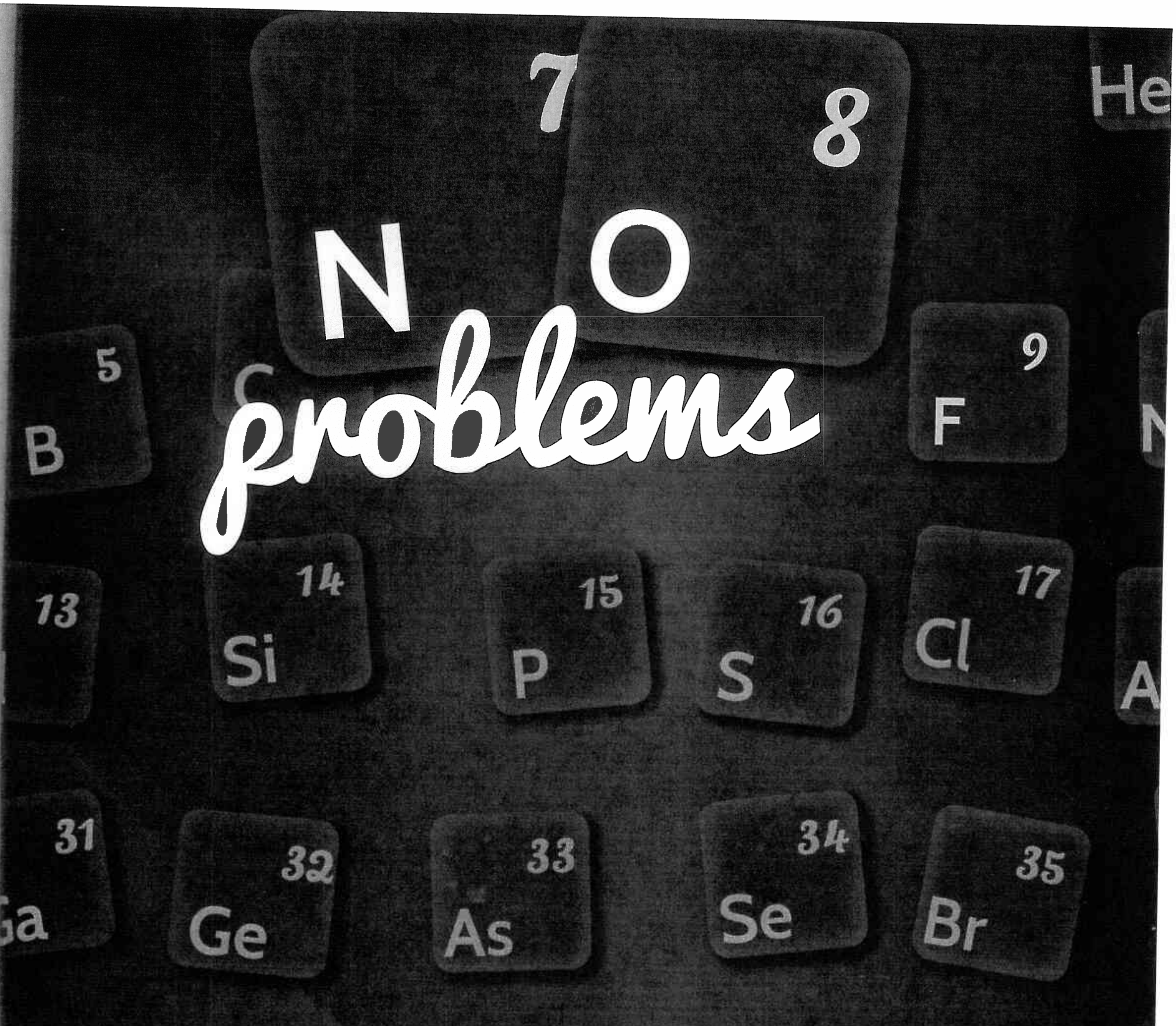
NO problems



G.B. Keller and L. Pennisi, Airflow Catalyst Systems, US, outline the challenges posed by NOx and NO_2 and survey potential solutions.

NOx refers to seven different compounds of nitrogen and oxygen. The compounds that are the highest concentration and most familiar to those in the mining industry are NO and NO_2, as these are the two compounds that are most often measured by portable gas analysers. NO_2 is the only oxide of nitrogen that is regulated by the US Environmental Protection Agency (EPA) and other regulatory bodies. It serves as a surrogate for the family of compounds, because it is the most prevalent form of NOx in the atmosphere. NO_2 exposure is also regulated by the US Mine Safety and Health Administration (MSHA).

NOx control is important in opencast mining applications because it is a major contributor to smog, acid rain and ground level ozone. It is also a dangerous pollutant itself and can contribute to inflammation of the respiratory tract. NO_2 can dissolve in water to form nitric acid and, in the presence of sunlight, reacts with oxygen in the air to form ozone. Ground level ozone – as contrasted with stratospheric ozone, which we need to shield the earth from solar radiation – is also dangerous to the human respiratory system and is the primary constituent of smog.

In an underground environment, mine safety personnel are obviously not concerned with NO_2 reacting with sunlight to form ozone. They are concerned, rather, with the buildup of dangerous concentrations of NO_2 arising from the exhaust of internal combustion engines and the reaction products of explosives used in mine operations. Underground NO_2 is still a dangerous pollutant, and can cause respiratory distress in miners when exposed to levels above those mandated. Assuming that the level and type of explosives are not going to change, the only means to reduce NO_2 production is to manage NO_2 emissions from internal combustion engines used in mine equipment. NO_2 emissions reduction and proper ventilation practices are both necessary to maintain NO_2 levels below those mandated by MSHA.

The management of NOx/NO_2 emissions is challenging. The EPA and the MSHA regulate NO_2, and the priorities by type of mine may differ. Measurement methods are inconsistent and difficult to capture accurately. The location at which emissions are measured (tailpipe versus operator) will differ significantly due to the natural equilibrium state that the NO-to-NO_2 ratio desires. For these reasons, it is important to understand how NO_2 is formed, the appropriate way to think about this emission and the options available to reduce NO_2/NOx in an underground mining environment.

NOx formation

Combustion of fuel using air as the source of oxygen produces, among other things, NO and NO_2 (the sum of which is typically, and correctly, referred to as NOx, though as mentioned above, there are seven different compounds). There are several different reactions that may form NOx, but the majority of the NOx formed in combustion processes is referred to as thermal NOx, meaning it is formed by the combination of atmospheric nitrogen and oxygen at the high temperatures found in combustion chambers. This rate of NOx production increases exponentially with increasing temperature; however, significant amounts of NOx are not formed below a flame temperature of around 1538°C (2800°F). The amount of NOx that is formed is also dependent upon the amount of oxygen and nitrogen present. As will be discussed, these dependencies lead to a possible means of reducing NOx formation. Interestingly, the type of fuel used has very little effect on NOx formation in internal combustion engines, meaning that users of alternative fuels, such as biodiesel, will still need to concern themselves with NOx emissions.

The exhaust gas temperature from diesel engines is well below that found in the combustion chamber, and therefore well below the temperature necessary to form NOx. It can therefore be assured that the amount of total NOx present at the outlet of the combustion chamber is the maximum that will be achieved. That is, additional NOx is unlikely to be formed along the exhaust path.

Some 95% of the NOx formed during combustion is NO. Were it to remain NO, there would be no cause for concern. Unfortunately, much of this NO is later transformed (oxidised) to NO_2.

If most of the NOx coming from the combustion chamber is NO, then where does the NO_2 come from? Most of the NO_2 is formed in response to well-defined equilibrium conditions that define the amount of NO and NO_2 that will be present in a gas mix at a given temperature and in the presence of oxygen. For convenience of understanding, a new relationship must be defined. Since the amount of total NOx is nominally fixed at the outlet of the combustion chamber, it is convenient to consider the NO-to-NO_2 ratio. Figure 1 presents an illustration of thermodynamic equilibrium between NO and NO_2 as the temperature increases.

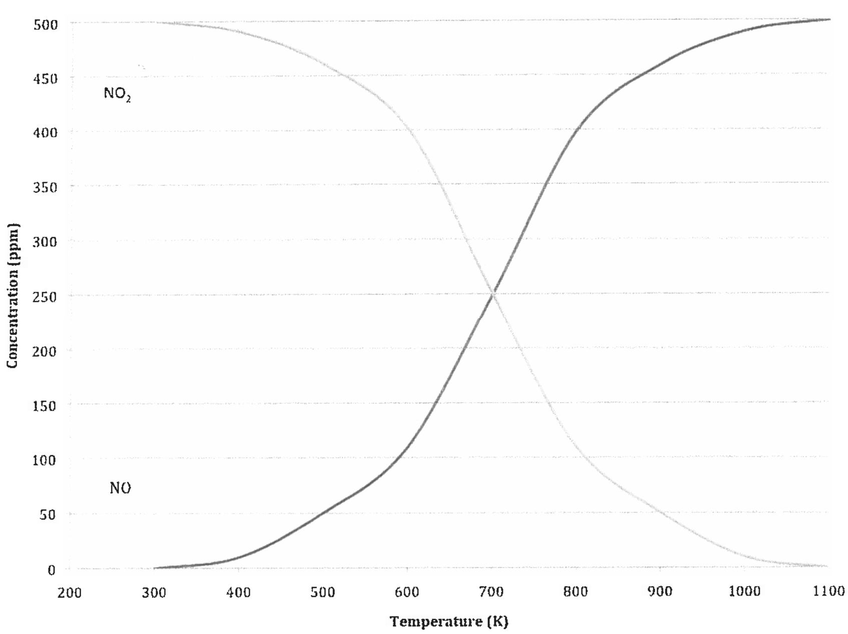


Figure 1. Thermodynamic equilibrium between NO and NO_2.
Source: Adapted from Gómez-García *et al.* (see bibliography).

Depending on the use of emissions treatment products in the exhaust stream, the NO-to-NO_2 ratio may decrease (NO_2 increase) as a result of precious-metal catalysing the oxidation of NO to NO_2.

From the relationship described in Figure 1 between NO and NO_2, an obvious problem arises. As the mixture cools, the NOx changes from almost all NO to almost all NO_2; precisely the compound that miners are trying to avoid. For that reason, it is more appropriate to consider NOx reduction as a whole – not NO_2 in isolation.

Methods to control NOx

A variety of methods are commercially employed to reduce NOx in diesel engine exhausts. These methods can generally be separated into two major categories:

- Combustion modification, which adjusts conditions inside the cylinder to reduce NOx formation.
- After-treatment, which attempts to modify the exhaust gases after the combustion chamber and before they are vented to the atmosphere.

Despite recent advances in engine and after-treatment technology, the control of NOx, particularly NO_2, remains a serious challenge. What follows is a review of current technology and some thoughts for moving forward.

Combustion modification

By modifying the air-to-fuel ratio, it is possible to manipulate the amount of pollutants in the exhaust gas. A lean mixture (increased air-to-fuel ratio) will produce higher flame temperatures as the ratio approaches ideal, and also increases the amount of NOx produced, but will reduce particulate emissions. The opposite is also true. A rich mixture (decreased air-to-fuel ratio) will produce lower flame temperatures as the ratio moves away from ideal, and consequently, reduced NOx formation. Particulate emissions will increase since there is not enough oxygen in the mixture to oxidise the hydrocarbons (fuel).

Exhaust gas recirculation (EGR) consists of routing a portion of the exhaust flow back into the air intake. The primary benefit of this technique is reduced cylinder temperatures due to increased specific heat of the charge air. To a lesser degree, NOx is reduced due to dilution of incoming charge air with exhaust gas.

Selective catalytic reduction

Selective catalytic reduction (SCR) is a process in which urea, also called diesel exhaust fluid (DEF) is injected into the exhaust stream. The urea is hydrolysed to ammonia, which, in the presence of a catalyst, reduces the NOx to elemental nitrogen and oxygen. This process is expensive, requiring complicated auxiliary controls, additive injectors and storage tanks. In addition, some SCR systems require the addition of an ammonia slip catalyst, as there may be excess ammonia left due to an overdose of urea. SCR is used on surface vehicles, both on and off highway and for stationary applications, but is a challenging solution for underground coal mining.

Passive NOx reduction

A passive NOx reduction system reacts NOx with hydrocarbons in the presence of a catalyst. These systems are sometimes referred to as lean NOx catalysts (LNC). In a passive system, it is most desirable to use hydrocarbons present in the exhaust itself; however, this often does not result in desired levels of NOx reduction, and additional hydrocarbon, such as raw diesel fuel, must be injected. This type of system may also refer to, or be supplemented by, a lean NOx trap (LNT). In this system, the washcoat contains zeolyte or a similar compound, which adsorbs NOx. The NOx is then released when conditions are more appropriate for its reduction, such as when the exhaust gas is at an elevated temperature.

AirFlow Catalyst Systems is currently conducting internal research to better address the passive abatement of NOx in the diesel exhaust stream. AirFlow's programme focuses on the reduction of NOx using both mechanical and chemical means. Internal research is identifying the main levers in the dynamic process of diesel combustion and optimising those levers that result in lower NOx formation while catalysing the NOx that is produced. Technology is now available to trap and passively oxidise particulate matter (soot) and reduce PM emissions by well over 93%. It would be logical, then, to adjust air-to-fuel ratios to take advantage of the hydrocarbons in the exhaust stream so the abatement system can utilise the hydrocarbons as NOx reductants. AirFlow believes that a multifunctional approach to NOx reduction will result in a passive system applicable to any internal combustion process.

Conclusion

The pathways of NOx formation are well understood, but abatement of NOx remains a difficult and persistent challenge. The acceptable NOx threshold will certainly be reduced, and so it is critical that effective and cost efficient solutions to control and abatement of NOx be discovered and incorporated into internal combustion engines. As with many issues, there are tradeoffs. For instance, controlling NOx within the combustion chamber can result in greater particulate pollution. For that reason, it is most likely that the best solution for control and abatement of NOx is multifaceted, and involves engine manufacturers, as well as manufacturers of exhaust after-treatment systems.

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