

INTENSIFICATION OF DIAMOND PURIFICATION FROM HYDROPHILIC MINERALS IN FOAM SEPARATION PROCESS

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Abstract

The reason for diamond loss in foam separation process consists in the fact that the diamond crystals fed to the foam separation are coated with hydroxides and carbonates. A combined method to restore the diamond hydrophobicity through thermal and electrochemical destruction of the mineral coat was proposed. This method provides for the conditioning stage in the foam separation process to enable decreasing the amount of the minerals coating diamonds surface from 3 to 10 times. Technological research showed that using products of diaphragm less electrolysis of recirculating water, with the thermal treatment of the foam separation feed enables increasing the recovery of diamonds in the foam separation concentrate from 76.5% to 83.7%.

Key words: *Diamonds; Foam separation; Heat treatment; Recirculating water; Conditioning.*

1. Introduction

Increasing efficiency of diamond-bearing kimberlite foam separation process for expanding the production of commercial bort diamonds can be achieved through increasing their floatability by removing hydrophilizing compounds from the diamond surface [1, 2]. To solve this problem, heat treatment of the foam separation feed is used, based on the thermomechanical destruction of diamond-mineral intergrowths due to their significantly differing linear thermal expansion coefficients [3]. The pulp heating intensifies chemical interaction of ion-molecular components of the pulp liquid phase with minerals formed on the diamond surface [4]. Such interaction can facilitate or hinder achieving the ultimate goal of the diamond surface purification of hydrophilizing minerals. This goal is potentially achievable through applying diaphragm less electrochemical treatment of recirculating water, which reduces the concentrations of both calcium and magnesium ions and ionic forms of carbonic acid [5]. The research objective was revealing the nature of the processes occurring on diamond surface at elevated temperatures, as well as determining

the parameters of the combination of the pulp heat treatment and the recirculating water electrochemical conditioning.

2. Methods of modeling and researching of mineral crystallization and dissolution processes on the surface of diamonds

Modeling and analysis of the processes occurring in the aqueous phase and on the surface of diamonds were carried out using thermodynamic calculation and construction of solid phases thermodynamic stability plots in $\lg [\text{CO}_3] - \text{pH}$ coordinates. We applied standard technique of thermodynamic modeling of the formation and dissolution of minerals for the construction of the thermodynamic stability plots [6]. The determination of the mineral stability boundaries included the formulation of chemical or electrochemical transition reaction, the calculation of the reaction Gibbs thermodynamic potential (ΔG°), the reaction equilibrium constant, and the determination of the relationship between the parameters of the reaction equilibrium constant equation. To determine the equilibrium constant at elevated

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temperatures, the integral form of the chemical reaction isobar equation was used [7]. The values of standard Gibbs thermodynamic potential ΔG° and enthalpy ΔH° of the reaction components were taken from the corresponding reference literature [8, 9].

In the laboratory tests, model solutions were used, simulating the foam separation cycle recirculating water in terms of the concentrations of calcium, magnesium, and chlorine ions. The recirculating water was preheated to 60-90°C, and soda was added to increase the solution pH and the concentration of bicarbonate ions. The precipitate formation intensity in the test solutions was measured by nephelometry method. The composition of the precipitates was determined by IR spectroscopy [10].

Chemical analysis of the minerals formed on the diamond surface was performed by X-ray photoelectron spectroscopy. When scanning the surface area, detection and chemical analysis of individual minerals or films were carried out. The elemental composition of mineral impurities on the surface of diamond crystals was determined using JXA-8230 Superprobe electron probe micro-analyzer [11].

The concentrations of calcium and magnesium ions, the sum of carbonate and bicarbonate ions in the aqueous phase were measured by the titration method. The aqueous phase pH was measured by potentiometric method using Anion-410 analyzer. The foam separation process was studied at the enlarged laboratory-scale plant at the "Yakutniproalmaz" Institute [12].

The impurities on the diamond surfaces were studied by using methods of optical microscopy, Auger and X-ray spectroscopy, infrared spectroscopy, and micro-X-ray spectroscopy. The chemical composition of mineral admixtures was determined by using a JXA-8800R microanalyzer.

The flotation activity of diamonds was determined in laboratory conditions by the methods of froth separation. Bench tests of the process of foam separation were carried out in the laboratory of the Institute "Yakutniproalmaz" at a pilot plant, which included sample preparation units, conditioning of recirculating water, agitation of ore with reagents and subsequent foam separation. At the first stage of the research, the composition of impurities on the surface of diamonds and the regularities of the processes of their formation were studied under the conditions of processing of refractory kimberlites [12].

3. Thermodynamic modeling of carbonate mineral crystallization and dissolution processes

The assaying findings and preferential location of the surface mineral formations on the defects of the diamond crystals enabled, for the analysis of the processes of their hypergene and technogenic hydrophilization, using the hypothesis of the formation and attachment of hypergene secondary minerals and salt-like substances on the diamond surface, with a broken crystal structure to be the most prone to the epitaxial growth [1, 13].

Thermodynamic modeling of carbonate mineral crystallization and dissolution processes occurring on the surface of diamonds was carried out through determining the conditions of phase transitions in the closed system with preset concentrations of ion-molecular components and by varying the two most important parameters: the aqueous phase pH and the concentrations of carbonic acid ion-molecular forms.

In the calculations, reactions proceeding with the participation of calcium and magnesium ions, carbonate and hydroxide minerals at temperatures of 25 and 83°C were taken into account.

In the calculations, the following ion concentrations obtained by assaying the ion-molecular composition of the pulp aqueous phase and the recirculating water were substituted into the equations: ($[\text{Ca}^{2+}]$ — 2150 mg/l ($5 \cdot 10^{-2}$ mol/l)); ($[\text{Mg}^{2+}]$ — 460 mg/l ($2 \cdot 10^{-3}$ mol/l)) [1].

The calculation outcome review showed that the pulp aqueous phase is supersaturated with calcium and carbonate ions, and the formation of calcium carbonate in the foam separation cycle is thermodynamically feasible (Fig. 1a). Acidifying the aqueous phase at the electrochemical treatment leads to decreasing the concentrations of calcium and bicarbonate ions by 30-40%. The heat treatment causes tenfold decrease in the concentration of carbonate ions. The values of the concentrations of bicarbonate and hydrogen ions (pH) lie around the boundary of calcium carbonate stability (Figure 1a, zone 3), i.e. the likelihood of calcium carbonate formation remains high. The combination of heat and electrochemical treatment allows solving the problem of preventing precipitation and dissolution of carbonate hydrophilizing impurities. As seen from Fig. 1a (zone 4), it is in this case that the conditions are reached when calcium carbonates become unstable.

The results of the calculations of the stability plot for magnesium carbonate hydroxide trihydrate

$\text{MgCO}_3\text{Mg}(\text{OH})_2\cdot 3\text{H}_2\text{O}$ (artinite) showed that this compound could be formed and was quite stable in the foam separation cycle (Fig. 1b, zone 1). Under conditions of heating to 85°C , the magnesium hydroxide stability region increases, and the precipitation region boundary pH value shifts to less alkaline conditions. In this case, the artinite stability boundary also shifts to less alkaline region.

Applying heat treatment with no solution acidifying leads to increasing probability of artinite precipitate formation (Fig. 1b, zone 2) due to shifting the mineral stability boundary to less alkaline conditions. Prevention of the artinite precipitate formation or its dissolution can be achieved through shifting the solution pH to acidic zone by adding acid or electrochemical treatment (Fig. 1b, zones 3, 4).

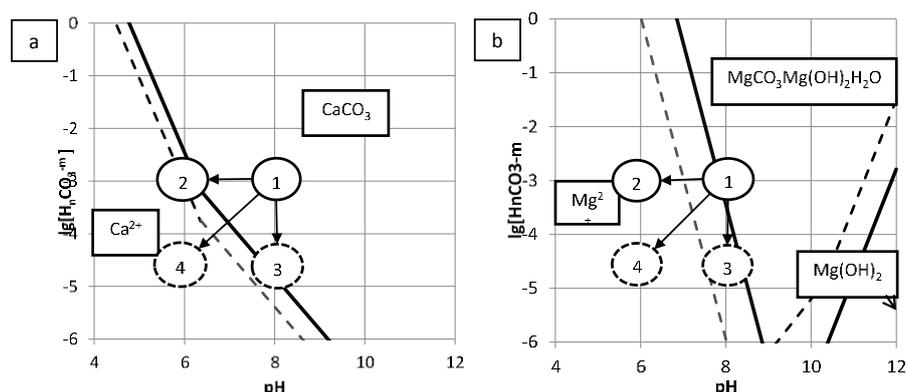


Figure 1 Plot of thermodynamic stability of calcite (a) and artinite (b) in the aqueous phase of the main foam separation process stages: 1 — initial regime; 2 — with electrochemically treated recirculating water; 3 — when using heat treatment; 4 — with the combined use of the electrochemical and heat treatment

—— - stability boundaries at $T = 25^\circ\text{C}$;

- - - - stability boundaries at $T = 83^\circ\text{C}$

The thermodynamic modeling outcomes showed that the effect of heat treatment is ambiguous. Increasing temperature leads, on the one hand, to decreasing the solubility of calcium and magnesium carbonates and carbonate hydroxides, but, on the other hand, to decreasing the solubility of carbon dioxide and, correspondingly, decreasing the concentration of bicarbonate ions and further to dissolution of these minerals. Decomposition of carbonate hydrophilizing compounds on the surface of diamonds at the heat treatment can be enhanced by simultaneously applying the electrochemical conditioning technique, which provides decreasing the concentration of calcium ions and carbonic acid, as well as shifting the solution pH to less alkaline zone.

4. The destruction covers on the surface of diamonds with the use of thermal treatment and with the use of electrochemically treated water products

To substantiate the feasibility of and select optimum conditions for thermochemical decomposition of

carbonate compounds when heating the pulp, tests on crystallization of salts from supersaturated model solutions simulating in composition the recirculating waters of Processing Plant No. 3 of the Mirny mining and processing combine were carried out. Soda was added to the initial solution with preset ion-molecular composition to provide precipitation of carbonate compounds from the supersaturated solution. The formed precipitates were dried and assayed by spectrophotometric technique using the IR-75 instrument.

Review of the IR spectra of the precipitates showed that in the common foam separation temperature area (14°C), the precipitates include carbonate and carbonate hydroxide compounds of calcium and magnesium. At 80°C , the amount of purely carbonate substances decreases, while the amount of hydroxide compounds remains stable or even possibly increases. Comparison of the test results with the calculated data allows concluding that the thermal conditioning leads to partial dissolution and decomposition of calcium and magnesium carbonate minerals and transformation of magnesium carbonate into magnesium carbonate hydroxide. In both

cases, the decomposition of the minerals occurs, and their mechanical or thermomechanical removal is facilitated.

The calculations show that maintaining the calcium carbonate dissolution conditions or preventing its crystallization on the surface of diamonds in the course of the pulp heat treatment requires maintaining weakly acid solution conditions (pH = 6-6.5).

To experimentally check the solution pH effect on the efficiency of thermal removal of the minerals from the surface of diamonds, laboratory tests were carried out on

diamonds from the "Internatsionalnaya" kimberlite pipe. The diamonds were treated at the solution working temperature of 60-90°C. After the treatment, the diamond surface was studied using JEOL JIB-Z4500 scanning electron microscope.

The study of the diamond crystal surface electron microscopic images showed that the 120-sec. heat treatment provides removing more than 90% of the mineral impurities from the diamond surface, and the surface concentration of calcium, magnesium, silicon, and iron decreases several times (Fig. 2, Table 1).

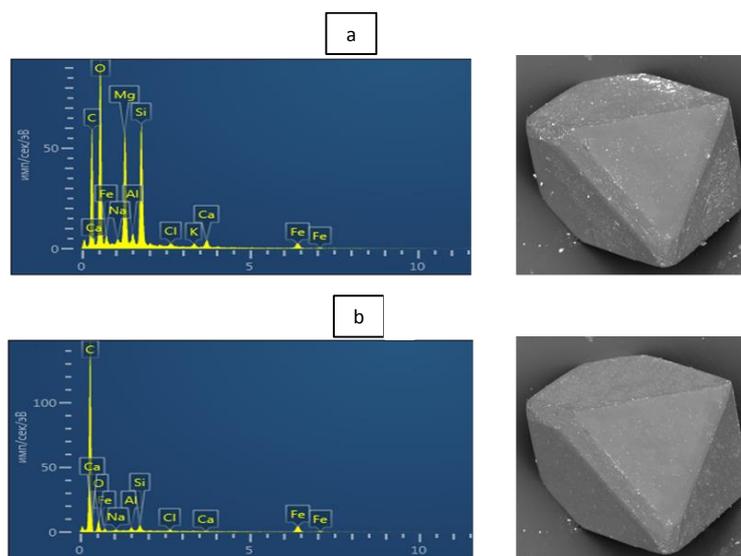


Figure 2 Change in the surface composition of diamonds heat treatment: 1- for treatment, 2 - after treatment at 80°C

Table 1 Change in the surface composition of diamonds heat treatment (at 80°C) [14]

Chemical element	Mass fractions of elements, %			
	Before treatment	After 30 s treatment	After 60 s treatment	After 120s treatment
C	88.08	90.9	92.70	94.50
O ₂	7.10	5.95	4.33	2.33
Ca	0.42	0.36	0.19	0.09
Fe	0.30	0.22	0.11	0.07
Si	0.58	0.33	0.23	0.18
Mg	0.24	0.21	0.13	0.07
Al	0.20	0.17	0.09	0.05

In the previous studies, we showed the possibility of using water electrolysis products for the desorption of surface films on diamond crystals [1, 5]. Taking into

account the findings of the present studies, testing of the products of the non-diaphragm electrolysis of recirculating water for removing the hydrophilic mineral formations from the diamond surface was performed. The recirculating water of the foam separation cycle accumulates various substances, including calcium and magnesium carbonate salts, which crystallize on the surface of diamonds and cause their technogenic hydrophilization [12].

The reason for the change in the hydrophobicity of diamonds is the cleaning of their surface in an aqueous medium that has passed the stage of electrochemical conditioning (Table 2). It was experimentally determined that the crystal surface, washed by the water electrolysis products, is characterised by low content of the impurity elements (< 5%) and oxygen content of less than 15% (Table 2) [12].

Table 2 Change in the surface composition of diamonds after interaction with the products of electrolysis of mineralized water in a non-diaphragm electrolyser

Chemical element	Mass fractions of elements, %			
	Before treatment	After treatment at power consumption, kWh/m ³		
		0.5	1	1.5
C	78.0	87.5	91.2	94.0
O ₂	9.4	6.8	4.3	3.3
Ca	1.4	1.06	0.39	0.19
Fe	1.3	1.12	0.61	0.37
Si	2.5	1.7	1.2	0.8
Mg	0.65	0.4	0.33	0.17
Al	0.4	0.27	0.19	0.1

5. Experiments and industrial test on foam separation of diamonds by using thermal and electrochemical non-diaphragm processing

To evaluate the efficiency and select the best mode of thermal and electrochemical conditioning of recirculating water in order to give them the ability to activate the surface of diamonds in the conditions close to industrial, a series of experiments were conducted on the flotation of the studied diamond crystals in mineralized water and products of its non-diaphragm processing. Bench tests of the process of foam separation of the studied mineral objects were carried out in the laboratory of the Institute "Yakutniiproalmaz" on a pilot plant [12], which included sample preparation units, conditioning of recirculating water, agitation of ore with reagents, and subsequent foam separation.

In the laboratory tests, an artificial diamond-kimberlite mixture was used. Preparation of the rough diamonds (size of -1.5+1 mm) included preliminary purification of their surface for each individual test. The diamonds recovered from the foam separation concentrate were washed in carbon tetrachloride, alcohol, and distilled water and treated with concentrated solution of hydrochloric acid which removed mineral films. For the diamond surface hydrophilization, the diamonds were aged in recirculating water at pH 8.5 exposed to air for 4 hours. After the preparation, the diamonds were mixed with a kimberlite sample of grain size of -1+0.5 mm and floated in a foam separation facility.

The laboratory tests confirmed the theoretical physicochemical study outcomes and showed that

maximizing the benefit from the heat treatment of the diamond foam separation feed is achieved when heated to 80-85°C. Application of the solution pH electrochemical regulation technique enabled achieving additional increasing the diamond recovery by 7.2-7.6% (Table 3).

Table 3 Diamond recovery into foam separation concentrate when using heat treatment and electrochemical diaphragmless conditioning of initial feed

	Heating Temperature °C	Thermal treatment only	With applying electrochemical diaphragmless conditioning of recirculating water by power consumption (kWh/t)			
			0.2	0.5	1.0	2.0
1	14	81.1	81.5	82.3	83.7	84.4
2	60	82.4	83.0	83.8	85.8	87.4
3	70	82.7	83.7	84.7	87.4	89.4
4	80	83.4	84.9	86.4	89.5	91.2
5	85	84.0	85.4	87.4	90.5	91.6
6	90	84.7	85.8	87.9	90.9	91.8

The research outcomes proved the feasibility of applying electrochemical treatment of the pulp aqueous phase for increasing the efficiency of diamond surface purification in the foam separation cycle and determined the optimum treatment conditions ($Q = 1.0-2.0$, $pH = 6.2-6.7$), at which maximum floatability of diamonds was achievable.

Industrial tests of the developed technology were carried out at Processing Plant No. 3 of the Mirny Mining and Processing Complex at a foam separation unit. During the tests, the capacity of the foam separation unit was 18.3 tons/hour. During the testing period, the following reagent consumption rates were maintained: F-5 naval special fuel oil, 980 g/t; Aeroflot butyl, 2.2 g/t; OPSB foaming agent, 80 g/t.

The flow sheet involved the PFM-10 foam separator heat treatment with superheated steam to a temperature of 80-85°C and electrochemical treatment of water supplied to EKWB-50 cell at current density of 200 A/m² and power consumption of 1.4 - 1.6 kWh/m³. The tests of the developed regime of foam separation preparation confirmed the feasibility of increasing the recovery of diamonds of the -2+0.5 mm size class from 76.5% to 83.7% (Table 4).

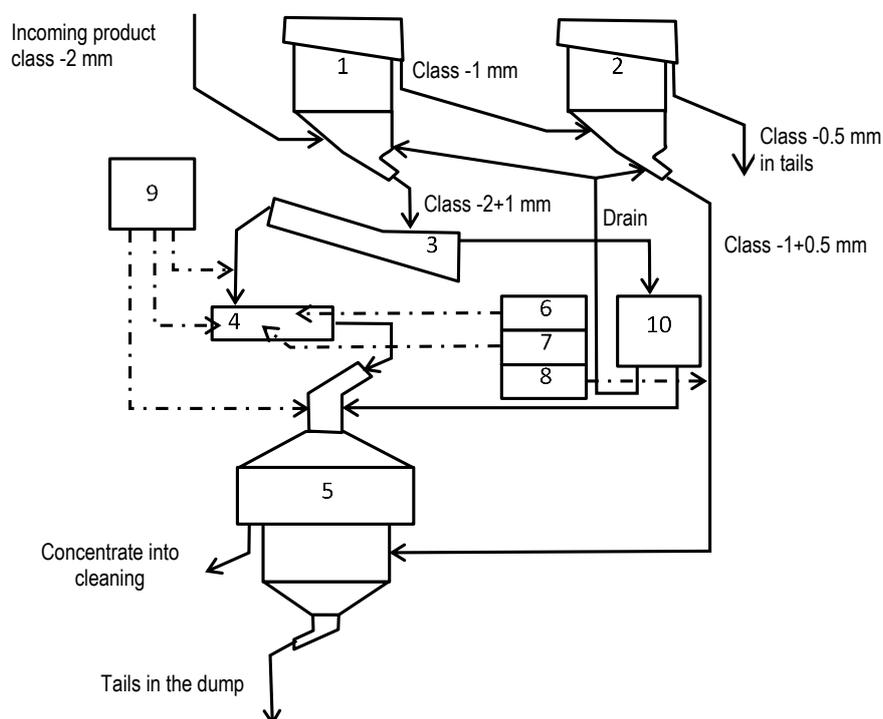


Figure 3 Flow diagram of the foam separation unit (industrial tests)
 1-classifier, 2-depulping machine, 3-dewatering classifier, 4-air conditioner, 5-foam separator,
 6-7-dosers of F-5 fuel oil and Aeroftot butyl into the conditioner, 8-doser of the foaming agent,
 9-water vapor generator, 10-diaphragmless electrolyzer

Table 4 Indicators of semi-industrial tests of foam separation with the use of the combined method for preparing the feed and recirculating water [15]

№	Foam separation process regime	The temperature of the input stream of foam separation, °C	Current density in the electrolyzer, A/m ²	Recovery of diamonds (-2+0.5 mm size class), %
0	Control tests (with no feed/recirculating water processing)	11-14	-	76.5
1	With feed heat treatment	80-85	-	77.5
2	With feed heat treatment and electrochemical conditioning of recirculating water	80-86	200	83.7

6. Conclusion

Based on the thermodynamic modeling and research test outcomes, applying electrochemical conditioning of recirculating water for increasing the efficiency of diamond surface purification of hydrophilizing compounds was substantiated. A regime including the stage of preliminary thermal conditioning of the foam separation feed at 80-85°C with decreasing

the solution pH to 6-6.5 through electrochemical treatment of the recirculating water was proposed. The results of the technological research showed that the heat treatment of the foam separation feed by superheated steam at temperature of 80-85°C and electrochemical processing of recirculating water at power consumption of 1.4-1.6 kWh/m³ allowed increasing the recovery of diamonds of (-2+0.5 mm size class from 76.5% to 83.7%.

Note

A part of this study was presented at the XIV International Mineral Processing and Recycling Conference, organized by the University of Belgrade, Technical Faculty in Bor, from 12th to 14th May 2021, Belgrade, Serbia.

7. References

- [1] Dvoichenkova, G., Chanturiya, V., Morozov, V., Podkamenny, Y., and Kovalchuk, O. (2019) Analysis of distribution of secondary minerals and their associations on the surface of diamonds and in derivative products of metasomatically altered kimberlites. *J. Polish Miner. Eng. Soc.*, 43 (1), 43-46.
- [2] Westhyzen, P., Bouwer, W., Jakins, A. (2014) Current trends in the development of new or optimization of existing diamond processing plants, with the focus on beneficiation. *J of the Southern African Institute of Mining and Metallurgy*, 114 (7), 539–545.
- [3] Kovalenko, E.G., Dvoichenkova, G.P., Polivanskaya, V.V. (2014) Substantiation of the application of the heat treatment method for improving the efficiency of the process of foam separation of diamonds. *Mining information and analytical bulletin (scientific and technical journal)*, No. 6, 158-164. In Russian
- [4] Makarsky, I.V., Adodin, E.I., Tarasova, L. (2011) Improvement of thermochemical methods of deep diamond purification. *Gorniy zhurnal*. - No. 1, 89-91. In Russian
- [5] Dvoichenkova, G.P. (2014) Mineral formations on the surface of natural diamonds and the method of their destruction on the basis of electrochemically modified mineralized waters. *J of Mining Science*. 4, 159-165.
- [6] Abramov, A.A. (2010) Flotation. Physical and chemical modeling of processes. *Gornaya kniga*, Moscow. In Russian
- [7] Timakova, E. (2016) Physical chemistry. Chemical thermodynamics. -NSTU(Ed), Novosibirsk. In Russian
- [8] Karapetyants, M.H., Karapetyants, M.L. (1968) Basic thermodynamic constants of inorganic and organic substances. - M., Chemistry. In Russian
- [9] Ravdel, A.A., and Ponomareva, A.M. (1983) Shot Reference of Physico-Chemical Values. 8th Edition, Chemistry, Moscow. In Russian
- [10] Chukanov, N., Chervonnyi, A. (2016) Infrared spectroscopy of minerals and related compounds, Springer Cham Heidelberg New York Dordrecht London, Springer Int. Publish. Switzerland.
- [11] Mahoney, J., Monroe, C., Swartley, A.M. (2020) Surface analysis using X-ray photoelectron spectroscopy, *Spectroscopy Letters*, 53 (10), 726-736.
- [12] Dvoichenkova, G. P., Morozov, V. V., Podkamenny, Yu. A., Chernysheva, E. N. (2020) The Formation of Crystalline Mineral Covers on the Surface of Diamonds and Their Destruction with the Use of Electrochemically Treated Water Products, *IOP Conference Series: Earth and Environmental Science*, 459 (2020) 052098.
- [13] Bardukhinov, L.D., Spetsius, Z.V., Lipashova, A.N. (2018) Structural defects and mineral inclusions in diamonds from nakyn and alakit-markhin field kimberlite pipes based on Raman and IR spectroscopy data. *Ores and metals*. 4, 76-86.
- [14] Dvoichenkova, G. P. (2014) Mineral formations on natural diamond surface and their destruction using electrochemically modified mineralized water, *Journal of Mining Science*, 50, 788–799.
- [15] Dvoichenkova, G.P., Kovalenko, E.G., Morozov, V.V., Podkamenny, Y.A. (2021) Destruction of crystalline mineral coatings on the surface of diamonds with the use of thermal and electrochemical treatment. In: XIV International Mineral Processing and Recycling Conference, 12-14 May 2021, Belgrade, Serbia, 78-83.

INTENZIVIRANJE PREČIŠĆAVANJA DIJAMANATA OD HIDROFILNIH MINERALA U PROCESU FLOTIRANJA

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Izvod

Razlog za gubitak dijamanata u procesu flotiranja je zato što su kristali dijamanata na ulazu u proces obloženi hidroksidima i karbonatima. Predložen je kombinovan model da bi se putem termalnog i elektrohemijskog razaranja mineralne obloge povratila hidrofobnost dijamanata. Ova metoda predviđa da će se količina minerala koji oblažu površinu dijamanta smanjiti 3 do 10 puta u fazi kondicioniranja u procesu flotiranja. Tehnološka istraživanja su pokazala da korišćenjem proizvoda elektrolize bez dijafragme recirkulišuće vode, uz termičku obradu ulaznog proizvoda procesa flotiranja, omogućava povećanje iskorišćenja dijamanata u koncentratu flotiranja od 76,5% do 83,7%.

Ključne reči: *Dijamanti; Flotacija; Termička obrada; Voda koja recirkuliše; Kondicioniranje.*
