# DECOMPOSITION OF THE PYRITE AND ARSENOPYRITE BY PRESSURE OXIDATION OF TETRAHEDRITE RAW MATERIALS

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One of the ways to process tetrahedrite concentrate is use hydrometallurgical method. A promising way seems to be pressure leaching which means that leaching at increased temperature. In the presented work the effects of temperature, time, concentration of the leaching solution and density of the slurry on the efficiency of pyrite and arsenopyrite decomposition by oxidative pressure leaching have been studied. At conditions chosen and studied, the degree of arsenopyrite decomposition was higher than it was in the case of pyrite.

Key words: tetrahedrite, pyrite, arsenopyrite, decomposition, pressure leaching

Razdvajanje pirita i arsenopirita oksidiranjem sirovina tetrahedrita pod tlakom. Jedan od načina obrade koncentrata tetrahedrita je hidromehanički način. Pokazuje se da ispiranje pod tlakom, tj. ispiranje uz povišenu temperaturu ima najviše izgleda da se i ubuduće upotrebljava. U ovom radu se proučavao utjecaj temperature, vremena, koncentracije otopine za ispiranje i gustoću mulja na učinkovitost razdvajanja pirita i arsenopirita pomoću oksidacije pri ispiranju pod tlakom. Pod odabranim i proučenim uvjetima stupanj razdvajanja arsenopirita je bio viši nego stupanj razdvajanja pirita.

Ključne riječi: tetrahedrit, pirit, arsenopirit, razdvajanje, ispiranje pod tlakom

## INTRODUCTION

In the presented work the effects of temperature, time, concentration of the leaching solution and density of the slurry on the efficiency of pyrite and arsenopyrite decomposition (coming from the real flotation sulphide concentrate) by oxidative pressure leaching have been studied. Methods of ores and concentrates pre-treatment by pressure oxidation have already been described in many works [1 - 4]. The technology of oxidation leaching in autoclaves is a complicated process. In dependence of leaching conditions several processes may run simultaneously in the closed autoclave, e. g. sorption of the gaseous oxygen in the solution, mass transport from the fluid volume to solid particles, diffusion of reagents through the boundary surface layers on the surface of solid particles, diffusion of the products of chemical reactions in the solution. Oxidation of sulphides runs by means of dissolved oxygen in liquid phase whereby sorption of oxygen by leaching solution plays an important role. Concentrates which contain pyrite and arsenopyrite are difficult treating materials. A number of works have been aimed at research of pyrite and arsenopyrite decomposition

within the range of much diluted slurries. Decomposition of the real flotation sulphide concentrate is an objective of the paper. The final outcome of pyrite and arsenopyrite decomposition depends on the conditions of a complex process which is effected by several particular processes. Processes of dissolution, oxidation, diffusion, precipitation and hydrolysis can be described by the following reactions:

$$2FeS_{2(s)} + 15/2O_{2(g)} + 8OH_{(aq)}^{-} = Fe_{2}O_{3(s)} + 4SO^{2}_{4(aq)} + 4H_{2}O_{(l)}$$
(1)

$$2FeAsS_{(s)} + 10OH_{(aq)} + 7O_{2(g)} = Fe_2O_{3(s)} + 2AsO^{3-}_{4(aq)} + 2SO^{2-}_{4(aq)} + 5H_2O_{(l)}$$
(2)

In the real concentrate interactions take place among products of the pressure oxidation of pyrite and arsenopyrite, i. e. among individual dissoluted components and grain surfaces.

## RAW MATERIAL USED

Real flotation sulphide concentrate from Pezinok was used for the experimental work. Chemical composition of the concentrate is given in Table 1.. The concentrate contained pyrite, arsenopyrite, tailings, silica, shale.

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Table 1. Chemical composition of the concentrate (wt. %)
Tablica 1. Kemijski sastav koncentrata (mas. %)

Fe	As	S	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Au	Sb	Cu
27.00	7.78	23.76	15.6	9.88	0.0041	0.23	0.17

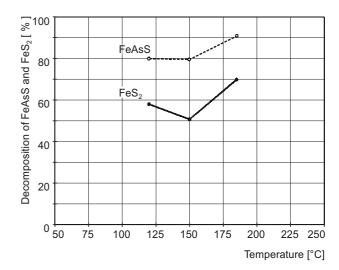
#### **EXPERIMENTAL**

Rotating autoclave LAMPART of 41 volume was used for the experimental work. Oxygen was introduced through a pressure reducer. After the concentrate was mixed with a relevant volume of the solution of NaOH slurries of different density with L:S from 5:1 to 20:1 were formed. The concentration of the leaching solution NaOH varied from 3.55 to 7.1 M and the temperature of experiments was between 120 and 185 °C. When the temperature reached the required values, the reaction time 90 - 300 minutes was measured. All experiments were carried out at constant initial pressure of oxygen 0.9 MPa which was sufficient for the course of oxidizing reactions in the system. The effects of individual parameters on the efficiency of pyrite and arsenopyrite decomposition was observed together with the possibilities of interactions in the process of sulphides oxidation.

#### DISSCUSSION

## Influence of temperature

The increase of the process temperature positively influences the quantity of oxidized pyrite and arsenopyrite. The ratio of pyrite and arsenopyrite in the real concentrate used for the experiments was 0.49 and the concentrate contained also tailings. Decomposition of sulphides and the effects of products coming from the decomposition process at temperatures 120, 150 and 185 °C were observed, the results are given in Figure 1.. Decomposition efficiency rises with increasing temperature for both sulphides. The value of pH stabilized at 13.8 at the temperatures 120 and 185 °C. At 150 °C there was a decline in value of pH on 12.6 which resulted in a decrease of sulphides decomposition efficiency (50.8 % in case of pyrite and 79.6 % in case of arsenopyrite) which probably caused by creation of a passive layer through which the mass transfer is hindered. The change in the value of pH brings about changes of conditions of the passive layer creation and thus a change of its qualitative parameters. The layer develops as a product of oxidation of the surface of pyrite grains with a direct creation of Fe<sub>2</sub>O<sub>3</sub> as a residue after oxidation and after leaching off sulphur into the solution or as a precipitate of the hydrated Fe<sub>2</sub>O<sub>3</sub> in case the leaching conditions have been changed. A compact passive layer creation might be connected with precipitation of hydrated oxide of iron from the boundary layer of the solution.



 $Figure \ 1. \quad \textbf{Influence of temperature on decomposition of pyrite and} \\ \quad arsenopyrite$ 

Slika 1. Utjecaj temperature na razdvajanje pirita i arsenopirita

#### Influence of time

The pressure oxidation was running at 185 °C when maximum efficiency of pyrite and arsenopyrite decomposition has been obtained. Reaction temperature hold time was 90, 180 and 300 minutes. The slurry was characterized by the ratio of S:L = 5: 1. Results are given in Figure 2.. During 90 minutes leaching 78.3 % of arsenopyrite and 48.9 % of pyrite was decomposed. Decomposition efficiency of pyrite dropped to 31.4 % after 5 hour leaching.

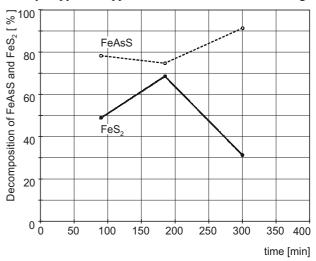


Figure 2. Influence of time on decomposition of pyrite and arsenopyrite

Slika 2. Utjecaj vremena trajanja oksidacije na razdvajanje pirita i arseno-pirita

## Influence of the concentration of leaching solution

The density of the slurry was L:S = 5:1. The excessive volume of NaOH necessary for the reaction course in a

closed autoclave was changed. With an increasing concentration of NaOH in the solution basicity its increases which positivelly affects the decomposition of arsenopyrite while in the case of pyrite it is just the reverse. Arsenic from the grain surface layer of arsenopyrite dissolves after oxidation in the form of As<sup>5+</sup>.

Due to the high basicity of the solution, arsenic does not precipitate back. Sulphur oxidizes to  $S^{6+}$  and the sulfate ions dissolve in the leach liquor. Iron remains in the undissolved residue in the form of hydrated  $Fe_2O_3$  that makes its surface porous and enables an undisturbed mass transfer. In consequence of arsenic and sulphur leaching off arsenopyrite decomposes. There is no compact passive layer on the surface.

Sulphur and iron oxidize on the pyrite grain surface and they are retained in the boundary layer in the solution due to the hydroxyl ions withdrawing. These are supplied from the solution by diffusion. They cause a change in boundary layer pH values that enables precipitation of Fe<sup>3+</sup> in the form of hydrated oxide which makes that the passive layer cuts back pyrite decomposition by oxidation. Diffusion of hydroxyl ions into the boundary layer is quicker in more concentrated NaOH solutions and precipitation of hydrated Fe<sup>3+</sup> ions is also better.

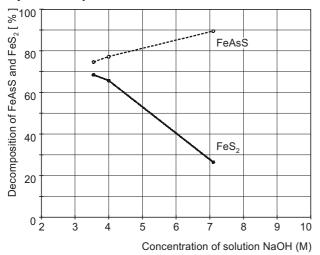


Figure 3. Influence of the concentration of leaching solution on decomposition of pyrite and arsenopyrite

Slika 3. Utjecaj koncentracije otopine za ispiranje na razdvajanje pirita i arsenopirita

## Influence of the density of the slurry

An excessive volume of the leaching agent which would be above its equimolar use may be achieved if the concentration of the leaching medium (NaOH) is not increased. Such an effect may be achieved by addition of different volumes of the solution with a given concentration to a constant quantity of the solid phase. The density of the slurry, i. e. L:S will change which means that concentration conditions will change, too. All dissolved components will behave like those present in a diluted solution and their behaviour will be very close to an "ideal solution". Interactions will decrease and the transition of components in the solution will be less influenced by undesired effects. The results of the influence of the density of the slurry on pyrite and arsenopyrite oxidation decomposition are given in Figure 4.. Obtained results have approved a favourable effect of slurry density decrease on pyrite and arsenopyrite decomposition in the process of sulphide concentrate oxidation leaching. At L:S = 20:1 99.3 % arsenopyrite and 80 % pyrite decomposed. To achieve their total decomposition, especially decomposition of pyrite, slurry density should be reduced as much as L:S = 30-40, however as high as L:S ratio that is practically not feasible.

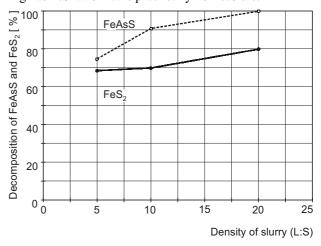


Figure 4. Influence of the density of the slurry on decomposition of pyrite and arsenopyrite

Slika 4. Utjecaj gustoće (L:S) početnog mulja na razdvajanje pirita i arsenopirita

### CONCLUSION

At conditions chosen of the study, the degree of arsenopyrite decomposition was higher than it was in the case of pyrite. Temperature, time and dilution of the slurry intensify the efficiency of sulphides decomposition. The changes of the parameters cause the creation of passive layer, the qualitative features of which depend on the concentration of the leaching solution.

In the equipment used for pressure leaching the highest efficiencies of the paralell decomposition of both sulphides was achieved at the following conditions: concentration of the leaching solution - 3.55 M NaOH, temperature of 185 °C, initial pressure of  $\rm O_2$  - 0.9 MPa, time - 180 minutes.

# V. MIKLOŠ at all.: DECOMPOSITION OF THE PYRITE AND ARSENOPYRITE BY PRESSURE ...

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