



# Mechanochemistry in hydrometallurgy of sulphide minerals

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Received 27 May 2004; received in revised form 13 July 2004; accepted 19 September 2004

Dedicated to Professor Klára Tkáčová in honour of her 70th birthday.

## Abstract

The paper handles with the impact of mechanochemistry on hydrometallurgy of sulphide minerals. Mechanochemistry is a branch of solid-state chemistry dealing with the processes which take place within solids as a result of the application of mechanical energy. The application of mechanochemistry to hydrometallurgy is illustrated with short theoretical background and selected examples involving selective leaching of Zn from sphalerite ZnS, Zn sorption on pyrrhotite  $\text{Fe}_{1-x}\text{S}$ , acid leaching of ZnS nanoparticles and selective Bi leaching from PbS concentrate. It is demonstrated that mechanochemical treatment of the sulphides leads to increased reaction rate, improved leaching selectivity and sorption efficiency and shows the enhanced leachability of nanocrystals.

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*Keywords:* Mechanochemistry; Hydrometallurgy; Sulphide; Zinc; Bismuth; Lead; Nanocrystal

## 1. Introduction

Mechanochemistry is a branch of chemistry which is concerned with chemical and physico-chemical transformations of substances in all states of aggregation produced by the effect of mechanical energy. This general definition has been formulated by Heinicke (1984) and is widely accepted nowadays. However, the origins of this science with many applications in extractive metallurgy go deep in the past. Takacs (2000) recently published a paper in

which the tracks of mechanochemical treatment of cinnabar HgS might be dated to the Aristotle era. In his book “On stones or de lapidus”, Theophrastus of Efesus (371–286 B.C.), a student of Aristotle, describes a method to recover mercury from cinnabar by mechanical energy. The metal is obtained from native cinnabar after rubbing in a brass mortar with a brass pestle in the presence of vinegar.

At present, mechanochemistry appears to be a science with a sound theoretical foundation which exhibits a wide range of potential application. Its benefits include lower reaction temperatures, increased reaction rate, increased dissolution and the formation of water soluble compounds. As a consequence, further processing can be performed in

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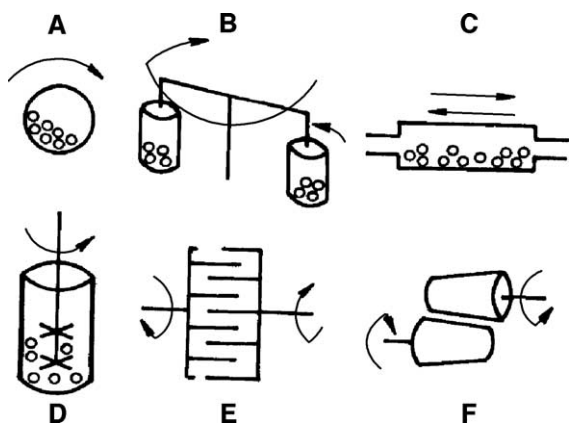


Fig. 1. Types of mills applied on mechanochemistry; A—ball mill, B—planetary mill, C—vibratory mill, D—stirring ball mill (attritor), E—pin mill, F—rolling mill (Boldyrev, 1986).

simpler and less expensive reactors during shorter reaction times (Welham, 1997, 2001; Baláž, 2000a).

The key factor in mechanochemistry is the application of a suitable mill which can work in different working regimes. In fact, there are various factors affecting the operation of milling process in mechanochemistry (Baláž, 2000a,b) and different types of mills are used (Fig. 1).

A brief description of the established technologies (LURGI-MITTERBERG, ACTIVOX, MELT, NENA-TECH, DYNATEC) applying mechanochemical principles for metals extraction from sulphide minerals was given recently (Baláž, 2003; Peacey et al., 2003). The aim of this review paper is to elucidate the recent progress of mechanochemistry in hydrometallurgy of sulphide minerals in Slovakia.

## 2. Theoretical background

Generally, the mechanochemical treatment of mineral leads to positive influence on the hydrometallurgical operations (Tkáčová, 1989; Baláž, 2000a, 2003). It has been documented by Zelikman et al. (1975) that the breaking of bonds in the crystalline lattice of the mineral brings about a decrease ( $\Delta E^*$ ) in activation energy and an increase in the rate of leaching

$$\Delta E^* = E - E^* \quad (1)$$

$$k^* = k \exp(\Delta E^*/RT) \quad (2)$$

where  $E$  is the apparent activation energy of the non-disordered mineral and  $E^*$  the apparent activation energy of the disordered mineral;  $k$ ,  $R$  and  $T$  stand for the rate constant of leaching for the non-disordered mineral, pre-exponential factor, gas constant and reaction temperature, respectively;  $k^*$  is the rate constant of leaching for the disordered mineral.

If  $E > E^*$ , then  $\exp(\Delta E^*/RT) > 1$  and thus it follows from Eq. (2) that  $k^* > k$ , i.e., the rate of leaching of a disordered mineral is greater than that of an ordered mineral.

It was Senna (1989) who analysed the effect of surface area and the structural disordering on the leachability of mechanically activated minerals. In order to solve the problem—whether surface area or structural parameters are predominant for the reactivity—the rate constant is divided by the proper surface area and plotted against the applied energy by activation (Fig. 2).

For example, if the rate constant of leaching divided by the surface area remains constant with respect to the applied energy, as shown in Fig. 2A, then the measured surface area may be the effective surface area and at the same time, the reaction rate is insensitive to the structural changes. If, on the other hand, the value  $k/S_i$  decreases with applied energy, as it is shown in Fig. 2B, then the surface area is probably not the effective surface area. In the third case, where  $k/S_i$  increases with increasing applied energy, as it is shown in Fig. 2C, the surface area  $S_i$ , may be again the effective surface area, with an overlapping effect of the structural imperfection, as a

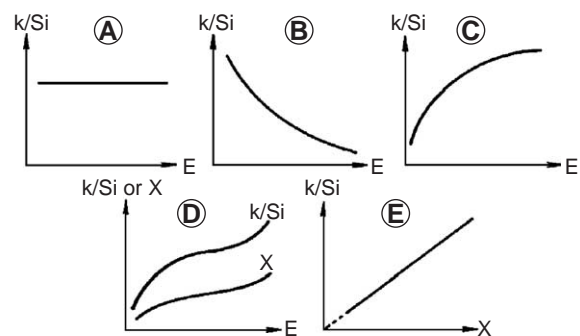


Fig. 2. The schematic diagrams representing the mutual dependence of physico-chemical characteristics and reactivity of mechanically activated solids:  $k$ —the rate constant of leaching,  $S_i$ —surface area,  $X$ —structural imperfections,  $E$ —applied energy (Senna, 1989).

result of mechanical activation. Alternatively, when  $k/S_i$  and  $X$  vary parallel to each other with  $E$ , as shown in Fig. 2D, or the value  $k/S_i$  is proportional to  $X$ , as shown in Fig. 2E, it seems more appropriate to accept the chosen  $S_i$  as an effective surface area.

### 3. Selective leaching of Zn from mechanically activated sphalerite ZnS

The selection of a leaching agent suitable for sphalerite has been given considerable attention (Warren et al., 1985; Crundwell, 1988; Chen et al., 2002; Hu et al., 2004). Strong oxidizing leaching allows leaching at atmospheric pressure, whereas the use of acids frequently necessitates the autoclave leaching in the presence of oxygen (Mizoguchi and Habashi, 1983).

The pretreatment of sulphides for hydrometallurgical operations can be performed by various methods (Havlík and Kammel, 2000; Havlík et al., 2001a,b). Exner et al. (1969) found that activation of the sphalerite by irradiation with ultraviolet rays raised the recovery of zinc in a subsequent high-pressure leaching. The authors pointed out the importance of solid-state properties of sphalerite for the progress of the leaching.

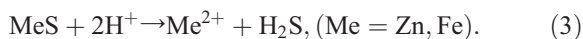
In paper (Baláž and Ebert, 1991) an attempt to study the correlation between the changes in surface and bulk properties of sphalerite due to mechanical activation with rate of oxidative leaching of this mineral was made. Hydrogen peroxide was selected as a model strong oxidative lixiviant for the leaching. This leaching agent selectively dissolves copper while iron, frequently present in the mineral in high amounts (Anthony et al., 1990) is precipitated.

This study reports the attempts to apply the non-selective leaching agent ( $H_2SO_4$ ) which dissolves zinc, as well as iron from sphalerite (15.53% Fe), and to assess the possible influence of sphalerite activation by milling on the leaching selectivity defined as Zn/Fe mass ratio.

The surface properties of sphalerite were studied using infrared spectroscopy. This method enables the identification of new compounds formed on the sulphide surface as a result of mechanical activation. Mechanical activation resulted in the appearance of  $ZnSO_4$  (1190, 1111 and  $1020\text{ cm}^{-1}$ ) or  $FeSO_4$  (1090, 1013, 620 and  $513\text{ cm}^{-1}$ ). The rest of the peaks can be

assigned to the admixture of  $SiO_2$ , moisture in the tablet of KBr and  $FeCO_3$  which can be created due to the reaction of activated mineral with atmospheric  $CO_2$ .

The acid non-oxidizing leaching of sphalerite with iron content obeys the principal equation



The final products of reaction (3) are influenced by several factors, e.g. concentration of hydrogen ions or temperature. In some cases the formation of elemental sulphur can be observed. In Fig. 3 the recoveries of Zn and Fe are plotted against leaching time.

Mechanical activation accelerates the recoveries of both metals. From leaching curves one can conclude that selectivity of leaching is also influenced. Two stages of leaching can be observed for mechanically activated sphalerite (Fig. 3). There is a sharp increase in Zn and Fe recovery as a consequence of high soluble sulphates. Decrease in Zn and Fe dissolution rate is characteristic for the second stage. This stage is attributed to the formation of metal-deficient polysulphide surface layers (Buckley and Woods, 1984) and is responsible for the course of leaching curves. The thickness of the polysulphide layer increases during the initial rapid leach period and reaches steady state during slow leach period. Of course, this interpretation is not in accord with Eq. (3).

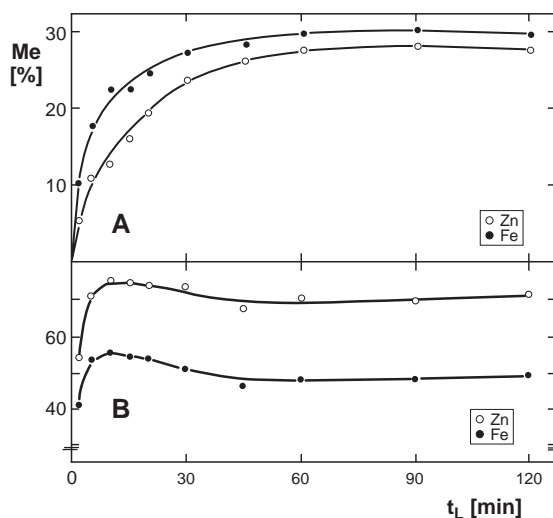


Fig. 3. Recovery of metals into solution Me, vs. time of leaching,  $t_L$  for ZnS: A—as-received, B—mechanically activated for 10 min.

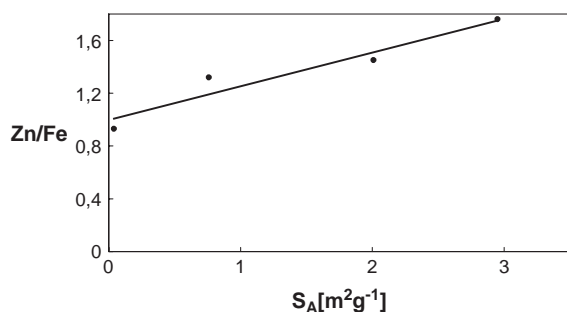


Fig. 4. Selectivity of leaching, Zn/Fe vs. specific surface area,  $S_A$  for mechanically activated sphalerite, leaching time 60 min.

Mechanical activation of minerals leads to an increase of specific surface area especially when the milling conditions are appropriately selected (Tkáčová, 1989). The relationship between sphalerite leaching selectivity defined as Zn/Fe and the specific surface area of mechanically activated sphalerite is shown in Fig. 4. There is a good linear relationship between both parameters which indicates the direct influence of surface disorder of the mechanically activated sphalerite on the selectivity of leaching.

#### 4. Zn sorption on pyrrhotite $Fe_{1-x}S$ synthesized by mechanochemical reduction of pyrite

The wastewater containing heavy metals causes one of the main problems for the environment. The hydrometallurgical research into heavy metals removal is oriented on the application of different sorbents including the waste from industry and agriculture. The sorption on mineral surfaces has been suggested as an alternative approach pointing out, that these materials could provide an inexpensive substitute for the treatment of wastewater with toxic metals content (Garcia-Sanchez and Alvarez-Ayuso, 2002).

The special properties of fine particles with a high surface area and their significant occurrence as the by-product waste from sulphide processing plants has led to the suggestion that they may act as sorbents for toxic metals (Zoubolis et al., 1993).

The mechanical activation is able to prepare sulphides with a high surface area and enhanced activity in hydrometallurgical processes (Baláž,

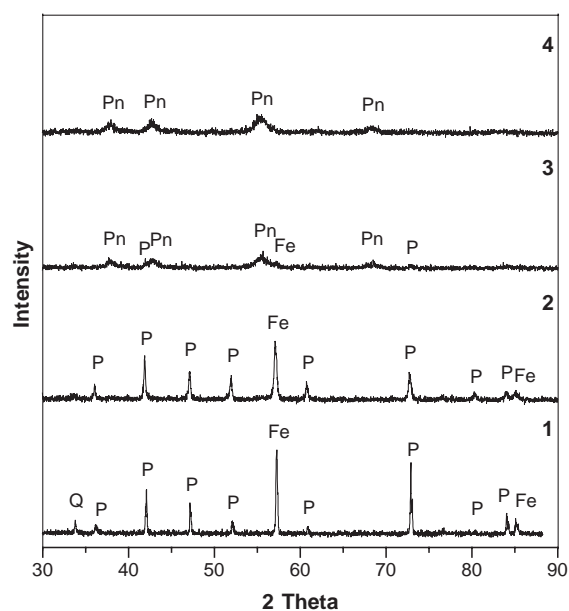


Fig. 5. XRD patterns of precursors and product of mechanochemical reaction (4) as a function of milling time: 1–0 min, 2–5 min, 3–25 min, 4–45 min, P—pyrite, Pn—pyrrhotite, Fe—iron, Q—quartz.

2000a). Pyrrhotite mineral after mechanical activation has been shown as an exceedingly efficient sorbent for sorption of platinum metals. A pyrrhotite concentrate was effectively used for Cu sorption from solutions using the unique properties of mechanically activated pyrrhotite (Kulebakin, 1988). In comparison with pyrrhotite, pyrite has a low economic significance in

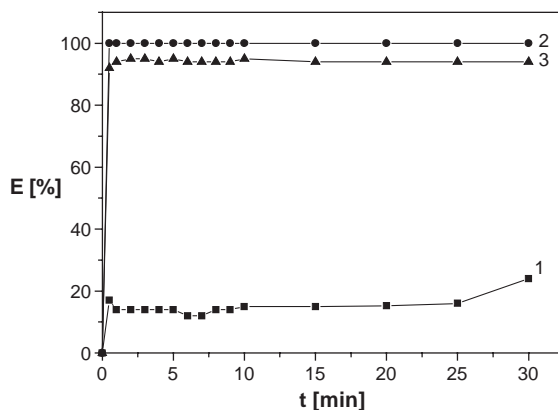


Fig. 6. Zinc sorption efficiency,  $E$  vs. time of sorption,  $t$  as a function of milling time: 1–0 min, 2–25 min, 3–45 min.

mineral processing plants, unless it is associated with uranium and gold. Its sorption capacity for toxic removal is negligible. This is the reason, why it is usually discarded into landfills in the mine area (Zoubolis et al., 1993).

This study reports the transformation of pyrite into pyrrhotite via mechanochemical reaction and testing prepared sorbent for zinc-ion removal. The simplified equation for pyrrhotite synthesis via mechanochemical reduction of pyrite with elemental iron is



The reaction (4) was performed in a planetary mill and in an argon atmosphere in order to prevent sulphur oxidation. The pyrite–pyrrhotite transformation is evidenced in Fig. 5.

The sorption tests with  $\text{ZnSO}_4$  solutions ( $25 \text{ mg L}^{-1}$ ) have been performed in order to verify the efficiency of as prepared sorbent. It can be seen that the total efficiency of Zn sorption was proved for mechanically synthesized pyrrhotite samples (Fig. 6).

The process was studied in more detail and the adsorption isotherm were determined (Aláčová, 2003). The isotherms were well fitted by the Freundlich equation (Fig. 7) what refers to the chemisorption of zinc ions as a rate determining step in a description of sorption mechanism.

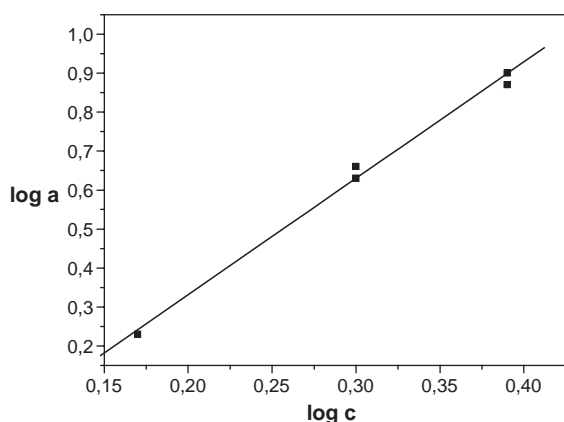


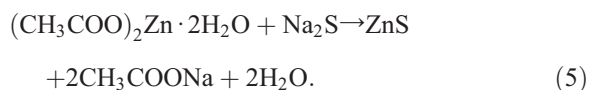
Fig. 7. Adsorption isotherms of Zn on mechanochemically pre-treated pyrrhotite, pH 2, sorption time=60 min, solid/liquid concentration= $5 \text{ g/L}^{-1}$ , c—the equilibrium concentration ( $\text{mg L}^{-1}$ ), a—sorption capacity ( $\text{mg g}^{-1}$ ).

## 5. Characterization and acid leaching of mechanochemically synthesized ZnS nanoparticles

In recent years, the preparation and characterization of different chalcogenides have attracted considerable attention mainly in case when these compounds are in the nanocrystalline state with grain sizes of up to about 100 nm. The novel characteristics of these materials are due to their extremely small particle size, where a large volume fraction of the atoms is located at the grain boundaries.

Zinc sulphide ZnS is an important semiconducting material for a variety of applications including optical coatings, solid-state solar cell windows, electrooptic modulators, photoconductors, sensors, etc. (Lan et al., 2003). Therefore, much research on physical properties of ZnS particles has been carried out (Baláž et al., 1997a,b; Dhas et al., 1999; Pawaskar et al., 2002).

However, the leaching of ZnS particles in nanocrystalline form has not been studied so far. This research was focused on the study of properties and non-oxidizing acid leaching of ZnS nanoparticles which were prepared by mechanochemical synthesis in a planetary mill according to the reaction



The conditions of mechanochemical synthesis are described in Baláž et al. (2003).

XRD patterns of reaction precursors and the washed reaction product are given in Fig. 8. One can clearly see the zinc sulphide phases which correspond to sphalerite (JCPDS 5-566) and wurtzite (JCPDS 5-0492). The average size of the particles is 2.1 nm. The broadening of diffraction peaks has been attributed to the small size of the nanoparticles, rather than the decrease of crystallinity.

The reactivity of the mechanochemically synthesized ZnS nanoparticles was tested by the non-oxidizing acid leaching which follows the reaction



Fig. 9A presents the plots of zinc fraction leached from the mechanochemically synthesized ZnS during 3, 5, 10 and 20 min of milling and that from

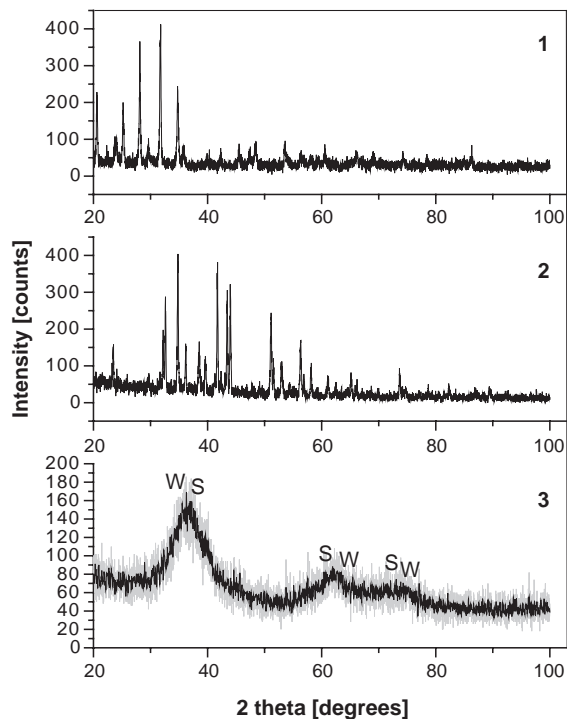


Fig. 8. XRD patterns of zinc acetate  $(\text{CH}_3\text{COO})_2\text{Zn} \cdot 2\text{H}_2\text{O}$  (1), sodium sulphide  $\text{Na}_2\text{S}$  (2) and mechanochemically prepared ZnS nanoparticles (3), milling time: 10 min, W—wurtzite, S—sphalerite.

chemically precipitated ZnS. The surface area of mechanically synthesized ZnS was as high as 91, 99, 117 and  $128 \text{ m}^2 \text{ g}^{-1}$  and of chemically precipitated ZnS  $8 \text{ m}^2 \text{ g}^{-1}$ .

The solubilization of Zn has a high starting velocity and after 10 min practically ceases. It is

obvious that while for chemically precipitated ZnS recovery of Zn increases, in case of the mechanochemically synthesized ZnS with the increasing milling time increases only the leaching kinetics. The dependence of Zn recovery for higher concentration of  $\text{H}_2\text{SO}_4$  is plotted in Fig. 9B. Clearly, the increasing concentration of leaching agent accelerates the extraction of zinc into leachate as well as leaching kinetics. However, the solubilization of Zn after 5 min practically ends. For the chemically precipitated ZnS a similar leaching behaviour to ZnS leached by 0.05 M  $\text{H}_2\text{SO}_4$  has been observed.

It follows from the presented results, that the increase in the surface area of mechanochemically synthesized ZnS does not manifest itself markedly in the following zinc leaching. The increasing milling time applied for the mechanochemical synthesis affects only the leaching kinetics. In this case the disordered ZnS nanostructure formation plays more significant role.

## 6. Selective Bi leaching from mechanically activated galena concentrate

Bismuth, widely used in chemicals, pigments and catalyst, is recovered only as a by-product. World output is about 6500 t/y principally from China (as a by-product in tungsten processing). Modest quantities are produced in Peru by pyrometallurgical way (Ellis, 2004).

Bismuth presence is very frequently associated with the occurrence of lead sulphide. However,

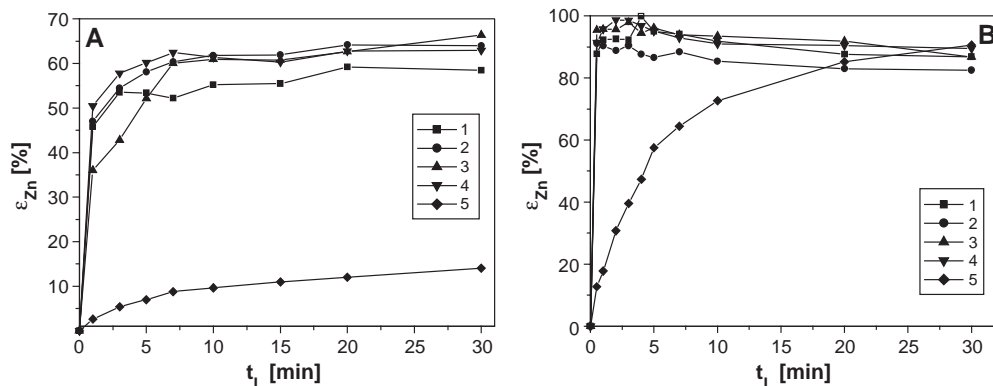


Fig. 9. Influence of leaching time,  $t_L$  on the zinc recovery,  $\epsilon_{\text{Zn}}$  from ZnS. 1, 2, 3 and 4: mechanochemically synthesized ZnS for 3, 5, 10 and 20 min, respectively; 5—chemically precipitated ZnS, leaching conditions: A—0.05 M  $\text{H}_2\text{SO}_4$ , B—0.5 M  $\text{H}_2\text{SO}_4$ , temperature: 323 K.



when lead is pyrometallurgically recovered from sulphide concentrates, bismuth is a harmful element. That is why selective leaching of bismuth makes sense. The key stage for Bi leaching from the concentrate is the way of its pretreatment and selection of leaching agent. HCl and (H<sub>2</sub>SO<sub>4</sub>+NaCl) belong among the fundamental leaching agents for Bi dissolution (Jansen and Taylor, 1995; Medkov et al., 1999).

The aim of this work was to examine the possibility of Bi leaching from lead sulphide concentrate (1.32% Bi, 51.3% Pb, 1.54% Cu, 8.42% Zn, 3.91% Fe, 2210 g t<sup>-1</sup> Ag and 18.75% S). Different leaching agents and mills have been tested in order to obtain selective extraction of bismuth with its high recovery into leach. The results are summarized in Table 1.

The results show that selectivity of Bi extraction was low at applying HCl and (H<sub>2</sub>SO<sub>4</sub>+NaCl) leaching agents despite of sufficient Bi recovery in several cases. However, with sodium thiosulphate solution

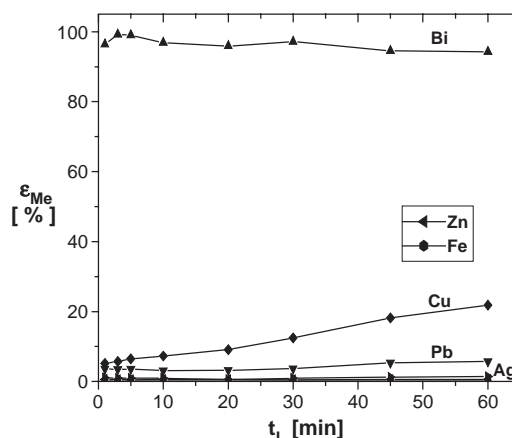


Fig. 10. Recovery of Bi, Cu, Pb, Zn, Fe and Ag,  $\varepsilon_{Me}$  vs. leaching time,  $t_L$  for lead sulphide concentrate mechanically activated in an attritor for 30 min, leaching temperature 25 °C.

applied at 25 °C and mechanochemical pretreatment made in an attritor it was possible to achieve 99% recovery of Bi even in 3 min of leaching time

Table 1

Specific surface area,  $S_A$ , leaching conditions (leaching time 60 min, solid/liquid ratio 1:400; 0.2 M HCl, H<sub>2</sub>SO<sub>4</sub>=15 g L<sup>-1</sup>, NaCl=200 g L<sup>-1</sup>, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>·5H<sub>2</sub>O=124 g L<sup>-1</sup>) and recovery of metals into leach,  $\varepsilon_{Me}$  for lead sulphide concentrate mechanically activated in different mills (leaching time 60 min)

Mill/milling time	$S_A$ [m <sup>2</sup> g <sup>-1</sup> ]	Leaching reagents	$T$ [°C]	$\varepsilon_{Me}$ [%]					
				Bi	Pb	Cu	Zn	Fe	Ag
–	0.7	HCl	25	1.8	3.7	0.2	1.2	7.6	0.6
			60	1.8	7.3	0.1	1.2	8.8	0.6
		H <sub>2</sub> SO <sub>4</sub> +NaCl	25	60	7.5	24	2	17	1.6
			60	99	55	6	2.6	27	2.7
		Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	25	38	3.5	5	2	1	0.6
			60	42	2	7	1	2.6	1.9
Eccentric vibration mill/15 min	1.5	HCl	25	1.8	11	0.1	3.5	19	0.6
			60	1.8	18	0.1	16	22	0.6
		H <sub>2</sub> SO <sub>4</sub> +NaCl	25	92	50	4	10	32	2
			60	87	76	5	17	25	1.6
		Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	25	47	2	6.5	0.5	1.6	2
			60	35	5.5	15	1	0.2	1.5
Planetary mill/15 min	2.9	HCl	25	1.8	11	0.1	4.1	13	0.6
			60	1.8	14	0.1	19	16	0.6
		H <sub>2</sub> SO <sub>4</sub> +NaCl	25	63	42	7.3	9.2	25	2
			60	48	50	4.5	21	25	2
		Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	25	57	3.6	12	1	3	1.6
			60	64	6.5	19	2	3	2
Attritor (stirring ball mill)/30 min	12	HCl	25	98	33	3	4	71	0.6
			60	98	33	2.5	7	80	0.6
		H <sub>2</sub> SO <sub>4</sub> +NaCl	25	99	57	4	7	87	1.5
			60	99	71	5	8	85	2
		Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub> ·5H <sub>2</sub> O	25	99	5	22	1	0.5	1
			60	99	53	10	1	2	1

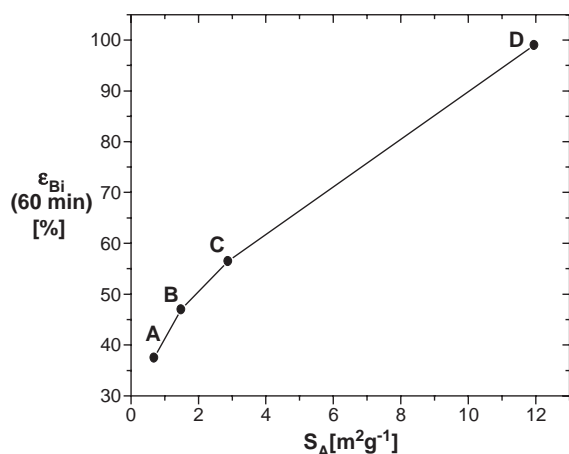


Fig. 11. Recovery of bismuth after 60 min leaching,  $\epsilon_{Bi}$  in sodium thiosulphate solution at 25 °C vs. specific surface area,  $S_A$  in various types of mills: “as-received” sample (A); eccentric vibration mill (B); planetary mill (C) and attritor-stirring ball mill (D).

(Fig. 10). With the exception of copper the recovery was 22%, the recoveries for all the other metals were 5% Pb, 1% Zn, 0.5% Fe and 1% Ag. It illustrates very good selectivity of sodium thiosulphate application towards Bi recovery.

The plot in Fig. 11 describes the effect of new surface area formation on recovery of Bi as a consequence of mechanical activation in different mills. The plot appears to be linear for all activated as well as non-activated samples of the concentrate. It probably suggests that Bi recovery is simply due to the increase of surface area. The highest value of Bi recovery was obtained for the sample with the highest surface area using milling in an attritor. It was shown by Beckstead et al. (1976) by milling of the chalcopyrite concentrate that the grind limit for ball milling was  $4 \text{ m}^2 \text{ g}^{-1}$ , whereas the specific surface area of attritor-ground products continues to increase to at least  $12 \text{ m}^2 \text{ g}^{-1}$ . These values are very close to our results. It is known that grinding in aqueous environment and/or the use of small mill balls (attritor) is more favourable for new surface formation whereas dry grinding and/or the use of larger mill balls (vibration mill and/or planetary mill) favour bulk disorder of concentrate (Baláž, 2000a; Tkáčová, 1989; Chodakov, 1972).

It follows from the presented results that the suitable leaching agent and the proper mechanical activation of lead concentrate can lead to excellent

results as for bismuth obtaining. It was possible to obtain over 90% Bi recovery after 3 min of leaching in  $\text{Na}_2\text{S}_2\text{O}_3$  solution for lead concentrate mechanically activated in an attritor.  $\text{Na}_2\text{S}_2\text{O}_3$  leaching agent is the most advantageous for the selective and fast extraction of Bi from the lead concentrate.

## 7. Conclusions

The data presented in this review paper show that hydrometallurgy of sulphides is an area suitable for verification of knowledge accumulated by mechanochemistry of minerals. The application of mechanochemistry to metallurgy is illustrated with a short theoretical background and some examples, involving selective leaching of Zn from sphalerite, Zn sorption on pyrrhotite, acid leaching of ZnS nanoparticles and selective Bi leaching from PbS concentrate. It is demonstrated that mechanochemical treatment of the sulphides leads to increased reaction rate, improved leaching selectivity and sorption efficiency and the enhanced leachability of nanocrystals.

## Acknowledgements

The support through the Slovak Grant Agency VEGA (grant 2/5151/5), Center of Excellence NANOSMART, APVT (grant 20-018402) is gratefully acknowledged. The authors wish to express their thanks to Prof. E. Gock and Ing. C. Villachica.

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