### **MDEC 2009**

## NO<sub>2</sub> Emissions in Mines

#### 1. Regulated Engine NOx Emissions

 $NOx = NO + NO_2$ 

NO – nitric oxide NO<sub>2</sub> – nitrogen dioxide

Nitrous oxide - N<sub>2</sub>O (laughing gas) is not a regulated emission

### 2. Exposure Limits for Nitrogen Oxides

ACGIH TLV (TWA 8hr): NO: 25 ppm NO<sub>2</sub>: 3 ppm

*N*<sub>2</sub>*O*: 50 ppm

### 3. NOx Composition in Diesel Exhaust (no catalyst)

Older technology, naturally aspirated: NO: 95% NO<sub>2</sub>: 5%

New, turbocharged diesel engines: NO: 85% NO<sub>2</sub>: 15%

### 4. Oxidation of NO to NO<sub>2</sub>

 $2NO + O_2 \leftrightarrow 2NO_2$ 

- reaction occurring spontaneously in the atmosphere
- equilibrium reaction

# 5. Impact of Oxidation Catalysts

- Oxidation catalysts greatly increase the NO/NO<sub>2</sub> reaction rate.
- Pt/Al<sub>2</sub>O<sub>3</sub> catalysts—common in diesel applications—are especially active.
- Pt-based catalytic filters widely used in US 2007 engines.

Conclusion: Emission controlled diesel engines have significantly increased NO $_2$  /NO ratio in their total NOx emission.

# 6. Implications of High NO<sub>2</sub> / NOx—Environmental Effects

- Suspected adverse effects, but the exact impact remains uncertain
- Future emission standards also require very low NOx; even at increased NO<sub>2</sub>/NOx ratios, the absolute NO<sub>2</sub> emissions will be reduced
- Little concern in regards to future emission standards
- Concerns exist in DPF retrofit applications with older high NOx engines
- California ARB: NO<sub>2</sub> must not be more than 20% of total NOx (based on uncontrolled engine emission baseline) for verified emission retrofit technologies

### 7. Occupational Health

- Increased diesel NO<sub>2</sub> may contribute to exceeding TLV levels
- MSHA PIB P02-7, July 16, 2002: "...particulate filters introduced into the underground [coal] mine (...) must not cause an increase in NO<sub>2</sub> concentrations in the raw exhaust."

### 8. Diesel Smoke Opacity Measurement—NO<sub>2</sub> Interference

 $NO_2$  absorbs green light and causes a false opacity reading. In DPF equipped engines, the majority of the opacity meter signal can be caused by  $NO_2$ , rather than by diesel soot.

#### 9. NO<sub>2</sub> Control—Diesel Oxidation Catalysts

- Selective formulations optimized for low sulfate emissions appear to have also low NO<sub>2</sub> production
  - Base metal/low Pt technology
  - Vanadium doped formulations
- But:
  - low sulfate formulations may have low effectiveness in controlling HC, CO, odor, etc.
  - low sulfate catalysts will be abandoned as ultra low sulfur fuels become available

#### 10. NO<sub>2</sub> Control—Diesel Particulate Filters

- Passive DPF systems
  - Less active formulations possible (e.g., base metal DPFs), but require higher regeneration temperatures
    - can be applied only on very hot vehicles
  - Wide consensus on using Pt in passive and quasi-passive DPF systems (US heavy-duty engines, EU passenger cars)
- Fuel additive regenerated filters
  - low regeneration temperatures, low NO<sub>2</sub>, but doping the fuel with additive often inconvenient
- Active DPF systems
  - There are no NO<sub>2</sub> problems, but no automated systems available for U.S. Mining market
  - Manually regenerated systems (electric off-board, shore power, ...)—no NO<sub>2</sub> increase, but high maintenance involved