

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»

№	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	<p>1.1 Compliance with priority areas of science development or government programs:</p> <p>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></p> <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>	The dissertation work was performed within the project AP08856414 «Solvometallurgical processing of copper smelter slag and tailings of their enrichment to obtain commercial products» funded by the Ministry of Education and Science of the Republic of Kazakhstan.
2.	Importance for science	<p><u>The work makes/does not make a significant contribution to science, and its importance is well disclosed / not disclosed</u></p>	The work makes a great contribution to the development of the processes of dry and wet mechanical activation of non-ferrous metallurgy, in particular, copper pyrometallurgy, waste. New knowledge about sulfuric acid leaching of waste copper slag, including in the presence of oxidizing agents, has been obtained.

3.	The principle of independence	Self-reliance level: 1) <u>High</u> ; 2) Medium; 3) Low; 4) No independence	<p>The applicant independently performed all experimental work on the mechanical activation of copper smelter slag, as well as the leaching of the original and activated slag. The interpretation of the research results and the formulation of conclusions were also carried out by the author independently. The significant contribution of the applicant to the preparation of scientific articles is expressed, among other things, in the first authorship of an article in the journal of the first quartile (Q1) Web of Science. Based on the foregoing, the level of independence in the performance of work is assessed as high.</p>
4.	The principle of internal unity	4.1 Justification of the relevance of the thesis: 1) <u>Justified</u> ; 2) Partially justified; 3) Not justified.	<p>The topic chosen for the dissertation work is very relevant both in the world and (in particular) in the Republic of Kazakhstan. Over the years of operation of copper smelters, a significant amount of waste copper slag has accumulated, for which there are no effective methods of processing. Existing routes are either very energy-intensive (high-temperature processes) or do not provide adequate recovery of copper and zinc (flotation). Therefore, the search for new ways to process waste copper slag is an important task.</p>
		4.2 The content of the thesis reflects the topic of the thesis: 1) <u>Reflects</u> ; 2) Partially reflects; 3) Does not reflect	<p>The introduction contains the main prerequisites for the implementation of the dissertation research. In the literature review, the author carried out a critical analysis of the existing ways of processing waste copper slag, and the emphasis was on hydrometallurgical approaches (following the direction of the dissertation work). The main part describes in detail the methods of conducting experiments on mechanical activation and leaching, as well as statistical processing of the results of experiments. Thus, the content of the dissertation fully reflects its topic.</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 purpose and objectives fully correspond to the theme of the dissertation work. The main purpose of the work was to determine the conditions for the mechanical activation of dump copper slag and further sulfuric acid leaching, including in the presence of oxidizing agents, providing an acceptable extraction of zinc and copper into an aqueous solution. To achieve this purpose, the corresponding tasks were set. The solution of the tasks set was necessary and sufficient.</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>The analysis of the main shortcomings of the existing methods for processing waste copper slag, given in the literature review, made it possible to formulate the purpose and objectives of the dissertation work. The validity of the set goal follows from the current state of affairs shown in the introduction. When determining the research scheme, the author used typical approaches commonly used to solve such problems: characterization of the starting material, material processing, characterization of solid and liquid products and intermediates. The experimental results are discussed from the standpoint of modern views in the field of mechanoactivation and leaching. All sections and provisions of the dissertation are fully interconnected.</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>; 2) partial analysis; 3) the analysis does not represent one's own opinions, but quotes from other authors 	<p>The author carried out a critical analysis of the new technological solutions proposed in the dissertation work for the selective low-temperature leaching of waste copper slag with sulfuric acid solutions. To increase the reactivity of the target copper and zinc minerals, it is proposed to use the mechanical activation of the initial slag. Based on the experiments carried out, a technological scheme for the hydrometallurgical processing of slag is proposed. Similar schemes for slag are not known in the scientific literature.</p>
5.	Scientific novelty principle	<p>5.1 Are the scientific results and provisions new?</p> <ol style="list-style-type: none"> 1) completely new; 	<p>The scientific results and provisions are partially new. The novelty of the results obtained is confirmed by the presence of publications in reputable scientific journal: Selective room-temperature leaching of copper from</p>

		<p>2) <u>partially new (25-75 % are new)</u>; 3) not new (less than 25 % are new)</p>	<p>mechanically activated copper smelter slag, <i>Journal of materials research and technology</i>, Q1.</p> <p>The level mark "partially new (25-75% are new)" is due to the presence of similar scientific articles on the mechanical activation of slags before leaching. For example: Mechanical Activation of Granulated Copper Slag and Its Influence on Hydration Heat and Compressive Strength of Blended Cement, 10.3390/ma12050772</p>
		<p>5.2 Are the dissertation findings new? 1) <u>completely new</u>; 2) <u>partially new (25-75 % are new)</u>; 3) not new (less than 25 % are new)</p>	<p>All scientific results and provisions in the dissertation are completely new. For the first time, a comparative study was carried out on dry and wet mechanical activation of waste copper slag in an attritor and a planetary mill; It has been shown that wet mechanoactivation is much more efficient than the dry one. The contribution of individual parameters of mechanical activation to the achievement of the main task is determined: an increase in the specific surface of the slag. For the first time, it was proposed to use potassium dichromate in combination with an aqueous solution of sulfuric acid for the selective extraction of copper from mechanically activated slag.</p>
		<p>5.3 Technical, technological, economic or management solutions are new and reasonable: 1) <u>completely new</u>; 2) <u>partially new (25-75 % are new)</u>; 3) not new (less than 25 % are new)</p>	<p>Technical, technological, economic or management solutions are partially new.</p> <p>The assignment of the "partially new" is due to the presence of technological solutions for processing copper-containing raw materials. The data is published in articles: DOI:10.3390/met8030150, DOI10.1016/j.hydromet.2020.105492</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>The main conclusions made in the dissertation are based on an adequate interpretation of the results obtained during the experiments. All the conclusions made do not contradict modern views in the field of mechanoactivation and leaching.</p>
7.	The main provisions	<p>It is necessary to answer the following</p>	<p>This provision is proven by the results of measurements of the specific</p>

for the defence	<p>questions for each provision separately:</p> <p><u>Provision 1 - Wet mechanical activation of 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>surface area of the material activated by dry and wet methods in a planetary mill and an attritor by the method of thermal desorption of nitrogen. The provision does not explicitly follow the known knowledge in the field of mechanoactivation, therefore it is not trivial. The level of application of the provision is medium. The provision is 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</u></p>	<p>The provision was proved by determining the extraction of zinc, copper and iron into solution during sulfuric acid leaching of the original, as well as mechanically activated slag. This provision does not explicitly follow the</p>

		<p><u>into solution 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? 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>known knowledge in the field of application of mechanoactivation in hydrometallurgy, therefore, it is not trivial. The provision is new since the literature has not previously described the effect of increasing the extraction of these metals into a solution of their mechanically activated slag in comparison with the initial one. The level of use of the provision is rated as medium. The provision is 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;</p>	<p>The provision is proved by comparing the degrees of extraction of copper, zinc and iron during sulfuric acid leaching of the initial and mechanically activated waste copper slag in the presence of potassium bichromate. The provision does not explicitly follow the available knowledge in the field of mechanoactivation and hydrometallurgy, therefore it is not trivial. The named effect has not been previously described in the scientific literature, therefore it is new. The level of applicability of the provision is assessed as medium. The provision is proven in an article in the journal of the first quartile (Q1) on Web of Science "Journal of Materials Research and</p>

		<p>3) rather unproven; 4) unproven. 7.2 Is it trivial? 1) yes; 2) <u>no</u>. 7.3 Is it new? 1) <u>yes</u>; 2) no. 7.4 Application level: 1) narrow; 2) <u>average</u>; 3) wide. 7.5 Is it proven in the article? 1) <u>yes</u>; 2) no.</p>	<p>Technology".</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?</p>	<p>The provision was proved experimentally: during sulfuric acid leaching of slag in the presence of potassium dichromate for 120 min, the degree of extraction of copper was more than 87%, while the degree of extraction of iron and zinc was several per cent. This fact is explained by the higher leaching rate of copper minerals than zinc and iron minerals under these conditions. This provision is confirmed by the fact that with an increase in the duration of leaching to 6-7 hours, the extraction of zinc and iron increases significantly. The provision is not obvious and could not be formulated without appropriate experiments, so the position is not trivial. The provision is new since it has not been previously described in the literature. The level of applicability of the provision is assessed as medium. The provision is 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>proven</u>;</p> <p>2) rather proven;</p> <p>3) rather unproven;</p> <p>4) unproven.</p> <p>7.2 Is it trivial?</p> <p>1) yes;</p> <p>2) <u>no</u>.</p> <p>7.3 Is it new?</p> <p>1) <u>yes</u>;</p> <p>2) no.</p> <p>7.4 Application level:</p> <p>1) narrow;</p> <p>2) <u>average</u>;</p> <p>3) wide.</p> <p>7.5 Is it proven in the article?</p> <p>1) <u>yes</u>;</p> <p>2) no.</p>	<p><i>* The main objectives of studying the kinetics of the leaching process are to determine the mechanism of dissolution of the components and to determine the limiting factor of the process, which determine the calculation of the activation energy. However, there is no data on these parameters in the dissertation work.</i></p> <p><i>* The choice of the reagent $K_2Cr_2O_7$ is not fully justified.</i></p> <p><i>* The choice of the Taguchi method is not justified, although there are many other methods of experimental design.</i></p> <ul style="list-style-type: none"> <i>• What is the drying temperature after mechanical activation? This temperature is very important for further processes and should be indicated in the dissertation.</i> <i>• Some images have very low resolution.</i> <p><i>* In Figure 3.7 (a), the duration of the process is written in Russian.</i></p>
8.	<p>8.1 The principle of reliability</p> <p>Reliability of sources and information provided</p>	<p>8.1 Choice of methodology - is justified or the methodology is described in sufficient detail</p> <p>1) <u>yes</u>;</p> <p>2) no.</p> <p>8.2 The results of the dissertation work were obtained using modern methods of scientific research and methods of processing and</p>	<p>The methodology used in the dissertation work is common in conducting this kind of research on mechanoactivation and leaching. Therefore, the choice of methodology is fully justified.</p> <p>Taguchi Orthogonal Array Design was used to design the experiments in mechanical activation in teaching. Analysis of Variance (ANOVA) was used to determine the contribution of mechanical activation parameters to the</p>

		<p>interpreting data using computer technologies:</p> <p>1) <u>yes</u>;</p> <p>2) no.</p>	<p>increase in slag surface during mechanical activation. Scanning electron microscopy, XRD analysis, ICP AAS measurements, specific surface area measurement and other modern techniques were used for analyzing, processing and interpreting data.</p>
		<p>8.3 Theoretical conclusions, models, identified relationships and patterns have been proven and confirmed by experimental research:</p> <p>1) <u>yes</u>;</p> <p>2) no.</p>	<p>The results of experiments on mechanical activation and leaching were used to confirm all theoretical conclusions, models, identified relationships and patterns. All conclusions drawn are consistent with each other.</p>
		<p>8.4 Important statements are <u>confirmed</u> / partially confirmed / not <u>confirmed by references to the current and reliable scientific literature</u></p>	<p>All statements formulated in the work are consistent with the results of modern research in the field of mechanoactivation and leaching, published in reputable scientific journals. All relevant references are available in the dissertation work.</p>
		<p>8.5 Used literature sources <u>are sufficient</u> / not sufficient for a literature review</p>	<p>All available references to the scientific literature are sufficient for a literature review. Of the 124 sources, most are articles from the last few years published in Q1 and Q2 Web of Science journals.</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 theoretical significance of the dissertation lies in the expansion of known knowledge in the field of dry and wet mechanical activation of oxide-sulfide systems, as well as sulfuric acid leaching of activated materials.</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 schematic diagram of waste copper slag processing developed in the dissertation, including mechanical activation and two-stage leaching, can be used at existing copper smelters. The lack of effective ways to process waste copper slag today makes this scheme attractive.</p>
		<p>9.3 Are the practice suggestions new?</p> <p>1) <u>completely new</u>;</p>	<p>The dissertation proposes a new concept for the processing of waste copper slag. The scheme involves mechanical activation of the slag in the attritor,</p>

		2) partly new (25-75% are new); 3) not new (less than 25% are new).	sulfuric acid leaching in the presence of potassium dichromate, separation of the solid residue from the solution. In the second stage, the solid residue is leached to extract the zinc into the solution. The scheme is new.
10.	The quality of writing and design	Academic writing quality: 1) high; 2) <u>average</u> ; 3) below average; 4) low.	The quality of the dissertation writing is rated as average. There are some inaccuracies in the description of terminology.

Conclusion:

1) to award the degree of Doctor of Philosophy (PhD) by specialty «6D072000 - Chemical technology of inorganic substances» Mussapyrova Lyazzat

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