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Mechanochemistry of sulphides

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At present mechanochemistry of sulphides appears to be a science with sound theoretical foundation exhibiting a wide range of opportunities in different area of science and technology. For *traditional applications* mechanochemistry is of exceptional importance in mineral processing and extractive metallurgy. Mineral disordering by high energy milling has a positive influence on the reaction kinetics and further phenomena, such as changing the reaction mechanism to reduce environmental impacts. Metal sulphides can be utilized nowadays, in *advanced applications* such as precursors for synthesis of high temperature superconductors, luminescent and solar energy materials, high-energy density batteries and further materials for opto-electronic and magnetic applications. Mechanochemistry in this case serves as a tool which can effectively control and regulate the solid state reactions for advanced materials preparation.

It is aim of this review paper to illustrate the progress in mechanochemistry of sulphides achieved in recent years in Slovakia.

1. Introduction

Sulphides play an important role in extractive metallurgy as sources of non-ferrous and precious metals. Mastering the processing of sulphides as well as their new applications as advanced materials (Table I) requires a deeper knowledge of their solid state properties. The new methods of solid treatment are studied in order to improve their technological processing. Among them, mechanochemical routes [1] strongly influence the field of the traditional as well as advanced applications of sulphides.

It is aim of this review paper to illustrate the progress in the mechanochemistry of sulphides, achieved in recent years in Slovakia. Three selected topics will be given covering the fields of gold and silver extraction [2–6], mechanochemical leaching of copper concentrates [2, 7–13] and nanosulphides preparation [14–18].

TABLE I Examples of sulphides utilization in technology

Traditional application
Chemical engineering
• hydrodesulphurisation (MoS_2, WS_2)
• hydrodenitrogenation (Co_9S_8)
• dehydratation (CuS, MnS, ZnS, PbS)
Mechanical engineering
• lubricants (MoS_2)
Mineral processing and extractive metallurgy
• pyrometallurgy ($CuFeS_2$, PbS)
• hydrometallurgy (ZnS, $Cu_{12}Sb_4S_{13}$)
• biohydrometallurgy (FeAsS, FeS_2)
Application as advanced materials
• high-energy density batteries (TiS_2)
• photoelectrochemical solar cells (FeS_2)
• solar energy conversion materials ($CuInS_2$)
• diagnostics materials (Ag_2S)
• luminescence materials (ZnS, CdS: Mn, Cu, Pb)
• precursors forsuperconductors synthesis (La_2S_3)
• intercalation compounds (TiS_2, TaS_2, NbS_2)

2. Enhancement of gold and silver recovery

The most frequent sulphides in which precious metals (Au, Ag) are present are pyrite FeS_2, arsenopyrite FeAsS and stibnite Sb_2S_3, other minerals, such as chalcopyrite, sphalerite and galena also contain small amounts of Au and Ag. The sulphidic minerals which occur in the form of sulfosalts (e.g. tetrahedrite $Cu_{12}Sb_4S_{13}$) cause considerable problems in the leaching of Ag. In this case, the classical cyanide leaching does not allow leaching of more than 5–10% Ag [19].

Some type of ore pretreatment is needed in order to improve the precious metal extraction (Fig. 1). Chemical and biological pretreatments consist of oxidizing roasting, pressure oxidation and bacteria attack. The goal of these is to disintegrate the sulphide and thus to facilitate the subsequent extraction of precious metals. Physical pretreatment consists of fine grinding of ore. If the gold encapsulated within the matrix of sulphide minerals is somewhat coarser in size, ranging from 1 to 20 microns, the liberation can be achieved by ultrafine grinding in an attritor [20]. Mechanochemical pretreatment based on the synergetic effect of mechanical activation and leaching has been verified as an effective tool for gold and silver extraction from refractory sulphidic ores [2].

The acid non-cyanide leaching of silver from silver bearing tetrahedrite $Cu_{12}Sb_4S_{13}$ physically pretreated by mechanical activation in a planetary mill and attritor was studied in paper [3]. Thiourea, $CS(NH_2)_2$ as

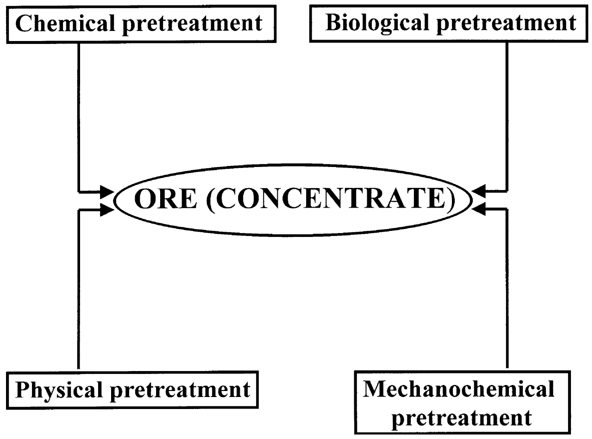

Figure 1 The different ways of sulphidic ore (concentrate) pretreatment.

an attractive alternative for cyanide because of its low toxicity and higher selectivity acts according to equation

$$Ag + 3CS(NH_2)_2 + Fe^{3+} \rightarrow Ag[CS(NH_2)_2]_3^+ + Fe^{2+} \quad (1)$$

The mechanically activated samples of tetrahedrite were subjected to thiourea leaching and the results are summarized in Figs 2 and 3. Under the activation and leaching conditions used the maximum recovery was achieved from the samples activated in a planetary mill. The recoveries from the samples activated in an attritor were lower. These results indicate that the disordering of the structure (which is greater in a planetary mill) is a decisive process from the viewpoint of Ag extraction.

Fig. 4 represents the quantitative relationship between the rate of thiourea leaching and surface/bulk properties of mechanically activated samples activated. The rate constant has been correlated with the empirical coefficient S_A/1-R which represents the surface/bulk disordering ratio form the mineral. The plot in Fig. 4 shows that the extraction of silver from tetrahedrite is a structure sensitive reaction. An equal rate of leaching can be attained by mechanical activation either in an attritor or in planetary mill. This observation is also of prognostic character because it enables us to propose suitable grinding equipment according to the demand for fineness or reactivity of the solid substances.

3. Antimony metal and copper concentrate production

Mechanochemical leaching integrates the milling and leaching operations into one common step. The synergistic effect has the important theoretical background as can be deduced from Fig. 5, which shows that are differences between the excitation period and the duration of excitation states. If the mechanical activation is separated from the chemical process (e.g. leaching) in time, then a number of highly excited states would have decayed before leaching. On the other hand, if the mechanical activation and leaching are integrated into a common step all the excitation states may be utilized. In addition to the improvement of grinding performance

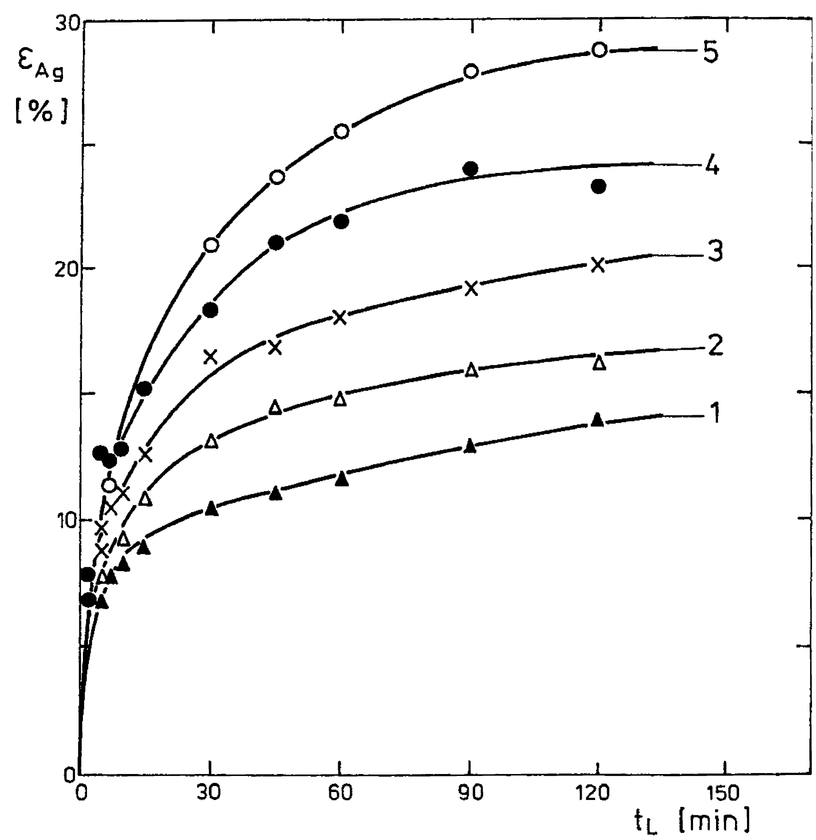

Figure 2 Silver recovery, ε_{Ag} vs. leaching time, t_L for tetrahedrite mechanically activated in an attritor. Mechanical activation: 1—10 min, 2—20 min, 3—40 min, 4—80 min, 5—160 min.

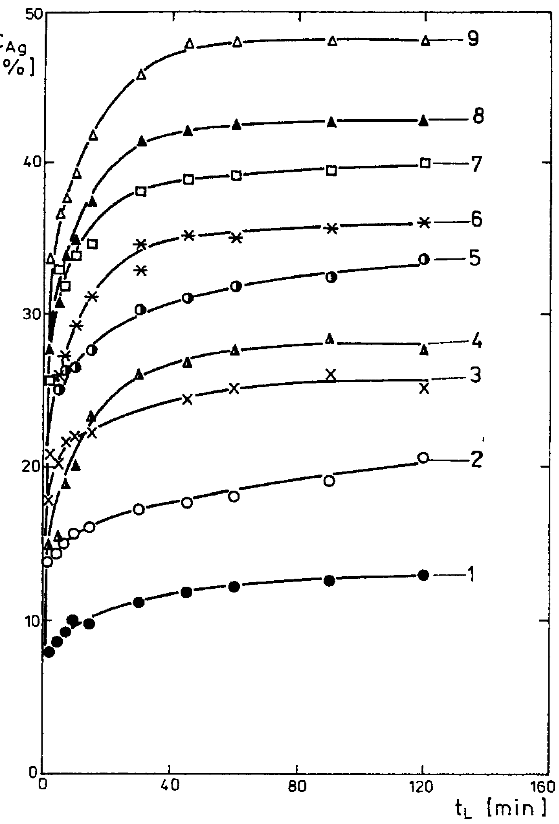

Figure 3 Silver recovery, ε_{Ag} vs. leaching time, t_L for tetrahedrite mechanically activated in a planetary mill. Mechanical activation: 1—2 min, 2—5 min, 3—10 min, 4—30 min, 5—15 min, 6—20 min, 7—60 min, 8—90 min, 9—45 min.

(the leaching agent works also as grinding additive) there is the possibility that a common grinding and leaching step contributes to operation at benefits and to the economy of the overall process.

The principle of mechanochemical leaching has been applied to the hydrometallurgical treatment of tetrahedrite Cu_3SbS_3 concentrates. The reaction of refractory tetrahedrite with Na_2S as an alkaline leaching agent is described by the equations

$$2Cu_3SbS_3(s) + Na_2S(l) \rightarrow 3Cu_2S(s) + 2NsSbS_2(l) \quad (2)$$

$$NaSbS_2(l) + Na_2S(l) \rightarrow Na_3SbS_3 \quad (3)$$

The reaction kinetics is slow and high temperatures and the long leaching times are needed to obtain high recoveries [21].

Simultaneous leaching and milling greatly intensify the whole process. The concept of mechanochemical leaching of tetrahedrites (process MELT) originally developed in the laboratory and semi-industrial attritors was further tested in a pilot plant unit in Slovakia. The flowsheet is given in Fig. 6 and consists of primary mechanochemical leaching and the subsequent operations for production of Cu-Ag-Au concentrate, Hg(As) cementation solid, antimony electrowinning and/or $Na[Sb(OH)_6]$ synthesis as well by products processing [2].

4. Preparation of sulphide nanoparticles

Nanoparticles of sulphides have been synthesized recently by different chemical routes with the aim to prepare materials with controlled particle morphology and size distribution [22–27]. The synthesis routes have used solvothermal synthesis with the addition of microwave, sonochemical and autoclave techniques.

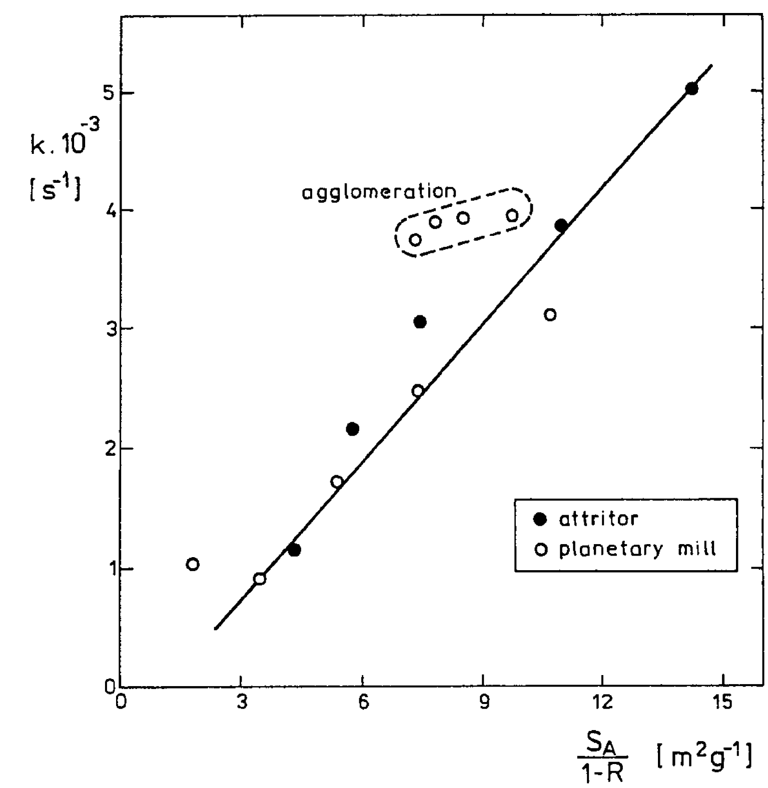

Figure 4 Rate constant of Ag leaching, k vs. surface/bulk disordering ratio, $S_A/1\text{-}R$, S_A—surface area, R—disordering of tetrahedrite structure.

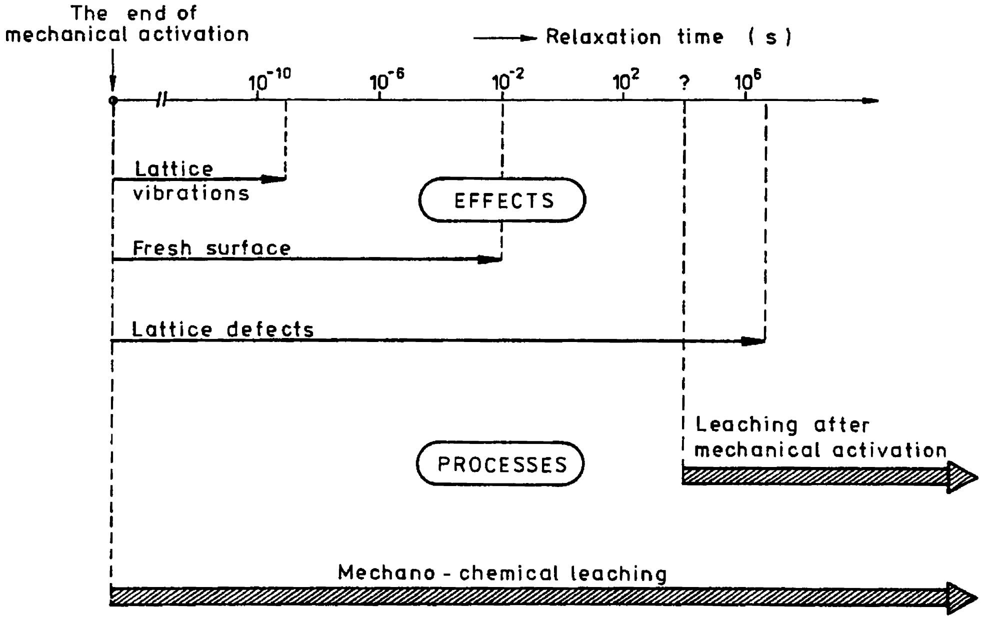

Figure 5 The period and the duration of excitation states after termination of mechanical activation.

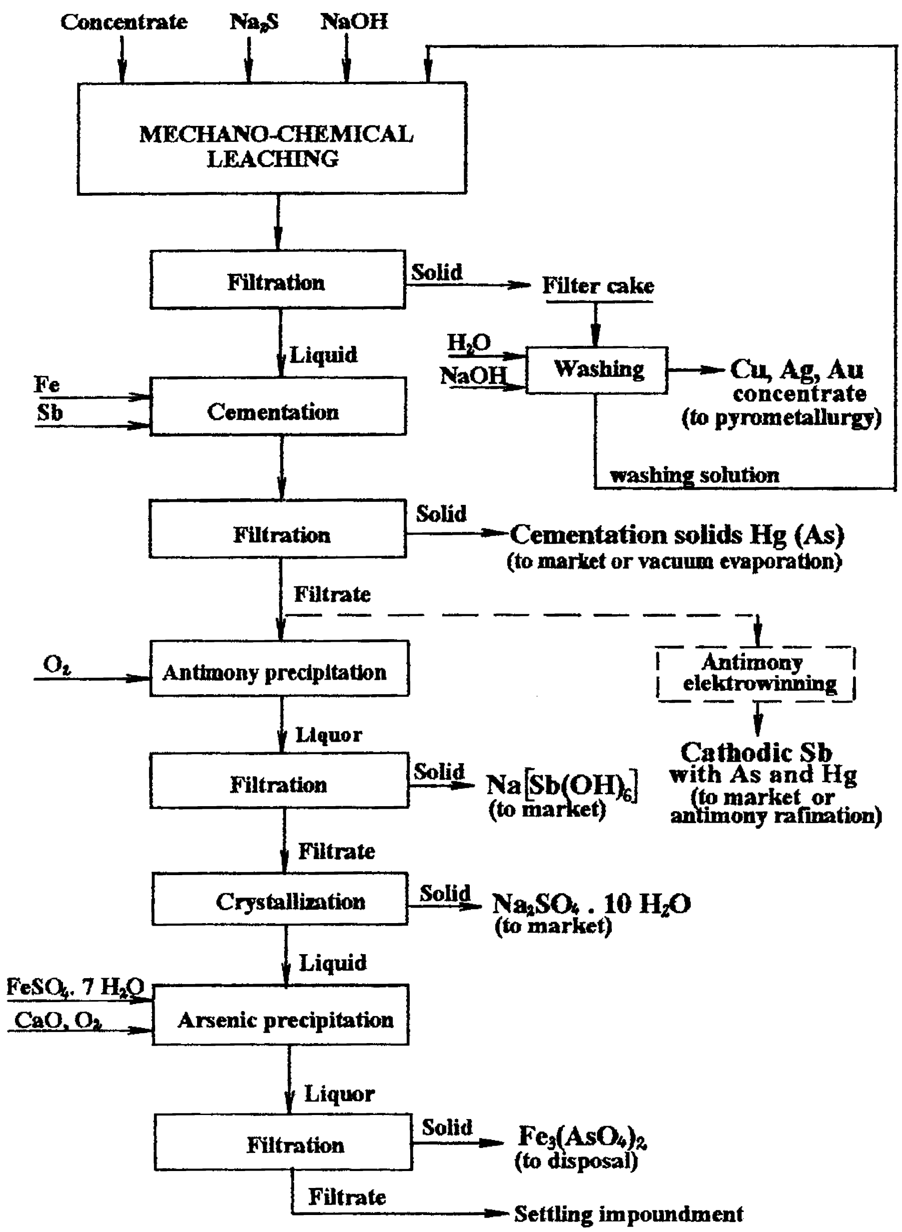

Figure 6 Flowsheet of the MELT process.

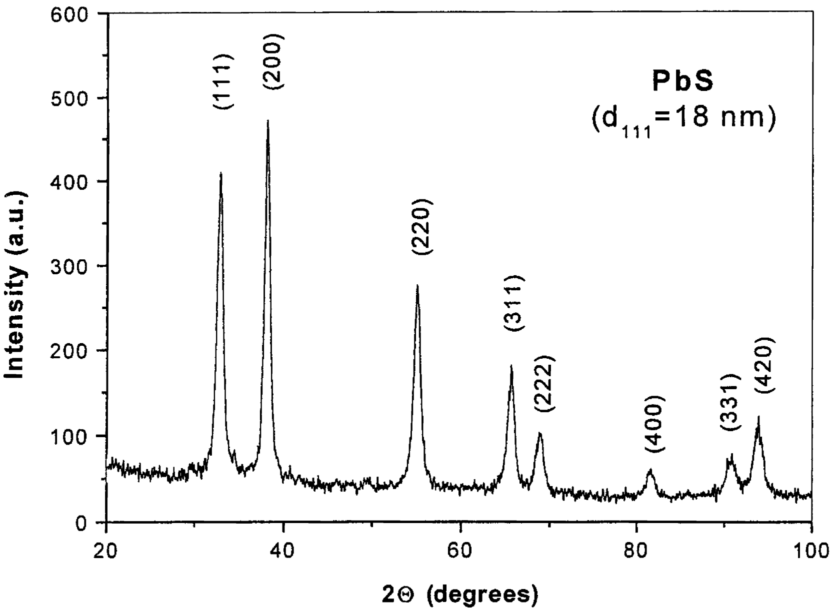

Figure 7 XRD pattern of the mechanochemically synthesized PbS nanoparticles (JCPDS 5-592: galena PbS).

The diverse possibilities of mechanochemical processes for sulphides preparation have been described recently in papers [14–18, 28–35]. In this type of synthesis, chemical reactions and phase transformations take place because of the application of mechanical energy. As a consequence, reactions which normally require high temperature will occur at low temperature without any externally applied heat. Mechanochemical processing belongs among the routes which can effectively control and regulate the course of solid state reactions.

A new mechanochemical route for sulphide nanoparticles preparation has been described in paper [17]. The synthesis is governed by

$$(CH_3COO)_2\mathit{Me} + Na_2S \rightarrow \mathit{Me}S + 2CH_3COONa \qquad (\mathit{Me} = \mathrm{Zn, Cd, Pb, Co, Cu}) \quad (4)$$

where after finalizing reaction (4), the solid metal nanoparticles can be directly obtained by washing the unreacted precursors and soluble product.

XRD pattern of PbS nanoparticles after the mechanochemical reaction of lead acetate $(CH_3COO)_2\,Pb{\cdot}3H_2O$ with sodium sulphide $Na_2S{\cdot}9H_2O$ and subsequent processing is given in Fig. 7. We clearly see the diffraction peaks corresponding unambiguously to galena PbS phase (JCPDS 5-592). The grain size of the PbS nanocrystallites was calculated from the Scherrer formula for (200) plane. The obtained value 18 nm is the same as estimated for PbS particles prepared by gas condensation [22].

5. Conclusions

1. Mechanical activation of silver bearing tetrahedrite $Cu_{12}Sb_4S_{13}$ has a positive influence on silver thiourea leaching. The leaching is a structurally sensitive solid-liquid reaction. An equal rate of leaching can be attained either in an attritor (i.e. in a mill producing larger surface and smaller disordering in bulk), or in planetary mill (where the disordering in bulk is great and the formation of new surface is minor).

2. Process MELT (mechanochemical leaching of tetrahedrites) has been developed and tested at pilot plant scale in Slovakia.

3. The simple, one-step process for crystalline PbS nanoparticles synthesis has been presented by the application of the mechanochemical processing route. The obtained nanoparticles were synthesized at laboratory temperature, atmospheric pressure and at a very short reaction time without the intervention of any solvent.

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