

## **MINERAL DRESSING**

### **EFFECT OF THE HYPERGENESIS OXIDATION ON THE PROCESSING BEHAVIOR AND PREPARATION CHARACTERISTICS OF COPPER-ZINC PYRITIC ORE**

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The paper presents the modeling and analysis of oxidation of copper-zinc pyritic ore sampled from the Valentorsky orebody. It is found that the oxidized samples contain copper and zinc sulfates that are leached under the sample and water contact. It is shown that sulfide floatability is decreased by the longer-term oxidation. The authors advise to improve nonferrous metals extraction by the joint leaching and ultrasonic treatment of oxidized compounds.

*Copper-zinc pyritic ore, oxidation, flotation*

Base metal ores are coming to depletion, and ore deposits with large oxidation zones enter on the scene, and the extraction in this case requires studying the structure of such zones, the minerals that occur in them and the processing behavior of these minerals. Studies of hypergenesis influence on flotation of copper-nickel and copper-zinc ores showed reduction in the extraction of valuable components with long-term oxidation [1, 2]. Kinetics of oxidation depends on structure of an ore: sulfide oxidation is more intensive in colloform ore as against granular-crystalline structured ore. Modeling of hypergenesis process detected mineral phases of copper, zinc and calcium sulfates that newly originate in natural and production-formed residual soil [3]. It seems important to know how oxidation in the conditions of hypergenesis influences physicochemical properties and flotation ability of copper-zinc pyritic ores.

#### **TEST SUBJECTS AND METHODS OF ANALYSIS**

The test copper-zinc pyritic ore occurs at the Valentorsky ore field composed mainly of sphalerite and pyrite, more seldom of chalcopyrite, and rare tellurium-bismite, fahlore and galena. Nonmetals are mainly quartz and carbonate sometimes. Sulfide make zonal ear-like aggregates where the inner core is crystalline sphalerite disordered with chalcopyrite, the interior-to-exterior space accommodates predominantly chalcopyrite with little pyrite and tellurium-bismite, while the exterior part is composed of sphalerite (sometimes rounded, botryoid, colloform) with rare crystalline pyrite in-grown along grain bounds, and very fine chalcopyrite in some grains. The in-between of the zonal aggregates is filled with

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a fine-grain mix of crystalline pyrite, fahlore, chalcopyrite and sphalerite. Some colloform sphalerites contain crystalline pyrite. The test samples contained zinc 36–44% and copper 5–6.5%. The structure of the test sulfide pyritic ore is illustrated in Fig. 1 and the mineral composition is described in Table 1.

Modeling of hypergenesis followed the mode of evaporation, when ore samples 30 g in weight were placed in thermostatically controlled cells under 45°C, periodically wetted with 25 ml/day distilled water and were kept in the cells for 3, 10, 20, 40 days and longer. In the end, the samples were dried and sealed in plastic bags in the argon environment. The floatability and electric testing included original ore and the oxidized samples. The phase composition was analyzed with the help of DRON-2 diffractometer (Cu K $\alpha$  radiation).

The leaching kinetics analysis included washing of the oxidized samples with distilled water at S:L = 7.5:100, measurement of the pH of the solutions, determination of the metal content and sulfation concentration in the aqueous phase.

The flotation tests involved flotation of 5 g samples in a flotation machine with chamber capacity 100 cm<sup>3</sup>, in a limestone medium with 300 mg/l CaO<sub>free</sub>. Butyl potassium ethyl xanthate was a collector, and methyl isobutyl carbinol was a foam enhancer. The foam removal took 5 min. Besides, electrochemical properties of the samples were studied by means of pH titration. The samples were bound to a pyrolitic graphite electrode. To take off the oxidized compounds, the oxidized samples were ultra sound treated in an ultrasonic bath, the treatment frequency was 35 kHz and power output was 150 W.

#### DISCUSSION OF THE TEST RESULTS

**The Valentorsky Ore Oxidates.** After the 3 days humidity–dryout treatment of the test samples, the X-ray phase analysis showed new-formed mineral phases; the longer the treatment was, the more intensive was reflexive action of the new phases: see Fig. 2 with a diffraction pattern of an ore sample after 20 days oxidation in evaporation mode. We see reflexes of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and biankite (ZnSO<sub>4</sub>·6H<sub>2</sub>O) [4]. Gypsum origination is related with the calcite presence. After the 40 days treatment, newgrowths of gypsum and gannigite (ZnSO<sub>4</sub>·H<sub>2</sub>O) were observed.

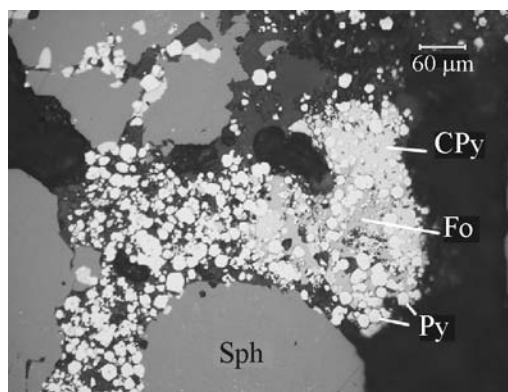


Fig. 1. Valentorsky sulfide ore. Legend: Py — pyrite; CPy — chalcopyrite; Sph — sphalerite; Fo — fahlore

TABLE 1. Valentorsky Field Ore Composition, %

Sphalerite	Pyrite	Chalcopyrite	Sphalerite+ chalcopyrite	Sphalerite+ pyrite	Pyrite+ chalcopyrite	Composite aggregates
38	15	5	15	15	12	4

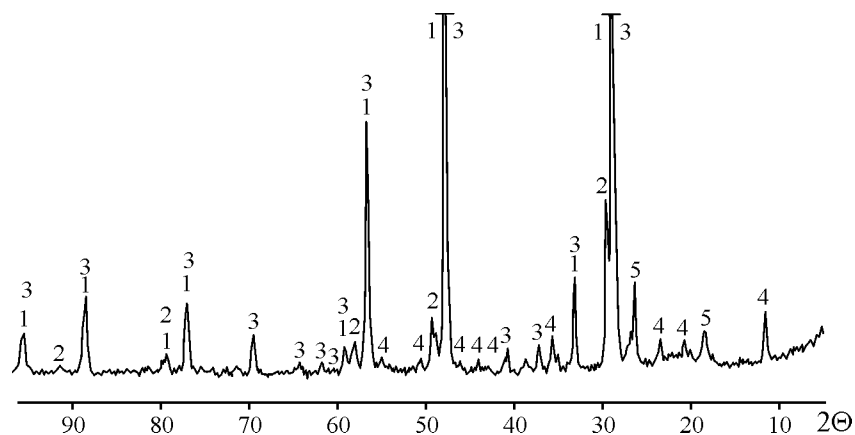


Fig. 2. Diffraction pattern of an ore sample after 20 days oxidation in the hypergenesis conditions: 1 — reflex of pyrite; 2 — reflex of chalcopyrite; 3 — reflex of sphalerite; 4 — reflex of gypsum; 5 — reflex of biankite

The chemical analysis results are given in Table 2. We see the higher concentration of heavy metals with the longer oxidation period. For instance, to zinc, the longer oxidation, 3 until 40 days, entailed an order higher concentration, from 600 to 660 mg/l. Acidity of the solutions grew, too.

In Fig. 3 there are calculated yields of heavy metals into solution depending on the experiment duration. The quickest oxidation is typical to sphalerite, which is confirmed with the indexes of water leaching of zinc and cadmium. Cobalt, present as an isomorphous admix in pyrite, even more intensively goes into solution. Chalcopyrite oxidation is very slow (cooper recovery in the solution was lower than 0.04%), which correlates with the references [5]. On the whole, the metal-to-sulfate conversion under the simulated hypergenesis had comparable intensity with the tests of ore samples taken from the Letnee orebody [2].

TABLE 2. Time Effect on the Ore Oxidation under the Hypergenesis Conditions on the Ion Composition of the Leaching Solutions

Oxidation time, days	Content, mg/l									pH
	Copper	Cobalt	Iron	Zinc	Cadmium	Magnesium	Sodium	Calcium	Sulfate	
3	0.011	0.029	0.011	61.006	0.140	1.137	-	6.861	125.64	6.36
10	0.032	0.061	0.017	190.583	0.466	1.814	0.473	8.966	271.35	5.56
20	0.0360	0.069	0.032	322.087	0.811	2.092	0.743	9.185	478.13	5.35
40	0.790	0.097	0.023	658.880	2.078	2.108	2.214	13.833	1090.6	4.83

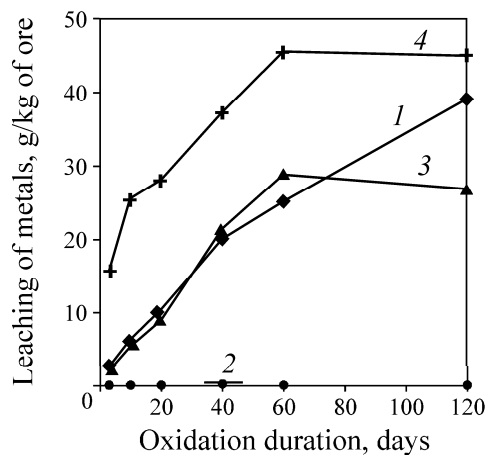


Fig. 3. The curves of the freshly arisen water-soluble heavy metals against the treatment duration in the hypergenesis simulation mode: 1 — zinc; 2 — copper; 3 — cadmium; 4 — cobalt

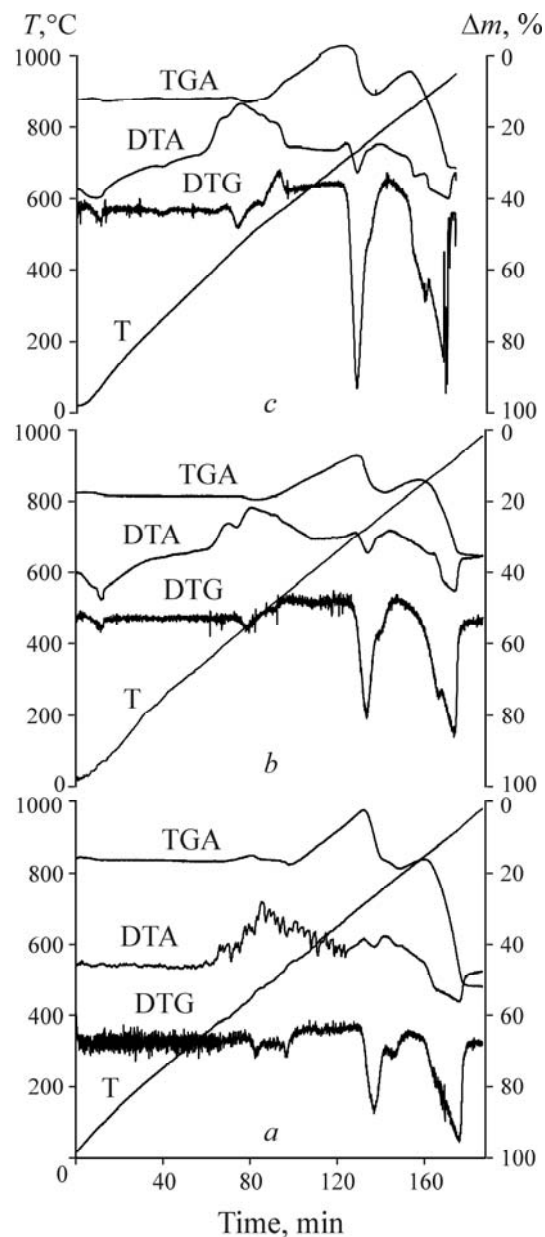


Fig. 4. The Valentorsky ore treatment: (a) untreated sample; (b) after 20 days oxidation; (c) after 40 days oxidation; TGA — thermogravimetric analysis; DTA — differential thermal analysis; DTG — differential thermogravimetric analysis

Oxidation of sulfides changed mineral composition of the Valentorsky field ore as per the differential thermal analysis and thermogravimetric analysis (Fig. 4). Weak low-temperature effects are associated with loss of water by sulfates (see Fig. 4, *b* and *c*). The thermogravimetric curves feature two zones of increase in mass, and distinction of the zones becomes more vivid in the longer treatment. Further on, under heating, we see a decrease in mass by nearly 10%. The increase in mass in the temperature ranges 450–650°C and 700–820°C is induced by oxidation of pyrite, chalcopyrite and sphalerite, with formation of sulfates  $\text{FeSO}_4$ ,  $\text{CuSO}_4$  and  $\text{ZnSO}_4$  [6, 7]. The decrease in mass in the next-following heating is due to oxidation of sphalerite and formation of  $\text{ZnO}$  [7]. While treatment gets longer, the tested ore samples lose a little  $\text{ZnS}$  as it becomes oxidized, which probably explains the decrease in mass in the ore samples (Fig. 4).

**The Oxidation versus Floatability of the Valentorsky Field Ore.** An ore sample was ground to  $-0.1$  mm size (Fig. 5). Figure 6 illustrates the influence of xanthate consumption and oxidation duration on the floatability of copper and zinc sulfates: the longer the oxidation simulating the hypergenesis, the less the extraction of copper and zinc into the flotation concentrate.

Results of mineralogical analysis of unoxidized ore concentrate and rewash discard are given in Table 3.

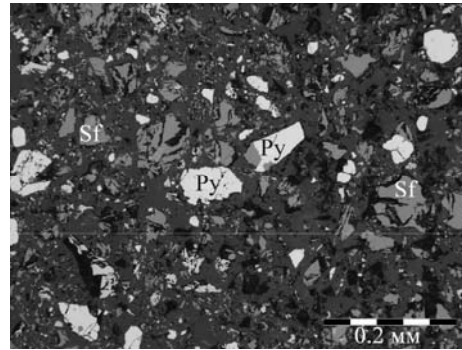


Fig. 5. Ground sample: general view

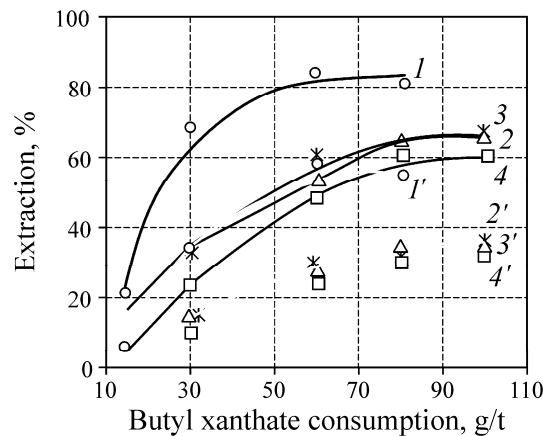


Fig. 6. The curves of the oxidation duration and butyl xanthate consumption against zinc and copper extraction from ores of the Valentorsky ore field: 1-4 — zinc; 1'-4' — copper; 1, 1' — untreated ore; 2, 2' — after 3 days oxidation; 3, 3' — after 10 days oxidation; 4, 4' — after 20 days oxidation

TABLE 3. Mineral Composition of Flotation Products of Unoxidized Ore (Reduced to 100 % of Sulfides)

Butyl xanthate consumption, g/t	Product	Content, %							Percent content of nonmetals in slurry
		Pyrite	Chalcopyrite	Sphalerite	Aggregates				
					Pyrite + chalcopyrite	Sphalerite + chalcopyrite	Sphalerite + pyrite	Composites	
30	Concentrate	5	5	72	0.5	7	6	5	Individual grains of quartz
	Rewash discard	21	21	17	10	13	7	11	60% quartz
80	Concentrate	10	10	38	3	19	3	17	Individual grains of quartz
	Rewash discard	53	10	15	9	2	1	5	65% quartz

Rewash discards contain sufficient amount of sulfides, with dominant large grains of pyrite and chalcopyrite. Aggregates, including composite aggregates, contain considerable amount of sulfides, too. With higher consumption of the collector, the content of pyrite, chalcopyrite and aggregates grow in concentrates. By the mineralogical analysis, sulfide grain release is insufficient when ore is ground to  $-0.1$  mm.

The potentiometric titration of untreated ore and of an ore sample after 43 days oxidation showed that electrolytic potential and pH ratio in the oxidized sample had drifted towards positive values, which indicated formation of oxidized compounds on the surface of sulfides as consistent with the X-ray phase analysis (Fig. 7).

It was found possible to remove the oxidized coatings by ultra sonic treatment. The 43 days-long oxidized sample was exposed to ultrasonic treatment for 2, 5 and 10 min, and to flotation with butyl xanthate consumption of 100 g/t. The results are presented in Fig. 8.

The ultrasonic treatment improved floatability of sulfides in the oxidized sample of the Valentorsky field ore. In the ultrasonic treatment time range from 2 to 10 min, the concentrate yield grows and reaches 65.6%, which is close to the result of 63.9% in the unoxidized sample treated in the same reagent mode. Copper recovery rose to 61.6% in the oxidized sample as against 46.8% in the unoxidized ore. The after-ultrasound recovery of zinc reached 75.7%, which is around the recovery from the unoxidized sample.

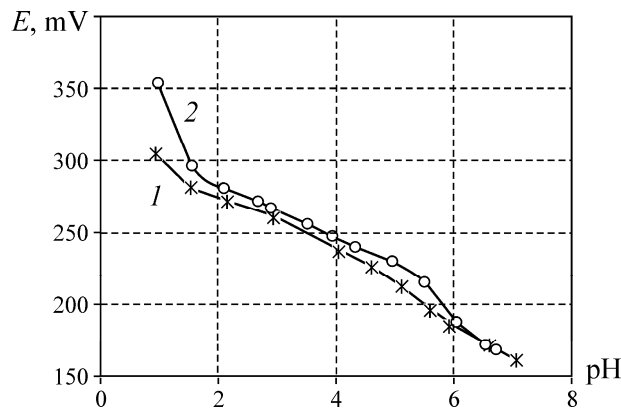


Fig. 7. Relation of electrolytic potential  $E$  (in relation to a chloride-silver electrode) and pH in the (1) unoxidized and in the (2) same ore sample after 43 days oxidation

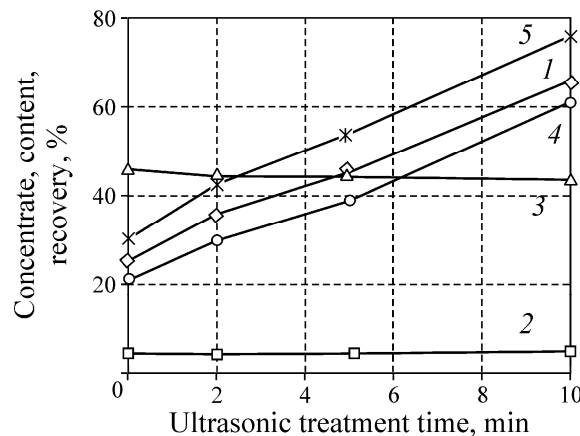


Fig. 8. Flotation ability of the oxidized ore sample in relation to its exposure to ultra sound: 1 — yield of concentrate; 2 — content of copper; 3 — content of zinc; 4 — copper recovery; 5 — zinc recovery

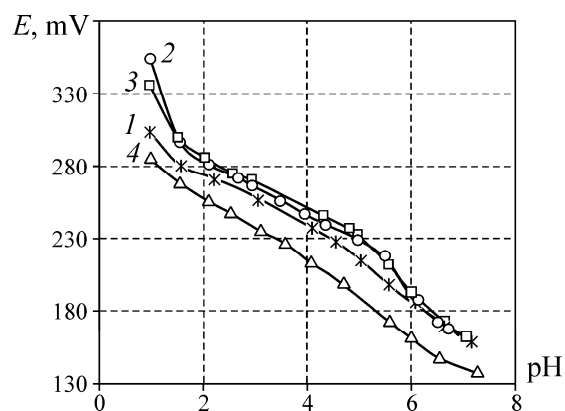


Fig. 9. The  $E$  and pH curves, the Valentorsky ore samples: 1 — unoxidized ore; 2 — after oxidation for 43 days; 3 — after 43 days oxidation followed with the 5 min ultrasonic treatment; 4 — after 43 days oxidation and 10 min ultrasonic treatment ( $E$  in mV relative to chloride-silver electrode)

The shifted curves of potentiometric titration in Fig. 9 confirm removal of oxidized compounds from the surface of a sample after 10 min ultrasonic treatment.

The water pre-leaching and ultrasonic treatment effect on the flotation extraction of metals showed that the three days leaching rises copper recovery from 14.3 % to 57.3 % and zinc recovery from 34.4 % to 76.6 % in flotation with 30 g/t butyl xanthate; the water leaching of the oxidized sample increased copper recovery to 59.8 % and zinc recovery to 61.1 %. The leaching and ultrasonic treatment application in turn results in much higher extraction than if used individually: copper recovery was 76.4 % and zinc recovery was 87.8 % after combined employment of the processes (see Fig. 10).

According to the potentiometric measurement, the  $E$ –pH curves, obtained for an unoxidized ore and a sample after 120 days oxidation, match (see Fig. 11) as metal sulfates from the mineral surface go to the solution. This conclusion agrees with the data of the liquid phase analysis (Table 2).

The influence of combining the leaching and ultrasound on the ore floatability after the ore oxidation for 3–120 days is illustrated in Fig. 12 (flotation involved 39 g/t butyl xanthate). The dashed lines show the recovery level for the unoxidized sample. In any oxidation duration, the leaching and ultrasonic treatment improved the copper recovery as compared to the unoxidized sample. The leaching and ultrasound result in the higher zinc extraction from the sample after 3 days and 43 days oxidation as against the unoxidized sample, while the 120 days oxidation ends with the lower zinc recovery by leaching as compared to the unoxidized sample, and the after-leaching plus ultrasound recovery is equal to the recovery from the unoxidized sample.

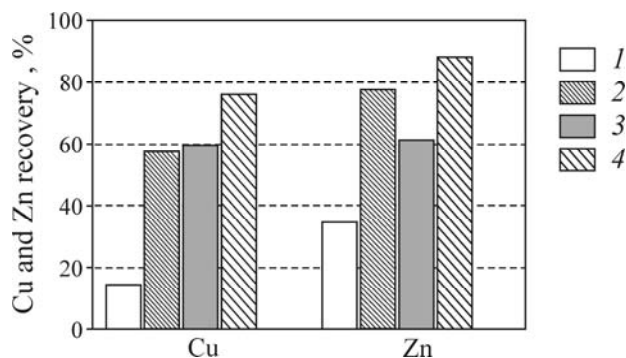


Fig. 10. Effect of leaching and ultrasonic treatment on copper and zinc recovery in the sample after 3 days oxidation: 1 — no treatment; 2 — ultrasonic treatment; 3 — leaching; 4 — leaching and ultrasonic treatment together

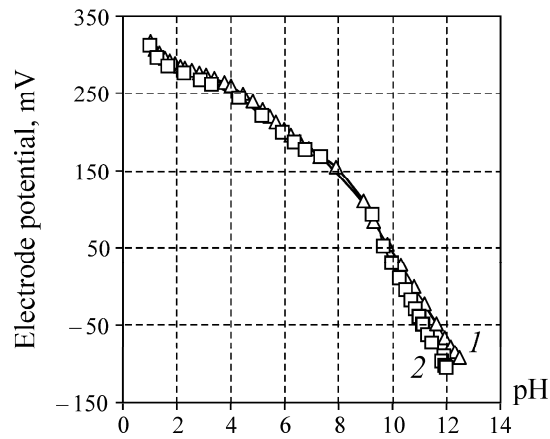


Fig. 11. The  $E$ -to-pH curves: 1 — unoxidized ore sample; 2 — the ore sample after the oxidation within 120 days ( $E$  in mV relative to chloride-silver electrode)

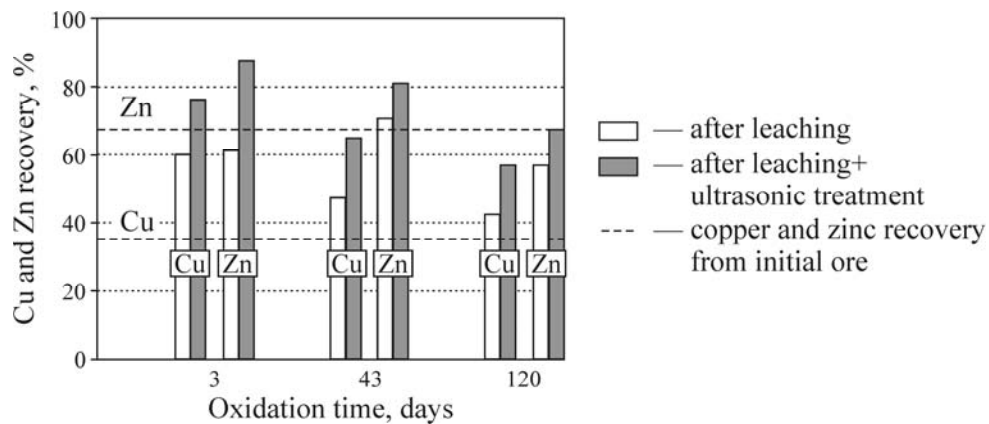


Fig. 12. Influence of the oxidation duration on the copper and zinc recovery from the sample subjected to leaching and ultrasonic treatment

Thus, on the strength of the performed research, the joint leaching and ultrasonic treatment yields higher results, though the effect is lower after the long-term oxidation.

## CONCLUSION

Based on the analysis into the influence of oxidation simulating the hypergenesis on the phase composition and surface properties of copper-zinc pyritic ore sampled at the Valentorsky orebody:

- 1) origination of sulfates of nonferrous metals is found;
- 2) it is shown that oxidation decreases copper and zinc sulfides recovery under flotation, but the recovery grows with longer-term oxidation;
- 3) it is recommended to improve flotation of oxidized ore by exposing it to the joint leaching and ultrasonic treatment.

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