

Article

Improvement of Working Conditions of Mining Workers by Reducing Nitrogen Oxide Emissions during Blasting Operations

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Abstract: The article presents comparison of the values of maximum permissible concentrations, revealed during the analysis of the national standards of Russia and Australia in the field of regulation of nitrogen oxides. The impact of poisoning of the workers of the quarry with nitrogen oxides after blasting operations are presented. A detailed review of studies of methods for reducing nitrogen oxide emissions is given. The way of decreasing emission of nitrogen oxides using highly active catalysts as a part of the profiled tamping is offered. Laboratory studies were carried out using a model explosive and pentaerythritol tetranitrate. The results obtained showed that zinc carbonate ($ZnCO_3$) is the most effective. The reduction in the amount of nitrogen oxide emissions was 40% of that released during experiments without the addition of catalysts.

Keywords: nitric oxide; maximum permissible concentration; catalyst; stemming; drilling and blasting operations



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1. Introduction

The modern world is a huge and complex mechanism in which such areas as IT, extraction of mineral resources and their processing are permanently developing [1,2]. These directions constantly intersect and complement each other [3,4]. Sustainable development of the environment cannot exist apart from the development of manufacturing industry, agriculture, economics and other industries [5,6]. The world production sector is represented mostly by various enterprises for the extraction and processing of mineral resources, as well as companies of the chemical industry, which have a great impact on sustainable development [7,8]. Significantly, that the extraction of solid and liquid mineral resources is the basis and is dominant of all industries in the modern world. Nowadays, the vast majority of the world energy industry is associated with the use of coal, oil and gas, and building and construction inextricably interwinds with the use of wall-stone, asbestos and other mineral resources mined in quarries [9]. It is important to note that the development of the mining industry inland makes it possible to pursue an economic policy in the field of import and export of extracted resources, which is an integral part of the GDP, and, accordingly, the sustainable development of the state itself [10–12].

While on the subject of underground and open pit mining, a special place is occupied by the extraction of minerals using drilling and blasting, which is the most widespread in the whole world. There are a number of hazardous and harmful factors in the deposits where blasting operations are carried out, the most common of which are the open pit slope failure [13] and air pollution of the working areas by the components of gases formed during the work of internal-combustion engines [14] or after the explosion, and which are a combination of oxide nitrogen, carbon dioxide, nitrogen dioxide and carbon monoxide. We can make a conclusion that as the number of open pit mines increases due to the elimination of mines in Europe and other continents, the risk of accidents due to acute poisoning with post blast gases increases too.

An increase in the concentration of nitrogen oxides and carbon monoxide in the air of working zones leads to acute poisoning and occupational diseases of the personnel of mining enterprises, as well as to the pollution of water basins and soils located within the area of influence of emissions [15–17]. Nitrogen oxides are the most dangerous among poisonous gases because at the same concentrations, they have higher toxic properties, especially nitrogen dioxide. Nitrogen dioxide belongs to a special hazard category primarily due to the fact that nitrogen dioxide is formed as a product of the chemical reaction of the compound of nitrogen oxide and oxygen during blasting operations, if reactions have a positive oxygen balance [18]. Firstly, oxidation reactions occurring in air are difficult to analyze, because it is necessary to jointly solve the problems of gas dynamics and materials' chemical kinetics [19]. Therefore, there are a significant number of factors that contribute to the occurrence of reactions with a positive oxygen balance, for example, the use of a poor or poorly mixed mixture of ammonium nitrate (AN); incorrect density of the explosive; deterioration of the quality of the explosive during storage or delivery or incorrectly selected explosive components. The nitrogen oxide cloud is yellow, orange or brown. However, in addition to the toxicity of the gas itself, it poses an increased danger to workers because of its slight solubility in water, therefore, this substance has a long latency period and nitrogen dioxide forms ammonium ions in combination with water. Either a group of chronic diseases (chronic cough, wheezing, bronchitis) or an acute poisoning (asthma) and death can be the consequences of nitrogen dioxide poisoning [20,21].

On the one hand, the sustainable development of the mining industry directly depends on the renewal or conservation of natural resources and it is confirmed by the basic concepts of a resource-based economy [22,23]. However, on the other hand, it is obvious that workers and human potentials are an integral part of the sustainable development of the production industry and a high-level safety during blasting can be achieved only when harmful emissions are reduced and controlled. Due to the significant number of factors affecting the formation of poisonous gases with high concentrations of nitrogen oxides, such as the management and control of the influence of wind and thermal forces that influence on the ventilation of the quarry, increased desorption of gases under the influence of pressure relief and destruction, meteorological conditions [24], as well as the lack of a unified approach to monitoring nitrogen dioxide to reduce the concentration of a toxic cloud, a risk-based approach can be used, because accidents of varying degrees with different occupational risk indices are possible in the different cases of nitrogen oxides formation [25].

Scientists have been solving the problem of reducing the harmful effects of nitrogen oxides on the health of workers for many decades. The impact of poisonous gases generated during blasting operations on the health of workers depends on the concentration of this gas, the numerical value of which depends on the explosive used and the oxygen balance of the mixture [26], as well as the blasting conditions and rock properties. In the modern mining industry, emulsion explosives are in great demand in blasting operations to destroy rocks. The transition to using these explosives was to ensure the minimum formation of nitrogen oxides close to zero, because the composition of emulsion explosives is created in such a way that the oxygen balance is approximately equal to zero. It should be noted that the minimum release of poisonous gases when using emulsion explosives is observed only with a certain balanced composition. So, to exclude the formation of nitrogen oxides and minimize the content of carbon monoxide in the composition of the explosion products, the oxygen balance of emulsion explosives should be in the range from -0.2 to -2.0% [27]. The analysis of the use of explosives based on emulsions is described in the works of many scientists [28,29]. Minimization of nitrogen oxides is possible only if there is a study of geological objects that are within the mining allotment, with a description of the properties, quality and structure of the rock mass [30]. The need to reduce harmful emissions in the air of working areas in open pits complimented by a significant excess of maximum permissible concentrations is described in the works of foreign scientists [31–33]. A lot of academic specialists have studied the risk-based approach to the exploitation of hazardous production facilities and have proposed the use of methods of spatial risk analysis [34]

and the concept of “Vision Zero” [35]. The dependence of the safety of blasting operations and production efficiency and economic indicators of the products is unconditional [36]. Although the use of organizational methods to reduce occupational injuries is effective, it requires significant economic costs [37], the concentration of nitrogen oxide emissions does not decrease and situations associated with abrupt changes in environmental factors are not excluded, and as a result, additional risks increase. As can be seen from the above, the study of such methods for reducing nitrogen oxide emissions using a risk-based approach, which are possible to apply both in Russia and abroad in the conditions of different regulatory and legal frameworks, is an urgent task, the solution of which saves the life and health of miners, so that the well-being of human resources is a prerequisite for sustainable development of production industry. Cases of acute poisoning from inhalation of significant concentrations in quarries during blasting operations are more common, therefore, the article discusses the issue of protecting personnel from acute poisoning.

2. Materials and Methods

It is important to note that the regulation of safety issues in the field of monitoring nitrogen dioxide is complicated by the fact that there is no consistent approach in the world: different countries validate different values of maximum permissible concentrations and the methods for calculating safe zones from exposure to toxic gases differ significantly.

Regarding comparative analysis, the statutory conditions of the Russian Federation and Australia were selected, caused by the association with the high competence of Australian blasting companies around the world. In Russia, the maximum permissible concentrations of hazardous substances are established by the Hygienic Standards GN 2.2.5.3532-18 “Maximum Permissible Concentrations (MPC) of Hazardous Substances in the Air of the Working Area” [38], and in Australia, the employer’s responsibilities to prevent the harmful and dangerous effects of hazardous substances are regulated in the “Workplace Exposure Standards for Airborne Contaminants” (Adoption Date: 27 April 2018) [39] in accordance with the Work Health and Safety Act (WHS) [40] and the Work Health and Safety Regulations (WHS Regulations) [41]. As a consequence, it is worthwhile to note that in Russia, the maximum permissible concentration of nitrogen dioxide is below and equals to 2 mg/m^3 , and in the Australian statutory conditions, the maximum permissible concentration equals to 9.4 mg/m^3 .

There are a number of methods to reduce emissions of gases generated after blasting operations, based on neutralization with various solutions, fixant additives and foams, but almost all of these methods are used to reduce emissions of sulfur oxides and carbon monoxide. Most of the methods for reducing nitrogen oxides are aimed at cleaning exhaust gases in metallurgy. In open pits, due to low costs, the methods of water stemming and pre-wetting of the block where the explosion will occur are most often used to form nitrous acid which settles on the ground. However, this method does not meet the requirements when there is a significant amount of toxic gases.

It is of importance to note the use of foam-gel stemming, which is made from 1.5–3.0% aqueous solutions of foam-gel-forming substances, and the modus operandi, of which does not differ from the previous one. In this case, the centers of neutralization of toxic gases in the atmosphere are small drops and bubbles of foam gel, which, in comparison with other methods, requires fewer components in preparation due to the fivefold foaming process [42]. Another topic includes researches related to methods of improving the quality of stemming in a borehole, because its use ensures the completion of secondary reactions and reduces the amount of gases released after the explosion, for example, the use of bend as stemming [43] or the using of pneumatic compression in a borehole for a length of 30–40 cm for stemming made from crude mineral salt [44]. Technologic methods of reducing the initial parameters of the dust and gas cloud are used in open pits, which are aimed to reduce the output of explosive detonation products from the drill hole collar: high face blasting in a compressed structure, blasting in boreholes with air gaps and using active stemming and funnel initiation of an explosive in a borehole. However, these

methods have a number of disadvantages: the use of active stemming is always closely associated with additional consumption of explosives; drilling and loading equipment does not always meet the requirements for blasting on high benches; it is difficult to mechanize such processes as the formation of charges with air gaps, and there are also restrictions on the use of this method in crumbling rocks and if there is a field water-cut [45]. Finally, a lot of researches on methods of reducing the amount of nitrogen oxides were based on the use of alkali earth metal salts introduced into the explosive, for the reason that, in this case, the salts reduce the explosion temperature and they are positive catalysts in the reaction of the combustion of ammonium nitrate and mixtures based on it, that is, in addition to increasing the combustion velocity, the extent of combustion increases too, which helps to reduce the amount of nitrogen oxides in the explosion products [46–49].

According to the generally accepted methods for calculating the parameters of the hazardous zone for toxic gases, it is worthwhile to note that these methods are based on the dependence on the parameters of wind flows and the ambient conditions and are aimed at reducing emissions of fine dust.

To sum up, in the field of reducing nitrogen oxide emissions directly during blasting operations in open pit mining, there is a very small number of theoretical studies. Most of the researches are aimed at finding ways to reduce emissions of carbon oxides and sulfur, or in these studies, toxic gases that are formed during underground mining are considered.

The use of high-activity catalysts is an effective way to reduce nitrogen oxide emissions, but the previous studies did not consider the result of using high-activity catalysts as part of a contoured stemming.

As is known, the explosion is accompanied by the release of a large amount of nitrogen oxides from the borehole. In turn, the use of contoured stemming during blasting operations in open pits solves two important problems: retention of gaseous explosion products in the charging cavity [50] and reduction of nitrogen oxide emissions due to the process of decomposition at a high temperature of explosion products in virtue of layer-by-layer burnout of the material, from which is a base of an interlayer when the explosion products pass through the axial channel of the contoured stemming.

As mentioned earlier, the use of alkaline earth metals as well as substances with their content can reduce the amount of nitrogen oxides. This chemical group includes the following elements: beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), zinc (Zn), barium (Ba) and others. On top of that, the ability of stemming to entrap the explosion products in the charging cavity allows the catalyst to stay in contact with the explosion products for a longer time and, while decomposing, neutralize nitrogen oxides. From there, the use of highly active catalysts as part of a contoured stemming can be used as a method for reducing nitrogen oxide emissions during blasting operations in open pits.

The borehole stemming design (patent No. 182481 dated 6 May 2018) was developed at the St. Petersburg Mining University. This design allows to reduce nitrogen oxide emissions during blasting operations by 40% [51].

At the first stage of the study, an experiment was carried out to determine the values of the concentrations of nitrogen oxides released during the explosion of a model explosive without the use of catalysts. The studies were carried using an explosion chamber with a carrying capacity of 5 L, designed for testing explosives in order to determine the composition of the explosion products and the concentration of poisonous gases (Figure 1).

The sample weight of the explosive was 1.2 g. The igniter with a sample of the explosive substance is installed inside the chamber in a plastic cap. After that, the chamber cover was tightly fixed with bolts. The hole for sampling with a gas analyzer is located on the cover itself, and at the time of the explosion, a special bolt was installed in this hole, which made it possible to seal the chamber in order to prevent the release of gaseous explosion products outside the chamber. A nearby gas analyzer was used to measure the concentration of nitrogen oxides. The finished installation is shown in Figure 2.



Figure 1. Explosion chamber (photo by the author R.S. Babkin).

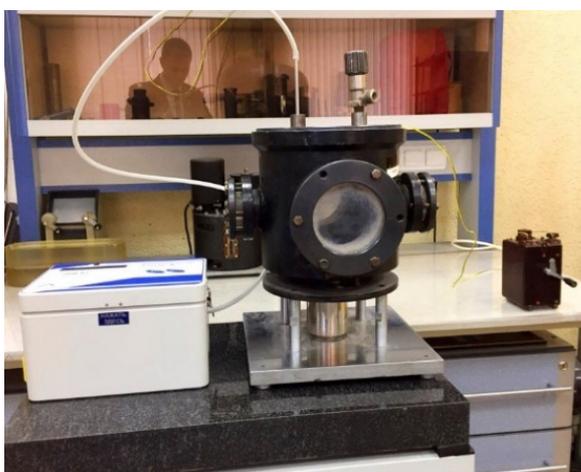


Figure 2. Laboratory setup for measuring the concentration of nitrogen oxides (photo by the author R.S. Babkin).

After the explosion, the follower of the gas analyzer for sampling was placed in a special hole, the principle of operation of which was to automatically perform measurements for some time with the results being displayed and saving them in the device's memory. Then, after each explosion, the chamber was ventilated and treated with a special cleaning compound.

The determination of the mass concentrations of nitrogen oxides released from the explosion of the model composition without the addition of a filler was a series of experimental explosions with averaging of the data obtained.

At the second stage of the study, experiments were carried out to confirm the effectiveness of the use of catalysts for reducing nitrogen oxide emissions using the same laboratory setup. The fillers were: magnesium carbonate (MgCO_3), calcium carbonate (CaCO_3) and zinc carbonate (ZnCO_3). Each of the selected fillers was used in studies to determine the

effectiveness of the application in order to reduce NO_x emissions. The fillers had the same dispersion and the same percentage in the composition of the sample, which was carried out by particle analysis of substances using an A-30 particle analyzer. At the preparatory stage before the study, the reagents were preliminarily degradation in size and have been dried in a thermal chamber at a temperature of 50 °C for 12 h.

To complete the study of the effect of using catalysts as part of a contoured stemming on nitrogen oxide emissions, in addition to conducting an experiment with a model explosive, it is necessary to carry out field experiments with a real explosive. The investigated explosive was pentaerythritol tetranitrate (PETN), a chemical compound (CH₂ONO₂)₄C, a blasting explosive with high sensitivity to impacts, a white crystalline powder with a molar mass of 316.25 g/mol and an oxygen balance of 10.12%.

To determine the amount of nitrogen oxides in the explosion products, an explosion chamber with a carrying capacity of 5 L was used, and a GANK-4 gas analyzer with an installed chemical cassette to determine the concentration of nitrogen oxides was used as a device for measuring the concentration of nitrogen oxides of the explosive under study (Figure 3).

A steel mortar with a diameter of 100 mm and a height of 100 mm was placed in an explosion chamber. A hole with a diameter of 6 mm and a depth of 60 mm was drilled in the center of the mortar.

An electric igniter placed in the lower part of the borehole was used as an initiator. Pentaerythritol tetranitrate weighing 1.02 g was placed in the charged part of the hole (36 mm). Quartz sand (21 mm) was used as part of the contoured stemming. The installation is shown in Figure 3.

Further, after conducting experiments without adding catalysts to pentaerythritol tetranitrate, laboratory studies were carried out using zinc carbonate to determine the concentrations of nitrogen dioxide in explosion products in order to prove, on a practical level, the effectiveness of using highly active catalysts as a way to reduce the concentrations of poisonous gases.



Figure 3. Scheme for measuring emissions of nitrogen oxides (photo by the author R.S. Babkin).

3. Results

The results of the conducted studies of the mass concentrations of nitrogen oxides released from the explosion of the model composition without the addition of catalysts are shown in Figure 4.

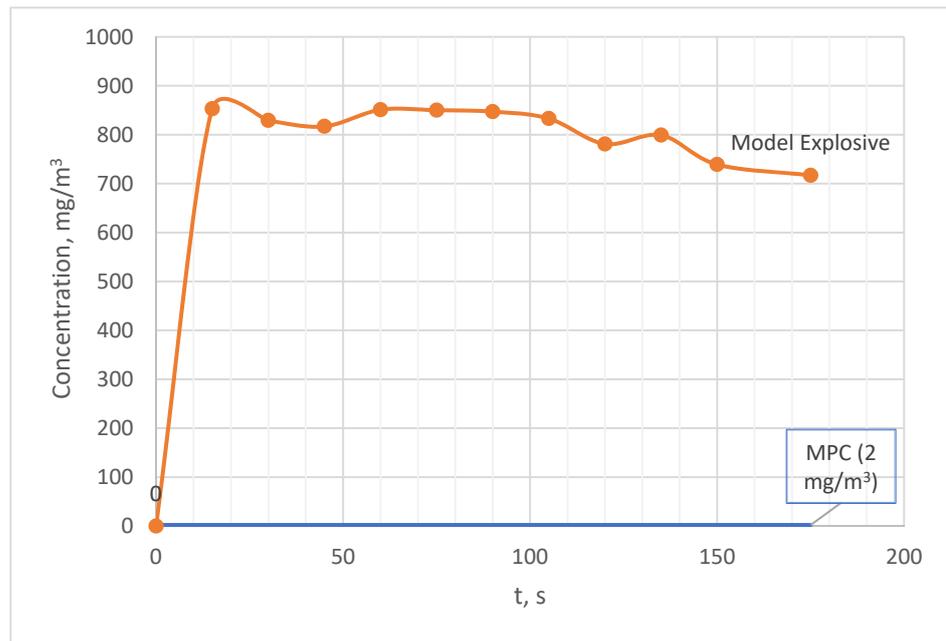


Figure 4. Dependence of the concentration of nitrogen oxides in the explosion products of a model explosive (compiled by the author R.S. Babkin).

The concentration of nitrogen oxides significantly exceeds the maximum permissible concentration of nitrogen dioxide in Russia (2 mg/m³).

The results of using various catalysts are shown in Figure 5.

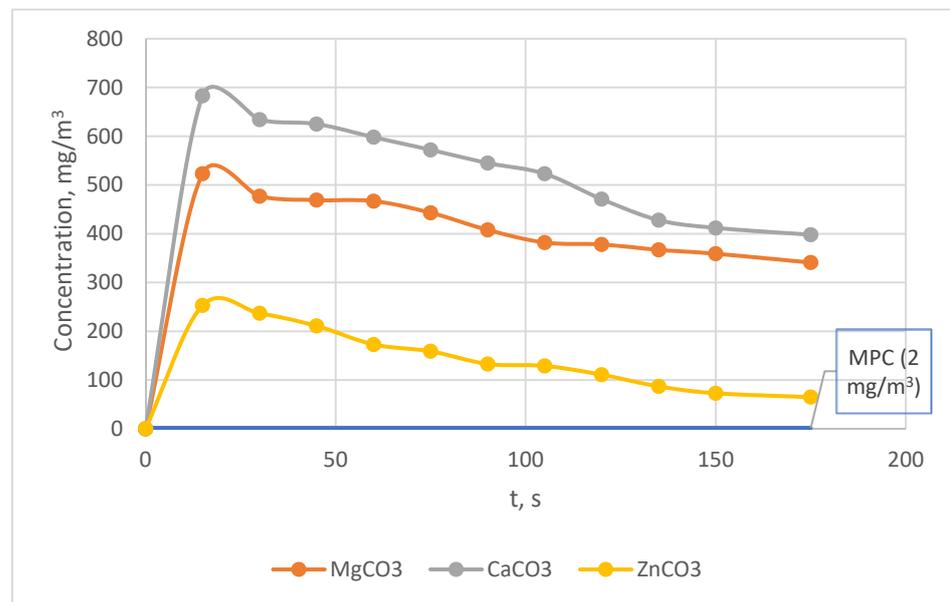


Figure 5. Dependence of the concentration of nitrogen oxides in the explosion products on the filler used (compiled by the author R.S. Babkin).

After the comparison with the maximum permissible concentration, it can be noted that zinc carbonate (ZnCO₃) is the most effective filler for reducing nitrogen oxide emissions and it allows you to reduce the concentration of released nitrogen oxides.

The results of the research on the content of nitrogen oxides in the explosion products of the explosive pentaerythritol tetranitrate without the use of catalysts are presented in Table 1.

Table 1. Concentration of nitrogen oxides in explosion products of a sample of pentaerythritol tetranitrate weighing 1.02 g (compiled by the author R.S. Babkin).

t, s	Concentration NO ₂ , mg/m ³	1	2	3	4	5
0		653	360	550	670	480
15		579	560	470	580	440
30		564	533	482	585	421
45		548	521	451	530	389
60		470	490	433	470	375
75		454	430	412	468	343
90		365	380	396	437	351
105		345	355	365	402	328
120		368	340	320	380	315
135		283	290	301	391	289
150		285	276	290	359	280
165		250	244	255	345	276
180		235	226	243	321	257
195		213	221	218	298	255
210		220	225	210	278	243
225		212	218	206	266	232
240		208	216	204	244	211
255		210	216	208	238	202

After adding zinc carbonate to the stemming in the amount of 20%, the results of the study to determine the concentration of nitrogen dioxide were as follows (Table 2):

Table 2. The concentration of nitrogen oxides in the explosion products of pentaerythritol tetranitrate with 20% zinc carbonate ZnCO₃ in the stemming (compiled by the author R.S. Babkin).

t, s	Concentration NO ₂ , mg/m ³	1	2	3	4	5
0		380	402	398	356	412
0		380	402	398	356	412
15		360	387	402	334	400
30		352	366	387	320	380
45		334	340	366	334	376
60		318	332	354	340	366
75		306	323	348	345	340
90		292	305	332	323	321
105		280	298	320	320	310
120		276	280	312	318	298
135		264	282	295	315	290
150		258	278	280	310	288
165		240	266	275	287	280

Table 2. Cont.

t, s	Concentration NO ₂ , mg/m ³	1	2	3	4	5
180		227	243	267	280	275
195		219	233	265	270	276
210		205	220	244	266	266
225		198	221	232	246	235
240		194	214	220	240	220
255		188	206	214	233	221

Based on the obtained results of nitrogen dioxide concentrations during research with pentaerythritol tetranitrate, the dependences of the concentration of nitrogen oxides in the explosion products in time during the explosion of a sample of pentaerythritol tetranitrate weighing 1.02 g, and a weighted portion of pentaerythritol tetranitrate with a 20% content of zinc carbonate ZnCO₃ in the stemming, were plotted. The diagram is shown in Figure 6.

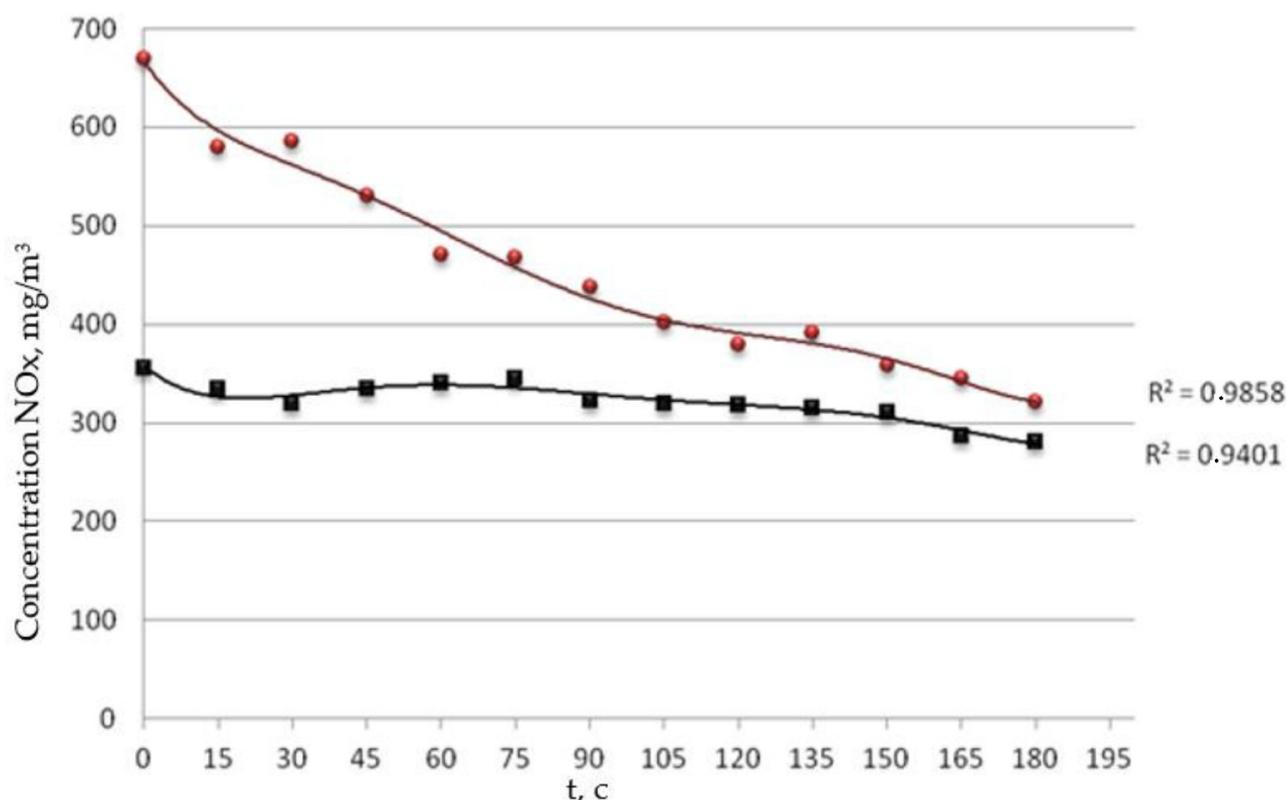


Figure 6. The dependence of the concentration of nitrogen oxides in the explosion products in time (compiled by the author R.S. Babkin).

4. Discussion

As mentioned earlier, firstly, methods of reducing the emissions of gases that are released into the atmosphere during blasting operations are mostly based on the neutralization process. For this, solutions, fixing additives and foams are used. The overwhelming majority of these methods are used to reduce emissions of sulfur oxides and carbon monoxide, that is, to reduce nitrogen oxides, they are mainly considered only in matters of combating waste gases in metallurgy. Secondly, technological methods that can be used in open pits are not effective, do not require additional expenditures of explosives, purchasing of special equipment, or they have a limited scope, for example, in deposits represented by fractured rocks or water-cut.

Of special interest were those researches in which methods of improving the quality of stemming in a borehole were considered, based on the properties of stemming to retain combustion products for a longer time.

Research shows that alkali earth metal salts, which are added to the explosive and catalyze the combustion of ammonium nitrate, reduce the explosion temperature.

Thus, it is possible to use highly active catalysts as part of contoured stemming due to a number of advantages inherent in both methods, described above, to reduce nitrogen oxide emissions directly during blasting operations in open pits.

According to the results of the study, it can be concluded that when an explosion of a model substance is carried out without the use of catalysts, a significant amount of nitrogen oxides is released. Over time, the nitrogen oxide concentration curve undergoes only small changes, which means that more time is required for ventilation. In the case of using catalysts, the emission of nitrogen oxide is reduced. The dependence of concentration on time in these cases is more pronounced, which indicates a high efficiency of the use of catalysts to reduce emissions of nitrogen oxides. This will reduce the risk of workers being poisoned by explosion products and reduce ventilation time, allowing more work to be done and less downtime. However, it is worthwhile to note that in order to further study the effect of highly active fillers, it is necessary to establish the most effective filler dispersion and its percentage in the contoured stemming.

5. Conclusions

Now it can be seen that by having considered the results obtained, it can be argued that the effectiveness of the use of catalysts as part of a contoured stemming in order to reduce emissions of nitrogen oxides released after blasting operations has been confirmed.

An important aspect is the obtained results of laboratory studies associated with the use of a real explosive instead of a model explosive, pentaerythritol tetranitrate (PETN), in order to prove the feasibility of using methods to reduce nitrogen oxide emissions. From the results of experiments without the addition of highly active catalysts, it can be seen that the concentration of nitrogen dioxide significantly exceeds the maximum permissible value, that is, it is necessary to use methods of protection against emissions of toxic gases.

From the above results, when adding catalysts to pentaerythritol tetranitrate, it can be seen that the use of zinc carbonate can reduce emissions of nitrogen oxides by more than 40%. Additionally, these studies confirm the possibility of conducting laboratory experiments using a pyrotechnic composition in a model explosive.

Summing up what has been said, the possibility of using catalysts as part of a contoured stemming in order to reduce nitrogen oxide emissions during blasting operations is possible, since this method shows a sufficient level of efficiency and does not require special means of mechanization or the cost of purchasing more explosives.

Obviously, the results obtained during experiments with a model explosive showed that zinc carbonate ($ZnCO_3$) is the most effective filler for reducing nitrogen oxide emissions during blasting operations. When conducting studies with pentaerythritol tetranitrate, the reduction in the amount of nitrogen oxide emissions was 40% of that released during experiments without the addition of catalysts, which confirms the possibility of using this method as a way to protect workers from exposure to poisonous gases generated after blasting operations.

One of the prerequisites for further research can be called the need to study the effect of dispersion and percentage of zinc carbonate in order to identify the most effective indicators for reducing the release of nitrogen oxides during blasting operations in open pit mines. In this case, the study will be aimed at finding the best properties of zinc carbonate, so it will be possible to further minimize emissions, which will preserve the life and health of human resources, which is an integral part of the sustainable development of the enterprise.

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