

Analysis on Nitric Oxide Emissions from Mining to Minimise Its Environmental Impact

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ABSTRACT : *High-energy materials like emulsions, slurries and ammonium-nitrate fuel-oil explosives (ANFO) which are largely composed of nitric oxide, perform a vital task in mining, quarrying, tunnelling and many other infrastructural activities. All these tasks lead to emission of toxic and detonable nitrate-based compounds. Although minor in the global sense, these negligible emissions are known to partake in causes of adverse health effects. The review emphasises on analysing the properties of these hazardous compounds, sources of their emission and practices on how to minimise their effects on the environment and health.*

IndexTerms - Explosives, Fuel Oil, Detonation, Denitrification

1. INTRODUCTION

1.1 Study of properties of nitric oxide

Nitric oxide is the simplest known molecule that detonates in all the three phases. Nitric oxide, being exothermic in its decomposition, decomposing to N₂ and O₂, with an energy release of approximately 3.02 MJ/kg. On comparing the detonating capacities of all the three phases with the results obtained from an instrumented-card gap test conducted by the Bureau of Mines, gaseous NO was observed to ignite at normal as well as raised pressures while liquid NO was discerned to be sensitive to weak shock waves. Solid NO exhibited greater tolerance while compared to liquid ones but were still subtly detonable.

For gaseous NO, with initiators weighing 43 X 10⁻³ kg or less, reaction velocities of the order of 1000 m/s were observed, but velocities more than 2000 m/s were observed for initiators weighing 60 X 10⁻³ kg or more. When boosted with a 50 X 10⁻³ kg tetryl donor, and with only the 0.08-mm Teflon as a gap, liquid boiling NO detonated at high velocity - approximately 5400 m/s. Detonations with velocities of 5400 and 5300 m/s were obtained in 230- and 300-mm-long charges at 128- and 255-mm gaps, respectively for non-boiling liquid NO. When boosted with a 50 X 10⁻³ kg tetryl donor, solid NO in charge lengths of approximately 510 mm, ignited at a velocity of approximately 6100 m/s at 1.0-, 26.7-, 52.1-, and 77.5-mm gaps.

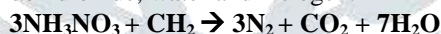
1.2 Sources of emissions of nitric oxide

Sources of nitric oxide may be broadly categorised into four – blast mines, vehicle exhausts, smouldering fires and drilling into stagnant water.

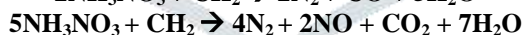
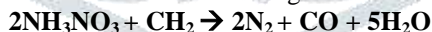
1.2.1 Fuel Oils

The main source of nitric oxide emission is from the fuel oils utilised in the blasting sites of mining industries. The estimated total NO emission from AN based explosive is 5x10⁴ t N/year. Although may seem insignificant, blast mines emit NO sufficient enough to exceed safety limits by 3000 times. Ammonium-Nitrate Fuel-Oil (ANFO) is employed in most of the open-cut coal mining industries.

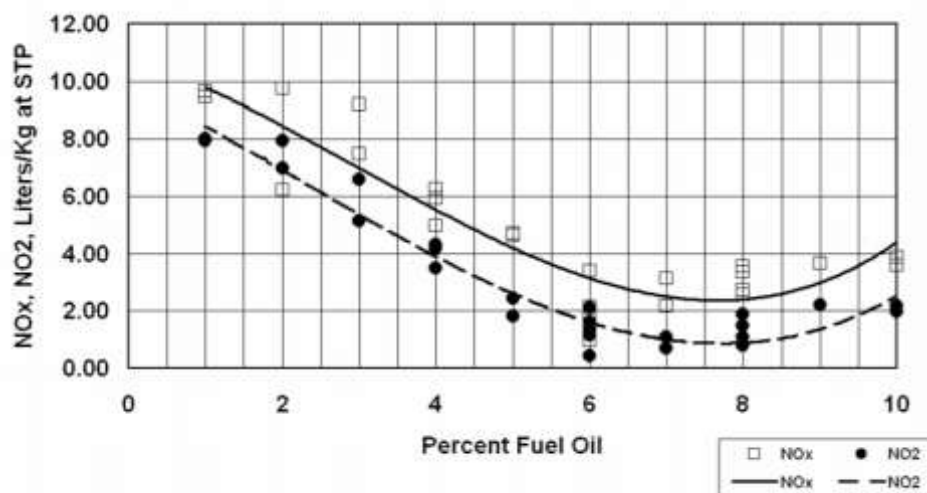
The explosion of ANFO primarily gives rise to carbon dioxide, water and nitrogen.



However, due to small stoichiometric changes, considerable amount of toxic gases such as CO and NO are emitted.



Due to expansion and subsequent cooling of detonation product gasses, the combustion reactions are quenched before they can go to completion. The quenching freezes out NO at concentrations higher than those expected for equilibrium. It is not possible to entirely prevent the release of nitric oxide in blasting; however, the quantities can be reduced. Some factors that lead to excessive NO production are incorrectly formulated explosives, use of deteriorated explosives, reaction in diameters below the critical diameter, loading wet boreholes with explosives that are not water resistant, mixing of explosive with drill cuttings at the top and bottom of the hole, and poor confinement.

Figure 1: Effect of fuel oil content on the quantity of nitrogen oxides produced by the detonating ANFO.

1.2.2 Explosives

Apart from emitting harmful NO into the atmosphere, NO is diffused into the water resources surrounding the mine sites as well. One chief source of nitrogen oxide are the explosives which find varied applications in the fields of construction, mining, quarrying etc. Most widely expended explosives are TNT and RDX. The explosives possess a threat to the environment as they easily infuse into soil and water thereby contaminating them. These explosives form by-products that causes mutation and genetic disorders to the species consuming them. In the survey conducted by the Geological Survey of Sweden, the nitrate levels in the groundwater around the Kiruna mining site ranges from 1.5 to 2mg/L. The NO concentration is high inside the mining site ranging between 16 to 34mg/L. When tested beneath the waste rock piles, the concentration varied from 22-26mg/L as the nitrogen leached from the rocks had a longer time to oxidise as it infiltrated into the mine. The mining pumping station showed the local minimum of 16-18mg/L. Nevertheless, the circulations of water in mining sites are complex and thus the exact mechanism cannot be identified. Still, the major underlying sources of water contamination with NO are due to AN-based explosives and leaching of waste rocks.

II. PRACTICES TO MINIMISE HAZARDS OF NITROGEN OXIDE

Nitrogen oxide finds sources in substances utilised in mining sites that cannot be eradicated totally. A viable solution will be to minimise the production of NO such that it is not harmful to the environment. Alternatives to existing materials are also worthwhile.

2.1 Minimisation of NO emission

Explosion reactions when quenched even before completion suspend NO in higher concentrations. Some factors that cause increased NO production are

2.1.1 Incorrectly formulated explosives

As already discussed, stoichiometric changes in explosive composition lead to emission of NO and CO. NO is emitted due to reduction in availability of fuel than required. Thus, appropriate amount of fuel and oxidisers must be expended by the manufacturers during explosive production.

2.1.2 Use of deteriorated explosives

Explosives that are beyond the manufacturer recommended shelf life or visibly deteriorated should not be used. Usage will result in an explosive that may not function as intended by the manufacturer and may produce excessive fumes.

2.1.3 Reaction in diameters below the critical diameter

When reactions occur below the critical diameter, the surroundings absorb energy from explosion front to quench the explosion. Also, the blasting agent may flow into cracks and crevices around the borehole where it may not detonate properly because the width of the cracks and crevices may be below the critical diameter.

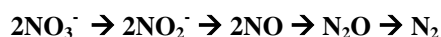
2.1.4 Loading wet boreholes with explosives that are not water resistant

Presence of water leads to curtailed detonation and results in excessive production of unwanted toxic gases.

III. DENITRIFICATION OF NITRATES

3.1. Using micro-organisms

Denitrification, the biological reduction of nitrogen oxides to dinitrogen gas, is also referred to as nitrate respiration and is mediated by several bacterial genera such as *Pseudomonas*, *Paracoccus*, *Flavobacterium*, *Alcaligenes*, and *Bacillus*. The nitrate ion is reduced to dinitrogen gas by the following pathway:



The denitrifying cultures are usually a mixture of various anaerobic micro-organisms each assisting various steps of the reaction. Commonly ammonia is first nitrified to nitrate which is again denitrified to nitrogen gas.

Table 1: Typical ammonia containing mine effects

| Type | Flow (m ³ /h) | NH ₃ (mg/l) | pH | SO ₄ ²⁻ (mg/l) | Fe (mg/l) | Zn (mg/l) | Hardness ^a |
|-------------|--------------------------|------------------------|----|--------------------------------------|-----------|-----------|-----------------------|
| Clean | 240 | 25 | 8 | 500 | 0.5 | 0.1 | 700 |
| Dirty | 240 | 25 | 7 | 2000 | 500 | 500 | 200 |
| Concentrate | 24 | 200 | 7 | 5000 | 1000 | 1000 | 1000 |

^aAs CaCO₃ equivalent, mg/l.

3.2 Iron mediated autotrophic denitrification

Iron mediated autotrophic denitrification possesses dual advantages of recovery of iron as well as removal of nitrate. The process begins with the bio-oxidation of iron from +2 oxidation states to +3 oxidation states followed by bio-precipitation of Fe (III) oxides. Released electrons are transferred to the nitrates that convert to inert nitrogen gas. Many microorganisms are capable enough to perform the process in an alkaline pH level.

3.3 Alkali metric neutralisation

Nitrogen oxide released by explosives can be prevented by addition of inexpensive neutralising additives to them. The neutralising additives include slaked lime, chalk CaCO₃ and soda Na₂CO₃. Azarkovich examined the neutralisation reaction of nitrogen oxide in a Dolgov bomb and an underground chamber when additives were added to the explosives. The resulting reactions showed a 40-80% decrease in the emission of NO₂ which was observed with the help of a electromagnetically relayed air sampling vessel.

3.4 Stabilising and scavenging additives

Oxley et al. incorporated formulations that stabilised AN that included grounded salt of sodium, potassium, ammonium and calcium, sulfates, carbonates, formates, oxalates etc. The more stabilising the additive was, the more selective was N₂ formation. Also nitrate additive especially potassium nitrate exhibited a 40% reduction in NO emission.

3.5 Re-Burning

In boilers, reburning achieved an overall decrease in NO release by 50-85%. Reburning occurs in three stages – initially the main fuel burns under fuel-lean condition and produces NO that reacts with hydrocarbon radicals in the reburning zone to eventually form molecular nitrogen. The combustion process is culminated by the addition of air to oxidise all the unreacted fuels and N-species.

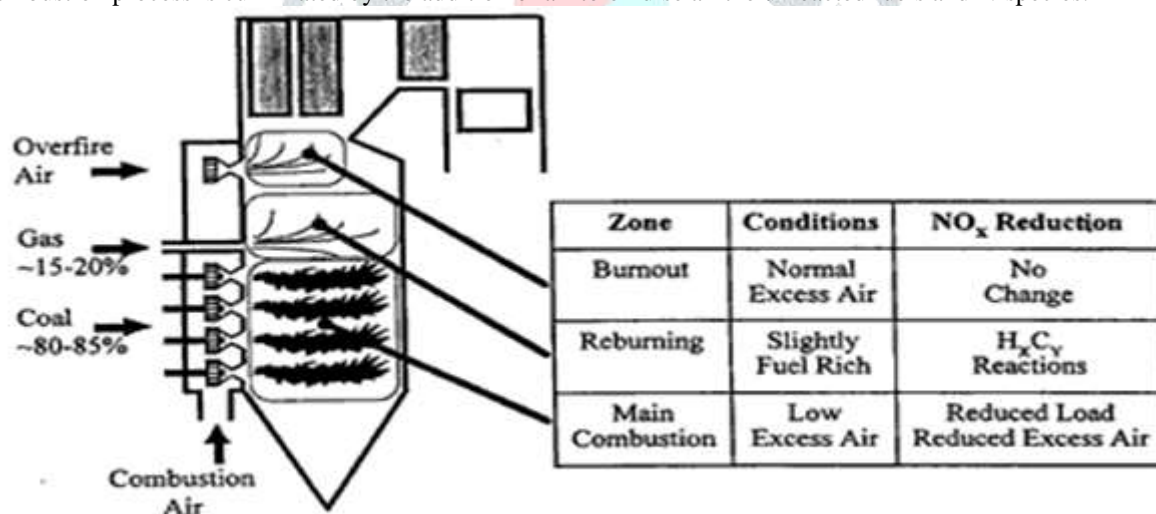


Figure 1: Typical gas reburning installation on a wall fired boiler

3.6 Spin Trapping

Generally used in monitoring reactions that encompass intermediacy of reactive radicals in low concentrations, spin trapping has been witnessed to remove radical species such as NO through the formation of stable adducts. Venpin et al. applied aromatic ortho substituted nitrocompounds such as nitrosobenzene sulfonate (NBS), dibromo-4-nitrosobenzene sulfonate (DBNBS) which triggered a 70% NO removal efficiency during sensitisation of AN emulsion blends.

IV. CONCLUSION:

The Miner should ensure whether they have placed the explosives technically as well as with respect to geological composites and stratigraphy where the different types of explosives will be compared and the low NO emission one must be chosen to the particular site. This can bring half of success in minimizing NO hazards. The neutralizers and NO emission controlling agents effectively work when the desirable pattern and best environment fitted to it. Bio-purification provides a notable play in controlling with irrespective to the geological composites. In future, the micro-orgasms should be developed and it will become more eco-friendly than any other methods.

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