Modification of Diamond Crystal Luminescence Parameters Using Luminophore-Containing Emulsions

V A Chanturia¹, O E Kovalchuk¹, V V Morozov⁴, G P Dvoichenkova²³

¹Geo-Scientific research Enterprise of PJSC “ALROSA”, Chernyshevskoye Chaussee, 16, Mirny, Republic of Sakha (Yakutia), 678171, Russia
²Mirny Polytechnic Institute (branch) of North-Eastern Federal University, Oyunskogo Street, 14, Mirny, Republic of Sakha (Yakutia), 678170, Russia
³Institute of Comprehensive Exploitation of Mineral Resources of Russian Academy of Sciences, Kryukovsky Tupik, 4, Moscow, Russia, 111020, Russia
⁴National University of Science and Technology “MISiS”, Leninskiy prospekt, 4, Moscow, 119049, Russia

E-mail: oleg.kovalchuk@mail.ru

Abstract. Based on luminophore combination being close to diamond in luminescence parameters, water-organic emulsions were synthesized that modified spectral-kinetic characteristics of low-luminescent diamond crystals. The combination of luminophores was used, including an organic luminophore, anthracene, and inorganic luminophore, K-35, the spectral and kinetic characteristics of which make it possible to achieve the required luminescence values of diamonds and ensure their maximum extraction in existing diamond-containing kimberlite X-ray separation process flows. Non-polar hydrocarbons were experimentally substantiated as an organic medium for the luminophores. Mathematical processing of the obtained results was performed and relationships between the composition of the luminophore combination and kinetic characteristics of the luminescent response were determined.

1. Introduction

Based on the experience of diamond recovery plant operation, it was found that there are some types of diamond crystals that were not recoverable in existing process flows of x-ray luminescent separation of kimberlite ores [1–4]. This is due to nonstandard values of their natural fluorescence [5, 6]. A team of specialists from ICEMR RAS, MPTI (under NEFU), institutes “Yakutniproalmaz”, and GSRE of PJSC “ALROSA” performed researches and developed methods for selective diamond surface modifications to improve their spectral-kinetic characteristics for more complete diamond recovery in the existing process flows of x-ray luminescent separation [7].

The research results presented in this paper proved the possibility of using luminophores for the purposeful regulation of diamond spectral characteristics. Wide variety of luminophores, demonstrating different spectral-kinetic characteristics [8–10] suggests that applying them to the surface of diamonds allows changing their processing properties and fluorescence ability. The proposed technology enables additionally recovering non-luminous diamonds and does not require changes in the existing process flows of x-ray luminescent separation, and is characterized by the use
of cheap chemical agents, simplicity, and environmental safety. This work was carried out as part of the RAS Presidium Basic Research Program No. I.48.

2. The research subjects and objectives
Plastic indicators composed of non-polar hydrocarbons and luminophores with maximum fluorescence range of 400-550 nm were studied [11]. Such characteristics comply with the requirements for the process flow of x-ray-luminescent separation of kimberlite ores [3].

At the second stage fluorescence parameters of low-fluorescent diamonds and kimberlite minerals after treatment by luminophore-containing aqueous-organic emulsions were studied. Spectral-kinetic characteristics of the indicators and diamonds were measured using POLYUS-M laboratory X-ray fluorescence separator [12].

The main objective was the selection of luminophores and their combinations which most accurately reproduce X-ray characteristics of diamonds (in kinetic and spectral parameters), and experimental assessment of the selectivity and stability of fixing luminophore-containing emulsions to the surface of diamond and kimberlite minerals.

3. Experimental findings and their discussion
The work concept consisted in activation of non-luminous and low-luminous diamonds based on selective fixing of certain combination of luminophores to the crystal surface for increasing their recovery in the process of X-ray fluorescence separation of diamond-bearing raw materials.

At the first stage of the study, in accordance with the developed technique, luminophores were selected that most accurately comply with the X-ray fluorescence spectral parameters of natural diamonds, recoverable in standard X-ray fluorescence separation process flows.

As control parameters, the allowable value range for diamond recording in X-ray fluorescence separation process was adopted (given in Table 1).

Table 1. Parameters of diamond recording in the existing X-ray fluorescence separation process [3, 6].

| Recorded parameter                             | Allowable value range |
|------------------------------------------------|-----------------------|
| Convolution of the fluorescence response      | from 0.1 to 1.0       |
| Fluorescence time constant of damping         | from 0.8 to 12.0 ms   |
| The ratio of the fluorescence components      | from 0.5 to 12.0      |

To measure the spectral-kinetic parameters of the luminophore-containing organomineral compositions, simulators were used, having the form of polymer capsules filled with a mixture of cetane, K-35 luminophores, and scintillation anthracene.

The results obtained by measuring the spectral-kinetic characteristics of the simulators fluorescence showed that the studied luminophore compositions possess high X-ray fluorescence in cetane medium. The data presented in Table 2 show that the studied organomineral compositions of luminophores demonstrate spectral-kinetic characteristics necessary for the required modification of the diamond fluorescence. For instance, the “convolution” parameter is within the selectivity range of 0.3–0.7, and the time constant of damping is within the selectivity range of 1.8–2.8 ms. Slow component (SC) has a pulse of 1235 - 7656 mV, and the fast component (FC), 14300 - 17391 mV. The ratio of FC and SC ranges (K) from 2 to 12.1.

The next objective of the experimental studies was to assess the selectivity and stability of fixing the organic luminophores to the surface of diamond and kimberlite minerals in the ore pulp. In the experiments, a collection of minerals was used, including: diamond, pyrope, olivine, epidote. The size of the mineral grains ranged from 2 to 3 mm.
Table 2. Spectral-kinetic characteristics of simulators filled with organomineral compositions of cetane and luminophores.

| Anthracene /K-35 ratio | Convolution | Response time of damping, ms | SC mV  | FC mV  | Ks  | Indication |
|------------------------|-------------|-----------------------------|--------|--------|-----|------------|
| 1 : 9                  | 0.3         | 2.0                         | 5954   | 14300  | 2.2 | +          |
| 1 : 9                  | 0.7         | 2.8                         | 7656   | 16980  | 2.0 | +          |
| 1 : 4                  | 0.5         | 1.8                         | 4630   | 16543  | 4.1 | +          |
| 1 : 4                  | 0.5         | 1.8                         | 4454   | 16366  | 4.8 | +          |
| 1 : 1                  | 0.5         | 1.8                         | 1235   | 17243  | 12.1| −          |
| 1 : 1                  | 0.5         | 1.8                         | 1405   | 17391  | 11.8| +          |

The experimental results obtained using the POLYUS-M separator showed that the luminophore-containing emulsion based on the mixture of Anthracene organic luminophore and inorganic luminophores is adsorbed on the surface of diamond crystals in the amount that allows them to be detected in the separator working medium. But, at the same time, some of the kimberlite minerals at certain concentrations of the luminophores are also detected as diamond crystals.

To reveal the optimum conditions for the selective fixing of luminophore-containing emulsions of the studied compositions, a series of additional experiments was performed at variable concentrations and ratios of the luminophores in the organomineral compositions. Analysis of the experimental results was performed by the standard regression analysis using two-parameter linear models.

The result of the dependences analysis presented in Figure 1 indicates the close connection of the SC with the K-35 luminophore concentration (determination coefficient $R^2 = 0.86$).

Figure 1. The SC fluorescence intensity on diamond as function of the concentration of anthracene (a) and K-35 (b) in cetane.

Taking into account the experiment objective, the FC to SC ratio as function of the luminophores ratios in cetane was analyzed. The preset FC to SC ratios (less than 12) are achieved at K-35 to anthracene ratio above 30-35 (Figure 2).
Figure 2. Dependences of FC to SC ratio on the K-35 to anthracene ratio in the emulsion organic phase: 1 - for diamond, measured in the separator; 2 - for diamond, calculated taking into account its own spectral characteristics; 3 - for the accompanying minerals, measured in the separator; 4 - boundary ratio for the condition of diamond detection based on FC to SC ratio.

To assess the effect of luminophore on various types of diamonds, analysis of the study results using the corrected FC and SC values, obtained by subtracting the own diamond response FC and SC intensity values from these components, obtained by measuring the fluorescent parameters of a diamond treated with the luminophores. The corrected FC to SC ratio (with subtracting own diamond fluorescence) is lower than the non-corrected ratio at the same ratios of the luminophores (Figure 4).

Mathematical treatment of the experimental results by the regression analysis (Matlab) using two-parameter linear dependence of the fluorescence response FC/SC ratio on the ratio of luminophores showed that achieving the FC to SC ratio values, at which the accompanying minerals are not extracted into the concentrate (FC/SC ≤1), requires maintaining the concentration of K-35 luminophore in the emulsion organic phase above 2-3 mg/ml and the ratio of the luminophores above 30-35.

The results obtained show the possibility of creating luminophores-containing compositions with spectral-kinetic characteristics close to those typical for natural diamonds.

4. Conclusions
Experimental studies have been performed, results of which substantiate the method of modifying spectral-kinetic characteristics of diamonds by luminophore-containing emulsions. Based on the method, the effectiveness of applying the combination of organic (anthracene) and inorganic (K-35) luminophores in cetane was established at different ratios of the components. Using POLYUS-M separator enabled determining the spectral-kinetic characteristics of the luminophores and their combinations (at different ratios) fluorescence on the surface of diamond and the kimberlite minerals. The research findings showed the possibility of achieving FC to SC ratios in the fluorescence response required for diamond detecting, by treating the minerals with the mixture of luminophores at K-35 to anthracene ratio above 30-35. It show the possibility of creating luminophores-containing compositions with spectral-kinetic characteristics close to those typical for natural diamonds.

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