determine the elemental composition and structural development of the samples. The focus was then on NAA using T-D neutron generator for offline leaching studies with radionuclide Mn-56. This chapter also describes the study of leaching of Zn with the use of radionuclide Zn -65 for real-time process tracking. These studies were verified by using XRF on NanoHunter II TXRF devices and portable EDXRF. The chapter also discusses ICP-MS analyzes for the extraction of metals from available substrates using ligands such as Aliquat 336, D2EHPA, MS, TAOT, TEP and TBP. Then, the results of experiments with the radionuclide Hf-181 were presented in the mixer-splitter system to track the online extraction of Hf from Ti ore. The chapter concludes with a discussion of the results of the simulation of the residence time distribution (RTD) to optimize the dynamics of phase flow, emphasizing its importance for the optimization of the hydrometallurgical process.

Chapter 5 and 6 contain a summary and conclusions, respectively.

In this parts is presented the key insights from the research carried out and the potential application of the results obtained.

The last part of the dissertation contains a bibliography, appendixes with a list of Figures and Tables, and a list of scientific papers published or submitted to the publications during doctoral studies.

Below are presented some of main conclusions:

X-ray Fluorescence spectrometers were effective in assessing the concentrations of most of the elements studied in solid materials. The studies also showed that extraction and suspension methods gave different results for each material. The results suggested that the selection of suspension or extraction methods based on specific metals and materials is important.

The efficiency of individual X-ray tubes was depending on the elements being determined.

Strong inorganic acid leaching effectively extracted Pb and Zn from Zn-Pb waste and Fe from Ti ore, with trace amounts of rare earth elements and other metals detected, indicating possibility for their recovery.

NAA demonstrated improved sensitivity and accuracy compared to TXRF with a leaching efficiency of $^{56}Mn^{2+}$. D - T neutron generator is proved as ideal for the determination of metals with relatively high thermal and fast neutron cross sections.

10% D2EHPA demonstrated the highest utility and efficiency in Ti ore nitrate solutions, achieving almost complete extraction of many REEs and transition metals. It is ideal for the batch extraction of such metals.

Aliquat 336 also performed well, particularly for transition metals and specific REEs, with solid recovery rates for several metals, although its range was narrower than D2EHPA.

10% TBP offered selective extraction for Zn^{2+} and Sc^{3+}, while TEP, TAOT and MS showed limited but specific efficiency for some metals under specific conditions. Extractions generally is increased with ligand concentration.

Aliquat 336 was the most effective general extractant in Zn-Pb waste chloride solutions, showing recovery of a wide range of critical and strategic metals.

TEP and TBP showed selective efficiency for some REEs and transition metals, with better efficiency at specific pH levels and temperatures.

TAOT and MS showed limited but specific efficiency, with TAOT being more suitable for specific metals at lower pH levels and MS showing better extraction at higher temperatures. All ligands performed well when their concentrations were maximized.

General conclusions:

The Author on the basis of the research presented in the thesis claims that the results obtained using analytical methods and extraction powered by radioisotope techniques were very useful in improving the efficiency of metal hydrometallurgical processes. The combination of TXRF, EDXRF, WDXRF, NAA, ICP-MS studies and the use of radionuclides effectively filled the existing knowledge gaps concerning these processes. This provided a solid base for improving the extraction of valuable metals from Ti ore and Cu, Zn-Pb waste, making it more efficient. The methods using radionuclides proved to be reliable in monitoring the recovery of metals online and at the same time monitoring the dynamics of the extraction processes. The studies using NAA provided valuable information allowing for increasing the efficiency of metal recovery processes and showed good prospects for use in laboratory and pilot hydrometallurgical operations. The NAA method based on neutron generation in the D-T reaction has also economic aspects. In addition, online measurements of leaching and extraction have shown great potential, and further studies using other radioisotopes are warranted. It was found that metal extractions from Ti ore and ZnPb wastes differ depending on the ligand, ligand concentration, temperature, pH and solution stirring rate. However, more ligands should be investigated to recover metals that have not yet been effectively extracted. Additional extraction parameters should also be investigated to improve the overall recovery of strategic and critical metals from the materials studied.

After reading the entire doctoral dissertation, I can state that I have no objections to the dissertation in terms of its content. I also have no major comments on the layout of the work and the way of presenting problems and discussing the obtained data. I provide minor comments on the work and technical details below. At the same time, I would like to emphasize that these have no impact on my very positive opinion of presented work. The comments below are rather of a more general nature and concern the universality of the work.

I wanted to draw attention to the graphical way of presenting results, which is now generally accepted. In some situations, I would draw a line between the points, thanks to which the tendency of changes in the dependencies could be observed more clearly. The results of the work are of technological importance and therefore I miss references to patents in the list of literature.

The author presented the conclusions in great details and I am somewhat lacking generalizations, although I understand that this is difficult and sometimes even impossible.

I would like to emphasize that the work was carried out at a very good and modern scientific level, which also proves the high level of the Scientific Laboratory in which the work was carried out and the knowledge and scientific experience of the Supervisor.

In the summary.

Mr, Nelson Kiprono Rotich, M.Sc. presented a very valuable, comprehensive work, in which the theory and experiment resulting from basic research were implemented in practice, with direct use of the developed method in industry. In addition, a great advantage of the work is the use of many complementary modern research methods in the experiment, leading to a more complete picture of the objects and technologies studied. The originality of the results and their value is evidenced by the fact that 4 articles were published in very good journals with international circulation. In addition, Mr. Nelson Kiprono Rotich, M.Sc. is a co-author of an article published in Science (IF 48) and another in the Journal of Human Evolution (IF 3, 7) and a work sent to Nature Communications (14,7). These additional works concern the activities of prehistoric man on the African continent. The entire scientific achievements of the doctoral student testify to his great commitment to the researched subject and a thorough foundation of knowledge in the research subject and at the same time a comprehensive interest in science. Mr. Nelson Kiprono Rotich, M.Sc. presented himself as an experienced experimenter, able to select and modify the appropriate research method, design the experiment and draw correct conclusions from the obtained results. It is also necessary to emphasize good knowledge and ability to use modern physicochemical techniques in research. The wide spectrum of measurement methods used in the research indicates very good scientific foundations, versatility and modern approach of the doctoral student to the research problem posed.

I declare that the doctoral dissertation of Mr. Nelson Kiprono Rotich, M.Sc. presented to me for review fully meets the conditions specified in the Act on Academic Degrees and Titles (Article 13 of the Act on Academic Degrees and Title and Degrees and Title in the Field of Art of 14 March 2003 in connection with Article 179 of the Act of 3 July 2018. Provisions introducing the Act "Law on Higher

Education and Science - Journal of Laws 2018 item 1669 as amended). **In connection with the above, I request the admission of Mr. Nelson Kiprono Rotich, M.Sc. to further stages of the doctoral procedure.**

In addition, I apply to the Scientific Council of the Institute to distinguish the work, taking into account that the results included in the reviewed dissertation are very valuable and innovative. They concern the application of radiation and conventional techniques in the analysis of strategic and critical metals in Ti, Zn-Pb ores and Cu wastes and the development of hydrometallurgical methods for the extraction of selected metals. The obtained results constitute a significant contribution to the global development of technologies for obtaining and recovering strategic and critical metals. This is evidenced by the publication of the obtained results of the dissertation in 4 articles published in the best scientific journals.

Andrzej Aleksander Czerwiński; Uniwersytet Warszawski

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Warszawa, 23.02.2025

Application for distinction of the doctoral dissertation of Mr. Nelson Kiprono Rotich, M.Sc.
Titled "The Role of Radiation and Conventional Techniques in the Development of Hydrometallurgical Processes for the Recovery of the Critical and Strategic Metals"

Referring to my review, considering that the results presented in the reviewed dissertation are very valuable and innovative. I apply to the Scientific Council of the Institute of Nuclear Chemistry and Technology to distinguish the dissertation of Mr. Nelson Kiprono Rotich, M.Sc. The obtained results concern the application of radiation and conventional techniques in the analysis of strategic and critical metals in Ti, Zn-Pb ores and Cu wastes and the development of hydrometallurgical methods for the extraction of selected metals. The obtained results constitute a significant contribution to the global development of technologies for obtaining and recovering strategic and critical metals. This is evidenced by the publication of the obtained dissertation results in 4 articles published in the best scientific journals with good IF impact factors. It should also be emphasized that in all these publications the PhD student is the first co-author, which indicates his main contribution to the creation of these works. These works are presented below:

1. Kiprono,N.R.;Kawalec,A.;Klis,B.;Smolinski,T.; Rogowski,M.;Kalbarczyk, P.; Samczynski, Z.; Norenberg, M.; Ostachowicz, B.; Adamowska, M.; et al. Radiation Techniques for Tracking the Progress of the Hydrometallurgical Leaching Process: A Case Study of Mn and Zn. ***Metals*** 2024, 14, 744. IF 2.6

2. Kiprono,N.R.,Smolinski,T.,Rogowski,M.,&Chmielewski, A. G. (2023). The State of Critical and Strategic Metals Recovery and the Role of Nuclear Techniques in the Separation Technologies Development. ***Separations***, 10(2), 112. Development: Reviewm IF 3.6

3. Kiprono,N.R.,Smoliński,T.,RogowskiM.,HerdzikKoniecko, I., Sudlitz, M., & Chmielewski, A. G. (2023). Kenya's Mineral Landscape: A Review of the Mining Status and Potential Recovery of Strategic and Critical Metals through Hydrometallurgical and Flotation Techniques. ***Minerals***, 14(1), 21. IF 2.5

4. Kiprono, N. R., Herdzik-Koniecko, I., Smoliński, T., Kalbarczyk P., Sudlitz M., Rogowski, M., Stosnach H & Chmielewski, A. G (2024). Recovery of metals from Titanium ore using solvent extraction process: Part 1- Transition metals. *Minerals.* IF 2.5

I would also like to add that Mr. Nelson Kiprono Rotich, M.Sc. is a co-author of 4 additional articles, including one published in Science (IF 48), the other in the Journal of Human Evolution (IF 3.7) and a paper submitted to Nature Communications (IF 14.7). These additional works concern the activities of prehistoric man on the African continent. The entire scientific achievements of the doctoral student testify to the great commitment of the doctoral

student in the researched subject and a solid foundation of knowledge in the research topic and at the same time a comprehensive interest in science.

Publications outside the subject of the doctoral dissertation

1. Kiprono, N. R., Gatari, M. J., Kareru, P., & Boman, J. (2023). Essential trace elements in the African spider plant (Cleome gynandra). A case study in Molo Ward, Nakuru, Kenya. ***X-Ray Spectrometry***, 52(2), 83-89.

2. Finestone, E. M., Plummer, T. W., Vincent, T. H., Blumenthal, S. A., Ditchfield, P. W., Bishop, L. C. **Kiprono, N. R** & Potts, R. (2023). New Oldowan locality Sare River (ca. 1.7 Ma) provides evidence of diverse hominin behaviors on the Homa Peninsula, Kenya. ***Journal of Human Evolution*** IF 3,7

3. Plummer, T. W., Oliver, J. S., Finestone, E. M., Ditchfield, P. W., Bishop, L. C., Blumenthal, S. A., ...**Kiprono N.R.** & Potts, R. (2023). Expanded geographic distribution and dietary strategies of the earliest Oldowan hominins and Paranthropus. **Science**, 379(6632), 561-566. IF 48

4. Finestone, E., Plummer, T., Ditchfield, P., Reeves, J., Braun, D., Bartilol, S., **Kiprono, N. R.**, Bishop, L., Oliver, J., Kinyanjui, R., Petraglia, M., Breeze, P., Lemorini, C., Caricola, I., Obondo, P. O., & Potts, R. (2024). Earliest evidence for long-distance stone resource transport by hominin toolmakers. ***Nature Communications***, Submitted

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