

Degasification and removal of dust at mass explosions in pits using a humate reagent in the internal and external storage

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The work is covering the results of research and industrial tests of environmental efficiency of water replacement in internal and external hydraulic wells in the quarries of mining enterprises for humic reagents. According to the results of experimental and industrial tests, it is substantiated that the efficiency of the use of humic reagent in the external water hammer in comparison with the use of technical water proved by dust suppression increases by 20.0%, neutralization of carbon monoxide by 59.4%, and neutralization of nitrogen oxides by 55.1%.

Keywords: mining ecology; quarry; mass explosion; humic reagent; water hammer; dust suppression; degassing

Introduction

When conducting massive blasting operations in quarries, a significant amount of dust and gases are released into the atmosphere, more than in other technological processes of mining production [2]. The dust and gas cloud that is formed during the explosion pollutes the atmosphere, not of the quarries and their industrial sites only, but also the territory of the adjacent residential areas. According to the Scientific Research Institute for the Occupational Safety and Environmental Protection in the Ore Mining and Iron and Steel Industries (Kryvyi Rih National University), massive blasting in quarries generates from 0.027 to 0.170 kg of dust per 1 m³ of the rock mass blasted. Dust suppression during massive blasting operations is mainly based on water stemming and irrigation of blocks with water before and after massive blasting [2].

Known methods and measures to reduce the dust release and gas emissions into the atmosphere when conducting massive blasting have not yet solved the above-mentioned environmental problem, which is corroborated by the definition of the problem of degassing and dust suppression during massive blasting in quarries as one of the priorities for industrial companies of the city of Kryvyi Rih in accordance with the decisions of the Scientific and Technical Environment-Protection Council under the Department of Environment Protection and Natural Resources of Dnipropetrovsk Regional State Administration (Par. 1, Protocol No. 2 dd. 09/06/2020) and the decisions of the Environment-Protection Planning Council under the Department of Environment Protection of the Executive Committee of Kryvyi Rih City Council (Par. 4.1 of the Protocol dd. 27/10/2017, Part II of the Protocol dd. 30/06/2018) as regards the implementation of measures of the City Program for Solving Environmental Problems of Kryvbas Basin and Improving the State of the Environment During the Period of 2016-2025.

To substantiate the efficiency of using a humate reagent for the dust and gas suppression theoretically during massive blasting, the authors' team conducted a theoretical study of the leading industrial adsorbents, the main of which is activated carbon (AC) and its modifications. It should be noted that AC is a unique universal absorber that is entirely permeated by an extensive system of pores of various sizes. Simultaneously, it is less selective than other adsorbents since it is neutral to both polar and non-polar adsorbed molecules. It also absorbs heavy metals (HM) well. As for gases, it absorbs chlorine, ammonia well, but not carbon monoxide, nitrogen, and hydrogen. Activated carbon is a relatively expensive adsorbent, and its use for industrial purposes is economically impractical.

That said, the search for more affordable adsorbents suitable for adsorption not only of gases that accompany industrial blasting operations (primarily carbon monoxide (I I), nitrogen oxides, hydrocarbons, ammonia, and others), but also for that of dust continues these days. Thus, the use of the carbon alkali reagent (CAR) and the peat hydroxide reagent (PHR) in the working humate mixture during massive blasting operations in quarries have shown their capacity to sorb gases and dust. The CAR is a product of brown coal processing. The CAR's main active components are sodium and potassium salts of humic acids and gelatinous substances that are finely dispersed carbon-humic compounds.

There is no generally accepted theory of the structure and composition of humic acids (HA). Those substances are known, but over the last two decades, interest in HA has increased again. This is due to their importance in the functioning of various ecosystems, viz. in maintaining the environment's ecological stability and the new data that show the efficiency of the use of HA in agriculture, medicine, and technological processes of mining companies. Based on the findings of research conducted by the Scientific Research Institute for the Occupational Safety and Environment Protection in the Ore Mining and Iron and Steel Industries (Kryvyi Rih National University) [2], the expediency of using a humate reagent that includes PHR and CAR is therefore justified.

The information on the chemical composition and structure of HA is currently not unequivocal. It is formed based on data from modern analysis methods: elemental analysis, electron paramagnetic resonance (EPR) spectroscopy, infrared (IR) spectroscopy, ultraviolet (UV) spectroscopy, nuclear magnetic resonance (NMR) spectroscopy, various types of chromatography, cryoscopy.

Common to HA of various origins is the presence of an aromatic nucleus and peripheral open chains consisting of carboxyl and carbonyl groups, hydroxyls of alcohol and phenolic nature, and a residue of nitrogen-containing amino acids [12]. Such a structure of HA explains their adsorption properties. While studying the CAR's adsorption properties, it was found that the absorption of carbon monoxide (I I)-CO as the leading most hazardous gas that is difficult to remove from the working area of the quarries obeys Langmuir's theory of adsorption [13]. A second-order equation describes the rate of the sorption process, is directly proportional to the equilibrium concentration of carbon monoxide (I I) in the gaseous phase and the S/V ratio in the aqueous suspension (S is the surface area of the sorbent, V is the volume of the sorbent). The proportionality of the sorption rate to the area/volume ratio indicates the homogeneous-heterophase nature of the sorption process.

The study of the integrated thermal effect of absorption of carbon monoxide (II) by a humate mixture with the CAR made it possible to conclude the type of adsorption [14]. It was established that the adsorption process of carbon monoxide (II) by the CAR is an exothermic one having a significant value of ΔN . It is equal to 179 kJ/mol, which makes it possible to conclude that chemisorption takes place there (i.e., physical sorption and chemical one). The capacity to sorb can be explained by the structure of the CO molecule that is extremely stable but has an atom of an element that can take part in forming a covalent bond using the donor-acceptor mechanism. The oxygen atom acts as an electron donor. Sorption of nitrogen and ammonia oxides is possible according to a similar mechanism, and in the case of ammonia, nitrogen is the donor.

The previous research by the Scientific Research Institute for the Occupational Safety and Environmental Protection in the Ore Mining and Iron and Steel Industries (Kryvyi Rih National University) has also shown that it is advisable to use a humate reagent with the CAR and PHR to prevent dust release from occurring on the surface of waste rock dumps and sludge storage facilities. The humate reagent contains HAs its composition which can be considered as fertilizers. Adding humate solutions to the soil will help form a plant microflora on the surface of rock dumps, ensuring dust binding in the future.

The presence in the humate reagent of electron-donor groups (-NH₂;-OH;>C=O;-COOH;-SH;>NH; \equiv N) therefore provides the possibility of the formation of strong compounds of those acids with metal ions including those of heavy metals such as Cu(2+),Ns(2+),Cd(2+), Pb(2+),Zn(2+),Fe(3+).

All heavy metals are pronounced chelating agents that form covalent bonds by the donor-acceptor mechanism with electron-donor groups present in a humate reagent structure.

Materials and methods

The main methods of dust suppression during massive blasting are currently based on water stemming of various types. Types of water stemming, methods, and techniques of their use were developed by the Scientific Research Institute for the Occupational Safety and Environment Protection in the Ore Mining and Iron and Steel Industries and the Ore Mining Scientific Research Institute (Kryvyi Rih National University) [3-9] and include external, internal and combined ones. The "Guidelines for the Use of Wet Charge Tamping During Blasting Operations in Quarries, Degassing of the Blasted Rock Mass and Cleaning of the Atmosphere from Harmful Explosion Products" provide technological recommendations for the use of stemming and organization of its use. At the same time, paper [10] gives figures on the efficiency of the dust and gas suppression measures during massive blasting operations. However, the listed measures to reduce dust release and gas emissions into the atmosphere when conducting massive blasting have not solved the above-mentioned environmental problem.

In order to implement scientific developments aimed at reducing emissions of pollutants into the atmosphere when conducting massive blasting operations, the Scientific Research Institute for Occupational Safety and Environmental Protection in the Ore Mining and Iron and Steel Industries and the Ore Mining Scientific Research Institute (Kryvyi Rih National University) proposed [3-9] and tested in industrial conditions the method of pre-wetting of the blocks using aqueous solutions of the PHR. In collaboration with the CERN LLC, the industrial-scale research of that method in 2019 in the quarries of Inguletskyi Iron Ore Mining and Processing Plant, the Central Iron Ore Mining and Processing Plant, and the Northern Iron Ore Mining and Processing Plant showed its efficiency that constituted 30-32% as regards dust suppression and 62-70% as regards degassing (carbon monoxide, nitrogen oxides). Consequently, it has been scientifically substantiated that the implementation of the tested measures in mining companies' conditions will reduce pollutant emissions into the atmosphere when conducting massive blasting operations.

In 2020, the Ore Mining Scientific Research Institute of Kryvyi Rih National University and the Scientific Research Institute for the Occupational Safety and Environment Protection in the Ore Mining and Iron and Steel Industries conducted industrial-scale tests during massive blasting operations in the quarries of the PJSC Northern Iron Ore Mining and Processing Plant in order to determine the efficiency of the method of dust and gas suppression by external and internal water stemming, as well as wetted stemming using a humate reagent.

The industrial-scale experimental tests were oriented to accomplishing the following tasks: determining the optimal consumption of a humate reagent when used in external water stemming; developing a rational technological process for the use of a humate reagent when applying the method of external water stemming; determining actual concentrations of pollutants, viz. dust (in the form of suspended particles) and gaseous pollutants (carbon monoxide and nitrogen oxides) in the air by conducting direct instrumental measurements at the blocks being blasted and along with the dust and gas cloud propagation torch; determining the efficiency of the dust and gas suppression by the method of external water stemming using a humate reagent.

A humate reagent contains components in a variable ratio depending on the air temperature, the type of rock to be blasted, and its strength; the mass % is: carbon alkaline reagent – 0.5-3.0; peat hydroxide reagent – 1.0-6.0; the rest is water.

The preparation of the humate reagent's working composition was carried out at the street sprinkler truck water filling station within the site of the quarry of the PJSC Northern Iron Ore Mining and Processing Plant. To obtain the humate reagent, a 30% liquid concentrate was used that had been prepared following the respective patent [1]. The components of the humate reagent are peat hydroxide reagent (PHR) according to Technical Specification TU U 08.9-35113654-003-2012; carbon alkali reagent (CAR) according to Technical Specification TU U 24.6-24709453-001-2001; balanced water.

The ratio of the mixture's components for obtaining a working composition of the humate reagent of a given concentration stands at 1 m³ to obtain 10 m³ of a solution of 3% concentration; to obtain 10 m³ of a solution of 6% concentration – 2 m³.

The humate reagent is pumped directly into the sprinkler truck's tank that delivers the working solution to the block to be blasted. The sprinkler truck tank must be filled in advance with water up to about a third of its capacity. After draining the concentrate, the truck tank is refilled to the required volume. Mixing of the humate reagent with water occurs when the truck tank is filled with water and transported to the quarry block. At the next stage, the sprinkler truck pumps the humate reagent into polyethylene hoses designed for external and internal water stemming and wets the stemming according to the current regulations. The external water stemming from the humate reagent is meant for the block's surface to be blasted, while the internal one for the dry blast borewells.

Placing dust and gas samplers at the block to be blasted is carried out after blasting borewells and preparing the external water stemming. Dust and gas samplers are installed in each section of the block. They are placed at a distance of 30-50 m from the farthest row of borewells in the direction of the air's predominant movement 1.5 to 2 hours before massive blasting. To ensure selective sampling from each section of the block (to ensure sampling before the start of intensive mixing of dust and gas clouds from those sections of the block), the dust and gas samplers are placed in each section of the block at the maximum distance possible. The location of the dust and gas samplers is shown in Figure 1.

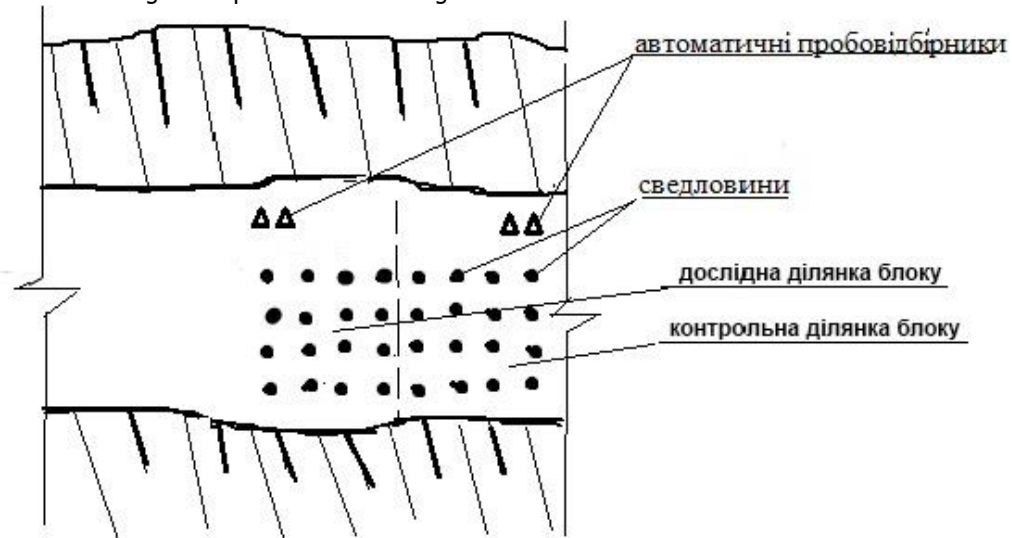


Figure 1. The layout of samplers at the block to be blasted.

Legend: автоматичні пробовідбірники – automatic sampling devices ; свердловини – borewells; дослідна ділянка блоку – experimental section of the block; контрольна ділянка блоку – reference section of the block

The dust and gas clouds' collection at the block of dust and gas samples is carried out in the automatic mode employing water and electromechanical dust and gas samplers. During installation, airflows' speed is measured with an anemometer, and the directions of flows are measured with ribbon flags. The electromechanical dust and gas sampling device design makes it possible to install at the input one dust intake cartridge for the AFA filter, while that of the water-based device makes it possible to install two cartridges with the AFA filters. The water-type dust and gas sampler's capacity that is filled with contaminated harmful gases is 10 L. Three dust samples are therefore taken in each section of the block, and a container is filled to analyze the air for the content of harmful gases that are the products of blasting agents' detonation. Switching on of the dust and gas samplers is triggered off by the action of the seismic shock from a massive explosion, which ensures sampling from the epicenter of the dust and gas cloud. Dust and gas sampling along the dust and gas cloud propagation torch outside the quarry is carried out in an open, well-aired on all sides low-dust area, on the quarry's leeward side. When determining pollutants' concentrations, sampling is carried out at the height of 1.7 m from the ground level. Simultaneously with air sampling, meteorological observations are conducted of the wind speed and direction, air temperature, and barometric pressure.

After the explosion, the start time of sampling is calculated based on the measured wind speed and distance to the block. At the end of the calculated time, the aspirator is turned on, and air sampling for dust and gas pollution is performed for 20 minutes. Dust samples are collected on the AFA-VP-10 filter, while gases are in oxygen bags.

Analyzing dust and gas samples is carried out by express method and laboratory one at the analytical and testing laboratory of the Scientific Research Institute for the Occupational Safety and Environment Protection in the era Mining and Iron and Steel Industries (Kryvyi Rih National University) that meets the requirements of the State Standard of Ukraine ISO 10012:2005 "Measurement Control Systems. Requirements for Measurement Processes and Measuring Equipment" (Certificate No. 08-0017/2018 dd. 17/05/2018).

Determining the concentration of dust (substances in the form of suspended particles) is performed following the regulatory document's requirements (RD 52.04.186-89. Pollution Control Guide, 1991). Determining the concentration of harmful gases is carried out by the express method using the following devices: carbon monoxide (CO), depending on the level of air pollution – Mini Warn, according to the operating instructions of the gas analyzer; MSI Vario-x, according to the operating instructions of the gas analyzer; nitrogen dioxide (NO₂) – Mini Warn, according to the operating instructions of the gas analyzer; MKI-20 NO₂, according to the operating instructions of the gas analyzer; nitric oxide (NO) – MKI-20 NO, according to the operating instructions of the gas analyzer. Dust and gas sampling and conducting measurements are carried out using the devices that have valid certificates of the State Metrological Calibration at the time of industrial-scale testing.

The results of the concentration of harmful substances in the dust and gas cloud after each massive blasting are recorded in a protocol. The application efficiency of a humate reagent when using external water stemming is determined according to the following formula:

$$E_{\text{PHR}} = \frac{C_0 - C_{\Phi}}{C_0} \cdot 100, \% \quad (1)$$

where E_{PHR} - efficiency of the dust and gas suppression when using a humate reagent, %; C_0 - the average concentration of harmful substances in the air without the use of a humate reagent, mg/m³; C_{Φ} - the average concentration of harmful substances in the air when using a humate reagent, mg/m³.

Results and Discussion

Results of the instrumental measurements of pollutants in the air during massive blasting using a humate reagent in water stemming

Calculating harmful gas emissions and dust release after blasting in Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant using a humate reagent was carried out according to the Protocol dd. 31/07/2020 on the R&D distribution between the Ore Mining Scientific Research Institute and the Scientific Research Institute for the Occupational Safety and Environment Protection in the Ore Mining and Iron and Steel Industries. The respective results are shown in Tables 1 and 2.

Table 1. Results of calculating harmful gas emissions in the dust and gas cloud after blasting in Gannivskiy quarry of the PJSC Northern Iron Ore Mining and Processing Plant using a humate reagent.

Sampling date	Gas type	Concentration, mg/m ³	The arithmetic mean concentration, mg/m ³	The volume of the BA, m ³	The volume of the dust and gas cloud, m ³	The specific gas formation, kg/kg of the BA
Part of the block, where a humate reagent was not used						
06/08/2020 Block No. 52	CO	27.5	27.5	17,157	978,180	0.00157
	NO ₂	24.7	24.7			0.00141
Part of the block, where a humate reagent was used						
Level -20/-30 m	CO	11.4	9.9	22,059	1,257,660	0.00056
	CO	8.4				
	NO ₂	8.6	7.9			0.00040
	NO ₂	7.2				

Description of the conditions of instrumental measurements of harmful substances in the air during massive blasting using a humate reagent in water stemming

Experimental Block No. 52 (Figure 2) is located at Level -20/-30 m that is represented by magnetite-silicate quartzites with a strength coefficient of 12 on the M. M. Protodyakonov scale. This block was divided into two parts. In the first section that contains 54 borewells, external water stemming in the amount of 24 m³ using a humate reagent (a mixture of 3% PHR and 3% CAR) was performed. In the second part of the block that contains 42 borewells, dust and gas suppression measures were not carried out. Dust and gas sampling devices were placed at 30-50 m from the block to be blasted.

The use of external water stemming with a humate reagent reduced dust release by 50.5%, the concentration of harmful gases by 66.0%, viz. carbon monoxide by 64.0%, and nitrogen oxides by 68.0%.

Table 2. Results of calculating the dust release after blasting in Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant using a humate reagent.

Data for calculating the dust concentration at the block being blasted										
Date	Airflow, according to the rotameter, l/min.	Volume of the air, l	Filter aliquot, mg	Concentration, mg/m ³	The arithmetic mean concentration, mg/m ³	The volume of the rock, m ³	Mass of the BA, kg	The volume of the dust and gas cloud, m ³	Specific dust release	
									kg/m ³ of the rock being blasted	kg/kg of the blasting agent
Part of the block, where a humate reagent was not used										
06/08/20 Block No. 52 Level -20/-30 m	5	3.7 / 3.3*	2.70	818	798	19,200	17,157	978,180	0.041	0.045
	3.5	2.6 / 2.3*	2.65	828						
	4.2	5 / 4.4*	3.35	761						
	4.2	5 / 4.4*	3.45	784						
Part of the block, where a humate reagent was used										
06/08/ 20 Block No. 52 Level -	5	3.7 / 3.3*	1.20	364	395	24,800	22,059	1,257,660	0.020	0.023
	3	2.3 / 2.0*	0.70	350						
	4.2	5 / 4.4*	1.55	352						

20/-30 m	4.2	5 / 4.4*	1.90	432
	4.2	5 / 4.4*	1.90	432
	4.2	5 / 4.4*	1.95	443

* – the volume of the air reduced to the standard conditions

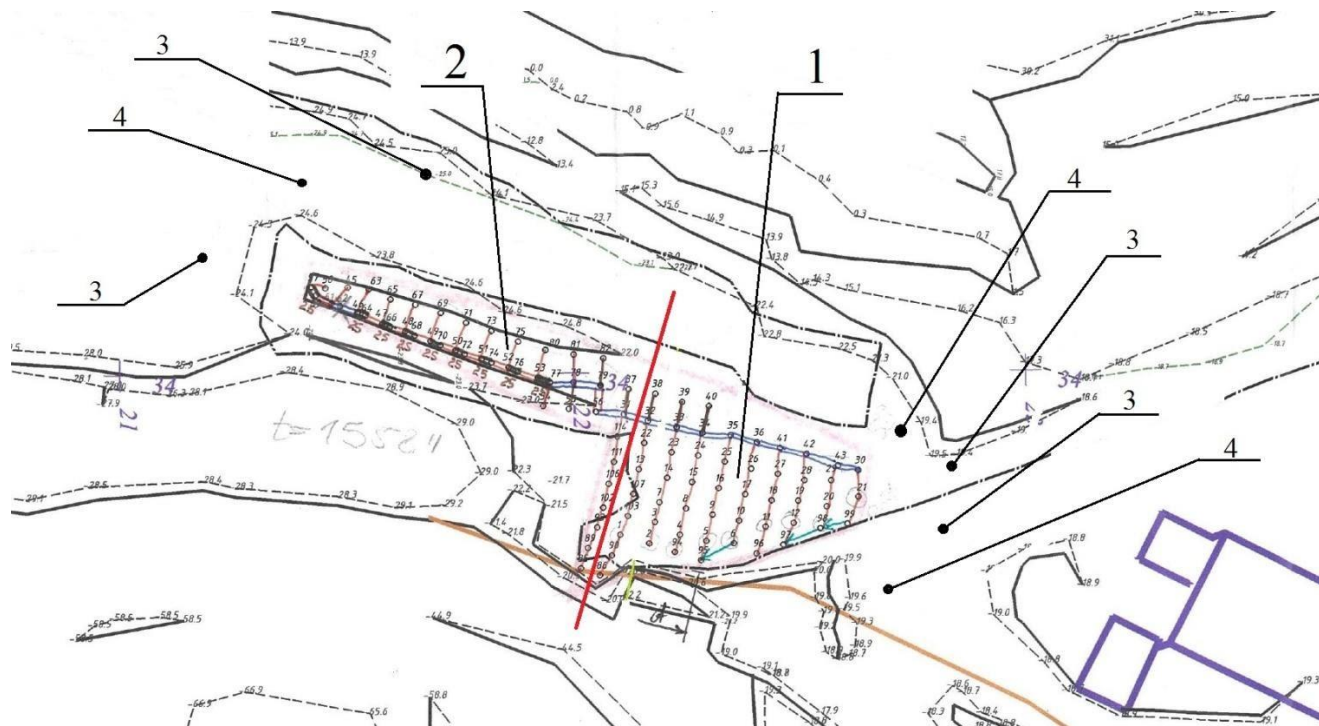


Figure 2. Diagram of the experimental block (Block No. 52 Level -20/-30 m dd. 06/08/2020), where: 1 – part of the block, where the humate reagent was used; 2 – part of the block without using a humate reagent; 3 – automatic dust detection (sampling) facilities; 4 – hydro-mechanical dust detection (sampling) facilities

Results of the instrumental measurements of pollutants in the air during massive blasting without the use of humate-based reagents in water stemming

Date and time of blasting: September 3, 2020, 1:00 p.m. Location of conducting massive blasting: Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant. Level and block: Level -30/-45 m, Block No. 64.1. Type and volume of rocks: magnetite-silicate quartzite – 35,000 m³.

The results of calculating dust release after blasting in Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant using water stemming are shown in Tables 3 and 4.

Table 3. Results of calculating the harmful gas emissions in the dust and gas cloud after blasting in Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant using water stemming.

Sampling date	Gas type	Concentration, mg/m ³	The arithmetic mean concentration, mg/m ³	The volume of the BA, m ³	The volume of the dust and gas cloud, m ³	Specific dust and gas formation, kg/kg of the BA
03/09/2020 Block No. 64.1	CO	27.1	27.1	31,030	1,582,944	0.00138
Level -30/-45 m	NO ₂	17.4	17.4			0.00089

Table 4. Dust release after blasting in Gannivskiy Quarry of the PJSC Northern Iron Ore Mining and Processing Plant using water stemming.

Data for calculating the dust concentration at the block being blasted					Specific dust release					
Date	Airflow, according to the rotameter l/min.	The volume of the air, l	Filter aliquot, mg	Concentration, mg/m ³	The arithmetic mean concentration, mg/m ³	The volume of the rock, m ³	The volume of the BA, m ³	The volume of the dust and gas cloud, m ³	kg/m ³ of the rock being blasted	kg/kg of the blasting agent
03/09/2020 Block No. 64.1 Level -30/-45 m	5	3.3 / 2.9*	1.60	551	553.75	35,000	31,030	1,582,944	0.025	0.028
	5	3.3 / 2.9*	1.40	483						
	3	2 / 1.8*	1.10	611						
	3.5	2.3 / 2.0*	1.14	570						

* – the volume of the air reduced to the standard conditions

Description of the conditions of instrumental measurements of harmful substances in the air during massive blasting using a humate reagent in water stemming

Experimental Block No. 64 (Figure 3) is located at Level -30 / -45 m that is represented by magnetite-silicate quartzites with a strength coefficient of 12 on the M. M. Protodyakonov scale. At that block containing 48 borewells, an external water stemming was made based on the rock mass volume of 18,000 m³. Dust and gas sampling devices were placed at about 50 m from the farthest borewells of the block to be blasted.

Measuring the concentration of pollutants in the atmosphere when conducting massive blasting on 03/09/2020 at Block No. 64.1 Level - 30 / -45 m in Gannivskiy Quarry was carried out to determine the efficiency of the use of a humate reagent in the external water stemming instead of industrial water (massive blasting on 06/08/2020 at Block No. 52 Level -20 / -30 m in Gannivskiy Quarry).

The efficiency of using the humate reagent was determined by the values of specific ("per unit") indicators. When using the humate reagent, the specific dust release constituted 0.020 kg/m³ of the rock mass, the release of carbon monoxide 0.00056 kg/kg of the BA, and nitrogen oxides 0.00040 kg/kg of the BA. When using regular external water stemming and wetting of the stemming with industrial water, the specific dust release constituted 0.025 kg/m³ of the rock mass, the release of carbon monoxide 0.00138 kg/kg of the BA, and that of nitrogen oxides 0.00089 kg/kg of the BA.

Consequently, the efficiency of using a humate reagent in the external water stemming constituted for the dust suppression 20.0%, for the carbon monoxide neutralization 59.4%, and the nitrogen oxides' neutralization 55.0%.

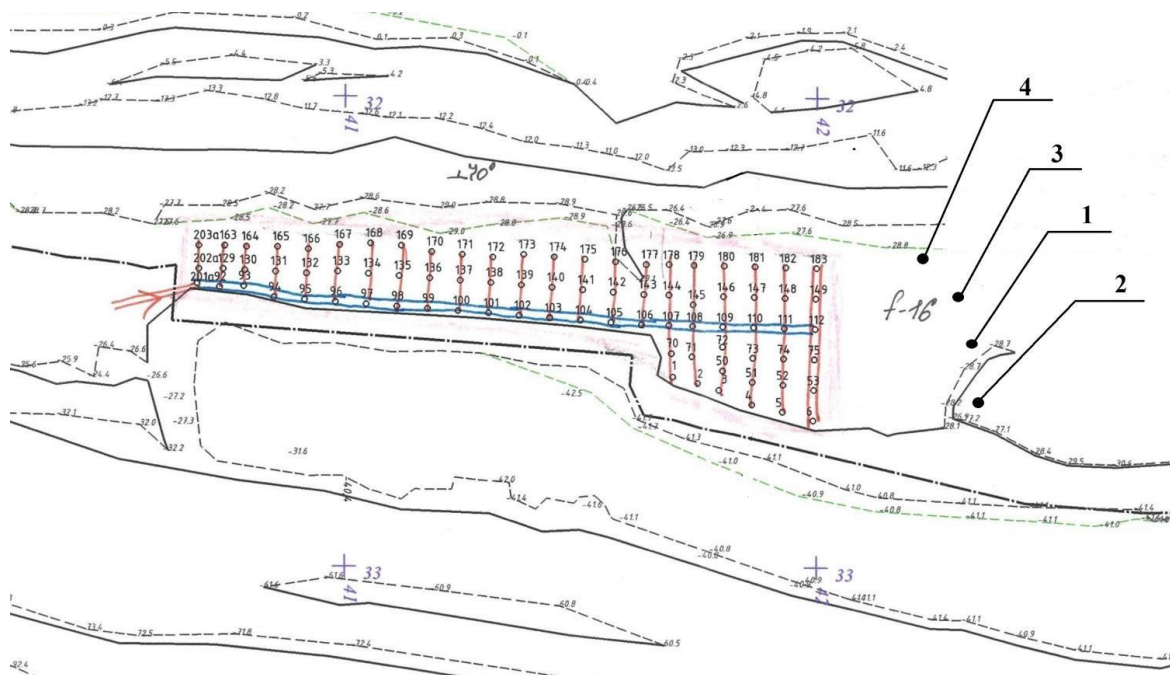


Figure 3. Diagram of the experimental block (Block No. 64 Level -30/-45 m dd. 03/09/2020), where: 1 – automatic dust detection (sampling) facility No. 1; 2 – automatic dust detection (sampling) facility No. 2; 3 – automatic dust detection (sampling) facility No. 3; 4 – automatic dust detection (sampling) facility No. 4.

Conclusions

The use of external water stemming with a humate reagent (a mixture of 3% aqueous solution of peat hydroxide reagent and 3% aqueous solution of carbon alkali reagent) reduced dust release by 50.5%, the concentration of harmful gases by 66.0%, viz. carbon monoxide by 64.0% and nitrogen oxides by 68.0%.

The efficiency of using the humate reagent was determined by the values of specific ("per unit") indicators. When using the humate reagent, the specific dust release constituted 0.020 kg/m³ of the rock mass, the release of carbon monoxide 0.00056 kg/kg of the BA, and that of nitrogen oxides 0.00040 kg/kg of the BA. When using regular external water stemming and wetting of the stemming with industrial water, the specific dust release constituted 0.025 kg/m³ of the rock mass, the release of carbon monoxide 0.00138 kg/kg of the BA, and that of nitrogen oxides 0.00089 kg/kg of the BA.

The efficiency of using a humate reagent in the external water stemming constituted for the dust suppression 20.0%, for the carbon monoxide neutralization 59.4%, and the nitrogen oxides neutralization 55.1%.

To ensure the maximum environment-protection effect when conducting massive blasting operations, the polyethylene containers with a diameter of 0.3-1 m filled with a humate reagent should be used to form the external water stemming of borewells with blasting agent (BA). The external stemming in polyethylene hoses is placed along the rows of borewells. The hoses' length is determined by the geometric parameters of the surface of the block to be blasted and the contour of the borewells. The technological process of performing external water stemming using a humate reagent does not differ from the regular implementation of stemming using water.


5. In order to reduce the dust release by more than 50.5% during massive blasting operations, to reduce the impact of atmospheric shock waves, and to improve the quality of rock crushing along the entire height of the ledge, it is advisable to form compacted to 2,450 kg/m³ stemming of the inactive parts of borewell blasting agent charges using 30% humate reagent (humate concentrate) and crushed rock of the 5-20 mm fraction.

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