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ELECTROCHEMICAL TREATMENT - BASIS OF HIGHLY EFFICIENT TECHNOLOGIES FOR MINERAL PROCESSING AND WASTEWATER TREATMENT

Purpose. Demonstration of the positive effect of an applied electrochemical impact on the i) flotation of lead-zinc (Pb-Zn) and copper-molybdenum (Cu-Mo) ores with the aim to improve the metals recovery from impoverished and lean ores, ii) treatment of wastewater from mineral processing to meet the environmental regulations.

Research methods. Laboratory, pilot scale and industrial experiments on electrochemically aided flotation and waste effluents treatment, instrumental analytical methods - pH and oxidation-reduction potential measurements, AAS and ICP-OES.

Scientific and practical value. An attempt to explain i) the improved flotability with the semiconducting properties of minerals, ii) removal of elements from waste effluents with the oxidation-reduction potential of the corresponding water pollutants.

A possibility to improve the flotation separation and to increase flotation recovery at decreased use, even avoidance, of some toxic flotation reagents and to decrease discharge of polluted water into environment.

Research results. Experimentally derived at laboratory level relation between i) flotation recovery of sulfide minerals and contact potential difference (CPD) between the mineral surface and an Au electrode; ii) copper, molybdenum and iron recovery in the flotation concentrate and the pulp oxidation -reduction potential (vs. SHE).

Data showing the positive effect of applying an electrochemical impact i) improved copper-molybdenum selection at pilot scale, ii) recovered copper and removed pollutants (arsenic, sulfates) from waste effluent at semi-pilot scale, iii) increased lead and zinc recovery at industrial scale.

Keywords: electrochemical impact, ore minerals flotation, mining and mineral processing wastewater treatment

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Problem and its connection with scientific and practical tasks. In the conditions of the increasingly impoverished ores and the more and more complex composition of polymetallic ores and at the same time the higher requirements for protection of environment and human health, it is necessary to create technological solutions for ore processing in order to increase extraction of valuable components while minimizing the amount of harmful reagents used. New effective technologies are also needed for the treatment of wastewater and leachate from technological processes, aimed not only at bringing waste effluents to regulatory requirements for environmental protection, but also the recovery of valuable components from them.

Analysis of recent achievements and publications. The idea to improve the technological results by applying an energy impact on the minerals before the flotation or on the flotation pulp has been laid down in the works of Plaksin and his colleagues [1], Carta and co-workers [2], Glembotsky and co-authors [3], Hoberg and Shneider [4], Rao and coauthors [5]. The theory and practice of imposing an electrochemical impact with the aid of electrodes immersed in the flotation pulp during the conditioning stage or directly during the flotation stage has been developed and presented to the scientific community by Chanturia and his colleagues [6,7], as well as by Abramov [8]. The aim of applying an energy impact is to change the minerals surface properties in a suitable manner, so to ensure higher activation of some minerals and deeper depression of others - both resulting in better minerals' selection. For example, different methods can be used to change the oxidation of molybdenite and chalcopyrite thus to ensure their better separation, such as application of plasma treatment [9], use of sodium hypochlorite [10], electrolysis or ozone treatment [11].

Statement of the problem. The current work presents our experience in the application of electrochemical treatment of flotation pulp in flotation of lead-zinc, copper-molybdenum-pyrite ores with minimizing the use of classical reagents. This leads to an increase in both the extraction of the main components and the noble ones, as well as a significant environmental and social effect. At the same time, a similar type of impact was applied in the processing of waste fluids - leaching acids generated during the processing of sulfide ores in metallurgical plants, as well as mineral processing wastewater that contains molybdenum and sulfates.

The motivation for our choice is that applying an electrochemical impact is easily realizable and controllable. The process fundamental nature is the charging (positively or negatively) of the mineral particles in the flotation pulp with the help of the working electrodes, immersed in the pulp or wastewater. In the case of flotation the charging can cause a proper activation or depression of mineral particles, thus leading to the improvement of the selection, recovery and concentrates' grade, as well as to the decreased use or substitution of reagents that are dangerous to humans and to the environment. In the case of wastewater treatment the imposed electrical potential causes reduction and oxidation processes to proceed on the electrodes thus leading to effluent purification and metals recovery.

Presentation of the main material and results. The changes caused by the electrochemical treatment of the flotation pulp are based on the semiconductor properties of the minerals. The flotation ability of a mineral-semiconductor can be expressed by the flotability coefficient K_f which depends on the Fermi level energy E_{F1} before flotation (or the Fermi level E'_{F1} after a preliminary treatment of the mineral, for instance by doping with proper donor or acceptor impurities, as well as treatment in an atmosphere of ozone or oxygen, operating as acceptors) and the Fermi level E_{F2} after flotation

$$K_f = \frac{E_{F1} - E_{F2}}{E_i}; \quad K'_f = \frac{E'_{F1} - E_{F2}}{E_i},$$

where E_i=E_g/2 is a mid-way of the forbidden band E_g, around which the Fermi level varies. If E_{F1} or E'_{F1} is situated near to E_i, and E_{F2} (after flotation) comes near to the bottom of conductivity band E_C or to the top of the valence band E_V, maximum flotability shall be achieved. If E_{F1} is far from E_i, good flotability would be achieved, if after proper preliminary treatment E'_{F1} gets close to E_i. Obviously, the difference $\left|E_{F1} - E'_{F1}\right|$ expresses energy flotation deficiency and determines the intensity of energy impact needed before flotation, in order to achieve maximum flotability of minerals [12].

When the mineral particle comes into contact with a charged metal electrode for milliseconds, the particle receives the charge of the working charged electrode, which leads to a change in its properties. The main impact is observed on the surface of the mineral-semiconductor particle. A bands' bending appears in the surface areas in one direction or another (fig. 1), which is associated with the enrichment or depletion of electrons in the near-surface area. This in turn effects the interaction of the mineral with a given reagent and as a result can lead to depression or activation of the mineral particle without the use of typical depressant reagents or activators.

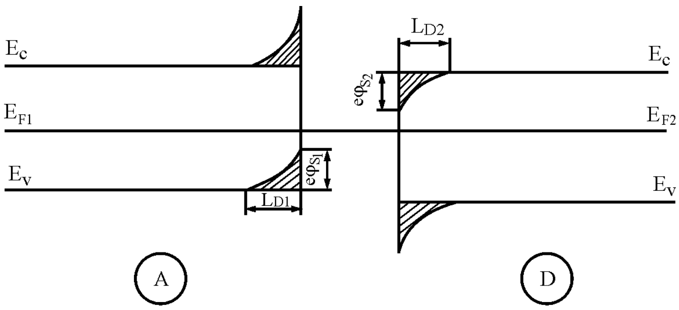

Fig. 1. Common view of the energy state of the mineral surface at activation (A) and depression (*D*): E_c - conduction band; E_v - valence band; $e\varphi_{s1}$ and $e\varphi_{s2}$ - surface barrier formed after the electrochemical impact; L_{D1} and L_{D2} - Debye length of screening

The measurement of the degree of bending of the energy zones on the mineral's surface is carried out using the method of contact potential difference (CPD) - the Kelvin-Zissman method. The measurement is performed against a standard electrode (a gold plate). The principle of this measurement is shown in fig. 2.

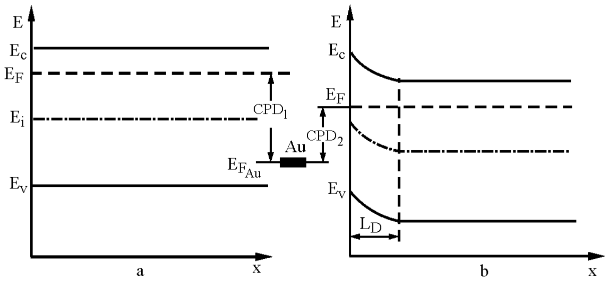

Fig. 2. Zone energy diagrams of n-type semiconductor mono-mineral sample: *a* - initial sample; *b* - after ozonation; E_C - bottom of conduction band; E_V - the top of the valence band; E_i - middle of the forbidden band; E_F - the Fermi level in n-type semiconductor; E_{FAu} - the Fermi level in a gold electrode; L_D - width of the near surface bending area (barrier layer)

The concept of changing the flotation properties of semiconductor minerals by modification of their surface (traced by measuring the CPD) through ozonation was tested. Investigations were carried out with mono-mineral samples of galena, sphalerite and chalcopyrite from Bulgarian deposits.

Samples were ground to 0.1 mm and put in a special porcelain chamber, filled with ozone, produced by a laboratory ozonator with an output of 6 g/h. The ozonation varied from 2 min for sample № 2 to 12 min for sample № 7 with a step of 2 min and from 13 min for sample № 8 to 20 min for sample No l5 with a step of 1 min, sample 1 was not treated. Immediately after the CPD measurement, ozonated samples were subjected to 5 minutes flotation under standard conditions (collector - potassium isobutyl xanthate - 40 mg/*L*, frother - pine-oil - 0.075 mg/*L*, distilled water - as flotation medium).

Typical experimental dependencies between the recovery ε and CPD of studied minerals *n*-PbS, *n*-ZnS and n-$CuFeS_2$ are shown in fig. 3.

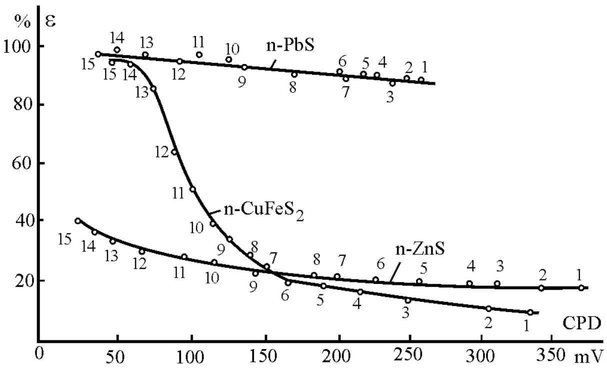

Fig. 3. Experimentally derived dependence of flotation recovery ε from the contact potential difference

As it can be seen in fig. 3, in the interval of CPD from 140 to 80 mV the recovery sharply increases from 10% to 90%. Further prolongation of ozonation lead to saturation, i.e. the curve tends to the maximum value of *ε*.

Hence, there is an optimum duration of the preliminary treatment, resulting in maximum recovery. For example, for *n-CuFeS*$_2$ under consideration the optimum time was 20 min.

In laboratory experiments on copper-molybdenum selection one kg of Cu-Mo-Py ore was used in laboratory experiments and the flotation was carried out with Denver flotation machine (3 *L*) and newly developed flotation cell [13]. Electrodes' immersion into the flotation pulp with the aid of auxiliary spaces of the new cell ensured the electrochemical impact. Graphite and stainless steel were used for anode and cathode correspondingly. The applied potential was controlled by a laboratory potentiostat. The ORP in all experiments, described in the paper, was measured with a laboratory

Metrohm pH-mV-meter and combined ORP electrode.

In the “classical” experiments Nockes (sodium dithiophosphate) was used to depress copper minerals, $Ca(OH)_2$ - to depress pyrite and Na_2CO_3 was the pH regulator.

In the both sets of experiments potassium xanthogenate was used as collector and the frother was Dowfroth. The experiments were conducted with different flotation times – from 1 to 7 min. The obtained rough concentrates for the different flotation times were collected, analyzed and results are presented in fig. 4.

Fig. 4 points at the relationship between the pulp potential, which changes by changing the degree of electrochemical impact and the extraction of copper and molybdenum minerals. This creates conditions for optimal selection without the use of the typical depressor of copper minerals - in this case Nockes.

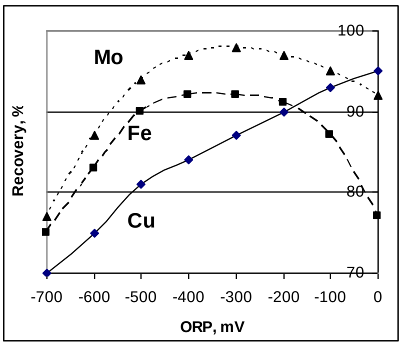

Fig. 4. Relation between the recovery of Cu, Mo and Fe in the flotation concentrate and the pulp ORP (vs. SHE): ▲ - Mo, ♦ - Cu, ■ - Fe

Copper recovery was increased with 6.7 %, molybdenum recovery was increased with 4.9 % with respect to “classical” experiments. In addition, silver recovery in copper concentrate was risen with 8.8 %.

The results of pilot studies with the same type of ore, conducted with 20 times more material, with a corresponding scaling of flotation conditions, are shown in table 1.

Table 1

Results from experiments on Cu-Mo selection, made under different conditions

Conditions	Nockes %	Recovery Mo, %	Recovery Cu, %	Machine
Standard (air)	100	94.05	19.04	Wemco
Elchem. treatment - 6 min; (air); 15 mA/cm^2	20	95.47	16.54	Wemco
Standard (N_2)	100	95.62	15.45	Wemco
Elchem. treatment - 6 min.; (N_2); 15 mA/cm^2	10	96.04	12.95	Wemco
Elchem. treatment - 6 min.; (N_2); 15 mA/cm^2	20	96.93	3. 24	Agitair

Elchem. = Electrochemical; 100 % Nockes = 2,5 g/L

In laboratory experiments on lead-zinc selection one kg of the sulfide lead-zinc ore, bearing 1.12 % Pb and 1.41 % Zn was used. Electrodes, immersed in the flotation pulp and made of different material, were used in experiments on zinc activation and depression. No other changes were made with respect to classical conditions except of replacement of sodium cyanide (NaCN) and copper sulphate ($CuSO_4$) addition by direct current imposing. Results are presented in fig. 5.

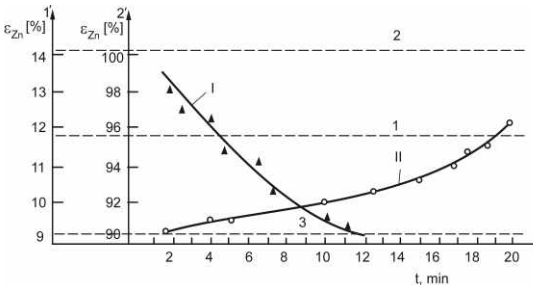

Fig. 5. Results from laboratory experiments on depression and activation of sphalerite without NaCN and $CuSO_4$ but with an applied electrochemical impact

The results shown in fig. 5, after additional extended laboratory experiments, made it possible to move to industrial study of the proposed technological approach. Denver 300 machines were used, the ore contained 2.17% Pb and 1.92% Zn.

A collective-selective flotation scheme was implemented. In the classical mode, without electrochemical treatment, the reagents were: sodium isobutyl xanthate 60 g/t, sodium sulfide (Na_2S) 55 g/t, $CuSO_4$ 135 g/t, frother T-80 40 g/t, zinc sulfate ($ZnSO_4$) 320 g/t, NaCN 20 g/t. In the flotation process with electrochemical impact, the reagents NaCN, $CuSO_4$ and $ZnSO_4$ were removed. Electrochemical activation and depression of zinc minerals were performed by introducing the corresponding electrode modules in the flotation cells (fig. 6). The results are shown in table. 2.

In addition to the improved results in the Pb-Zn selection (table 2), the recovery of silver in Pb concentrate was increased by 4.05 %.

a *b*

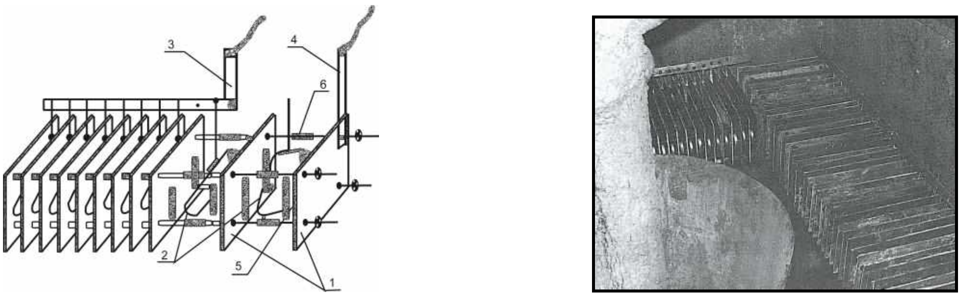

Fig. 6. Modules in the industrial experiments: **6*a*.** - A separate electrochemical module for depression of zinc minerals: *1*,*2* - working and auxiliary electrodes, respectively; *3*,*4* - power supply lines; *5* - studs regulating the distance between electrodes; *6* - rubber limiters; **6*b*. -** Photo from the industrial implementation - modules located in flotation machines

Table 2

Results from industrial experiments on Pb - Zn selection without lime, NaCN and $CuSO_4$

Parameter Flotation type	Ore		Pb Concentrate		Zn Concentrate		Tailings		ε_{Pb}, %	ε_{Zn}, %
	Pb, %	Zn, %	Pb, %	Zn, %	Pb, %	Zn, %	Pb, %	Zn, %		
Classical Technology	1.69	1.72	68.23	4.83	1.47	49.89	0.34	1.01	91.62	75.50
Electrochemical Impact	1.62	1.12	71.41	2.87	1.04	51.09	0.26	0.95	94.35	81.06

Another possibility for application of the electrochemical impact is to treat wastewater generated by the flotation of copper-molybdenum ores. The aim was to reduce the concentration of sulphates (with initial concentration 2000-2200 mg/L) and dissolved molybdenum (with initial concentration 1.9-2.2 mg/L). The treatment was carried out in electrolytic cells with graphite electrodes and anodic and cathodic compartments separated by a special ceramic membrane - fig. 7.

Fig. 7. General appearance of the enlarged laboratory plant

Sulfate concentrations in the range of 900-1100 mg/L and molybdenum concentrations in the range of 0.8-1.2 mg/L were found in the treated water. No additional chemicals were introduced in conditioned water and voluminous sludge was not formed.

The method is based on electromigration, electroosmosis, electrolysis and subsequent secondary processes.

Analyses showed that ions that migrated due to the electrical field application were predominately sulfate, molybdate, sodium, potassium, calcium and magnesium. Sulfate ions were concentrated in anolyte. Precipitation/co-precipitation of some low-soluble sulfates and/or sorption of sulfates on other solids precipitated in cathodic compartment additionally decreased their concentration in treated water. Anionic molybdenum species passed into anolyte.

Different polymolybdates were formed due to anolyte high acidity. They were precipitated or retained by the filter. The conditioned water met the standards with respect to its acidity - its pH value was 8.0-8.5.

The electrochemical impact was applied to recover copper (Cu) and arsenic (As) from washing acids from copper production without use of additional reagents. The washing acids contained these elements in high concentrations (over 10 g/L).

Generally, commercial copper (85-92 % Cu and 3.5-1.5 % As) was deposited on cathodes due to cathodic reduction of copper ions. After Cu separation, the electrode was changed and As was eliminated on cathode as harmless (under normal conditions) solid material, containing elemental As and some As species as a result of a series of reactions involving the reduction of arsenic species.

Conclusions and direction for further research. The following conclusions can be drawn from the presented results:

The use of electrochemical treatment of flotation pulp makes it possible to improve the selection and extraction of the main and noble components contained in the ore;

The technology makes it possible to eliminate the use (or reduce it to a safe minimum) reagents harmful to the environment and humans;

In the future it is possible to control and manage the flotation processes based on the information about the surface energy state of the mineral phase in the different stages of the process;

It is possible to purify wastewater and acids and neutralize them due to the electrochemical effects without the use of reagents, as the process is effectively manages by controlling the electrical parameters.

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ОЦІНКА СУЧАСНОГО СТАНУ ТА ПЕРСПЕКТИВНОГО РОЗВИТКУ ГІРНИЧОДОБУВНОГО КОМПЛЕКСУ УКРАЇНИ

Мета. Метою роботи є встановлення основних проблем, пов'язаних з тривалою та інтенсивною експлуатацією родовищ залізорудної сировини, та визначення основних пріоритетних напрямів перспективного розвитку підприємств гірничодобувного комплексу України, реалізація яких спрямована на стабілізацію виробничої діяльності, задоволення потреб внутрішнього та зовнішнього ринків залізорудною сировиною, зниження негативного тиску виробничої діяльності гірничодобувних підприємств на довкілля:

Методи дослідження. Використано комплексний метод, який включає в себе аналіз та узагальнення негативних факторів, які стримують подальший та ефективний розвиток підприємств гірничодобувного комплексу та вплив їх діяльності на довкілля, фактичний стан гірничих робіт та виробничих комплексів, які переробляють сировину, як основи для визначення пріоритетних напрямів сталого розвитку підприємств гірничодобувного комплексу на тривалу перспективу.

Наукова новизна. За рахунок комплексного підходу до вирішення основних проблем встановлена залежність впливу специфічних особливостей на ефективність виробничої діяльності, що дозволило визначити основні пріоритетні напрями подальшого більш ефективного розвитку гірничодобувних підприємств на тривалу перспективу.

Практична значимість. Реалізація пріоритетних напрямів перспективного розвитку гірничодобувних підприємств дозволить суттєво розширити сировинну базу та створити позитивні умови подальшої підтримки виробничих потужностей з видобутку та переробки залізорудної сировини, виробництву конкурентоспроможної товарної продукції, задоволення потреб внутрішнього ринку та збереження експортного потенціалу країни.

Результати. Комплексний підхід до встановлення основних проблемних питань та їх взаємозв'язок з подальшим збільшенням глибини розробки родовищ корисних копалин в складних гірничо-геологічних умовах дозволяє оптимізувати обсяги розкриття, транспортні схеми видачі гірничої маси на поверхню з подальшим розвитком різних видів транспорту, у тому числі в комбінаціях з поглибленням конвеєрних трактів циклічно-потокових технологій.

Ключові слова. Залізорудна сировини, коефіцієнт розкриття, комплексне використання надр, глибина розробки родовищ, транспортування, конвеєрні комплекси, збагачення, конкурентоспроможність товарної продукції, негативні наслідки виробничої діяльності на довкілля.

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Проблема та її зв'язок з науковими та практичними завданнями. Постійне зростання негативного тиску специфічних особливостей гірничорудного виробництва негативно впливає на ефективність роботи підприємств гірничодобувного комплексу і, насамперед, на конкурентоспроможність товарної продукції, яка і по теперішній час залишається дуже вразлива до будь-яких коливань на внутрішньому та зовнішньому ринках її споживання.

З інтенсивним зниженням глибини відпрацювання запасів залізорудної сировини в складних гірничо-геологічних умовах тиск цих негативних явищ тільки підсилюється. Незважаючи на те, що вирішенню проблем, які в процесі експлуатації родовищ корисних копалин накопичувалися десятиріччями, постійно приділялась особлива увага, питання щодо збереження сировинної бази, подальша підтримка діючих виробничих потужностей та підвищення ефективності роботи гірничодобувних підприємств залишаються актуальними і на теперішній час.