Assessment of Technological Efficiency of Application of Products of the Membrane-Less Treatment of Mineralized Waters in a Cycle of Froth Separation of Kimberlite Ores

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Abstract. Using the methods of electron microscopy and IR spectroscopy on the surface of diamonds from the tailings of froth separation, hydrophilic mineral formations have been diagnosed and the efficiency of electrochemical effects has been identified for their removal during processes beneficiation of refractory kimberlites.

It is shown that the application of the method of electrochemical conditioning of recycling water in the scheme of flotation of diamond-containing refractory ores makes it possible to clean the surface of diamonds from hydrophilic mineral formations and, accordingly, to increase their recovery into a froth separation concentrate by 5.2% for slightly changed kimberlites and by 23.5% for intensely altered kimberlites.

1. Introduction

The existing technologies of processing primary and man-made diamond deposits are quite standard and determined by the properties of the valuable diamond component, the composition of the enclosing rocks, and also by the low content of diamonds in the initial ores with the high value of the crystals [1]. The need to achieve a diamond recovery rate of more than 98% with a high content of fine crystals determines the depth of processing of diamond-bearing ores at the level of 0.5 mm [1, 2].

Based on the experience of kimberlite ore processing plants, it is established that the main diamond losses are represented by crystals of the -5 mm grade, where up to 40-45% of their total content is concentrated in, that is more than 15% of the value of commercial output [1, 2].

In the current schemes for processing kimberlite ores, diamonds of -5 + 2 mm and -2 + 0.5 mm in size are recovered at the final stages in testing operations by the methods of grease and froth separations based on the contrasts of the hydrophobic-hydrophilic state of the surface of separated components [2, 3].

For a number of years, IPKON RAN, MPTI, NEFU, Yakutnipralmaz and NIGP AK ALROSA research institutes conducted a number of studies of processes of beniciciation of altered kimberlites of the upper horizons, which results taking into account [4] established the following:

- the content of altered minerals in kimberlite ores leads to the formation of hydrophilic films on the surface of crystals that reduces the degree of natural hydrophobicity of diamonds, which, accordingly, increases their losses in basic operations of beneficiation [5, 6];
- the crystallization process is adopted as a mechanism of adhesion of mineral formations to the surface of diamonds, which intensity is primarily due to the material composition of kimberlite ores and the conditions of their processing [7-9];
- the composition of mineral formations on the surface of the studied diamonds, recovered from the tailings of the basic operations of grease and froth separation, is identical to the composition of altered minerals of the processed kimberlite ores and is formed by clayey finely dispersed talc-smectite minerals [10, 11].

Thus, the task of reducing losses of -5mm grade diamonds in modern conditions of involving refractory diamond-containing raw materials in the process of beneficiation is topical and requires the use of new innovative methods of destruction and dissolution of mineral formations on the surface of diamond crystals to restore their natural properties.

2. Research Targets
The following items have been studied as research targets:
- Mineral formations on diamonds recovered from froth separation tailings during the processing of refractory altered kimberlites of deep horizons,
- Properties of the crystal surface under the conditions of their processing by electrochemical impacts.

3. Research methods and techniques
The experimental assessment of the surface of the recovered crystals was made using optical, electron microscopy, IR and UV spectroscopy methods.

The study of the substance on the surface of diamonds was carried out by comparing the reference infrared spectra of passing layered minerals with mineral adhesion streaks on diamonds. The chemical composition of the adhesions is determined by the method of micro-X-ray spectral analysis.

The assessment of process efficiency of the developed technical solutions for the destruction and dissolution of mineral formations from the surface of diamond crystals was made by a cycle of bench and industrial tests in the laboratory of the Yakutniproalmaz Institute and in the froth separation scheme at the beneficiation plant No.3 of Mirny MPP of AK ALROSA.

4. Discussion of findings
Figure 1 shows pictures of diamonds recovered from the tail products of froth separation during the processing of kimberlite ores, and the IR spectrum of their surface.

The presented photographs show that practically all the studied crystals are characterized by the presence of mineral films on their surface, which are layers of finely dispersed clay minerals located on the plane of the crystals and in the region of various defects of their surface.

The IR spectrum of the surface of one of the studied crystals shown in the Figure is typical for the most of the crystals studied.

In the IR absorption spectra of the ground mass of the diamonds studied, intense bands of about 1000 cm\(^{-1}\) and 500 cm\(^{-1}\) are observed in the range (1000-1200) cm\(^{-1}\), which are typical for the [SiO\(_4\)]\(^4-\) groups. Layered silicates are characterized by an intense band at 1,000 cm\(^{-1}\) and weaker bands of 1,111 cm\(^{-1}\) and 900 cm\(^{-1}\).

Taking into account the results of the previously performed experimental works [12-15], a comparative analysis of the surface properties of crystals sampled from tailings of the froth separation of kimberlites of the upper and lower horizons of one of the pipes of Western Yakutia was conducted.

The integrated analytical studies disclosed that in the processing of altered kimberlites of different horizons, diamond crystals not recovered by the froth separation method generally have an inhomogeneous surface with mineral formations represented by magnesium silicates, calcium, magnesium and iron carbonates. The number, size, conditions and strength of adhesion of the diagnosed mineral formations are quite different and conditioned by the degree of change of the processed kimberlite ores. The linear size of the diagnosed mineral formations varies from 16 μm to
120 μm in the lower horizons to the talc-smectite-type slurry adhesions in the upper horizons of kimberlite rocks.

Taking into account the previously obtained data [6-8] and the results of the series of studies completed, the area, thickness and strength of mineral films on the diamond surface are determined as the main components in the mineral impurity formation system on the surface of diamond crystals.

![Figure 1. Photos of studied diamonds and an example of the IR spectrum of mineral formations on their surface.](image)

To identify the conditions for deposition and adhesion to the surface of diamonds of mineral formations in order to justify the method of their destruction and dissolution, a thermodynamic analysis of the stability of the main diagnosed minerals under the research conditions was performed [16, 17].

The thermodynamic analysis of chemical reactions involving minerals forming films on diamonds has been conducted by plotting the diagrams of stable compounds in the lg [CO3] - pH coordinates given in Fig. 2, whose analysis shows that:

- in the recycling water and the liquid phase of the pulp under the research conditions, the formation of a magnesite - magnesium hydroxide and carbonate is unlikely with the least probability (Figure 1a), while the most stable are the mixed calcium, magnesium, iron carbonates (Figure 2b-d), and the formation of dolomite, siderite and iron hydroxide is possible under all conditions studied;
- for the decomposition (dissolution) of carbonate and hydroxydcarbonate sediments on the surface of diamond crystals, the main condition is a decrease in the concentration of bicarbonate ions, and a shift in the pH of the aqueous system used in to acidic media.

Taking into account the structural and chemical features of fine-dispersed mineral impurities found on the surface of the diamonds studied, as well as the mechanism of their formation and adhesion as a crystallization process, a method of destruction and dissolution of formed films has been proposed based on the application of electrolysis products of aqueous systems previously tested as activator reagents enabling to restore the natural hydrophobicity of the diamond surface [15].

An experimental assessment of the effectiveness of the application of electrochemically treated aqueous systems to create conditions for the destruction and dissolution of mineral formations on the surface of diamond crystals was made using collections of natural diamonds of altered kimberlites of deep horizons. Taking into account the results of the studies conducted for the processing conditions of kimberlite ores of the upper horizons [14, 15, 21], the products of membraneless treatment of mineralized recycling water, characterized by a change in the value of Eh from + 650 mV to + 900 mV, with the intervals of pH values from 5.8 to 6.8 were used in the experiments.

Figure 2. Diagrams of thermodynamic stability of diagnosed mineral formations on the surface of diamonds in the conditions of technological processes of their recovery: a - magnesium trihydrohydroxocarbonate; b - calcite; c-dolomite; d-siderite.
The results of the experiments performed (Table 1) identified the possibility of reducing the content of impurity elements and the area of the restricting film from 83% to 15% on the surface of diamonds as a result of their treatment with products of membraneless electrolysis of mineralized water systems.

The experimental data obtained are confirmed by analytical methods for diagnosing the surface of diamond crystals under the test conditions shown in Fig. 3.

Photographs obtained by the electron microscopy method, as well as the nature of the IR spectra of the surface of crystals, convincingly demonstrate the effectiveness of the application of electrolysis products of aqueous systems to remove hydrophilic mineral impurities from the surface of diamonds.

Table 1. Change in the composition of the film on the diamond surface after treatment with water electrolysis products.

| Degree of hydrophobicity, % | Content, %, atomic | Σ min. impurities, C | Film area, % |
|----------------------------|-------------------|---------------------|-------------|
|                            | C | Si | Fe | Mg |                         |             |
| 1 - hydrophilic diamonds   | 13.2 | 57.5 | 5.2 | 6.3 | 6.5 | 0.30 | 83.2 |
| II - hydrophobic diamonds (after treatment with water electrolysis products) | 89.7 | 85.3 | 1.1 | 0.4 | 1.5 | 0.034 | 14.9 |

Figure 3. The surface of a diamond with mineral formations (A) and after their destruction by water electrolysis products (B), diagnosed by electron microscopy (1) and IR spectroscopy (2).
5. Conclusion
The results of analytical and technological studies confirmed the effectiveness of the use of electrochemically modified aqueous systems for the destruction and dissolution of mineral formations on the surface of natural diamonds in both the upper and deep horizons of altered refractory kimberlite ores:
- the results of bench tests of froth separation carried out in the laboratory of the Yakutniproalmaz Institute of ALROSA enabled increasing the extraction of diamonds from 10% to 68.9% with the supply of electrochemically treated recycled water to the flotation process.
- the results of industrial tests carried out in the froth separation circuit No. 3 of the beneficiation factory of Mirny MPP have identified that the use of electrochemically treated recycling water in the process of flotation of refractory diamond-containing kimberlites from the Mirny and Internationalnaya pipes enables increasing the recovery of diamonds into the froth separation concentrate by 5.2% and 23.5% respectively.

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