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MECHANOCHEMISTRY AND PREPARATION OF NANOCRYSTALLINE MATERIALS

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The possibility of application of mechanochemistry in extractive metallurgy and material science is illustrated. Surface oxidation of mechanically activated sulphides, sorption properties of $CaCO_3$ after mechanical activation, gold leaching from mechanochemically pretreated Cu-Pb-Zn complex concentrate and pilot plant tests of mechanochemical technology (process MELT) have been selected as examples of application of mechanochemistry in physical chemistry and extractive metallurgy. The mechanochemical reduction of Cu_2S with the aim to prepare nanocrystalline copper can serve as an example of a novel process for preparation of advanced materials in materials science.

Key words: *mechanochemistry, leaching, sorption, reduction, mineral*

Mehanokemija i priprema nanokristaliničnih materijala. U radu su prikazane mo-gućnosti primjene mehanokemije na procese ekstrakcije u metalurgiji i znanosti o materijalima. Za primjer takve primjene mehanokemije u fizičkoj kemiji i metalurgiji ekstrakcije odabrani su oksidacija površine mehanički aktiviranih sulfida, apsorpciona svojstva $CaCO_3$ nakon mehaničkog aktiviranja, izdvajanje zlata luženjem prethodno mehanokemijski pripremljenog kompleksnog koncentrata Cu-Pb-Zn i pilot-pogonskog testiranja mehanokemijske tehnologije (proces MELT). Mehanokemijska redukcija Cu_2S radi pripreme nanokristalnog bakra može u znanosti o materijalima poslužiti kao primjer neuobičajenog procesa za pripremanje poboljšanih materijala.

Ključne riječi: *mehanokemija, luženje, sorpcija, redukcija, mineral*

INTRODUCTION

Mechanochemistry as a branch of solid state chemistry which enquiring into processes which proceed in solids due to the application of mechanical energy. The central problem of the solid state chemistry is the relationship between structure and reactivity of solids. Mechanochemistry helps us to solve this problem by the intentional formation of defects in the structure of solid substances by the application of mechanical forces using intensive milling equipments.

At present, mechanochemistry appears to be a science with a sound theoretical foundation which exhibits a wide range of potential application. There is a great number of publications on this topic concentrated in several monographs and papers [1 - 5].

The purpose of this paper is to elucidate the recent progress of mechanochemistry in extractive metallurgy and preparation of advanced materials.

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SURFACE OXIDATION OF MECHANICALLY ACTIVATED SULPHIDES

The disordering of surface layers of sulphide minerals occurs during mechanical activation in the presence of air oxygen. The first surface layers of these sulphides are degraded to some extent [6]. However, this disordering is not uniform and a great variety of different species are formed on the surface of disordered sulphides, e. g. oxides, hydroxioxides, hydroxides, sulfites, thiosulphates, oxisulphates, hydroxisulphates and sulphates have all been reported [1].

Photoelectron (XPS) spectra of mechanically activated lead sulphide PbS have been studied. Pb, S and contaminating C and O are seen in the survey XPS spectrum of PbS in Figure 1. The sulphate sulphur enrichment on surface is illustrated in Figure 2., where spectra of S2p electrons for both samples are given. While about 42 % of hexavalent sulphur is present in the surface layer of non-activated PbS, it increased to 70 % in the activated sample. However, based on the shape of spectrum we may suppose the presence of oxidative sulphur species also between S^{2-} and S^{6+} peaks. This was well documented in our previous work devoted to mechanical activation of galena

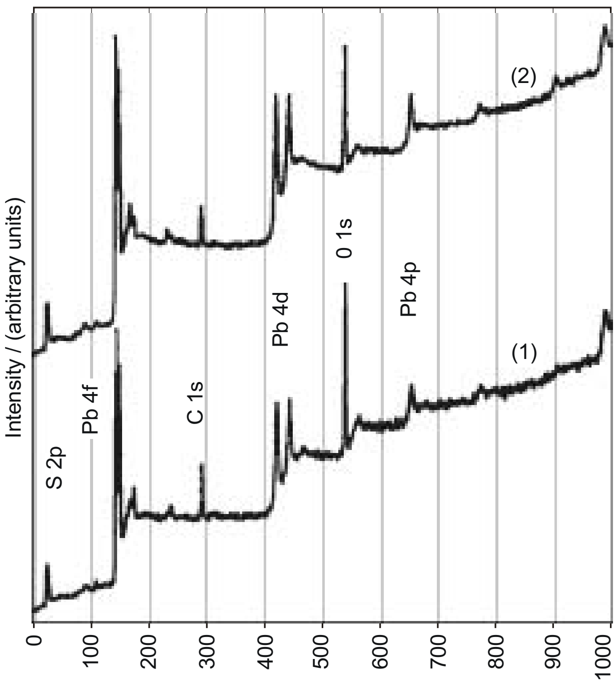

Figure 1. **XPS survey spectrum of PbS, mechanical activation: 1 - 0 min, 2 - 15 min**

Slika 1. **XPS spektar površine PbS, mehaničko aktiviranje: 1 - 0 min, 2 - 15 min**

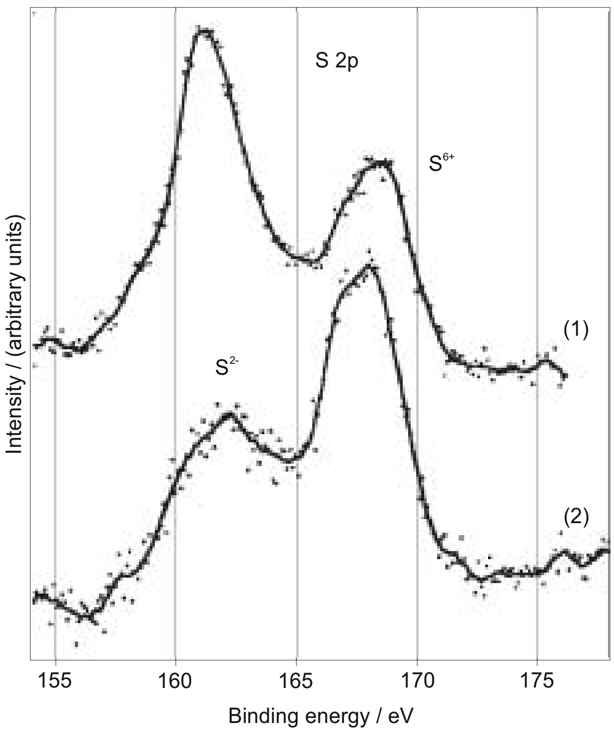

Figure 2. **S2p XPS spectrum of PbS, mechanical activation: 1 - 0 min, 2 - 15 min**

Slika 2. **S2p XPS spektar PbS, mehaničko aktiviranje: 1 - 0 min, 2 - 15 min**

[1]. The model developed in paper [7], where point defects and adsorption sites on surface of PbS are presented, can also be partly accepted for our obser-vation bearing in mind the fact, that mechanical activation is always connected with the creation of surface defects in solids.

SORPTION PROPERTIES OF $CaCO_3$ AFTER MECHANICAL ACTIVATION

The special properties of fine particles with a high surface area and their significant occurrence as by the product waste from mineral processing plants hawe lead to the suggestion that they may be utilized as sorbents for toxic metals [8]. The application of mechanical activation to industrial minerals with the creation of new surface area and structure disordering is the innovative procedure to enhance the sorption efficiency of fines for toxic metals removal.

The physico-chemical properties of calcite $CaCO_3$ mechanically activated in a planetary mill, as well as the sorption ability of this mineral for zinc removal from $ZnSO_4$ model solution, have been studied.

Table 1. **Time of mechanical activation, t_M, specific surface area, S_A and content of crystalline phase, X of mechanically activated $CaCO_3$**

Tablica 1. **Vrijeme mehaničkog aktiviranja, t_M, određeno područje površine, S_A i sadržaj kristalne faze, X u mehanički aktiviranom $CaCO_3$**

t_M / min	S_A / m^2g^{-1}	X / %
0	1,8	100
3	6,7	32
7	4,4	22
15	3,1	16

The specific surface area and the content of crystalline phase (structure disorder) are given in Table 1. The specific surface area increases for the first three minutes and then the decrease is observed probably as a result of aggregation

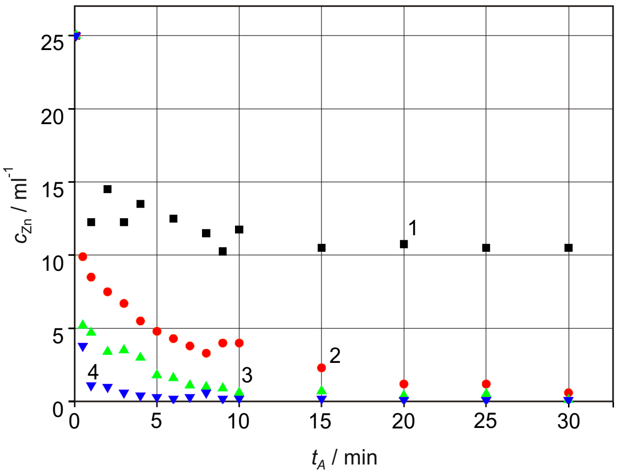

Figure 3. **Concentration dependance of Zn, c_{Zn} vs. time of sorption, t_A. Mechanical activation: 1 - 0 min, 2 - 3 min, 3 - 7 min, 4 - 15 min**

Slika 3. **Ovisnost koncentracije Zn, c_{Zn} o vremenu sorpcije, t_A. Mehaničko aktiviranje 1 - 0 min, 2 - 3 min, 3 - 7 min, 4 - 7 min, 4 - 15 min** of mechanically activated particles. However, in spite of that, the increase of structure disordering can be observed in a whole interval of mechanical activation under study.

The sorption isotherms for zinc sorption from $ZnSO_4$ solution (pH = 2,0) on mechanically activated calcite are given in Figure 3. There is a strong evidence of positive influence of mechanical activation on the rate as well as the efficiency of sorption. While only 58 % of Zn was adsorbed from zinc solution after 30 minutes treatment, only three minutes were needed for 98 % retention of Zn. In comparison with data in Table 1., the preferential influence of structural disordering on zinc sorption can be unambiguously deduced.

GOLD LEACHING FROM MECHANOCHEMICALLY PRETREATED COMPLEX SULPHIDE CONCENTRATE

The technologies hitherto used encounter a problem in processing complex sulphide concentrates containing gold in an economic way providing sufficient recovery. One of the problems of gold extraction from sulphidic minerals is associated with the form in which the metal occurs. Gold in sulphides may be physically included in intercrystalline spaces of sulphides that result from defects in their structure, or it can be chemically bonded in solid solutions and compounds.

Chemical, biological and physical pretreatments are applied as intervention steps directed to the sulphide, the goal of which is to change the composition and particle size of the gold-bearing sulphides and thus, to facilitate subsequent leaching. Simultaneously, with examination of the above mentioned pretreatments, new processes of mechanochemical pretreatment are being successfully applied to fundamental research, as well as to plant operations [1].

The possibility of mechanochemical pretreatment of Cu-Pb-Zn gold bearing sulphide concentrate in order to enhance the leachability of gold in ammonium thiosulphate lixiviant (as an alternative for cyanide leaching) has been verified.

Leaching of gold in thiosulphate solution results in the formation of a stable complex and is described by the equation:

$$Au + 2S_2O_3^{2-} \rightarrow Au(S_2O_3)_2^{3-} + e^- \qquad (1)$$

The dissolution step in ammonium thiosulphate solution is an electrochemical reaction and is promoted by the presence of cupric ions. It is possible to achieve more than 90 % recovery of gold in leach even in a few minutes for mechanically activated samples while the recovery of only 54 % Au was obtained under equal leaching conditions in the case of as received concentrate (Figure 4.). The mechanical activation proved to be a very effective method

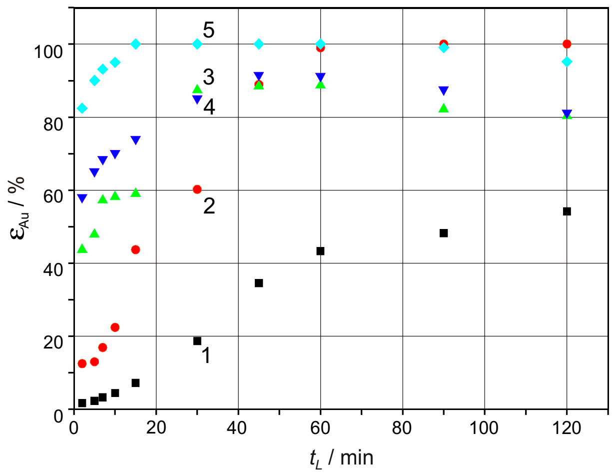

Figure 4. **Recovery of Au into leach, ε_{Au} vs. leaching time, t_L for mechanically activated samples. Energy input by milling, E_M: 1 - 0 kWh/t (as-received concentrate), 2 - 225 kWht/t, 3 - 449 kWh/t, 4 - 898 kWh/t, 5 - 1497 kWh/t**

Slika 4. **Oporavak Au u lužini, ε_{Au} prema trajanju luženja, t_L za mehanički aktivirane uzorke. Unos energije valjanjem, E_M: 1 - 0 kWh/t (koncentrate u primljenom stanju), 2 - 225 kWht/t, 3 - 449 kWh/t, 4 - 898 kWh/t, 5 - 1497 kWh/t**

of sulphide concentrate pretreatment before extraction of precious metals into leach liquor. The process of thiosulphate leaching is nontoxic and moreover brings kinetic advantage over classical cyanide leaching [1, 9].

PROCESS MELT: MECHANOCHEMICAL TECHNOLOGY

The possibility of integrating the individual operations within a whole technological flowsheet is not new. The process CIL (carbon-in-leach) is used in hydrometallurgy for gold recovery. Granular activated carbon is added to the leaching tanks so that it can adsorb the gold cyanide complex as soon as it is formed thus integrating leaching and sorption into a common operation.

If the mechanical activation is separated from the leaching in time, then a number of highly excited states in solids would have decayed before leaching. On the other hand, if the mechanical activation and leaching are integrated into a common step all the excitation effects may be utilized. In addition to the improvement of milling performance (the leaching agent works also as grinding additive) there is the possibility that a common milling and leaching step contributes to operation benefits and to the economy of the overall process.

Alkaline leaching of tetrahedrite mineral Cu_3SbS_3 in Na_2S solution dissolves selective antimony leaving copper in the solid residue:

$$2\,Cu_3SbS_3 + Na_2S \rightarrow Cu_2S + 2\,NaSbS_2 \qquad (2)$$

$$NaSbS_2 + Na_2S \rightarrow Na_3SbS_3 \qquad (3)$$

The soluble Na_3SbS_3 with trivalent Sb is oxidized to pentavalent antimony due to the oxidizing power of polysulphides present in the leach liquor as indicated in equation:

$$(x-1)\,Na_3SbS_3 + Na_2S_x \rightarrow (x-1)\,Na_3SbS_4 + Na_2S \qquad (4)$$

The process has a high selectivity with copper and precious metals remaining in the solid residue which is by composition suitable feed for a smelter treatment.

The concept of mechanochemical leaching of tetrahedrite (process MELT) developed and verified in laboratory and semi-industrial attritors Figure 5. was further tested in pilot plant unit in Slovakia [1, 10, 11]. The pilot plant tests

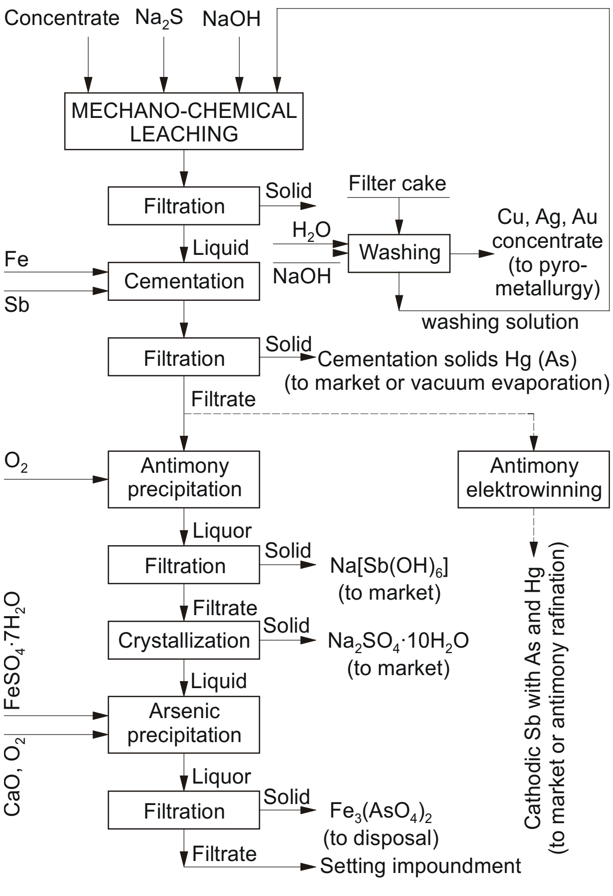

Figure 5. **Flowsheet of the MELT process**
Slika 5. **Tehnološka shema MELT procesa**

have shown that with alkaline Na_2S solution applied at 86 °C and atmospheric pressure, 30 minutes is required for total extraction of Sb from tetrahedrite. The other valuable metals (Cu, Ag, Au) form the main economic components of solid residue. The liquid/solid ratio (2,5...4,8) and power inputs (150 to 250 kWh/t of concentrate) applied in optimized mechanochemical experiments are acceptable from the view point of plant operation [1, 12].

PREPARATION OF COPPER NANOPARTICLES BY MECHANOCHEMICAL REDUCTION OF COPPER SULPHIDE

Mechanical alloying is a novel high-energy ball milling synthesis route that can be used to prepare various interesting advanced materials in nanorange dimensions. The properties of these products can differ considerably from those of the polycrystalline powders prepared by conventional methods. The principles and applications of the method were reviewed recently by Suryanarayana [13].

Ball milling also induces chemical reactions. The mechanochemical reduction of copper sulphide Cu_2S with elemental iron has been studied [14].

The reaction is thermodynamically possible, as the enthalpy change is negative, ΔH = - 21 kJ for the "ideal" stoichiometry:

$$Cu_2S + Fe \rightarrow 2\ Fe + FeS \qquad (5)$$

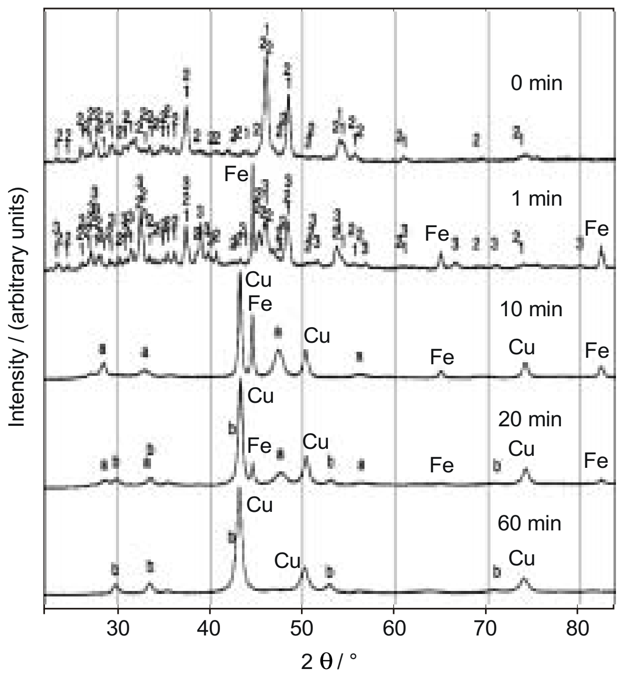

Figure 6. **XRD patterns as a function of milling time. The lines of the copper sulphides djurleite $Cu_{1,94}S$(1), chalcocite Cu_2S(2) and tetragonal $Cu_{1,83}S$(3); cubic (a) and hexagonal (b) FeS; and the metals copper (Cu) and iron (Fe) are marked**
Slika 6. **XRD obrasci kao funkcija vremena prolaska kroz valjaonicu. Označene su crte sulfida bakra $Cu_{1,94}S$(1), Cu_2S(2), $Cu_{1,83}S$(3); kubičnog (a) i heksagonalnog (b) FeS; te metali bakar (Cu) i željezo (Fe)**

Most of the reaction takes place during the first 10 minutes (Figure 6.) of milling and only FeS and Cu are found after 60 minutes.

The main chemical process is accompanied by phase transformations of the sulphide phases as a result of milling. As for copper sulphide phases, djurleite is partially transformed to chalcocite and a tetragonal copper sulphide phases before reduction.

The cubic modification of FeS was formed first, transforming to hexagonal during the later stages of the process. The formation of off - stoichiometric phases and the release of some elemental sulphur by copper sulphide are also probable.

Platelets of Cu - FeS composite particles are formed as aggregates, tenths of micrometers in diameter. However, the average grain size of the freshly formed copper is between 10 and 25 nanometers depending on milling conditions.

CONCLUSIONS

The presented results have shown that after successful application to extractive metallurgy of minerals, mechanical activation is heading for new fields of study such as preparation of composites, nanocrystalline and amorphous substances which create technological background for the 21st century.

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