
MINERAL
DRESSING

Modification of Properties of High Luminous Diamonds with Luminophore-Bearing Compositions towards Enhanced Selectivity of X-Ray Luminescence Separation

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Abstract—The found interaction mechanism between a mineral–diamond mixture and a modifying agent includes the stage of adhesive attachment of luminophore at grains of diamonds and kimberlite. The selected compositions of modifying agents and the modification process parameters ensure efficient attachment of luminophore-bearing compositions at diamonds. The proposed criterion of selective action of modifying agent on spectral characteristics of diamonds enable choosing modes of recovery of weak and high luminous diamonds from kimberlite ore in X-ray luminescence separation. The rational variation parameters are determined for the organic collector composition, water phase of a modifying agent and for the process of modifying treatment of diamond–kimberlite products before the X-ray luminescence separation. The test of the selected compositions of modifying agents and the diamond-bearing product treatment modes proved almost complete extraction of weak and high luminescence diamonds to concentrate at minimized yield of kimberlite.

Keywords: Weak and high luminescence diamonds, kimberlite, luminescence property modification, luminophores, modifying agents, interaction mechanism, selectivity criterion.

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INTRODUCTION

Improving the recovery of weak and high luminescence diamonds provides a significant increase in the productivity of diamond mining enterprises. [1]. The use of up-to-date technologies for modifying the spectral characteristics of diamonds, including luminophore-bearing compositions, is a prospective trend [2]. An important condition for the effective application of the developed technology is the selective effect of modifying agents on diamond crystals. Selective attachment of a luminophore-bearing composition at diamonds is largely similar to selective attachment of a collector during diamond flotation in froth separation of diamond-bearing materials. In both cases, the efficiency is determined by the attachment strength of organic liquid (collector) at the hydrophobic surface of diamonds with a minimum attachment at the kimberlite surface [3].

The process mechanism relates this system to conditioning the initial feed of froth separation in dense media and to attachment of finely dispersed collector drops at the diamond surface in the bulk of flotation pulp [4, 5]. The main distinction from the froth separation is the need to retain the luminophore grains by collector drops, which restricts the use of collector attachment regulators on the surface of kimberlite minerals. The stability of such aggregates is ensured by the intense adhesive interaction of diamonds and luminophores with an organic liquid (collector). It is achieved at maximum values of the three-phase contact angle in the mineral–collector drop–water medium system. [6].

Another distinction is the absence or minimization of the air phase when treating a mixture of diamonds and kimberlite with luminophore-bearing compositions. In addition to transporting diamonds to the froth layer, the air phase redistributes the collector between floatable and non-floatable minerals. This system differs from flotation and froth separation by a rather coarse size of processed material (2–5 mm versus 0.5–2 mm in froth separation).

The problem of selecting an organic collector is solved using the energy approach, which determines the use of organic liquids with a surface energy close to the energy of the diamond-water phase interface. It is advisable to use oil products with a surface energy in the range of 28–45 mJ/m², for example, diesel fuel, petroleum-based mineral oils, hexadecane and their mixtures as such collectors [7].

This paper aims at defining the mechanism and conditions for the selective attachment of a luminophore-bearing composition at the surface of weak and high luminescence diamonds in the water medium in the presence of kimberlite minerals, determining the effect of ion-molecular composition of the water phase (pH, Eh, salinity) on the stability and selectivity of attachment, and selecting the optimal composition of the water phase of luminophore-bearing emulsions.

1. RESEARCH PROCEDURES

The interaction between diamonds, luminophores, and organic liquids in the water medium was studied by the methods of luminescence and combined (ultraviolet-visible light) microscopy that ensure the observation and recording of images of macro- and micro-objects using the photoluminescence effect [8]. In these studies, a luminescent microscope Micromed 3 LYUM was used.

The influence of agents on surface hydrophobicity of objects under study was estimated by measuring the contact angles [9]. The mineral surface was treated with the water system in question, a drop of organic matter was applied, and the contact angle was measured. The measurements were carried out on an OCA 15EC Package 1 unit with a direct dosing module SD-DM, the measurement results were processed using the SCA 20 package.

To study the oil receptivity of diamonds, kimberlite minerals, and luminophores, we used a setup [6] that provided the supply of dispersed organic liquid to the working zone, in which the components under study (diamonds, luminophores) were attached, the organic liquid floated up with the attached components, and the floated fractions were subsequently unloaded into the receiver.

The efficiency of luminophore attachment at the surface of diamonds and kimberlite minerals was estimated from the luminescence images of objects under study, in ultraviolet radiation. Images of diamonds and kimberlite minerals after treatment with luminophore-bearing media were performed on a Luch-1F luminoscope equipped with UV radiation sources with a wavelength of 273 and 365 nm. The resulting images were diagnosed by a visual analysis, which allowed estimating the concentration of luminophore and its distribution on the surface of test samples. [6, 7].

To determine the results of modifying the diamond surface with luminophore-bearing compositions and the possibility of extracting diamonds, a portable Polyus-M separator which reproduces the settings of industrial X-ray luminescence separators was used. [10]. The analog-to-digital registration system provided the possibility of operating both in the amplitude-time mode and in a special mode of increased selectivity, using the kinetic characteristics of a signal: convolution S_v , decay time constant τ_s , slow component amplitude A_{SC} , fast component amplitude A_{FC} , and the ratio of component amplitudes K_A [11].

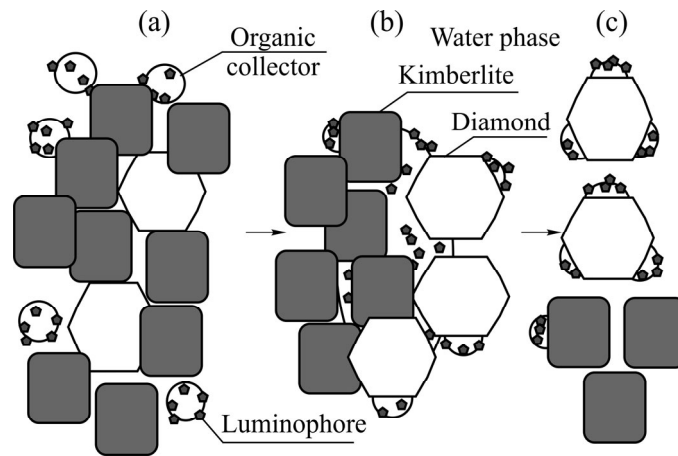


Fig. 1. Interaction of luminophore-bearing composition with diamond crystals and kimberlite grains: (a) addition of emulsion composition; (b) formation of aggregates (diamond–collector–kimberlite–luminophore); (c) removal of excess composition.

2. MECHANISM OF INTERACTION OF LUMINOPHORE-BEARING COMPOSITION WITH DIAMONDS AND KIMBERLITE MINERALS

The modifier of kinetic and spectral characteristics of diamonds represents a composition of inorganic and organic luminophores in an organic collector, which is mixed with a water phase containing dispersing agents. The dispersion degree of a luminophore-bearing composition in the water phase is characterized by the predominance of collector drops 100–500 μm in size, which ensures the stability of primary collector aggregates with grains of inorganic luminophore 10–40 μm in size and implementation of the adhesion-hysteresis mechanism for attaching the composition at the diamond surface.

When diamonds are treated with an emulsion of luminophore-bearing composition, due to hydrophobic interactions in the water phase, group aggregates of diamonds are formed, in which individual crystals are interconnected by a luminophore-bearing liquid [6, 7]. When treating diamond–kimberlite products, the resulting organic–mineral aggregates contain both diamond crystals and grains of kimberlite minerals (Fig. 1b). When excess collector is removed in a turbulent hydrodynamic mode, organic–mineral aggregates disintegrate with the separation of individual diamond and kimberlite grains, on which drops of a luminophore-bearing composition are retained (Fig. 1c).

The interaction energy of the organic collector of luminophore-bearing composition with diamonds is much higher than with kimberlite, which causes a predominant luminophore attachment at diamonds and, to a lesser extent, at kimberlite grains (Fig. 2a). When the excessive composition is removed by washing, the concentration of luminophores on the surface of diamond crystals (coverage 15–40%) significantly exceeds the similar value for kimberlite grains (1–5%, Fig. 2b).

The mechanism of luminophore attachment at diamond and kimberlite grains can be represented by two main subprocesses. The main interaction involves the adhesion of an organic collector to naturally hydrophobic minerals. Such minerals include phlogopite, talc, non-oxidized sulfide minerals [12]. Luminophore-bearing composition is attached at the grains of such minerals. The second-type mechanism includes the pulling of an organic liquid into cracks of water-unfilled polycrystalline kimberlite samples.

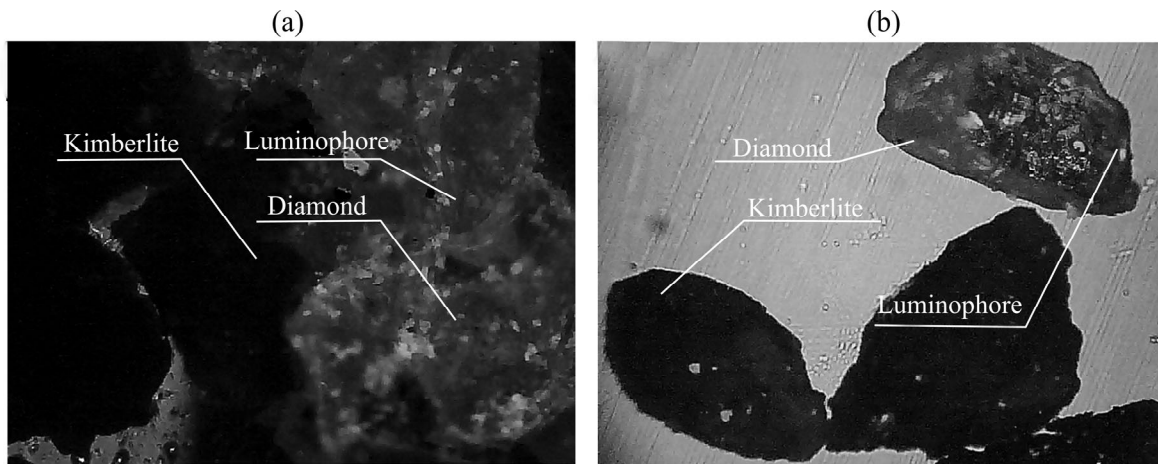


Fig. 2. (a) Aggregate of luminophore-bearing composition with diamond crystals and kimberlite grains and (b) isolated diamond crystals and kimberlite minerals after removing the excessive composition.

A liquid with a polarity close to that of a solid has a high selective wettability towards this surface. Taking this regularity into account, the main condition for the selective attachment of a collector with luminophores at diamonds will be proximity of the surface energy of the diamond–water interface to the surface energy of the collector–water interface. On the contrary, the attachment of collector at the surface of kimberlite minerals can be prevented by increasing the energy difference between the kimberlite minerals–water and collector–water interfaces. Obviously, the required energy shift must be accompanied by a decrease in the surface energy of diamonds and an increase in the surface energy of kimberlite minerals.

To achieve the result, it is necessary to increase the hydrophilicity of all mineral components of kimberlite due to the adsorption of ionized surfactants on them, or adhesion of organic compounds with a significant concentration of polar groups in hydrocarbon radicals.

Previous studies showed that the required stability of luminophore compositions and organic collectors, as well as high attachment strength of luminophores at diamonds, is achieved using organic (alkyl sulfates and alkyl sulfonates) and inorganic (polyphosphates) dispersing agents [6, 7]. The fundamental difference of reagents, which determines their behavioristic features in water-dispersed systems, is the presence of a long hydrocarbon radical in alkyl sulfates (Fig. 3).

When alkyl sulfates and alkyl sulfonates are attached at hydrophobic minerals, surfactant molecules are located on the interfacial surface according to the polarity equalization rule: the polar group of the molecule is in polar water, the non-polar group is directed towards the hydrophobic solid. Due to the adsorption of surfactant molecules, the interfacial solid–liquid σ_{s-l} and water–collector σ_{w-c} tensions decrease. According to Young's equation:

$$\cos \theta = \frac{\sigma_{s-c} - \sigma_{s-l}}{\sigma_{l-c}}, \quad (1)$$

the contact angle decreases, i.e. the solid surface is better wetted by the surfactant solution compared to pure water and becomes less hydrophobic and less oleophilic.

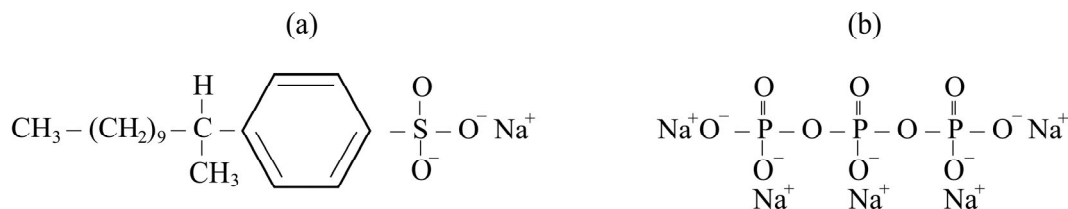


Fig. 3. Structural formulas of (a) sodium alkyl sulfate and (b) polyphosphate.

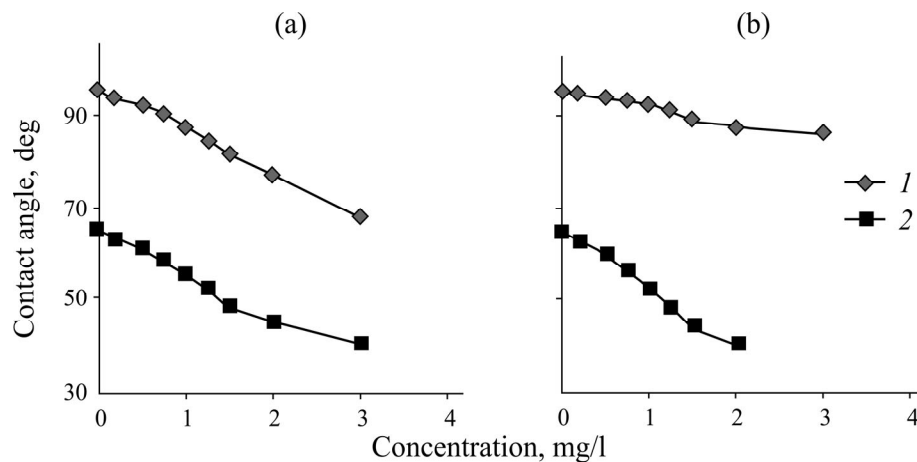


Fig. 4. Effect of (a) alkyl sulfate and (b) hexametaphosphate concentration on contact angle of diamond (1) and phlogopite (2).

There is no adsorption of alkyl sulfate surfactants on the surface of well-wettable hydrophilic minerals. In this case, the surface wettability increases to a lesser extent and only due to a decrease in the surface tension at the liquid–collector σ_{c-l} interface.

Thus, heterogeneous surfactant molecules are adsorbed on the surface of the diamond–water and collector–water interfaces with a decrease in the surface tension at the diamond–water interface σ_{d-w} resulting in a decrease in contact angle θ .

This result was confirmed experimentally by measuring the contact angle in the mineral–organic collector–water phase system, in which the mineral surface was preconditioned with a surfactant solution. Experimental results showed that almost any addition of alkyl sulfates causes a decrease in hydrophobicity of the surface of naturally hydrophobic minerals (Fig. 4a) and the desired selective effect is not observed.

The effect of polyphosphates on the mineral–water phase–collector disperse system is different. The basic action of polyphosphates is their attachment at the surface of naturally hydrophilic minerals by the mechanism of cation exchange, when a strong chemical bond with doubly charged mineral cations (calcium, iron, magnesium) is formed [12, 13]. The effective action of sodium tripolyphosphate or sodium hexametaphosphate is also explained by the intense adsorption of polyphosphate ions at the boundary of silicon–oxygen tetrahedra (for example, naturally hydrophobic layered aluminosilicates), which is due to the similarity in the structure and size of tripolyphosphate anions and silicon–oxygen tetrahedra of clay minerals [14]. Polyphosphates also allow hydrophilizing the surface of phosphate minerals [12].

The research results showed a fundamentally different effect of hexametaphosphate on surface properties of minerals in comparison with alkyl sulfates. The decrease in the contact angle on diamond is expressed to a much lesser extent and, on the contrary, a very intense hydrophilization of the phlogopite surface is observed (Fig. 4b). There are no changes in the hydrophobicity and oil receptivity of naturally hydrophilic minerals (the contact angle is not detected, and a drop of organic liquid is released from the mineral).

The obtained results allowed concluding the need to select regulating agents of the mineral–water phase–collector disperse system that do not contain a significant apolar radical and prone to the formation of chemical bonds with kimberlite mineral cations.

The efficiency of collector attachment at the mineral surface is also significantly affected by other factors related to the composition of the collector, the water phase and the temperature of the medium. These factors include the fractional composition that regulates the adhesion rate and the strength of collector attachment at diamonds. It is found that the best result is achieved when using light medium-viscosity oil products, which are a mixture of medium and high molecular weight fractions containing linear and cyclic hydrocarbons [6, 7].

An important condition for the stable retention of luminophores in an organic collector attached at the diamond surface is the high oil receptivity of their surface, which is achieved by pretreatment with hydrophobizing xanthate agents and unsaturated fatty acids [7]. The above factors regulate the interaction of luminophore-bearing composition with diamonds. However, in many cases, improved attachment of an organic collector with luminophores at the diamond surface is accompanied by a similar effect in relation to hydrophobic kimberlite minerals or polymineral kimberlite grains containing hydrophobic minerals.

The main factors regulating the interaction in water-disperse systems are additions of chemical reagents that prevent the attachment of organic non-ionized substances at the mineral surface. Reagents including polyphosphates, silicates, natural organic polymers (starch, carboxymethylcellulose, polysaccharides), lignosulfonates, etc. were selected to suppress the attachment of luminophore-bearing composition on hydrophobic kimberlite minerals [12, 15–17]. An important condition was the justification and practical selection of the composition parameters of emulsion water phase (pH, salinity, Eh, temperature) that ensure the selective attachment of luminophore-bearing compositions at diamonds.

3. CRITERIA FOR SELECTIVE ATTACHMENT OF LUMINOPHORE-BEARING EMULSION AT DIAMONDS AND KIMBERLITE MINERALS

The system under study is characterized by a combination of factors that determine the final result—luminophore attachment selectivity. This system is complex, as it is necessary to consider an important factor in the stability of luminophore-bearing composition. This relationship is illustrated by the data in Fig. 5, showing the influence of sodium polyphosphate concentration on the oil receptivity of diamonds, kimberlite and luminophore, estimated by the criterion of extraction and oil flotation of these components with an organic liquid that forms the basis of luminophore-bearing composition [6].

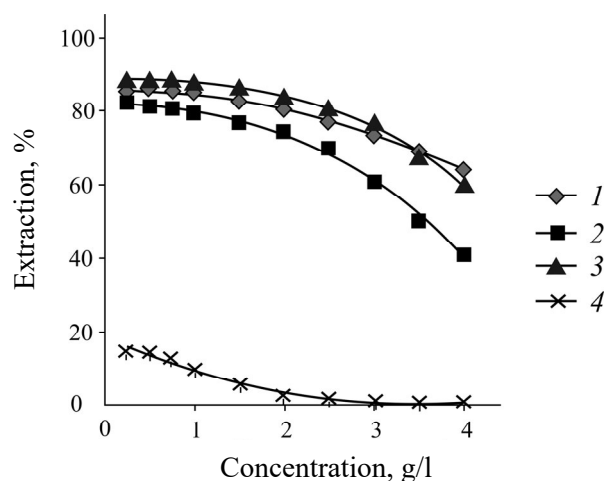


Fig. 5. Influence of sodium polyphosphate concentration on the extraction of diamonds (1), luminophore FL-530 (2), luminophore E-515-115 (3), kimberlite (4) composition of heavy gas oil of catalytic cracking (HGCC) (75%) and diesel technical fraction (DTF) (15%).

Increasing the concentration of sodium polyphosphate over 0.5 g/l causes a decrease in the extraction of kimberlite grains by an organic collector; at concentrations of more than 1 g/l, the extraction of luminophores by the organic collector and diamond flotation are reduced. These processes are aimed at decreasing the attachment of luminophore-bearing composition both at the surface of diamonds and kimberlite grains.

The criterion for evaluating the process selectivity was chosen using the dependence of extraction of X-ray luminescence separation of diamond crystals and kimberlite grains into the concentrate on the concentration of luminophore-bearing composition on their surface. To estimate the process selectivity, a combination of visual analysis of mineral surface coverage with luminophores and recoverability analysis of diamonds and kimberlite was used in Polyus-M separator.

The results of the visual analysis showed that with an increase in the concentration of luminophore-bearing emulsion of sodium polyphosphate in the water phase, the amount of luminophore attached at diamond and kimberlite grains decreases (Table 1).

Sodium polyphosphate, on the one hand, is an additional stabilizer of the luminophore-bearing composition-water disperse system; on the other hand, it prevents the adhesion of an organic collector with luminophores on it, attaching at the surface of kimberlite minerals. The results of visual analysis data were compared with the data of X-ray luminescence separation of diamonds and kimberlite grains, and it was found out that a sufficiently high level of coverage of diamond surface with luminophores was provided and almost complete diamond recovery was maintained when sodium polyphosphate concentration was increased in the range of 0–1.5 mg/l. A noticeable decrease in the coverage of kimberlite grain surface with luminophores in the same concentration range, and a decrease in the yield of kimberlite into diamond concentrate to a technologically acceptable level (less than 1.5%, Table 1) were observed.

A further increase in the polyphosphate concentration (more than 1.5 g/l) causes a worse luminophore attachment both at the surface of diamonds and kimberlite due to a decreased attachment stability of the organic collector, which results in a reduced diamond recovery and kimberlite yield into the concentrate of X-ray luminescence section (XLS). The analysis showed that the loss of diamonds in XLS is observed when the surface concentration of luminophores on diamonds decreases to less than 15%. For kimberlite, surface luminophore concentration of 3% was selected as the boundary value. When it is exceeded, the yield of kimberlite into the concentrate is increased by more than 1.2% and the quality of diamond concentrate is deteriorated. Such a large difference in the boundary concentrations of luminophores on the mineral surface is explained by fluctuations in the properties of diamonds and kimberlite minerals, in particular, the presence of hydrophilized diamonds and monomineral grains of naturally hydrophobic kimberlite minerals.

Table 1. Results of visual analysis of diamond and kimberlite coverage with luminophores and their recovery in Polyus-M separator, %

| Sodium hexametaphosphate concentration, g/l | Coverage of diamonds with luminophores | Extraction of diamonds into XLS | Coverage of kimberlite with luminophores | Extraction of kimberlite into XLS |
|---|--|---------------------------------|--|-----------------------------------|
| 0 | 36.3 | 100 | 18.1 | 6.3 |
| 0.5 | 32.3 | 100 | 5.3 | 2.5 |
| 1.0 | 26.5 | 100 | 3.4 | 1.5 |
| 1.5 | 14.9 | 99 | 3.1 | 1.2 |
| 2.0 | 11.4 | 95 | 2.8 | 1.0 |
| 3.0 | 10.3 | 90 | 2.1 | 0.5 |

The obtained data made it possible to determine that selectivity of X-ray luminescence separation will be achieved at a surface luminophore concentration on diamonds of at least 15% and surface luminophore concentration on kimberlite minerals of no more than 3%.

Thus, a certain value of the surface concentration of luminophores attached at diamonds and kimberlite can be taken as a selectivity criterion for the separation of diamonds and kimberlite minerals in XLS. In this case, the selectivity criterion is represented by two parameters: the concentration of luminophores on diamonds (more than 15%) and the concentration of luminophores on kimberlite (less than 3%). If these conditions are satisfied, weak and high luminous diamonds and kimberlite will be effectively separated in XLS with a high extraction of diamonds into a quality concentrate.

4. CHEMICAL METHODS TO CONTROL LUMINOPHORE ATTACHMENT AT DIAMOND AND KIMBERLITE SURFACE

Polyphosphates were tested in the studies when developing and selecting the optimal compositions of modifying agents [3, 6]. In addition to polyphosphates (trisodium phosphate, sodium hexametaphosphate SHMP), organic polymer reagents (carboxymethyl cellulose CMC), polysaccharides (starch), water-soluble silicates (liquid glass), alkyl sulfates and alkyl sulfonates (oxyethylidenediphosphonic acid HEDP, sulfonol) can be used to control the surface properties of minerals. These reagents are used in various industries to stabilize disperse systems and suppress the floatability of rock-forming minerals [12, 16, 17]. An important factor in the state of water-disperse systems is the ionic strength of the solution (salt content) and pH of the medium [18].

The dispersing agents were selected in accordance with their capability to prevent the luminophore attachment at the surface of kimberlite minerals, taking into account a possible similar effect on diamonds. A visual analysis in ultraviolet light, which allowed determining the coverage of a mineral surface with luminophores, was used to estimate the efficiency of luminophore attachment at minerals.

The luminophore-bearing composition contained an organic collector with luminophore (0.5–1.0%), water (99.0–99.5%). The concentration of luminophore in the collector was 100 mg/ml. The water phase of the emulsion was tap water with a salt content of 0.5 g/l and the same water after adding a mixture of sodium chloride (5 g/l) and calcium chloride (5 g/l). The added components brought drinking water closer in composition and properties to mineralized water of ALROSA diamond mining company. In all experiments, 0.5 g/l of Progress synthetic detergent (mixture of secondary alkyl sulfonates) was added to the water phase, which provided a stable emulsion of the organic collector with luminophores in the water phase.

The study results showed that sodium hexametaphosphate, sulfonol, carboxymethylcellulose, and water glass are highly capable of preventing the attachment of luminophores at the surface of kimberlite grains in weakly mineralized water systems (Table 2). These reagents reduce the coverage of kimberlite grain surface with luminophores from 18 to 0.5% in tap water.

The permissible level of luminophore surface concentration on kimberlite (3%) is achieved at a reagent concentration of more than 1 g/l.

When using highly mineralized water, the result of using dispersing agents changes markedly (Table 3). On the one hand, mineralized water is a factor that reduces the luminophore attachment at the kimberlite surface from 18 to 7%, on the other hand, the effectiveness of dispersants, especially those interacting with calcium ions, decreases and the required level of kimberlite coverage with luminophores is achieved at a reagent concentration of 1.0–1.5 g/l.

Table 2. Results of visual analysis of reagent effect in weakly mineralized tap water to check the luminophore attachment at kimberlite surface

| Agent | Concentration of agents, g/l | | | | | | |
|---------------------|---|-----|-----|-----|-----|-----|------------------------------------|
| | 0 | 0.5 | 1.0 | 1.5 | 2.0 | 3.0 | Average in the interval of 0.5–3.0 |
| | Coverage of kimberlite surface with luminophores, % | | | | | | |
| Tripolyphosphate | 18.1 | 5.3 | 2.4 | 2.1 | 1.8 | 1.1 | 2.5 |
| SHMP | 16.8 | 4.2 | 1.7 | 1.4 | 1.0 | 0.8 | 1.8 |
| HEDP | 16.8 | 4.7 | 2.4 | 1.5 | 0.9 | 0.8 | 2.0 |
| Corn starch | 16.5 | 4.8 | 2.2 | 1.6 | 1.4 | 1.0 | 2.1 |
| CMC | 17.2 | 3.8 | 1.9 | 1.4 | 1.0 | 0.5 | 1.8 |
| Sulfonol | 18.4 | 2.9 | 2.0 | 1.2 | 1.0 | 1.0 | 1.6 |
| Sodium metasilicate | 18.0 | 3.9 | 1.9 | 0.9 | 0.8 | 0.6 | 1.3 |
| Lignosulfonate | 17.6 | 5.4 | 3.3 | 2.6 | 2.0 | 1.4 | |

Table 3. Results of visual analysis of reagent effect in highly mineralized tap water to check the luminophore attachment at kimberlite surface

| Agent | Concentration of agents, g/l | | | | | | |
|---------------------|---|-----|-----|-----|-----|-----|------|
| | 0 | | 0 | | 0 | | 0 |
| | Coverage of kimberlite surface with luminophores, % | | | | | | |
| Tripolyphosphate | 7.5 | 3.5 | 2.1 | 1.5 | 1.4 | 1.2 | 1.94 |
| SHMP | 7.0 | 3.9 | 2.6 | 1.6 | 1.0 | 0.9 | 2.00 |
| HEDP | 7.1 | 3.6 | 3.0 | 1.9 | 1.4 | 1.2 | 2.22 |
| Corn starch | 6.5 | 3.5 | 3.1 | 2.2 | 1.4 | 1.0 | 2.24 |
| CMC | 6.4 | 3.1 | 2.5 | 1.8 | 1.1 | 0.7 | 1.84 |
| Sulfonol | 7.1 | 4.1 | 3.2 | 1.8 | 1.4 | 0.9 | 2.28 |
| Sodium metasilicate | 7.9 | 4.8 | 3.4 | 2.1 | 1.3 | 1.2 | 2.56 |
| Lignosulfonate | 7.6 | 4.8 | 3.5 | 2.2 | 1.5 | 1.2 | 2.64 |

Tripolyphosphate, hexametaphosphate, and CMC have a greater dispersing capability. When comparing the efficiency of reduced luminophore attachment at the kimberlite surface, preference should be given to modes involving the use of weakly mineralized water. Reagents that ensure a decrease in surface luminophore concentration on kimberlites to a level of 3% or less were selected as the most promising, which allows extracting kimberlite grains into a concentrate at a level of 1% corresponding to the industrial performance of XLS. Such dispersing agents are SHMP, sodium metasilicate and CMC. The selected composition of the reagents reduces the intensity of luminophore attachment at the diamond surface to a lesser extent, which is confirmed by the retention of luminophore concentration at a level of 16.5–33.0%

5. TEMPERATURE EFFECT ON SELECTIVITY OF LUMINOPHORE ATTACHMENT AT DIAMONDS AND KIMBERLITE

The temperature of the medium is an important factor that ensures the efficiency and selectivity of attachment of luminophore-bearing composition at diamonds and kimberlite. It affects the interface energy in disperse systems [19], while the viscosity of organic liquids determines the possibility and rate of their spreading over the mineral surface, and the capability to retain on it in a turbulent water medium [20, 21].

Table 4. Effect of temperature on the efficiency of luminophore attachment at kimberlite surface

| Composition of organic collector | Temperature, °C | | | | | |
|---|-----------------|------|------|------|------|------|
| | 15 | 20 | 25 | 30 | 35 | 40 |
| Coverage of diamond surface with luminophores, % | | | | | | |
| HGCC | 27.0 | 29.2 | 31.5 | 32.0 | 31.5 | 29.7 |
| DTF | 22.0 | 24.2 | 27.5 | 28.0 | 26.9 | 25.7 |
| HGCC (85%), DTF (15%) | 27.4 | 31.4 | 33.0 | 32.1 | 31.2 | 28.7 |
| Coverage of kimberlite surface with luminophores, % | | | | | | |
| HGCC | 3.0 | 3.8 | 4.3 | 4.0 | 2.1 | 1.5 |
| DTF | 4.6 | 5.3 | 5.0 | 4.6 | 2.8 | 2.3 |
| HGCC (85%), DTF (15%) | 3.1 | 3.5 | 3.3 | 2.8 | 2.0 | 1.5 |

HGCC—heavy gas oil of catalytic cracking; DTF—diesel technical fraction.

By analogy with froth separation, the fractional composition and temperature of the medium must be interrelated. Less viscous organic fluids are apparently effective at lower temperatures of the medium and vice versa. To test this hypothesis, we performed studies on the treatment of diamond-kimberlite products with luminophore-bearing compositions, in which collectors of different fractional compositions were used. The studies were carried out in the temperature range of 14–45 °C typical for water systems in process flows of diamond factories [4, 22].

The efficiency of luminophore attachment was estimated visually, and the selectivity criterion was the level of luminophore attachment at the kimberlite surface (3%). The above-described composition of the emulsion (before Table 2) was used in our studies. Sodium hexametaphosphate at a flow rate of 1 g/l was used as a dispersing agent. The study results showed that an increase in temperature from 15 to 35°C strengthens the attachment of luminophores at diamonds for all compositions of the organic collector (Table 4). The efficiency of luminophore attachment at kimberlite rises to a lesser extent. Increasing the temperature of the medium from 30 to 40°C slightly reduces the concentration of luminophores at the diamond surface, and it is more significant for kimberlite. The concentration of luminophores on the kimberlite surface decreases to 1.5–2.3%, which creates conditions for increasing their selective attachment at diamonds at elevated temperatures. Thus, increasing the temperature of the medium to 30–40 °C contributes to a more selective attachment of luminophores at diamonds.

The practice of using compound organic collectors in flotation includes regulating agents, whose effect improves the efficiency of attachment of organic collectors at the diamond surface [23]. Sodium butyl dithiophosphate (BDTP) and diethyl ketone (DEK) were considered as such components.

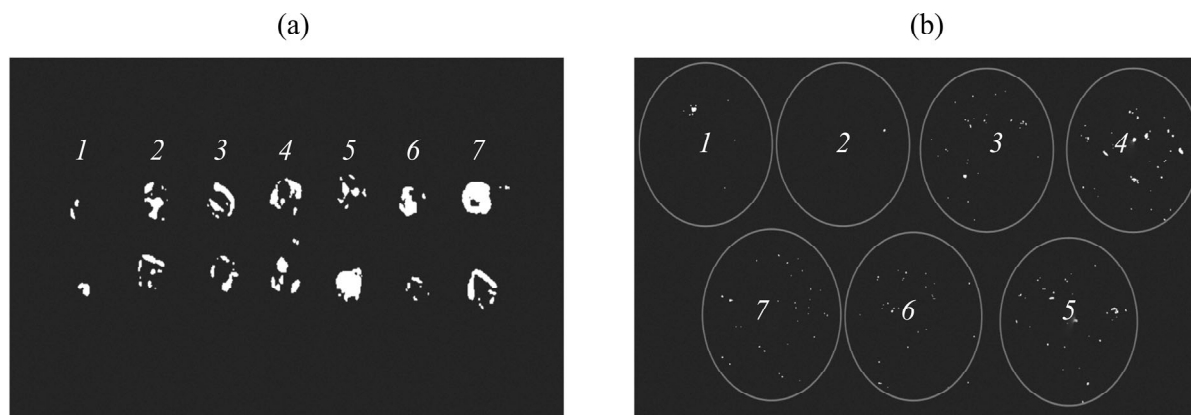
Additions of heavy gas oil of catalytic cracking to the collector showed a positive result. The coverage of diamond surface with luminophores increased by 5.0–6.7%, and the same value for kimberlite grains increased slightly (by 0.5–0.6%).

6. MODES FOR SELECTIVE MODIFICATION OF KINETIC AND SPECTRAL CHARACTERISTICS OF DIAMONDS FOR THEIR RECOVERY IN X-RAY LUMINESCENCE SEPARATION

Experiments were carried out to select optimization trends for treating diamond materials with luminophore-bearing agents. Using the method of mathematical statistics, according to the criterion of covering the surface of minerals with luminophores, the parameters of the composition of dispersing agent were selected: pH of the medium, temperature, concentration of hexametaphosphate (SHMP), mass fraction of luminophore in the collector, mass fraction of collector in the emulsion.

Table 5. Parameters of diamond material treatment in the selected modes

| Treatment mode | SHMP, g/l | HGCC, % | DTF, % | DEK, % | Acid, ml | BDTP, mg/l | T, °C | C_{lf}^{\min} |
|--|-----------|---------|--------|--------|----------|------------|-------|-----------------|
| Control | 1.5 | 0 | 100 | 0 | 0 | 0 | 24 | 5.0 |
| With HGCC-based collector | 1.5 | 85 | 15 | 0 | 0 | 0 | 24 | 3.0 |
| With acidification of the medium (pH 4.45) | 1.5 | 85 | 15 | 0 | 2 | 0 | 24 | 3.0 |
| With aeroflot additives | 1.5 | 85 | 15 | 0 | 0 | 20 | 24 | 6.0 |
| With heating of the medium (35 °C) | 2.0 | 85 | 10 | 0 | 0 | 20 | 40 | 3.5 |
| With DEK additives | 1.5 | 80 | 10 | 10 | 0 | 0 | 24 | 3.0 |
| Combined | 2.0 | 80 | 10 | 10 | 2 | 20 | 40 | 3.5 |


Fig. 6. Images and results of the visual analysis of (a) diamonds and (b) kimberlite samples for seven final experiments using optimal modes.

In this study, to increase the efficiency of luminophore attachment (E-515-115 based composition) at diamonds, the use of butyl aeroflot and diethyl ketone additives was tested. The modes that provide effective technologically acceptable attachment of luminophores (at least 15%) at the diamond surface in XLS and no more than 3.0% on the kimberlite surface were selected by varying the significant parameters.

The results of statistical processing determined six most significant factors and six local minima of luminophore surface concentration on kimberlite C_{lf}^{\min} , each of them is achieved with a certain reagent composition and process flow pattern (Table 5).

The visual analysis of diamonds and kimberlite samples showed that the selected modes provide the required high concentration of luminophores (33–45%) on the surface of diamonds (Fig. 6a) and the allowable concentration of luminophores on the surface of kimberlite grains (0.5–3.0%).

The selected reagent compositions and treatment modes were tested for preparing a diamond material for its X-ray luminescence separation (Table 6). During the tests, a series of weak and high luminescence diamonds was prepared, which were not detected by the diagnostic units of Polyus-M separator.

Approbation of the selected modes and verification of diamonds and kimberlite recoverability on Polyus-M1 separator confirmed their efficiency—a complete recovery of weak and high luminescence diamonds with a kimberlite recovery of no more than 1.5%. In terms of selectivity, the best results were obtained in modes with acidification and heating of the medium, addition of organic collector dispersing agents, and in combined mode. These results allowed determining the rational parameters for varying the composition of the organic collector and the water phase of the modifying agent, as well as treatment parameters for diamond-kimberlite products before the X-ray luminescence separation.

Table 6. Approbation of selected reagent compositions and treatment modes for preparing diamond material for X-ray luminescence separation and verification of diamonds and kimberlite recoverability on Polyus-M1 separator, %

| Treatment mode | Surface coverage | | Recovery | |
|--|------------------|------------|----------|------------|
| | diamonds | kimberlite | diamonds | kimberlite |
| Without treatment | — | — | 10 | 0 |
| Control | 22.0 | 5.0 | 50 | 1.0 |
| With HGCC-based collector | 33.0 | 3.0 | 90 | 0.5 |
| With acidification of the medium (pH 4.45) | 35.0 | 3.0 | 100 | 1.0 |
| With aeroflot additives | 42.0 | 6.0 | 100 | 2.5 |
| With heating of the medium (35 °C) | 40.0 | 3.5 | 100 | 1.5 |
| With DEK additives | 35.0 | 3.0 | 100 | 1.0 |
| Combined | 45.0 | 3.5 | 100 | 1.5 |

CONCLUSIONS

It is experimentally confirmed that the mechanism of interaction of a diamond-mineral suspension with a modifying agent (luminophore-bearing composition) consists in the formation of mixed organic-mineral complexes containing diamond crystals and grains of kimberlite minerals, subsequent disintegration of the resulting complexes when the excess collector is removed in a turbulent hydrodynamic mode and separation of diamond grains and kimberlite with modifying agent drops attached at their surface.

It is found that the mechanism of luminophore attachment at diamond and kimberlite grains includes:

—adhesion of an organic collector, which is the basis of a luminophore-bearing composition, on minerals with natural hydrophobicity;

—penetration of an organic liquid with dissolved luminophore into water-unfilled cracks of polycrystalline samples.

The possibility of modifying the spectral characteristics of weak and high luminous diamonds with luminophore-bearing compositions and controlling the selectivity of luminophore attachment by adding regulating agents for stability of water-mineral disperse systems is shown.

A two-parameter criterion for the selectivity of luminophore-bearing emulsion attachment at diamonds and kimberlite minerals expressed in terms of boundary surface concentration of luminophores attached at diamonds (not less than 15%) and kimberlite (not more than 3%) is proposed and experimentally justified.

Rational compositions of modifying agents containing HGCC-based collectors with additives of low and high molecular weight organic liquids, as well as reagents that prevent the attachment of luminophore at kimberlite grain surface (sodium hexametaphosphate, sodium metasilicate and CMC) are selected. The process parameters (temperature, pH of the medium) that ensure the selective attachment of luminophore-bearing compositions at diamonds are determined.

The optimal parameters for varying the composition of an organic collector and water phase of the modifying agent, as well as parameters for treating diamond-kimberlite products before the X-ray luminescence separation are determined. Approbation of the selected compositions of modifying agent and treatment modes confirmed their efficiency: complete recovery of weak and high luminescence diamonds was achieved with a kimberlite extraction of no more than 1.5%.

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