1. Introduction

Copper production process is a complex process in which obtaining blister copper containing 99.99% pure element requires multiple processes [1-3]. Each process produces a lot of waste material, the utilization and the most efficient use can rationally manage resources to maximize profits and reduce harmful effects on the external environment. A thorough analysis of qualitative and quantitative waste and develop a suitable concept of their use and processing [4] to minimize production costs, environmental degradation, and increase profits.

2. Analysis of the problem

Copper production process, from extraction of the mine in the form of ore, it starts a series of processing procedures, preparing a result of copper concentrate.

After mining the ore, copper mining plants produced a number of waste. Most, as even 77% of soil material from the drill shaft, less than 12% oversize floors, scrap iron and its alloys is not more than 6.2%, while dredging soil, and unsorted municipal waste related to constitute no more than 4, 8%. Materials formed at this stage constitute almost 80% of all mining waste.

Ore extracted from the mine has a varied content of copper, which in ores slate - carbonate varies from 0.7% to as much as 16% Cu [5, 6]. After the concentrate process (flotation process) concentrate is obtained with a content of 25 - 35% Cu [7, 8]. Meanwhile, this is only the initial stage of a long journey element, where after each stage created certain waste.

THE INFLUENCE OF THE CHEMICAL COMPOSITION OF SELECTED WASTE MATERIALS FROM THE PRODUCTION OF COPPER ON THE FINAL ENVIRONMENTAL ASSESSMENT

This article presents qualitative and quantitative analysis of the waste produced by KGHM Polska Miedź. The waste has been analyzed according to its chemical composition and balanced in order to be reused and recycled. Special attention has been paid to mining industries producing the biggest amount of waste and ore enrichment businesses generating waste, which isn’t reused nowadays. Laboratory research has been conducted on flotation waste, different kinds of slags, waste gases and water slag extracts. Attention has been drawn to the possibility of using a computer program SLAG - PROP for analyzing physicochemical features, technological features and the refining of the acquired waste. Consequently, the further way of utilization of waste has been shown. From this point of view, analyses of DTA and TG slags in an oxide coating seem especially interesting. Having a particular composition they can be successfully utilised in the refining processes of copper pyrometallurgy.

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copper. Despite the fact that Huta Miedzi Głogów also generates waste to a large extent they are recycled in manufacturing processes so that their number is negligible. Meanwhile, the greatest problem may constitute waste described above. The tests were subjected to various waste from flotation tailings through warehouses slag at ending gases. Attention was also drawn to the possibility of using the properties for SLAG-PROP [10] allows to indicate the content of the chemical composition of various materials and their physical, chemical and refining processes pirometallurgy.

First study were subjected to flotation waste. They consist mainly oxides and metallic elements. The detailed composition of the flotation tailings was presented in the table [Tab. 1]. Due to the composition of these wastes can be further processed and re-used. They are subject to recycling processes, recovery, combustion, but are also deposited in landfills, put into deep wells, or stored in areas of the plant. Accurate management of flotation tailings are presented in Table 2 [Tab. 2].

Since waste flotation are mainly liquid for the purposes of the redevelopment is used in the appropriate containers. With the flotation tailings recovered even 2/3 of the materials. A smaller part is recycled and re-used. About 1/3 of the materials is stored. As shown in Table 2, adequate protection are also subject to hazardous materials, which represent a small percentage of all waste materials.

Another material that has been subjected to thorough study was slag shaft. In addition to the metallic elements, its main composition, they are of course oxides, including primarily silicon oxides SiO₂ from 39% to 48.3%. The iron oxide present in the slag shaft at about 10% does not constitute a direct threat to the environment. It should be noted, however, that the higher amounts may affect the way an environmental irritant. Finally, alumina Al₂O₃ present in an amount less than 15% is not dangerous but may also be used for the production of aluminum. From a legal point of view, it is important that the amount of lead and sulfur in the product output were a minimum. Table 3 [Tab. 3] given the chemical composition of the slag shaft.

| Type      | Amount       | Type      | Amount       |
|-----------|--------------|-----------|--------------|
| SiO₂      | 39 – 48.3 %  | Cr        | 510 ppm      |
| CaO       | 15,18 – 20 % | Co        | 600 – 770 ppm|
| Fe₂O₃     | 9.3 – 11.3 % | Mo        | 296 ppm      |
| Al₂O₃     | 11.0 – 13.95 %| Sn        | 18 ppm       |
| MgO       | 7.3 – 9.6 %  | Ag        | 20 – 33 ppm  |
| S         | 0.17 – 0.8 % | V         | 836 ppm      |
| Zn        | 0.26 – 0.74 %| As        | 120 ppm      |
| Pb        | 0.12 – 0.29 %| Au        | 2 ppm        |
| Cu        | 0.16 – 0.57 %| Cd        | 5 ppm        |
| Ni        | 50 – 60 ppm  | Re        | 1 - 2 ppm    |

It is noteworthy that in the material a small amount of precious metals such as gold Ag and silver Au. But these are very minor part at the level of 33 parts per million for silver and only 2 parts per million for gold.

The last type of slag that has been subjected to the test chemical composition is blast furnace slag. According to current regulations, its composition should contain at least 2/3 of the oxides of calcium, magnesium and silicon. Another material that has been tested was granulated slag. Its chemical composition is not as “rich” as slag shaft and as can be seen from Table 4 [Tab. 4] representing its chemical composition, it is present in a lesser amount of oxide.

| Type      | Amount       | Type      | Amount       |
|-----------|--------------|-----------|--------------|
| K₂O       | 3.74 %       | Zn        | 0.59 %       |
| Na₂O      | 0.67 %       | Ag        | 6 g/Mg       |
| Pb        | 0.089 %      | Fe        | 5.39 %       |
| Cu        | 0.63 %       | Ni        | 0.01 %       |
| As        | 0.007 %      | S         | 0.021 %      |
| Co        | 0.04 %       |           |              |

It also is devoid of silica, which is bound within the framework of complex chemical compounds. In contrast to the slag shaft is greater in the amount of lead Pb at 0.89%, and the same copper Cu 0.63%. In the noble metal is here only silver Ag at a very low level, which is about 6 grams per tonne.

The last type of slag that was analyzed was a blast furnace slag. According to current regulations, its composition should contain at least 2/3 of the oxides of calcium, magnesium and silicon. Analyzing the chemical composition of this material, which is presented in Table 5 [Tab. 5], it can be assumed that these values are met, as their total is 86.2%.
In addition to these compounds it contains other oxides, a relatively lack of it free of metallic elements, which when properly maintained pyrometallurgical processes, it can be assumed that as a whole go to the metal bath. It should be noted that the blast furnace slag is characterized by low natural radioactivity. The research shows that the rate of radioactivity for natural radioactive isotopes ranges from 0.53 Bq to 0.66 Bq, in turn, for radium from 90.69 Bq to 131.51 Bq. Officially, these standards are not exceeded and do not constitute a direct threat, so they can be used in residential construction.

Another waste product were analyzed gases. Their main harmful materials are oxides of sulfur. It is these compounds pose the greatest threat to the environment being the cause of, among others, acid rain. Hence, a high priority is to install equipment for flue gas desulphurization, and ultimately the management of waste that did not have them stored in large quantities. It should also be noted that the waste gases are substantial amounts of dust, which also should not be released into the environment only by the proper equipment should be captured for the purpose of reprocessing. In the context of the development of waste dust created relevant extract water from flue gas desulphurisation plant. Their composition is mainly iron Fe, copper Cu, Pb Lead and arsenic As, as well as other compounds in a smaller amount, which may be on-site plants processed and used as fluxes in the pyrometallurgical processes. As can be seen the chemical composition of exhaust gases it is very diverse and includes not only oxides but different metallic elements. Hence, the formation of an aqueous extract of the flue gas desulphurisation system proved particularly beneficial.

The final analysis of the study was to undergo qualitative - quantitative water extracts from the slag. Here, an important parameter is the ability of elution of harmful substances and heavy metals from the slag. You can say that the process can be properly maintained the level of the individual compounds and the same elements to keep within the limit. It should be noted that all the compounds and the elements are at the right level, at most, the whole reaction solution beyond the standard norms. The boundaries define the reaction solution in the range of 6.5 - 9.0 pH, whereas in the case of the test solution had a pH of 11.2. It was therefore higher than the maximum value of 2,2 units.

Table 6 [Tab. 6] given chemical composition of exhaust gases, a study of the chemical composition of water extracts of slags together with the boundaries of the limit values is presented in Table 7 [Tab. 7].
hand too high viscosity of the material will hinder the passage of inclusions and impurities into the slag, thereby refining its effects will be much worse. In addition to the viscosity are also significantly different properties even as the melting point, wettability, surface tension or electrical conductivity. Interestingly, in this context it represents a computer program SLAG - PROP to evaluate the physicochemical, refining and technology properties of slag. Such a computer analysis of the properties of slag begins with selecting the analysis, as shown in Figure 1 [Fig. 1].

### TABLE 7
The chemical composition of water extracts of slags and their limits

| No. | Type          | Unit of measure | Test result | The limit value |
|-----|---------------|-----------------|-------------|-----------------|
| 1.  | Phosphorus    | mg P/l          | 0,12        | 3               |
| 2.  | Ammonia nitrogen | mg N<sub>NO3</sub>/l | <0,05 | 10              |
| 3.  | Sodium        | mg Na/l         | 19          | 800             |
| 4.  | Potassium     | mg K/l          | 2,5         | 80              |
| 5.  | Iron          | mg Fe/l         | <0,04       | 10              |
| 6.  | Antimony      | mg Sb/l         | 0,00007     | 0,3             |
| 7.  | Arsenic       | mg As/l         | 0,00041     | 0,1             |
| 8.  | Barium        | mg Ba/l         | 0,024       | 2               |
| 9.  | Zinc          | mg Zn/l         | 0,00464     | 2               |
| 10. | Chromium      | mg Cr/l         | 0,0026      | 0,5             |
| 11. | Cadmium       | mg Cd/l         | 2E-06       | no requirements |
| 12. | Cobalt        | mg Co/l         | 0,00013     | 1               |
| 13. | Copper        | mg Cu/l         | 0,0012      | 0,5             |
| 14. | Manganese     | mg Mn/l         | 0,00015     | no requirements |
| 15. | Molybdenum    | mg Mo/l         | 0,00092     | 1               |
| 16. | Nickel        | mg Ni/l         | 0,00042     | 0,5             |
| 17. | Lead          | mg Pb/l         | 0,00005     | 0,5             |
| 18. | Mercury       | mg Hg/l         | 0,00128     | 0,03            |
| 19. | Selenium      | mg Se/l         | 0,0031      | 1               |
| 20. | Thallium      | mg Ti/l         | 0,00001     | 1               |
| 21. | Vanadium      | mg V/l          | 0,0067      | 2               |
|     | Reaction      | pH              | 11,2        | 6,5-9,0         |
|     | Chloride      | mgCl/l          | 2,04        | 1000            |
|     | Sulphureous   | mgSo4/l         | 102,23      | 500             |
|     | Solute Total  | Mg/l            | 360         | no requirements |

It should also be noted that the system has the ability to double-track action. By selecting “Enter the criteria,” the user can search the database looking for the best composition of the mixture of slag for him interesting properties. The user indicates his choice property eg. Viscosity, and then entered limit values, which is the minimum and the maximum. After approval of his choice program performs filtering database and then displays his list of areas that meet the criteria specified by the user. With the acquisition of such rapid information, you can not conduct additional research and painstaking research to obtain information on the suitability of the product constituting the waste slag production process for a particular purpose, provided knowledge of the relevant parameters of the application. Meanwhile, in the figure below 3 [Fig. 3] shows the result obtained by the user when selecting an area marked number 362. In this case the area selected is a blend of slag composition: Al<sub>2</sub>O<sub>3</sub> (10 – 15%), CaO (30 – 35%) and SiO<sub>2</sub> (50 – 55%).

The proposed program Slag - prop also has another very important environmental aspect. A huge database, which has in the context of physical, chemical, refining, and even technology properties allows the user to quickly reach the interesting information. At this point, there is no need for additional, often painstaking research and the result obtained in a few seconds. It should be noted that any conduct of the study involves not only the use of energy or other media, but also results in waste generation as the samples used, gases, dusts, etc. The database is detrimental fact is eliminated.

Thanks to the program, following the process of refining the particular metal, you can directly reach the best available and well-established coating extraction matrix oxide. The program, which represents a broad properties of mixtures of slag used in the vast majority of ingredients are
not characterized by a high toxicity in the process of refining. Here the user to deal with 6 different components which are oxides, including the basic layout of the base Al2O3 - CaO - SiO2, then the two salts, the type of chlorides, eg. NaCl, and three types of fluoride, which do not pose a health risk, while maintaining proper precautions.

The company KGHM undoubtedly introduces a large amount of pollutants into the environment. The process of mining is a major interference with the natural ecosystem, which is gradually changed. Note, however, that the production with which we are dealing in the company is producing at a very high level, which in the case of some products it belongs to the world leaders. Such production can not be deprived of the price you have to pay not only in the amount of environmental fees, but also the prices for the same high exploitation of nature. Continuous development of the company, however, allows to improve processes and gradually reduce pollution of the environment. As indicated by studies [11-13] of 80 years - the last century through appropriate concepts, improvements and changes to a large extent managed to reduce the amount of emissions particularly sulfur oxides, and particulate matter and lead. Emissions to the environment of metals such as copper, cadmium, and arsenic has large decrease. Conduct further work related to the monitoring and analysis of quality - quantitative waste, as well as the development of new concept will allow for even better environmental effects.

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