

Review of the official reviewer

for the dissertation work by Mussapyrova Lyazzat «Technology of hydrometallurgical processing of copper smelter slag», submitted for the degree of Philosophy Doctor by specialty «6D072000 - Chemical technology of inorganic substances»

The research chosen as the topic of the Doctoral Dissertation is very actual. Recently, significant research has been launched worldwide to develop new, environmentally friendly recycling technologies, driven on the one hand by reducing the carbon footprint and on the other hand by giving new metal resources.

The structure of the Dissertation is proportionate and formally appropriate, its style is good, the figures are illustrative, they are suitable for the interpretation and evaluation of the results, for drawing, the conclusions are adequate.

I conclude that the dissertation is a careful, high-quality work that satisfies the formal and content requirements, which contains a number of new and novel thesis-based findings, which are well-supported. It is very important to emphasize that the basis of the dissertation is a large number of experimental works done by the candidate.

Regarding the Candidate's publishing activity, it can be stated that it has several full-length articles and proceedings, most of which have been published in English-language journals, such as WoS journal with Impact Factor that shows high-quality publishing activity.

The dissertation contains new scientific results, I accept the results formulated in the theses (for all theses) as new scientific results. Based on all this, I propose to submit the dissertation to public discussion, and in case of a successful defense, I support the award of the PhD degree.

№	Criteria	Criteria eligibility (it is necessary to mark one of the answer options)	Justification of the position of the official reviewer
1.	The topic of the thesis (as of the date of its approval) corresponds to the development of science and/or government programs	1.1 Compliance with priority areas of science development or government programs: 1) <u>The thesis was completed within the framework of a project or target program financed from the government budget (indicate the name and number of the project or program)</u>	The dissertation work was carried out within the framework of the government grant funding for the following project: AP08856414 «Solvometallurgical processing of copper smelter slag and tailings of their enrichment to obtain commercial

		<p>2) The thesis was completed within the framework of another government program (indicate the name of the program)</p> <p>3) The dissertation corresponds to the priority area of the development of science, approved by the Higher Scientific and Technical Commission under the Government of the Republic of Kazakhstan (indicate the direction)</p>	products».
2.	Importance for science	<p><u>The work makes/does not make a significant contribution to science, and its importance is well disclosed</u> / not disclosed</p>	The work makes a significant contribution to the development of science, in particular, to understanding the processes of mechanical activation of waste copper slag and subsequent selective sulfuric acid leaching of the activated material.
3.	The principle of independence	<p>Self-reliance level:</p> <p>1) <u>High</u>;</p> <p>2) Medium;</p> <p>3) Low;</p> <p>4) No independence</p>	The level of independence in the performance of work is rated as high. The dissertator independently performed all experimental work on mechanical activation, leaching, as well as the corresponding physical and chemical studies. The author independently interpreted the results of the experiments and formulated conclusions from the dissertation work. In addition, the dissertation student made a significant contribution to the preparation of scientific publications.
4.	The principle of internal unity	<p>4.1 Justification of the relevance of the thesis:</p> <p>1) <u>Justified</u>;</p> <p>2) Partially justified;</p> <p>3) Not justified.</p>	The relevance of the study is justified by the current lack of acceptable technologies for extracting valuable non-ferrous metals from waste copper slag. Meanwhile, this by-product of the pyrometallurgical production of copper is a potential resource for metals such as copper and zinc. The author gave weighty arguments in favour of choosing the topic of the dissertation.
		<p>4.2 The content of the thesis reflects the topic of</p>	The content of the dissertation fully reflects its topic. The

	<p>the thesis:</p> <ol style="list-style-type: none"> 1) <u>Reflects</u>; 2) Partially reflects; 3) Does not reflect 	<p>literature review provides information about the main object of research (that is, dump copper slag), a critical analysis of the existing ways of processing slag, including hydrometallurgical ones, is carried out. In the main part of the work, the dissertator investigated the issues of increasing the reactivity of slag by mechanical activation, as well as the extraction of copper and zinc by leaching the activated material.</p>
	<p>4.3. The purpose and objectives correspond to the topic of the thesis:</p> <ol style="list-style-type: none"> 1) <u>correspond</u>; 2) partially comply; 3) do not match. 	<p>The goal and objectives are fully consistent with the topic of the dissertation. Following the goal, it was necessary to determine the conditions for the mechanical activation of waste copper slag and subsequent leaching with an aqueous solution of sulfuric acid; it was important to use relatively low temperatures. All tasks are aimed at achieving this goal.</p>
	<p>4.4 All sections and provisions of the thesis are logically interconnected:</p> <ol style="list-style-type: none"> 1) <u>fully interconnected</u>; 2) the connection is partial; 3) there is no connection 	<p>All sections and provisions of the dissertation are fully interconnected. The literature review identifies the main disadvantages of hydrometallurgical methods for processing dump copper slag, based on which the goals and objectives of the dissertation are formulated. In the "Experimental Part" the dissertator indicated the methodology for conducting experiments, as well as the methods used to characterize solid and liquid materials. The "Results and Discussion" section is devoted to the search for optimal conditions for mechanical activation and leaching, which provide a high extraction of copper into solution, as well as selectivity concerning copper.</p>
	<p>4.5 The new solutions (principles, methods) proposed by the author are reasoned and evaluated in comparison with the known solutions:</p> <ol style="list-style-type: none"> 1) <u>there is a critical analysis</u>; 	<p>New technological solutions for the extraction of copper and zinc from copper smelter slag are argued and critically evaluated in comparison with the known ones. An increase in the reactivity of copper and zinc minerals in slag during</p>

		<p>2) partial analysis;</p> <p>3) the analysis does not represent one's own opinions, but quotes from other authors</p>	<p>mechanical activation has been proven by leaching experiments. The increase in selectivity of leaching for copper in the presence of potassium dichromate is caused by a significant difference in the rates of leaching of copper, zinc, and iron.</p>
5.	Scientific novelty principle	<p>5.1 Are the scientific results and provisions new?</p> <p>1) <u>completely new</u>;</p> <p>2) partially new (25-75 % are new);</p> <p>3) not new (less than 25 % are new)</p>	<p>All scientific results and provisions in the dissertation are completely new. The effect of mechanical activation of copper smelter slag on its subsequent sulfuric acid leaching in the presence of potassium dichromate has not been studied before.</p>
		<p>5.2 Are the dissertation conclusions new?</p> <p>1) <u>completely new</u>;</p> <p>2) partially new (25-75 % are new);</p> <p>3) not new (less than 25 % are new)</p>	<p>All conclusions of the dissertation work have not been previously formulated and are completely new.</p>
		<p>5.3 Technical, technological, economic or management solutions are new and reasonable:</p> <p>1) <u>completely new</u>;</p> <p>2) partially new (25-75 % are new);</p> <p>3) not new (less than 25 % are new)</p>	<p>The technical and technological solutions proposed in the dissertation are completely new and reasonable. For the first time, for the processing of copper smelter slag, it was proposed to carry out the mechanical activation of the source material, followed by sulfuric acid leaching in the presence of potassium bichromate.</p>
6.	Validity of key findings	<p>All the main <u>conclusions are/are not based on scientifically significant evidence</u> or reasonably well substantiated</p>	<p>All the main conclusions in the dissertation are based on the results of the experiments and their competent interpretation. The conclusions of the dissertation work are consistent with modern views in the field of mechanoactivation and hydrometallurgy.</p>
7.	The main provisions for the defence	<p>It is necessary to answer the following questions for each provision separately:</p> <p><u>Provision 1 - Wet mechanical activation of</u></p>	<p>This provision is fully proved by the results of experiments on dry and wet mechanical activation of waste copper slag, as well as subsequent measurements of the specific surface area of the activated material. The provision is not trivial, since it</p>

	<p><u>copper smelter slag in a planetary mill and attrition mill leads to a more significant increase in its specific surface area than dry mechanical activation.</u></p> <p>7.1 Is the provision proven? 1) <u>proven</u>; 2) rather proven; 3) rather unproven; 4) unproven.</p> <p>7.2 Is it trivial? 1) yes; 2) <u>no</u>.</p> <p>7.3 Is it new? 1) <u>yes</u>; 2) no.</p> <p>7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide.</p> <p>7.5 Is it proven in the article? 1) <u>yes</u>; 2) no.</p>	<p>does not explicitly follow the known knowledge in the field of dry and wet mechanoactivation. The provision is new because it has not been previously described in the scientific literature. The level of application of the provision is average since it can be used to increase the specific surface area of other solid materials that have a structure similar to slag. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science "Journal of Materials Research and Technology".</p>
	<p><u>Provision 2 - Dry and wet mechanical activation of copper smelter slag increases the degree of zinc, copper and iron recovery into solution during sulfuric acid leaching.</u></p> <p>7.1 Is the provision proven?</p>	<p>The provision has been experimentally proven: indeed, the degree of extraction of zinc, copper and iron during sulfuric acid leaching of mechanically activated slag is higher than during leaching of the original slag. The provision is not trivial, since the increase in the degree of extraction during mechanoactivation is not obvious. The scientific literature</p>

	<p>1) proven; 2) rather proven; 3) rather unproven; 4) unproven.</p> <p>7.2 Is it trivial? 1) yes; 2) <u>no</u>.</p> <p>7.3 Is it new? 1) <u>yes</u>; 2) no.</p> <p>7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide.</p> <p>7.5 Is it proven in the article? 1) yes; 2) no.</p>	<p>does not describe an increase in the degree of extraction of zinc, copper and iron during the mechanical activation of waste copper slag, so the provision is new. The provision's usage is rated as average. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science "Journal of Materials Research and Technology".</p>
	<p><u>Provision 3 - The presence of potassium dichromate increases the degree of copper, zinc and iron recovery from the original and mechanically activated copper smelter slag during sulfuric acid leaching.</u></p> <p>7.1 Is the provision proven? 1) <u>proven</u>; 2) rather proven; 3) rather unproven; 4) unproven.</p> <p>7.2 Is it trivial?</p>	<p>The provision has been fully proved experimentally: in the presence of potassium bichromate, the recovery of copper, zinc, and iron were higher in the leaching of both the original and mechanically activated slag. The provision is not trivial, since it does not explicitly follow the available knowledge in the field of mechanoactivation and hydrometallurgy. The provision is new because it has not been previously described in the scientific literature. The level of applicability of the provision is assessed as average. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science "Journal of Materials Research and Technology".</p>

	<p>1) <u>yes</u>; 2) <u>no</u>. 7.3 Is it new? 1) <u>yes</u>; 2) <u>no</u>. 7.4 Application level: 1) <u>narrow</u>; 2) <u>average</u>; 3) <u>wide</u>. 7.5 Is it proven in the article? 1) <u>yes</u>; 2) <u>no</u>.</p>	
	<p><u>Provision 4 - Leaching of copper smelter slag in sulfuric acid solution in the presence of potassium dichromate makes it possible to selectively extract copper into the solution, thereby separating it from zinc and iron. This phenomenon is caused by the higher dissolution rate of copper sulfide minerals, in comparison with the dissolution rate of iron (mainly fayalite) and zinc (mainly zinc ferrite) - containing minerals under the investigated conditions.</u></p> <p>7.1 Is the provision proven? 1) <u>proven</u>; 2) <u>rather proven</u>; 3) <u>rather unproven</u>; 4) <u>unproven</u>.</p>	<p>The provision has been fully proved experimentally: the use of potassium bichromate in the sulfuric acid leaching of waste copper slag made it possible to separate copper from zinc and iron. The author explains this fact by a higher rate of dissolution of copper sulfide minerals than the rate of leaching of zinc and iron minerals. This explanation looks logical, taking into account the nature of zinc and iron minerals in the slag. Undoubtedly, the provision is not trivial: it is not obvious and could not be formulated without appropriate experiments. The provision has not been previously described in the scientific literature. The level of applicability of the provision is assessed as average. The provision is fully proven in an article in the journal of the first quartile (Q1) on Web of Science "Journal of Materials Research and Technology" and in Patent for Utility model "Melting for processing copper smelting slags", N5741, publ.12.02.21.</p>

		<p>7.2 Is it trivial? 1) <u>yes</u>; 2) <u>no</u>.</p> <p>7.3 Is it new? 1) <u>yes</u>; 2) <u>no</u>.</p> <p>7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide.</p> <p>7.5 Is it proven in the article? 1) <u>yes</u>; 2) <u>no</u>.</p>	
8.	8.1 The principle of reliability	8.1 Choice of methodology - is justified or the methodology is described in sufficient detail 1) <u>yes</u> ; 2) <u>no</u> .	The choice of methodology is fully justified. All approaches used in the dissertation work are generally recognized for research in the field of mechanoactivation and leaching.
	Reliability of sources and information provided	8.2 The results of the dissertation work were obtained using modern methods of scientific research and methods of processing and interpreting data using computer technologies: 1) <u>yes</u> ; 2) <u>no</u> .	All results of the dissertation work were obtained using modern methods. Materials were characterized by scanning electron microscopy, X-ray phase analysis, atomic absorption spectrometry, and laser light diffraction. Taguchi Orthogonal Array Design was applied to design the experiments. Analysis of Variance (ANOVA) was used to determine the contribution of mechanical activation parameters to the increase in slag surface during mechanical activation.
		8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research:	All theoretical conclusions, models, identified relationships and patterns are confirmed experimentally. The shrinking sphere model is used to describe the leaching process; the

		<p>1) <u>yes</u>;</p> <p>2) no.</p>	<p>legitimacy of its use is not in doubt. Based on the found kinetic characteristics of leaching processes, the limiting stages are determined, depending on the conditions.</p>
		<p>8.4 Important statements <u>are confirmed</u> / partially confirmed / not <u>confirmed by references to the current and reliable scientific literature</u></p>	<p>All important statements are consistent with modern views in the field of mechanoactivation and hydrometallurgy and are also confirmed by references to articles in high-reputable journals.</p>
		<p>8.5 Used literature sources are sufficient / not sufficient for a literature review</p>	<p>The list of references includes 124 sources; most of the sources are articles from the last few years published in the Q1 and Q2 Web of Science journals. The sources used are sufficient for a literature review.</p>
9	Practical value principle	<p>9.1 The thesis has theoretical value:</p> <p>1) <u>yes</u>;</p> <p>2) no.</p>	<p>The dissertation has theoretical value. The results of the work expand the existing knowledge in the field of mechanical activation of technogenic metallurgical materials, in particular, copper slag, as well as its sulfuric acid leaching.</p>
		<p>9.2 The thesis is of practical importance and there is a high probability of applying the results obtained in practice:</p> <p>1) <u>yes</u>;</p> <p>2) no.</p>	<p>The dissertation is of great practical importance. Hundreds of millions of tons of copper smelter slag have been accumulated in the world, for which there are no effective processing technologies. The original technological solutions proposed in the dissertation work can form the basis of new hydrometallurgical industries. With a high degree of probability, these productions can be organized at existing copper smelters.</p>
		<p>9.3 Are the practice suggestions new?</p> <p>1) <u>completely new</u>;</p> <p>2) partly new (25-75% are new);</p> <p>3) not new (less than 25% are new).</p>	<p>The author proposed a new concept for the processing of copper smelter slag, including mechanical activation in an attritor and subsequent two-stage sulfuric acid leaching in the presence of potassium dichromate. In the first stage, mainly copper is extracted into the solution; in the second stage, zinc</p>

			and iron are transferred into the solution. The proposed scheme is completely new.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) <u>average</u> ; 3) below average; 4) low.	In general, the quality of writing a dissertation is assessed as quite acceptable. The existing individual inaccuracies are because English is not native to the author.

My questions and comments for the PhD dissertation:

- In Paragraph 2.1. The particle size distribution curve would be useful to see.
- In Paragraph 2.3. A more detailed description of the mills would be required since it is a comparative investigation. Schematic drawing.
- There are numerous literature data and figures in the Results and discussion, on spite of the title is related to own results. However, most of them are from the papers of the PhD candidate.
- Temperature unit sometimes degree centigrade sometimes Kelvin. Uniform unit would be more comparable.
- For the better comparability of the two mills a specific energy density value would be useful.
- In Figure 3.19 : What is the reason of the big portion of coarse material size fraction remained in the AM and PM samples beside the submicron fraction?
- In the case of attrition mill, or stirred media mill the material filling ratio should be used instead of ball to powder ratio which takes into consideration the porosity of grinding media.
- In the abbreviation, please specify ICP AAS, this is a bit confusing.

Decision: I support the award of the PhD degree by specialty «6D072000 - Chemical technology of inorganic substances» to Mussapirova L.

Gábor Mucsi,
Professor, Dean of the Faculty of Earth Science and Engineering,
University of Miskolc, Hungary



signature

(seal of the organization)