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Review article

Atmospheric emission of NO_x from mining explosives: A critical review

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HIGHLIGHTS

- NO_x forms in unbalanced blasting, deflagration and sensitisation of mining explosives.
- Atmospheric emission of NO_x from mining explosives amounts to 50 000 t pa.
- New technologies can mitigate atmospheric emission of NO_x from mining explosives.
- Research needs include source measurement, sampling techniques and new formulations.

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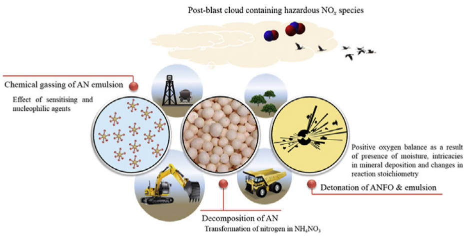
GRAPHICAL ABSTRACT



ABSTRACT

High-energy materials such as emulsions, slurries and ammonium-nitrate fuel-oil (ANFO) explosives play crucial roles in mining, quarrying, tunnelling and many other infrastructure activities, because of their excellent transport and blasting properties. These explosives engender environmental concerns, due to atmospheric pollution caused by emission of dust and nitrogen oxides (NO_x) from blasts, the latter characterised by the average emission factor of 5 kg $(\text{t AN explosive})^{-1}$. This first-of-its-kind review provides a concise literature account of the formation of NO_x during blasting of AN-based explosives, employed in surface operations. We estimate the total NO_x emission rate from AN-based explosives as 0.05 Tg (i.e., 5×10^4 t) N per annum, compared to the total global annual anthropogenic NO_x emissions of 41.3×10^6 t N y^{-1}. Although minor in the global sense, the large localised plumes from blasting exhibit high NO_x concentration (500 ppm) exceeding up to 3000 times the international standards. This emission has profound consequences at mining sites and for adjacent atmospheric environment, necessitating expensive management of exclusion zones. The review describes different types of AN energetic materials for civilian applications, and summarises the essential properties and terminologies pertaining to their use. Furthermore, we recapitulate the mechanisms that lead to the formation of the reactive nitrogen species in blasting of AN-based explosives, review their implications to atmospheric air pollution, and compare the mechanisms with those experienced in other thermal and combustion operations. We also examine the mitigation approaches, including guidelines and operational-control measures. The review discusses the abatement technologies such as the formulation of new explosive

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mixtures, comprising secondary fuels, spin traps and other additives, in light of their effectiveness and efficiency. We conclude the review with a summary of unresolved problems, identifying possible future developments and their impacts on the environment with emphasis on local and workplace loads.

1. Introduction: mining and its environmental impact

1.1. Mining

High-energy-density materials (HEDMs) have revolutionised the world's mining, infrastructure and aviation industries. These materials generally consist of explosives, propellants and pyrotechnics. They generate high temperature and pressure via complex combustion phenomena involving physicochemical phase changes, complemented by rapid exothermic reactions (Agrawal, 2010; Klapötke, 2007; Kubota, 2002). Technically, the term “explosion” defines a sudden release of energy confined in (but not limited to) HEDMs, accompanied by dramatic discharge of expanding gases (Fordham, 1966) that enables impacting work done on the surroundings.

HEDMs fall into two broad categories, namely, the low and the high explosives. The salient features entrenched in this classification include the reaction velocities and pressures achieved during the combustion processes (Akhavan, 2011; Kubota, 2002). Low explosives, otherwise known as fast-burning or deflagrating substances, burn in a regular but less shattering manner, while exhibiting relatively low reaction velocities between 0.01 and 400 m s^{-1}, and bar-range pressures. Typical examples of low explosives comprise black powders, smokeless powders, propellants and pyrotechnic mixtures. On the contrary, high explosives demonstrate superior rates of reaction, i.e., velocity of detonation (VOD) ranging from 1000 to 9000 m s^{-1}, as well as higher pressure of explosion. High explosives generate supersonic detonation waves, designed to perform useful work on the surrounding rocks. The sensitivity of high explosives to detonation serves as a convenient criterion to subdivide them into three main classes (Agrawal, 2010; Badgujar et al., 2008; Cardarelli et al., 2008):

(i) Primary high explosives (primers) represent extremely sensitive materials that easily explode with the application of shock, spark, fire, friction, impact and heat. They remain dangerous to handle and find use in comparatively small quantities in primers, detonators and percussion caps. Examples of primary high explosives include mercury fulminate, lead azide, lead styphnate, silver azide, tetrazene, and diazodinitrophenol.

(ii) Secondary high explosives (base explosives) display relative insensitivity to mechanical shock, friction or flame, but shock waves of primary explosives in detonators can set them off. Common examples comprise nitroglycerine, dynamite, nitroglycol, nitromethane, pentaerythritol-tetranitrate (PETN), TNT, RDX, and HMX. Dynamite constitutes mostly liquid nitroglycerine absorbed onto a porous solid material such as diatomaceous earth, rendering it relatively safer for transportation and operational handling as compared to pure nitroglycerine. PETN serves as a benchmark for classifying explosives, i.e., explosives that exceed the sensitivity of PETN are usually considered as primary explosives.

(iii) Tertiary high explosives (blasting agents) exhibit the least sensitivity. They cannot reliably detonate by application of practical quantities of primary explosive, requiring a booster of secondary explosives. This class consists of oxidisers such as ammonium nitrate (AN), ammonium perchlorate (AP), ammonium dinitramide (ADN), etc., and their corresponding fuel-composite mixtures.

Tertiary high explosives excel other high explosives for their stability, demanding more energy to set off. Blasting agents afford variety of civilian applications involving local displacement of earth crusts, structural demolitions and building implosions, spanning large-scale mineral extraction, quarrying, tunnelling, and many other construction operations. AN-based blasting agents display desirable compromise between production, handling, safety, economic, and performance characteristics as compared to nitrated hydrocarbon compounds, i.e., molecular explosives.

AN-fused high energy products include emulsions, slurries and ammonium-nitrate-fuel-oil (ANFO) mixtures. Owing to their excellent transport and blasting properties, they represent nearly 90% of the total explosives employed worldwide in the civilian sector (Mahadevan, 2013). A mixture of a well-balanced bulk ANFO usually consists of 5.7 wt % fuel oil in an oxidising AN matrix, whereas, formulations of emulsion and slurry explosives consist of additional components that improve the contact between the oxidising salt and the fuel, and sensitise these materials. For instance, emulsion explosives contain droplets of supersaturated aqueous phase of AN dispersed in continuous oil phase (a mixture of fuel and emulsifier). The literature (Mahadevan, 2013; Oommen and Jain, 1999; Oxley et al., 2002; Sudweeks, 1985) provides further information on the composition, manufacturing and underlying properties of these materials. Volatile oils give the greatest sensitivity towards the reaction. However, petroleum fractions with low flash points pose hazards. Therefore, the optimum choice incorporates fuel oils similar to those used in diesel engines, i.e., No 2 distillate fuel oil or biodiesel. As seen by comparing the exothermicity of overall Equations (1) and (2), the fuel component of AN explosives increases their energy density (Attalla et al., 2008; Mahadevan, 2013).

$$NH_4NO_3 \rightarrow N_2(g) + 2H_2O + ½O_2(g),\quad \Delta H_r = -1440\ \mathrm{kJ\ kg^{-1}} \tag{1}$$

$$3NH_4NO_3 + CH_2 \rightarrow 3N_2(g) + CO_2(g) + 7H_2O,\quad \Delta H_r = -3900\ \mathrm{kJ\ kg^{-1}} \tag{2}$$

Heating of solid ammonium nitrate from room temperature proceeds through three recrystallisation phase changes leading to melting at around 169 °C and subsequent evaporative decomposition, usually completed by 300 °C, in laboratory studies involving thermogravimetric analysers, depending on sample size and heating rate. Unlike other solid explosives (Beckstead et al., 2007), the elementary reactions associated with the evaporative decomposition of ammonium nitrate remain incompletely understood, but appear to advance initially both by ionic and radical mechanisms in the condensed phase (Izato and Miyake, 2015). In comparison, the ensuing gas-phase reactions attracted considerable research interest that has led to adequate grasp of their behaviour. The only comprehensive, but still a semi-detailed model of reactions in