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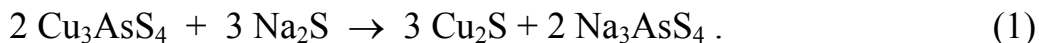
## CHARACTERIZATION OF THE SOLID RESIDUE OF ENARGITE $\text{Cu}_3\text{AsS}_4$ AFTER ALKALINE LEACHING

The characterization of solid after alkaline leaching of enargite  $\text{Cu}_3\text{AsS}_4$  is discussed. X-ray diffractometry for characterization of the physico-chemical transformations in bulk of source enargite concentrate resulted from alkaline leaching was used. The surface layers of the samples of enargite concentrate were investigated with XPS spectroscopy. The leaching of mechanically activated enargite concentrate with  $\text{Na}_2\text{S}$  leads to total extraction of arsenic (the content of As in a solid after leaching is 0.06%) and then decomposition of enargite ( $\text{Cu}_3\text{AsS}_4$ ) with formation of new phases of copper sulphide and jarosite. XPS spectroscopy measurements did not registered the occurrence of arsenic in any chemical form in the sample of solid taken from leaching system.

*Key words*- enargite, alkaline leaching, solid residue, physico-chemical transformations

### INTRODUCTION

Enargite  $\text{Cu}_3\text{AsS}_4$ , like tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , belongs among the minerals important for copper metallurgy. The alkaline leaching of enargite with sodium sulphide follows the equation:



This leaching process is selective. Arsenic passes into leach while produced copper sulphide represents the raw material suitable for pyro-treatment (BALÁŽ et al., 1995). The contents of pentavalent and trivalent forms of arsenic depend on the presence of polysulphides in leaching solution (HISKEY et al., 1988).

In our previous study we have shown that the alkaline leaching of enargite enables the recovery of arsenic in solution exceeding 90 % (ACHIMOVÍČOVÁ et al., 1998; BALÁŽ et al., 1999; BALÁŽ et al., 1998). Moreover, it has been found that the mechanical activation of mineral by

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grinding in stirring ball mill 60 minutes enhances the rate of arsenic extraction.

The aim of this study is to estimate the bulk and surface properties of solid from alkaline leaching of mechanically activated enargite concentrate by means of X-ray diffractometry and XPS spectrometry.

## EXPERIMENTAL

### Materials

The investigations were carried out with enargite concentrate (El Indio, Chile) of the following chemical composition: 38.64% Cu, 12.03% As, 0.95% Fe, 0.58% Sb, <0.004% Pb, 0.006% Zn, 21.28% SiO<sub>2</sub>.

### Mechanical activation

The mechanical activation of the source of enargite concentrate was performed in a stirring ball mill (attritor) Molinex PE 075 (Netzsch, Germany) under the following conditions: weight of concentrate 20 g, 2000 g of iron balls (diameter 2 mm), 200 ml of water, 60 min, 1000 revolutions/min.

### XRD analysis

The qualitative examination of transformations in bulk of enargite concentrate after alkaline leaching was by using a diffractometer Rigaku Rad 3 (Japan) under the conditions: radiation CuK $\alpha$ , 40 kV, 20 mA and rate of goniometer 1°/min.

### XPS analysis

The XPS measurements were carried out using an ESCA 3 Mk II instrument (VG Scientific, Great Britain) in a vacuum of 10<sup>-6</sup> Pa. The AlK $\alpha$  radiation ( $h\nu = 1486.6$  eV) was used for electron excitation, the transmission energy of the electron analyzer was 20 eV and input slit width was 4 mm. The surface stoichiometry was calculated from integral intensities of photoelectron lines As (3d), Cu(3p), S(2p) and C(1s), measured individually in the regime of high resolution. To eliminate the sublimation of the elements the samples were cooled to liquid nitrogen temperature during spectra accumulation.

### Chemical leaching

The leaching was investigated in a 1000 ml glass reactor containing 400 ml of leaching solution (100 g l<sup>-1</sup> Na<sub>2</sub>S + 50 g l<sup>-1</sup> NaOH and 4 g of enargite concentrate. The leaching was performed for 120 and 30 minutes at 90°C and at stirring rate of 500 min<sup>-1</sup>. Samples (5 ml) of the solution were withdrawn at appropriate time intervals for determination of the dissolved elements by atomic absorption spectroscopy.

## RESULTS AND DISCUSSION

The physico-chemical transformations in bulk of enargite concentrate after alkaline leaching were evaluated by the method of X-ray diffractometry. The X-ray analysis of the as-received sample of enargite concentrate and of the solid residue of this concentrate mechanically activated for 60 minutes and subjected to 30 minutes leaching showed considerable changes in structure of solid phase after leaching with  $\text{Na}_2\text{S}$ . Figs 1 and 2 represent diffractograms of the as-received sample of enargite concentrate and of the solid residue after leaching. Then reveal that the diffraction lines of enargite  $\text{Cu}_3\text{AsS}_4$  disappeared and the lines of new phases of copper sulphide  $\text{Cu}_{3.9}\text{S}_{2.8}$  and jarosite  $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$  appeared.

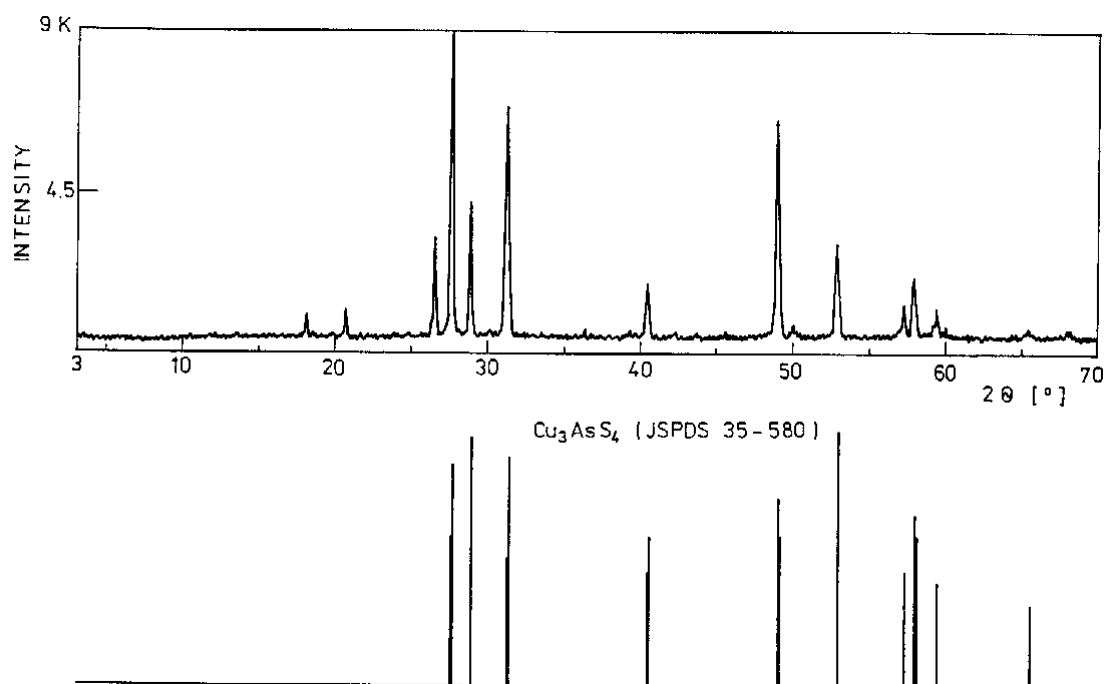


Fig.1 Diffractogram of the as-received sample of enargite concentrate  
Rys.1 Dyfraktogram otrzymanej próbki koncentratu enargitu

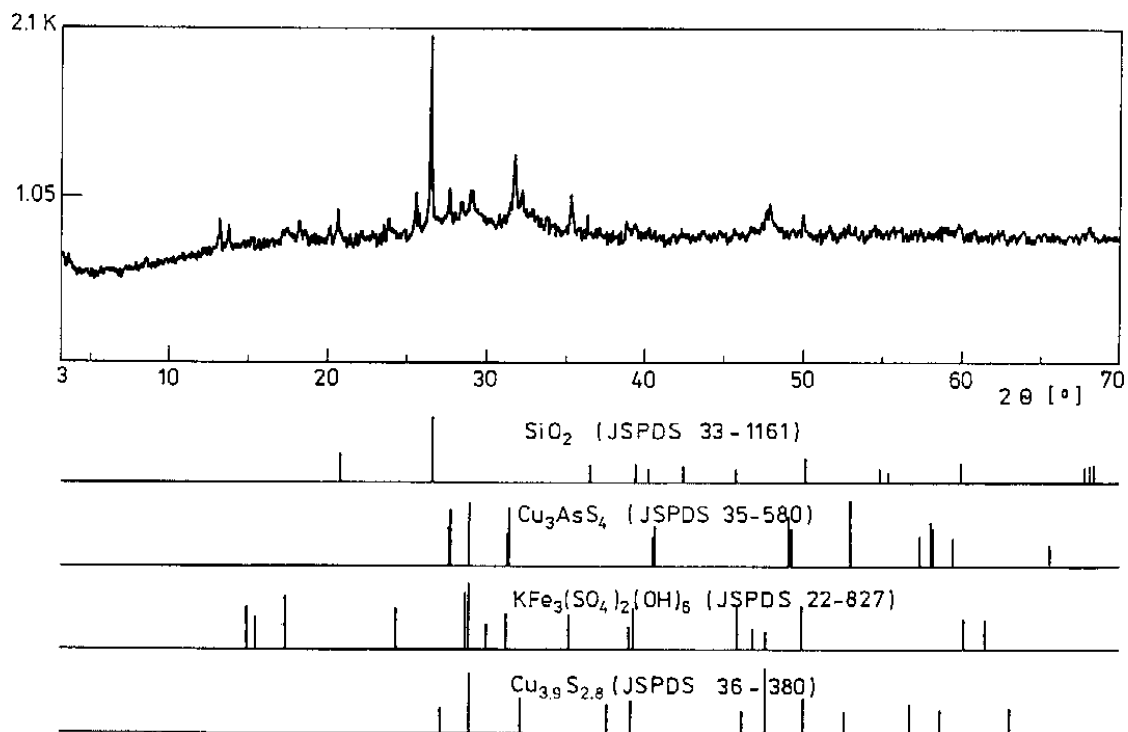


Fig.2 Diffractogram of the solid residue after alkaline leaching of the enargite concentrate mechanically activated 60 minutes

Rys. 2 Dyfraktogram ciała stałego pozostałego po alkalicznym ługowaniu koncentratu enargitu po mechanicznej aktywacji przez 60 minut

The surface layers of the samples of enargite concentrate were investigated by XPS spectroscopy. The survey XPS spectra in Fig. 3 demonstrate the presence of arsenic, copper, sulphur and carbon in surface layers of the samples. Moreover, the above elements as well as silicium and sodium were also identified (Table 1). Silicium originated from quartz in the sample (21.28%) and sodium cause from leaching medium ( $\text{Na}_2\text{S}$ ). Its original relative value 6.0 (sample 3) decreased to 0.5(sample 4) after washing the sample with water.

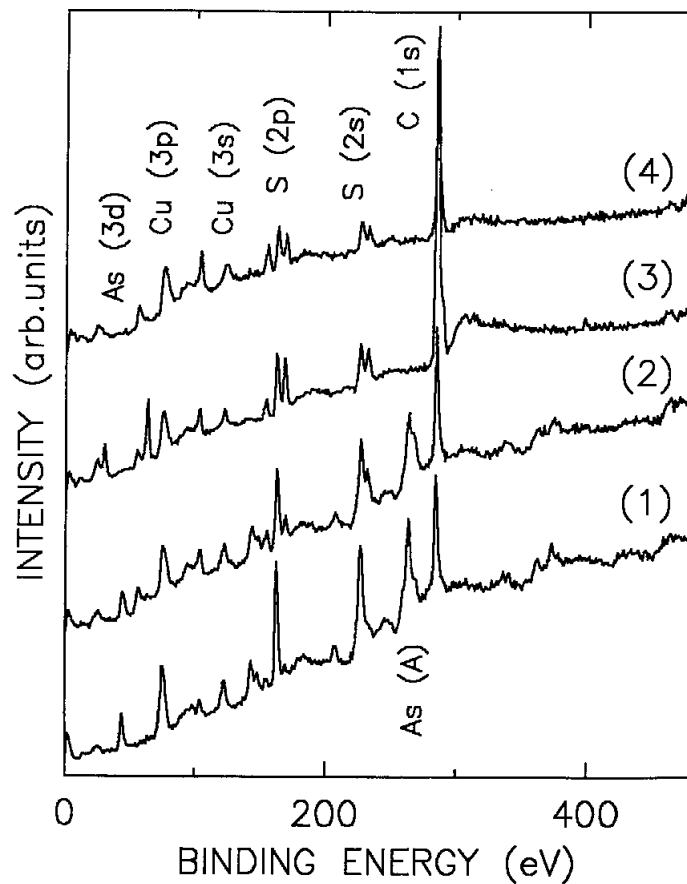


Fig.3 The survey XPS spectra of enargite concentrate: (1= as-received sample; 2=enargite ground for 60 min.; 3=enargite ground for 60 min. and subsequently leached; 4=solid residue after grinding, leaching and washing with H<sub>2</sub>O)

Rys.3 Widmo XPS koncentratu egargitu ( 1- otrzymana próbka, 2- enargit mielony przez 60 minut, 3- enargit mielony przez 60 minut a następnie ługowany, 4- ciało stałe pozostające po mieleniu, ługowaniu i przemyciu wodą)

Table 1 Relative atomic concentrations of elements in samples of enargite concentrate. Concentrations of elements are referred to Cu concentrations: (1= as-received sample, 2 = enargite ground for 60 min., 3 = enargite ground for 60 min. and subsequently leached, 4 = solid residue after grinding, leaching and washing with H<sub>2</sub>O)

Tabela 1 Względna zawartość atomów pierwiastków w próbkach koncentratu enargitu. Zawartości pierwiastków odniesione są do zawartości Cu: ( 1- otrzymanej próbki, 2- enargitu pomieleniu przez 60 minut, 3- enargitu po mieleniu przez 60 minut i ługowaniu, 4- ciało stałe powstające po mieleniu, ługowaniu i przmyciu wodą)

Sample No.	As	S	O	C	Si	Na
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1	0.6	1.8	1.8	3.7	0.2	-
2	0.7	2.1	6.5	5.8	0.6	-
3	-	3.4	17.6	20.0	1.0	6.0
4	-	1.7	9.2	6.5	1.0	0.5

In the course of leaching the sodium sulphide ( $\text{Na}_2\text{S}$ ) degrades to the sulphate and, therefore, an increased content of oxygen and hexavalent sulphur appears in sample 3 (Fig.4). The water-soluble  $\text{Na}_2\text{SO}_4$  can be removed by washing and thus the content of oxygen and sulphur in sample 4 decreases. Samples 2 and 4 are contaminated by iron which is originated from abrasion during milling (Fig.5).

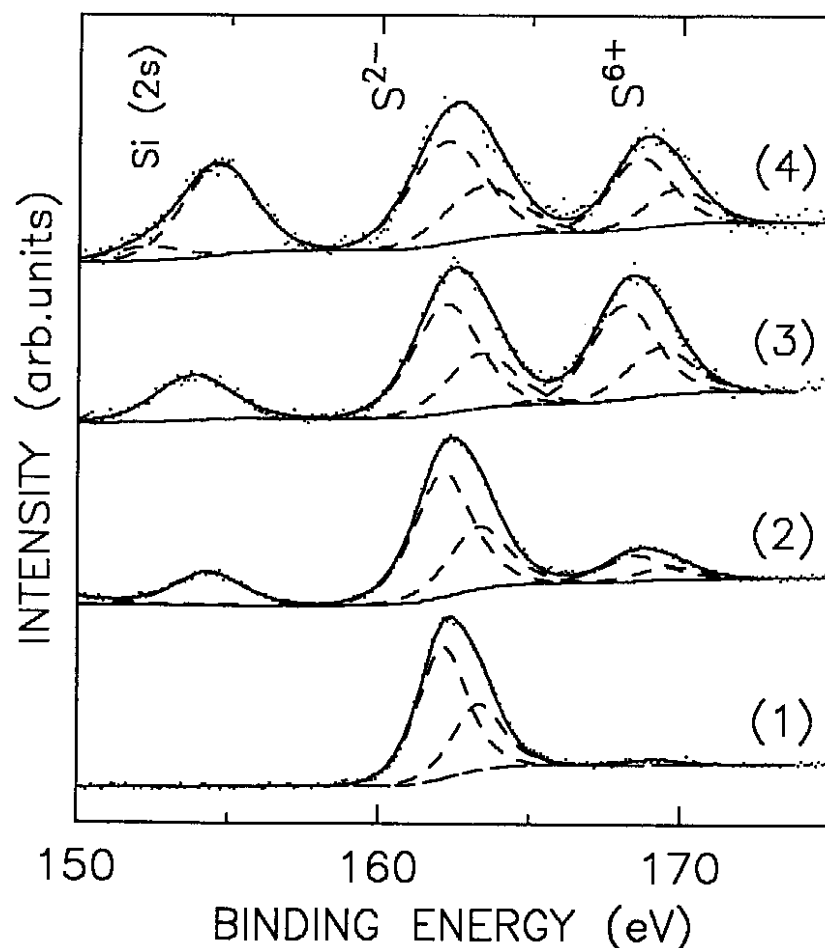


Fig.4 XPS S(2p) spectra of enargite concentrate: (1= as-received sample; 2=enargite ground for 60 min.; 3=enargite ground for 60 min. and subsequently leached; 4=solid residue after grinding, leaching and washing with H<sub>2</sub>O)

Rys. 4 Widmo XPS (2p) anargitu: (1- otrzymana próbka, 2 enargit mielony przez 60 minut, 3-

enargitu mielony przez 60 minut a następnie ługowany, 4- stała pozostałość po mieleniu, ługowaniu i przemyciu wodą)

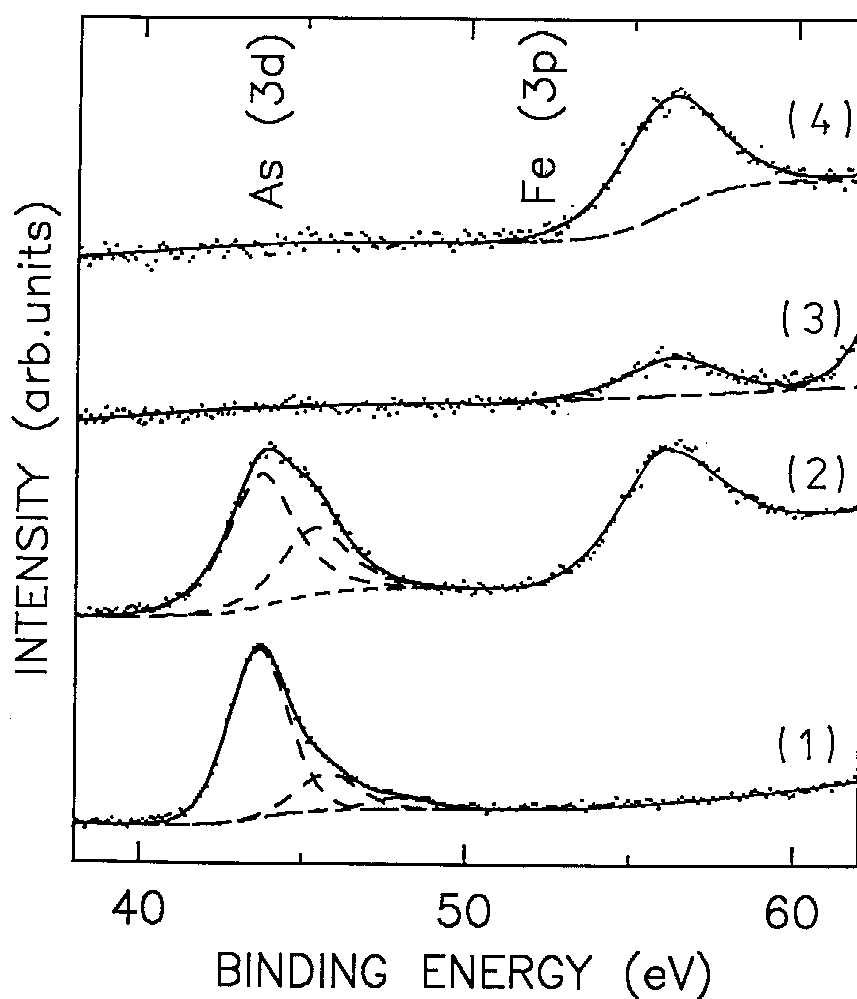


Fig.5 XPS As(3d) and Fe(3p) spectra of enargite concentrate:(1= as-received sample; 2=enargite ground for 60 min.; 3=enargite ground for 60 min. and subsequently leached; 4=solid residue after grinding, leaching and washing with H<sub>2</sub>O)

Rys.5 Widmo XPS As(3p) i Fe(3p) enargitu: (1- otrzymana próbka, 2- enargit mielony przez 60 minut, enargit mielony przez 60 minut następnie ługowany, 4- ciało stałe pozostałe po mieleniu, ługowaniu i przemyciu wodą)

The XPS spectra and their quantitative evaluation unambiguously made evident the effectiveness of alkaline leaching of enargite. Arsenic was not present in the samples of solid after leaching and the original trivalent form of arsenic was transformed into the pentavalent form in the course of mechanical activation (Table).

The effectiveness of alkaline leaching of enargite concentrate can also be evaluated the results of chemical analysis of the solid residue from leaching of mechanically activated sample. It appears that the content of arsenic in a solid residue fell on 0.06%.



Table 2 Relative concentration of sulphur and arsenic oxidative states in the enargite concentrate samples (1 = as-received sample, 2 = enargite ground for 60 min., 3 = enargite ground for 60 min. and subsequently leached, 4 = solid residue after grinding, leaching and washing with H<sub>2</sub>O)

Tabela 2 Względna zawartość siarki i arsenu na różnych stopniach utlenienia w próbkach enargitu (1- otrzymana próbka, 2- enargit mielony przez 60 minut, 3- enargit mielony przez 60 minut i następnie ługowany, 4- ciało stałe pozostałe po mieleniu, ługowaniu i przemyciu wodą)

Sample No.	Sulphur		Arsenic	
	S <sup>2-</sup>	S <sup>6+</sup>	As <sup>3+</sup>	As <sup>5+</sup>
1	97	3	82	18
2	83	17	67	33
3	54	46	-	-
4	65	35	-	-

## CONCLUSION

The changes in the bulk and surface of enargite were investigated resulted by alkaline leaching with Na<sub>2</sub>S. It has unambiguously been evidenced by the method of X-ray diffractometry and XPS spectroscopy that the application of alkaline leaching is evidently efficient from the view-point of arsenic extraction from enargite concentrate because no arsenic was found in any chemical form in the sample subjected to leaching. Moreover, this application is selective because copper remains in the solid residue.

## ACKNOWLEDGEMENT

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Przedyskutowano charakterystyczne cechy stałej pozostałości po alkalicznym ługowaniu enargitu  $\text{Cu}_3\text{AsS}_4$ . Dla charakteryzacji fizykochemicznych transformacji w ciele stałym posłużono się rentgenowskim dyfraktogramem koncentratu anargitu, otrzymanego po ługowaniu. Warstwy powierzchniowe próbek koncentratu enargitu badano przy pomocy spektroskopii XPS. Ługowanie mechanicznie aktywowanego koncentratu enargitu  $\text{zNa}_2\text{S}$ , prowadzi do całkowitej ekstrakcji arsenu (zawartość As w ciele stałym po ługowaniu wynosi 0.06%). Następnie zachodziła dekompozycja enargitu  $\text{Cu}_3\text{AsS}_4$  z utworzeniem nowych faz siarczku miedzi i jarosytu. Pomiary wykonane techniką XPS nie odnotowały występowania arsenu oraz innych związków chemicznych w próbce ciała stałego otrzymanego po ługowaniu.