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## COMBINED PROCESSING OF POLYMETALLIC RAW MATERIALS WITH INCREASED CONTENT OF PRECIOUS METALS

Using thermogravimetric, x-ray, and chemical methods interactions has been studied and the products identified of heating of  $\text{CuFeS}_2\text{-NH}_4\text{Cl}$ ,  $\text{PbS-NH}_4\text{Cl}$ , and  $\text{ZnS-NH}_4\text{Cl}$  mixtures in air. Results of investigations of individual sulphides have been utilized as the base for the selection of a technological pattern for oxidizing chlorinating roasting with ammonium chloride of natural material containing copper, lead, and zinc sulphides as well as iron and precious metals. Leaching of resultant sinters have outlined, in principle, a possibility for the selective removal of non-ferrous and precious metals. Moreover, depending on the content of metals and on their distribution, the solutions and the solid residues can be used in different unit operations of lead and zinc production. The results can contribute to the development of technologies for selective removal of the metal values from low grade raw materials with elevated content of precious metals.

### INTRODUCTION

Processing of sulphide raw materials containing copper, zinc, lead and precious metals is a challenging technological task. Contemporary metallurgy takes into account, in more or less acceptable manner, the complex removal of metal values from such raw materials only if the content of non-ferrous metals exceeds 10-20 per cent (1). The extension of resources of non ferrous and precious metals calls for the development of new methods for the rational utilization of low grade raw materials.

The technological flow-sheets of such new processes must involve the separation of metals at the initial stages and subsequently their concentration in final products. Depending on their chemical composition the products should be suitable for a further processing at respective stages of the classical production of copper, zinc and lead.

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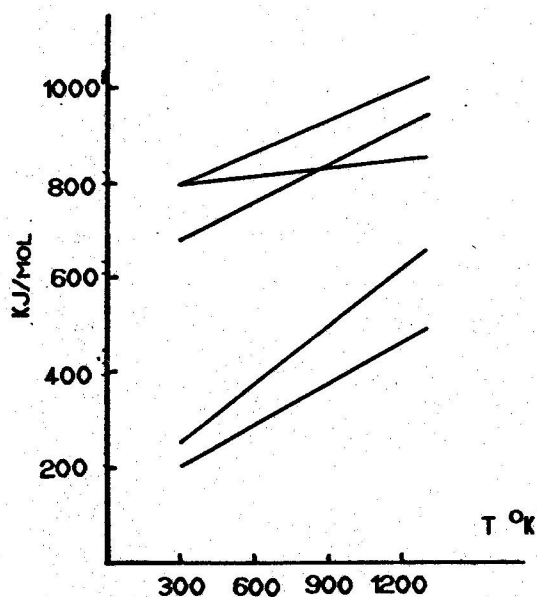


Fig. 1.

Dependence of  $\Delta G$  on number of the straight line corresponds to the (number of reaction in the text).

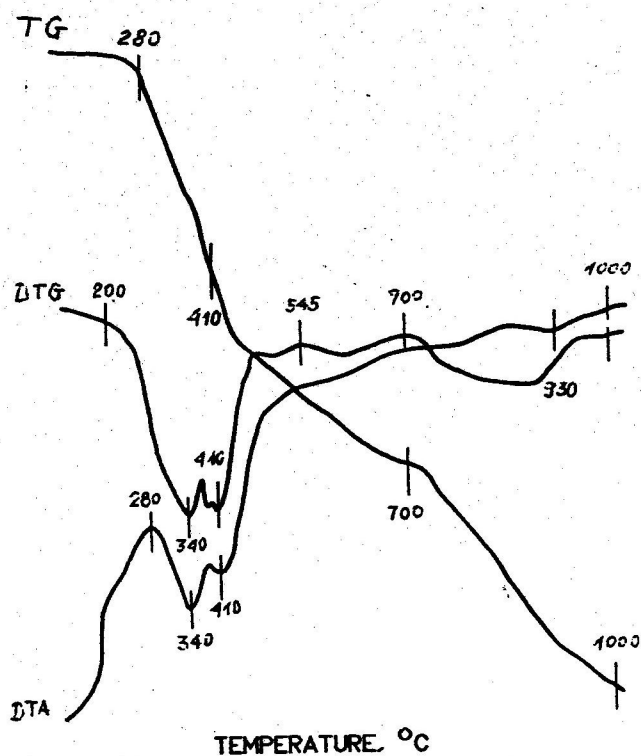


Fig. 2.

Derivatogram of reaction products in  $\text{CuFeS}_2\text{-NH}_4\text{Cl}$  system.

Therefore, a study is presented on the behaviour of  $\text{CuFeS}_2$ ,  $\text{PbS}$  and  $\text{ZnS}$  in chlorination roasting with ammonium chloride to determine the possibilities for the removal of copper, lead, zinc, and precious metals from a low grade polymetallic ores and other raw materials.

## EXPERIMENTAL

Investigations have been carried out with pure minerals and with various flotation products obtained by processing of ores containing chalcopyrite, sphalerite, galena, and precious metals. Ore-processing products containing copper, lead, and zinc sulphides of total content of up to 10%, as well as iron and precious metals, were roasted with ammonium chloride under air. Experiments were carried out using the granulated concentrate to reduce considerably the dusting, to provide better penetration of gases, and to create better contact conditions between the components of concentrate, chlorinating agent and gaseous phase. The granulation was made with a cup granulator. The amount of ammonium chloride was always kept 2.5 times higher than the stoichiometric quantity calculated for reactions 2, 4, and 5. A vertical furnace with a reactor were used to provide the necessary conditions for a completing of the processes studied. The granules were placed in the quartz reactor with an uniform access of air to all zones of the reaction. Temperature was ranging from  $250^\circ\text{C}$  to  $750^\circ$  whereas the quantity of air was from 0.8 to 1.0 in relation to air theoretically required for the complete oxidation of metal sulphides in the sample. Products were then subjected to hydrometallurgical processing by leaching with aqueous hydrochloric and sulphuric acids of varying concentrations. Filtrates were then analysed by atomic absorption spectroscopy to determine lead, copper, zinc and iron concentrations.

Differential-thermal, thermo-gravimetric, X-ray, and chemical analyses have been used to determine the products of interactions in the heated in air  $\text{CuFeS}_2\text{-NH}_4$  and  $\text{ZnS-NH}_4\text{Cl}$  systems. The thermograms were taken with the Paulik-Paulik-Erdy system in air under following conditions: heating rate  $10^\circ\text{C}$  per minute; sensitivity:  $1/5$  for DTA,  $1/5$  for DTG, and 500 mg for TG. The molar ratio of mineral to ammonium chloride was 1:2. Various reactions are expected to take place during the heating of mixtures of chalcopyrite, sphalerite and galena with ammonium chloride in the presence of oxygen.

## RESULTS AND DISCUSSION

Figure 1 shows the changes of mass (G) versus temperature for the

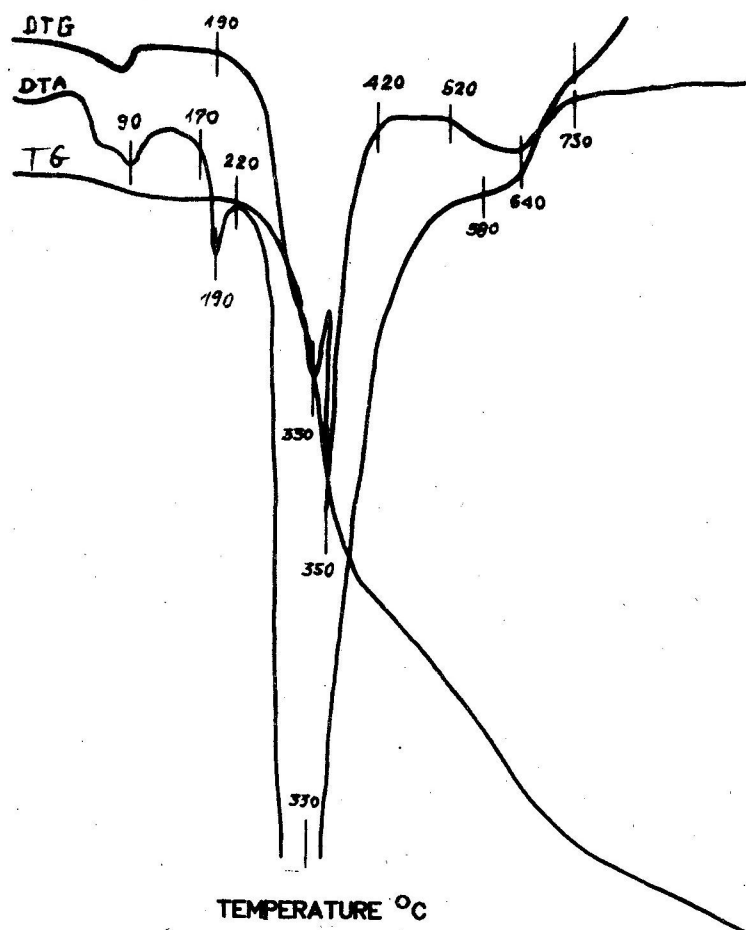


Fig. 3. Derivatogram of reaction products in  $\text{ZnS-NH}_4\text{Cl}$  system.

following reactions:

1.  $\text{CuFeS}_2 + 2\text{NH}_4\text{Cl} + 3\text{O}_2 \longrightarrow \text{CuO} + \text{FeCl}_2 + \text{NH}_3 + \text{H}_2\text{O} + 2\text{SO}_2$  (1)
2.  $\text{CuFeS}_2 + 2\text{NH}_4\text{Cl} + 3.25\text{O}_2 \longrightarrow \text{CuCl}_2 + 0.5\text{Fe}_2\text{O}_3 + 2\text{NH}_3 + \text{H}_2\text{O} + 2\text{SO}_2$  (1)
3.  $\text{CuFeS}_2 + \text{NH}_4\text{Cl} + 3\text{O}_2 \longrightarrow \text{CuCl} + 0.5\text{Fe}_2\text{O}_3 + \text{NH}_3 + 0.5\text{H}_2\text{O} + 2\text{SO}_2$  (3)
4.  $\text{ZnS} + 2\text{NH}_4\text{Cl} + 1.5\text{O}_2 \longrightarrow \text{ZnCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2$  (4)
5.  $\text{PbS} + 2\text{NH}_4\text{Cl} + 1.5\text{O}_2 \longrightarrow \text{PbCl}_2 + 2\text{NH}_3 + \text{H}_2\text{O} + \text{SO}_2$  (5)

Calculations have been made with first approximation according to the equation  $\Delta G = \Delta H - T\Delta S$ . The phase transformations of the components involved in the reactions were taken into account within the studied range of temperature. Adequate values of thermodynamic constants have been taken from (2,3).

Figure 1. shows that from the thermodynamical point of view the interactions of minerals with ammonium chloride are fully possible while the probability of chlorination is the highest for  $\text{CuFeS}_2$  and the lowest for  $\text{PbS}$ .

Derivatograms in Fig.2 and 3 indicate that the reaction begins at low temperature and is accompanied by a considerable decrease of the mass of the samples. The comparison of results of chemical identification of products exhibited that up to  $400^\circ\text{C}$  the main products of interaction of  $\text{CuFeS}_2$  and  $\text{NH}_4\text{Cl}$  were  $\text{CuCl}$  and  $\text{Fe}_2\text{O}_3$ . Above  $500^\circ\text{C}$ , copper chloride begins to decompose to  $\text{CuO}$ , while above  $700-750^\circ\text{C}$ , copper ferrites are intensively formed [4].

A small endothermic effect is observed at  $190^\circ\text{C}$  on the differential thermal curve for the mixture of  $\text{ZnS}$  and  $\text{NH}_4\text{Cl}$  (Fig.3) and more distinct endothermic effect can be detected at  $350^\circ\text{C}$ . The mass of the feed sample was found to decrease by 73.33% in the temperature ranging from  $200$  to  $1000^\circ\text{C}$ . The first endothermic effect is not related to a mass loss and corresponds to the polymorphic transformation of ammonium chloride. The solid phase interactions between the source components are most likely to begin at that temperature.  $\text{ZnO}$  and  $\text{ZnCl}_2$  become the major products of interaction when the temperature increases. Chloride zinc complexes and ammonium chloride are also expected to exist within a certain temperature range.

The change in composition of mixture of galena and ammonium chloride at temperatures up to  $360^\circ\text{C}$  was shown in Fig.4. Several maxima of diffraction values related to galena ( $d, \text{\AA} = 3.41, 2.96, 2.09, 1.78, 1.48, 1.36, 1.32$ ) and to  $\text{PbCl}_2$  ( $d, \text{\AA} = 3.57, 2.76, 2.50, 2.26, 2.21, 2.14$ ) were identified in a sample heated at  $360^\circ\text{C}$ . This suggests that within the temperature range from  $240$  to  $400^\circ\text{C}$  the following reaction takes place:

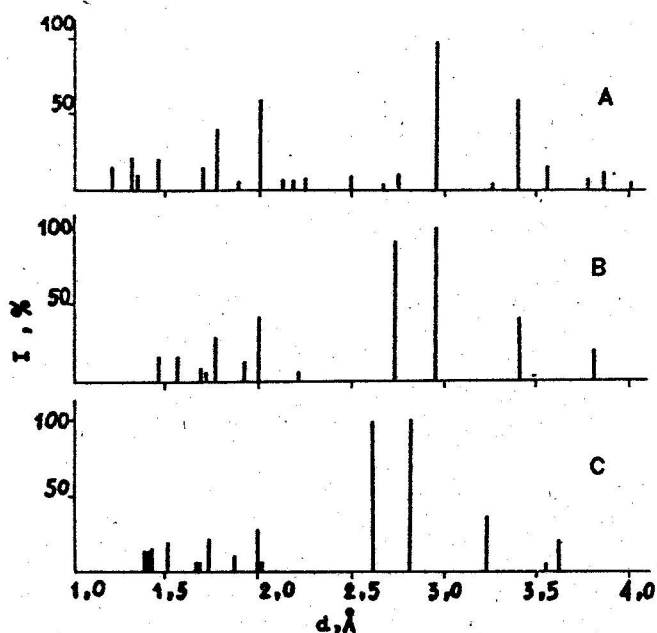


Fig. 4. Diffractogram of reaction products in  $\text{PbS-NH}_4\text{Cl}$  system.

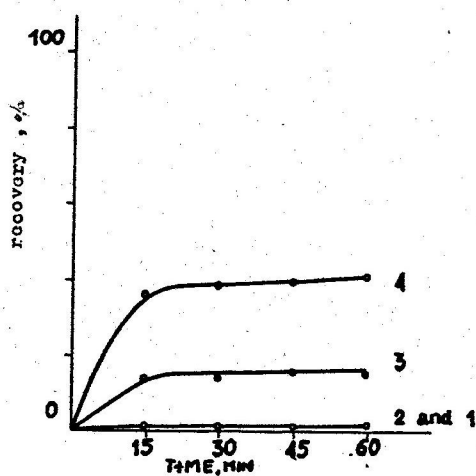


Fig 5. Recovery-time relationships for leaching of Pb (1), Fe (2), Cu (3), and Zn (4) from solids sintered at  $500^{\circ}\text{C}$  (leaching medium- $\text{H}_2\text{O}$ ; leaching temperature- $80^{\circ}\text{C}$ )



The observed results for individual pure sulphide minerals were the base for the subsequent investigations with natural raw materials.

Results of leaching of sinters with water, aqueous hydrochloric and sulphuric acids are summarized in Figures 5-10. It is well visible from Fig. 5 that when the sinter has been leached with water, the degree of removal of copper and zinc changed from 8.52% to 16.35% and from 35.08% to 42.44%, respectively. Lead and iron practically remained in the residue (Fig. 5). The extension of leaching process, to more than 15 minutes did not affect the degree of metals recovery. Obviously, treatment of the sinters with water cannot result in the complete removal and separation of metal values.

Results of leaching of sinters with hydrochloric acid (Figures 6-8) indicate that the degree of metal removal increases but their selective separation is impossible. No change in the degree of removal of copper and zinc was observed when HCl concentration increased from 1 to 10% while removal of lead and iron increased insignificantly.

Results of investigations showed that at experimental conditions the maximum degree of leaching was reached within 5-6 minutes. When the temperature of roasting was kept in the range of 350-400° the degree of metals recovery was essentially enhanced (Fig. 8.). This observation correlates with the results on chlorinating roasting of individual minerals.

In all experiments iron was observed to dissolve insignificantly in hydrochloric acid solutions, at concentration of HCl corresponding to the highest degree of extraction of zinc. After chlorinating roasting at temperatures above 500°, the degree of removal of zinc reaches 80%. When the chlorinating roasting of the concentrate was performed at temperatures ranging from 300 to 750°C, 32% of copper and 45% of lead was subsequently leached. Therefore, when leaching with HCl solutions is applied, only the non-ferrous metals can be separated from iron.

When the sintered solids were leached with sulphuric acid the observed recoveries were higher than those for HCl. Figures 9 indicate that the increase in the concentration of sulphuric acid from 30 to 180 g/l did not substantially affect the degree of removal of metals from the sinter. Decrease in lead recovery was, however, observed when concentration of  $\text{H}_2\text{SO}_4$  increased from 30 to 60 g/l (Fig. 9). The recovery of zinc was found to be about 90%. Copper was only partially leached while lead, iron, and precious metals remained in the solid phase. No effect of sintering temperature exceeding 300-400°C was observed on

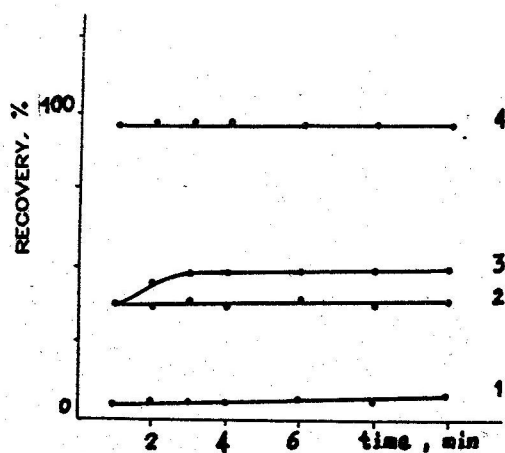


Fig. 6. Influence of HCl concentration on recovery of Fe (1), Cu (2), Pb (3), and Zn (4) from sinter obtained at 500°C (leaching time 15 min).

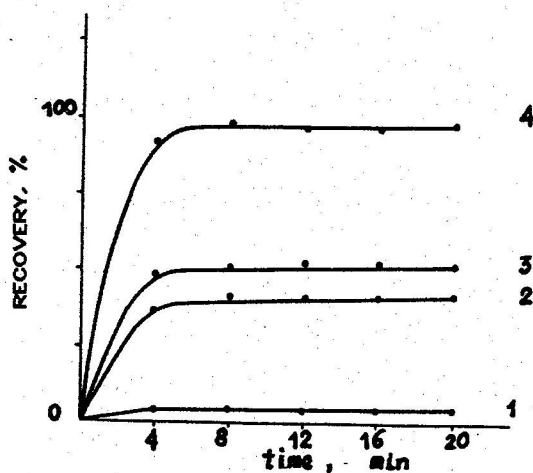


Fig. 7. Recovery-time relationships for leaching of Fe (1), Cu (2), Pb (3), and Zn (4) from sinter obtained at 500°C (leaching medium - 5% HCl).



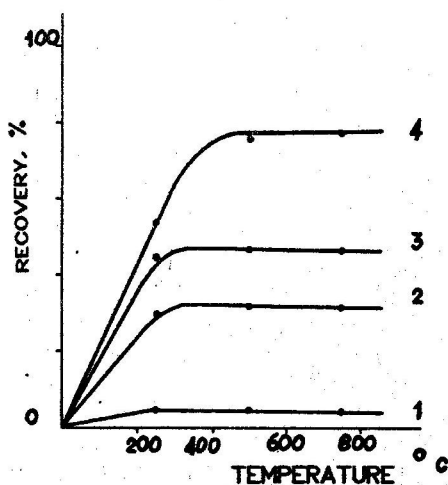


Fig. 8.  
Effect of temperature of roasting  
on the subsequent leaching of a  
sintered solid with 2.5 % HCl after  
15 min. (2-Cu; 3-Pb; 4-Zn)

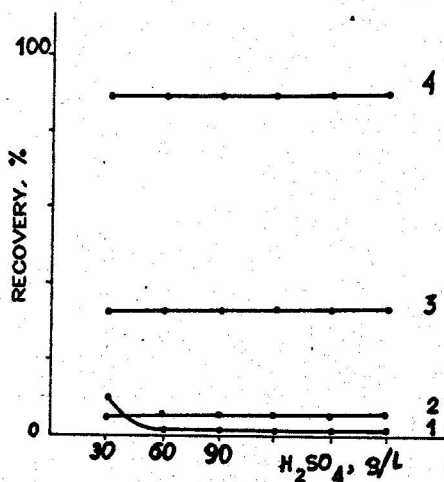


Fig. 9.  
Effect of H<sub>2</sub>SO<sub>4</sub> concentration on the  
recovery of metals from a solid  
sintered at 500°C (leaching time-15  
min. 1-Pb, 2-Fe, 3-Cu, 4-Zn)

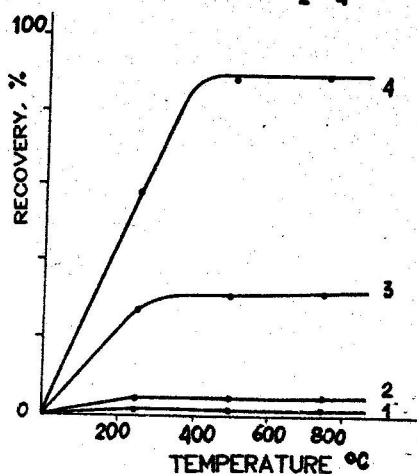


Fig. 10.  
Effect of temperature of roasting  
on the subsequent leaching  
of sinter with aqueous sulphuric acid.  
(H<sub>2</sub>SO<sub>4</sub> concentration - 30 g/l,  
leaching time-15 min., 1-Pb, 2-Fe,  
3-Cu, 4-Zn)

leaching with sulphuric acid solutions (Fig.10). Therefore, when the sinters resulting from chemical and thermal processing by chlorinating roasting are leached with aqueous sulphuric acid (45-60g/l) zinc can be separated from lead, iron, and precious metals. Moreover, depending on the content of metals and on their distribution, the liquid and solid phases resulting from the processing of polymetallic concentrates, according our procedure, can be utilized in different unit processes of lead and zinc production.

### CONCLUSIONS

1. Products of chemical interaction in  $\text{CuFeS}_2\text{-NH}_4\text{Cl}$ ,  $\text{PbS-NH}_4\text{Cl}$ , and  $\text{ZnS-NH}_4\text{Cl}$  systems, heated in air were identified by means of thermogravimetric analysis.
2. Results of investigation on individual sulphides can be applied as the base for the further selection of the technological method of oxidizing chlorinating roasting with ammonium chloride of natural raw materials containing copper, lead and zinc sulphides as well as iron and precious metals.
3. Leaching experiments of resultant sinters exhibited the selective removal of non-ferrous and precious metals. Moreover, depending on metals content and on their distribution, the liquid and solid phases obtained can be utilized in different unit operations of lead and zinc production.
4. Results of this study contribute to the development of technologies for selective removal of metal values from low grade raw materials with elevated content of precious metals.

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## STRESZCZENIE

Penev P., Boteva A., Angelova V., 1990. Kombinowana metoda przeróbki polimetalicznej rudy zawierającej metale szlachetne. Fizykochemiczne Problemy Mineralurgii 22; 173-183.

Metodami termograwimetrycznymi, rentgenowskimi i chemicznymi badano produkty spiekania siarczków:  $\text{CuFeS}_2$ ,  $\text{PbS}$  i  $\text{ZnS}$  z  $\text{NH}_4\text{Cl}$  przy dostępie powietrza. Otrzymane spieki ługowano  $\text{HCl}$  i  $\text{H}_2\text{SO}_4$  i stwierdzono możliwość selektywnego usuwania metali nieżelaznych i szlachetnych. Zaznaczono, że stałe pozostałości po ługowaniu mogą być użyte w różnych technologiach produkcji  $\text{Zn}$  i  $\text{Pb}$ .