



## BENEFICIATION AND PROCESSING OF NATURAL AND TECHNOGENIC RAW MATERIALS

Research paper

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### Optimizing composition and application conditions of agents for modifying spectral characteristics of diamonds in X-ray luminescence separation

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#### Abstract

One of the research areas focused on improving the efficiency of diamond-bearing kimberlite beneficiation processes involves the utilization of technology aimed at enhancing the recovery of weakly and anomalously luminescent diamonds during the X-ray luminescence separation process using luminophore-containing chemical agents. The objective of this research was to select the optimal composition of agents that modify the spectral characteristics of minerals and the conditions for their application. A crucial factor for process efficiency is the effective attachment of modifying agents to diamond crystals while avoiding similar attachment to kimberlite mineral surfaces. This is achieved through the use of organic collectors with an optimal composition, characterized by their ability to both adhere to the diamond surface and retain inorganic luminophore grains. The evaluation of luminophore attachment efficiency was performed using visimetric analysis in the UV range. The capability of diamonds to retain luminophore collector droplets or films on their surfaces was evaluated using a technique to measure the three-phase limiting wetting angle. The spectral and kinetic characteristics of diamonds and their recovery during the X-ray luminescence separation process were determined using a separator “Polyus-M”. The feasibility of purposefully modifying the spectral characteristics of weakly and anomalously luminescent diamonds through luminophore-containing compositions based on zinc sulfides and zinc orthosilicate has been confirmed through the conducted studies. By considering the criterion of selectivity in the attachment of luminophore emulsion to diamonds and kimberlite minerals, calculated based on the measured surface concentrations of luminophores on the minerals, the optimal ratios between the masses of inorganic luminophore, organic collector, and the aqueous phase of the emulsion were determined. Dispersing agents that offer selective binding of luminophores to diamond crystals were identified, and rational parameters for the composition of the organic collector were established. The temperature range for treating diamond-containing material was defined. As a result of bench testing the modifying agents with the selected composition and conditions for their application in the diamond-containing material treatment cycle before XRF separation, it was confirmed that the recovery of anomalously and weakly luminescent diamonds could exceed 90%, while keeping the yield of kimberlite minerals in the concentrate below 1%.

#### Keywords

diamonds, kimberlite, spectral characteristics, luminophores, modifying agent, selectivity, luminescence, separation

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## ОБОГАЩЕНИЕ, ПЕРЕРАБОТКА МИНЕРАЛЬНОГО И ТЕХНОГЕННОГО СЫРЬЯ

Научная статья

**Оптимизация состава и режима применения реагентов-модификаторов спектральных характеристик алмазов в процессе рентгенолюминесцентной сепарации****В.А. Чантурия  , В.В. Морозов  , Г.П. Двойченкова   ,  
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г. Москва, Российская Федерация* [dvoigp@mail.ru](mailto:dvoigp@mail.ru)**Аннотация**

Одним из направлений повышения эффективности процессов обогащения алмазосодержащих кимберлитов является применение технологии, способствующей извлечению слабо и аномально люминесцирующих алмазов в процессе рентгенолюминесцентной сепарации с применением люминофорсодержащих реагентов. Задача исследований заключалась в выборе рационального состава реагентов-модификаторов спектральных характеристик минералов и режима их применения. Основным условием эффективности процесса является интенсивное закрепление реагентов-модификаторов на кристаллах алмазов без аналогичного закрепления на поверхности кимберлита, что обеспечивается применением органических коллекторов оптимального состава, характеризующихся способностью как адгезионно закрепляться на поверхности алмазов, так и удерживать зерна неорганических люминофоров. Оценка эффективности закрепления люминофоров выполнена с использованием методики визиометрического анализа в УФ излучении. Оценка способности алмазов удерживать на поверхности капли или пленки коллектора с люминофорами выполнена с использованием методики измерения величины трехфазного краевого угла смачивания. Спектрально-кинетические характеристики алмазов и их извлечение в процессе рентгенолюминесцентной сепарации были определены на сепараторе «Полюс-М». В результате проведенных исследований установлена возможность целенаправленного модифицирования спектральных характеристик слабо и аномально светящихся алмазов люминофорсодержащими композициями на основе сульфидов цинка и ортосиликата цинка. С использованием критерия селективности закрепления люминофорсодержащей эмульсии на алмазах и минералах кимберлита, рассчитываемого по величинам измеренных поверхностных концентраций люминофоров на минералах, определены оптимальные соотношения между массами неорганического люминофора, органического коллектора и водной фазы применяемой эмульсии. Выбраны реагенты-диспергаторы, обеспечивающие селективное закрепление люминофоров на алмазных кристаллах. Установлены рациональные параметры состава органического коллектора. Определены границы температурного режима процесса обработки алмазосодержащего материала. В результате стендовой апробации реагентов модификаторов выбранного состава и режимов их применения в цикле обработки алмазосодержащего материала перед процессом РЛС установлена возможность достижения извлечения аномально и слабо люминесцирующих алмазов более чем на 90 % при значениях выхода кимберлита в концентрат, не превышающих 1 %.

**Ключевые слова**

алмазы, кимберлит, спектральные характеристики, люминофоры, реагент-модификатор, селективность, люминесценция, сепарация

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## Introduction

A crucial resource for enhancing the efficiency of diamond mining enterprises lies in mitigating the so-called “methodical losses” of diamonds. These losses are linked to substantial and fundamental deviations in the raw material’s parameters from the settings of the utilized equipment. In the context of X-ray luminescence separation (XRF), methodological losses of diamonds arise from their unique composition and structure, leading to the absence or, conversely, excessive concentration of lattice defects or impurities, which induce distinct X-ray luminescence patterns [1, 2].

A promising trend for improving the efficiency of X-ray luminescence separation of diamonds involves the development of technologies to modify their spectral characteristics through the use of luminophore-containing modifying agents [3, 4]. This technology is design to target the recovery of weakly and anomalously luminescent crystals, characterized by X-ray luminescence of low intensity or significantly differing from the characteristics of the majority of diamonds.

The core components of these modifying agents are luminophore-containing compositions that incorporate both inorganic and organic luminophores, each possessing characteristics conducive to the desired alterations of the kinetic parameters of a diamond’s X-ray luminescence signal [5].

The primary criterion for selecting luminophores for the implementation of this technology is their ability to endow diamonds with X-ray luminescence signal parameters that closely resemble those of natural crystals and fall within the acceptable ranges of detector settings in X-ray luminescence separators.

An important condition for enhancing the effectiveness of this developed technology [3–5] is to establish selective conditions for the attachment of modifying agents to diamond crystals. This entails maintaining a satisfactory level of luminophore attachment to diamonds while minimizing their attachment to kimberlite mineral surfaces. The realization of this condition, adopted as the main approach to address the specified objectives, is achieved through the experimentally supported selection of organic collector components included in the modifying agents. These collectors are characterized by their capacity to be selectively adhered to the diamond surface while retaining inorganic luminophore grains within their structure. To determine the selectivity of luminophore attachment at the surfaces of diamonds and kimberlite, a method of visiometric analysis has been developed [4].

The necessary stability of diamond – collector – luminophore aggregates is achieved through hydrophobizing treatment of inorganic luminophores and by selecting the composition of organic fluids used as collectors [6]. The assessment of the adhesive ability of a collector to the diamond surface, which determines the ability of diamonds to retain the luminophore-containing composition on their surfaces, is conducted using the technique of measuring the three-phase limiting wetting angle in the system composed of mineral – collector drop – aqueous medium [7].

The ultimate objective of this research was to select the parameters of modifying agents and the conditions for their application that ensure the required selectivity in the X-ray luminescence separation process. This goal was attained by selecting rational agent compositions applicable for modifying the characteristics of the main types of non-extractable diamonds. This involves determining the composition and mass ratios of luminophores, collector and aqueous phase, identifying the composition of the organic collector, and choosing selective attachment regimes for luminophores on diamond crystals. This included the use of dispersing agents for the organic phase and agents to control collector attachment to kimberlite minerals.

## Research methods

The treatment of diamond-containing kimberlite products with modifying agent was carried out using a specialized apparatus designed and manufactured with the support of the Russian Science Foundation under Grant No. 21-17-00020.

The intensity of luminophore attachment to diamonds was determined by assessing their surface concentration. This measurement was carried out using both luminescence and combined (ultraviolet-visible light) microscopy techniques, allowing for observation and registration of images of the elements within a luminophore-containing composition through the utilization of the photoluminescence effect [8, 9]. In this particular study, a “Micromed 3 LUM” luminescent microscope was employed.

The impact of control agents on the hydrophobic and oleophilic properties of the surfaces of both diamonds and hydrophobic minerals in kimberlite was evaluated through the measurement of limiting wetting angles [10]. Initially, the mineral surfaces were treated with the examined aqueous system, followed by the application of an organic substance droplet to the treated surface. The addition of the aqueous phase increased the level of the water-air

interface. Next, the limiting wetting angle and droplet size were measured within the mineral – collector drop – aqueous phase system.

These measurements were conducted using an “OCA 15EC Package 1” unit with an SD-DM direct dosing module. The measurement results were processed using the SCA 20 software package.

The efficiency of luminophores attachment to the surface of diamonds and kimberlite minerals was assessed based on images of luminescence produces by the examined objects under ultraviolet radiation. This assessment was carried out using a UVC-254/365 instrument equipped with UV light sources emitting at wavelengths of 254 and 365 nm. The obtained images were subjected to visimetric analysis, allowing for the estimation of luminophore concentration and distribution characteristics on the surface of the analyzed samples [2, 4].

To determine the spectral and kinetic characteristics of diamonds and kimberlite, as well as the recoverability of diamonds, a portable X-ray luminescence separator “Polyus-M” was employed. This equipment’s capabilities aligned closely with those of industrial X-ray luminescence separators [11, 12]. The built-in analog-to-digital registration system of the “Polyus-M” separator facilitated the separa-

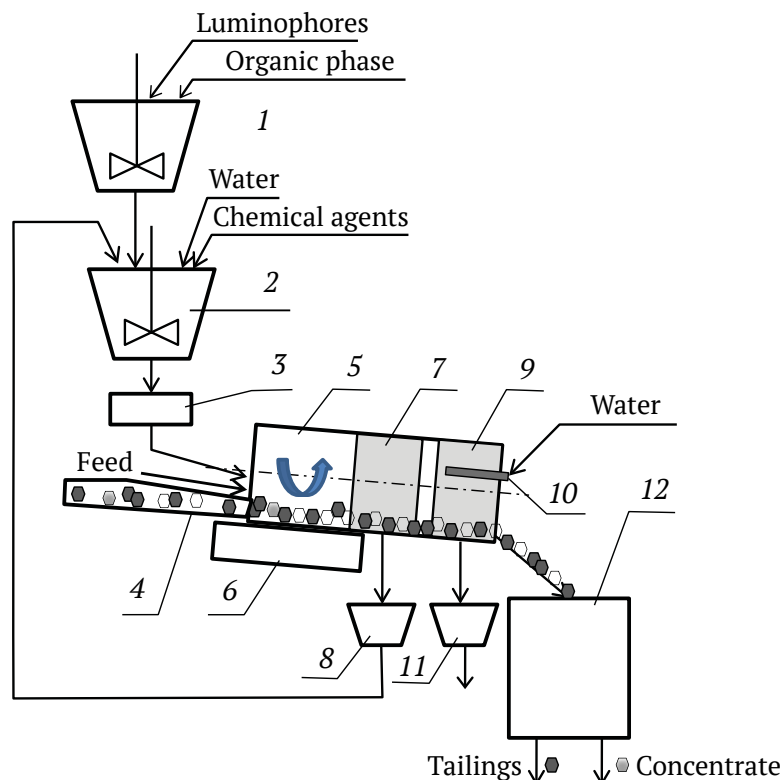
tion process within the “selective” regime, which involved the use of kinetic characteristics of the X-ray luminescence signal, including the convolution  $S_V$ , attenuation time constant  $\tau_{att}$ , amplitude of the slow component  $A_{SC}$ , amplitude of the fast component  $A_{FC}$ , and the ratio of amplitude components  $K_A$  [4, 12].

## Findings and Discussion

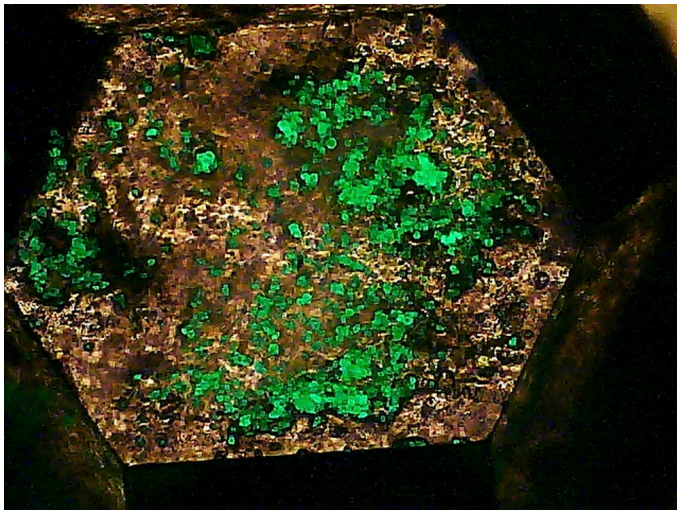
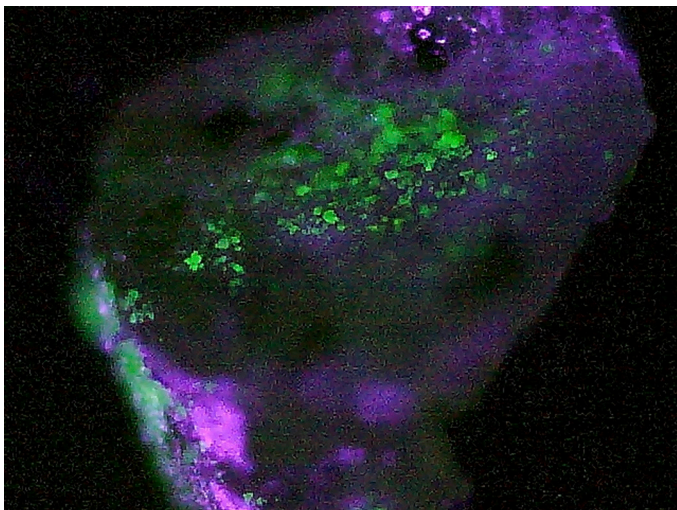
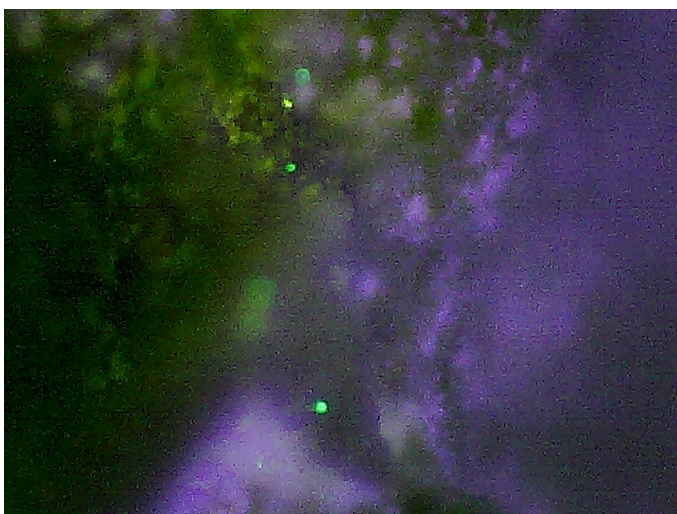
### 1. Justification of process parameters for applied luminophores and compositions

One notable aspect of the research was the use of a specialized laboratory setup that performed the tasks of processing diamond-containing material with a modifying agent, separating the conditioned emulsion, and washing the treated material prior to the X-ray luminescent separation (XRF) operation (Fig. 1).

The use of this setup enables the processing and separation of diamond-containing material under conditions closely resembling industrial settings. The experimental methodology involved treating a mineral mixture in an emulsion of a modifying agent for 1 min, washing it with water for 30 s, subsequent drying, visimetric analysis, and capturing spectral and kinetic characteristics using the “Polyus-M” separator.



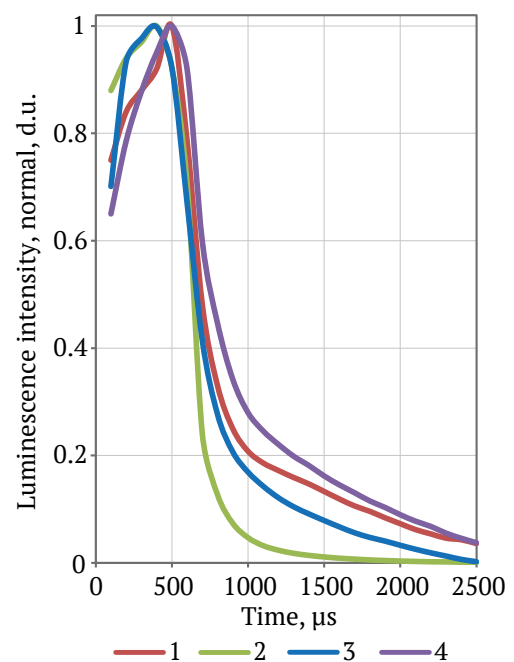
**Fig. 1.** Diagram of the setup for researching the technology of preparing diamond-containing products for the XRF process using modifying agents, where 1 – composition preparation unit; 2 – emulsion preparation unit; 3 – emulsion heating device; 4 – loading device; 5 – unit for diamond-containing material treatment with emulsion; 6 – roller drive; 7 – perforated section for removal of conditioned emulsion; 8 – emulsion receiver; 9 – perforated section for separation of washing water; 10 – distributor of washing water; 11 – receiver of washing water; 12 – X-ray luminescent separator

*a**b**c*

**Fig. 2.** Images in combined illumination of the surface of investigated minerals with attached luminophore (luminophore in green): *a* – synthetic diamond, *b* – natural diamond, *c* – kimberlite grains

The employed setup ensures effective contact between the emulsion and the diamond surface, allowing for the secure fixation of the luminophore composition on it. Our examination of the distribution and attachment of luminophores to the surface of diamond crystals, carried out using the Micromed-3-Lum microscope, revealed that the most pronounced fixation of luminophores was observed in the regions of crystal irregularities, both on synthetic and natural diamonds (Fig. 2, *a, b*). On the surface of kimberlite minerals, we observed the accumulation of luminophores at specific points, attributed to the fixation of an organic collector on naturally hydrophobic minerals (2, *c*).

The primary technological criterion for selecting of luminophore and collector compositions was their ability to confer the necessary spectral and kinetic characteristics upon diamonds for detection. The degree of resemblance between the waveform of the X-ray luminescence signal and that of a natural diamond served as the optimality criterion for a luminophore-containing composition. This criterion is illustrated in the graphs in Fig. 3, which demonstrate that the use of modifying agents with different composition (MLA-1, based on FL-530, and MLA-3, based on E-515-115) results in distinct shapes of the kinetic curves of the X-ray luminescence signal. Notably, within the conditions under consideration, the obtained characteristics closely resemble those of naturally recovered diamonds.



**Fig. 3.** Spectral and kinetic characteristics of diamonds before and after treatment: *1* and *2* – initial normal and anomalously luminescent diamonds, respectively; *3* and *4* – anomalously luminescent diamonds after treatment with modifying agents MLA-1 and MLA-3, respectively



The selection of luminophores for the studied compositions under study considered the need to alter the spectral characteristics of both types of non-extractable diamonds (weakly and anomalously luminescent). Previous research had indicated the promising potential of luminophores based on zinc orthosilicate, zinc sulfides, and cadmium sulfides for this purpose [6]. In this study, our objective was to validate and assess the effectiveness of the selected modifying agent compositions for the aforementioned categories of non-extractable diamonds.

The results of our investigations into the influence of the used luminophore compositions on the resulting spectral and kinetic characteristics of diamonds are presented in Table 1 and Fig. 4. These findings allowed us to assess the technological feasibility and efficiency of using the main types of modifying agents in the diamond-containing material treatment process preceding the X-ray luminescent separation procedure.

As evident from the provided data, in the case of weakly luminescent diamonds, the best outcomes were observed with the luminophore compositions of

modifying agents MLA-3 and MLA-4, both based on zinc sulfides. This is supported by the diagram in Fig. 3, which indicates that the resulting spectral and kinetic characteristics of weakly luminescent diamonds underwent a significant shift towards the detection range. This shift was attributed to the increased amplitudes of the fast and slow components.

The most favorable outcomes for anomalously luminescent diamonds were observed for MLA-1 and MLA-2 agents (based on zinc orthosilicate). However, the resulting signal form diamonds treated with the MLA-1 agent, particularly concerning the ratio of fast and slow components  $A_{SC}$  weakly luminescent diamonds, approaches the boundary of the detection zone (see Fig. 4, line 4).

In scenarios where both types of diamond crystals are simultaneous present in the initial diamond-containing product, the MLA-2 and MLA-3 agents prove to be the most effective for the purposeful modification of diamond luminescent properties. These agents endow the diamonds with spectral and kinetic characteristics that fall within the identification zone of the the detection system (see Fig. 4).

Table 1

Change in spectral and kinetic characteristics of diamonds resulting from treatment with modifying agents of different composition

No.	Mineral	Component	Before treatment	After treatment	Increase	$K_A$ before treatment	$K_A$ after treatment
<b>MLA-1 (FL-530-G3 in CCHGO and BF)</b>							
1	Weakly luminescent diamond	$A_{SC}$	109	574	465	3.88	1.27
		$A_{FC}$	423	730	307		
2	Anomalously luminescent diamond	$A_{SC}$	287	688	401	21.01	9.23
		$A_{FC}$	6030	6353	323		
<b>MLA-2 (FL-530-G3 and anthracene in a ratio of 25-40 : 1 in CCHGO and BF)</b>							
3	Weakly luminescent diamond	$A_{SC}$	102	545	443	4.20	2.01
		$A_{FC}$	428	1095	667		
4	Anomalously luminescent diamond	$A_{SC}$	287	810	523	21.25	8.66
		$A_{FC}$	6100	7011	911		
<b>MLA-3 (E-515-115-G5 in CCHGO and BF)</b>							
5	Weakly luminescent diamond	$A_{SC}$	100	488	388	4.00	4.80
		$A_{FC}$	400	2340	1940		
6	Anomalously luminescent diamond	$A_{SC}$	347	720	383	17.64	10.18
		$A_{FC}$	6120	7330	1210		
<b>MLA-4 (FK-110-G5 in CCHGO and BF)</b>							
7	Weakly luminescent diamond	$A_{SC}$	110	455	345	3.83	4.29
		$A_{FC}$	421	1954	1533		
8	Anomalously luminescent diamond	$A_{SC}$	326	647	321	18.53	10.83
		$A_{FC}$	6040	7008	968		
<b>MLA-5 (FK-1 in CCHGO and BF)</b>							
9	Weakly luminescent diamond	$A_{SC}$	109	425	316	3.65	5.09
		$A_{FC}$	398	2163	1765		
10	Anomalously luminescent diamond	$A_{SC}$	339	695	256	17.55	10.10
		$A_{FC}$	5950	7020	1070		

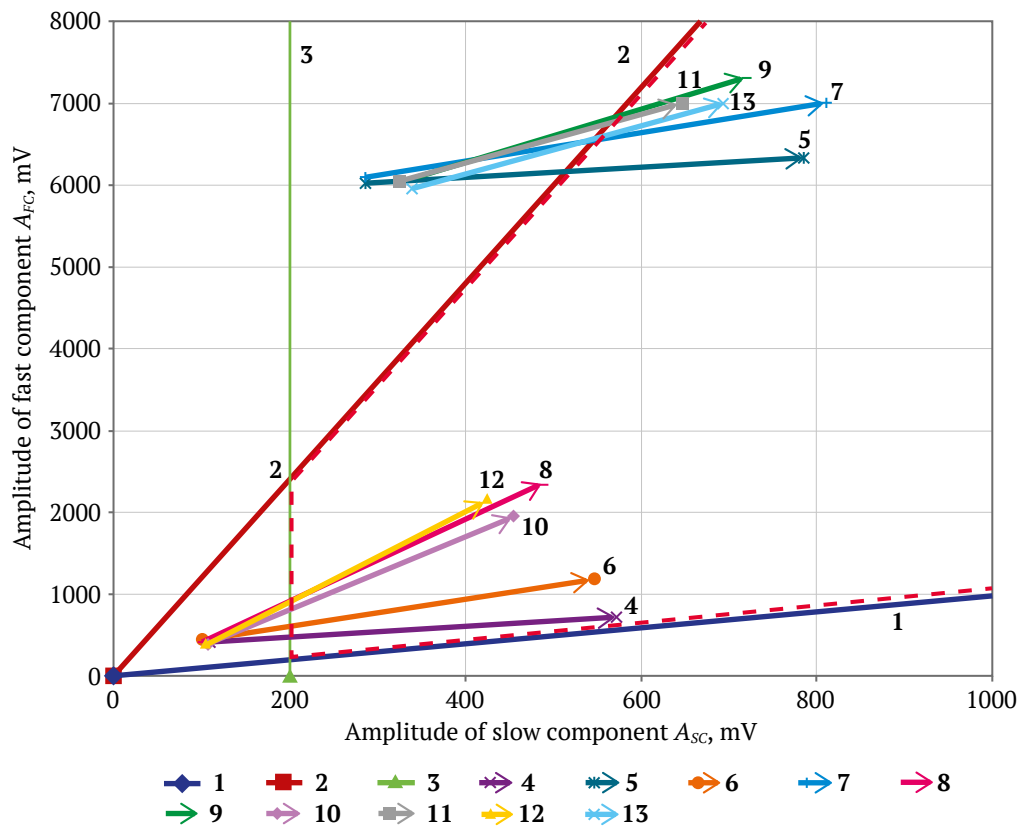
A separate series of studies was dedicated to experimentally substantiate the optimal fractional composition of an organic collector, which would ensure the maximum attachment of a luminophore-containing composition to diamonds. In order to unveil the underlying patterns of how an organic collector with a fractional composition based on CCHGO and BF influences the efficiency of luminophore attachment and aid in the reasonable selection of a chemical agent composition, a set of physicochemical investigation was carried out. This analysis included the measurement of the adhesive activity of the collector as the primary influencing factor. To assess and compare adhesion activity, the results of limiting wetting angle measurements in the diamond – collector drop – aqueous phase system were employed.

An analysis of the research findings revealed that an increase in the proportion of BF in the collector leads to an elevation in the value of the limiting wetting angle, signifying heightened adhesive activity. However, despite this increase in the limiting wetting angle, when the mass fraction of BF in the compound exceeds 15%, there is a decrease in the size of the

collector droplet retained on the diamond surface after the liquid level rises (Table 2).

This result can be mainly attributed to the following factors: a decrease in the viscosity of the collector, resulting in a reduction of the hysteresis effect, and a decrease in density, leading to an increase in detachment force as the liquid level rises.

The extreme pattern of luminophore fixation intensity dependence on the mass fraction of BF in the organic collector correlates with a similar dependence of the size of the retained collector droplet on the mineral surface on the compound composition (see Table 2). The likely explanation for this correlation is the pivotal role played by the amount of organic collector attached to a diamond surface. Pure CCHGO exhibits lower adhesion activity to a diamond surface compared to compounds containing BF, which results to a lower quantity of fixed compound and, consequently, a reduced amount of luminophore on the diamond. Increasing the proportion of BF in the collector beyond 15% leads to reduced detachment from the diamond surface. This reduction can be attributed to the increasing density difference relative to the aque-



**Fig. 4.** Diagram showing changes in amplitude spectral and kinetic characteristics of non-extractable diamonds after treatment with luminophore-containing modifying agents: 1 – lower boundary of the positive diamond identification area based on  $K_A$ ; 2 – upper boundary of the positive diamond identification area based on  $K_A$ ; 3 – boundary of the positive diamond identification area based on  $A_{SC}$ ; 4, 6, 8, 10, 12 – shifting characteristics of weakly luminescent diamonds; 5, 7, 9, 11, 13 – shifting characteristics of anomalously luminescent diamonds after treatment: 4, 5 – MLA-1; 6, 7 – MLA-2; 8, 9 – MLA-3; 10, 11 – MLA-4; 12, 13 – MLA-5; [red dashed box] – area of positive identification (detection)

ous phase (with a density of BF at 0.867 g/cm<sup>3</sup>, while CCHGO has a density of 0.965 g/cm<sup>3</sup>, and water has a density of 1 g/cm<sup>3</sup>), as well as a decrease in viscosity (by 45–58%), which reduces the hysteresis stability of mineral – collector aggregates in a turbulent medium.

**2. Selection of conditions for increasing the selectivity of luminophore attachment to diamonds and kimberlite mineral surfaces**

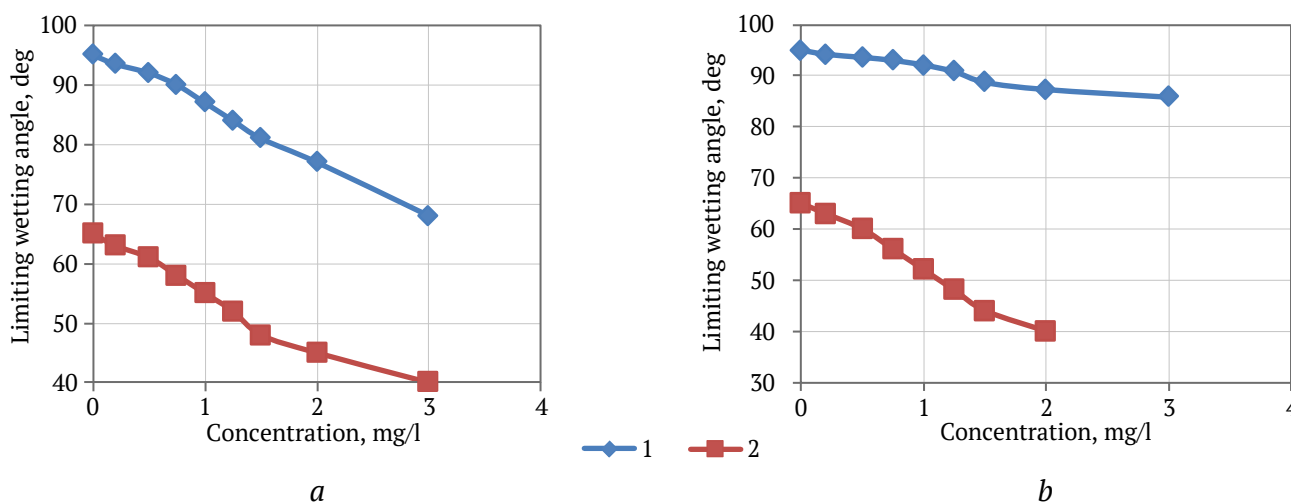
To address the challenge of increasing the selectivity of luminophore attachment to diamond surface, we conducted a study involving agents from various groups, including polyphosphates, silicates, natural organic polymers, and lignosulfonates. These agents are known to hinder the fixation of apolar and weakly polar reagents on hydrophobic minerals [13, 14]. We also carried out experimental investigations to substantiate and select of parameters of the aqueous phase in the modifying agent emulsion (pH of the medium, mineralization, Eh) to facilitate the more selective fixation of apolar and weakly polar reagents on minerals [15, 16].

In the current research, the use of surfactants (alkyl sulfates, alkyl sulfonates) for dispersing the organic phase of the modifying agent is grounded in their mechanism of action on the properties of the diamond surface. According to principles in solution physicochemistry, heteropolar surfactant molecules adsorb at the interfaces of diamond-water and collector-water, aligning their apolar radicals with the hydrophobic phase and their polar groups with the aqueous phase. This results in a reduction of interfacial surface tension at both solid-liquid and water-collector interfaces. As per Young's equation [17] this leads to a decrease in the limiting wetting angle, indicating that the solid surface becomes better wetted by the surfactant solution compared to pure water. Experimental evidence supported this effect in the mineral – organic collector – aqueous phase system, where the additions of alkyl sulfonates was found to reduce the hydrophobicity of a mineral surface (Fig. 5, a) [18]. In contrast, for hydrophilic minerals, due to the reverse orientation of surfactant

Table 2

**Variation of physicochemical characteristics and efficiency of organic collector attachment to diamonds with varying collector fractional composition**

No.	BF fraction in compound collector	Limiting wetting angle, deg	Density, g/cm <sup>3</sup>	Dynamic viscosity measured, mPa s, 24 °C	Average size of a drop on diamond, mm	Surface concentration of luminophore, %
1	0 (CCHGO only)	85	965.0	167.0	1.5	16.9
2	5	87.5	961.1	154.5	1.65	21.7
3	10	90.0	957.2	133.0	1.62	24.4
4	15	92.0	951.3	110.3	1.33	24.5
5	20	93.3	947.4	92.1	0.96	22.1
6	25	94.3	942.5	72.0	0.75	20.4
7	30	95.0	937.6	64.1	0.65	18.6
8	100	97.5	867.0	3.64	0.4	15.5



**Fig. 5.** Influence of alkyl sulfate (a) and hexametaphosphate (b) concentrations on limiting wetting angles of diamond (1) and phlogopite (2)



molecules, there is a possibility of surface hydrophobization [19]. This is a detrimental factor as it increases the oleophilicity of kimberlite minerals, thereby promoting the attachment of the luminophore-containing composition to them.

Polyphosphates exert a distinct influence on the mineral – aqueous phase – collector disperse system. The basis of polyphosphates action is their attachment to the surface of naturally hydrophilic minerals through a cation exchange mechanism, forming strong chemical bond with divalent cations (e. g., calcium, iron, magnesium) of a mineral [20, 21]. The effective action of sodium polyphosphate can also be attributed to the intensive adsorption of polyphosphate ions at the boundary of silicon-oxygen tetrahedra layers (e.g., natural hydrophobic layered aluminosilicates). This is due to the structural and size similarity between tripolyphosphate anions and the silicon-oxygen tetrahedra of clay minerals [22]. Additionally, polyphosphates enable the hydrophilization of phosphate mineral’s surfaces.

The results of the studies revealed a fundamentally different effect of hexametaphosphate on the surface properties of minerals compared to alkyl sulfates. While there is a much smaller reduction in the value of the limiting wetting angle on diamonds, an intense hydrophilization of the phlogopite surface is observed instead (Fig. 5, b). Notably, the addition of hexametaphosphate does not lead to hydrophobization and an increase in oleophilicity of naturally hydrophilic kimberlite minerals (there is no detachment of organic liquid from the minerals).

Organic polymers, such as carboxymethylcellulose (CMC), exhibit significant over both diamond

surfaces and hydrophobic kimberlite minerals. This results in a substantial decrease in the limiting wetting angle (by 10–23°) on these minerals as the agent concentration increases to 3 g/L (Fig. 6, a). Chemical agents from the alkylphosphonate group show promise. Limiting wetting angle measurements indicate that within the concentration range of 0 to 1 g/L, these chemical agents (e.g., oxyethylene diphosphonic acid – OEDP) substantially reduce the hydrophobicity (oleophilicity) of phlogopite, with a relatively smaller change in the condition of the diamond surface (Fig. 6, b). This characteristic can be attributed in many ways to the formation of coordination bonds between the agent anions and Ca and Mg cations in the crystal lattice of the minerals.

The results obtained lead to the conclusion and confirmation on the feasibility of employing dispersing agents that lack a prominent apolar radical in their structure and interact with kimberlite minerals through the formation of chemical or coordination bonds.

Laboratory testing of the selected dispersing agents demonstrate their effectiveness. The optimal outcomes, marked by the highest selectivity of luminophore attachment at an agent consumption of 1.5 g/L, were achieved with oxyethylene diphosphonic acid (OEDP), hexametaphosphate, metasilicate, and sodium tripolyphosphate (Table 3).

The attachment selectivity was calculated using the following equation:

$$SLF_{DK} = \frac{C_{LD}}{15} - \frac{C_{LK}}{3}.$$

The designations of the variables in the equation are given in Table 3.

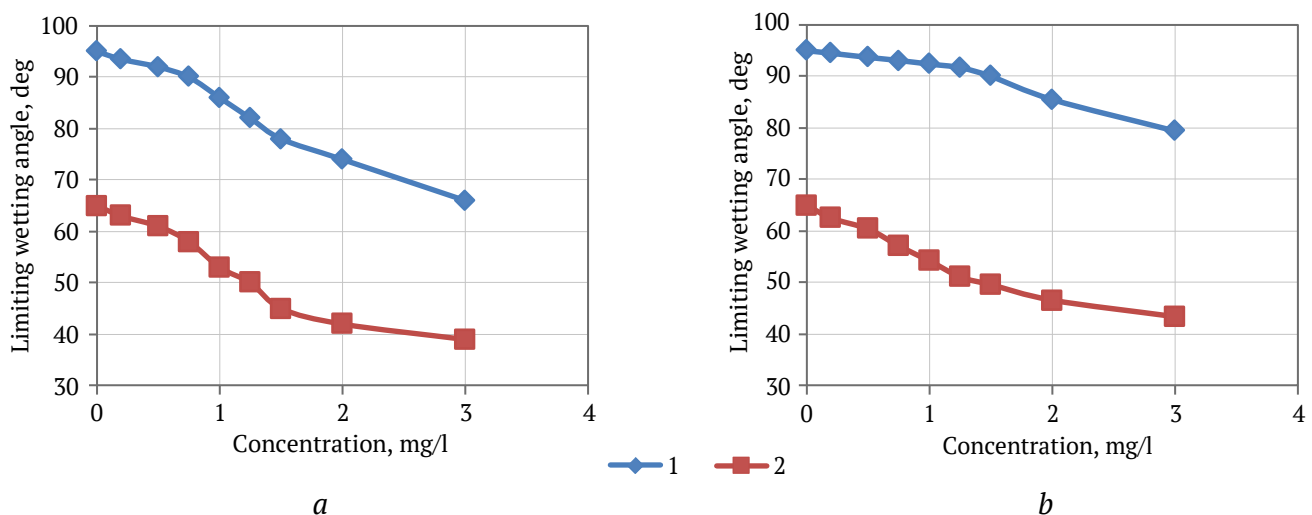


Fig. 6. Influence of CMC concentration (a) and OEDP concentration (b) on the limiting wetting angle of diamond (1) and phlogopite (2) in the aqueous phase of the modifying agent emulsion

**3. Selection of temperature conditions for treating diamond-containing products with modifying agents**

The temperature of the medium used in the process of preparing and treating diamond-containing material with modifying agent significantly influences the intensity and selectivity of luminophore attachment to the surfaces of both diamonds and kimberlite minerals. This influence is primary due to alterations in the physical and chemical properties of the complex composition organic liquids, which are petroleum-based products [23]. The medium's temperature impacts various aspects, including interface energy and wettability of minerals in dispersed systems, the viscosity properties of a collector, its ability to spread over surface, and the stability of attachment in turbulent media [24, 25].

In order to determine the optimal temperature conditions, studies were conducted involving the

treatment of diamond-bearing kimberlite products with emulsions of modifying agents, employing petroleum products of varying fractional composition as collectors.

The efficiency of luminophore attachment was assessed based on the surface concentration of the attached luminophors, which was determined using visimetric methods. Unlike the studies described in [17], the treated diamond-mineral product was subsequently subjected to X-ray luminescence separation using a "Polyus-M" separator. The study results confirmed that increasing the treatment temperature from 15 °C to 40 °C enhanced luminophore attachment to both diamonds and kimberlite minerals for all organic collector compositions (Table 4). However, it was observed that when the medium temperature exceeded 40 °C, the efficiency of luminophore attachment to diamonds slightly decreases.

Table 3

**Impact of dispersing agents on surface concentration and selectivity of luminophore attachment to the surface of diamonds and kimberlite minerals**

No.	Dispersing agent	Concentration of luminophore on diamond surface ( $C_{LD}$ ), %		Concentration of luminophore on kimberlite mineral surface ( $C_{LK}$ ), %		Attachment selectivity, $SLF_{DK}$ , decimal quantity	
		Agent concentration, g/l					
		0	1.5	0	1.5	0	1.5
1	Tripolyphosphate	38	21.8	7.5	1.5	0.03	0.95
2	Hexametaphosphate	39.3	23.5	7	1.6	0.29	1.03
3	OEDP (etidronic acid)	38.3	25.5	7.1	1.9	0.19	1.07
4	Corn starch	38	20.4	6.9	2.2	0.23	0.63
5	CMC	37.4	18.5	6.7	1.8	0.26	0.63
6	Sulfonol	37.8	19.5	7.1	1.8	0.15	0.70
7	Sodium metasilicate	39.4	22.5	7.9	2.1	-0.01	0.80
8	Lignosulfonate	38.9	20.3	7.6	2.2	0.06	0.62

Table 4

**Results of visimetric analysis of the temperature effect on the efficiency of luminophores attachment to the surface of diamonds and kimberlite minerals**

No.	Composition of organic collector	Temperature, °C					
		20	25	30	35	40	45
		Covering of diamond surface with luminophore, %					
3	CCHGO (85%) BF (15%)	17.4	28.4	33	34.1	36.2	35.7
		Kimberlite minerals surface covering with luminophore, %					
6	CCHGO (85%) BF (15%)	2.4	2.6	2.8	2.9	3.2	3.5
		Attachment selectivity, conditional units.					
9	CCHGO (85%) BF (15%)	0.43	1.03	1.27	1.31	1.35	1.21
		Diamond recovery, %					
12	CCHGO (85%) BF (15%)	80	85	90	95	95	95
		Kimberlite recovery, %					
15	CCHGO (85%) BF (15%)	1.0	1.1	1.3	1.3	1.3	1.3

Notes: CCHGO is catalytic cracking heavy gas oil; BF is bunker fuel or technical grade diesel fraction.

The analysis of the data for calculating luminophore attachment selectivity indicates that the highest selectivity in attaching luminophore to both diamonds and kimberlite occurs when the treatment temperature ranges from 30 to 45 °C. The analysis of the results from X-ray fluorescence separation of the diamond-containing kimberlite product confirmed the findings from the visimetric analysis and demonstrated the feasibility of achieving maximum diamond recovery within the temperature range of 30 to 45 °C (see Table 4) without a significant increase in kimberlite recovery. Based on these results, it is recommended to conduct the treatment of diamond-containing products at elevated temperature.

#### 4. Selecting the agent emulsion component composition for modifying spectral and kinetic characteristics of diamonds

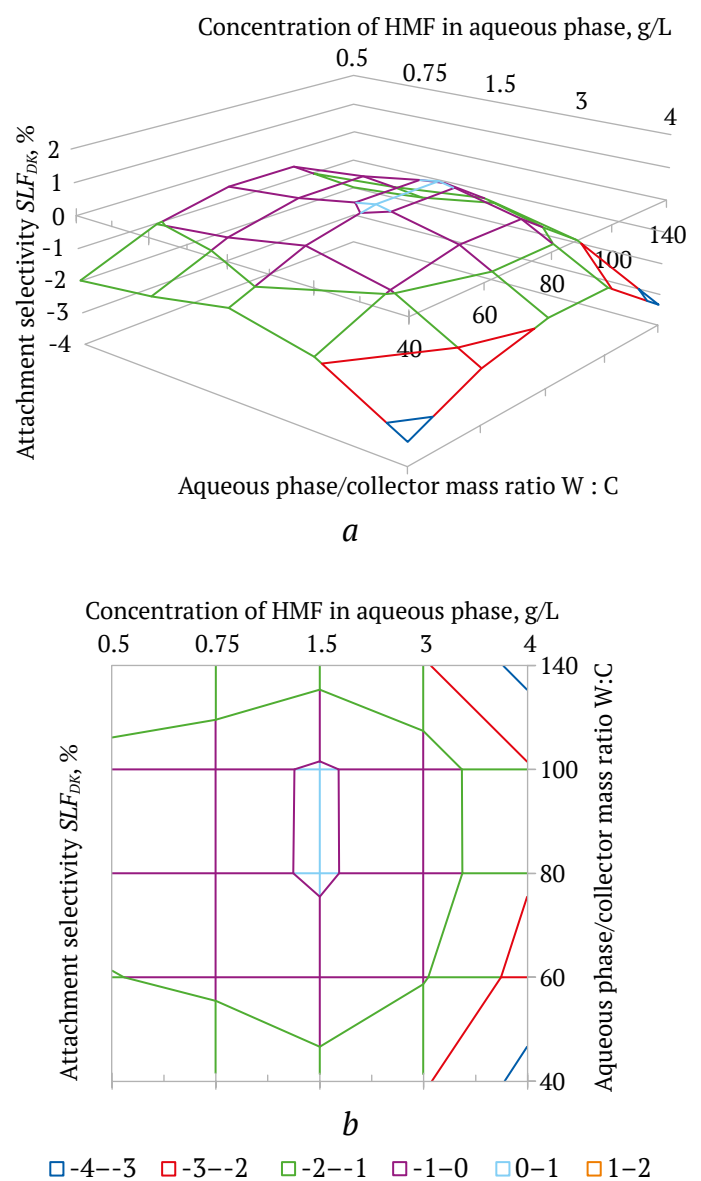
The key technological parameters of the selective modification regimes for the spectral and kinetic characteristics of diamonds include the following characteristics of the modifying agent: the luminophore -to- collector ratio; the collector -to- aqueous phase ratio, and the concentration of the dispersing agent. Recognizing the potential interplay among these factors and the need to identify the optimal modifying agent composition, a second-order factorial experiment method was employed. The initial factorial experiment matrix (second-order orthogonal central composite design) was constructed following standard procedures, with the inclusion of zero and star points [26]. This experimental design encompassed 15 trials.

Mathematical analysis of experimental results, conducted in Excel, facilitated the determination of the region with optimal relationships between the components of the MLA-3 modifying agent within the emulsion process. A water : collector ratio of 90:1. Was chosen as optimal, alongside an optimal concentration of 1.5 g/L for HMF (Fig. 7). The collector-to-luminophore ratio was set at 9:1. These selected parameters closely align with values derived from prior laboratory studies and used as coordinates at the center of the matrix (60:1, 10:1, and 1.5 g/L).

The results demonstrated that the application of an aqueous emulsion of modifying agents, namely MLA-1 based on FL-530-G3-G5 luminophore and MLA-3 based on E-515-115-G5 luminophore, with the selected parameters for the component composition of the modifying agent emulsion using sodium hexametaphosphate as a dispersing agent, brings about the desired alterations in the spectral and kinetic characteristics of weakly and anomalously luminescent diamonds (Table 5).

The findings from tests carried out at a Polyus-M separator showed the high efficiency of the developed modifying agents and treatment protocols for diamond-kimberlite products. This allowed for the recovery of 80–95% of weakly and anomalously luminescent diamonds into the X-ray luminescence separation concentrate, without a significant increase in the recovery of kimberlite into the concentrate (see Table 5).

Thus, the research results validate the effectiveness of the chosen technology for preparing diamond-containing products for the XRF process and enable the determination of the optimal composition of a modifying agent and the parameters for the treatment of diamond-containing kimberlite products.



**Fig. 7.** 3D graphs (a) and cross-sections (b) depicting the relationships between selectivity of luminophore attachment ( $SLF_{DK}$ ) and the mass ratio of aqueous phase to the collector (W:C) and hexametaphosphate (HMF) concentration

Table 5

**Testing results of luminophore-based modifying agents FL-530 (MLA-1) and E-515-115 (MLA-3) for diamond-bearing kimberlite products**

No.	Modifying agent composition	Mineral	Sv	$\tau_z$ , ms	$A_{SC}$ , mV	$A_{FC} - A_{air}$ , mV	$K_A$	Recovery, %
1	Without luminophores	Diamond (w)	0.15	4.3	120	564	5.7	40
		Diamond (an)	–	0.1	not measured	1,022	$\geq 50$	20
		Kimberlite	–	–	not measured	<50	–	0.75
2	MLA-1 (FL-530 + CCHGO + BF)	Diamond (w)	0.22	1.6	329	1,216	4.7	80
		Diamond (an)	0.17	0.6	275	1,469	6.3	90
		Kimberlite	–	–	not measured	<50	–	0.9
3	MLA-3 (E-515-115-G5 + CCHGO + BF)	Diamond (w)	0.26	2.3	258	1105	5.0	95
		Diamond (an)	0.18	0.5	168	1465	9.9	90
		Kimberlite	–	–	not measured	<50	–	0.5
4	Parameters of XRF selective regime	Diamond	0.1–1	0.1–10	More than 100	–	0.2–12	Recovery

Notes: w, an – are weakly and anomalously luminescent diamonds, respectively,  $A_F$  is amplitude of fast component of air X-ray luminescence signal (background); not measured – values were not measured.

### Conclusions

The effective composition and application conditions of modifying agents in the preparation of diamond-containing material for X-ray luminescence separation have been determined based on the research findings.

The feasibility of purposeful modification of the spectral characteristics of weakly and anomalously luminescent diamonds, coexisting in diamond-containing material, has been established through the use of luminophores based on zinc orthosilicate and zinc sulfides (MLA-1 and MLA-3). These luminophores provide diamond crystals with spectral and kinetic characteristics that fall within the identification zone of the detection system.

The composition of the diamond collector (85% CCHGO and 15% BF) in the luminophore-containing compound, as well as the temperature treatment conditions (30–45 °C) for the diamond-containing product, were selected to ensure intensive and selective attachment of luminophores to the surface of diamond crystals.

The results of mathematical processing, using the criterion of luminophore-containing emulsion

attachment selectivity to diamonds and kimberlite minerals, calculated based on the measured surface concentrations of luminophores on these minerals, have allowed the determination of the optimal component ratios in the modifying agent emulsion. These ratios are as follows: water:collector = 90:1, collector:luminophore = 9:1, with a concentration of HMF at 1.5 g/l.

Dispersing agents (oxyethylene diphosphonic acid, hexametaphosphate, metasilicate, and sodium tripolyphosphate) were selected to ensure selective attachment of luminophores to diamonds through weakening the attachment of luminophores to the surface of kimberlite minerals.

The results from the tests carried out at a Polyus-M separator have confirmed the high efficiency of the modifying agents with the developed composition and application conditions for treating diamond-containing material. This process enables the recovery of low and anomalously luminescent diamonds into the X-ray luminescence separation concentrate at a level of 80–95%, without increasing the recovery of kimberlite minerals into the concentrate.

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