Türkiye 14 Madencilik Kongresi / *14th Mining Congress of Turkey,* 1995 , ISBN 975-395-150-7

BIOGE01J^IAT<UJLOGY OF METALS

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ABSTRACT: Biotechnology of metals allows to process waste ores, difficult-to-dress concentrates, and purify industrial waste waters. Dump bacterial leaching of copper and zinc is used in industrial scale. In semi-industrial scale tank method of the following concentrates was tested: gold-pyrite, gold-arsenopyrite, copper-arsenic, tin-copper-arsenic, copper-zinc. Bacterial leaching of these products provides selective recovery of 90-98% Au and 70-90% Ag, and allows to decrease of the content of sulfide arsenic from 4-18% to 0.2-0.3%. Subsequently concentrates can be processed by traditional means. It is possible to extract up to 82% Cu, 80% Zn, and 75% Cd from copper-zinc concentrates, and up to 90% Zn from zinc-containing tailings of concentrating mills at pulp density 40%.
Biosorbents created on the base of bacterial biomass allow to recover non-ferrous, rare, and noble metals, and radionucleides from process or waste waters. Solid biosorbents possess high capacity and can be prepared from the wastes of different biotechnological industries.

INTRODUCTION

Critical ecological situation has arisen in non-ferrous metallurgy as well as in other industrial branches. Considerable amounts of wastes are being accumulated while mining, ore dressing operators and metallurgy. For instance in SNG only in non-ferrous metallurgy over 18 bl-»—tons of mining production wastes, 3.6 bin tons of dressing tailings, 414 mln tons of slags, and 230 mln tons of ore slurry have been accumulated. About 6 mln tons of harmful substances are ejected into the atmosphere and about 0.5 bin m^3 of sewage is discharged into reservoirs annually. In one of the regions where pyrometallurgy is intensively developing the rate of ecosystem mighty destruction zone reaches 1-1.5 km annually. The content of nickel and copper in mushrooms, berries, and plants at a distance of 10-20 kms from the factory reaches 25 maximum allowance concentration, that makes them absolutely unfeasible for using as food. pollution of reservoirs by copper (100 maximum allowance concentration), suspended and mineral substances are increasing also. Sick rate of the population by diseases of endocrine system, blood, organs of senses, skin ar-e*- 1.3-2.7 times higher than average in the country. There are a lot of such examples in the world. Only essentially new technologies can charge the nowadays practice of mineral materials treatment. Such technologies are biohydrometallurgical ones.

<u>Microorganisms and fields of their using in biohydrometallurav.</u>

At the present time the following microorganisms and important processes for biohydrometallurgy are known (Table 1):

a) oxidation of sulfide minerals, elemental sulfur, and ferrous iron by chemolithotrophic bacteria (Thiobacilli, Leptospirilli, moderately thermophilic bacteria, and archaea);
b) production by organotrophic microorganisms of organic compounds, peroxides, etc., which destruct non-sulfide minerals, oxidize or reduce the elements with variable valency (organotrophic bacteria);
c) sorption or precipitation of different elements.

Chemistry of bacterial processes of minerals transformation.

Chemolithotrophic bacteria oxidize inorganic substrates that are energy source for their living activity.

$$4Fe^{2+} + O_2 + 4H^+ \xrightarrow{\text{bacteria}} 4Fe^{3+} + 2H_2O \quad [1]$$

$$2FeS_2 + 15/2\ O_2 + H_2O \xrightarrow{\text{bacteria}} Fe_2(SO_4)_3 + H_2SO_4 \quad [2]$$

$$FeS_2 + 2Fe^{3+} \xrightarrow{\text{chemically}} 3Fe^{2+} + H_2O \quad [3]$$

$$S^0 + H_2O + 3/2\ O_2 \xrightarrow{\text{bacteria}} H_2SO_4 \quad [4]$$

These reactions proceed also chemically at normal temperature and pressure but in the presence of bacteria reactions proceed -at a thousand- and even million-fold rate. Sulfuric acid produced as the result supports favorable pH for bacteria and leaching process. So it is no need to add it from without. Fe^{3+} produced in these reactions not only create high redox potential in solutions or in the pulp. As the result the system favorable for metals leaching from sulfide ores and concentrates is created.

Heterotrophic bacteria need organic compounds such as wastes of other industries. These bacteria are of great interest in destruction of non-sulfide minerals and biosorption of minerals from ores.

Table 1. Microorganisms important for biohydrometallurgy.

Microorganisms	Processes
Bacteria gen. Thiobacillus & Leptospirillum (T.ferrooxidans, T.thiooxidans, L.ferrooxidans and others)	Oxidation of sulfide minerals, S_Q, Fe^{2+}, at pH 1.4-3.5, T = 5-35°C
Moderately-thermophilic bacteria gen. Sulfobacillus and close organisms	Same at pH 1.1-3.5 and T = 30-55°C
Thermoacidophilic archaea gen. Acidianus, Metallosphaeras and Sulfurococcus	Same at pH 1.0-5.0 and T = 45-96°C
Organotrophic microorganisms and metabolites (fungi, bacteria, yeast, alga)	Destruction of non-sulfide minerals, boxites dressing, precipitation and biosorption of metals from solutions

Naturally occurring processes o£ dump and underground metal leaching from ores.

In depleted mines there remains!' a part of rich ore and, as a rule, waste ores. As a result of oxidation processes sulfide minerals transfer into easily soluble sulfate compounds and sulfuric acid is formed. These solutions are ecologically dangerous if we take into account their amounts and the content of heavy metals ions in them . Table 2 reports the data of heavy metals discharge into an Australian river from the mine after mining was stopped. The main source of metals were low-grade ore dumps (6) . River fauna was either poor or nonexistent at a great length of the river.

Table 2. Annual pollution load bv the East Finnish river (61.

Season	1971-72	72-73	73-74
Pollution load (tons)			
Cu	77	67	106
Mn	84	77	87
Zn	24	22	30
SO_4	9100	8300	11400

The same situation is observed in other regions. In the Degtyarsk deposit on the level of solution flow rate from 123 to 144 mm^3/h due to natural (spontaneous) oxidation processes 0.8-1.43 tons copper and 0.4-1.4 tons H_2SO_4 were discharged daily. Discharge of iron .and zinc reached 1.5 and 1.2 tons respectively. At some deposits these solutions outflow to the cementation plant where only copper was extracted and farther to the neutralization plant. But at many deposits mine waste discharges flow to reservoirs, rivers etc. polluting the environment.
On the other mine dump over 300 thousands tons of copper and 160 thousand tons of zinc are contained. About 216 tons of copper and up to 144 tons of zinc flow out of the, dumps into the river together with mine waste waters annually. Time span of such environmental pollution due to natural leaching of copper could be about 1.500 years and that of zinc about a thousand years. There are a lot of such examples. It is evident that strict control over the state of dumps and mines and organization of work solutions recovery from metals is necessary. Another approach to solving ecological problems is organizing of bacterial-chemical metal leaching and their recovery as commercially used product with further recycling of solutions or their discharge with preliminary treatment.
This method of copper as well as uranium recovery has been used or is being tested on pilot plant in a number of countries (USA, Canada, Peru, Australia, Mexico, Bulgaria, USSR, and others).

Biohydrometallurav of non-ferrous metals.

At present time dump, underground, and tank leaching of non-ferrous metals from low-grade ores or difficult-to-dress concentrates are well known. The number of quite new technologies of complicate ores and concentrates processing were designed.

Dump and underground leaching.

In several countries this technology is used in industrial scale (6,15,16,17). The content of copper in the ore is equal to 0.4%. Peculiarity of the technology for copper bioleaching is the using of solutions containing *T. ferrooxidans* and other bacteria, and also Fe^{3+} obtained by the reaction [5]. The last process is carried out in ponds or in ore bodies in deposits (Fig. 1,2).
Excess of Fe^{3+} is precipitated due to the reaction of hydrolysis:

$$Fe_2(SO_4)_3 + 6H_2O \rightleftharpoons 2Fe(OH)_3 + H_2SO_4 \qquad [5]$$

This allows^to economize sulfuric acid and support pH in the range 1.6-1.8. Solving of technological problems on the mine Kounradsky allowed to increase the capacity of one site by 2.400 tons per season of copper with the net cost 3 times less than by pyrometallurgical method.
Recovery of copper from solution is carried out with the help of scrap iron according to the reaction:

$$Fe^0 + CuSO_4 = \downarrow Cu + FeSO_4 \qquad [6]$$

Fe^{2+} is again oxidized by bacteria to Fe^{3+} by the reactions mentioned above. Extraction method of copper recovery from solutions is now used in practice.

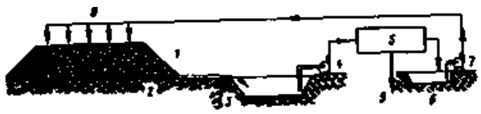

Fig.l. Scheme of heap leaching operation. 1- heap; 2- ground surface; 3- pregnant solution collecting pond; 4,7- pump; 5- cementation launders; 6- spent solution pond; 8- dump irrigation system.

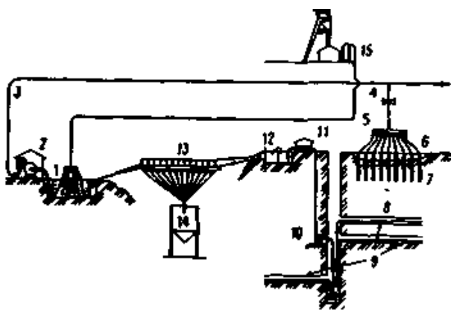

Fig.2. Scheme of in-situ leaching operation. 1- air sparging of recycled solution; bacterial oxidation of Fe^{2+}; 2- pump station; 3- solution distribution line; 4- valve; 5- solution distribution manifold; 6- solution lines; 7- injection wells; 8- orebody; 9- drainage gullies; 10- pregnant solution pump; 11- limnographic station; 12- clarification tanks; 13- precipitation launder; 14- cement copper binds; 15- compressor station.

<u>Tank method of concentrates processing.</u>

<u>a).Removal of As as harmful impurity from concentrates.</u>
Many concentrates containing non-ferrous metals, contain arsenopyrite also. This imped their processing by traditional means. Bacterial leaching of these products allows to decrease the content of sulfide arsenic from 4-18% to 0.2-0.3%. This provides their following processing by traditional means (Fig.3).

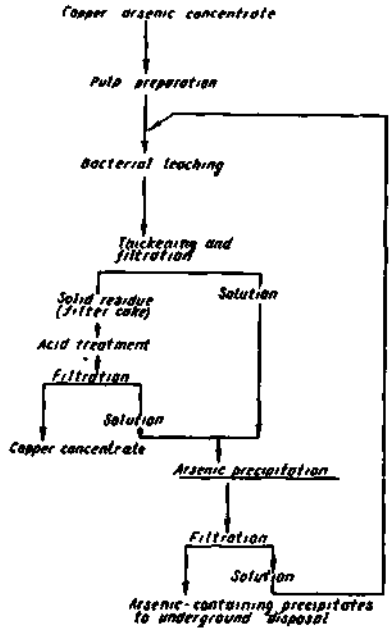

Fig.3. Flowsheet of bacterial leaching of arsenic from a copper-arsenic concentrate.

<u>b).Selective technology of complex copper-zinc. copper-nickel. and copper-molvbdenium concentrates.</u>
This technology will solve the problem of polymetallic ores processing. For example, it is possible to recover 90% and more of nickel from collective copper-nickel concentra- tes with 3-4% Ni. Sorption methods provide 95-98% nickel extraction from solutions. Copper can be extracted from solid phase by pyrometallurgical means (13).
Copper-zinc concentrates contain 6-7% Cu and 13-14% Zn. Bioleaching of such concentrates at pulp density 20% allows to obtain solutions with zinc content 20-70 g/1 and copper content 3-7 g/1.

Cadmium is bioleacned practically fully. **Its content in solution reaches 0.10-0.15 g/1. Solid phase after bioleaching is presented by high-quality copper concentrate and copper-cadmium cake , that can be processed by pyrometallurgical means (Fig.4). As the result of this complex technology total recovery of copper reaches 82% , zinc - up to 80%, cadmium - up to 75%. It is possible to extract up to 90% Zn from zinc-containing tailings of concentrating mills at pulp density 40%. Zinc concentration in solution reaches 38 g/1.**

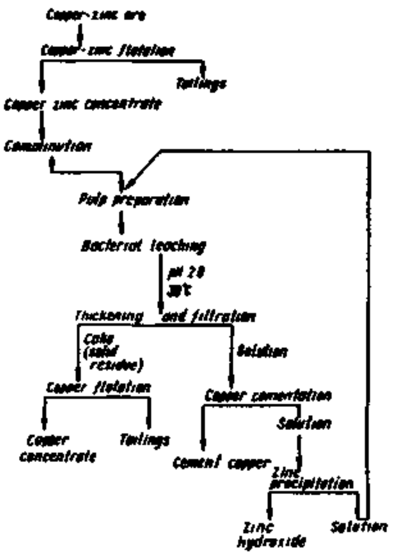

Fig.4. **Combined flowheet** for **processing** a copper- zinc **ore** using **bacterial** leaching.

On **the** above « mentioned examples it is shown that bacterial processes can be constituting part of hydrometallurgical or pyrometallurgical technologies.

Biohvdrometallurqy of gold-containing concentrates.

Tank method.

Bacterial leaching in reactors is one of the most effective methods of releasing finely dispersed gold from arsenopyrite-pyrite concentrates in different countries RSA, USA, Canada, and Russia (1,3,5,13,14,18). In several countries this technology is used in industrial scale - RSA, Brasilia, Ghana, Australia, USA (3,5). In Russia, a direct-flow scheme is used with liquid and solid phases passing simultaneously through a successive series of tanks: airlifts, or reactors with mechanical stirring (Fig.5).

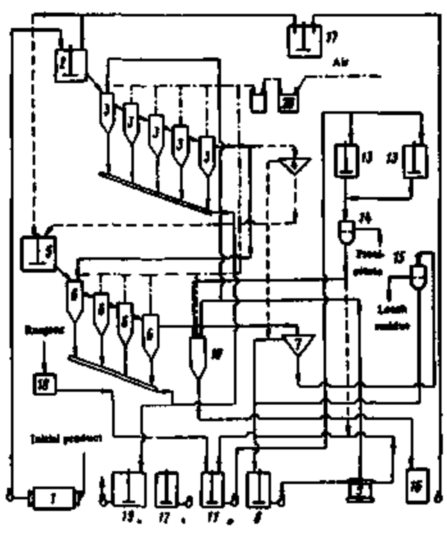

Fig.5. Flowsheet of semi-industrial bacterial leaching plant. 1- ball mill; 2,5- conditioning tanks; 3,6- pachuka tanks for leaching; 4,7- dewatering cones; 8- leaching solution tank; 9- biomass separator; 10- pachuka tanks for solution with biomass; 11- solution purification tank; 12- stand-by tank; 13- setting tank; 14,15- vacuum filters; 16,17- recycle solution tanks; 18- pachuka discharge tank; 19- stirrer; 20- liquid-ring vacuum pump.

Bacterial oxidation of sulfide minerals takes place in tanks. Next liquid and solid phases are separated. Gold is recovered from solid sediment (cake) by the method of cyanidation (Fig.6).

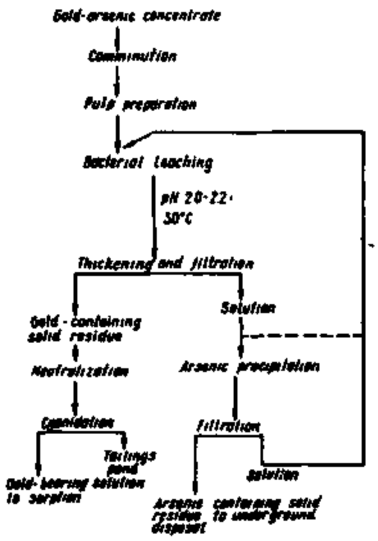

Fig.6. Flowsheet for treatment of a gold-arsenic concentrate **using** bacterial leaching.

In semi-industrial conditions different types of concentrates **were** tested: gold-pyrite with 56.5 g/ton Au; gold-arsenic with 30% As, containing sulfides of stibium, other non-ferrous metals; pyrrotite, and active carbon compound (4-20%). The content of gold in **them** varies from 8 to 100 g/ton, **and** silver - 30-150 g/ton. The rate of pyrite oxidation reaches 75%, **and** arsenopyrite - 98% within **70-120** hours. This allowed to recover by the method of cyanidation 90-98% Au and 70-90% Ag dependent on concentrate type.

Biosorption.

The method lays with the **use** of microbial biomass and created on their basis solid **granulated** biosorbents for collective or selective recovery of **non-ferrous,** rare, and noble metals, **and** radionucleiâes from process or waste waters (4,8,12,18).. **Dead** biomass of bacteria, **yeasts, and** fungi and created on their **basis** solid biosorbents **are used as** sorbents. The capacity of biosorbents reached at optimal **conditions** of sorption are as following (mg/g dry biomass): Sc - 1-40, Y - **1-36,** Ce - 48, Mn - 25, Pb - 70, Zn - 40, **Cu - up to 125, Ni - 0.72, Cr - up** to **169,** Mo and W - up to 200, U and Th - 30-220. Biosorbents are also effective for sorption of Cs, Pu, Sr, As, Ga, and other radionucleiâes. Addition of biosorbents to **ionites** provides selective desorp**tion of Sm,** Y, Er, Cs, and other **metals.** Often living or dead **biomass is** used for metals sorption.

Solid biosorbents have major **advantages.** They are stable, **convenient** for transportation. The **dignity** of biosorbents is that they **can** be obtained from the wastes of different biotechnological industries. This not only decrease their **cost** but also allows to solve ecological problems of other industries. Biosorbents are unharmful **and** do not affect man and environment, because they are produced on **the** base of dead biomass already used by man.

CONCLUSION

Application of microbiological and **other** hydrometallurgical methods for **the** extraction of metal values **from** low-grade ores introduces **considerable** changes into the existing practice of processing raw **materials.**

First and foremost, vast reserves of **refractory** and lost ores as well **as wastes** of concentrating mills **and** composite sulfide concentrates will become eligible for processing. The bacterial leaching technology may present a solution for utilization of refractory deposits of rich ores and large deposits in **remote** regions. This new method of metals extraction seems economically feasible. It ensures a higher standard of production technology, and provides for an integrated and **more** comprehensive utilization of mineral raw materials as compared to **the** classical methods of metals **extraction.** It also eliminates to a **large** extent the necessity for a **large** number of people working underground and the discharge of **noxious** gases into the atmosphere.

REFERENCES

1.Aslanukov R.Y., Karavaiko G.I. G.I., **Fil**imonov N.V., P ivovarova T.A., Dementyev V.A., Voronina O.B. 1993.Tsvetnye Metally (In Russian). **"11: 21-23.**

2.Aslanukov R.Y, Sedelnikova G.V., **Pivovarova T.A.,** Karavaiko G.I., **Voronina O.B.,** Makarov S.B. 1992. **Tsvetnye Metally** (In Russian) **4: 27-29.**

3.Dew D.W., Miller D.M., Van Answegen-Randol. 1993. Beaver Creek'93: **229-237.**

4.Brierley C.L., Brierley J.A. **1993. In:** Biohydrometallurgical **technolo-** gies. Torma A.E., Apel **M.L.,** Brierley C.L. (Ed) TMS, II: **35-44.**

5.**Had** R.P., Wright F.R. 1989. In: **Biohydrometallurgy-89**. J.Salley, **McCready,** Wichlasz P.L. (Ed). **GANMET.** Sept.89-10: 533-549.

6.Harries J.R., Ritchie A.I.M. **1990.** In:Biohydrometallurgy, Proc. **Int.** Seminar. Karavaiko G.I., **Rossi G.,** Avakyan Z.A. (Ed). **M.**, **CIP:** 335-356.

7.Karavaiko G.I., Kuznetsov S.I., **Golomzik** A.I. 1977. The bacterial **leaching** of metals from ores. **Technology Ltd. England:**203.

8.Karavaiko G.I., Kareva A.S., **Avakyan Z.A.,** Zakharova V.l. 1991. In: IX Int. Symp. Biohydrometallurgy'91. **Duarte** J.C., Lawrence R.W. (Ed). FORBITEC, Portugal: 4-50.

9.Korenevsky A.A., Karavaiko G.I **1990. In:** Proc. 5th Europ. Congr. Biotechnol. Christiansen, Munck L., Villadsen J (Ed). Copenhagen. 1: **561-564.**

10.Korenevsky A.A., Karavaiko G.I. 1993. Mikrobiologya (In Russian). **62:** 709-716.

11.Korenevsky A.A., Sorokin V.v., **Karavaiko** G.I. 1993. Mikrobiologya (In **Russian)**.62: 1085-1092.

12.Laskorin B.N., Karavaiko G.I., **Molchanova** T.V., Polyakova O.P., **Rodionov** V.V., Sharapov B.N., **Vodolazov L.I.,** Sharapova N.A., **Konoplyova** L.V. 1992. Tsvetnye **Metally (In Russian)**. 4: 30-31.

13.Polkin S.I., Adamov E.V., Panin **V.V.**, **Karavaiko** G.I., Yudina I.N., **Aslanukov R.Y.,** Grishin S.I. 1985. In: Biogeotechnology of Metals. **Proc. Int.** Seminar and Int. Training Course. Karavaiko G.I., Groudev S (Ed). CIP, M.: 239-258.

14.Polkin S.I., Panin V.V., Adamov E.V., Karavaiko G.I., Chernyak A.S. 1975. In: Proc. 11th Int. Mineral processing Congress. Cagliary: 901-923.

15.Radjibayev M.G., Plaxa N.E., Sheveleva L.D., Karavaiko G.I., Kamalov M.R., Bubnov B.B. 1992. Tsevetnye MetaLly (In Russian). 4: 10-12.

16.Rossi G. 1989. In: Biogeotechnology of Metals. Manual. Karavaiko et al (Ed). M., CİP: 211-303.

17.Rossi G. 1990. Biohydrometallurgy. Mc Graw-Hill Book Company GmbH: 609.

18.Torma A.E., Oolman T. 1992. Intern. Materials Rev. 37: 187-193.

Volesky B. FEMS Microbiol. Rev. 14:291-302.