

ZAŠTITA MATERIJALA MATERIAL AND ENVIRONMENT PROTECTION I ŽIVOTNE SREDINE



ČASOPIS: ZAŠTITA MATERIJALA I ŽIVOTNE SREDINE

SADRŽAJ

Glavni urednik: Dr Darko Vuksanović,
Univerzitet Crne Gore, Metalurško-
tehnološki fakultet

Uređivački odbor:

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Dr Miomir Pavlović, Srbija
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Dr Nada Blagojević, Crna Gora
Dr Aleksandar Joksimović, Crna Gora

Izdavački savjet:

Dr Jelena Pješčić – predsjednik
Dr Ivana Bošković
Mr Dragan Radonjić
Dr Filip Kokalj
Mr Igor Jovanović

Za izdavača:

Prof. dr Darko Vuksanović

Izdavač:

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CONTROL OF COPPER ACID MAIN DRAINAGE BY MEANS OF IMMOBILIZING AGENTS: ELECTROCHEMICAL STUDY ON A GRAIN MODEL

Perica Paunović, S. Hadži Jordanov and A. T. Dimitrov

*Faculty of Technology and Metallurgy, University "Sts. Cyril and Methodius"
Ruger Bosković Str., 16, 1000 Skopje, R. Macedonia*

Abstract

The nature of processes that take place on top of copper bearing grains during the suppression of copper acid drainage from mine tailings was studied on a grain model. Cyclic voltammetry (C.V.) was employed as an experimental technique suitable for indirect measuring of copper leaching.

Experiments were done in sulfuric acid (pH=2) at electrodes that progressively approach the real situation during acid main drainage, starting with Cu-metal, then with CuO and finally with CuO covered with CaSO₄.

Oxidation was found to be the only process that takes place on metallic copper electrode anodically polarized up to 2 V vs. Cu/CuSO₄ reference electrode. Dissolution is intensive and reaches up to 50 mA.cm⁻². When the same was repeated, but on CuO electrode, anodic currents were some 4 times lower than on the bare metallic surface. This indicates that the electrode material is not completely oxidized to copper(II)oxide and the Cu(0) or Cu(I) residues are oxidized during the anodic polarization. This explains the diminished dissolution.

Dissolution is further restricted at electrodes covered with CaSO₄. It is some 20 times lower than on the bare oxide electrode. When the second layer of CaSO₄ was applied, anodic currents were another 15 times lower. Total decrease of anodic currents when transition is made from Cu-metal to CuO covered with 2 layers of CaSO₄ reaches up to 7.500 times.

C.V. measurements produced a proof that mechanical blockage is the way how lime prevents leaching of copper bearing grains in immobilization experiments.

Key words: acid rain drainage, copper mine tailings, immobilization by CaSO₄, cyclic voltammetry, grain model

1. Introduction

The exploitation of copper ore deposits causes severe environmental pollution problems, such as accumulation of enormous quantities of mine and flotation tailings and generation of wastewater that contaminate surface and groundwater with high loads of toxic and heavy metals [1-3]. Especially dangerous is the process of acid mine drainage, where oxidation and occasional leaching of sulfide minerals exposed to the combined action of rainfalls, air and bacterial action occurs. The generated acid is consumed by acid-consuming minerals resulting in the precipitation of gypsum and metal hydroxides, oxy-hydroxides and other complex compounds (e.g., Cu(OH)₂ at pH 5÷6, PbSO₄, Ca₃(AsO₄)₂, FeSbO₄·2H₂O, etc.).

There are three main approaches for the control of AMD such as [4]: the Preventive approach, the Containment approach and the Remedial one. The essence of the first approach is to prevent acid generation. The prevention of AMD includes the following methods: *i*) excluding the contact of sulphides with oxygen or water [5], i.e. to avoid oxygen diffusion (the use of organic, composite and vegetative covers); *ii*) eliminating the bacteria responsible for the catalytic reactions [4, 6] and *iii*) by controlling pH using alkaline additives, such as fly ash [7], limestone [8] etc. The aim of the containment approach [9] is to prevent the migration of AMD to the environment (soil and groundwater) by preventing the water flow through the construction of diversion trenches, or by using porous reactive walls that remove

contaminants from groundwater. Remedial methods [4, 10] aim to collect and treat the contaminated drainage, either by active or using passive treatment methods.

Republic of Macedonia is rich in poly-metallic complex sulfide ore deposits. They are used for production of base and precious metals, as e.g. copper, zinc, lead, silver and gold. The exploitation of sulfide ores requires a complex treatment during which the low-grade ore is enriched. This is achieved by flotation aimed at the removal of copper bearing particles in the ore. As a result of flotation, copper concentrate is produced which is later transformed into blister copper and finally into electrolytic copper of 99.95-99.97% Cu purity.

Copper works in Bučim, near town of Radoviš, is in operation since 1979. Open pit mining is

applied with a capacity of some 4 million t/y ore with an average content of 0.25% Cu, 0.9g/t Ag, 0.4g/t Au, etc. Flotation efficiency is 1.2% (m/m) and the separation of useful components is 85%, 35%, and 60% respectively for Cu, Ag and Au. As a result, a quantity of an average of 40,000 t/y Cu-concentrate, containing 20% Cu, 30 g/t Ag; 30 g/t Au is produced annually. After metallurgical treatment, that takes place elsewhere, annual metal production averages 8,000 t/y Cu, 800 kg/y Au, 800 kg/y Ag.

The studied wastewaters reached concentrations of up to 840 mg/l Cu²⁺, 360 mg/l Mn²⁺, etc. In order to control the acid mine drainage process, stabilization of copper bearing grains in mine tailings was studied. As a stabilizing agents lime, fly ash and limestone were used.

2. Experimental

In this study, the following investigations were performed: *i*) leaching of mine tailings in percolated columns with diluted sulfuric acid, within the effect of addition of stabilizing agents (lime, fly ash and limestone) on the prevention of copper leaching was studied and *ii*) electrochemical measurements of grain immobilization, within the nature of processes that take place on top of copper bearing grains was studied on modeled surfaces by means of cyclic voltammetry.

A sample of mine tailings that contains 0.132 % Cu (CuO being 0.01 %) was subjected to homogenization and size reduction. Three

fractions were chosen for leaching experiments: *i*) < -10 mm, *ii*) < -3.3 mm and *iii*) < -1.25 mm.

Sample size was 0.5 ÷ 4 kg per column, with use of 0.1 to 0.2 kg of foundry sand as a drainage bed. Immobilizers were added in the following percentage to the tailings sample: lime, 5-7%, Fly Ash, ~10% and CaCO₃, 7%.

Leaching was performed by means of 0.1 M H₂SO₄, with compensation for spend acid. Solid to liquid ratio was typically 1:1 to 1:2 [11, 12]. The conditions under was performed the leaching are shown in Table 1. Leaching was studied over a period of 250 days into columns such as in Fig. 1.

Table 1 Conditions of the leaching

Sample	pH	Immobilizers	%Cu in the waste	M _{total} (Cu), mg
1	7	no	< 0.1	0.442
2	1	no	< 0.1	633.827
3	1	875 g fly ash 250 g casting sands	< 0.1	563.23
4	1	650 g lime	< 0.1	43.094
5	2	no	< 0.1	16.8825
6	2	875 g fly ash 250 g casting sand	< 0.1	15.7145
7	2	650 g lime	< 0.1	3.0625

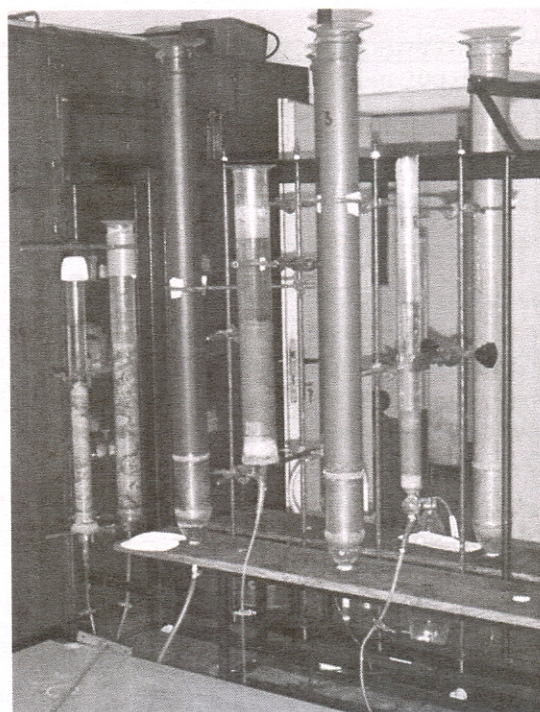


Figure 1. Photos of used columns

Electrochemical measurements were performed using AMEL equipment (Function Generator AMEL 568, Potentiostat/Galvanostat 2053 and software package SOFTASSIST 2.0). The counter electrode was of platinum wire and the reference electrode – Cu/CuSO₄. The electrolyte was an aqueous solution of H₂SO₄ (p.a., Merck) in ultrapurified and deionized water, with pH = 2 at room temperature. As a working electrodes Cu, CuO and CuO/CaSO₄ were used. Cu electrode was a wire with working surface area of 0,5 cm². For preparation of CuO electrode, sintered CuO

was used ($\rho = 5.92 \text{ g/cm}^3$). After implementation of electric contact, the electrode was inserted in plastic envelope and insulated by polyester resin. The working surface circle was 0.125 cm². CuO/CaSO₄ electrode was made by the same procedure as CuO electrode, with additional application of CaSO₄. CaSO₄ was formed by applying a layer of Ca(OH)₂ on top of CuO, and immersion in solution of H₂SO₄, pH = 2. Two CuO/CaSO₄ electrodes were prepared, with one and with two CaSO₄ layers.

3. Results and discussion

3.1 Leaching in percolated columns

Rates of copper leaching without addition of immobilizer are shown in Fig. 2.

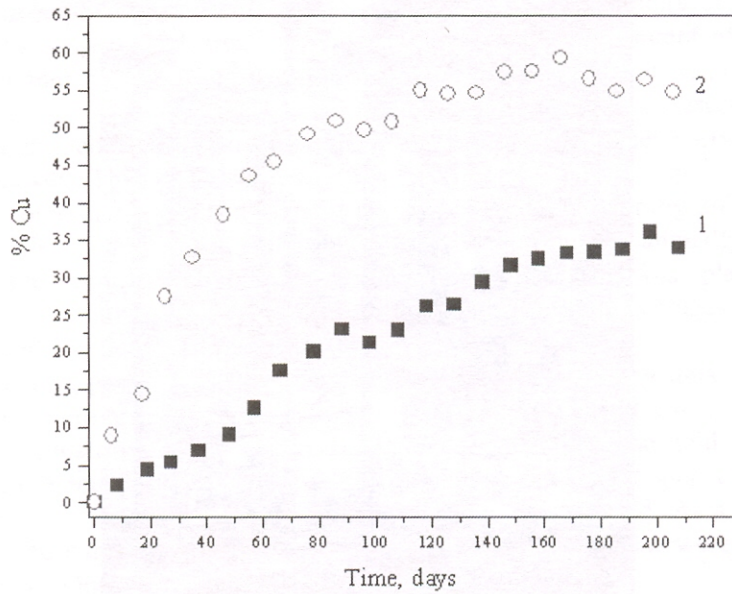


Figure 2. Rate of unrestricted copper leaching
 1 - 0.72 kg Sample 3 + 0.36 L 0.1 M H₂SO₄
 2 - 4 kg Sample 1 + 2 L 0.1 M H₂SO₄

The effect of grain size on the rate of unrestricted copper leaching is shown in Table 2.

Table 2 Effect of grain size on the rate of unrestricted copper (%) leached in 200 days

Grain size	% Cu leached in 200 days	Relative leaching rate
- 10 mm	34,5	1
- 3.3 mm	38	1.10
-1.25 mm	57,6	1.67

Rates of copper leaching with addition of immobilizers are shown in Fig. 3.

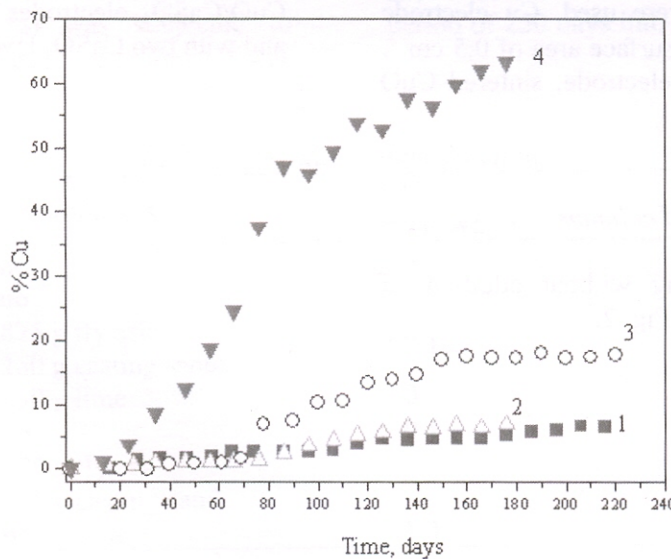


Figure 3. Rate of copper leaching with addition of immobilizers
 1 - ■ (75 kg Sample 1 + 6% lime) + 2L 0.1 M H₂SO₄
 2 - ▲ (2,65 kg Sample 1 + 5% lime) + 2 L 0.1 M H₂SO₄
 3 - ○ (4 kg Sample 1 + 8% flyash) + 2 L 0.1 M H₂SO₄
 4 - ▼ (0,465 kg Sample 2 + 7% limestone) + 0,35 L 0.1 M H₂SO₄

Table 3 Effect of the type of immobilizer on the quantity of copper (%) leached in 200 days

Immobilizer	Grain size	% Cu leached in 200 days	Reduction of leaching rate, %
Lime, 6%	- 10 mm	7	79,7
Lime, 5%	- 3.3 mm	7	81,6
Fly ash, 8%	-10 mm	17,5	49
Limestone, 7%	- 3.3 mm	30	21

The effect of applied immobilizer on the rate of copper leaching is shown in Table 3. According to the results shown in Figs. 2 and 3 and Tables 2 and 3, one can indicate regularities that govern the immobilization of copper bearing grains. Immobilization by addition of fly ash (875 g fly ash + 250 g casting sand) lowers the rate of copper leaching to only 59% compared with unrestricted Cu bearing grains (Fig. 2). The most effective immobilizer is lime. Applied in 6%wt. of the Cu bearing grains, it lowers the copper leaching rate to only 13% as compared to the unrestricted Cu leaching. In the case of 5% wt. lime, the lowering is 10%, in the case of 8% wt. fly ash it is 18% and in case of 7% wt. limestone it practically does not prevent Cu leaching (Fig. 3). When the size of copper bearing grains was reduced from -10 mm to -3.3 mm and -1.25 mm, the leaching rate over a span of 200 days increased from 34,5% available Cu to 38% and

57,6% respectively. This indicates that the leaching rate is determined dominantly by the surface area of Cu bearing grains that are subject of leaching. As smaller the grains, as higher is the leaching rate. When the grain size was reduced from -10 mm to -1.25 mm, the leaching rate was increased for 67% (Table 2).

Lime (added in 6% wt.) reduced the leaching rate of -10 mm fraction for 63% more effectively than fly ash to the same granulation (Table 3) In the case of smaller grains, -3.3 mm, lime (added 5% wt.) reduced the leaching rate almost 4 times more than limestone (added in 7% wt., see Table 3). All identified regularities are understandable in terms of the increase of grain surface exposed to leaching in H₂SO₄ and different effectiveness of selected immobilizers in preventing the copper bearing grains leaching.

3.2 Electrochemical study of grain immobilization

The nature of processes that take place on top of copper bearing grains was studied at modeled surfaces in order to demonstrate diminishing of the active surface available for chemical leaching in real acid main drainage conditions and to verify the effect of stabilizing agents.

Cyclic voltammetry for characterization of surface processes was used as a method that effectively demonstrates the diminishing of copper oxide active surface available for chemical leaching in acid mine drainage conditions. Experiments were

done in sulfuric acid (pH=2) as a more aggressive medium than under real conditions, at three electrode systems, i.e. Cu, CuO and CuO/CaSO₄ electrode. Shown in Fig. 4 are the microphotographs of the cross section of CuO/CaSO₄ electrode with one (Fig. 4 a) and two layers (Fig. 4 b) of gypsum. The white cover (gypsum) is in contact with the electrolyte. This layer inhibits the migration of ions from electrolyte to the CuO (black area), that protect its leaching.

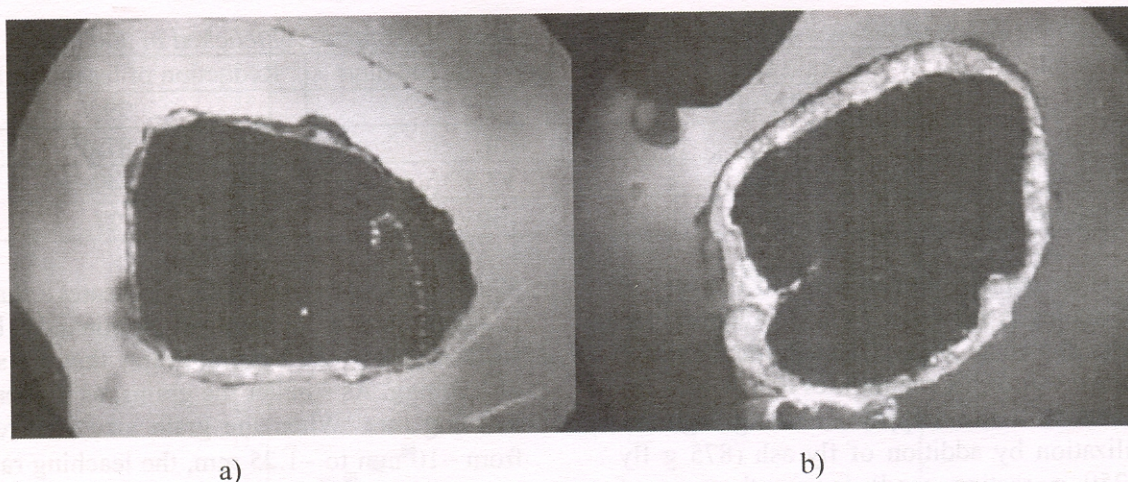


Figure 4. Microphotographs of CuO grain (black) covered with a layer of CaSO₄.
 a) One CaSO₄ layer; b) Two CaSO₄ layers

Electrochemical behavior of Cu-metal electrode, when the potential is cycled up to 1 V around the rest potential is shown in Fig. 5.

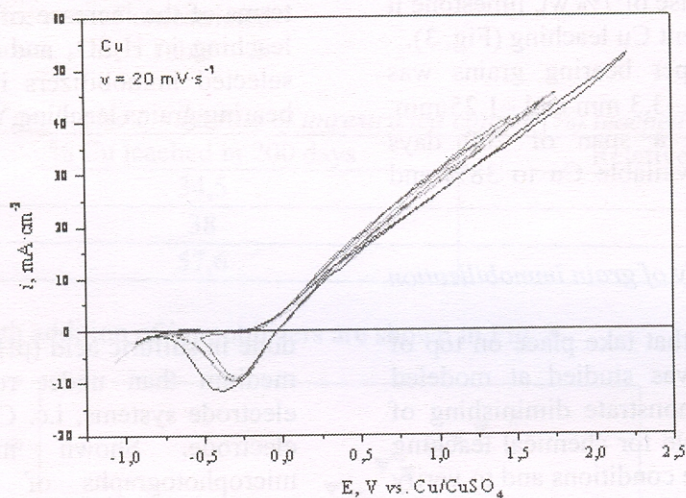


Figure 5. Cyclic voltammogram of Cu-metal in H₂SO₄, pH = 2

From Fig. 5 one could see that only Faradic process, i.e. Cu-metal oxidation (dissolution) takes place when the potential is made more positive than typically 0 V vs. Cu/CuSO₄ reference electrode. The oxidized Cu is then reduced back to metallic state during the cathodic polarization. Its quantity is exhausted pretty soon, so that a maximum is registered at the cathodic

part of the curves and at potentials near -1.1 V hydrogen evolution starts to develop.

Electrochemical behavior of CuO electrode, when the potential is cycled up to 1 V around the rest potential is shown in Fig. 6. For comparison the plot taken at Cu-metal electrode (Fig. 5) is also present in Fig. 6. It is obvious that the anodic currents taken at CuO electrode are some 4 times lower than on the bare metallic surface.

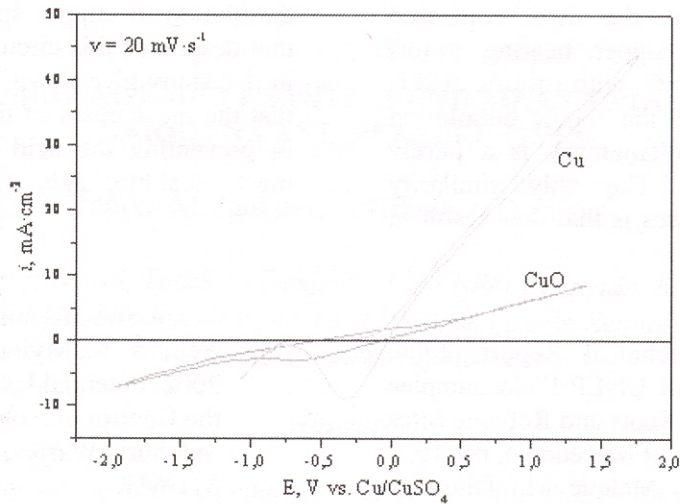


Figure 6. Cyclic voltammogram of CuO in H_2SO_4 , $pH = 2$

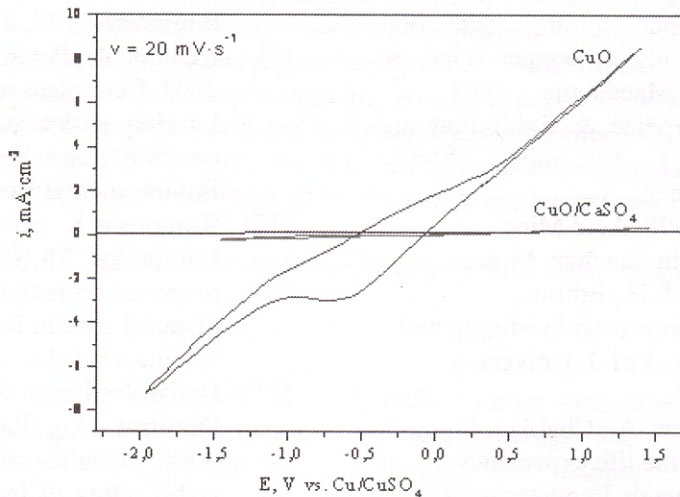


Figure 7. Cyclic voltammogram of $(CuO + 1 \text{ layer } CaSO_4)$ in H_2SO_4 , $pH = 2$

Electrochemical behavior of CuO electrode covered with 1 layer of $CaSO_4$, when the potential is cycled up to 1 V around the rest potential is shown in Fig. 7. For comparison the plot taken at CuO electrode (Fig. 6) is also present in Fig. 7. It is obvious that the anodic currents taken at the electrode covered with one layer of $CaSO_4$ are some 20 times lower than on the bare oxide electrode.

4. Conclusions

Cyclic voltammetry measurements shown above produced a proof that mechanical blockage is the way how lime prevents leaching of copper bearing grains in previously performed immobilization experiments.

When a second layer of $CaSO_4$ was applied onto the CuO electrode, further lowering of anodic currents occurs. They are now lower for another 15 times.

Total decrease of anodic currents when transition is made from electrode of Cu-metal to electrode of CuO covered with 2 layers of $CaSO_4$ reaches 6.000 to 7.500. This is really an impressive figure.

Thus, acid mine drainage process could be effectively controlled by applying lime, $Ca(OH)_2$, that forms an insoluble and compact layer of gypsum, $CaSO_4$, on top of the copper bearing grains.

One should admit that the two compared processes, leaching of copper bearing grains (containing presumably CuO) with sulfuric acid is a chemical process, while the anodic dissolution registered with cyclic voltammetry is a purely electrochemical process. The only similarity between these two processes is that they result in

dissolution of copper species, but we do believe that despite of this circumstance results presented in this study give strong support to the conclusion that the mechanism of the action of immobilizers in preventing the acid mine drainage is purely mechanical blockage.

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