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**Technology of hydrometallurgical processing of
copper smelter slag**

6D072000 - Chemical technology of inorganic
substances

Dissertation submitted in fulfilment of the requirements
for the degree of
Doctor of Philosophy (Ph.D.)

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CONTENT

LIST OF ABBREVIATIONS

XRD – X-ray diffraction
SEM - scanning electron microscopy
ICP AAS - atomic absorption spectroscopy
S: L ratio – solid to liquid ratio
MA – mechanical activation
SCM - shrinking core model
RS - rotation speed
B : P - ball to powder ratio
BET – Brunauer-Emmett-Teller theory
SSA - specific surface area
S/N ratio – signal-to-noise ratio
ANOVA - Analysis of Variance
F test – Fisher test
FWHM - full width half maximum
XRF – X-ray fluorescence

INTRODUCTION

General description of the work

The dissertation work is devoted to the development of conditions for low-temperature sulfuric acid leaching of copper smelter slag, as a technogenic raw material for the production of zinc and copper. The peculiarities of the mineralogical composition of the said slag make it difficult for its hydrometallurgical processing, including the use of sulfuric acid solutions. For the first time to increase the reactivity of copper and zinc minerals present in the slag, dry and wet mechanical activation of the initial slag in a planetary mill, as well as in an attrition mill, was applied. Potassium dichromate was used as a leaching agent to intensify the leaching process, as well as to increase the selectivity towards copper. Optimization of the experiments was performed using the Design of Experiments (DoE) method, namely Taguchi Orthogonal Array Design. This made it possible to obtain optimum conditions for the selective extraction of copper into solution, the maximum value of which was 87.31 %. Changing the leaching conditions to improve the processability of the process reduced copper recovery to 68.30 %, which is a relatively high indicator for room-temperature copper slag leaching. A schematic diagram of the processing of copper smelter slag by wet mechanical activation in an attrition mill with subsequent two-stage leaching with an aqueous sulfuric acid solution in the presence of potassium dichromate is proposed.

The relevance of the work

Exhaustion of the ore base of non-ferrous metals, in particular zinc and copper, makes it necessary to find new sources of these raw materials. Such a source can be copper smelter slag, which is formed in significant quantities during the pyrometallurgical production of copper [1]. The content of copper and zinc in the waste slag reaches 2 and 5 wt. % or more, respectively, which is comparable to the content of the indicated metals in the ore, or even exceeds this value. The main method for recovering copper from waste copper slag is flotation enrichment, with obtaining a concentrate containing about 8-10 % copper. The relatively low content of copper in the concentrate, as well as the almost complete loss of zinc with the tailings, does not allow us to consider flotation enrichment as an acceptable method for processing these slags. Another method that has practical application is slag depletion in electric furnaces; this method is not economically feasible due to high energy consumption. Hydrometallurgical processing of copper smelter slag, which is the processing of material with an aqueous solution of chemical reagents, seems attractive [2-4]. A significant amount of sulfuric acid produced in copper smelters as a by-product makes it preferable to use this particular reagent for slag leaching. However, sulfuric acid leaching of slag requires the use of elevated (up to 80-90 ˚C) temperatures; besides, a significant amount of iron passes into the solution, which complicates further processing of the pulp. Thus, the development of conditions allowing hydrometallurgical processing of waste copper slag without the use of elevated temperatures, with selective extraction of copper into solution, seems to be a very urgent and important task for copper producers.

Purpose of the work: to find optimum conditions for mechanical activation of copper smelter slag and its subsequent low-temperature sulfuric acid leaching, providing high extraction of copper and zinc into solution.

Tasks of the work:

1) Determination of a model describing the leaching of components of waste copper slag in a sulfuric acid solution. Determination of the main kinetic parameters of the leaching reactions of copper-, zinc- and iron-containing minerals;

2) Determination of the effect of potassium dichromate on the copper, zinc and iron recovery into a sulfuric acid solution during leaching. Establishing the influence of the form of copper in the slag on the degree of the mentioned metals recovery into solution;

3) Revealing the influence of dry and wet mechanical activation of copper smelter slag in a planetary mill and attrition mill on the change in the specific surface area (SSA) of copper smelter slag. Determination of mechanical activation parameters that have the greatest impact on SSA. Establishing conditions for the greatest increase in SSA of copper smelter slag;

4) Revealing the effect of mechanical activation of copper smelter slag on the copper, zinc and iron recovery into a sulfuric acid solution in the presence of potassium dichromate;

5) Optimization of conditions for mechanical activation of copper smelter slag and its subsequent sulfate leaching in the presence of potassium dichromate to maximize the degree and selectivity of copper extraction;

6) Development of a schematic diagram of sulfuric acid leaching of copper smelter slag in the presence of potassium dichromate.

The object of the research is copper smelter slag samples collected from the «Kazakhmys Smelting» company (Balkhash, Central Kazakhstan).

The subject of the research is the processes occurring during dry and wet mechanical activation of copper smelter slag, as well as during leaching of initial and mechanically activated slag with sulfuric acid solutions, including in the presence of oxidants.

Research methods

Mechanical activation and sulfuric acid leaching were employed to treat the initial slag. The characterization of the initial, intermediate and final materials was carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic absorption spectrometry (AAS), nitrogen adsorption for specific surface area (SSA) measurement, light scattering technique for particle size distribution analysis and magnetization measurements. Taguchi Orthogonal Array Design, as well as Analysis of Variance (ANOVA) as statistical methods were applied to measure the variations of the experimental design and determine individual interactions of control factors during mechanical activation and leaching processes.

The research hypothesis was as follows: As known, mechanical activation is accompanied by a change in the internal energy and specific surface area of the processed material. Consequently, it was expected that the mechanical activation of the copper smelter slag would lead to a change in the reactivity of its components during leaching. In turn, the presence of potassium dichromate will not only intensify the process of dissolution of target minerals due to oxidizing ability but also, possibly, will allow to selectively extract one of the components due to the difference in leaching rates of the present metals.

The scientific novelty of the research results obtained is ascertained by the fact that for the first time:

-the main kinetic parameters of the reactions of copper, zinc and iron recovery into solution during sulfuric acid leaching of copper smelter slag have been determined;

-the influence of dry and wet mechanical activation of copper smelter slag on the specific surface area, as well as on leachability in a sulfuric acid solution was revealed;

-the possibility has been shown and the reason has been found for the selective extraction of copper into solution during the sulfuric acid leaching of copper smelter slag in the presence of potassium dichromate.

Theoretical significance. The results of the dissertation research expanded the known knowledge in the field of mechanical activation of copper smelter slag and hydrometallurgical leaching of copper, zinc and iron.

Practical significance. The developed technical solutions for sulfuric acid leaching of copper smelter slag have prospects for practical use in industry and will expand the raw material base of copper and zinc.

The main provisions for the defence:

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;

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;

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;

4) Leaching of copper smelter slag in sulfuric acid solution in the presence of potassium dichromate makes it possible to selectively extract copper into 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.

The personal contribution of the author of the work consists in the collection, processing and analysis of literature data on the topic of the thesis, direct planning and implementation of the experimental part. The applicant took part in the analysis, interpretation and presentation of the obtained research results and their discussion, as well as in the preparation of scientific articles.

Approbation of work

The results of the thesis were reported and discussed at international scientific conferences, such as the IX Scientific Conference of Young Scientists "Innovations in chemistry: achievements and prospects – 2018", and the 10th International Beremzhanov Congress on Chemistry and Chemical Technology – 2019.

Publications

The main research results on the topic of the dissertation are presented in 8 published works, including:

- one article in an international journal with a non-zero impact factor (IF = 5.039 Q1) according to the Web of Science database;
- one article in an international journal included in the Scopus database and having a percentile above 25;
- one article published in scientific journals recommended by the Committee for Control in the Sphere of Education and Science;
- two patents for a useful model of the Republic of Kazakhstan;
- two abstracts at international conferences;
- one article in an international journal.

Relation of the thesis with research and government programs

The dissertation work was carried out as part of the research carried out jointly at the Department of General and Inorganic Chemistry of al-Farabi Kazakh national university and Institute of Geotechnics, Slovak Academy of Sciences, as well as within the framework of the grant funding project of the Science Committee of the Ministry of Education and Science of the Republic Kazakhstan (No. AP08856414).

Volume and structure of the thesis.

The thesis consists of an introduction, four sections, a conclusion, and a list of references. The work is presented on 100 pages, contains 36 figures, 22 tables, and 124 bibliographical references.

1 LITERATURE REVIEW

1.1 Characterization of copper smelter slag

1.1.1 Copper smelter slag generation

The pyrometallurgical cycle for copper manufacture incorporates a few preparing stages: (i) getting copper concentrate (copper mineral improvement), (ii) heating the concentrate to deliver copper matte, (iii) changing over copper matte to rankle copper, and (iv) treatment of rankle copper with getting anodic copper, (v) electrolytic processing of rankling copper to create cathode copper (99.5-99.9 % Cu).

The main parts of commercial copper concentrate incorporate, remarkably sulfide copper minerals, for example, chalcopyrite ($CuFeS_2$), bornite (Cu_5FeS_4), and chalcocite (Cu_2S). Likewise, concentrates conclude other components, for example, iron sulfides (FeS, FeS_2, and so on), silicon dioxide (SiO_2), zinc sulfide (ZnS), calcium and magnesium carbonates ($CaCO_3$, $MgCO_3$), aluminium oxide (Al_2O_3), and others.

Smelting of copper concentrates is performed in proper metallurgical furnaces, in an oxygen atmosphere (air). Under these conditions, the oxidation of sulphur and iron happens with the arrangement of Cu-rich molten matte according to the following reaction:

$$2CuFeS_2 + 3.25O_2 \longrightarrow Cu_2S \times 0.5FeS + 1.5FeO + 2.5SO_2 \qquad (1.1)$$

The addition of silicon flux (SiO_2) makes iron bind in the form of fayalite ($2FeO \times SiO_2$ or Fe_2SiO_4):

$$2FeO + SiO_2 \longrightarrow 2FeO \times SiO_2 \qquad (1.2)$$

Streams of oxides (for example, CaO, $CaCO_3$) are added to decrease the viscosity of the melt. In terms of its softening in the heater, two liquid products are obtained: liquid matte rich in copper and copper smelter slag. The matte is a melt of copper and iron sulfides. Copper slag is an alloy of ferrosilicates, rich in iron, as well as silicon, and slightly mixed with various oxides. The main part of this slag is a FeO-SiO_2 binary system.

Depending on the process of segregation (the difference in density) these products are classified: matte as heavier, is at the bottom, and lighter slag is located on the top.

These furnaces are used as metallurgical units for melting copper concentrates: reflective furnace, autogenous melting furnace (Vanyukov furnace), electric furnace, etc. The selection of the furnace depends on the concentrate that will be treated.

1.1.2 Content of copper smelter slag

Copper slags are characterized by a complex chemical and mineralogical content due to the different compositions of concentrates, fluxes, as well as the technological cycle of their production [5-11].

K. Sanakulov and A. Hasanov investigated the mineralogical content of copper smelter slag from some copper smelter factories [12]. The major minerals of the slag were fayalite and magnetite.

Magnetite has the form of dendrites and octahedrons, the size of which reaches 250-280 microns. Magnetite is most often occurred in the form of precipitates in crystals bound with fayalite and copper sulfides, which have a size in the range of 10-100 microns. Fayalite is a prismatic crystal, sometimes granular, saturated with magnetite ($\approx$ 30%) and silicate phase (up to 30-50 %) with a size of 25$\times$ 160 microns.

In addition, small droplets of matte and secondary sulfide compounds are present in significant quantities in the slag. These compounds are formed as a result of the separation of dissolved sulfides from slag during their crystallization. Reflective slag is saturated with fayalite in the form of crystals with a size of 30 $\times$ 150-200 microns and silicate magnetite with a size of 20-30 microns. Sulfide particles of size 1-30 μm are distributed in the vitreous mass and are associated with magnetite crystals.

Differences in the chemical composition of the copper smelter slag depend on the following factors: (i) the composition of copper concentrates, (ii) the composition of the charge, (iii) the characteristics of the melting equipment (furnace) and (iv) the technological mode of the melting process [13-20]; The content of alkali metals can also change depending on their amount in the initial material [21]. Due to the low efficiency of melting, the material in the slag contains a relatively large amount of sulphur [22]. Also, the long-term contact of the slag with the surrounding medium affects its composition due to chemical and physical processes occurring during long-term storage [23].

There are two types of phases in the slag: the first phase, which is formed as a result of melting of copper concentrate in the furnace; and the second one, that forms as a result of the effects of the surrounding environment (e.g., by the action of weather).

Fayalite and silicate glass are the main source phases of slag. Pure crystalline fayalite (Fe_2SiO_4) corresponds to 70.51 % of iron oxide (II) and 29.49 % of silicon dioxide. The phases of the olivine group are also present, mainly kirschsteinite ($CaFeSiO_4$) and forsterite (Mg_2SiO_4) [24-27]. Other common phases encompass spinel ($MgAl_2O_4$), hematite (Fe_2O_3), viscite (FeO) and magnetite ($Fe^{2+}Fe^{3+}O$)$_2$ $_4$ [24–28]. Metallic elements are mainly represented as sulfides of copper, such as bornite, chalcopyrite and chalcocite, as well as pyrrhotite ($Fe_{(1-X)}S$), sphalerite ((Zn, Fe)S), galena (PbS) and wurtzite ((Zn, Fe)S) [25-35].

The phase composition of the copper slag strongly depends on the stage of copper production.

M. Shabalina studied the copper slag from the Sredneuralsk plant [29]. The size of the granules of copper-bearing mineral (represented by fayalite and its vitreous structure) in the silicate-slag mass was below 0.08 mm, and the size of the main granules was in the range 0.005-0.04 mm. Minerals in the slag are found in the form of fine impregnation with silicate slag at 90 % (fayalite, glass) and magnetite. Minerals are represented by bornite (Cu_5FeS_4), chalcopyrite ($CuFeS_2$), chalcocite

(Cu_2S), covellite (CuS) and cuprite (Cu_2O). Grains of chalcopyrite have a size of 0.005-0.01 mm and represent 6 % of the mass of copper minerals. Bornite and chalcocite are in close contact with chalcopyrite and rock grains and they make up about 23 % of the total mass. Covellite in size of 0.005-0.01 mm represents 22 % of the mass. Sulfur and metallic copper with size 0.005-0.01 mm make up about 3-5 mass %. The content of magnetite in the slag was 5-10 %. Noble metals were present in the form of mixtures with copper minerals. Iron is distributed as follows: 90 % fayalite, 5-10 % magnetite, a small amount is present of goethite and pyrrhotite.

It should be noted that the content of copper and zinc in copper smelter slags is the same as the content of these components in the ore. This fact allows us to consider copper smelter slag as an important resource for the extraction of precious metals.

1.1.3 Physical properties

The physical and mechanical properties of slag strongly depend on the cooling method [36].

The colour of chilled slag in the air is black and glassy. The specific gravity of the iron varies from 2.8 to 3.8. The specific weight of copper slag is higher than that of an ordinary agglomerate. The absorbency of the material is low (0.13 %). Copper slag consists of stable angular particles, the size of which is mainly 4.75–0.075 mm [37, 38]

Granulated copper slag is porous, thus it possesses a lower specific weight and a higher absorption capacity than copper slag prepared by air cooling.

1.2 Common principles of leaching copper smelter slag

1.2.1 Leaching methods

The first stage of hydrometallurgical slag treatment is the crushing of the original material. Two goals are achieved.

First of all, during the crushing the surface of the contact, the solid-liquid contact surface increases, which increases the speed of the heterogeneous chemical reaction according to the equation [39]:

$$-\frac{dM}{d\tau} = k \times F \times C \qquad (1.3)$$

where $\dfrac{dM}{d\tau}$ is the change in the amount of the leachable component in the original material; k - is the rate constant of the heterogeneous reaction; F - contact area "solid-liquid"; C is the concentration of the extracting agent in the solution.

Crushing also leads to the "disclosure" of the target minerals in the slag and makes them available for the extracting agent.

Consecutive main methods of leaching for crushed slag are as follows:
- Leaching without prior heating (roasting) under atmospheric pressure (preferably in heated pulp).

- Burning in the presence of a chemical reagent and extraction of the roasted material under atmospheric pressure to increase the solubility of the target components in the aqueous solution;
- Autoclave leaching (at high pressure and temperature).
- Bacterial leaching.

1.2.2 Leaching models

For extraction of metals from various minerals it is possible to use several models [40]:
- shrinking core model,
- variable-activation energy models.
- kinetic models,
- thermodynamic models,
- empirical models.

The shrinking core model (SCM) is considered the most promising when describing the leaching process. According to this model, the particles are spherical and become smaller evenly during the process. Thus, they preserve the spherical shape.

Concerning the model, Safari and co-workers demonstrated the following [41]:
- The solid particle interacts with the liquid reagent with the formation of the soluble product. The size of the particle is thus getting smaller until it completely disappears during the reaction.
- The solid particle interacts with a liquid reagent to form an insoluble product. In this case, the interacting nucleus compresses, but the particle size does not change.
- As a result of the interaction of the solid particle with the reagent on the surface, a gel-like layer is formed.

For SCM, the rate of the reaction can be controlled by three stages: mass transfer in the fluid surrounding the solid particle (Eq. 1.4), chemical reaction on the surface of the particle (Eq. 1.5), and mass transfer in the layer of solid products of chemical reaction (Eq. 1.6):

$$1 - (1 - X_{Me})^{2/3} = k_{exp}\tau \tag{1.4}$$

$$1 - (1 - X_{Me})^{1/3} = k_{exp}\tau \tag{1.5}$$

$$1 - 3(1 - X_{Me})^{2/3} + 2(1 - X_{Me}) = k_{exp}\tau \tag{1.6}$$

where X_{Me} is the metal fraction of the slag that has reacted, k_{exp} is the experimental apparent rate constant (min^{-1}), and τ is the time (min).

If the kinetics of the dissolution process is controlled by diffusion (equations 1.4 and 1.6), then the apparent experimental constant can be calculated according to the following equation [42]:

$$k_{exp} = \frac{DC_A}{R_0^2 \rho} \tag{1.7}$$

where D is the diffusion coefficient of the mineral, C_A the concentration of the reagent in the solution, ρ is the density of the extracted mineral and R_0 the radius of the unreacted particle.

For chemically controlled reaction the apparent experimental rate constant will be:

$$k_{exp} = \frac{k_S C_A}{R_0 \rho} \tag{1.8}$$

where k_S is the rate constant of the reaction. Since the SCM seems to reasonably represent reality in a wide variety of situations, we have decided to apply the kinetic equations associated with this model in the experimental section.

1.2.3 Mechanism of silicates dissolution

Most of the copper slag consists of silicates, including quartz SiO_2 and fayalite Fe_2SiO_4. Therefore, it seemed important to consider the dissolution processes of these minerals in this literature review.

As described in [43, 44], the disintegration of silicate minerals in acidic or alkaline solutions leads to one of the following: (i) complete destruction of the silicate structure, (ii) partial destruction of the silicate structure, or (iii) no dissolution.

The mechanism of dissolution of silicates remains the topic of scientific discussion until now. The model suggested by Crunwell [45] precisely describes the process of dissolution of silicates in acidic and alkaline media. The specificities of the suggested model are as follows: (i) the difference of potentials in the Helmholtz layer affects the rupture of the surface of the bond and the remodelling of the solvate film around the ion, (ii) the processes of cation and anion formation during the solubility of the solid occurs separately and in parallel, and (iii) the separate cation-anion processes depend on the potential differences at the boundary of the section.

It turned out that the order of the reaction for H^+ and OH^- ions is close to 0.5.

Thus, the rate of silicates leaching can be determined by the following equation [42]:

$$rate = k_H[H^+]^{0.5\pm0.1} + k_{OH}[OH^-]^{0.5\pm0.1} \tag{1.9}$$

where k_H and k_{OH}, are the rate constants for the reaction with acid and hydroxide, respectively.

Accordingly [45], the following simple stages of silicate dissolution in acidic solutions exist: atoms of the metal react with water to form solvated cations, and silicate groups react with water with the formation of hydrated anions.

For the dissolution of silicate in alkaline solutions, the following stages are needed: atoms of the metal react with hydroxide ions with the formation of hydrolyzed cations, and silicate groups react with water with the formation of hydrated anions.

As a result of the reaction, the bonds are broken in two places: between a group of silicates and the solid lattice and between an atom of metal and a solid lattice.
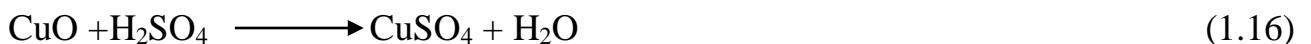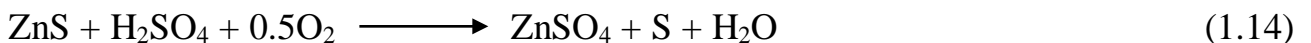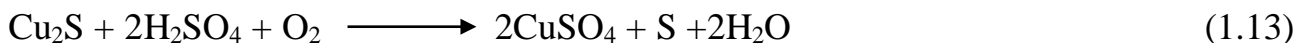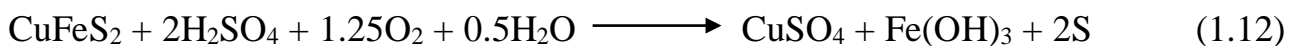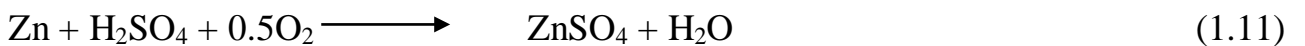
In the work [46] fayalite, synthesized with the use of powders of metallic Fe, Fe_2O_3, and SiO_2, was subjected to mechanical activation in the planetary ball mill at 400 rpm with a ball/powder (B:P) ratio of 5 for 45 minutes. This process led to partial amorphization of the initial sample. As a result of mechanical activation, the rate constants of the iron leaching in sulfuric acid solution (50-80 g$\times$ L^{-1}) increased and the activation energy of the leaching process decreased, i.e. mechanical activation enhances the reactivity of fayalite in H_2SO_4 solution.

1.3 Sulfuric acid leaching
1.3.1 Sulfuric acid leaching without additives

A suitable way for the leaching of copper slags seems to be the use of an aqueous solution of sulfuric acid [47]. This reagent is a by-product of non-ferrous metallurgy enterprises, is produced in large quantities, and is relatively inexpensive. Besides, sulfuric acid is an effective solvent for many iron compounds and non-ferrous metals. It is not surprising that most researchers choose this reagent in their experiments for the leaching of copper slags.

Target reactions in the leaching of copper slag with sulfuric acid are reactions of dissolution of zinc and copper minerals that are present in the slag:

$$Cu + H_2SO_4 + 0.5O_2 \longrightarrow CuSO_4 + H_2O \qquad (1.10)$$

$$Zn + H_2SO_4 + 0.5O_2 \longrightarrow ZnSO_4 + H_2O \qquad (1.11)$$

$$CuFeS_2 + 2H_2SO_4 + 1.25O_2 + 0.5H_2O \longrightarrow CuSO_4 + Fe(OH)_3 + 2S \qquad (1.12)$$

$$Cu_2S + 2H_2SO_4 + O_2 \longrightarrow 2CuSO_4 + S + 2H_2O \qquad (1.13)$$

$$ZnS + H_2SO_4 + 0.5O_2 \longrightarrow ZnSO_4 + S + H_2O \qquad (1.14)$$

$$ZnO + H_2SO_4 \longrightarrow ZnSO_4 + H_2O \qquad (1.15)$$

$$CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O \qquad (1.16)$$

As a result of these reactions, soluble sulfates of copper and zinc are formed. Processing of the obtained solutions by hydrometallurgical methods, including electrolysis, allows the restoration of metallic zinc and copper.

The results of studies on the extraction of copper and zinc from brass slag with sulfuric acid solutions were shown in [48]. The evaluation of the effect of acid concentration, particle size, reaction time, L:S ratio, as well as temperature on the recovery of metals, was made. The optimal concentration of H_2SO_4 for Zn recovery is

25-35 % and 30-45 % for Cu recovery. At 30 % H_2SO_4 and 35 °C, 90 % of copper passes into a solution.

The researchers of [49] studied the possibility of extraction of valuable metals with sulfuric acid from slag with the composition as follows (in mass %): Fe 40, Cu 5.11, Zn 1.53. The main phases identified in the copper slag were Fe_3O_4, Fe_2SiO_4 and the copper-consisting phase. An also small amount of ZnO, Pb_2O_3 and precious metals-containing compounds were also present. The size of the particles of copper slag before extraction was 120 mesh (124 microns). It was found that the optimal conditions for extraction were obtained upon leaching copper slag with 7 times higher concentration than the theoretical amount of 30 % H_2SO_4 at 90 °C for 2 hours. Under these experimental conditions, the solubility of Fe, Cu, Co and Ni was 92.83 %, 96.76 %, 93.62 % and 63.41%, respectively.

1.3.2 Leaching with sulfuric acid and hydrogen peroxide

Extraction of non-ferrous metals, iron removal and gaining well-processed pulp from copper smelter slag was carried out by the extraction with sulfuric acid in the presence of hydrogen peroxide (H_2O_2) at atmospheric pressure [50]. By using the proposed techniques, both silica gel arrangement and iron co-extraction are evaded. The function of H_2O_2 is in the oxidation of slag parts:

$$CuS + 2H_2SO_4 + 2H_2O_2 \longrightarrow CuSO_4 + 2H_2SO_3 + 2H_2O \qquad (1.17)$$

$$2FeSO_4 + H_2O_2 + 2H_2O \longrightarrow 2FeOOH + 2H_2SO_4 \qquad (1.18)$$

On the one hand, hydrogen peroxide, as an oxidant, helps to extract the necessary components of slag to the solution (Eq. 1.17). On the other hand, these agents oxidize iron (II) to iron (III), with iron precipitating out of the solution prevalently as iron metal hydroxide FeOOH (Eq. 1.18). The separation of iron from zinc and copper contributes to the effective treatment of the solution after extraction.

This setup was used for leaching of copper smelting slags of the Balkhash Copper Plant (Kazakhstan) in the past [51].

The conditions of experiment were: pH 2.4, particle size 90 % < 74 μm, S: L = 10 g: 1 L. After 50 minutes of the leaching in the sulphuric acid, process peroxide was added to the solution to reduce the possibility of side reactions. After the addition of hydrogen peroxide, a precipitate was obtained. XRD analysis of the leach residue indicated the presence of unreacted fayalite and magnetite. The reflections of iron metal hydroxide (FeOOH), gypsum ($CaSO_4 \times 2H_2O$) and hematite (Fe_2O_3) were also observed.

The effect of the following parameters on copper and iron recovery was observed: hydrogen peroxide consumption, pH, leaching time and particle size. The pulp temperature was 60 ± 3 °C. The economic efficiency of the leaching process was indicated by the consumption of hydrogen peroxide. The theoretically required consumption of hydrogen peroxide can be determined using a stoichiometric method.

Semi-quantitative XRD analysis showed that the content of copper and zinc sulfides was about 2-5 % and iron oxides content was 40.1 %.

The authors calculated that the theoretical consumption of hydrogen peroxide will be about 150 kg per 1 ton of slag. This calculation was performed without considering the decomposition of hydrogen peroxide (Equation 1.19):

$$H_2O_2 \longrightarrow 0.5O_2 + H_2O \qquad (1.19)$$

Because of this, the actual consumption of hydrogen peroxide should be higher than the theoretical one.

Figure 2 shows the effect of hydrogen peroxide consumption on the recovery of zinc, copper and iron.
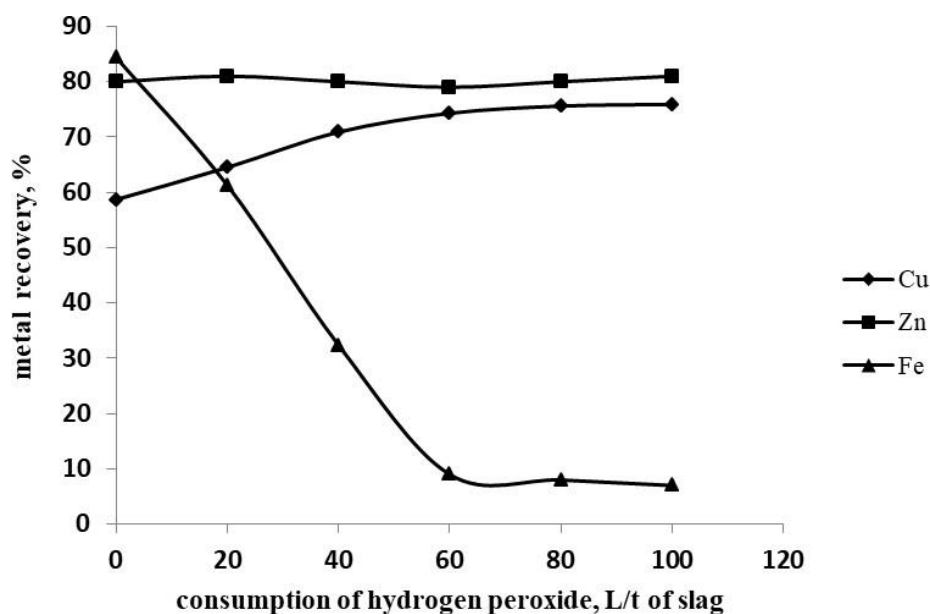
Figure 1.1 **-** Dependencies of the metal recoveries on H_2O_2 consumption [51]

The addition of hydrogen peroxide in an amount of 60 L/t increased the copper recovery to 76 % (7 % more than in the absence of hydrogen peroxide). Zinc also passes into the solution, however, iron is retained in the leaching residue.

The influence of hydrogen peroxide consumption on the extraction degree of iron, copper, zinc and silicon into solution, is shown (Table 1.1).

In the presence of hydrogen peroxide at a flow rate of 60 L/t slags, it can be observed that the pH solution in the range of 2.0–2.3 practically does not affect the content of copper and zinc in the solution. Simultaneously, the pH of the solution plays important role in the extraction degree of iron and silicon into the solution.

An increase of sulfuric acid amount in the system reduces the degree of hydrolysis of Fe (III), thus its content in the solution increases.

Table 1.1 - Dependencies of metal ion content of leach solution (mg/L) on the pH of the solution, at the H_2O_2 consumption of 60 L/t slags [51]

pH	Metal ion content, mg/L			
	Cu	Zn	Fe	Si
2.4	47±2	127±5	190±5	158±5
2.3	78±2	309±5	276±5	214±5
2.2	79±2	309±5	337±5	352±5
2.0	79±2	310±5	1214±12	473±5

The reaction of orthosilicic acid decomposition occurs:

$$H_4SiO_4 \longrightarrow 2H_2O + SiO_2 \qquad (1.20)$$

The formed silicon dioxide was obtained in the form of a precipitate, while the content of dissolved silicon in the solution decreased. Raising the pH of the solution to a value of 2.4 decreases the iron and silicon content in the solution, which is preferable; however, the content of copper and zinc in the solution sharply decreased, which, on the contrary, is undesirable. Therefore, the next experiments on leaching were done at pH 2.3.

The influence of leaching duration on the extraction degree of copper, zinc, iron and silicon is shown in Table 1.2; without changing the following parameters: temperature 60 °C, particle size 90% < 74 microns, S: L = 10 g: 1 L, pH = 2.3.

Table 1.2 - Dependencies of metal ion content of leach solution (mg/L) on the leaching duration, at the H_2O_2 consumption of 60 L/t slags [51]

Leaching duration, min	Metal ion content, mg/L			
	Cu	Zn	Fe	Si
40	24±1	160±3	220±5	62±3
50	49±2	246±5	238±5	184±5
60	78±2	309±5	276±5	214±5
70	79±2	310±5	272±5	210±5
80	79±2	310±5	274±5	210±5

After 1 hour, almost the maximum metal content in the solution is reached. A slight difference in iron content in solution after 40 min and after 80 min leaching was observed. This is could be explained by the fact that as time passes, the amount of deposited iron increases; with this iron content in the solution decreases.

The cost of the grinding material is considered to be proportional to the degree of grinding. Therefore, it was very important to study the effect of slag particle size on the parameters of the leaching process.

Table 1.3 shows the effect of particle size on the recovery of zinc and copper.

Table 1.3 - Dependencies of zinc, copper, and iron recovery on the particle size (temperature 60 ^{0}C, leaching duration 60 min, S: L = 10 g : 1 L, pH 2.3, H_2O_2 consumption 60 L/t slag) [51]
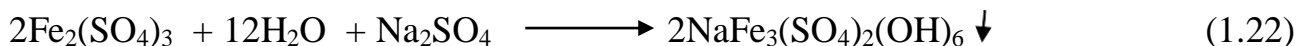
Particle size (μm)	Cu	Zn	Fe
90% <50	77.4±2.3	81.7±2.3	9.6±1.5
90% <74	76.1±2.3	80.9±2.3	9.7±1.5
90% <104	53.7±2.3	59.5±2.3	9.9±1.5
90% <147	42.4±2.3	50.1±2.3	9.5±1.5

As expected, the reduction in particle size increased the recovery of zinc and copper into the solution. Grinding the slag to 50 μm practically did not lead to an increase in the extraction of these metals; therefore, the particle size of 74 μm can be considered optimal. In the investigated range of particle sizes, the extraction of iron into solution remained constant; at the same time, the mass of the sediment increased with declining particle size. This fact could be explained as follows: as the size of the slag particles decreases, the degree of dissolution of iron that exists passes into the solution increases. The iron (II) is oxidized to iron (III) in hydrogen peroxide media; then iron (III) becomes sediment.

1.3.3 Leaching with sulfuric acid and sodium chlorate

Yang and his colleagues studied the addition of sodium chlorate to sulfuric acid when extracting copper from smelter slag [52]. Slag samples described in this study were gathered from a smelter in Guangdong Province, China, which generates more than
10,000 tons of slag annually. The leaching was performed on slag particles with a diameter of 180 microns. Sodium chlorate was obtained as a proficient reagent to avoid the polymerization of silicic acid. This was conceivable because of oxidation of Fe (II) to Fe (III) with the help of $NaClO_3$ following by the formation of the $2NaFe_3(SO_4)_2(OH)_6$ jarosite; while the solution is neutralized with calcium hydroxide, under these conditions the disintegration of silicic   acid (Eq. 1.21) happens:

$$6FeSO_4 + NaClO_3 + 3H_2SO_4 \longrightarrow 2Fe_2(SO_4)_3 + NaCl + 3H_2O \qquad (1.21)$$

$$2Fe_2(SO_4)_3 + 12H_2O + Na_2SO_4 \longrightarrow 2NaFe_3(SO_4)_2(OH)_6 \downarrow \qquad (1.22)$$

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + H_2O \qquad (1.23)$$

Apparently, Fe (III) is precipitated in the form of $NaFe_3(SO_4)_2(OH)_6$.

The general process proposed includes the washing of crushed slag with an aqueous solution of H_2SO_4 and $NaClO_3$ with the subsequent stage of neutralization with $Ca(OH)_2$ to keep the pH at the value around 2.0 (1.23). In these cases, the process of coagulation of iron ions (III) according to Eq. (1.22).

The described method was applied to the copper smelter slag of the Balkhash Copper Plant [50]. Fayalite (Fe_2SiO_4), ferrosilite ($FeSiO_3$), and franklinite ($ZnFe_2O_4$) were detected as the main components of the slag sample. The chemical composition of the slag is presented in Table 1.4.

Table 1.4 - Chemical composition of the copper smelter slag sample (wt. %, for Au and Ag g/t)

Si	Fe	Zn	Cu	Ca	Mg	Pb	Au	Ag	S	Al	As
13.85	39.46	4.50	1.14	0.78	0.16	0.69	0.12	4.81	1.05	1.52	0.11

The effect of H_2SO_4 consumption (g / g slag) on the extraction of copper and zinc into the solution is shown in Figure 1.2.
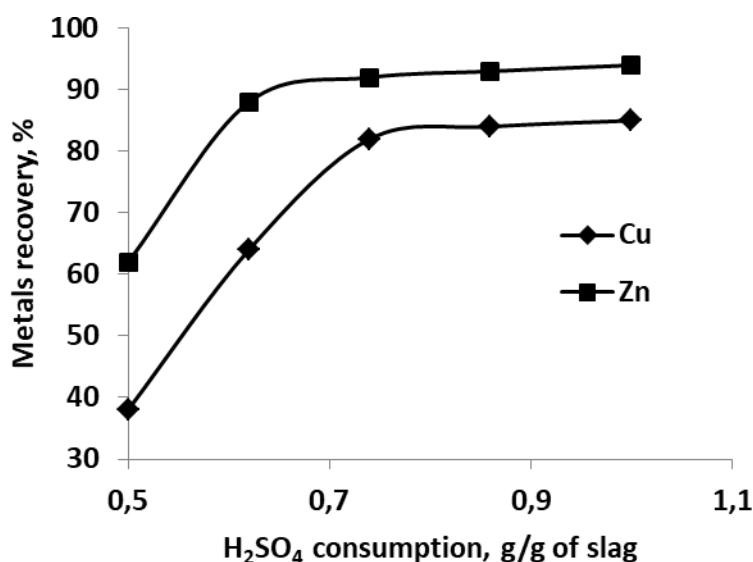

Figure 1.2 - Dependence of copper and zinc recovery on the sulfuric acid consumption (leaching duration 3.5 h) [51]

Figure 1.2 indicates that copper and zinc recovery increases with increasing the sulfuric acid consumption and gains a plateau at 0.74 g H_2SO_4 / g slag for copper and 0.62 g H_2SO_4 / g slag for zinc. The maximum recovery of copper and zinc is 84 and 93%, respectively.

The influence of sulfuric acid consumption on the recovery of iron and silicon in the solution after leaching is shown in Figure 1.3.

The consumption of sulfuric acid practically does not influence the iron content in the solution. However, the results of X-ray structural analysis of the solid residue showed that the amount of jarosite in the solid phase increases, as acid is used in the system. Thus, iron dissolves and forms jarosite. Apparently, the iron content in the solution in the range of 38-42 mg/L corresponds to the equilibrium content under these conditions.
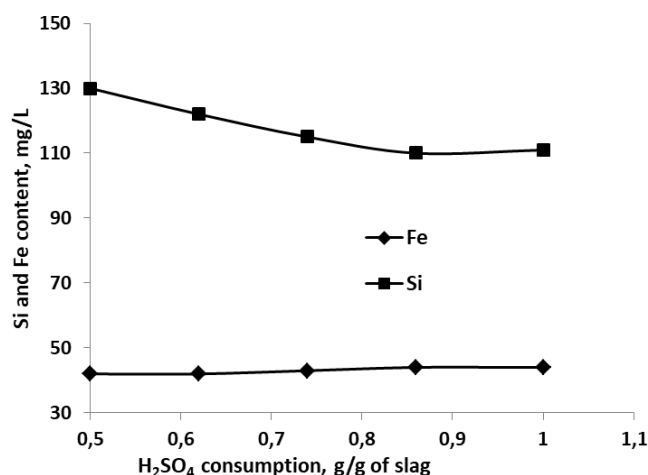
Figure 1.3 - Dependence of silicon and iron content in the filtrate on the sulfuric acid consumption (leaching duration 3.5 h) [51]

A slight decrease in the amount of silicon in the solution with increasing sulfuric acid content can be explained by the fact that a decrease in the pH of the solution moves the equilibrium of the reaction (1.20) to the right. This leads to the precipitation of silicon from the solution.

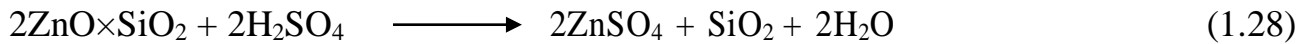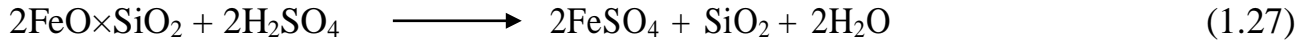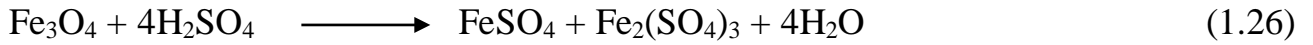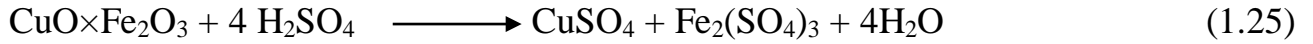1.3.4 Leaching with sulfuric acid and potassium dichromate

Potassium dichromate ($K_2Cr_2O_7$) is a simple inorganic chemical agent extensively used as an oxidizer in various industrial conditions.

The scientists of [53] worked with this reagent to extract precious metals from converter slag from the Maden, Elazig and Ergani plants in Turkey. The sample of slag contained 0.45 % Co, 4.36 % Cu, 52.18 % Fe, 1.92 % S and 0.64 % Zn The particle size was below 74 μm. This slag was exposed to leaching in a flask with constant stirring (400 min^{-1}) in mixed media of $K_2Cr_2O_7$ and H_2SO_4. Different concentrations of $K_2Cr_2O_7$ and H_2SO_4 were used. When $K_2Cr_2O_7$ was added, the leachability of the copper was more effective, and there was a decrease in the content of Co, Fe and Zn. Treatment of crushed slag (< 74 μm) is carried out in a flask with a stirrer (400 rpm) at ambient temperature in a flask with 1.0 M H_2SO_4 (L/S: 100) resulted in the following metals' recovery into solution (mass %): Cu 20.5, Co. 66.6, Fe 62.1, Zn 65.7. In the same conditions with 0.3 M $K_2Cr_2O_7$ following metal conversion was obtained (mass. %): Cu 81.15, Co 12.0, Fe 3.15, Zn 10.27.

The fact that the recovery of Co, Fe and Zn is declined in the presence of dichromate ions is determined by the passivation on the surface of slag with ions of $Cr_2O_7^{2-}$ and/or $HCrO_4^-$. Accordingly to the author's clarification, Co, Fe and Zn are mainly occurring in silicate and ferrite matrices. Adsorption of $Cr_2O_7^{2-}$ and $HCrO_4^-$ ions passivates the surface of zinc and iron minerals and prevents their dissolution.

1.3.5 Leaching with sulfuric acid and iron (III) sulfate in the presence of ultrasound

Beşe studied the combined use of sulfuric acid and iron sulphate (III) with the ultrasound for the leaching of copper converter slag from Black Sea Copper Works in Turkey [54]. The following reactions were assumed during the process:

$$CuS + Fe_2(SO_4)_3 \longrightarrow CuSO_4 + 2FeSO_4 + S \qquad (1.24)$$

$$CuO{\times}Fe_2O_3 + 4\,H_2SO_4 \longrightarrow CuSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (1.25)$$

$$Fe_3O_4 + 4H_2SO_4 \longrightarrow FeSO_4 + Fe_2(SO_4)_3 + 4H_2O \qquad (1.26)$$

$$2FeO{\times}SiO_2 + 2H_2SO_4 \longrightarrow 2FeSO_4 + SiO_2 + 2H_2O \qquad (1.27)$$

$$2ZnO{\times}SiO_2 + 2H_2SO_4 \longrightarrow 2ZnSO_4 + SiO_2 + 2H_2O \qquad (1.28)$$

The following conditions were found to be optimum: 65 $^{\circ}$C, 0.2 M acid concentration, 0.15 M ferric sulfate concentration and 180 min response time. In this case, the extraction of Cu, Zn, Co, and Fe from the slag without ultrasound, was 80.41 %, 48.28 %, 64.52 %, and 12.16 %, and with the help of ultrasound 89.28 %, 51.32 %, 69.87 %, and 13.73 %, respectively. The ultrasonic energy most probably positively affects the disintegration of base metals in copper converter slag.

1.3.6 Calcination with sulfuric acid

The roasting of slag with sulfuric acid followed by leaching is described in some papers [55-57]. The work [55] studied the extraction of copper and iron from a reverberation furnace slag.

A two-stage extraction procedure was performed. The first thing to do was to burn the slag in the media of sulfuric acid at temperatures from 150 to 800 $^{\circ}$C. The second stage was to lixiviate a calcine with distilled water. The maximum recovery of copper was about 94 %. For this process, the slag was heated at 250 $^{\circ}$C with the amount of sulfuric acid that exceeds stoichiometric requirements (more than 33 %). The excretion of calcine with water was carried at 50 $^{\circ}$C. About 55 % of the iron is also dissolved. On the other hand, for calcine formed at a sulfation temperature of 600 $^{\circ}$C the extraction degree of copper was still relatively high (about 79 %) and iron relatively low (about 6 %). It was found that the passing of copper and iron from calcine into solution goes at high speed and is accomplished within an initial couple of moments. The water temperature does not affect the extraction of copper and iron from calcine in the range of 30 to 85 $^{\circ}$C.

The traditional scheme of extraction of metals in hydrometallurgy includes some processes before the leaching stage, as well as preliminary treatment. Most of them have a mechanical character, which increases the leachability of the valuable component with the help of an alkaline agent. Sorting represents its key stage in the extraction scheme, and on its way can influence the selection of the method of extraction and/or convenient preliminary processing of the solid phase. One of the effective approaches to increase the leachability of minerals in hydrometallurgy is considered the mechanical activation of the initial slag.

1.4 Mechanical activation of solids

Mechanical activation is used, in general, for increasing the chemical transformation of inorganic and high-molecular compounds.

It is connected with the field of reactions caused by mechanical energy, often referred to as Mechanical or Mechanochemical Activation. The activation depends on the breakage process and the rate at which energy is applied to the system. In contrast to rough grinding, where the aim is size contraction, mechanical activation deals with structural changes that are occurred with the help of mechanical energy. Fine grinding is an intermediate option between rough grinding and mechanical activation. Mechanical activation has been attempted in a variety of disciplines, such as extractive metallurgy, waste utilisation, mechanical alloying, advanced ceramics, catalysis, coal gasification, paints and dyes, fertilizers, drugs and pharmaceuticals, organometallic synthesis, and many others. The changes in solids during the rough grinding of mechanical activation are listed below:
- Milling of the particles to a very small size.
- Formation of large new surfaces.
- Formation of dislocations and defects in the crystalline structure.
- Phase transformations in polymorphic materials.
- Chemical reactions: decomposition, ionic exchange, oxidation-reduction, etc.

Mechanical activation of minerals can be used in various stages of metal extraction both in pyrometallurgy and hydrometallurgy. Mainly, applications are connected with leaching ores and minerals, minimisation/utilization of wastes from metal extraction or related industries [58].

1.4.1 Factors affecting solids during mechanical activation

It is now generally accepted those solid bodies are simultaneously affected by three features: structural disorder, structural relaxation and structural mobility [58].

Structural relaxation plays an influential role in the reactivity of solid bodies. Scientists gave a representation of the states that slowly change after the cessation of the action of mechanical forces as a result of activation. Relaxation curve for activated solid bodies, in which different parts of the curve correspond to different characteristic periods of relaxation, has been drawn (Figure 1.4).

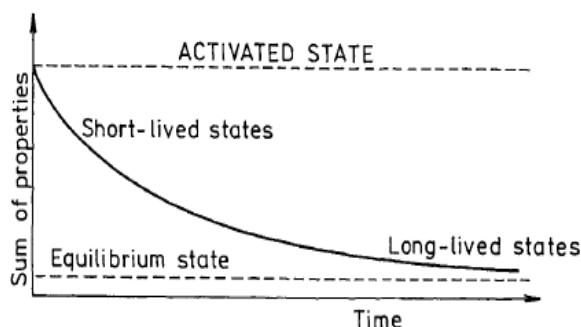Figure 1.4 - A generalized relaxation curve of mechanically activated state [58]

According to this theory, it is impossible to affect the reactivity of activated solid bodies by states, which time of relaxation is less than the time of the reaction. And on the contrary, some long-lasting states (for example, the surface layer) during the reaction can be considered stable, and their action must be subjected to

mechanical activation. There were different processes described primarily for the types of relaxation processes: heating, formation of a new surface, aggregation, recombination, adsorption, imperfections, chemical reactions between neighbouring particles, and so on.

The speed of these relaxation processes can change, and the processes can pass from one mode of relaxation to another (Figure 1.5).

Molchanov analyzed the multistage nature of mechanical activation [59]. It was assumed that the amount of stored energy will change at each stage and that the four potential stages of mechanical activation will be separated from each other.

Step I. This is the effect of the application of the force to the destruction of the structure and a lesser extent the strength of the given substance. In crystalline substances, atoms deviate from their "normal" state. Crystalline lattice is chaotic, intermolecular, interatomic and interstellar distances, angular orientations in the structure are changing.

Step II. This includes the appearance of a new surface. Structural damage and the appearance of cracks in solid bodies are interesting for several reasons. It is interesting not only as a process that leads to a change in energy status but also as a process, as a result of which the mechanical energy of the mill is transformed into the surface energy of the main substance.

Step III. (fine grinding). The appearance of a new surface and the accumulation of energy at the boundary of the subdivision affect the thermodynamic properties of matter and essentially change the structure and properties of the solid body.

Step IV. (ultrafine grinding). At this stage, the solid body loses its originality and becomes a substance, which reflects different structures, properties, and sometimes different compositions. In this case, it is better to use the term mechanochemical activation instead of mechanical activation.

It is assumed assumed that the processes under the influence of mechanical activation can be divided into primary and secondary. The initial process (for example, the increase of internal and surface energy, the increase of surface areas, and the reduction of the coherent energy of solid bodies) increases the reactivity of the substance. Secondary processes (for example, aggregation, adsorption, and recrystallization) occur spontaneously in activated systems and can occur during crushing, as well as after crushing.
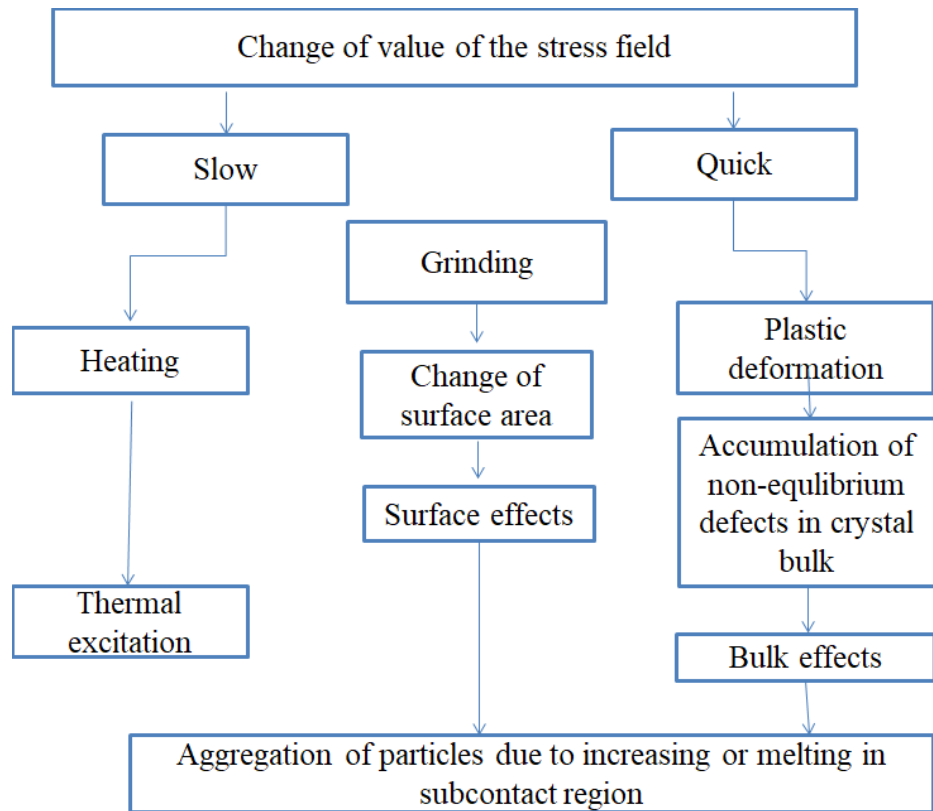
Figure 1.5 - Flowsheet of changes of relaxation processes [59]

Thus, mechanical activation can be considered as a multi-step process, in which the energy parameters and the amount of stored energy of solid bodies change at each stage.

1.4.2 Equipment used for mechanical activation

The multi-step nature of mechanical activation demands the use of equipment with different modes of operation (commonly called high-energy mills). The main categories of stress applied during activation are pressure, movement (attrition), impact (impact) and impact (collision) (Figure 1.6).

Figure 1.6 - Main stress types in mills, R1 - compression, R2 - shear (attrition), R3 – impact (stroke), R4 - impact (collision) [60]

In fact, various factors affect the work of the crushing process, for example:
• type of mill (Figure 1.7)
• types of grinding tools (balls, rods or other shapes)
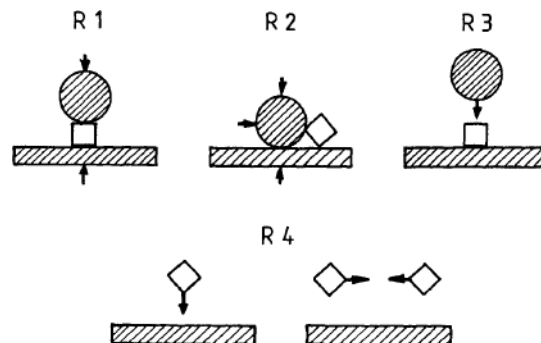• grinding material (for example, stainless steel, tungsten carbide, zirconium oxide, aluminum oxide, silicon nitride)
• atmosphere of crushing (for example, air, inert gas, regenerative gas)
• crushing mode (dry or wet)
• correlation of the dimensions of the activated material from the ball
• the ratio of the weight of the activated material to the ball
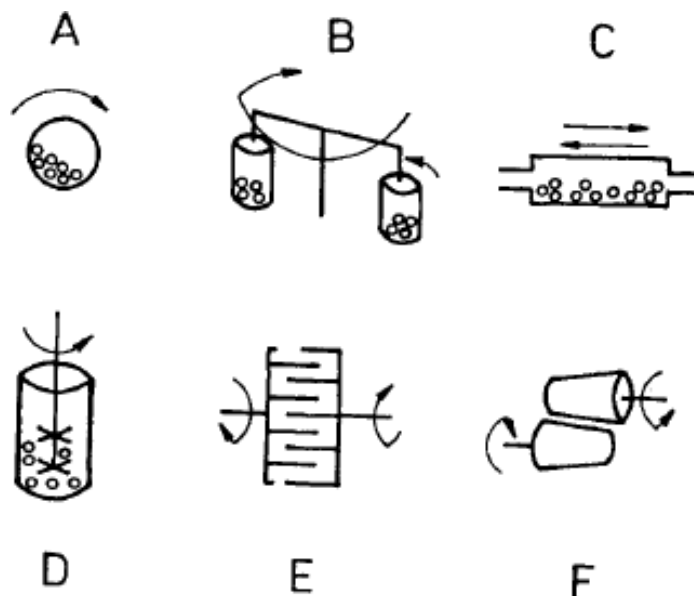• grinding temperature
• speed of milling and crushing time

Figure 1.7 - Types of mills for mechanical activation and the stress types,
A- ball mill (R1-R4), B - planetary mill (R1-R4), C - vibratory mill (R1-R4),
D - stirring ball mill – attrition mill (R1-R4), E - pin mill (R4),
rolling mill (R1-R2) [60]

1.4.3 Structural changes of mechanically activated minerals

Mechanical activation of minerals allows reducing the decomposition temperature or creates a degree of disorder. In this process, a complex influence of superficial and voluminous properties arises. Activation of minerals positively affects the kinetics of the leaching reaction, leading to an increase in the measured surface area and other phenomena, especially the weakening of pollutants in the surrounding environment. At present, it is unknown whether the kinetics of heterogeneous reactions is determined by the area of contact, or by the structure of the mineral. The required change in structure can be attained by mechanical activation of the mineral, usually by intensive grinding. The breaking of the bonds in the crystal lattice of the mineral leads to a reduction in activation energy (ΔE *) and an increase in the rate of leaching.

$$\Delta E^* = E - E^* \tag{1.29}$$

where E is the apparent activation energy of the ordered mineral and E* is the apparent activation energy of the disordered mineral.

The connection between the rate of leaching and temperature is usually described by the Arrhenius equation

$$k = Z \exp(-E/RT) \tag{1.30}$$

We can write for a disordered mineral

$$k = Z \exp(-E^*/RT) \tag{1.31}$$

and after substituting for E* from (1.30) we obtain

$$k^* = k \exp(\Delta E^*/RT) \tag{1.32}$$

It is clear that $\exp(\Delta E^*/RT) > 1$ and thus it follows from Eq. (1.29) that $k^* > k$, i.e., the rate of leaching of a disordered mineral is greater than that of an ordered mineral.

Senna analyzed the impact of surface area and the structural disordering on the leachability of mechanically activated minerals [61]. In order to figure out the issue - whether surface area or structure of mineral are prevailing for the reactivity, the rate constant was divided by the surface area and plot against the applied energy by activation (Figure 1.8).

If the leaching rate constant divided by the surface area remains constant regarding the applied energy, as shown in Figure 1.8a, so the measured surface area can be the effective one and thus the reaction rate is non-sensitive to structural changes. If, on the other hand, the k/S_i value decreases with the applied energy, as shown in figure 1.8 b, at that point the surface area is likely not the effective surface area.

In the third case, when k/S_i grows with the applied energy, appeared as in Figure 1.8c, the S_i can again be the effective surface area with overlapping structural interactions due to mechanical activation.
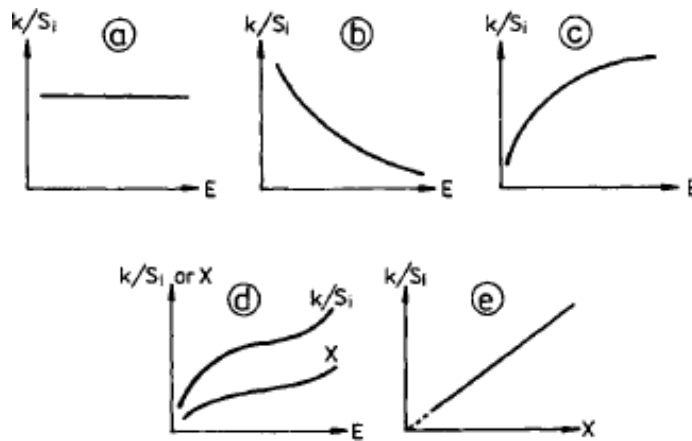
Figure 1.8 - The schematic diagrams representing the mutual dependence of physicochemical characteristics and reactivity of mechanically activated solids (k - the rate constant of leaching, Si- surface area, X - structural imperfections, E - applied energy) [61]

Alternatively, when k/S_i and X change parallel to each other with E, as shown in Fig. 1.8d or the k/S_i value is proportional to X, as shown in Fig. 1.8e seems to be more appropriate taking the selected S_i as the effective surface area.

Chalcopyrite (CuFeS₂)

Chalcopyrite belongs to the group of the most exploited copper sulfide minerals. Its infusible nature often requires a pre-activation stage. Dutrisak summarized activation methods and they can be separated into three main categories: replacement of chalcopyrite with other sulphides by adding or removing Cu, Fe or S, catalyzing the reaction with a small amount of Ag and increasing the leaching rate by fine crushing and/or initiated lattice deformation [62].

Effect of structural disorder in mechanically activated minerals with the close-packed sublattice for their reactivity has been the subject of detailed study since the early 1980s. Spinels and perovskites were taken as models. Literature containing data on spinels are called mechanically induced magnetic order-disorder transformation a threshold phenomenon that occurs at sufficiently high-stress intensity. Due to the crystallographic shift in the oxide sublattice, the inversion of the cation sublattice occurs. Changing interatomic distances leads to structural metastability. In this way relationship between the changes in magnetic properties and reactivity can be expected. Based on the similarity of the structure of spinels and chalcopyrite, chemical reactions with the participation of mechanically activated chalcopyrite have been studied.

In further studies, the influence of structural metastability on the effects influencing the technological behaviour of the finely ground chalcopyrite was investigated. It is known that surface oxidation occurs during and after energy-intensive grinding of sulfides in the air.

During the experiment for the material crushed in the attrition mill, an 11-fold increase in the initial speed of acceleration of the specific surface area from 0.59 to

$17 \ m^2/g$ (i.e. 28-fold) was observed. In the case of grinding in a vibrating mill, despite an eightfold increase in the specific surface area, the increase in k_0 was increased by more than 30 times, i.e. only from 0.59 to $4.7 \ m^2/g$.

Zinc ferrite ($ZnFe_2O_4$)

The grinding of zinc ferrite in a high-energy planetary ball mill is accompanied by a change in the shape of the diffraction lines from the start.

According to [63] the mechanically induced transfer of cations into metastable positions can be identified by determining a change in the Zn/Fe ratio passing into the leachate during dissolution in acids. The degree of inversion, determined by the fraction of tetrahedral positions occupied by Fe^{3+} cations, monotonically increases from zero in the initial sample to 0.94

In other words, the ordinary spinel is almost completely reversed after 24 minutes of grinding. An inversion degree d=0.67 was found after 5 min of grinding by the Rietveld structure refinement.

The transition of zinc ferrite to a metastable state is the result of mechanically induced inversion and deformation in the geometry of the octahedron. Mechanically induced inversion is reversible and the stresses around the bonds formed can be relaxed during heating. Chemical changes are one of the possible relaxation channels. The rate of dissolution of zinc and iron in dilute acid increases exponentially with an increase in the specific surface area, as well as with an increase in the degree of inversion of mechanically activated zinc ferrite. The deformation in the octahedron of zinc ferrite can hypothetically be associated with the selective acceleration of the dissolution of Zn. Dissolution rate ratio, $k_{Zn} > k_{Fe}$. 1 can serve as an indicator of the formation of a metastable substance that differs markedly from normal and partially activated zinc ferrite in structure and chemical behaviour.

The extraordinary chemical behaviour of mechanically activated zinc ferrite is manifested in its decomposition at temperatures that are 50 % below the temperature of its synthesis. Based on the approximate correspondence between the relative participation of the maximally deformed cation-anion bonds with a bond angle of 180 °C and the relative amount of decomposed ferrite, these maximally deformed bonds can be taken as the places where partial decomposition is localized. Decomposition occurs simultaneously with the return of Zn and Fe cations to equilibrium positions. The increased mobility of cations in a narrow temperature range can be an important factor in stimulating the low-temperature decomposition of mechanically activated zinc ferrite [63].

Olivine (($MgFe$)$_2SiO_4$)

Mechanical activation of olivine was performed in planetary (PM), attrition (AM) and nutating (NM) mills and the dependence of specific surface area SA of the samples on the time of mechanical activation are represented in Figure 1.10. These plots show that the new surface formation is affected by both the time of mechanical activation and the milling conditions (type of mill). The increase in specific surface area for the olivine sample milled is detected in an attrition mill (Figure 1.10 a) is much higher than for the sample milled in planetary and nutating mills (Figs.1.10 b, c). The disintegration of olivine by mechanical activation is accompanied by an increase in the number of particles and by the generation of fresh,

previously unexposed surfaces [64]. By application of the three mills, the common features in plots in Figures 1.10 (a, b, c) can be identified. After the first stage where the increase in surface area is almost proportional to the milling time, the second stage is manifested. Here, the new surface area formation is slowed down. This effect is the most pronounced in a planetary mill and literature is attributed to particle enlargement (aggregation and/or agglomeration). In some cases when very intensive milling is applied, the changes in the crystal structure and mechanochemical reactions appear in this stage [65].
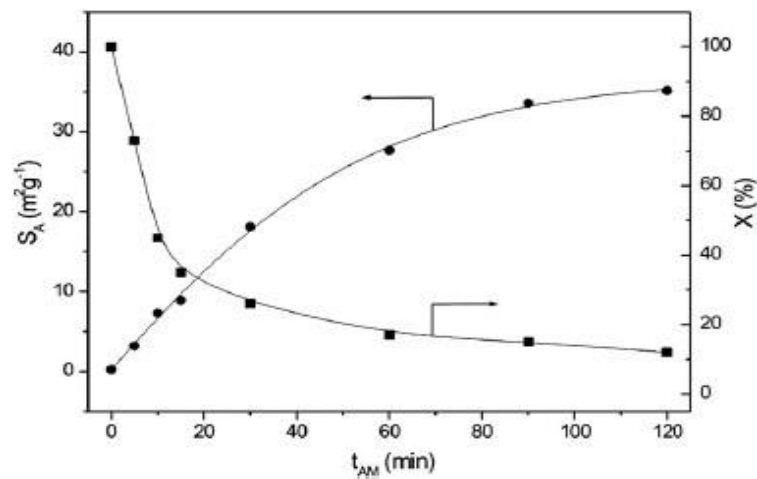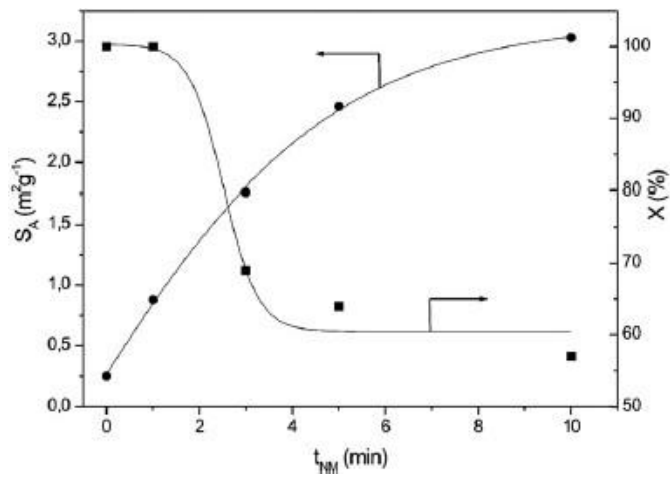

(a)
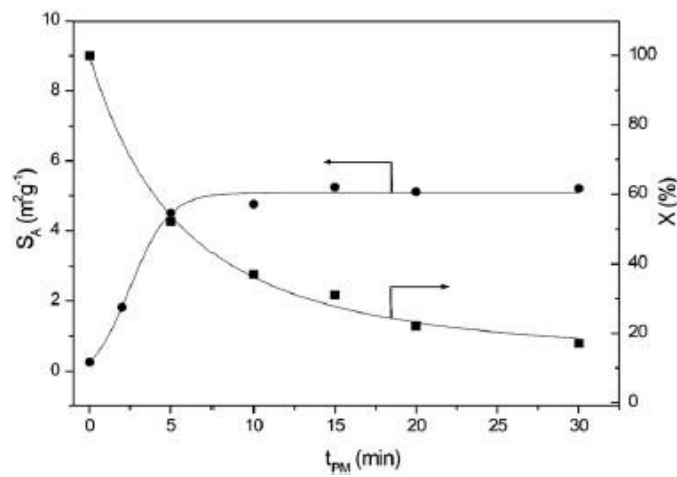
(b)

Figure 1.9 - Specific surface area S_A and content of crystalline phase X of olivine as a function of milling time: a) attrition mill, b) planetary ball mill, c) nutating mill, Page 1;

Figure 1.9 , Page 2 [66]

During milling, the particles are rounded, fractured and diminished. Some large particles still exist but an overall reduction in size appears to have occurred as a result of high-energy milling. The attrition milled samples show the most significant reduction in size which is in agreement with the results of olivine milling published in paper [66]. In some cases, the evidence of well-bonded aggregates can be seen.

The mutual dependence of new surface area S_A formation and the content of crystalline phase X of the mechanically activated olivine in various mills is depicted in Figure 1.10. The two-stage process of the new surface area formation can be deduced from the plots in Figure 1.10. In the first stage characteristic for dry milling, the increase of S_A values with olivine deterioration (decrease of X values) is very small. In the second stage characteristic for wet milling (in presence of H_2O) only small changes in values of X bring about the massive increase of S_A. However, some limiting values of X are required in this case: X < 55% and X < 35% for nutating mill and attrition mill, respectively.

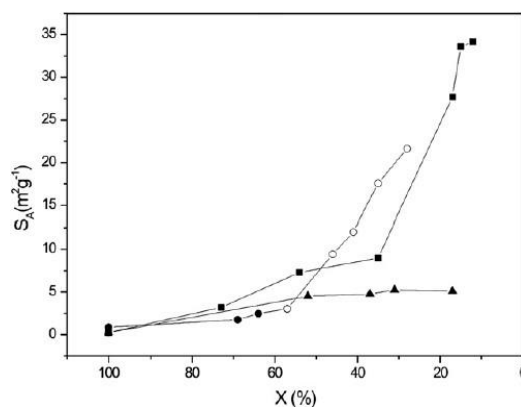Figure 1.10 - Specific surface area S_A of olivine as a function of the content of crystalline phase X: ($\blacksquare$) attrition mill, ($\blacktriangle$) planetary mill, ($\bullet$) nutating mill (dry milling), ($\circ$) nutating mill (wet milling with H_2O) [66]
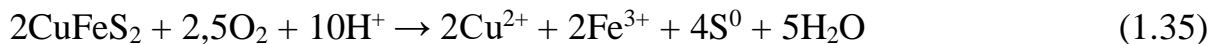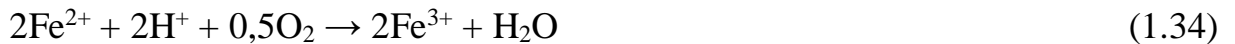
Milling in an attrition mill seemed to be very promising from the point of view of induced physico-chemical changes: both S_A and X values are the most different in comparison with the as-received sample ($S_A = 35.2 \ m^2g^{-1}$ vs. $0.25 \ m^2g^{-1}$ and X = 12 % vs. 100 %). The same is valid for the maximum value of the crystalline phase at planetary milling (X = 17 %). The corresponding values of milling energy for attrition mill and planetary mill are relatively high in comparison with the values for nutating milling. However, the values of S_A and X are not the same.

1.4.4 Influence of mechanical activation on leachability of minerals
Chalcopyrite (CuFeS₂)
The following minerals are mostly distributed in the content of copper smelter slag. Iron was occurred in the form of fayalite and magnetite, the copper and zinc mainly in the form of sulfides.

Chalcopyrite is known as the main topic of copper mining research. The leaching of chalcopyrite can be stated as follows [67]:

$$CuFeS_2 + 4Fe^{3+} \rightarrow Cu^{2+} + 5Fe^{2+} + 2S^0 \tag{1.33}$$

$$2Fe^{2+} + 2H^+ + 0{,}5O_2 \rightarrow 2Fe^{3+} + H_2O \tag{1.34}$$

$$2CuFeS_2 + 2{,}5O_2 + 10H^+ \rightarrow 2Cu^{2+} + 2Fe^{3+} + 4S^0 + 5H_2O \tag{1.35}$$

The main disadvantage of chalcopyrite leaching is its low leachability due to the forming of a passivation layer (for example, bimetallic sulfides, polysulfide, elemental sulfur and jarosite) on the surface of this mineral [68].

Mechanical activation (MA) before leaching is one of the effective methods that can enhance the leaching of minerals. The advantages of mechanical activation, such as using lower temperatures, obtaining water-soluble substances, new surface formation and lattice defects, makes it possible to use simpler and relatively less expensive reactors with shorter run times, which are economically viable reasons for this pretreatment.

There is an optimal time for MA during which the maximum leaching efficiency occurs.

The early raise in the leaching efficiency is connected to an increase of free energy of particles (due to an increase in lattice defects, structural disorder) [69], which in turn increase the reactivity.

The reason for the decrease in leaching efficiency after reaching the particular amount (6 hours) can be related to the effect of agglomeration and some agglomerated particles on the surface, which are partially activated. The maximum structural disordering of mechanically activated samples occurs within 6 hours after activation; a longer activation time does not cause any further changes. This behaviour is consistent with the maximum leaching efficiency (42 % for 7 hours of leaching, which is 2.4 times higher than in the case without MA), which occurs during 6 hours of activation, as the optimal activation time [70]

In this work [71], the process of chalcopyrite leaching was studied using mechanochemistry. With an increase in the mass ratios between the oxidant (i.e. $Fe_2(SO_4)_3 \cdot H_2O$) and chalcopyrite, the rate of copper leaching increased significantly, for example, after grinding, only 8 % of copper can be recovered within 2 hours without adding an oxidizing agent, while more than 40 % of copper can be recovered at a mass ratio of more than 1: 1. At a temperature below 338 K, copper extraction increases with increasing temperature. However, with an increase in temperature from 338 K to 348 K, lower copper recovery was observed. Aggregation of fine particles was observed after prolonged grinding, however, the copper extraction from the chalcopyrite did not decrease, for example, more than 98 % of the copper was leached out within 1.5 hours after grinding with $Fe_2(SO_4)_3 \cdot x$ H_2O for 2.0 hours. Acid was not required to leach ground chalcopyrite. The leaching results showed that the increased copper recovery after mechanical activation was associated not only with a decrease in particle size but more significantly, with a phase transformation through a solid phase reaction with the formation of much more readily soluble $CuSO_4$.

Sphalerite (ZnS)

This study examines the influence of mechanical activation on the extraction of zinc from sphalerite in an alkaline solution containing lead carbonate. Treatment under mechanical activation along with chemical leaching in one operation (mechanochemical leaching) is more effective than separate mechanical activation and subsequent chemical leaching. A new hydrometallurgical process for the recovery of Zn from sphalerite in an alkaline solution by chemical conversion with $PbCO_3$ was carried out. In the presence of $PbCO_3$, S in sphalerite can be converted to PbS and Zn can be converted to $Na_2Zn(OH)_4$ in alkaline solution in an agitated ball mill. And then precipitation PbS in the leach residue can be converted back to $PbCO_3$ in a Na_2CO_3 solution. It has been found that over 86 % of Zn can be recovered from sphalerite when the leaching process is carried out in 6 M NaOH solution at 90 °C with the addition of $PbCO_3$ and a stainless steel ball with a diameter of 5 mm as an activating medium, the mass ratio of the ball to powder 30:1, Pb / ZnS 0.9: 1 [72].

In another work, the leaching kinetics of mechanically activated sphalerite under pressure was studied. X-ray diffraction and scanning electron microscopy were applied to describe the effects of the treatment on crystal structure and morphology, respectively. In comparison with a non-activated sample, the activated samples demonstrated different physicochemical properties and higher reaction efficiency and increased recovery degree of Zn. The activation energy of sphalerite decreased from 69.96 to 45.91, 45.11, and 44.44 kJ / mol with an increase in the activation time from 0 to 30, 60, and 120 minutes, respectively. Reaction orders for H_2SO_4 solutions of sphalerite samples activated during 0, 30, 60 and 120 minutes were 1.832, 1.247, 1.214 and 1.085, respectively, indicating that the dependence of the sphalerite leaching process on H_2SO_4 can be reduced using mechanical activation [73].

Zinc ferrite (ZnFe₂O₄)

There is a study that estimates the influence of using mechanochemical reduction to recover zinc from zinc ferrites by alkaline leaching. The change of zinc ferrite to a metastable state after mechanochemical reduction with metallic iron

promotes the rapid dissolution of zinc from activated zinc ferrites in an alkaline solution. Zinc ferrites were subjected to mechanochemical reduction under conditions of a molar ratio 2:1 of Fe: $ZnFe_2O_4$, using stainless steel balls 5 mm in diameter as an activating medium at a ball to powder ratio of 25: 1. Following leaching at 6 mol/L. NaOH solution at 90 °C resulted in more than 70 % Zn recovery. These results can be used for further development of a hydrometallurgical process for the extraction of zinc from zinc ferrites in an alkaline solution. Mechanically induced inversion and dislocation in octahedral geometry resulted in the transition of zinc ferrite to a metastable state. More than 70 % of the zinc was recovered from mechanochemically reduced zinc ferrites, compared to inactivated samples (less than 2 % alkaline leach extraction) and samples after 2 hours activated in a planetary ball mill (13 % alkaline leach extraction) [74].

Indium-bearing zinc ferrite IBZF *(In $_x$ Zn $_{(1-x)}$ Fe$_2$O$_4$)*

Synthetic indium zinc ferrite was mechanically activated using a stirring ball mill and then investigated for the behaviour and kinetics of indium leaching from indium-bearing zinc ferrite. The impact of changes in the crystalline phase, lattice deformation, particle size, specific surface area and morphology caused by mechanical activation (MA) was also studied. The activated IBZF presented different physicochemical characteristics in comparison with the non-treated one and was dissolved in sulfuric acid easier than the non-milled sample. MA increased the leaching ability of IBZF. Upon mechanical activation of IBZF for 30 and 60 min, the activation energy decreased from 68.8 kJ / mol (for the non-milled sample) to 54.4 and 44.7 kJ / mol, respectively. The leaching process for unmilled IBZF was determined by a chemical reaction, but after MA treatment it became a hybrid controlled process. The reaction orders of starting and activated for 30 and 60 min, IBZF dissolution in relation to the concentration of H_2SO_4 were 0.69, 0.58 and 0.54, respectively [77].

Olivine ($Mg_{1.86}$ Fe$_{0.134}$ Ni$_{0.006}$ SiO$_4$*)*

This work studies how mechanical activation of olivine can enhance the surface reactivity of a mineral, and presents how such technology can lead to new olivine products. The olivine material considered in this study contains pure olivine crystals ($Mg_{1.86}$ Fe$_{0.134}$ Ni$_{0.006}$ SiO$_4$) obtained from the North Cape Minerals denote deposit at Eheim in Western Norway. After activation in a planetary mono mill, activated olivine products were visually examined using scanning electron microscopy (SEM) and characterized relative to particle size, specific surface area (BET) and X-ray diffraction (XRD). Surface reactivity of activated olivine products was detected using acid leach experiments in which the initial acid consumption rates were certain. The initial dissolution phase of olivine can be shown using first-order kinetics. Prolonged dry grinding of pure olivine crystals leads to highly aggregated compounds that were more reactive concerning dissolution in acid despite their lower BET surface areas. Compared to olivine milled for 1 min, 60 min milling raised the initial reaction rate by a factor of 9.0, while the corresponding increase in specific surface area was just 1.8 times. Results from leaching experiments and XRD analysis propose that the observed over-proportional increase in reactivity with respect to surface area is

largely due to structural disordering (i.e. mechanical activation) of olivine surfaces [75].

Kaolin residue

The influence of mechanical activation on the leaching of the residual kaolin in hydrochloric acid (20 wt. %) was studied in [76]. SEM images demonstrated that mechanical activation causes the conversion of the kaolin residue from needle-like particles to spherical particles. The particle size decreased as a result of milling. XRD spectra from the raw residue decreased after 4 hours of mechanical activation. Thus, mechanical activation enhanced acid leaching by altering the physicochemical properties. The apparent activation energy for leaching untreated and milled residues were determined to be about 43 kJ/mol and 24 kJ/mol, respectively, indicating that the leaching process of the raw residue was regulated by a chemical reaction on the surface, and the milled residue was controlled by a diffusion process. Mechanical activation significantly increased the activity of the kaolin residue and affected the leaching kinetics, which lowered the leach temperature and leach time [76].

Hemimorphite (Zn_4 (SiO_7)($OH)_2$ ·H_2O)

Mechanical activation of hemimorphite led to an increase in specific surface area due to grinding to submicroscopic particle sizes and a significant increase in structural disorder. The crystallite size declined with extended grinding time, while the lattice deformation became larger. Agglomeration was the cause of the average particle size increase beyond the minimum value during prolonged treatment. The transformation of the crystalline structure into an amorphous state brought a decrease in endothermic peaks. The growth of amorphous layers and a decrease in the particle size caused the degeneration and broadening of the X-ray diffraction patterns of hemimorphite. Alkaline leaching demonstrated that the extraction of zinc from hemimorphite increased with increasing grinding time, and the mechanochemical grinding mode is better for zinc recovery than dry grinding. This was due to the increased specific surface area and amorphization of mineral particles. The grinding and leaching steps were separated during dry grinding. In the case of mechano-chemical milling, the mechanical activation and chemical leaching were integrated into one step. Chemical leaching of non-milled hemimorphite was investigated with regards to the concentration of leaching agents and a solid to liquid ratio in the range of 0,083. The extraction of zinc increases with an increase in the concentration of the solution. After leaching for 420 min at 313 K, the maximum recovery was 85.69 %, when the leach solution contained 5.0 mol / L NH_4Cl, 2.5 mol / L NH_3 • H_2O, while for 4.0 mol / L NH_4Cl, 2.0 mol/L NH_3·H_2O and 3.0 mol/L NH_4Cl, 1.5 mol/L NH_3·H_2O it accounted for only 67.03 % and 49.35 %, respectively. The dissolution of hemimorphite rose with leaching time at the beginning of the process. However, after 2 hours, the extraction of zinc slowed down, and within 2-3 hours a flat stage began, at which it stopped. After this stage, zinc recovery increased slowly and reached a high rate after about 6-7 hours.

Comparative studies were carried out between chemical leaching after mechanical activation and mechano-chemical leaching samples at the solution concentration of 5.0 mol/L NH_4Cl, 2.5 mol/L NH_3·H_2O and solid/liquid ratio of 0,083. The extraction of zinc (88, 12 %) of hemimorphite confirmed the positive

effect of mechanical activation on its alkaline leaching, and the mode of mechanochemical leaching (90, 10 %) is more encouraging.

This could be explained as follows. During mechanical activation, the crystal structure of a mineral is usually disordered and the generation of defects or other metastable forms.   These defects are unstable and possess different relaxation times. If the process of mechanical activation was separated from leaching in time, a large number of highly excited states formed during milling would decay before leaching. In the first stage of leaching, the rate of diffusion and mass transfer was high due to the high concentration of the solution. As the reaction proceeds, the residue insensible spreads the surface of the particles, and the concentration of the solution further decreases. This led to a slowdown in the rate of diffusion and mass transfer, which could not provide a sufficient amount of ammonia for the zinc-ammonia complex. This is how the flat stage appeared. However, after 3 hours, zinc recovery increased again as the ammonia reached the solid-state surface. As mentioned before, the phase at 2–3 h limited the leaching efficiency of hemimorphite [78].

Mechanochemistry in hydrometallurgy of sulphide minerals

The preparation and characterization of various chalcogenides have received much attention, mainly in the case of nanocrystalline state compounds with grain sizes up to about 100 nm. The new characteristics of these materials are due to their extremely small particle size when a large volume fraction of atoms are located at the grain boundaries. Zinc sulphide ZnS is a main semiconducting material for a variety of applications such as optical coatings, solid-state solar cell windows, electro-optic modulators, photoconductors, sensors, etc [85-95]. Therefore, much research on the physical properties of ZnS particles has been done [79- 83].   However, the leaching of ZnS particles in nanocrystalline form has not been investigated so far. The study [84] was devoted to studying the properties and non-oxidizing acid leaching of ZnS nanoparticles which were prepared by the mechanochemical synthesis in a planetary mill according to the reaction

$$CH_3COO_2Zn + 2H_2O + Na_2S \rightarrow ZnS + 2CH_3COONa + 2H_2O \qquad (1.36)$$

The average size of the particles sphalerite and wurtzite was 2.1 nm. The broadening of diffraction peaks is explained by the small size of nanoparticles, and not by a decrease in crystallinity. The reactivity of mechanochemically synthesized ZnS nanoparticles was tested by nonoxidative acid leaching that follows the reaction

$$ZnS + H_2SO_4 \rightarrow ZnSO_4 + H_2S \qquad (1.37)$$
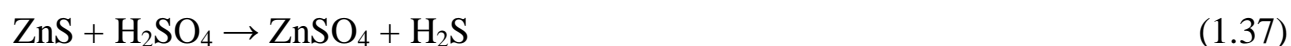
The surface area of mechanically synthesized ZnS reached values of specific surface area as, 91, 99, 117, and 128 m^2/g, and that of chemically deposited ZnS was 8 m^2/g. These samples were mechanochemically synthesized during 3, 5, 10 and 20 min of milling. The solubilization of Zn has a high starting point and after 10 min practically ceases.   An increase in the surface area of mechanochemically synthesized ZnS does not manifest itself noticeably during the subsequent leaching of zinc. The increasing

grinding time used for mechanochemical synthesis only affects the leaching kinetics. In this case, the formation of a disordered ZnS nanostructure plays a more significant role [84].

1.5 General information about copper smelter slag

1. Copper smelter slag is characterized by a complex composition, the main component is a fayalite matrix in which zinc and copper minerals are interspersed. The composition of the slag strongly depends on the conditions of smelting the charge and the cooling regime of the slag.

2. The leaching mechanism of silicate materials, including fayalite, in acidic or alkaline solutions could have resulted in one of the following: complete dissolving of the silicate structure, partial destruction of the silicate structure, or no dissolution. The following processes of silicate dissolution in acidic solutions occur: interaction atoms of the metal with water to give solvated cations, and interaction of silicate groups with hydrogen cations to form hydrated anions. For the dissolution of silicate in alkaline solutions, the next stages occur: atoms of the metal react with hydroxide ions to give hydrolyzed cations, and silicate groups react with water with the formation of hydrated anions.

3. Leaching with sulfuric acid requires elevated temperatures ($\approx$ 90 °C) to achieve acceptably (more than 90 %) copper recovery. Using hydrogen peroxide (150 kg per 1 ton) with sulfuric acid can reduce the leaching temperature to 60 °C, on the other hand, this reagent is relatively expensive.

4. Sodium chlorate was obtained as an effective reagent to avoid the polymerization of silicic acid due to oxidation of iron ions to the jarosite. However, this reagent couldn't be used on an industrial scale because of its high price.

5. The potassium dichromate could be used to selectively extract copper during leaching. However, the need to utilization chromium-containing solutions after leaching reduces the possibility of using this method.

6. During roasting of slag with sulfuric acid, highly soluble sulfates are formed, which in turn facilitate the leaching process. But its practical implementation is impeded by high energy consumption.

7. Using mechanical activation of minerals before leaching allows to reduce the decomposition temperature or creates a degree of disorder. The increased mobility of cations in minerals in a narrow temperature range can be an important factor in stimulating the low-temperature decomposition of mechanically activated samples.

8. The optimal conditions of mechanical activation for the aforementioned minerals were investigated. Agglomeration of particles was obtained after a prolonged time of activation. The influence of the types of grinding mills on the structure of minerals and leaching was investigated. In most cases, milling in an attrition mill seemed to be very promising from the point of view of induced physico-chemical changes and industrial application.

9. The impact of changing surface area and the structural disordering due to mechanical activation on the leachability minerals have been confirmed. To find out if the surface area or structure of the mineral is predominant for the reactivity, the rate constant divided by the surface area and plotted as a function of the applied

energy upon activation were taken as an indicator. The rate of dissolution of many minerals increases with an increase in the specific surface area.

10. The leach results for some minerals showed that the increased metal recovery after mechanical activation was associated not only with a decrease in particle size but more significantly, with a phase transformation through a solid phase reaction with the formation of much more readily soluble products. Additionally, after mechanical activation physicochemical properties of minerals had changed, which in turn showed higher reaction efficiency due to reducing activation energy.

2 MATERIALS AND METHODS

2.1 Characteristics of raw material

The investigation was carried out with the different samples of copper smelter slag collected from Kazakhmys Smelting (Balkhash, Central Kazakhstan). The slag sample was milled and sieved to reach the particle size ≤ 100 μm. In the end, more than 90 % of particles were smaller or equal to 100 μm.

2.2 Chemical reagents

Sulfuric acid (96 %), potassium dichromate (≈ 99 %), hydrogen peroxide (3 %) and sodium bicarbonate was purchased from Sigma-Aldrich and used without further purification. Distilled water was used in all washing and cleaning procedures.

2.3 Mechanical activation

Mechanical activation. Planetary ball mill *Activator-2SL* (Activator, Russia) and attrition mill (attritor) Molinex PE 075 (Netzsch, Germany) were used for mechanical activation of slag samples. The volume of the steel milling chamber of the planetary and attrition mill was 0.25 L and 0.5 L, respectively. Milling chambers contained 150 g (planetary ball mill) and 2000 g (attrition mill) of iron balls with a diameter of 2 mm.

Initial experiments were performed both in dry and wet mode. The slag sample was placed in a milling chamber and activated in the air environment under the pre-determined conditions (ball-to-powder ratio, duration of treatment, rotation speed). In the case of wet milling, 100 mL (planetary ball mill) or 200 mL (attrition mill) of distilled water was placed in a milling chamber before activation. After the treatment, the solid component was separated from water by decantation and the solid residue was dried at 105 °C to constant weight.

To optimize the milling conditions of mechanical activation of copper slag, three factors at three levels were selected and changed (Table 2.1).

Table 2.1 - Experimental parameters of mechanical activation and their levels

Level	Rotation speed (A), rpm	Sample mass (B)	Duration of treatment (C), min
Upper (3)	1200	150	120
Middle (2)	900	100	75
Lower (1)	600	50	30

The initial values were determined based on the preliminary experiments. As better results were obtained with wet milling, optimization was performed just with this setup. Taguchi orthogonal array (3^3) was created using the Minitab14 software (Minitab, Ltd., United Kingdom) and subsequently, nine experiments with different combinations were planned.

2.4 Leaching experiments without mechanical activation

2.4.1 Sulfuric acid leaching

The batch leaching tests in sulfuric acid solution were performed in a 200 mL round bottom glass reactor with ports for thermometer and mechanical stirrer (300 min^{-1}). 20 g of the ground (-200 mesh) slag sample was placed into the reactor filled with 2 L of the sulfuric acid solution with a given concentration. A water bath was used for maintaining the temperature of the pulp. After the predetermined time, a liquid sample was taken from the reactor to determine the concentration of Cu, Zn and Fe. These values were then used to calculate the recovery degree of mentioned metals into the solution.

2.4.2 Sulfuric acid leaching in the presence of dichromate

The batch leaching tests of the slag sample with a combination of H_2SO_4 and $K_2Cr_2O_7$ were performed by shaking in 500 mL flasks. A mixture of a slag sample (15g) and a leaching solution of a predetermined concentration of the aforementioned leaching agents were stirred at 450 min^{-1} at the predetermined temperature.

2.5 Leaching experiments with mechanical activation

2.5.1 Sulfuric acid leaching of mechanically activated slag sample

50 g of copper-containing slag was mixed with 200 ml of water. The resulting mixture is introduced into a 500 mL steel drum in an attrition mill Molinex PE 075 NETZSCH (Germany), loaded with iron balls with a diameter of 2 mm and a total weight of 2 kg. The suspension is subjected to mechanical activation (MA) at a rotation speed of 500 rpm, 600 rpm, 750 rpm and different time duration. The suspension obtained after MA is filtered off, dried, and the dry material is leached with an aqueous solution of 1M H_2SO_4 at a temperature of 52 ± 1 ° C for 1 hour. The degree of copper extraction into the solution was determined by inductively coupled plasma atomic emission spectroscopy.

2.5.2 Sulfuric acid leaching of mechanically activated slag sample in presence of hydrogen peroxide and sodium bicarbonate

The conditions of mechanical activation were: ball to powder ratio – 20:1 (300 g of iron balls and 15 g. of slag sample), rotation speed - 600 rpm, duration of mechanical activation - 20, 40, 60, 80, 100 min.

5 g mechanically activated slag was subjected to leaching with 100 mL 1 M H_2SO_4 for 2 hours. Then 10 mL 30 % H_2O_2 was added and mixed in 1 hour. Afterwards, 13.85 g NaHCO$_3$ was added to the solution and leached for 1 hour.

2.5.3 Sulfuric acid leaching of mechanically activated slag sample in the presence of potassium dichromate

The batch leaching tests of initial and/or mechanically activated slag samples with a combination of sulfuric acid and potassium dichromate were performed in a 250-mL round-bottom glass reactor with a port for a thermometer. A magnetic stirrer was used to stir the slurry. The reactor was kept at 25 ±2 °C. Again, Taguchi design using Minitab14 software was used, however, this time four factors at three levels were optimized (Table 2.2).

The redox potential and pH of the leach solution were measured during leaching by using a pH meter/ionomer ИТАН (Russia) equipped with a glass redox

combination electrode (Ag/AgCl was a reference electrode and platinum rod tip was a working electrode). The electrode was immersed into an as-prepared leaching solution (in the absence of a slag sample) and kept for 15-20 minutes until a constant oxidation-reduction potential and pH were reached. Then, pH and redox potential values were recorded every 20 minutes during leaching.

Table 2.2 - Experimental parameters of leaching and their levels

Level	$K_2Cr_2O_7$ concentration (A), [M]	H_2SO_4 concentration (B), [M]	Leaching time (C), [min]	Liquid-to-solid ratio, L:S (D)
Upper (3)	0.5	1	120	75:1
Middle (2)	0.15	0.5	60	100:1
Lower (1)	0.03	0.1	30	200:1

To assess the efficiency of leaching, the recovery of metals, α_{Me} and selectivity of copper leaching ε_{Cu} were calculated using the following formulas:

$$\alpha_{Me} = C_x/C_o * 100 \ [\%] \tag{2.1}$$

Where C_x (g/mL) is the concentration of the metal in the solution, C_o (g/mL) is the initial concentration of metal in the slag and Me = Cu, Zn, Fe.

$$\varepsilon_{Cu} = \alpha_{Cu} / (\alpha_{Zn} + \alpha_{Cu} + \alpha_{Fe}) * 100 \ [\%] \tag{2.2}$$

2.6 Materials characterization

XRD analysis. The XRD patterns were recorded by a D8 Advance diffractometer (Bruker, Germany) with CuKα (40 kV, 40 mA) radiation. XRD patterns were measured in the 2 theta range 5-70° with step size 0.03° and step time 6 s. For phase analysis, the JCPDS-PDF2 database and the Diffracplus EVA software has been used.

SEM imaging. Scanning electron microscopy was performed using a Quanta 200i 3D (FEI Company, USA). The accelerating voltage was set to 20 kV; a through-the-hole detector was used for imaging. Samples were prepared by spreading dried powders evenly on rectangular pieces (5×5 mm^2) of standard (100) silicon wafers: small powder amounts were placed on one silicon wafer; a second piece was used to distribute the powders by rubbing the two surfaces against each other.

ICP AAS measurements. Atomic absorption spectrometry (AAS) using AA-6200 spectrometer (Shimadzu, Japan) was applied for the determination of copper, iron and zinc concentration in liquid samples. The content of selected elements in the initial slag was also determined by AAS using a SPECTRAA L40/FS spectrometer (Varian, Australia).

Specific surface area measurement. Specific surface area (SSA) was determined by using the nitrogen adsorption technique (ANOVA 1200e, Quantachrome

Instruments) using the BET method. The measurements were done at the Institute of Geotechnics, Slovak Academy of Sciences, and Kosice, Slovakia.

Particle size distribution. The grain size analysis was performed using a particle size laser diffraction analyzer Mastersizer 2000E (Malvern, Malvern, UK) in the dry mode. The measurements were done at the Institute of Materials Research, Slovak Academy of Sciences.

Magnetization. Magnetization of selected samples was measured through a vibrating sample magnetometer (Cryogenic Limited, London, UK). The measurements were done at the Institute of Experimental Physics, Slovak Academy of Sciences.

2.7 Statistical methods

2.7.1 Design of Experiments (DoE) using Taguchi Orthogonal Array Design

The Taguchi method [97] uses the S/N ratio to measure the variations of the experimental design. The objective of using the S/N ratio as performance measurement is to develop products and processes insensitive to noise factors. The S/N ratio indicates the degree of the predictable performance of a product or process in the presence of noise factors. Regardless of the category of the performance characteristics, a greater S/N value corresponds to better performance.

The design of experiments (DOE) is a methodology for applying statistics to experimental work. Among DOE methods, Taguchi is one method that must be considered [97] due to its ability to reduce the number of experimental runs to a reasonable amount (on the contrary to full factorial design). This is advantageous in terms of cost and time as a result of using orthogonal arrays (selecting a number of independent factors and a number of their levels). This method uses the quality loss function that is defined in terms of the deviation of a design parameter from an ideal or target value. The value of this loss function is further transformed into a signal-to-noise (S/N) ratio, which can be characterized into three different categories: nominal-the-best, larger-the-best and smaller-the-best, depending on what is required. Before the experiments can be conducted, a set of factors and their levels (usually more numerical values of factors) are defined. This methodology is being intensively applied in the processes using ball milling [98].

The signal-to-noise ratio of each experimental run is calculated based on the following equation "Larger is better", as the largest values of process results (specific surface area and recovery of copper into solution) are the desired results.

$$\frac{S}{N} = -10 \log \frac{\sum_{i=1}^{n} \frac{1}{y_i^2}}{n} \tag{2.3}$$

where n is the number of observations, y_i is the observed data, S/N – a signal to noise ratio.

The effects of the level of each factor on the quality characteristics can be analyzed using S/N ratios. Another requirement in the calculation of optimum values is to determine the optimum levels. The optimum levels can be determined by

evaluating three different levels of the control factors according to the results from the combinations generated by the orthogonal array.

2.7.2 Analysis of Variance (determination of contribution)

ANOVA is a statistical method used for determining individual interactions of all control factors. In the analysis, the percentage distributions of each control factor were calculated in order to show their individual contributions to the response The performed experimental plan was evaluated at a confidence level of 95% [97].

Statistically, there is a tool called an F test named after Fisher to see which design parameters have a significant effect on the quality characteristic. In the analysis, the F ratio is a ratio of mean square error to residual and is traditionally used to determine the significance of a factor.

3 RESULTS AND DISCUSSION

3.1 Leaching of untreated copper smelter slag
3.1.1 Sulfuric acid leaching
Slag sample characterization

The copper smelter slag sample used in this work was obtained from a copper smelting plant of the town of Balkhash located in the central part of Kazakhstan. Fe_2SiO_4 - 29.4 wt. %, $FeSiO_3$ - 26.7 wt. %, Fe_3O_4 - 9.3 wt. %, $ZnFe_2O_4$ - 15.1 wt. % were identified by XRD analysis (DRON-3) as major components of the slag sample. Most of the copper was in the form of copper sulfides, such as Cu_2S, Cu_5FeS_4 and $CuFeS_2$
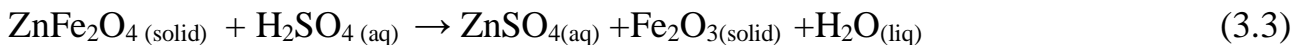
Leaching chemistry

A conspicuous route for the extraction of copper from copper slags is by all accounts the use of sulfuric acid [50]. This reagent is a result of non-ferrous metallurgy ventures, is delivered in enormous amounts, and is generally cheap. What's more, sulfuric acid is a good solvent for some iron mixes and non-ferrous metals. The main reactions of minerals with sulfuric acid are shown below.

Low-temperature oxidative pressure leaching of chalcopyrite promotes the elemental sulfur formation and sulfuric acid consumption [96]. The total chemical reaction of the low-temperature process is as shown in Equation 1.12.

The dissolution of silicates, such as olivines, contributes to an increase in solution pH. The pH increase is related to acid-consuming hydrolysis reactions, which are common in solid/water interactions [101].

$$2FeO{\times}SiO_2 + 2H_2SO_4 \rightarrow 2FeSO_4 + H_4SiO_4 \tag{3.1}$$

$ZnFe_2O_4$ is slightly soluble in a dilute solution of sulfuric acid however, at a high concentration (1 M), peak reduction is responsible for the reaction of the same phase in sulfuric acid solution [99].

$$ZnFe_2O_{4\,(solid)} + 4H_2SO_{4\,(aq)} \rightarrow ZnSO_{4\,(aq)} + Fe_2(SO_4)_{3(aq)} + 4H_2O_{(liq)} \tag{3.2}$$

$$ZnFe_2O_{4\,(solid)} + H_2SO_{4\,(aq)} \rightarrow ZnSO_{4(aq)} + Fe_2O_{3(solid)} + H_2O_{(liq)} \tag{3.3}$$

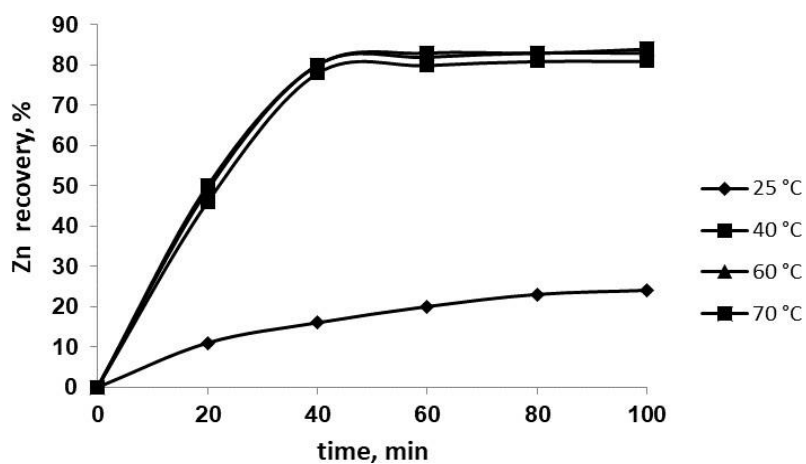$$ZnFe_2O_{4\,(solid)} + H_2SO_{4(aq)} + H_2O_{(liq)} \rightarrow ZnSO_{4(aq)} + 2Fe(OH)_{3(solid)} \tag{3.4}$$

Kinetics
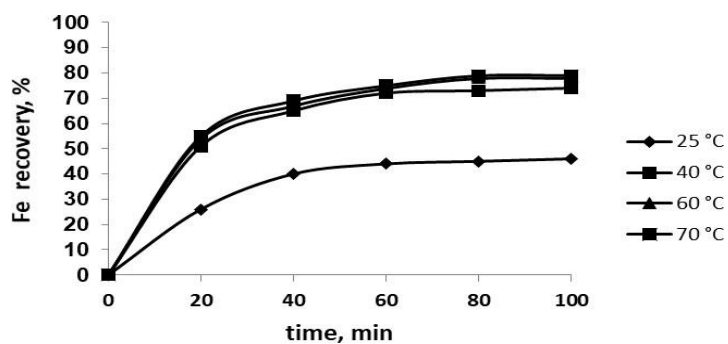
The influence of temperature and leaching process duration on the recovery of copper, zinc and iron into the solution at pH = 2.4 is presented in Figure 3.1.
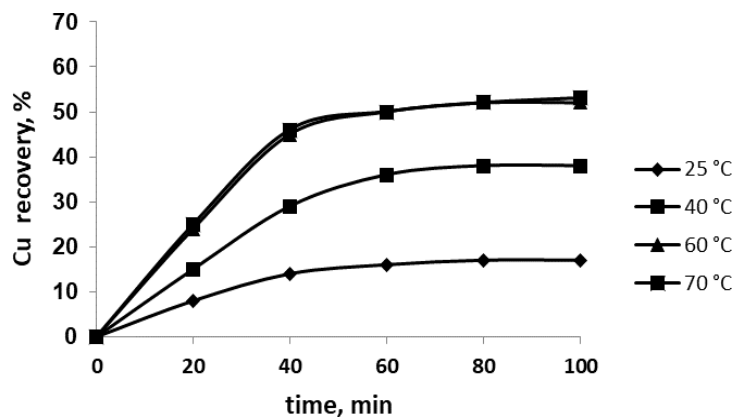
a)

b)

c)

Figure 3.1 **-** Influence of the temperature and leaching process duration on recovery metals in sulfuric acid solution (10 g. of slag (-200 mesh), 300 rpm): (a) Cu, (b) zinc, (c) iron [100]

It can be seen, increasing the temperature and duration of leaching to the particular values resulted in an increase in the recovery of Cu, Zn and Fe into the solution. Values of metals extraction reach the plateau after 1 hour of leaching. The increase in temperature above 60 °C in all cases had practically no effect on the extraction of the metals into the solution. The maximum extractions achieved under the mentioned conditions were, wt. %: Cu 53.2; Zn 84.2: Fe 79.7.

Shrinking core model (SCM) was used to determine the kinetics of the process [41].

The good linear tendency for $1 - (1 - X_{Me})^{1/3} = k_{exp}\tau$ vs. time dependence indicates that the rate of leaching of all the mentioned metals at all the temperatures studied is controlled by the chemical reaction on the particle's surface (Figure 3.2).

From the data presenting the following kinetic parameters of the processes were calculated: (i) the reaction rate constants (k) at the three temperatures studied, (ii) apparent values of the activation energy (E_a), and (iii) the values of the pre-exponential factor (A) (Table 3.1) [100].

Table 3.1 - Kinetic parameters of leaching slag sample in 1M sulfuric acid solution [100]

T, K.	Cu			Zn			Fe		
	k, min^{-1}	$E_a, kJ/mol$	A, min^{-1}	k, min^{-1}	$E_a, kJ/mol$	A, min^{-1}	k, min^{-1}	$E_a, kJ/mol$	A, min^{-1}
298	0.0013			0.0030			0.0022		
313	0.0020	28.1	111.4	0.0045	23.1	236.7	0.0028	16.5	174.2
343	0.0029			0.0062			0.0034		
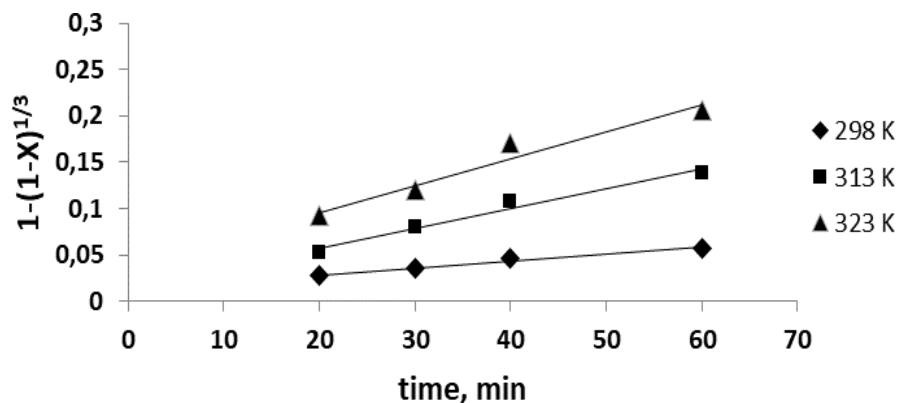
(a)

Figure 3.2 - Plot of $1 - (1 - X_{Me})^{1/3} = k_{exp}\tau$ vs. time for Cu, Zn and Fe recovery according to SCM at different temperatures:
a) Cu; b) Zn; c) Fe, page 1; [100]
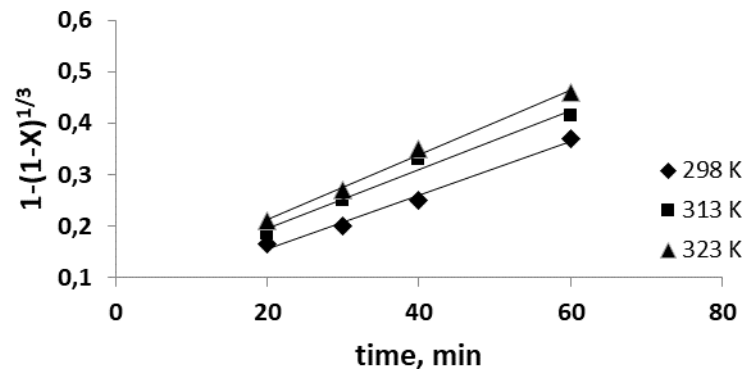
(b)

(c)

Figure 3.2 , Page 2 [100]

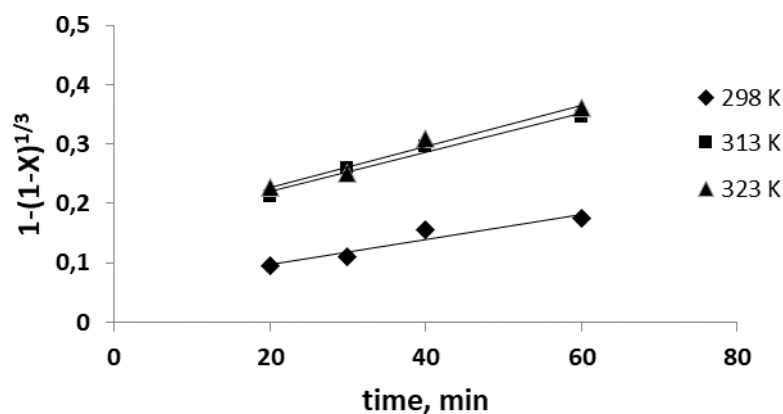The consumption of sulfuric acid is one of the most important parameters determining the economics of the leaching process. The deficiency of acidity of the solution not only reduces the degree of extraction of the target components into the solution but also leads to a decrease in the rate of the leaching process. Excess acid leads to difficulties in processing the final solution; in addition, the overrun of sulfuric acid is economically inexpedient. Consequently, it was important to determine the maximum pH of the solution, which ensures maximum recovery of zinc and copper into the solution.

Figure 3.3 demonstrates the pH dependence on the recovery of Cu, Zn and Fe into solution during the sulfuric acid leaching process under the following conditions: temperature 70 °C, leaching duration 1h. At pH = 2, 5 the recovery of metals into the solution within 1 h was, wt. %: Fe 84. 7 %, Zn 73. 9 %, Cu 48. 8 %. The decrease in pH to 2. 4 did not change the extraction of iron into the solution; at the same time, extraction of zinc and copper increased to 79, 6 % and 53, 2 %, respectively. A further decrease in pH to a value of 2.3 led to an increase in the extraction of copper to 58. 7 %, while the values of extraction of iron and zinc remained at the same level. A decrease in pH below 2. 3 did not lead to changes in the extraction of the metals.
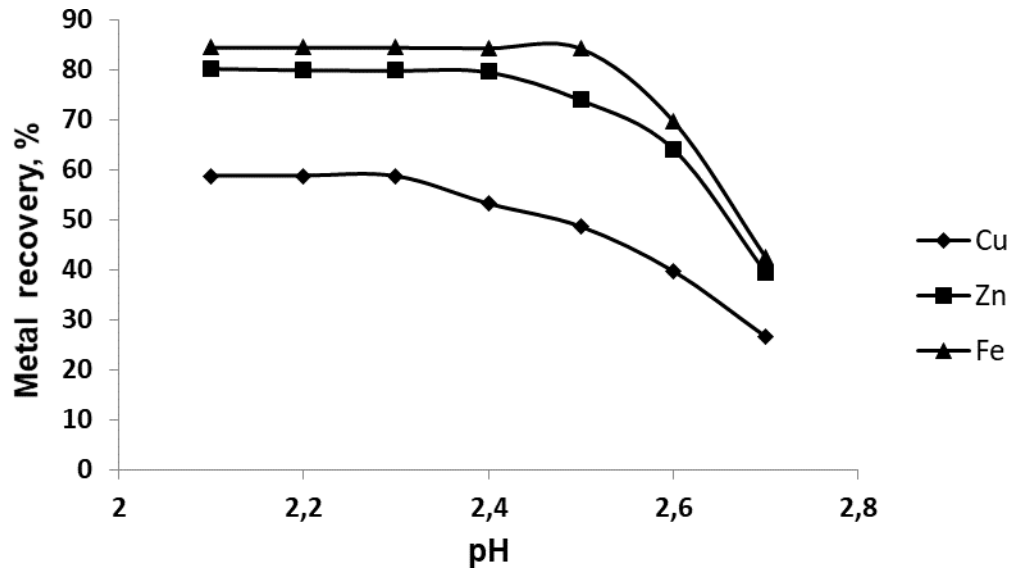
Figure 3.3 - Dependence of metals recovery on the pH of solution [100]

Sulfuric acid leaching can be used to recover Cu, Zn and Fe to the solution after grinding the initial slag to the particle size -200 mesh. Increasing the temperature and duration of leaching to the particular values resulted in an increase in the recovery of Cu, Zn, and Fe into the solution [100].

3.1.2 Sulfuric acid leaching of non-activated slag sample in presence of potassium dichromate

Slag sample characterization

In this section, another slag sample was used. Fayalite (29.6 wt. %), ferrosilite (26.3 wt. %), magnetite (9.5 wt. %), and zinc ferrite (14.9 wt. %) were identified by XRD analysis (DRON-3) as major components of the slag sample. Most of the copper was in the form of copper sulfides, such as chalcocite, bornite, and chalcopyrite (1.1 wt. %).

The slag sample was crushed and then sieved. The fraction of – 200 mesh of the slag was subjected to further treatment. The bulk density of the slag sample obtained by dividing the weight of the sample by its volume was 3100 kg m^{-3}.

Leaching chemistry

Potassium dichromate is a powerful oxidizing agent in an acidic medium. In the presence of dilute sulfuric acid, it liberates nascent oxygen.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + \text{Nascent oxygen } 3(O) \qquad (3.9)$$
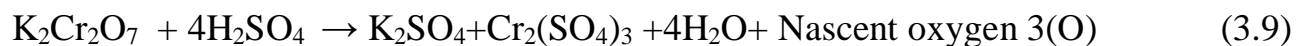
The reduction of dichromate ion in acidic solution:

$$Cr_2O_7{}^{2-} + 14\,H^+ + 6\,e \rightarrow 2Cr^{3+} + 7\,H_2O \qquad (3.10)$$

The standard redox potential of dichromate ion ($E_0 = 1.33$ V) is adequate to oxidize almost all metal sulfides [101].

The positive effect of the presence of potassium dichromate on copper recovery can be explained by the interaction of $Cr_2O_7^{2-}$ with copper sulfide minerals in an acidic medium following Eq. 3.11 (on an example of chalcocite dissolution):

$$3\ Cu_2S + 5\ K_2Cr_2O_7 + 23\ H_2SO_4 \leftrightarrow 6\ CuSO_4 + 5\ Cr_2(SO_4)_3 + 5\ K_2SO_4 + 23\ H_2O \qquad (3.11)$$
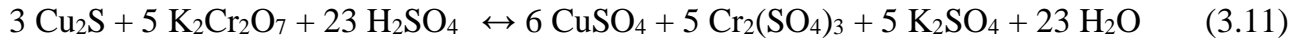
To demonstrate the oxidation-reduction processes, Eq. (3.12) can be rewritten as follows:

$$3\ Cu_2S + 5\ Cr_2O_7^{2-} + 46\ H^+ \leftrightarrow 6\ Cu^{2+} + 10\ Cr^{3+} + 3\ SO_4^{2-} + 23\ H_2O \qquad (3.12)$$
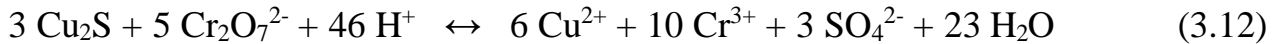
The equilibrium constant of Reaction (3.11) can be used to estimate the completeness according to the following equation:

$$\Delta_r F_T^0 = -RTlnK_c + RTlnC\ _{products}\ /C\ _{reactants} \qquad (3.13)$$

where $\Delta_r G_T^0$ is the free energy of the reaction, R is the universal gas constant, T is the absolute temperature, and K is the equilibrium constant of a chemical reaction. This requires an excess of potassium dichromate and sulfuric acid in comparison with the stoichiometrically calculated amounts [52].

Leaching kinetics

The dependences of Cu, Zn, and Fe recovery into solution with H_2SO_4 and $K_2Cr_2O_7$ concentrations presented in Figure 3.4 (a-c) demonstrate that the recovery of Fe and Zn increases significantly with the increase of the acid concentration up to 0.5 M in absence of dichromate.
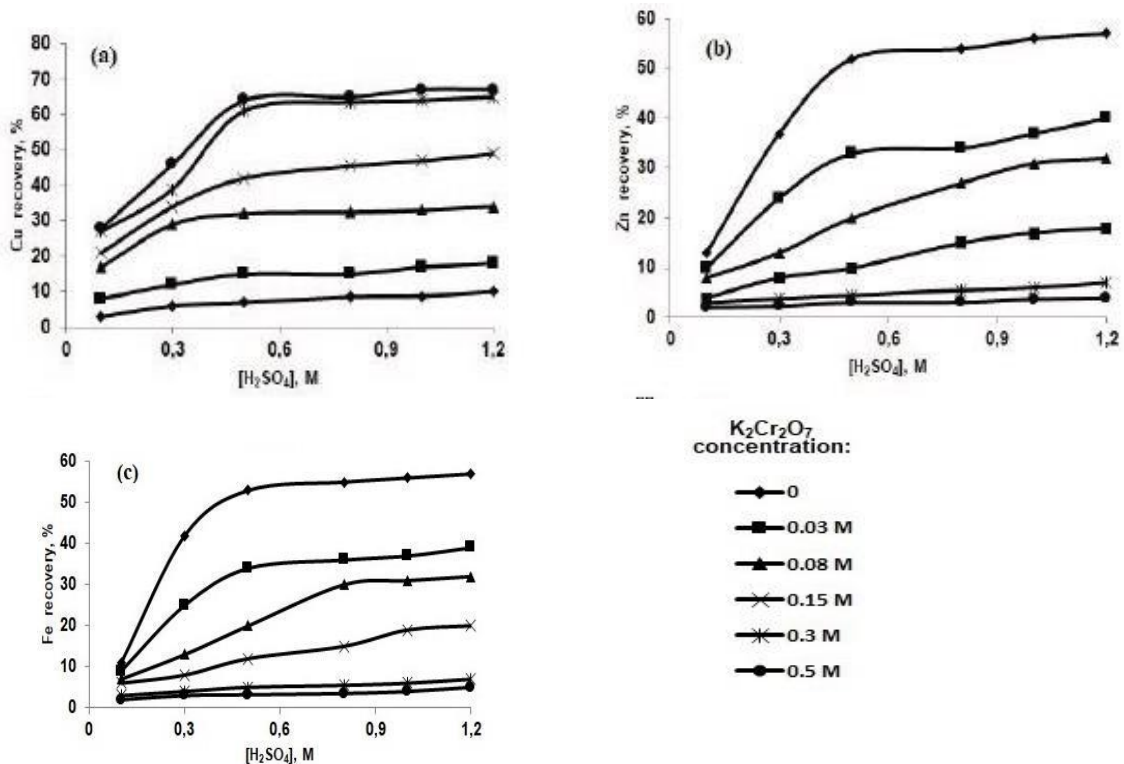

Figure 3.4 - Influence of H_2SO_4 and $K_2Cr_2O_7$ concentrations on the metals recovery (S:L = 15 g: 1 L, 120 min, 298 K) [102]

The maximum values of extraction of zinc and iron are 57 % and 56 %, respectively. The increase of Cu recovery is not significant and these values remain at the level of 8 % – 9 % up to 1.2 M sulfuric acid. The presence of $K_2Cr_2O_7$ in the solution has a positive impact on the recovery of copper; this value reaches 68% when 0.5 M $K_2Cr_2O_7$ is added to the solution. The recoveries of both Zn and Fe, on the contrary, decrease in presence of $K_2Cr_2O_7$ and reach 4 %-5 % when 0.5 M of dichromate is added. This fact is in agreement with the results obtained by Altundogan and co-workers [53] who studied the leaching of a converter slag under similar conditions. The mentioned scholars point out that the fact of Fe and Zn recovery decrease in presence of dichromate ions is due to passivation of the slag particles surface by adsorbed $Cr_2O_7^{2-}$ and/or $HCrO_4^-$. The adsorption of these ions inhibits the probability of the contact of H_3O^+ ions with major mineral phases of the slag. Another version of the very low extraction of iron reported in ref. [103] is the formation of a sparingly soluble jarosite analogue.

Table 3.2 demonstrates the mineralogical composition of the solid residue after leaching under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4, a solid: liquid ratio = 15 g: L, 120 min, 298 K [102]. The weight of the washed and dried precipitate is 16.5 g. It is seen that a hardly soluble compound $KFe_3(CrO_4)_2 (OH)_6$ is formed as a result of the solid precipitate leaching. According to the stoichiometric calculations, the iron content in $KFe_3(CrO_4)_2(OH)_6$ is 45 % of the iron in the original slag. Thus, the extraction of iron from the slag into the solution during the leaching process is 50 %. Thus 90 % of this amount is precipitated as $KFe_3(CrO_4)_2(OH)_6$. This fact confirms the version stated in [103].

Table 3.2 - A mineralogical composition of the solid residue after leaching (0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4, S: L = 15 g: 1 L, 120 min, 298 K) [102]

Compound	wt. %
Fe_2SiO_4	21.7
$FeSiO_3$	21.0
$ZnFe_2O_4$	12.2
Fe_3O_4	7.6
$CaSiO_3$	2.1
$CaSO_4$	1.6
$KFe_3(CrO_4)_2(OH)_6$	18.4
ZnS	1.0
$CuFeS_2$	0.9

It is found that the linear dependence of the degree of Cu recovery on the leaching duration at 298 K, 318 K and 358 K is determined by Eq. (3.6) by SCM theory.

This fact means that the limiting stage of copper leaching from the slag refers to the mass transfer to the fluid layer that surrounds the solid particle.

The processes of extraction of zinc and iron are limited by the chemical reaction on the surface of the particle by Eq. (3.7).

The apparent rate constants of the reactions of copper, zinc and iron recovering at the three temperatures investigated are given in Table 3.3.

Table 3.3 - Experimental apparent rate constants of the reactions of Cu, Zn, and Fe recovery from the slag [102]

Temperature, T/K	Experimental apparent rate constant, $k \times 10^{-3}$/min^{-1}		
	Cu	Zn	Fe
298	0.724	0.626	0.619
318	1.971	1.915	2.017
358	6.857	12.250	12.140

The calculated values of E_a refer to 34.60 kJ/mol for Cu, 43.96 kJ/ mol for Zn and 44.33 kJ/mol for Fe. The kinetics of the nonferrous metals and iron extraction from the copper converter slag by sulfuric acid leaching in presence of potassium dichromate is studied in [102]. The value of the activation energy of Cu recovery found by this method is close to that found in ref. [103]. The values of E_a referring to Zn and Fe recovery under the conditions investigated are determined for the first time.

The maximum copper recovery (68 %) was obtained in case of leaching under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4, a solid-to-liquid ratio = 15 g: 1 L, 120 min, 298 K. The results obtained in the present work can be used for selective extraction of copper from copper smelter slag.

Sulfuric acid leaching of slag, as a rule, is characterized by low efficiency and has some disadvantages. For example, the known method of leaching for converter slag with a solution of sulfuric acid under an oxygen pressure of 0.45-0.59 MPa and a temperature of 130 °C is economically unacceptable to extract copper from poor slags with a copper content of about 0.5 - 1.5 % [105].

The sulfuric acid in a combination of hydrogen peroxide does not allow using this method for processing waste slags of copper smelting production due to the high consumption (more than 60 litres per 1 ton of slag) [50].

In the work of Deng and Ling T. Y. (2007) [104] they heated the pulp to 250 °C, however, this method doesn't allow to use this in large scale production due to the high cost of the process.

In the work [106], sodium chlorate was used, and steam or steam-water emulsion was supplied to the resulting mixture. The disadvantage of the method is the use of steam or steam-water emulsion for heating the reaction mixture, which reduces the economic feasibility of using the method for processing waste slags.

Consequently, to intensify the leaching process the method of mechanical activation was used recently. Mechanical activation is understood as increasing the free energy of solid systems by mechanical effects, changing the inner morphology of solids, e.g. reducing the particle size of dispersed systems, or increasing the specific surface area by deformation.

For this reason, mechanical activation was be applied as the main procedure to reduce the duration of leaching treatment and give the possibility not to use high temperatures.

3.2 Influence of mechanical activation on leachability of copper smelter slag

Mechanical activation is a method of high-energy mechanical action on a solid. Grinding during impact, impact-abrasion, or abrasion leads to the accumulation of structural defects in solid particles, phase transformations, and even amorphisation of crystals, which affects their chemical activity.

Assumptions for using MA, as follows: 1) to increase specific surface area; 2) to obtain amorphous phase; 3) to obtain particles with more reactive abilities during possible mechanochemical reactions.

In this dissertation work, mechanical activation has been applied to copper smelter slag sample before sulfuric acid leaching, independently, as well as in the presence of oxidants.

3.2.1 Sulfuric acid leaching of mechanically activated copper slag

To avoid these disadvantages with sulfuric acid leaching researchers in their work [106] had subjected the copper smelter slag to mechanical activation in a planetary ball mill at a speed of at least 350 rpm and a duration of at least 45 minutes. The product of mechanical activation is then leached with an aqueous solution of sulfuric acid. It is assumed that mechanical activation of slag leads to partial decomposition of fayalite [107]. Firstly, the silicon content in the liquid part of the pulp decreases, which improves its filterability. Secondly, mechanical activation leads to the "opening" of copper-containing slag minerals, which makes them more accessible to the leaching agent (sulfuric acid).

The considered method of processing copper-containing slag has two significant disadvantages. The first one is associated with significant difficulties in the implementation of a continuous process of mechanical activation of slag in a planetary mill. Due to the design features of such a mill, when processing industrial volumes of material (tons per hour), the equipment quickly fails. The second disadvantage is associated with the high energy consumption of planetary mills. The indicated disadvantages of the method do not allow it to be used in industry for processing relatively poor copper slag.

The objective of this work [108] is to develop a method for extracting copper from copper smelter slag, which makes it possible to reduce the energy consumption of the process in comparison with the previous work [109], and also to exclude the

use of a planetary mill as an apparatus in which it is difficult to process dump slag on an industrial scale in a continuous mode.

The technical result is a decrease in the energy consumption of the process of extracting copper from copper smelter slag, as well as the choice of an apparatus that allows processing dump slag on an industrial scale in a continuous mode.

Attrition mill, being a high-energy mill for mechanical grinding, mixing and agglomeration of materials due to the impact of balls and abrasion is used, as a planetary mill, for the mechanical activation of materials.

Examples from Table 3.4 show the influence of the rotation speed, as well as the duration of the MA process, on the degree of copper extraction into the solution.

Comparison of the experimental results for examples 1-10 shows the following (Table 3.4). At a rotational speed of 500 rpm, the degree of copper extraction into the solution does not exceed 45 ± 1%. At a rotational speed of 600 rpm and an MA duration of 70 min, the extraction of copper into solution is 56 ± 1%, and this value practically does not increase with an increase in the MA duration to 120 min. An increase in the rotational speed of the attritor shaft to 750 rpm does not increase the degree of copper extraction into the solution but worsens the economic performance of the method due to an increase in the energy consumption of the MA process.

Table 3.4 – Influence of the rotational speed of the attrition mill and the duration of the MA process on the degree of copper extraction into solution [108]

Example	Rotation speed, orb./min	Duration of mechanical activation, min	Copper recovery, %
1	600	70	56±1%
2	500	75	38±1%
3	500	90	44±1%
4	500	120	45±1%
5	600	60	41±1%
6	600	90	56±1%
7	600	120	57±1%
8	750	60	52±1%
9	750	90	57±1%
10	750	120	57±1%

To find the effect of the mode of mechanical activation (dry or wet), experiments were performed on both modes [110, 111].

3.2.2 Influence of dry and wet mechanical activation for sulfuric acid leaching
Mineralogical composition determined by DRON -3, were as follows: Fe_2SiO_4 - 76.3 wt. %), Fe_3O_4 23.7 wt. %. From the XRD analysis (Figure 3.5), it can be seen a sharp (75-90%) decrease in the intensity of reflexes of fayalite and magnetite on the X-ray MA slag in comparison with the original sample.

The X-ray powder diffraction patterns of the considered slag sample showed that it is composed of different phases. A well-specified phase indicated from the XRD picture is fayalite (Figure 3.5), which is the most abundant phase composing this material and traces of some compounds such as chalcopyrite, sulfides of zinc and copper are distributed in small quantities. The very high background and weak intensities of the diffraction lines of the mentioned phases showed a significant amorphous content of the slag. Silicate phases are displayed as major and sulfides as minor phases.

The influence of MA duration (in case of dry milling 20 min. and wet milling 45 min.) and the presence of water (30 mL) on the structure and morphology of the sample were investigated. The results of SEM analysis are shown in Figure 3.6.

As can be seen from Figure 3.6 after 20 minutes of dry milling, the change in size is insignificant, after 40 minutes the size of the crystallites sharply decreases by about 1000 times. As 1 hour passes, the particles agglomerate again. The agglomerate formation is common during dry grinding and is usually explained by the agglomeration of the structurally modified particles following the initial reduction of particle size. This happens because of the tendency of the activated material to reduce its surface free energy.
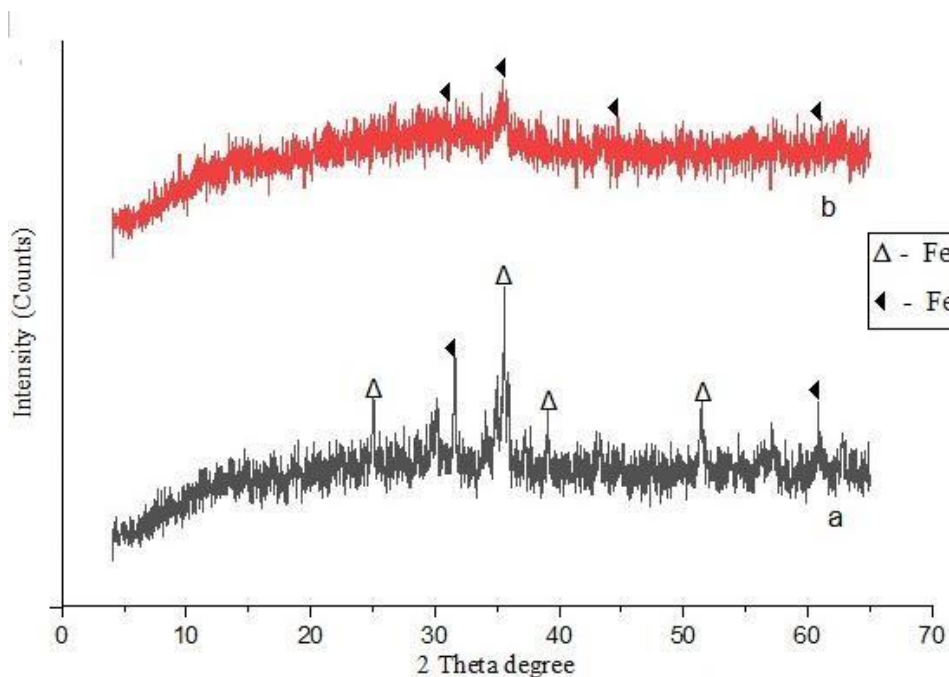

Figure 3.5 - XRD spectrum of initial (a) and
mechanically activated slag samples in dry (b) [110]

A greater degree of amorphisation occurs during wet milling than dry milling. Grinding in water favours the formation of finer particles giving a greater specific surface area [111].
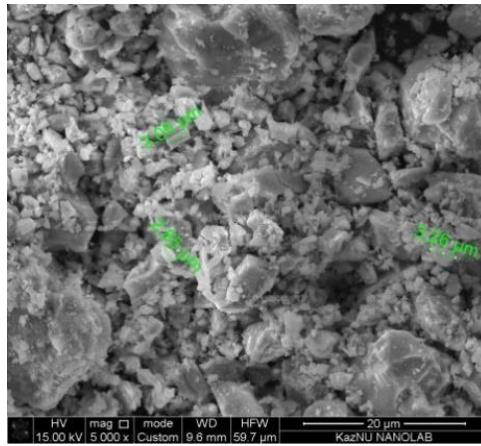
Initial
(a)
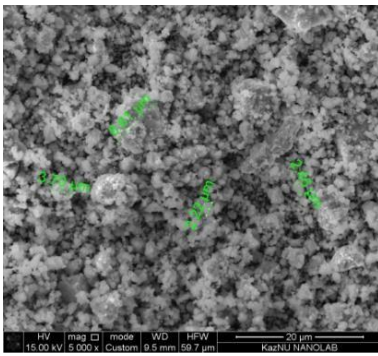
t$_{MA}$=20 min
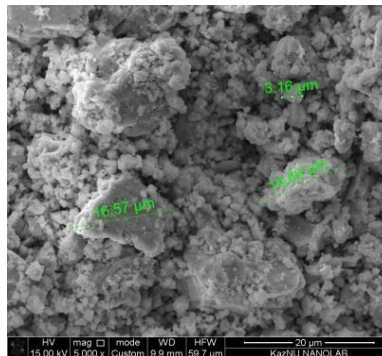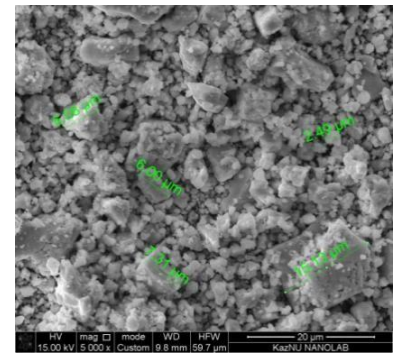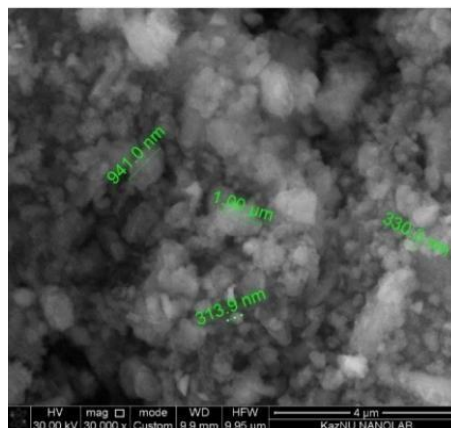

t$_{MA}$=40 min
dry milling
(b)

t$_{MA}$= 60 min

t$_{MA}$= 45 min
wet milling
(c)

Figure 3.6 - SEM pictures of initial (a) and mechanically activated slag
samples in dry (b) and wet (c) conditions [110,111]

The results of leaching experiments are presented in Fig. 3.7 (a-c). It was found that from dry mechanically activated slag about 47 % Fe, Zn and Cu passed into the solution after 45 min of leaching, as the degree of extraction of the specified components from the initial sample did not exceed 17-20 % for 90 min. This effect can be partially explained by amorphisation and decomposition of the sample during mechanical activation [107].

In the case of a wet mechanically activated sample [111], after 1 hour of leaching 91 % Cu, 89 % Zn passed into the solution. The silicon content in the liquid part of the pulp, found by the method of optical emission spectroscopy within inductively coupled plasma, was less than 40 mg/L, which provides easy filterability of the pulp. Leaching of the original slag without the use of MA, under the above-mentioned conditions, led to the formation of a hard-to-filter gel. The degree of extraction of copper and zinc did not exceed 47 and 40%, respectively.
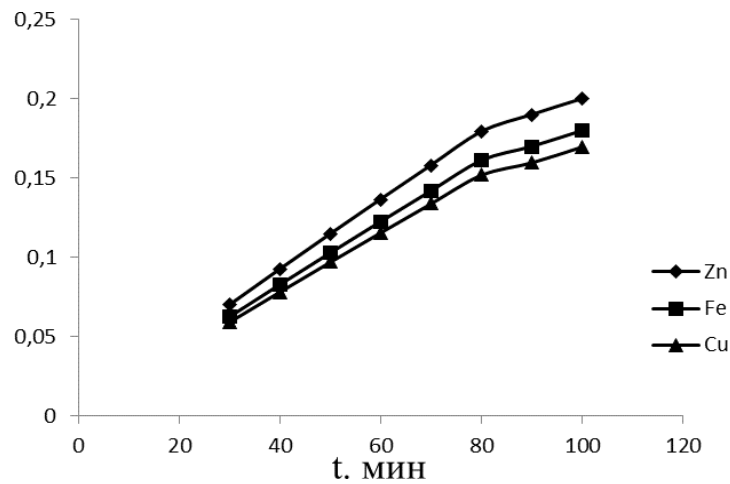
(a)
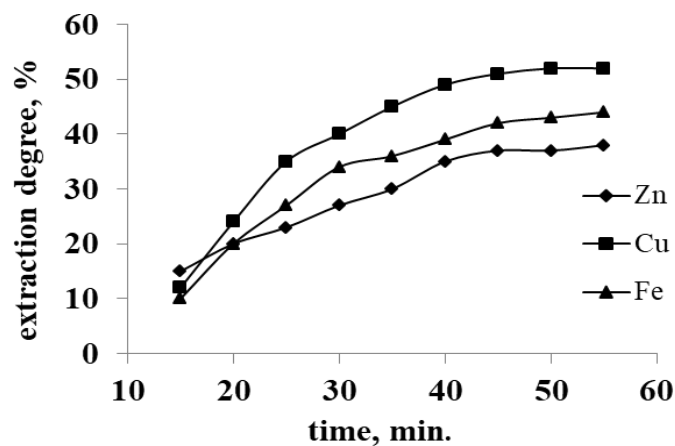
(b)

Figure 3.7 - Kinetics of leaching of a slag sample before and after mechanical activation at T = 298 K: a) initial slag; b) dry milling; c) wet milling :
Page 1 [110,111]

(c)
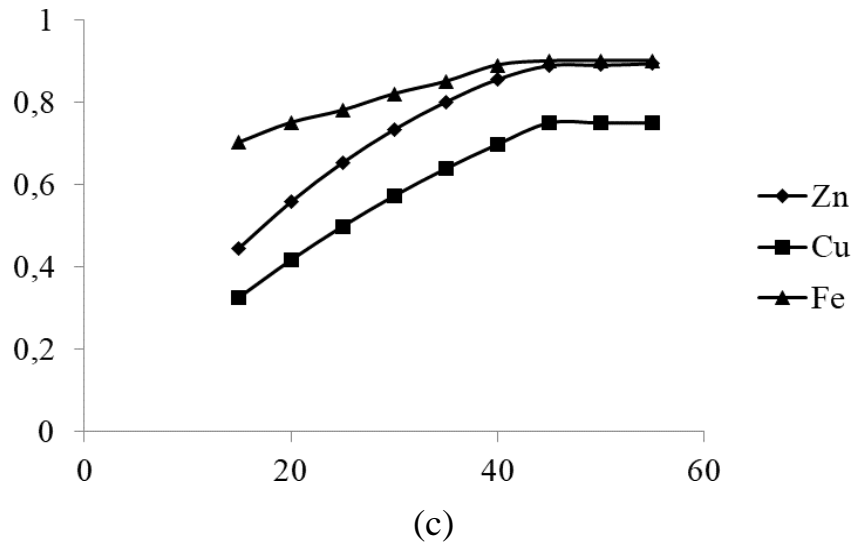
Figure 3.7 – Page 2 [110,111]

We associate an increase in the degree of extraction of zinc and copper into a solution with a partial amorphisation of the minerals of the slag, mainly fayalite. This fact is confirmed by XRD analysis (Figure 3.5). A possible reason for the decrease in pulp viscosity is the decomposition of fayalite, with the formation of iron oxide (II) and silicon dioxide [107].

3.2.3 Sulfuric acid leaching of mechanically activated slag sample in presence of hydrogen peroxide and sodium bicarbonate

Slag sample characterization and its mechanical activation

The results of the semi-quantitative analysis of XRD (Figure 3.8) showed that the slag sample consists of major phases, as well as Fe_2SiO_4, $CuFe_2O_4$, and minor phases, as $CuFeS_2$, ZnO, Na_6ZnO_4, ZnS. Identification of compounds: $CuFeS_2$, ZnO and Na_6ZnO_4 was carried out along one line. This reduces the accuracy of identification.

Particle size and shape are factors that determine surface area. Mostly the reactions involved in the processing of minerals are heterogeneous (i.e. the reaction takes place at the interface between the phases), and therefore it occurs that the rate will change with the interfacial area.
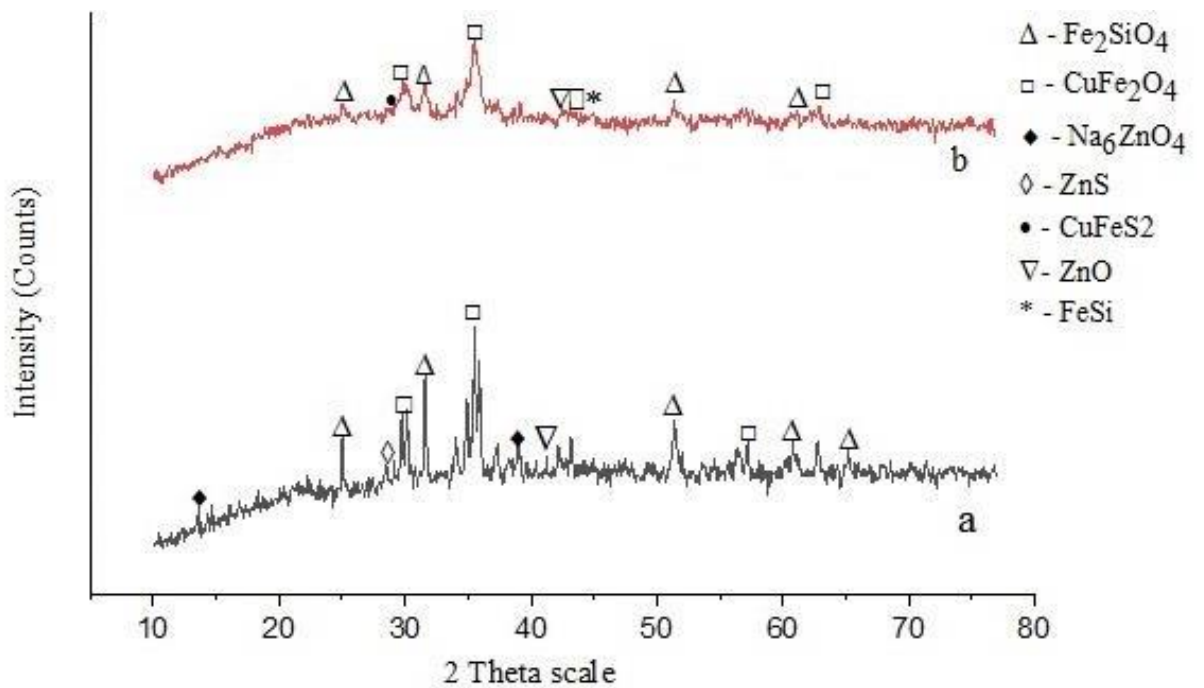
Figure 3.8 - XRD spectrum of initial (a) and mechanically activated (b)
(dry milling – t_{MA}= 20 min) slag sample

After mechanical activation, the phase of the crystals has not changed (Figure 3.10b), the size of micro crystallites has decreased by half. The sizes of crystal lattices have slightly changed (Table 3.5).

Table 3.5 - Lattice parameters and microcrystallite sizes of the mechanically activated sample (dry milling)

Initial			t_{MA} = 20 min		
Fe_2SiO_4					
micro crystallite sizes					
L=940 Å			L=490 Å.		
a=4.8109 Å,	b=10.4765Å	c=6.0857Å	a=4.8160 Å,	b=10.4690 Å,	c=6.0990 Å.
$CuFe_2O_4$					
micro crystallite sizes					
L=770 Å.			L=310 Å		
a=8.3670 Å.			a=8.3642 Å.		

Leaching kinetics is affected by the particle size of the material that is leached, and generally, a smaller particle size gives faster leaching kinetics, since finer particles have a larger surface area. Thus, we expected that a decrease in the size of micro crystallites of minerals should increase the leachability of the slag sample.

Leaching experiments

Hydrogen peroxide was used for the oxidation of sulfides. On the other hand, this reagent oxidizes iron (II) to iron (III), with iron precipitating out of the solution predominantly in the form of iron metal hydroxide FeOOH. By using this reagent,

both silica gel arrangement and iron co-extraction are evaded. Sodium bicarbonate was used to neutralize and precipitate zinc and iron compounds in the slurry before filtration.

During the first stage of sulfuric acid treatment without additional agents, fayalite will form silicic acid, as shown in Equation 3.2, chalcopyrite promote the elemental sulfur formation (Equation 3.1), and sulfate, oxides and hydroxides of iron could be formed after leaching of zinc ferrite (Equation 3.3-3.5). Further reactions occur during the next stages of leaching.

$$2FeSO_4 + H_2SO_4 + H_2O_2 \rightarrow Fe_2(SO_4)_3 + 2H_2O \qquad (3.15)$$

$$2CuFeS_2 + 18H_2SO_4 + H_2O_2 \rightarrow 2Cu^{2+} + 2Fe^{2+} + SO_4^{2-} + 18H_2O \qquad (3.16)$$

$$2CuFeS_2 + 10H^+ + 5H_2O_2 \rightarrow 2Cu^{2+} + 2Fe^{2+} + S + 10H_2O \qquad (3.17)$$

$$6CuSO_4 + 2H_2O_2 \rightarrow 2Cu_3(SO_4)_2(OH)_2 + 2SO_2 + 2O_2 \qquad (3.18)$$

$$Fe_2(SO_4)_3 + NaHCO_3 \rightarrow Na_2SO_4 + Fe(HCO_3)_3 \qquad (3.19)$$

$$H_2SO_4 + 2NaHCO_3 \rightarrow 2CO_2 + 2H_2O + Na_2SO_4 \qquad (3.20)$$
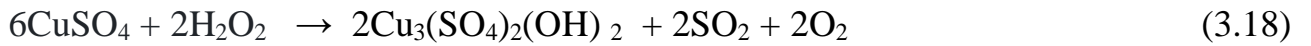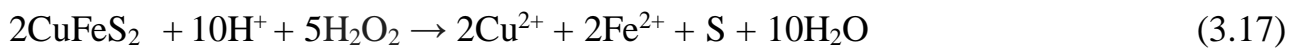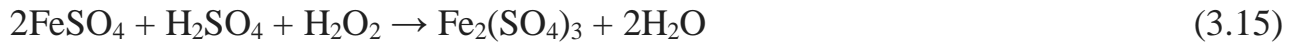
XRD analysis of the residue (Figure 3.11) after leaching showed the presence of $Cu_3(SO_4)_2(OH)_2$, $CaSO_4 \cdot 2H_2O$, Na_2SO_4, $CaCO_3$. The contents of mentioned compounds were, 11, 4 %, 41,7%, 16,8 %, 14,1 %. The weak intensity of the peaks indicated the predominance of the amorphous phase in the solid residue.
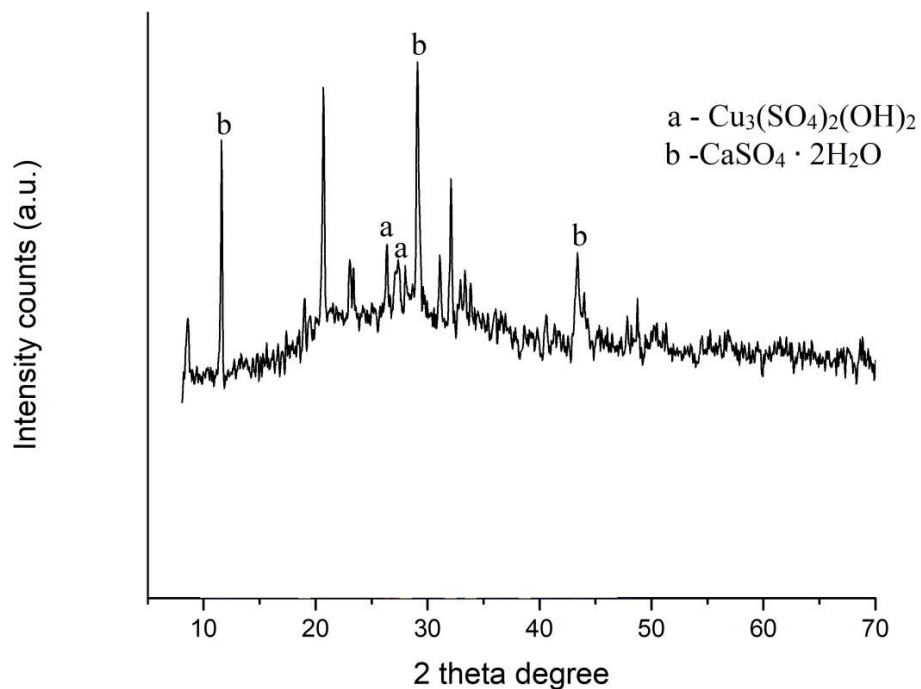
Figure 3.9 - XRD spectrum of solid residue after leaching treatment

After leaching 56, 4 % of copper have passed into solution. A practically large part of iron and zinc compounds have been dissolved, more than 50 % were obtained in the solution.

By using sulfuric acid and hydrogen peroxide, both silica gel formation and iron co-extraction are avoided during leaching of copper smelter slag.

3.3. Sulfuric acid leaching of mechanically activated slag in the presence of dichromate

3.3.1 Characterization of slag sample

The content of targeted metals in the initial copper smelter slag determined by atomic absorption spectrometry was as follows: 1.2 % of copper, 22.9 % of iron, 0.48 % of zinc and 37.4% of silicon. Also, 1.25 % of potassium has been detected.

The X-ray powder diffraction pattern of the used slag sample showed that it is composed of different phases (Figure 3.12), namely of fayalite, Fe_2SiO_4, ferrosilite, $FeSiO_3$ and further phases which crystallize in the same system and therefore their diffraction peaks significantly overlap (in particular, zinc ferrite, $ZnFe_2O_4$ cuprospinel $CuFe_2O_4$ and magnetite Fe_3O_4). In addition, chalcopyrite $CuFeS_2$ is also present in small quantities. The very high background and weak intensities of the diffraction lines of the mentioned phases hint at a significant content of amorphous material in the slag [112].

a - Fe_2SiO_4 (87-0315)
b - $CuFeS_2$ (80-7740)
c - $ZnFe_2O_4$ (82-1049),
    $CuFe_2O_4$ (74-8585),
    Fe_3O_4 (75-0033)
d - $FeSiO_3$ (72-1509)
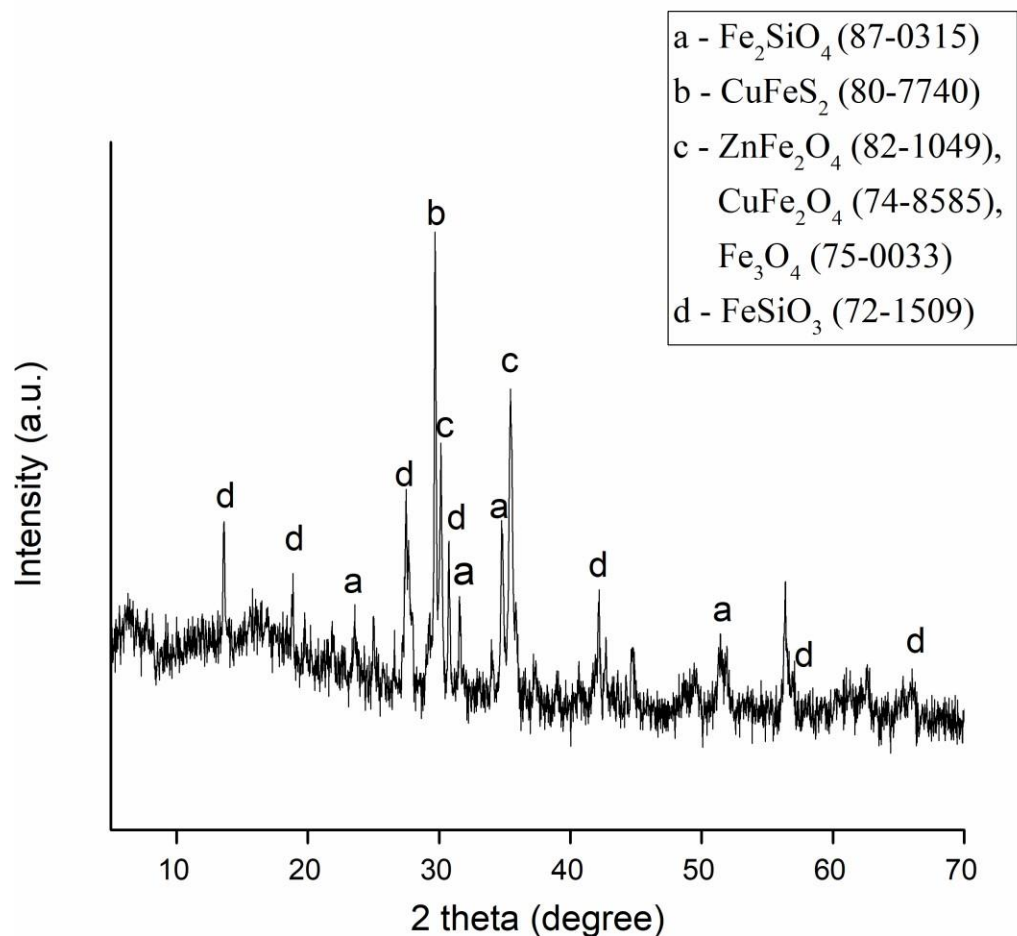
Figure 3.10 - XRD pattern of the starting slag [112]

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3.3.2 Mechanical activation

Selection of the mill type and mode of milling (dry or wet)

At first, mechanical activation in a dry mode in both types of mills was performed. The results of the specific surface area analysis are in Table 3.6.

Table 3.6 -   Specific surface area values for slag subjected to the treatment of different mills in dry conditions [112]

Rotation speed, [rpm]	Ball-to-powder ratio	Duration of treatment, [min]	SSA, $[m^2/g]$
Initial slag			
-	-	-	1.7
Attritor			
600	20:1	20	2.6
600	20:1	100	2.2
Planetary ball mill			
600	20:1	20	4.9
600	20:1	100	4.1

From Table 3.6, it can be seen that upon attrition milling, under dry processing for 20 minutes, at a ball-to-powder ratio of 20:1 and 600 rpm leads to an increase in SSA to 2.6 m^2/g. Increasing the milling time to 100 min reduces SSA to 2.2 m^2/g due to agglomeration. The agglomerate formation is common during dry milling and usually occurs after the initial reduction of particle size, due to the tendency of the activated material to reduce its surface free energy. Massive and compact agglomerates form during intensive dry milling [65]. The planetary ball milling led to higher SSA values (4.9 and 4.1 m^2/g for the slag milled for 20 and 100 min, respectively). Nevertheless, the increase of SSA value using dry milling was not very significant.

In Figure 3.13, SEM images of slag subjected to dry milling in planetary and attrition mills for 20 min are compared. It appears that slightly finer particles are formed in the case of planetary milling (Figure 3.13 b).
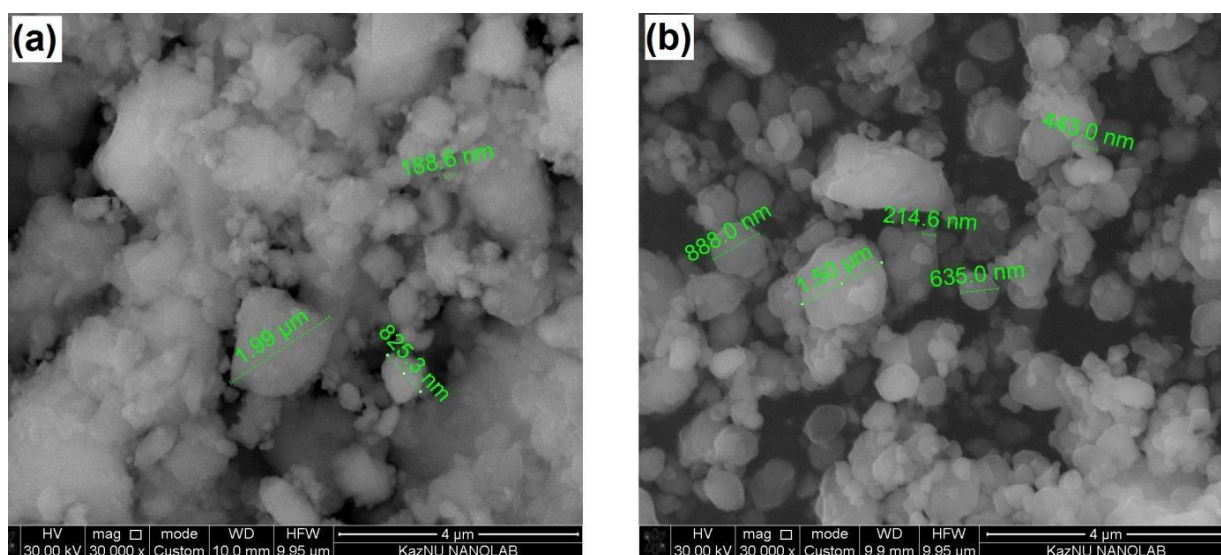
Figure 3.11 **-** SEM images of milled slag samples (dry milling - 20 min, 600 rpm, B : P – 20: 1) in an attrition mill (a) and planetary ball mill (b) [112]

It is known that wet milling can efficiently increase the SSA value [113, 114]. Milling in water favours the formation of finer particles giving a greater SSA, unlike the surface area obtained by dry milling, which changes a little after prolonged milling. Despite the better results obtained for planetary ball milling, it would be difficult to use this mill at an industrial scale due to the high energy demands. Consequently, we have performed the milling under wet conditions in attrition. This time a significant increase of SSA value to13.0 m^2/g has been observed. The duration of this experiment was set to 75 min, as this is an intermediate milling time (between 20 and 100 min used for planetary milling).

The effect of mechanical activation on the crystallinity of the slag was investigated by XRD (Figure 3.14).

The results obtained from XRD measurements showed a reduction in peak height together with peak broadening in both dry-milled samples, and that the amorphisation is more pronounced for the planetary ball milled slag. Activation in the planetary ball mill resulted in a material with a greater disorder, compared to the attrition mill as a result of the high energies applied. The structural disorder due to the increasing abundance of X-ray amorphous content is expressed by decreasing the intensity of diffraction lines. The broadening of diffraction peaks is mainly due to the instrumental effects, crystallite size and lattice strain [65].

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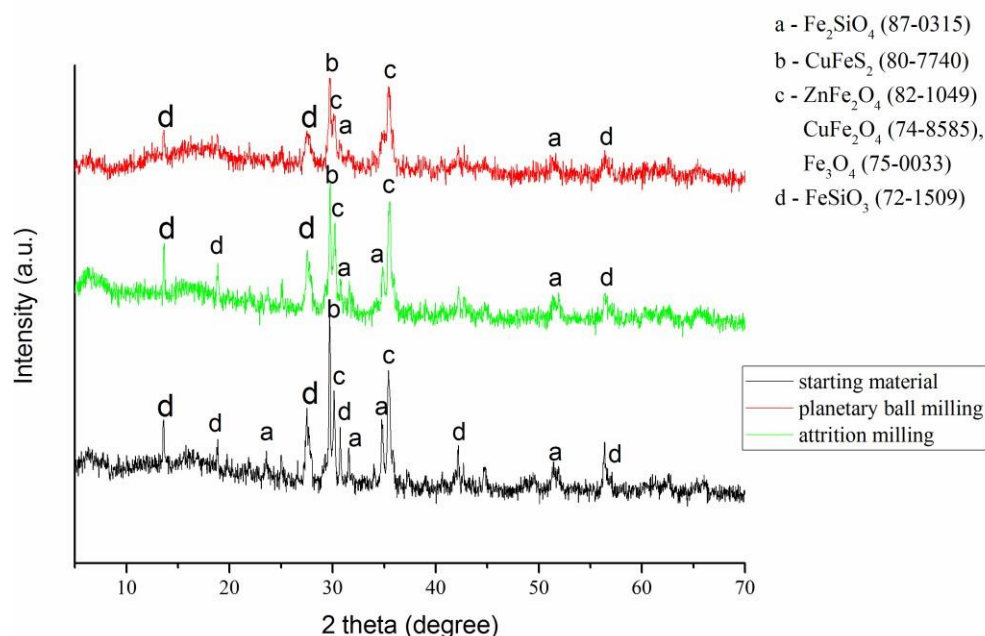
Figure 3.12 - XRD pattern of the slag sample, starting and subjected to dry
mechanical activation in an attritor and planetary ball mill at 600 rpm
for 20 min [112]

Accounting for the scalability of the attrition mill, and the higher SSA values
obtained from wet milling, this type of mill was chosen for further optimization of the
mechanical activation in wet conditions.

Optimization of wet milling in attrition mill

The optimization of three milling parameters (rotation speed, ball-to-powder
ratio and milling time) was carried out using 9 experiments according to Taguchi
design (Table 3.7).

The observed SSA values were much higher than that of dry-milled slag in all
cases (Table 3.6). Moreover, in 8 out of 9 cases, the observed SSA values were
higher than in the case of a preliminary experiment using wet attrition milling.

Wet mechanical activation of the slag led to some changes in the XRD patterns
(Figure 3.13). The conditions of mechanical activation were the following: M0 –
starting slag sample; M1 – 600 rpm, 50 g, 30 min.; M2 - 600 rpm, 100 g, 75 min.; M3
- 600 rpm, 150 g, 120 min.; M4 – 900 rpm, 50 g, 75 min.; M5 - 900 rpm, 100 g, 120
min.; M6 - 900 rpm, 150 g, 30 min.; M7 – 1200 rpm, 50 g, 120 min.; M8 - 1200 rpm,
100 g, 30 min.; M9- 1200 rpm, 150 g, 75 min. Increasing the ball-to-powder ratio and
milling duration reduced the intensity of the main peaks in the diffractogram. This
fact was especially characteristic of the rotation speed of 1200 rpm. A decrease in the
intensity of diffraction peaks is due to a decrease in the content of the crystalline
phase of minerals due to their amorphisation. Jancke and co-authors demonstrated
that mechanical treatment of $ZnFe_2O_4$ decreased intensity of peaks on diffraction

patterns of milled samples and the broadening of diffraction lines was also observed [118].

Table 3.7 - Specific surface area for copper smelter slag subjected to different milling conditions according to Taguchi design [112]

Experiment number	Rotation speed [rpm]	Sample mass [gram]	Duration of treatment [min]	SSA, [m^2/g]
M1	600	150	30	7.4
M2	600	100	75	13.0
M3	600	50	120	3.8
M4	900	150	75	17.2
M5	900	100	120	20.6
M6	900	50	30	21.6
M7	1200	150	120	43.7
M8	1200	100	30	36.6
M9	1200	50	75	59.4

The obtained SSA values have been taken as responses; the results have been analyzed by the Minitab software using the Taguchi method by *larger-the-better* characteristics (Figure 3.14).

The optimum parameters can be clearly seen from the highest mean values. This accounts for rotation speed 1200 rpm, slag mass of 50 g (the highest ball-to-powder ratio 40) and milling time 75 min, which are the conditions of the experiment M9. Therefore, for the subsequent leaching stage, the sample treated at 1200 rpm, sample mass 50 g (*i.e.* ball-to-powder ratio 40:1) and milling time 75 min was chosen.

To determine the influence of individual parameters, the analysis of variance (ANOVA) has been applied (Figure 3.15).

From ANOVA calculations, the rotation speed has a greater influence (88 %) than other parameters, such as milling time (4 %) and mass of samples (2 %). Of the three parameters studied, only the influence of rotation speed is significant (p-value = 0.002). The influence of the other two factors is not significant (the p-value for sample mass and milling time is 0.940 and 0.875, respectively).
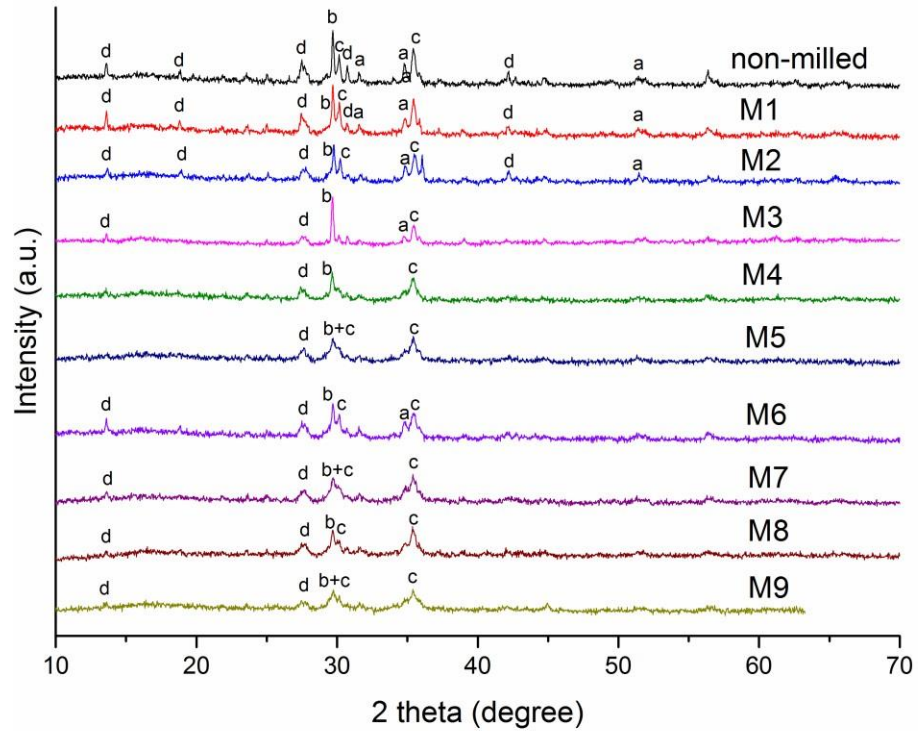
Figure 3.13 - XRD patterns of the starting slag and the slag powders after nine optimization experiments of wet mechanical activation in an attrition mill. Phase identification: a – Fe_2SiO_4 (87-0315), b – $CuFeS_2$ (80-7740), c – $ZnFe_2O_4$, (82-1049), $CuFe_2O_4$ (74-8585) or Fe_3O_4 (75-0033), d– $FeSiO_3$ (72-1509) [112]
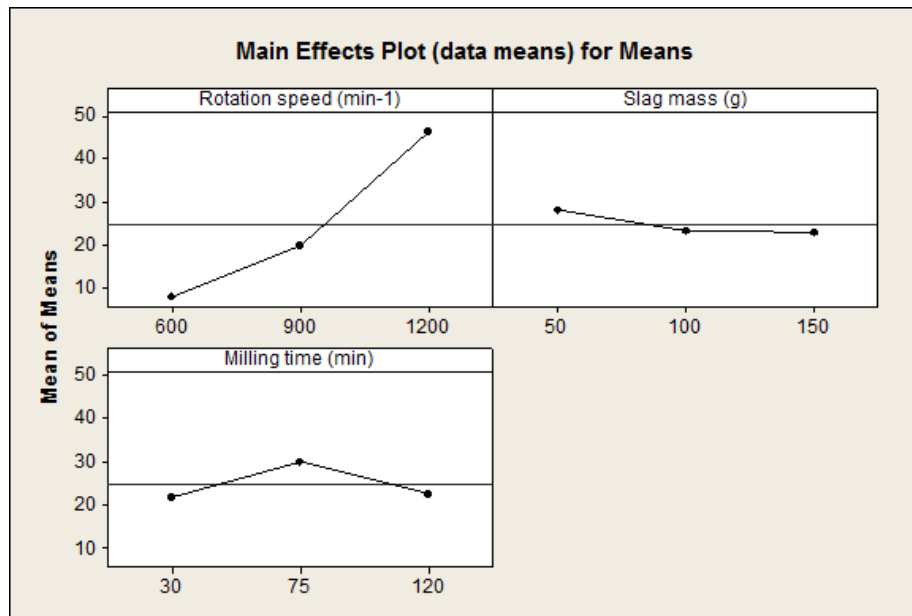

Figure 3.14 - Results of Taguchi calculations in Minitab (mean values) for mechanical activation of slag in AM[112]
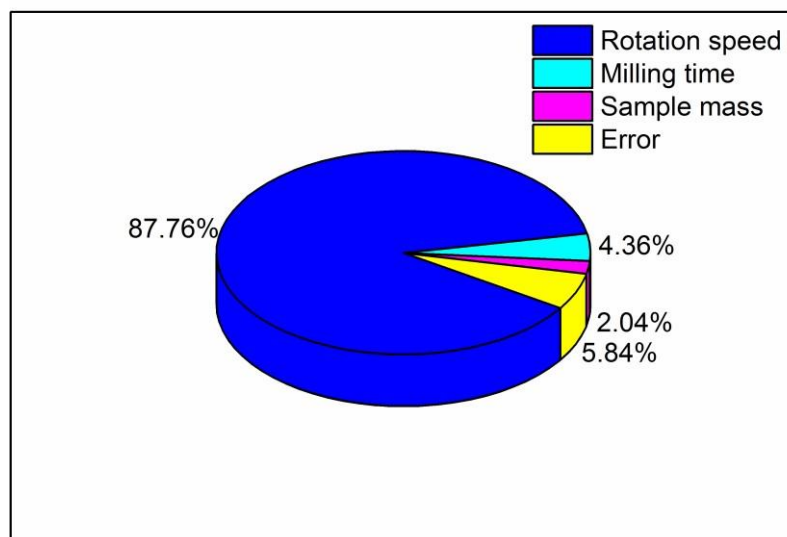
Figure 3.15 - Contribution of rotation speed, sample mass and milling time to the increase of specific surface area according to ANOVA calculations in Minitab [112]

Comparison of wet milling in attrition mill and planetary ball mill under the optimized conditions

After the optimization in an attrition mill, the optimum conditions (*i.e.* that of experiment 9 in Table 3.7) were used also for planetary ball milling (except ball-to-powder ratio which was 20 in this case). The XRD patterns of slags treated under optimum conditions in both mills are provided in Figure 3.16. In the following discussion, the abbreviations AM and PM are used for the milling in attritor, and planetary ball milling, respectively, performed under optimized conditions.

The degree of amorphisation of PM slag is very significant, as the peaks of fayalite have disappeared and that of chalcopyrite is barely visible. The SSA value of this sample was determined to be 126.0 m^2/g. The fact that planetary ball milling is more efficient than milling in an attritor has been confirmed also under the optimized conditions, as the degree of amorphisation is lower for attrition milling (*e.g.*, traces of fayalite peaks can still be detected). Moreover, there also seems to be a clear correlation between amorphisation n detected by XRD and an increase in the specific surface area values. In general, SiO_2 and one or more from $CuFe_2O_4$, $ZnFe_2O_4$ and Fe_3O_4 phases (represented by peak c) are quite resistant to the effect of milling.

To investigate the effect of mode of milling (wet or dry) and type of mill (planetary or attrition), the selected peaks from the XRD patterns assigned to the identified phases have been subjected to peak fitting. Namely, as a representative of SiO_2, and $CuFeS_2$, the peak at around 13.5 and 29.7 °, respectively has been selected. For Fe_2SiO_4 and $ZnFe_2O_4$, two peaks have been selected. For the fayalite (Fe_2SiO_4) phase, the diffraction peaks at around 31.5 and 34.5° were considered, and for the group of three indistinguishable phases (namely zinc ferrite ($ZnFe_2O_4$), cuprospinel $CuFe_2O_4$ and magnetite Fe_3O_4), the diffraction peaks at around 30.2 ° and 35.5 ° were selected. For simplification, just $ZnFe_2O_4$ is used in the figure and discussion below. Using the Pseudo-Voigt function in Origin software, the peak heights and their full-

width half maximums (FWHMs) for the selected peaks have been obtained. The results for the non-milled slag, those of the milled in a dry mode in both mills (XRD patterns are in Figure 3.12) and the slag samples treated in a wet environment in both devices (XRD patterns are in Figure 3.16) are shown in Figure 3.17.
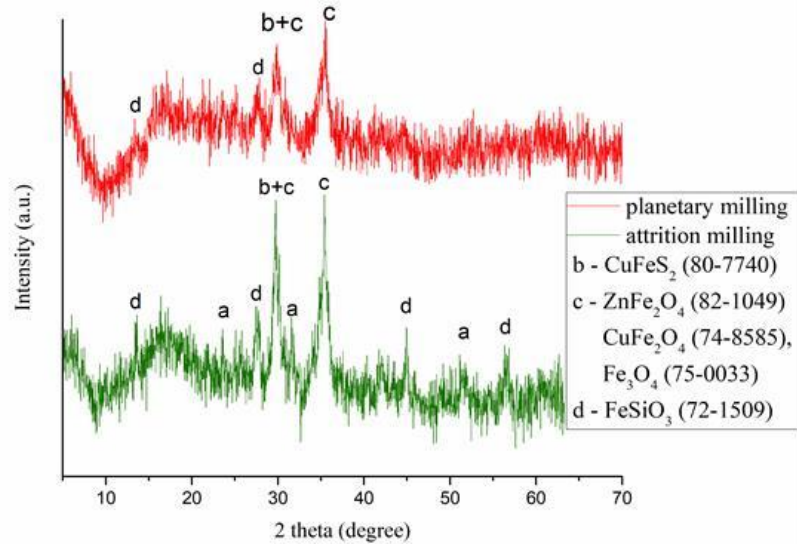
Figure 3.16 - XRD patterns of slag milled in a planetary ball mill (red) and the attritor (green) under optimized conditions in a wet environment (conditions for planetary milling: 1200 rpm, sample mass 7.5 g (ball-to-powder ratio 20), duration 75 min; for attrition milling: 1200 rpm, sample mass 50 g (ball-to-powder ratio 40), duration 75 min) [112]

As it can be seen, the height of almost all selected peaks decreases as a result of milling. The reduction of peak height can be put into the following order (starting with the smallest reduction): dry milling in attrition < dry milling in a planetary ball mill < wet milling in attrition < wet milling in a planetary ball mill. This order is in perfect correlation with the specific surface area values (the largest one was evidenced for the slag milled under a wet environment in a planetary ball mill). The most pronounced decrease was evidenced for the chalcopyrite phase. A good correlation was evidenced between the peaks for both Fe_2SiO_4 and $ZnFe_2O_4$. The Fe_2SiO_4 peak at 31.5 ° and that representing ferrosilite, $FeSiO_3$, could not be detected in the slag treated in PM, under wet conditions, due to complete amorphization. The least influenced phase was SiO_2.
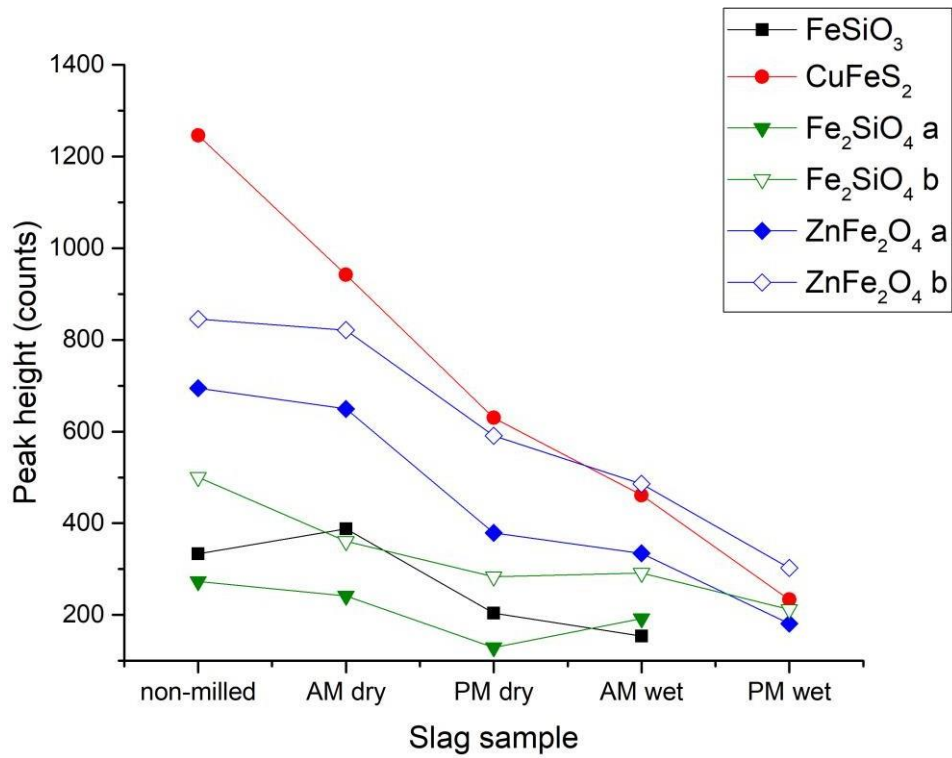
(a)
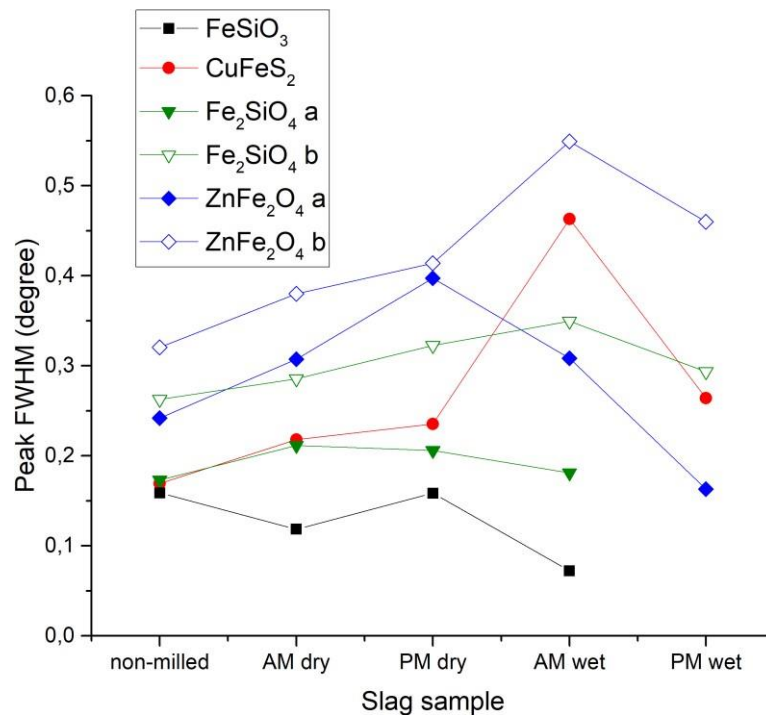
(b)

Figure 3.17 - Results of the peak fitting for different phases
in selected slag samples [112]

The FWHM values presented in Fig. 3.17 b show more-or-less the opposite
trend, *i.e.* with changing from dry to wet environment and from attrition to planetary

mill, FWHM values increase, *i.e.*, the peaks become broader. This relates to both reduction of crystallite size of the corresponding phases, and also as a result of introduced microstrain. The values detected for PM slag treated under wet conditions seem to decrease, however, most of the considered peaks are almost completely amorphized (see a red pattern in Fig. 3.16), and so the validity of these results is questionable. The FWHM values for $FeSiO_3$ do not follow the trend of other investigated phases.

The SEM images of the PM and AM slag are provided in Figure 3.18.
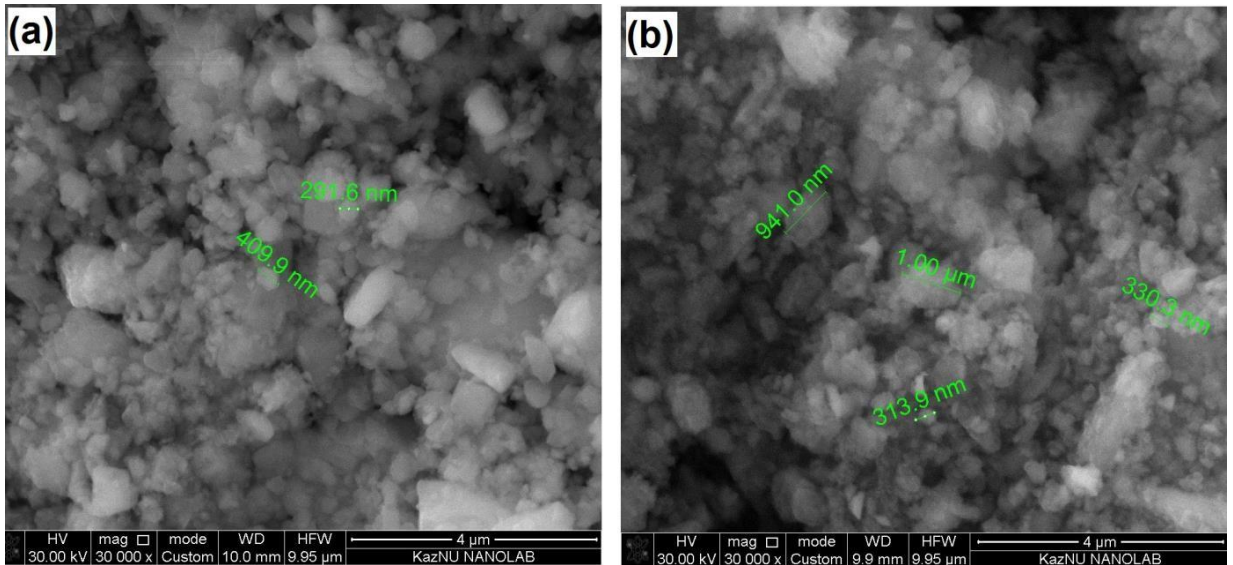
Figure 3.18 - SEM images of AM slag (a) and PM slag (b) [112]

As can be seen from Figure 3.21, the morphology of both samples is more-or-less similar, although slightly finer particles can be evidenced for PM slag (Figure 3.18b).

The particle size distribution curves for the untreated, AM and PM slag are shown in Figure 3.19. Most particles in the original slag were in the range 50 – 1000 µm in size. By using milling, the fraction of submicron particles could be significantly increased at the expense of those larger than 100 µm. For both milled samples, bimodal distribution has been observed; with the two maxima around 1 and 100 µm. Slightly finer particles have been obtained using attrition milling.

To determine whether the milling process has caused any change in magnetic properties of the material, the magnetization values for three samples (untreated, AM and PM slag) has been recorded in the magnetic field ranging from 0 to 5 T (Figure 3.20). As Figure 3.20 shows, the magnetization curves of each sample exhibit a ferromagnetic nature with a high magnetic susceptibility at low fields and a tendency to reach a saturated magnetization at high field values. This behaviour confirms the presence of the above-revealed ferrite phases ($CuFe_2O_4$, $ZnFe_2O_4$ and Fe_3O_4), which are obviously the main contributors to the prevailing ferromagnetic signal.
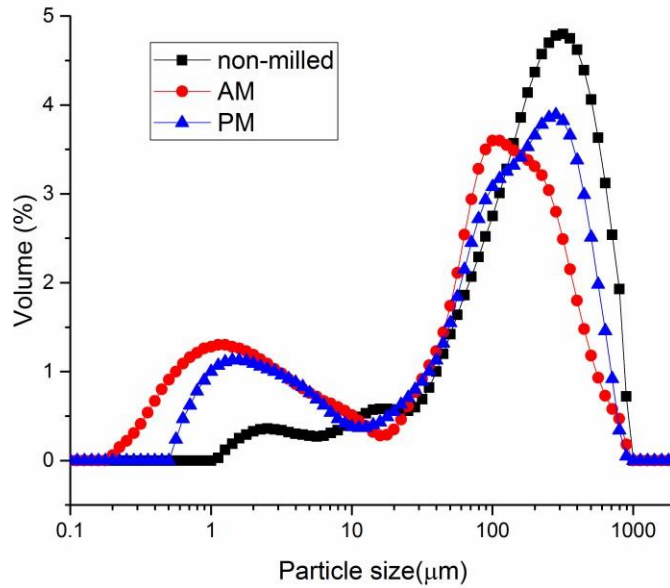
Figure 3.19 - Particle size distribution of starting, AM and PM slags [112]
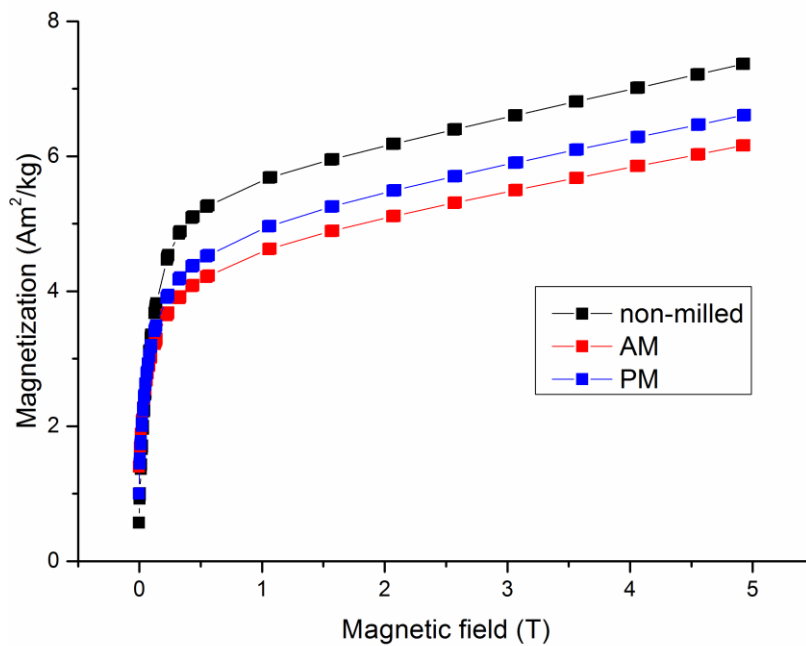
Figure 3.20 - Magnetization curves of starting, AM and PM slags at the laboratory temperature in the magnetic field of 0-5 T [112]

The magnetization value could be slightly decreased using milling, namely the decrease from 7.3 Am^2/kg detected for the starting slag at 5 T, to 6.6 and 6.1 Am^2/kg for PM and MA slags has been evidenced. The milling process thus results in a noticeable reduction of the specific magnetization, of the sample due to introducing defects and also some chemical changes (this will be demonstrated in increased solubility of the metals shown later on). On the other hand, the magnetization

reduction may reflect the decrease in the particle size and the increase in the SSA, as it is known that surface atoms have reduced magnetic exchange coupling [119].

The AM slag and PM slag have been subjected to leaching experiments, as they possess the highest SSA values (namely, 59.4 m^2/g for the sample treated in attritor and 126.0 m^2/g for the sample treated in a planetary ball mill. High specific surface area is a great prerequisite for subsequent efficient leaching [65, 120].

3.3.3 Leaching experiments

The process of Cu, Zn and Fe recovery from copper smelter slag of Balkhash copper plant by leaching with H_2SO_4-$K_2Cr_2O_7$ system has been already investigated [102]. The maximum achieved copper recovery in the absence of dichromate ions, using only 1M H_2SO_4, was only 9.8 % and a significant amount of Fe and Zn was also leached out. Namely, the recoveries of Fe and Zn increased significantly with the increase of the acid concentration to 0.5 M in the absence of dichromate and reached values of 57 % and 56 % for zinc and iron, respectively. The presence of dichromate decreased the Zn and Fe recoveries. Presumably, this result is due to the adsorption of dichromate ions on the surface of the mineral. The copper recovery, on the contrary, increased in the presence of dichromate and reached 68 % in case of leaching under the following conditions: 0.5 M $K_2Cr_2O_7$ + 1 M H_2SO_4, a liquid-to-solid (L:S) ratio 67, 120 min, 298 K. The recoveries of Fe and Zn under these conditions were 4 and 5 %, respectively.

We have applied almost the same leaching conditions as described in [105102] (with the exception of the L:S ratio which was 75 in the present case) to get the following recoveries of metals into solution: Zn – 2.1 %, Cu – 34.2 %, and Fe – 4.9%. The obtained Cu recovery in the present case was almost two times lower than that in [105]. This difference can be explained by the chemical composition of the slag samples. In the slag sample used in [102], copper was present not only in the form of refractory chalcopyrite ($CuFeS_2$) but also in the forms of better soluble bornite (Cu_5FeS_4) and chalcocite (Cu_2S). The last two minerals are more readily oxidized in an acidic environment than chalcopyrite [121, 122]. The calculated Cu selectivity for the selected experiment in [112] was 83.19 %.

In order to increase Cu recovery and selectivity, a series of leaching experiments were carried out with samples of mechanically activated slag.

Leaching chemistry

The oxidative dissolution of chalcopyrite in sulfuric acid with dichromate addition produces, presumably due to different stoichiometry of the equations, either elemental sulfur as shown in equation 3.21 or sulfate according to equation 3.22:

$$6CuFeS_2 + 5Cr_2O_7{}^{2-} + 70H^+ \leftrightarrow 6Cu^{2+} + 6Fe^{3+} + 12S + 10Cr^{3+} + 35\ H_2O \qquad (3.21)$$

$$6CuFeS_2 + 17Cr_2O_7{}^{2-} + 142H^+ \leftrightarrow 6Cu^{2+} + 6Fe^{3+} + 12SO_4{}^{2-} + 34Cr^{3+} + 71\ H_2O \quad (3.22)$$
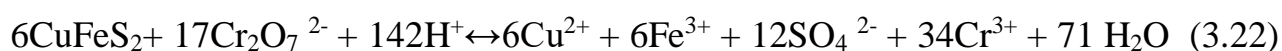
The chromate ion acts as a reducing agent.

Optimization of leaching conditions

Similar to mechanical activation, the selected parameters of leaching have been optimized using a Taguchi design (Table 3.9). In this case, the following parameters were modified: $K_2Cr_2O_7$ concentration, H_2SO_4 concentration, leaching duration and liquid-to-solid (L:S ratio). Again, the *larger-the-better* characteristics have been used when analyzing the results from the Taguchi calculations. For comparison, the results from the initial experiment described above are listed (experiment entitled as L0). In the experiment L1, the same leaching conditions as in L0 have been used, (with exception to the above-mentioned difference in L: S ratio), so the observed change can be ascribed purely to the effect of mechanical activation.

Table 3.9 demonstrates the results of slag leaching in a sulfuric acid solution in the presence of potassium dichromate. For all studied samples, the extraction of copper into solution significantly exceeded the extraction of zinc and iron and the results were much better than in the case of initial non-activated slag (L0). The highest copper recovery was 77.2% (experiment L8 for PM slag) and the highest Cu selectivity was 89.1% (experiment L9 for AM slag). In comparison with the experiments performed without the use of mechanical activation reported in [101], the Cu recovery of 15 % and 20 % has been achieved under the conditions of L8 and L6, respectively. In our study, we recovered 76.4 % of Cu in experiment L8 and 77.2 % of Cu in experiment L6, so a significant improvement has been achieved due to the effect of mechanical activation.

When comparing Cu recoveries with the starting slag, the degree of copper extraction increased from 15 % to 77 % for the sample treated in a planetary ball mill and changed from 20 % to 76 % in the case of attrition mill.

Table 3.9 - Leaching results for copper smelter slag subjected to different leaching conditions according to Taguchi design for PM and AM slag [112]

Experiment number	[$K_2Cr_2O_7$], M	[H_2SO_4], M	Leaching duration, min	L:S	Metal recovery, %						Cu selectivity, %	
					Cu		Zn		Fe			
					PM	AM	PM	AM	PM	AM	PM	AM
L0	0.5	1	120	75	34.2		2.1		4.9		83.0	
L1	0.5	1	120	75	55.1	68.9	3.0	2.6	7.2	7.11	84.4	87.6
L2	0.5	0.5	60	100	61.4	64.8	3.3	2.3	9.2	8.71	83.2	85.5
L3	0.5	0.1	30	200	63.5	63.7	2.9	2.2	16.2	14.30	76.9	79.4
L4	0.15	1	60	200	65.8	70.0	3.4	2.4	17.0	19.6	76.4	76.1
L5	0.15	0.5	30	75	52.1	75.1	2.7	2.6	7.1	7.0	84.2	88.7
L6	0.15	0.1	120	100	73.2	76.4	3.0	2.2	9.2	8.72	85.7	87.5
L7	0.03	1	30	100	67.6	70.5	2.8	2.1	9.4	9.01	84.7	86.4
L8	0.03	0.5	120	200	77.2	75.1	3.4	2.4	17.5	18.0	78.7	78.6
L9	0.03	0.1	60	75	68.5	73.5	3.1	2.1	7.1	6.9	87.1	89.1

The optimum conditions for recovery and selectivity were determined using a Taguchi design (Figure 3.21).
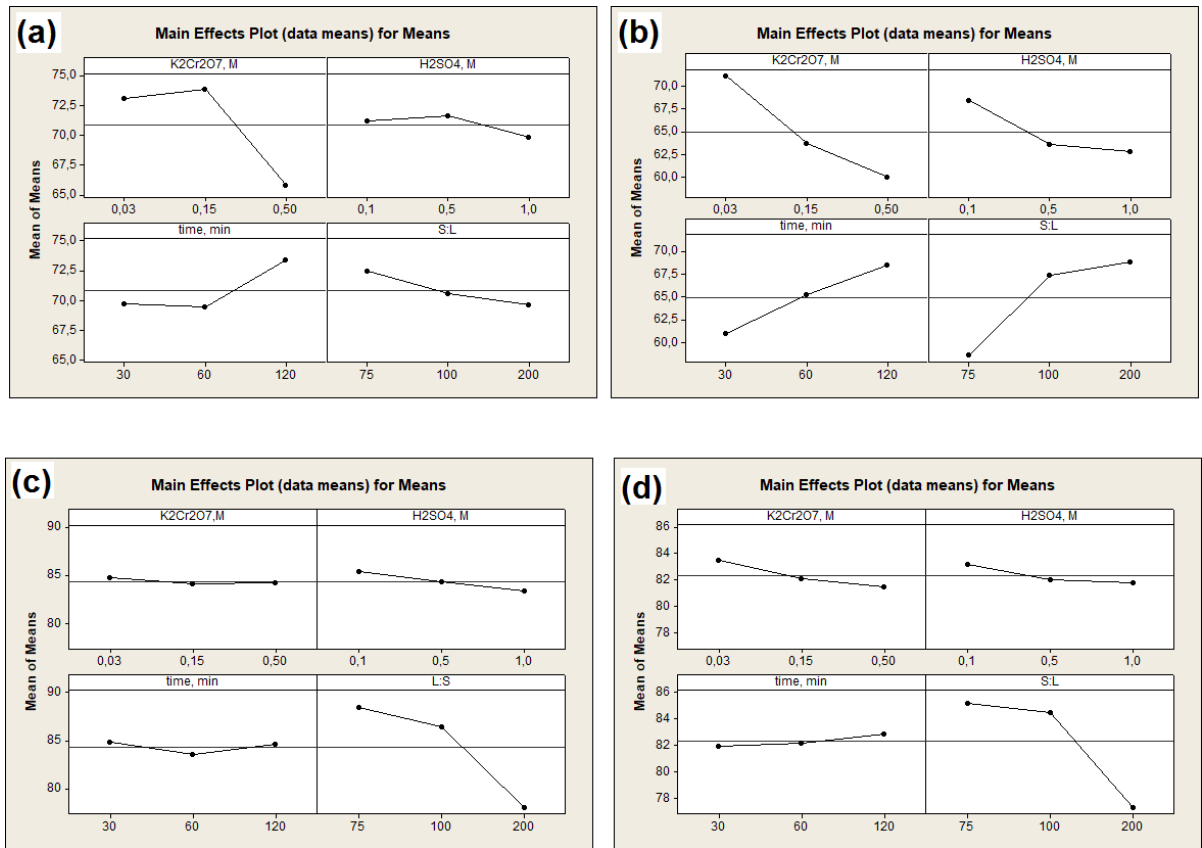
Figure 3.21 - Results of Taguchi calculations in Minitab (mean values) for leaching: (a)Cu recovery in attrition mill, (b) Cu recovery in planetary ball mill, (c) Cu selectivity in attrition mill, (d) Cu selectivity in planetary ball mill [112]

Different parameters were found to be ideal for Cu recovery in attrition and planetary milling. The following conditions were found to be optimal in attrition mill for Cu recovery: $[K_2Cr_2O_7] = 0.15$ M, $[H_2SO_4] = 0.5$ M, leaching duration 120 min, liquid-to-solid ratio 75:1. In the case of planetary ball milling, the optimum leaching conditions were, as follows: $[K_2Cr_2O_7] = 0.03$ M, $[H_2SO_4] = 0.1$ M, leaching duration 120 min, liquid-to-solid ratio 200:1. Just the longest duration of leaching was the most appropriate for both PM and AM slag and all the other optimum parameters were different. It seems that the activation in AM and PM yields a material with different properties, where the individual components are affected by the pretreatment method to a different extent. On the other hand, the optimum parameters for selectivity were the same in all cases, with exception of leaching time, where the shortest was the best for AM - and the longest was the most suitable for PM-pretreated slag. Namely, $[K_2Cr_2O_7] = 0.03$ M, $[H_2SO_4] = 0.1$ M and liquid-to-solid ratio 75:1 were optimal for both pretreatments. The optimum parameters for recovery and selectivity are in most cases different, so it is impossible to find a combination to get both the highest recovery and selectivity.

The contribution of individual parameters on both Cu recovery and Cu selectivity was calculated by ANOVA (Figure 3.22).
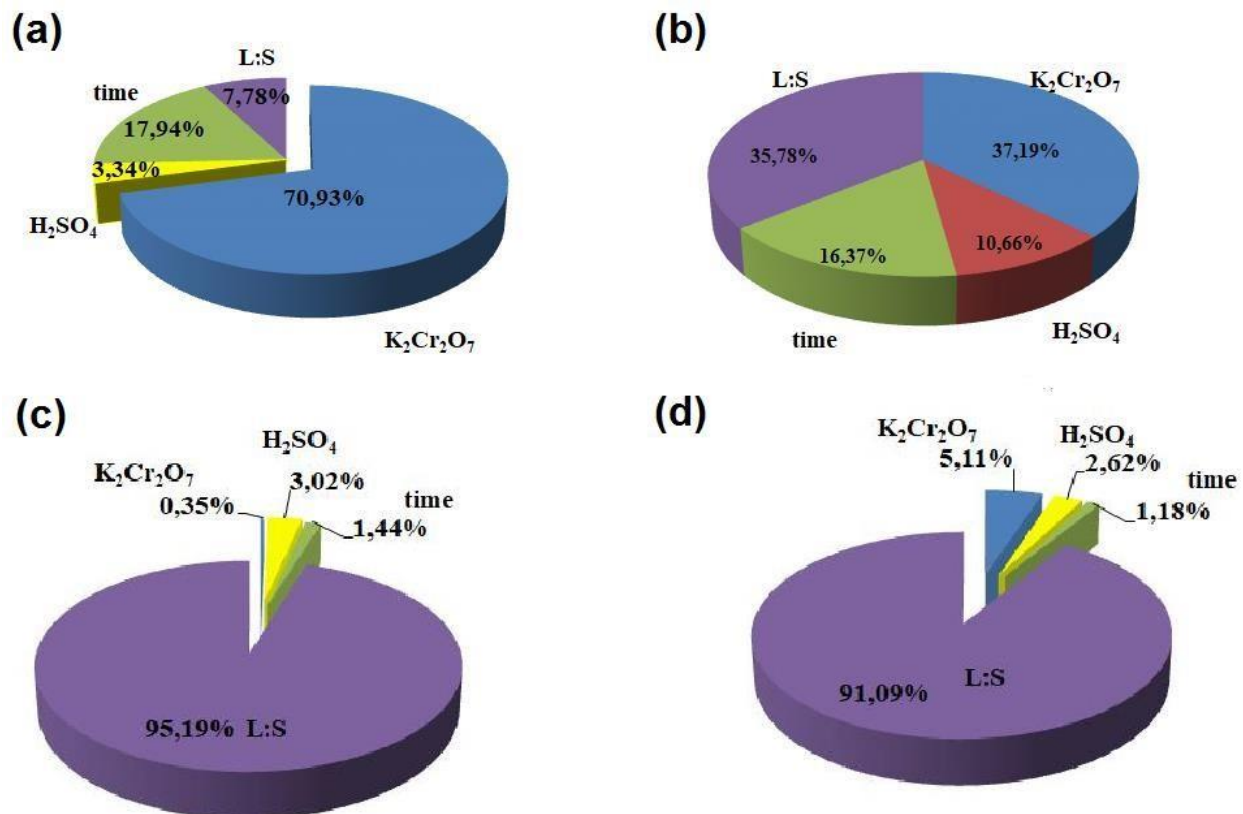
Figure 3.22 - Results of ANOVA calculations in Minitab for leaching: (a) Cu recovery in attrition mill, (b) Cu recovery in planetary ball mill, (c) Cu selectivity in attrition mill, (d) Cu selectivity in planetary ball mill [112]

From Figure 3.22, we can see that in the case of AM, the concentration of $K_2Cr_2O_7$ is the most important parameter (70.9 %) for Cu recovery, with a p-value of 0.025. The contribution of other parameters is not significant (p values for leaching time, L: S ratio and H_2SO_4 concentration was 0,552; 0,784 and 0,903, respectively). In the case of PM, the concentration of $K_2Cr_2O_7$ and L: S ratio] have the same influence on recovery degree (37.19 % and 35.78 %, respectively). The p values for these parameters were 0.248 and 0.265, both of which are not significant but are much smaller than the other two p values (p-value was equal to 0.585 and 0.713 for leaching time and H_2SO_4 concentration, respectively).

The Cu selectivity is governed mostly by the L: S ratio (the contribution of this parameter is higher than 90 %). It is the only significant parameter with p values of 0.000 and 0.001, for AM and PM slag, respectively).

Experiments performed under the optimum leaching conditions

Subsequently, leaching experiments have been performed, under optimum conditions, for both PM and AM slags, and with both optimum parameters for Cu

recovery and Cu selectivity. These results, together with the predicted values, are shown in Table 3.10. Labels „s" and „r"describe whether the experiment has been performed under the optimum conditions for selectivity and recovery, respectively.

Table 3.10 - The results of copper smelter slag leaching with regards to metals recovery and Cu selectivity performed under the optimized leaching conditions (predicted values from Minitab software are also provided) [112]

Experiment number	Mill type	[K$_2$Cr$_2$O$_7$], M	[H$_2$SO$_4$], M	Leaching duration, min	L:S	Recovery, %				Cu selectivity, %	
						Zn	Cu		Fe	predicted	experimental
							predicted	experimental			
OL1-s	AM	0.03	0.1	30	75	1.5	90.4	87.3	2.7	95.6	95.4
OL2-s	PM	0.03	0.1	120	75	1.3	87.8	84.6	2.3	96.0	95.9
OL3-r	AM	0.15	0.5	120	75	2.6	78.8	78.2	2.4	94.6	94.0
OL4-r	PM	0.03	0.1	120	200	1.3	82.0	77.5	0.4	98.0	97.9

Under the optimum conditions, high Cu recoveries with great selectivity can be achieved following the proposed experimental setup. The differences between the predicted and experimental values are very small, which means that the proposed method for finding the optimum conditions has been very successful in this case.

An increase of copper extraction from mechanically activated slag in comparison with the untreated slag has been achieved, and is associated with partial destruction of the fayalite matrix and the release of target minerals; besides, mechanical activation increases the reactivity of minerals.

A low extraction of iron and zinc into a sulfuric acid solution in the presence of potassium dichromate was expected as this observation has been previously reported in [53] and [102]. The authors of [53] propose two hypotheses explaining this observation. The first is associated with the adsorption of dichromate ions onto the surface of the fayalite matrix; according to the authors' assumptions, adsorbed ions block the surface of iron and zinc minerals, thereby preventing their dissolution. The relatively high copper recovery is due to the presence of copper minerals in a separate phase (not in the fayalite matrix). The second hypothesis is that formation of insoluble compounds such as $KFe_3(CrO_4)_2(OH)_6$ occurs.

The high recovery of copper was confirmed also by the XRD analysis of selected leaching residue (from experiment OL3, see Fig. 3.23), which indicated the presence of $FeSiO_3$ and all or some of the following phases: zinc ferrite $ZnFe_2O_4$, cuprospinel $CuFe_2O_4$, magnetite Fe_3O_4. The XRD pattern is very similar to that of PM slag presented in Fig. 3.23. The absence of fayalite peaks is explained by their amorphization during the mechanical activation of the slag. The elemental

composition of the residue determined by AAS was as follows, wt. %: Fe 22.1, Si 38.9, Zn 0.41, and Cu 0.13. For comparison, leaching residues from other experiments have been analyzed (Table 3.11), but the results were very similar, with exception of the residue from experiment L0, where a larger amount of Cu (due to non-efficient leaching) was observed.
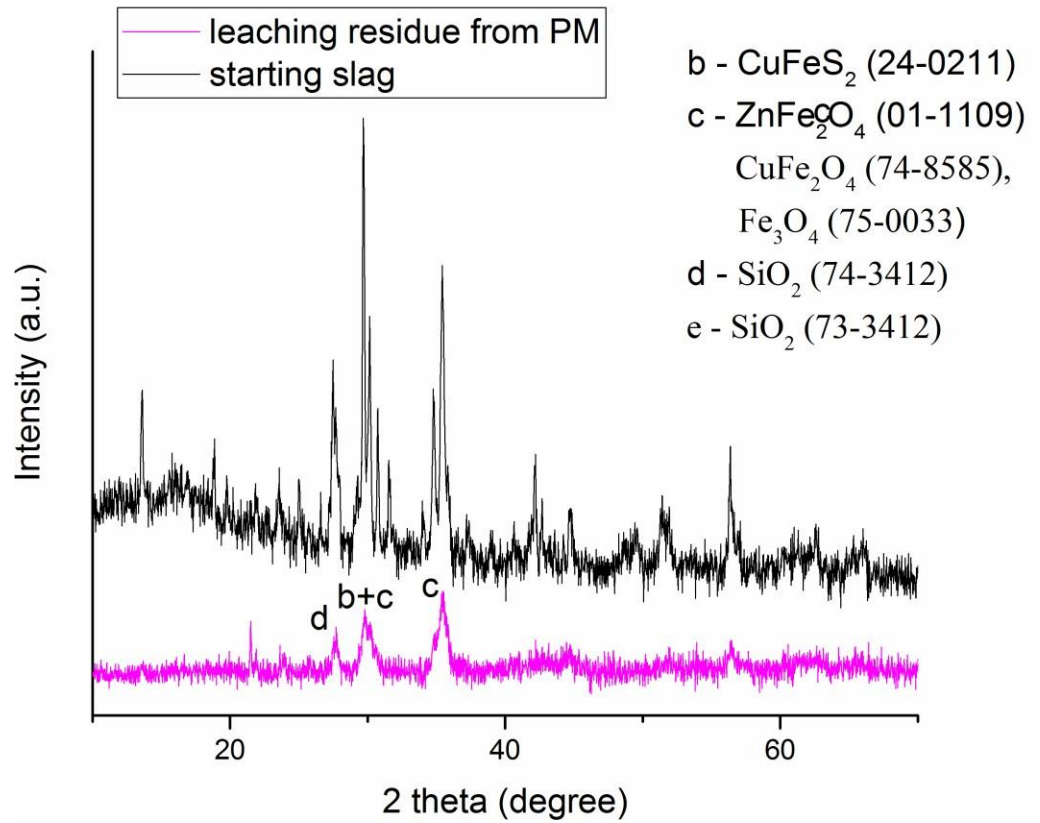
Figure 3.23 - XRD pattern of solid residues after leaching treatment [112]

With regards to chromium, Cr (III) ions do not form a solid precipitate but remain in solution under strongly acidic conditions (pH <1) as in our case. Therefore, chromium was not detected in the residues washed with water.

Table 3.11 - Elemental analysis of selected leaching residues by AAS method [112]

Experiment	Fe	Si	Zn	Cu
L0	22.6	37.4	0.47	1.19
OL3	22.1	38.9	0.41	0.13
OL4	21.8	39.2	0.40	0.14
OL13	22.3	37.6	0.42	0.17
OL14	22.5	37.8	0.41	0.16

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Justification of using potassium dichromate in leaching

To determine the effect of potassium dichromate on metal recovery, comparative leaching experiments using the optimized conditions in the absence of dichromate were carried out. The experiments were performed both under the optimum conditions providing the highest Cu recovery and the highest Cu selectivity for mechanically activated slags (AM and PM). Also, to demonstrate the effect of mechanical activation, experiments were carried out for the untreated slag. The results are presented in Table 3.12. Labels „s"and „r"describe whether the experiment has been performed under the optimum conditions for selectivity and recovery, respectively.

Table 3.12 - The results of copper smelter slag leaching with regards to Cu, Fe and Zn recovery and Cu selectivity under the optimized conditions, in the absence of potassium dichromate [112]

Experiment	Mill type	[H$_2$SO$_4$], M	Leaching duration, min	L:S	Recovery, %			Cu selecti vity, %
					Zn	Cu	Fe	
OL5-r(AM)	non-milled slag	0.5	120	75	1.2	6.1	1.4	70.1
OL6-r(PM)	non-milled slag	0.1	120	200	0.9	3.9	1.0	67.2
OL7-r	AM	0.5	120	75	2.3	28.3	2.2	86.3
OL8-r	PM	0.1	120	200	1.2	24.8	2.1	88.3
OL9-s	AM	0.1	30	75	1.4	13.7	2.5	77.8
OL10-s	PM	0.1	120	75	1.1	23.4	2.1	88.0

Comparison of the leaching results from the experiments OL1-OL4 performed in the presence of dichromate (Table 3.10) and OL7-OL10 performed in its absence (Table 3.12) showed that the presence of potassium dichromate increased Zn and Fe recovery by a factor of 1.1-1.2, whilst Cu recovery was increased by a factor of 2.8-6.4 (for AM sample) and 3.1-3.6 (for PM sample). Leaching of non-milled slag (experiments OL5 and OL6) resulted in 4.6-6.4 times lower Cu recovery compared to the milled samples, and more than 6 times lower recovery than that in the case of dichromate presence in the initial experiment (L0 in Table 3.11, although in this case 1 M H$_2$SO$_4$ has been used). Cu selectivity remained reasonably high (higher than 67% for all the experiments OL5-OL10), being higher for the milled slags, but as the Cu recoveries are low, it is not important.

Generally, the presence of potassium dichromate had a positive effect on the leaching of all the considered metals, however, the greatest effect was observed for Cu recovery. Noteworthy are the metal recovery values at a leaching duration of

30 min (experiment OL9): Zn and Fe recoveries were comparable to those observed at 120 min leaching, however, Cu recovery was less than 14 % (90.4 % Cu recovery was observed for AM sample under the same conditions (OL1, Table 3.10)).

To provide additional information, oxidation-reduction potential (RP) and pH has been measured for experiments OL3-OL10 (Figure 3.24).
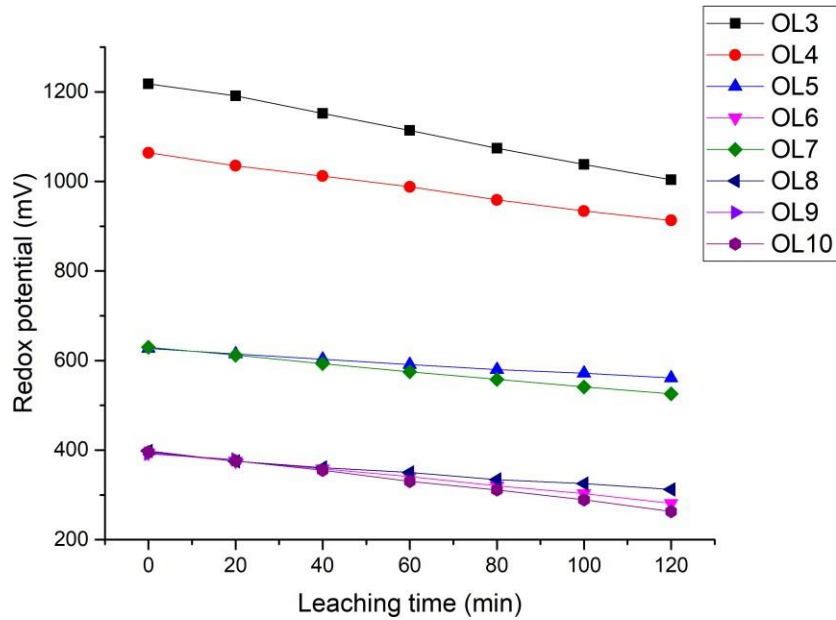
(a)
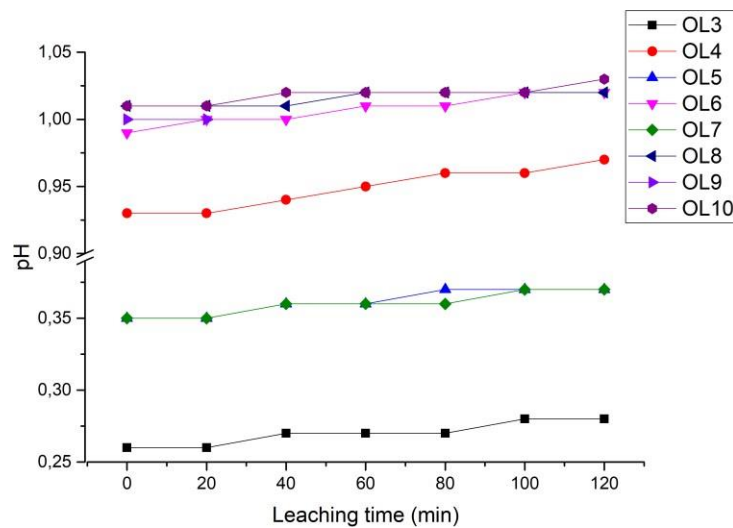
(b)

Figure 3.24 - Change of redox potential (a) and pH (b) for selected experiments [112]

Due to the presence of potassium dichromate (a strong oxidizing agent), the stock solutions at OL3 and OL4 had a much higher RP value than solutions at OL5-OL10. The differences in the values of RP and pH among the experiments can always be understood in terms of a difference in the concentrations of dichromate and

sulfuric acid (the higher concentrations result in higher RP and lower pH). In all cases, there was a linear decrease in RP and a more-or-less linear increase in the pH of the solution. This is due to the consumption of leaching agents (H_2SO_4 and $K_2Cr_2O_7$). Upon leaching in the presence of potassium dichromate, the solution changed colour from orange to dark green, which indicated the reduction of $Cr_2O_7^{2-}$ ions to Cr^{3+}; which confirms the participation of dichromate in the oxidation process during leaching according to Equation 3.21 and 3.22. In the absence of dichromate, the solution was transparent during the whole experiment.

In general, dichromate ions are a strong oxidizing agent, and, being adsorbed on the surface of minerals, should oxidize them (especially in the presence of sulfuric acid). Therefore, the hypothesis based on the surface passivation of iron and zinc minerals looks doubtful. We hypothesized that the significant difference between the recovery rates of copper, as well as iron and zinc, can be explained by the different rates of mineral dissolution. To test this hypothesis, we conducted an additional experiment under the conditions providing the highest selectivity (OL 4 in Table 3.11), however, the leaching time, in this case, was 8 hours. The extraction of metals into solution was found to be: Zn - 65.7 %, Cu - 79.3 % and Fe - 57.63 %, indicating that kinetics play a role here. Namely, the dissolution rate of chalcopyrite (copper mineral), which is much higher than the dissolution rate of iron and zinc minerals. An increase in the duration of leaching practically does not increase the extraction of copper into the solution. On the contrary, the extraction of zinc and iron, sharply increase and become comparable to the extraction of copper. It means that the protection of Zn and Fe offered by dichromate ions is only temporary.

The role of dichromate seems to play a key role also with regards to the mechanical activation process, namely the fact that less dichromate leads to improved Cu recovery (Fig. 3.21 a, b). This effect is more significant when planetary ball milling has been used. In fact, two hypotheses might be considered as a reason for this phenomenon. The first one is based on the fact that chalcopyrite can be possibly oxidized during milling, due to which less oxidizing power is required during subsequent leaching. The other one is that an increased presence of dichromate enhances the passivation of Cu (e.g. through precipitation as the spinel $CuFe_2O_4$). However, mainly the first one is highly probable, as it is known that during milling in air, the surface layer of oxidized species is formed in general (as an example, e.g. the synthesis of nanocrystalline copper sulfides where the surface layer containing sulfate species has been evidenced, might be used [121]). With regards to leaching, there are technologies in extractive metallurgy where a similar effect was observed. The need to decrease the high oxygen consumption in hydrometallurgical operations is important from an economical point of view. This is an advantage of mechanical activation when applied as a separate operation before oxidative leaching [122] which is also our case. For example in ACTIVOX[R] process was developed in Australia as an alternative to the pretreatment of sulphidic concentrates by roasting and bacterial oxidation [122]. The leaching conditions in the autoclave after mechanical activation

led to the reduction of oxygen consumption from 2.2 kg of O_2 per kg of sulphur to 1.5 kg of O_2 per kg of sulphur.

Lowering L: S ratio

The L: S values used to optimize the leaching process are extremely high for the industry. Therefore, it was deemed important to check the effectiveness of the proposed method of copper smelter slag hydrometallurgical processing, at lower L:S ratios (in particular, L:S = 10, as it is acceptable for industrial use). The results are presented in Table 3.13. In this case, the experiments were performed under the optimized conditions for Cu recovery. Label „r" means that the experiment has been performed under the optimum conditions for recovery.

Table 3.13 - The results of copper smelter slag leaching with regards to Cu, Fe and Zn recovery and Cu selectivity under the optimized conditions for Cu recovery, at L:S =10 [112]

Experiment	ill type	$[H_2SO_4]$, M	$[K_2Cr_2O_7]$, M	Leaching duration, min	Recovery, %			Cu selectivity, %
					Zn	Cu	Fe	
OL11-r(AM)	non-milled slag	0.5	0.15	120	1.9	25.6	2.2	86.2
OL12-r(PM)	non-milled slag	0.1	0.03	120	1.7	23.8	1.9	86.9
OL13-r	AM	0.5	0.15	120	2.5	73.7	2.4	93.8
OL14-r	PM	0.1	0.03	120	1.0	71.9	0.8	97.6

Comparison of the data presented in Table 3.11 (OL3 and OL4) and Table 3.13 (OL13 and OL14) showed that L:S reduction from 75 to 10 (for AM sample) and from 200 to 10 (for PM sample) reduced Cu recovery from 78.2 to 73.7 % for AM, and from 77.5 to 71.9 % for PM. Thus, the reduction in Cu recovery was only slight, and the proposed methodology is potentially applicable in industry, whereby the use of L: S = 10 is preferred over L: S = 75 and L: S = 200 for obvious reasons.

The Cu recoveries for the non-milled sample were more than 3 times lower than when using milled slags (OL11 and OL12, Table 3.13), which justifies the need for mechanical activation of the slag before leaching.

Thus, in a sulfuric acid solution in the presence of potassium dichromate, the rate of dissolution of copper minerals is much higher than the rate of dissolution of iron and zinc minerals. This circumstance can be used to separate copper from zinc and iron during the leaching of waste copper slag.

Following conclusions could be made from the results of Chapter 3.3:

(1) Dry and wet mechanical activation of copper smelter slag in both planetary ball mill and attritor resulted in an enhancement of the specific surface area, with the greatest effect in the case of the wet mechanical activation in a planetary ball mill. Employing conditions of 1200 rpm, ball-to-powder ratio 40:1 and 75 min, the SSA of the slag sample increased 68.2 times;

(2) Mechanical activation of the slag led to an increase in the degree of extraction of copper into solution during leaching with the sulfuric acid solution in the presence of dichromate ions, whereas that of Fe and Zn only increased marginally;

(3) Leaching of both, the initial and mechanically activated slag in the system under study made it possible to selectively extract copper into the solution. The selectivity for copper is due to the higher dissolution rate of copper minerals compared to iron and zinc minerals;

(4) The samples obtained using optimized conditions have been subjected to leaching and the following conditions were found to be optimal for Cu recovery in attrition mill (in parentheses for copper selectivity): $[K_2Cr_2O_7] = 0.15$ (0.03) M, $[H_2SO_4] = 0.5$ (0.1) M, leaching duration 120 (30) min, liquid-to-solid ratio 75:1 (75:1). Under these conditions, copper recovery reached 87.31%, and Cu selectivity was 95.44 % upon mechanical activation in attritor. In the case of planetary ball milling, the optimum leaching conditions were different (in parentheses for Cu selectivity): $[K_2Cr_2O_7] = 0.03$ (0.03) M, $[H_2SO_4] = 0.1$ (0.1) M, leaching duration 120 (120) min, liquid-to-solid ratio 200:1 (75:1) and the copper recovery and selectivity was 84.63 % and 97.87 %, respectively;

(5) Different types of mills have a different impact on the individual components of the slag, resulting in different optimum leaching parameters for slag activated in an attritor or planetary ball mill;

(6) Upon L: S ratio reduction to value 10, and an only slight decrease in Cu recovery has been evidenced (namely it dropped from 78.2 to 73.7 % upon the use of attrition milling and from 77.5 to 71.9 % for planetary milling), which predetermines the proposed methodology to be potentially applicable in the industry;

(7) The additional experiment was performed under the conditions providing the highest selectivity, however, the leaching time, in this case, was 8 hours. The extraction of metals into solution was found to be: Zn - 65.7 %, Cu - 79.3 % and Fe - 57.63 %, indicating that kinetics play a role here.

The overview information on results and leaching conditions of different copper smelter slag samples are presented in the following Table 3.14.

Table 3.14 - The general information on leaching conditions of slag samples

Sample #	Mineral composition	Chemical composition, wt. %	Treatment conditions	Metals recovery, %
1	Major: Fe_2SiO_4, $FeSiO_3$, Fe_3O_4 Minor: $ZnFe_2O_4$, Cu_2S, Cu_5FeS_4, $CuFeS_2$	Fe – 22.50, Cu – 1.18, Zn – 1.17, Si – 33.95, S – 1.06.	*Leaching* Liquid-to-solid ratio 100; leaching duration 1 h; T= 343 K, pH=2.3, rotation speed 300 min^{-1}	Zn - 79.6, Cu - 58.7, Fe - 84.7.
2	Major: Fe_2SiO_4, $FeSiO_3$, Fe_3O_4 Minor: $ZnFe_2O_4$, Cu_2S, Cu_5FeS_4 $CuFeS_2$, Al_2SiO_5, $CaSiO_3$, ZnS, $MgSiO_3$	Fe – 23, 88, Cu – 1.20, Zn – 0.52, Si – 39.79, Ca – 0.76, Mg – 0.18, S – 1.11, Al – 1.49.	*Leaching* Liquid-to-solid ratio 67; leaching duration 2 h; T= 298 K, rotation speed 450 min^{-1}, 1 L of the 0.5 M sulfuric acid solution	Fe - 56, Cu – 8,7 Zn – 57.
3	-//-	-//-	*Leaching* Liquid-to-solid ratio 67; leaching duration 2 h; T= 298 K, rotation speed 450 min^{-1}, 1 L of the 0.5 M sulfuric acid solution, 0.5 M $K_2Cr_2O_7$	Fe - 5,0 Cu – 68,0 Zn – 4.1.
4	Major: Fe_2SiO_4 Minor: Cu_2S, Cu_5FeS_4	Fe – 23.76, Cu – 1.80, Zn – 0, 42, Si – 35.54, Ca – 0. 89, S – 1.16,	*Mechanical activation* B: P – 40:1, 200 mL water, <u>rotation speed</u> <u>500 rpm, MA duration 120 min.</u>	Cu- 45 ± 1.

		Al - 1.43.	*Leaching* leaching duration 1 h; T= 325 ± 1K, 1 M sulfuric acid solution, L:S	
5	-//-	-//-	*Mechanical activation* B: P – 40:1, 200 mL water, <u>rotation speed 600 rpm, MA</u> duration 90 min. *Leaching* leaching duration 1 h; T= 325 ± 1K, 1 M sulfuric acid solution, L:S	Cu-56 ± 1.
6	Major: Fe_2SiO_4 , Fe_3O_4 Minor: $CuFeS_2$, $MgSiO_3$, $CaSiO_3$, ZnO	Fe – 20.88, Cu – 1.12, Zn – 0.50, Si – 33.45, Ca – 0.62, Mg – 0.15, S – 1.14.	*Mechanical activation (dry mode)* B: P = 25:1 (steel balls with a total mass of 250 g), rotation speed 400 rpm, MA duration – 20 min. *Leaching* 1 M sulfuric acid, L:S = 4:1, at ambient temperature, 45 min of leaching	Cu - 47, Fe - 45, Zn – 38.
7	Major: Fe_2SiO_4 Minor: $CuFeS_2$, $MgSiO_3$, $CaSiO_3$, ZnS	Fe – 22.68, Cu – 1.52, Zn – 0.42, Si – 31.40, Ca – 0.69, Mg – 0.13, S – 1.10.	*Mechanical activation (wet mode)* B: P - 20:1, 30 mL of water, RS - 450 rpm, duration - 45 min. *Leaching*	Cu - 91, Zn – 89.

			1M sulfuric acid, ambient temperature, leaching duration 1 h, particle size 90% < 200 mesh, L:S = 100.	
8	Major: Fe_2SiO_4 Minor: $CuFe_2O_4$, $CuFeS_2$, ZnO, Na_6ZnO_4, ZnS	Fe – 28, 56, Cu – 1.02, Zn – 0.40, Si – 32.44, Ca – 0.62, Mg – 0.15, S – 2.78.	*Mechanical activation* B: P – 20 :1 (300 g. iron balls and 15 g. of slag sample), RS - 600 rpm, t_{MA} = 20 min. *Leaching* 5 g. mechanically activated slag sample, 100 mL 1 M H_2SO_4, leaching duration 2 h, treatment with 10 mL 30 % H_2O_2 in 1 hour, treatment with 13,85 g $NaHCO_3$ for 1 h.	Cu - 56. 4, Fe - 50.89, Zn - 50.76.
9	Major: Fe_2SiO_4 Minor:, $CuFeS_2$, $ZnFe_2O_4$, SiO_2	Fe - 22.9, Cu - 1.20, Zn - 0.48, Si - 37.4%, K - 1.25 %	*Mechanical activation in Attritor* RS - 1200 rpm; B:P – 40:1; duration - 75 min., amount of added water - 200 mL (optimal conditions) *Leaching* Optimal conditions for Cu recovery in attrition mill (in parentheses for copper selectivity): $[K_2Cr_2O_7]$ = 0.15 (0.03) M, $[H_2SO_4]$ = 0.5 (0.1) M, leaching duration 120 (30) min, liquid-to-solid ratio 75:1 (75:1).	Cu - 87.31, (selectivity 95.44), Fe – 2.7, Zn – 1.5. Cu -78.2, (selectivity 94.0), Fe – 2.4, Zn – 2.6. (under optimal conditions for selectivity and recovery, respectively).
10	-//-	-//-	*Mechanical activation in Planetary*	Cu - 84.6,

			ball mill – Activator 2SL RS - 1200 rpm; B:P – 40:1; duration - 75 min., amount of added water - 100 mL (optimal conditions) *Leaching* Optimal conditions for Cu recovery in Planetary ball mill (in parentheses for copper selectivity): $[K_2Cr_2O_7]$ = 0.03 (0.03) M, $[H_2SO_4]$ = 0.1 (0.1) M, leaching duration 120 (120) min, liquid-to-solid ratio 200:1 (75:1).	(selectivity 95.9), Fe – 2.3, Zn – 1.3. Cu -77.5, (selectivity 97.9), Fe – 0.4, Zn – 1.3. (under optimal conditions for selectivity and recovery, respectively)
11	-//-	-//-	0.5 M H_2SO_4, 120 min. L:S 75 non-milled	Cu - 6. 1, Fe - 1,4, Zn - 1.2.
12	-//-	-//-	0.1 M H_2SO_4, 120 min. L:S 200 non-milled	Cu - 3. 9, Fe - 1,0, Zn – 0.9.
13	-//-	-//-	0.5 M H_2SO_4, 120 min. L:S 75 AM	Cu – 28.3, Fe - 2,2, Zn – 2.3.
14	-//-	-//-	0.1 M H_2SO_4, 120 min. L:S 200 PM	Cu – 24.8, Fe - 2,1, Zn – 1.2.
15	-//-	-//-	0.1 M H_2SO_4, 30 min. L:S 75 AM	Cu – 13.7, Fe - 2,5, Zn – 1.4.

16	-//-	-//-	0.1 M H_2SO_4, 120 min. L:S 75 PM	Cu – 23.4, Fe - 2,1, Zn – 1.1
17	-//-	-//-	0.5M H_2SO_4, 0,15 M $K_2Cr_2O_7$, 120 min. L:S 10 non-milled	Cu - 25.6, Fe - 2,2, Zn - 1.9.
18	-//-	-//-	0.1 M H_2SO_4, 0,03 M $K_2Cr_2O_7$, 120 min. L:S 10 non-milled	Cu - 23.8 Fe - 1,9, Zn – 1.7.
19	-//-	-//-	0.5M H_2SO_4, 0,15 M $K_2Cr_2O_7$, 120 min. L:S 10 AM	Cu - 73.7 Fe - 2,4, Zn – 2.5.
20	-//-	-//-	0.1 M H_2SO_4, 0,03 M $K_2Cr_2O_7$, 120 min. L:S 10 PM	Cu - 71,9, Fe - 0.8, Zn – 1.0

In order to improve the manufacturability of the process for extracting copper from slag, we leached the slag mechanically activated in the attritor (L: S = 10, $[H_2SO_4]$ = 0.5 M, $[K_2Cr_2O_7]$ = 0.15M) under the following conditions: L: S = 10, $[H_2SO_4]$ = 0.1M, $[K_2Cr_2O_7]$ = 0.03M. The extraction of metals into solution was, %: Cu - 68.3, Zn - 0.9, Fe - 0.8.

3.4 Recommendations for the processing of waste copper slag by sulfuric acid leaching

The results presented in this dissertation work show the probability of sulfuric acid leaching of copper smelter slag, previously subjected to wet mechanical activation. The use of potassium dichromate makes it possible to achieve selectively leaching namely, the separation of copper from zinc and iron during leaching.

Table 3.15 shows the material balance for the studied metals (copper, zinc, iron) during leaching of 100 g mechanically activated slag in attrition mill under the following conditions: L: S = 10, $[H_2SO_4]$ = 0.1M, $[K_2Cr_2O_7]$ = 0.03M.

Table 3.15 - Balance of base metals for MA copper slag leaching

Input	Weight, g		
	Cu	Zn	Fe
Copper slag	1.196	0.479	22.914
Total	1.196	0.479	22.914
Output			
Solution	0.817	0.004	0.183
Solid residue	0.362	0.454	21.729
Losses	0.017	0.021	1.002

The content of the studied metals, as well as chromium, in the solution, was, g / L: Cu 0.817, Zn 0.004, Fe 0.183, Cr 8.756. The sulfuric acid content in the final solution was 7.4 g / L (pH = 1.12).

The extraction of copper from solutions with the specified content of the mentioned metals and pH is recommended to be processed by hydrolytic precipitation, cementation or sulfide precipitation [123]. After copper extraction, it is proposed to introduce an oxidizing agent (preferably hydrogen peroxide) into the solution to convert (oxidize) Cr^{3+} to Cr^{6+}, reinforce it with sulfuric acid and use it for leaching.

When iron accumulates in solution, it may precipitate in the form of jarosite; neutralization of the solution to pH = 1.5-2.4 creates conditions for the formation of jarosite [124]:

$$3Fe_2(SO_4)_3 + K_2SO_4 + 12H_2O = 2K\ Fe_3(SO_4)_2(OH)_6 + 6H_2SO_4$$
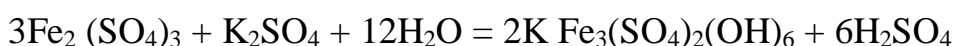
Based on the foregoing, the following scheme of hydrometallurgical processing of copper smelter slag by wet mechanical activation and subsequent sulfuric acid leaching is proposed (Fig.3.25):
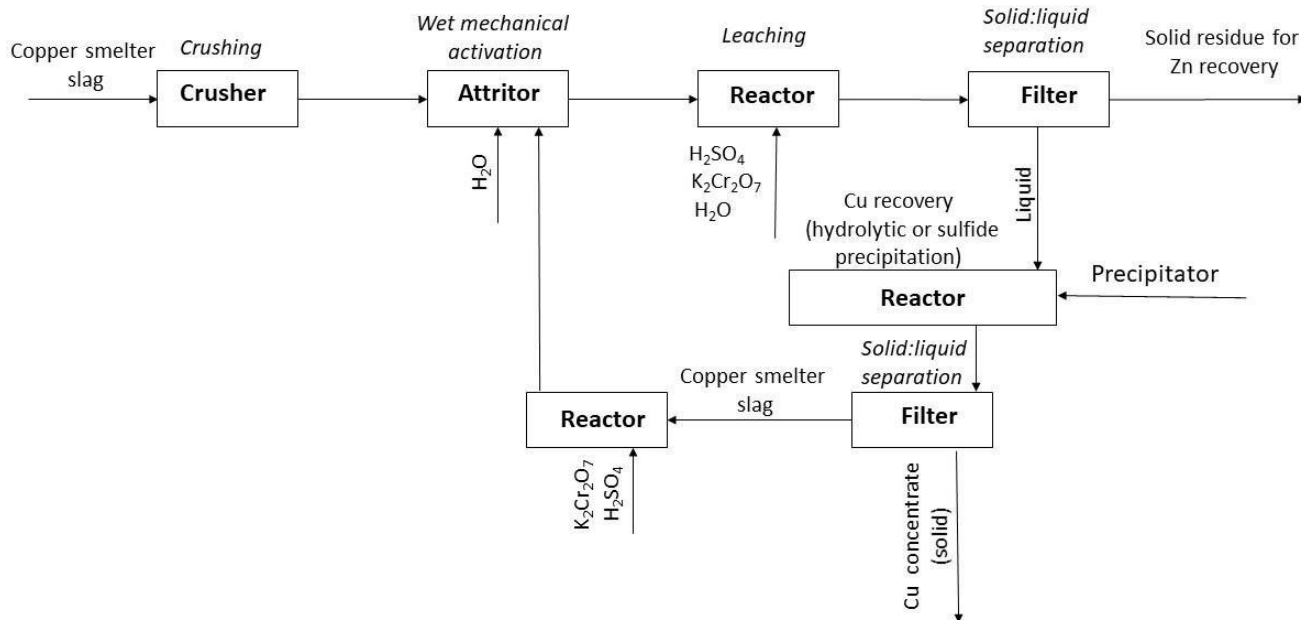
Figure 3.25 – Principal scheme of hydrometallurgical processing of copper smelter slag (1st stage)

The following conditions are applied:
1) MA: attritor mill; milling duration 75 min; ball-to-powder ratio 40:1, rotation speed 1200 rpm
2) Leaching: L: S = 10, $[H_2SO_4] = 0.1M$, $[K_2Cr_2O_7] = 0.03M$.

The solid residue after copper recovery is subjected to further leaching (2nd stage) under the same leaching conditions as copper leaching (Fig. 3.26).

Figure 3.26 - Principal scheme for the 2nd stage of the leaching

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The above schemes will make it possible to selectively extract copper (68.3% recovery) at the 1st stage of leaching mechanically activated copper smelter slag, and then extract zinc (65.7% recovery) from the residue of the first leaching stage.

CONCLUSIONS

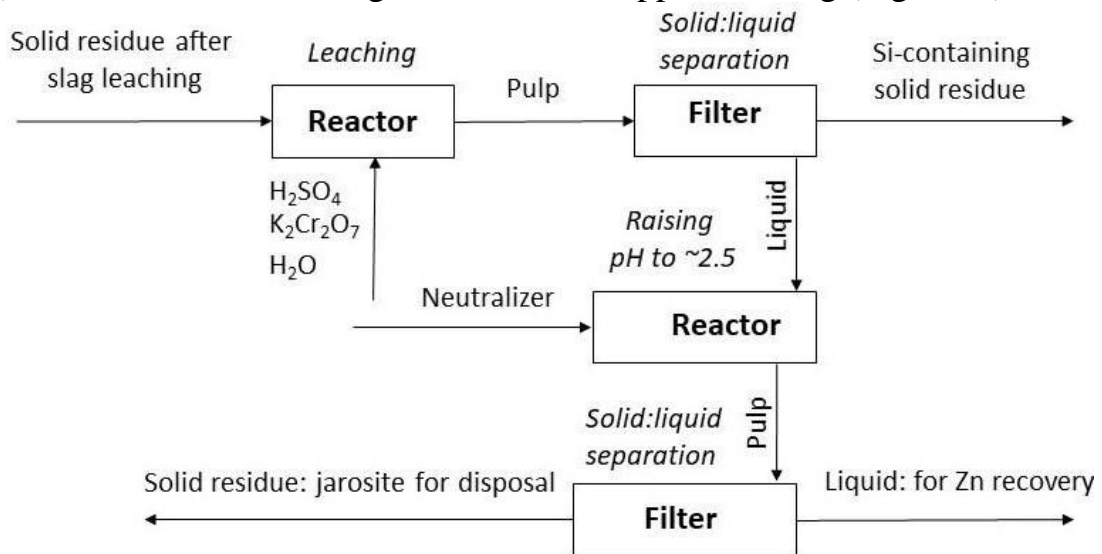Based on the data presented in this dissertation work, the following conclusions were made:

1) Sulfuric acid leaching of copper, zinc and iron from copper smelter slag is described by a shrinking core model; the rate of leaching of these metals into the solution at 298, 313 and 323 K is controlled by the rate of the chemical reaction. The activation energies of the leaching reactions of copper, zinc and iron were 28.1, 23.1, and 16.5, kJ/mol, respectively. The maximum extractions of the metals achieved at 70 °C, leaching duration of 1hour, final pH of 2.3, the rotation speed of 300 rpm, were, %: Cu 58.7, Zn 84.2, Fe 79.7;

2) The presence of $K_2Cr_2O_7$ in the sulfuric acid allows selectively separating copper from zinc and iron during leaching. Copper recovery is highly dependent on the copper-bearing mineral present in the slag: covellite and chalcocite are more easily leached than chalcopyrite. From chalcopyrite-, covellite- and chalcocite-containing copper slag, under the conditions of the liquid-to-solid ratio of 67, leaching duration 2 hours, T= 298 K, rotation speed 450 rpm, $[H_2SO_4]$ = 0.5 M, $[K_2Cr_2O_7]$ = 0.5 M, the extractions of metals were, %: Cu 68.0, Zn 4.1, Fe 5.0. From chalcopyrite-containing slag, under the same conditions (except for liquid-to-solid ratio, which was 75 in this case), the extractions of metals were, %: Cu 34.2, Zn 2.1, Fe 4.9;

3) Dry and wet mechanical activation of copper smelter slag in both planetary ball mill and attritor resulted in an enhancement of the specific surface area, with the greatest effect in the case of the wet mechanical activation in a planetary ball mill. Under the conditions of 1200 rpm, ball-to-powder ratio 40:1 and 75 min, the SSA of the slag sample increased 68.2 times;

4) Mechanical activation of the slag led to an increase in the degree of extraction of copper into solution during leaching with the sulfuric acid solution in the presence of dichromate ions, whereas that of Fe and Zn only increased marginally. The selectivity for copper is due to the higher dissolution rate of copper minerals compared to iron and zinc minerals;

5) The samples obtained using optimized conditions have been subjected to leaching and the following conditions were found to be optimal for Cu recovery in attrition mill (in parentheses for copper selectivity): $[K_2Cr_2O_7]$ = 0.15 (0.03) M, $[H_2SO_4]$ = 0.5 (0.1) M, leaching duration 120 (30) min, liquid-to-solid ratio 75:1 (75:1). Under these conditions, copper recovery reached 87.31%, and Cu selectivity was 95.44 % upon mechanical activation in the attritor. Upon L: S ratio reduction to value 10, and an only slight decrease in Cu recovery has been evidenced (namely it dropped from 78.2 to 73.7 % upon the use of attrition milling and from 77.5 to 71.9 % for planetary milling), which predetermines the proposed methodology to be potentially applicable in the industry;

6) The technological scheme of hydrometallurgical processing of copper smelter slag is proposed. The scheme includes the crushing of the initial slag, wet mechanical activation of the slag in the attritor, two-stage leaching in sulfuric acid solution in the presence of potassium dichromate, as well as filtration processes. The

following conditions are applied at the 1st stage: wet mechanical activation in attritor mill (milling duration 75 min; ball-to-powder ratio 40:1, rotation speed 1200 rpm); leaching (L: S = 10, $[H_2SO_4]$ = 0.1M, $[K_2Cr_2O_7]$ = 0.03M). The solid residue after copper recovery is subjected to further leaching (2nd stage) under the same leaching conditions as the 1st stage. The scheme makes it possible to selectively extract copper (68.3 % recovery) at the 1st leaching stage, and then extract zinc (65.7 % recovery) from the residue at the 2nd leaching stage.

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