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«HIGH-ENERGY EMULSION INDUSTRIAL EXPLOSIVES WITH INCREASED WATER-RESISTANCE»

Urgency of the research

Extensive exploitation of natural resources is a continuous process driven by the economy's ever-growing demand for raw materials, which has led to a several-fold increase in the extraction of mineral resources by blasting methods and, consequently, to growth in the production and use of industrial explosives (hereinafter, IEs). According to the Annual Report «On the Activities of the Federal Service for Environmental, Technological and Nuclear Supervision in 2024», the annual quantity of IEs manufactured onsite at the point of use from non-explosive components (typically ammonium nitrate as the oxidizer and liquid petroleum products as the fuel) amounts to 2,1 million tonnes, which is one of the significant drivers of increasing anthropogenic pressure on the environment and the deterioration of its condition.

Contrary to the common belief that environmental pollution from the use of IEs, including ammonium-nitrate-based ones (hereinafter, AN-IEs), occurs only after detonation, contamination begins as soon as the column of an uncased AN-IE bulk charge formed during mechanized loading comes into contact with the rock and/or borehole waters. Charging water-filled boreholes is not uncommon and, by some estimates, may account for a third of all drilling-and-blasting (hereinafter, D&B) operations. The rate at which water-soluble components of AN-IEs are leached depends on a number of technological factors during D&B: the time, temperature, and area of contact between the charge and water; the level and filtration rate of the water and the height of the water column in the borehole; the degree of fracturing of the rock mass; the mineral composition of the rock in contact with the AN-IE charge and etc. However, the dominant factor governing the migration of water-soluble AN-IE components into the water in contact with the charge is the explosive's formulation, which determines its water-resistance.

In addition to adverse environmental impacts, contamination of mined ores and rock materials resulting from the use of AN-IEs – due to the partial loss of ammonium nitrate from the charges – creates problems in the processing of certain minerals. For example, experience in mining and processing apatite-nepheline ores shows that nitrate (NO_3^-), nitrite (NO_2^-), and ammonium (NH_4^+) ions entering the flotation pulp with the ore and recycled water adversely affect froth flotation because these species accumulate in the process medium. According to analyses carried out by the Laboratory of Flotation Reagents of the Mining Institute of the Kola Science Center of the Russian Academy of Sciences, the concentrations of nitrogen compounds in the recycled water of a mining enterprise located in Murmansk Oblast averaged in 2020 as follows: 44 – 75 mg/dm³ NO_3^-, 0,7 – 3,5 mg/dm³ NO_2^-, and 1 – 3 mg/dm³ NH_4^+. This led to a decrease in the yield of the target product (apatite–nepheline concentrate) from 98 % to 93 %, which is economically significant at the enterprise's scale of production.

The Constitution of the Russian Federation enshrines the following provisions: «everyone shall have the right to a favorable environment, reliable information about its condition…» (Chap. 2, Art. 42), and «everyone shall be obliged to preserve nature and the environment, and to treat natural wealth with care» (Chap. 2, Art. 58). The rational use of natural resources and the reduction of environmental pollution, including from industrial activities, are established in the Russian Federation by Federal Law No. 7-FZ of 10 January 2002 «On Environmental Protection» (Chap. 1, Art. 3) and by Presidential Decree No. 400 of 2 July 2021 «On the National Security Strategy of the Russian Federation» (Chap. 4, Art. 83, para. 7). Legal regulation of relations in the field of environmental management is set forth in the provisions of Federal Law No. 74-FZ of 3 June 2006 «Water Code of the Russian Federation», Federal Law No. 96-FZ of 4 May 1999 «On the Protection of Atmospheric Air», Federal Law No. 136-FZ of 25 October 2001 «Land Code of the Russian Federation», Government Decree No. 1391 of 10 September 2020 «On Approval of the Rules for the Protection of Surface Water Bodies» and Government Decree No. 94 of 11 February 2016 «On Approval of the Rules for the Protection of Groundwater Bodies». The provisions of GOST 17.1.3.06-82 and GOST 17.1.3.13-86 establish general requirements for the protection of groundwater and surface waters. These standards list industrial sites, boreholes, and other mine workings among the sources of water pollution. Monitoring studies conducted by Rosvodresursy (the Federal Agency for Water Resources) from 2008 to 2020 established that areas of intensive mining activity experience sustained contamination of the environment with nitrogen compounds. According to the latest State Report «On the Status and Use of Water Resources of the Russian Federation…», in quantitative terms the discharges of nitrogen compounds into water bodies amounted to: nitrate-ion – 375 thousand tonnes, nitrite-ion – 5,1 thousand tonnes, and ammonium nitrogen – 297 thousand tonnes. Information from SanPiN 1.2.3685-21 and GOST 12.1.005-88 indicates that these pollutants are among the chemicals that can enter water from materials and reagents – specifically, from charges of AN-IEs. On the basis of these data, most water resources within the operating zones of mining enterprises have been assigned a low water-quality class under GOST R 58556-2019.

Accordingly, it is becoming increasingly important to resolve environmental issues related to nitrogen-compound contamination of the environment – particularly water resources – during D&B operations using AN-IEs, as well as, in some cases, the technological issues of processing contaminated ore at mining and processing enterprises that employ AN-IEs for extraction.

In accordance with Decision of the Council of the Eurasian Economic Commission No. 57 of 20 July 2012 «On the Adoption of the Technical Regulation of the Customs Union «On the Safety of Explosives and Products Based Thereon» (together with «TR CU 028/2012. Technical Regulation of the Customs Union. On the Safety of Explosives and Products Based Thereon»), water-resistance (W, kg/m^2) is a mandatory controlled indicator subject to quantitative determination during tests confirming the safe handling of explosives. For AN-IEs, this parameter, in physical terms, represents the specific amount of nitrate-ion (kg) released from a unit surface area of the explosive charge (S_{area}, m^2) over a specified period of contact between the charge and water. At the same time, the determination of water-resistance for most IEs is regulated by GOST 14839.13-2013; for high-energy emulsion explosives, by GOST 32411-2013. Water-resistance is included among the key controlled physicochemical parameters in their testing and production.

Among all types of AN-IEs, emulsion explosives (hereinafter, EEs) are the most water-resistant. Nevertheless, over their service life they partially lose this property due to their metastable nature. In reverse «water-in-oil» emulsions, to which EEs belong, this process depends primarily on the properties of the dispersion medium – the oil phase – which maintains the emulsion structure and shields the finely dispersed ammonium nitrate from external influences. To stabilize the oil-phase shell in such colloidal systems, specialized surface-active agents (surfactants) – emulsifiers and stabilizers – are used. The choice of their type and concentration determines the water resistance and stability of EEs.

In this context, within the domain of AN-IEs, the shift to using EEs offers broad technological opportunities for regulating the performance characteristics of both the high-energy formulations themselves and the methods by which they are applied. Moreover, controlling the water-resistance of high-energy EEs – whose explosive performance approaches that of TNT-containing industrial explosive compositions – will make it possible to address the environmental and technical problems associated with their use.

Objective of the work: to substantiate formulation and technological approaches to enhancing the water-resistance of EEs during production and use, in order to minimize contamination of the environment and mined rock materials by water-soluble components.

Research tasks:

Investigate the problem of the limited water-resistance of EEs.

Analyze the factors that influence the water-resistance of EEs.

Substantiate formulation-based methods for improving the water-resistance of EEs, including the use of special types of emulsifiers and stabilizing additives that enhance the physicochemical stability of high-energy emulsions and prevent the leaching of soluble substances into the environment.

Develop a methodological algorithm for determining the water-resistance of EEs using a chromatographic method, both to identify the optimal formulation and as an alternative to the standard titrimetric method.

Provide a quantitative assessment of the enhanced water-resistance metric for EEs.

Confirm the feasibility of ensuring increased water-resistance of EEs while simultaneously maintaining the technological feasibility of their production and application.

Academic novelty

A study was conducted that identified the key governing relationships determining and regulating the water-resistance of EEs. Methods for improving EE water-resistance were substantiated, including formulation techniques for configuring the fuel phase of high-energy emulsions, thereby enhancing the physicochemical stability of EEs.

For the first time, evaluation criteria for enhanced water-resistance of EEs are proposed.

An original methodological algorithm for the quantitative determination of water-resistance using high-performance ion chromatography is proposed, and its effectiveness for identifying the optimal formulation of a water-resistant EE is substantiated.

Theoretical and practical significance

A study of the factors influencing the water-resistance of EEs was carried out, expanding theoretical knowledge of EE – environment interactions and providing deeper insight into the causes of nitrogen-compound migration that leads to environmental and technological issues when EEs are used.

Methods for increasing the water-resistance and stability of EEs were substantiated. The results make a significant contribution to understanding the relationship between an EE's formulation and its water-resistance – knowledge that is important for developers of new, environmentally safe mining technologies.

Developing of the proposed methods for improving the water-resistance and stability of EEs will markedly reduce the leaching of pollutants into the environment, thereby enhancing the quality of D&B operations, the chemical purity of mined feedstock, and the environmental safety of mining enterprises.

Implementing the original methodological algorithm for precise quantitative determination of water-resistance will make it possible to optimize EE formulations with a view to increasing their water-resistance.

The findings can be used in developing new regulatory and methodological documents for industrial safety and environmental protection, which will influence the legislative framework and production standards governing the handling of IEs.

Postulates presented in the thesis:

1. The possibility of increasing the water-resistance of emulsion explosives is experimentally confirmed by optimizing the formulation and the method of dispersing components during the preparation of high-energy water-in-oil (W/O) emulsions. Control of the emulsion explosives water-resistance is achieved by modifying the composition of the combustible component (the emulsion's fuel phase).

2. As an analytical tool for identifying the optimal formulation of water-resistant emulsion explosives, the applicability of a developed methodological algorithm is substantiated – using a chromatographic method to determine nitrate-ion concentration in water samples that have been in contact with a high-energy W/O emulsion based on a concentrated ammonium nitrate solution.

3. Quantitative criteria are established that define the concept of enhanced water-resistance for high-energy W/O emulsions based on a concentrated ammonium nitrate solution.

4. Technological approaches to the production of water-resistant emulsion explosives are substantiated using data on the correlation of the water-resistance of high-energy W/O emulsions with their dispersity (droplet-size distribution) and dynamic viscosity.