

Acid leaching of oxide–sulfide copper ore prior the flotation – A way for an increased metal recovery

Miroslav D. Sokić¹, Vladan D. Milošević¹, Velizar D. Stanković², Vladislav Lj. Matković¹, Branislav R. Marković¹

¹Institute for Technology of Nuclear and Other Mineral Raw Materials, Belgrade, Serbia

²University of Belgrade, Technical Faculty, Bor, Serbia

Abstract

The copper mine Cerovo – East Serbia, as well as the other ore bodies in its vicinity, contains a significant amount of oxide copper minerals in their upper layers (>40%). Processing of such mixed ores by the existing concentration technologies leads to a substantial copper losses (<60%). Reduction of “oxide copper”, by acid leaching prior the flotation concentration, can increase the overall copper efficiency up to more than 70% in the single-stage leaching, achieving an efficiency in the flotation concentration stage higher than 75%. Based on the performed experimental results, the flow sheet for processing of the mixed oxide-sulfide copper ore is proposed.

Keywords: oxide–sulfide copper ore, leaching, flotation, increase of copper recovery.

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Many copper mines contain, beside sulfide ore as a main quantity in deeper layers, a certain amount of oxide deposit in upper layers, as well as oxide–sulfide blend in the middle of an ore body. In order to recover the copper metal oxide ore parties are usually processed by leaching, followed by solvent extraction, and electrowinning, while the rest of ore deposit is processed by flotation, having considerable technological problems, and usually a low percent of copper recovery may be achieved. Hence, the major fraction of oxide and a part of sulfide minerals may be lost and thus making the process economy less advantageous. Such case is found in the copper ore deposit “Kraku Bugaresku”, an ore field in Eastern Serbia, a property of Mining and Smelting Copper Co., Bor, Serbia. This ore field contains several smaller ore bodies, named “Cerovo – C₁₋₄”, having oxide cap on the top, followed by a layer of oxide-sulphide mixture, before coming deeper into the main sulfide ore deposit. So far, only the ore body C₁-Copper Mine Cerovo is opened, this body is under exploitation. The majority of oxide–sulfide batches from “Cerovo – C₁₋₄” ore bodies contain carbonate minerals, with some cuprite and chrysocolla which may easily leach. From all ferrous minerals the hematite and limonite are predominant, including some parts of lodestone. The oxide batches are placed on the surface, and upon the body opening they are the first to be excavated. Potential content of copper oxide batches in the C₁ to C₄ ore bodies is estimated to

be 18000 t of copper, including a part that is already extracted during the ten years of C₁ ore body (Open pit Cerovo) exploitation [1].

Three sources of copper losses are noticed during the exploitation of C₁ ore body, which also generates technical and environmental problems that will appear in each of the other ore bodies:

- Barren surface layer and associated gangue material, with copper content below 0.2%;
- Oxide–sulfide ore from the current ore excavation containing various percentages of oxide and sulfide minerals, in a range from few percents up to 60% of oxide.
- Mine water collected at the open pit bottom, as well as the one drained as an acid mine drainage (AMD), due to a spontaneous self-leaching of the out of balance ore stored as a dump at the open pit edge, as is illustrated in Figure 1.



Figure 1. A photograph of the dump, formed of out of balance ore (top part), and the pond (lower part of the photo), formed by collecting the AMD.

Correspondence: M.D. Sokić, Institute for Technology of Nuclear and Other Mineral Raw Materials, 86 Franchet d'Esperey Street, 11000 Belgrade, Serbia.

E-mail: m.sokic@itnms.ac.rs

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Each of these copper sources needs a different approach related to their technological treatment. Flo-

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tation of sulfide minerals from copper ore, containing a high percent of oxide copper, generates technical problems in the concentration process, decreasing the level of copper content, which is already low. In order to increase the overall efficiency of copper concentration process from such ore blend it is necessarily to treat the part of copper oxide either by leaching of grinded ore prior the flotation or by leaching the flotation tailing coming out from the concentrator.

Direct leaching process of copper oxides or complex ores attracts considerable scientific and engineering attention, which plays an important role in the sustainable development of copper industry. Sulphuric, hydrochloric and nitric acid, as well as the ammonia are usually used as the leaching agents in a various copper ore leaching processes [2–12]. Copper oxides easily react with sulphuric acid solutions at the room temperature producing Cu^{2+} in the aqueous phase. Energy consumption can also become an important factor of economy when the leaching process occurs, considering the heating and agitation of the input suspension. The kinetics of copper minerals leaching was recently published by several authors, for example Sokić *at al.* kinetics of copper leaching from chalcopyrite [7], Bingol and Canbazoglu kinetics of copper leaching from malachite [10,11], while Quast has published the kinetics of copper leaching from atacamite [12]. Also some researchers studied the processing of copper oxides wrapped by silicate and limonite [13,14]. This kind of ore is usually processed by mill running and then smelting, and the copper recovery is about 35% during the mill running process. Sun *at al.* [14] performed the copper leaching from low grade copper oxide ore by sulphuric acid, and they have obtained leaching percent of copper over 90%. Compared with the copper leaching efficiency of about 35% in the mill running technology the leaching process has achieved a better economic result.

In the present study the leaching of oxide-sulfide copper ore was considered, and a modification of the existing process was performed by inserting the leaching process between the ore milling and the flotation sections. Therefore, a higher overall efficiency of the copper removal, from such minerals blend, was obtained. Through this study, the influence of some parameters, affecting the leaching process, and the flotation process of the leach residue were defined. Finally, the oxide-sulfide copper ore, used in the experimental part, was taken from the current mine works in the Copper Mine Cerovo.

EXPERIMENTAL

Equipment and chemicals

The leaching experiments were carried out in a glass reactor, presented in Figure 2, equipped with the

teflon mechanical stirrer, the condenser, the thermometer, the glass funnel for feeding a solid sample and the sampling device. Such set-up provides stable hermetic conditions, and allows leaching at the chosen constant temperature as well as at the constant stirring rate.

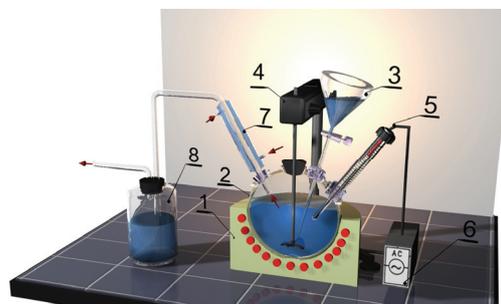


Figure 2. Experimental set-up for the leaching process at atmospheric pressure: 1 – electrical heater, 2 – glass reactor, 3 – glass funnel, 4 – mechanical stirrer, 5 – contact thermometer, 6 – cut off relay, 7 – condenser, 8 – absorber.

Sulphuric acid, analytical grade was used to prepare the leach solution by dissolving it in distilled water. Since the initial H_2SO_4 concentration was the key parameter of leaching, the stock solution with the concentration of 0.3 M was prepared and further diluted to get the desired initial concentration of H_2SO_4 .

In flotation concentration of the leaching residue standard chemicals were used, save as in the concentration plant Veliki Krivelj. These are the potassium-ethyl-xanthate (PEX) as the collector, and the DOW 250 as the frothing agent. These chemicals were of a technical grade. Lime milk (technical grade) was used for adjusting the pH value of suspension before the flotation.

Time was measured by a chronometer. Atomic absorption spectrophotometer (AAS – Perkin Elmer, model Analyst 300) was used for chemical analysis of the leaching samples. Chemical analysis of the ore samples, as well as of the leaching residue, the concentrate, and the flotation tailing were all analyzed in laboratories of the Institute of Mining and Metallurgy Bor.

Leaching procedure

Ore samples, at first were disintegrated and then sieved through a set of standard laboratory sieves. The fraction $<74 \mu\text{m}$ was used in the leaching experiments. Prior the leaching the chemical analysis was done in order to determine the initial concentrations of oxide, sulfide and total copper. Also, the percent of moisture, the contents of Fe, S, and SiO_2 were determined.

The measured volume of the leaching solution with a chosen initial H_2SO_4 concentration was poured into the reactor. The weighted mass (1372 g) of disintegrated and sieved ore was joined to the leaching solu-

tion (2.5 dm³), and the time of leaching was measured. The solution samples were taken in a predetermined time intervals for chemical analysis on Cu²⁺, Fe²⁺ and Zn²⁺. After completing the leaching process, solid residue was filtered, than washed and further processed by flotation in order to separate and concentrates copper sulfide minerals from gangue minerals.

Leaching time was in a range of 20 to 240 min, while the initial H₂SO₄ concentration in the leaching solution varied from 0.05 M to 0.3 M. The particle size was 90% –74 µm; stirring velocity 300 rpm, while the phase ratio was S:L = 1:2. These three process parameters were kept constant in all experiments. All experiments were performed at the room temperature.

The leach residue, that followed each of leach experiments, was conducted in the laboratory flotation cell of the following characteristics: Denver DR12, 1350 rpm, a small impeller and average air consumption. All experimental parameters were scaled down, adding the same flotation agents to the conditioned suspension, and the proportional quantities as they are used at the industrial scale. Also, the process time of each flotation stage was the same as it is on the industrial scale in the concentrator “Veliki Krivelj”. The aim was to get an insight how high is the copper recovery from the ore, liberated from oxide minerals, in the leaching stage. Potassium ethylxanthate (PEX) was used as a flotation reagent, while as an aero promoter AP 3418 was used, both as collectors, while as a frothing agent DOW 250 was used. After completing both leaching and flotation processes, chemical analysis of the obtained products – leach solution, concentrate and flotation tailing, was carried out and the mass balance was evaluated. Finally, the copper distribution along the both stages was determined.

RESULTS AND DISCUSSION

Oxide–sulfide copper ore was sampled from the ore body Cerovo C₁ (south deposit) and used in this study. The chemical composition of the ore sample is presented in Table 1. From Table 1, it can be seen that the high copper concentration is in the sample, as well as the high copper oxide content, while the sulfide copper concentration is lower. The iron concentration is also high, what may be related to the presence of hematite and other iron oxides. Low sulphur content indicates a low content of pyrite. Also, the content of impurities in the ore, such as zinc, lead, arsenic and cadmium is low, which is very convenient for its processing.

Table 1. Chemical composition of the ore sample (%)

Cu	Cu _{ox}	Cu _{sulf}	Fe	Zn	Pb	As	Cd	S	SiO ₂
0.68	0.45	0.23	4.37	0.016	0.023	0.004	<0.0025	1.33	60.36

Leaching of oxide-sulfide copper ore

The influence of time and H₂SO₄ concentration on the leaching degree of oxide copper, leached out from the ore sample, was determined and presented in Figure 3.

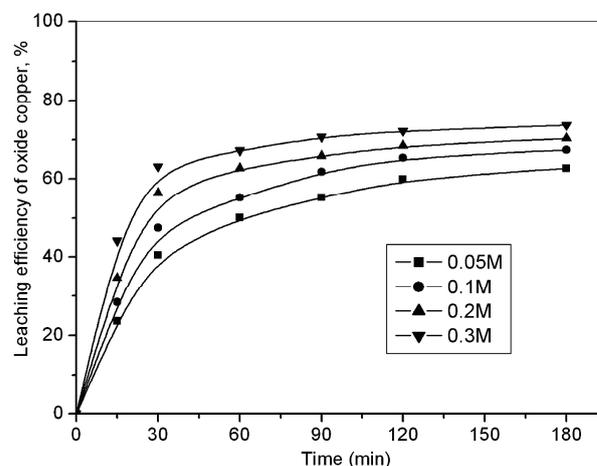


Figure 3. Leaching efficiency vs. process time for different H₂SO₄ concentrations in the leaching solution.

As expected, a copper extraction increases with the process time, tending to achieve a plateau value after approximately two hours for all here used initial concentrations of H₂SO₄ in the leaching solution. The higher concentrations the higher copper leaching percentages were obtained. The highest extraction percentage of 73.8% was achieved at the H₂SO₄ concentration of 0.3 M. One can see that after 180 min increment of leaching degree is almost negligible and the process occurs very slowly. From an engineering point of view, the optimal process time could be chosen between 1.5 and 3 h, depending on the used initial concentration of H₂SO₄. However, increasing the concentration of H₂SO₄ over 0.2M is not justified due to its higher consumption in undesired reactions with earth-alkali carbonates present in the ore, as well as with higher acidity of the leach solution. The leach solution has to be adjusted to a desired value (pH 2), to be prepared for further processing by ion exchange and/or solvent extraction [15].

The chemical composition of the leach liquor and leach residue, obtained after leaching of the ore sample at 120 min and 0.2 M of H₂SO₄, is presented in Table 2.

Obtained copper concentration in the leach solutions was usually in the range 1.2–1.7 g/dm³, for other experimental conditions. Concentration of leached fer-

Table 2. Chemical composition of the leach liquor and leach residue

Leach part	Cu	Cu _{ox}	Cu _{sulf}	Fe	Zn	Moisture
Liquor	1.62 g/l	–	–	1.39 g/l	7.75 mg/l	–
Residue	0.41%	0.176%	0.23%	4.06%	0.013%	22.24%

rous/ferric ions is approximately equal to the copper ions concentration, while the concentration of zinc ions was for more than two orders of magnitude less.

Flotation of the leach residue

In the residual solid part, after completing the leaching process and phase separation by filtration, lime milk was added in order to adjust the pH value up to 9.5. Then after, the residue was processed by flotation in order to separate the copper sulfide minerals from the gangue and produce the concentrate. Frothing agent D 250 was used as needed while the consumption of PEX collector was 40 g/t. Figure 4 presents the influence of flotation time on the flotation efficiency of sulfide copper, for five experiments with the different amount of the PEX collector of 15, 20, 25, 30 and 35 g/t. The maximum sulfide copper removal in the flotation process was 78%, for 20 min of treating, and amount of the PEX collector of 30 g/t. Similar results were obtained by Chen *et al.* [16]. They have studied chalcopyrite recovery from cleaner flotation as a function of collector dosage, and their result showed that with the increase of collector, chalcopyrite recovery slightly increase and then decrease. Besides the valorization of oxide copper, the utilization of sulfide copper in flotation process increases 2–4% by introducing the leaching process, because it has a positive effect on the surface of the sulfide mineral grains.

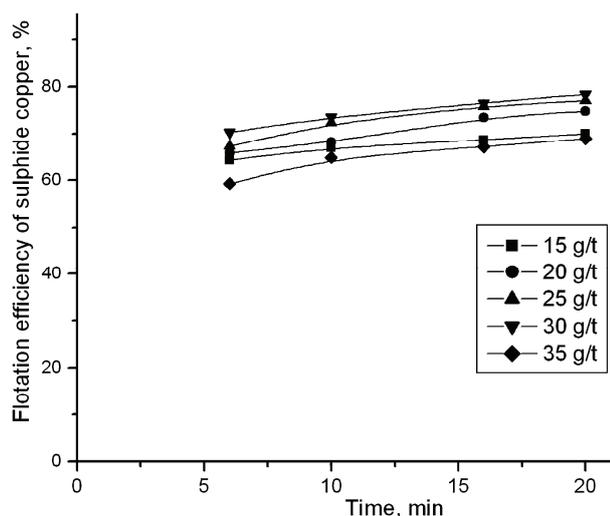


Figure 4. Influence of the time of treatment on the sulfide copper flotation efficiency, from leach residue, for five experiments with the different amount of the PEX collector.

The chemical composition of the sulfide copper concentrate and the flotation outflow are presented in Table 3. Base concentrate with a 5% of Cu was obtained, and after a three-stage rinsing the final concentrate with over 20% of Cu, for smelting process, was obtained. In the base concentrate total copper recovery, during the ore processing (leaching and flotation), is approximately 75%.

Table 3. Chemical composition (%) of the flotation products obtained at the content of 30 g/t PEX

Flotation product	Cu _{total}	Cu _{ox}	Cu _{sulf}
Base concentrate	5.06	0.6	4.46
Outflow	0.23	0.16	0.07

Process proposal

Based on these, preliminary, experimental results, on an enlarged laboratory scale the schematic flow sheet of mixed oxide-sulfide copper ore processing was proposed and presented in Figure 5. Also, the copper distribution and its recovery, along some particular stages, are shown.

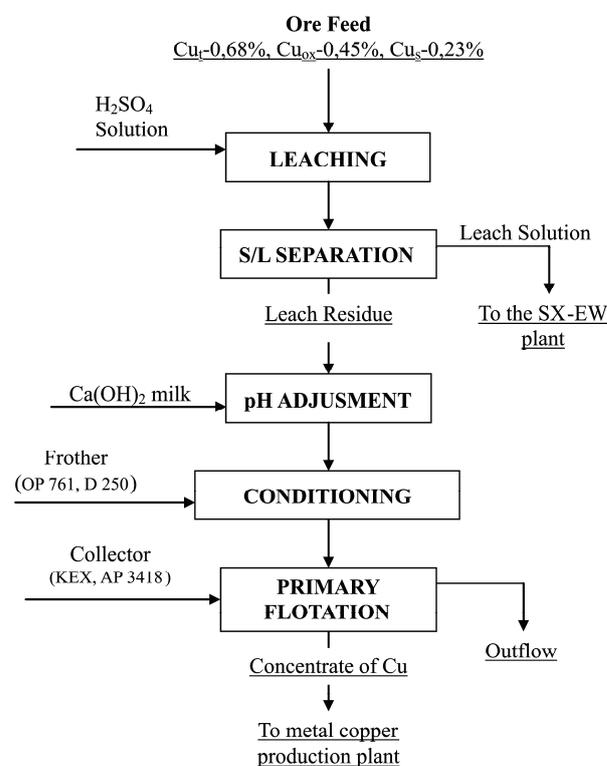


Figure 5. Schematic flow sheet of the oxide-sulfide copper ore processing.

CONCLUSION

Copper Mine Cerovo, as well as the other ore bodies in its vicinity, contains significant amount of oxide copper minerals (>40%) in the upper layers. Processing of such mixed ores by the existing concentration technologies leads to the oxide copper losses. In order to increase an overall degree of copper utilization, a study of the copper oxides leaching from oxide-sulfide ore followed by flotation of copper sulfide minerals from the leach residue was presented. Maximum copper oxide extraction during the single leaching stage was 73% with 0.3 M H₂SO₄ leaching solution and after 180 min. Maximum sulfide copper extraction in the flotation process was 78% for 20 min and amount of the PEX collector of 30 g/t. Achieved total copper recovery in the ore leaching and flotation process is about 75%. Introducing the leaching process prior to the flotation process is the main reason for increases in the total copper recovery. This is due to the valorization of most of the oxide copper, and improved efficiency of the sulfide copper flotation. Copper concentration in the leach solutions was in the range 1.2–1.7 g /dm³, and content of copper in the concentrate after flotation was about 5%.

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IZVOD**KISELO LUŽENJE OKSIDNO–SULFIDNE RUDE BAKRA PRE FLOTACIJE – NAČIN ZA POVEĆANJE ISKORIŠĆENJA METALA**Miroslav D. Sokić¹, Vladan D. Milošević¹, Velizar D. Stanković², Vladislav Lj. Matković¹, Branislav R. Marković¹¹*Institut za tehnologiju nuklearnih i drugih mineralnih sirovina, Beograd, Srbija*²*Univerzitet u Beogradu, Tehnički fakultet, Bor, Srbija*

(Stručni rad)

Rudnik bakra Bor, lokalitet Cerovo, sadrži više rudnih tela koja sadrže značajnu količinu oksidnih minerala bakra u svojim površinskim slojevima (> 40%). To su najvećim delom karbonatni minerali, uz nešto kuprita i hrizokole, a od minerala gvožđa preovlađuju hematit, limonit i nešto magnetita. Prerada mešanih sulfidno-oksidnih ruda stvara tehnološke probleme pri flotiranju, smanjujući ionako nizak stepen iskorišćenja, pa ukupni gubici na bakru dostižu i do 60%. U cilju povećanja ukupnog stepena iskorišćenja bakra, prilazani su rezultati luženja oksidnog bakra iz oksidno-sulfidne rude i flotacije sulfidnog bakra iz čvrstog ostatka luženja. Maksimalno iskorišćenje oksidnog bakra tokom jednostepenog luženja sa 0,3 M rastvorom H₂SO₄ i vremenu od 180 min je 73%, a sulfidnog bakra u procesu flotacije je 78%, za 20 min i dodatak PEX kolektora od 30 g/t koncentrata. Ukupno iskorišćenje bakra u procesima luženja i flotacije rude iznosi oko 75%. Koncentracija bakra u lužnom rastvoru iznosi 1,2–1,7 g / dm³, a sadržaj bakra u koncentratu nakon flotacije je oko 5%. Na osnovu izvršenih eksperimentalnih rezultata predložena je tehnološka šema za preradu mešovite oksidno-sulfidne rude bakra.

Ključne reči: Oksidno–sulfidna ruda bakra • Luženje • Flotacija • Povećanje iskorišćenja bakra