During the past couple of years the Technical Services Department of Exchem Explosives has received a number of enquiries regarding the nature of after-blast fumes. These enquiries have been driven by two concerns:

1. **Site-related health and safety**
   The advent of risk assessments and the introduction of programmes such as the quarry industry’s ‘Hard Target’ initiative have led to the re-examination of many activities that make up the rock extraction process.

2. **Public comment from people living close to blasting operations**
   Increasing environmental awareness and the availability of Internet-based information has led to members of the public investigating all aspects of blasting operations. In the last year this has led to a number of ‘objectors’ asking about toxic fumes from blasting.

A recent paper by Santis reviewed US accident statistics since 1992 for incidents relating to the use of explosives. The incidents detailed 11 occasions where after-blast fumes had seriously affected a member of the public, three occasions where a worker had been affected, and one workplace fatality. Such papers are readily available and make perfect ammunition for those ‘objectors’ working to prevent the use of explosives in mines, quarries, civil engineering etc.

Although all explosives have the potential to produce toxic fumes, initial work has focused on ammonium nitrate fuel-oil (ANFO) mixtures. This focus is driven by the fact that the use of ANFO allows the user to make choices regarding the type of AN prill to be used and the mixing procedure to be followed. This paper examines how these choices can impact the quality and quantity of after-blast fume.

### Background on fumes from blasting

**For every kilogram of ANFO that is detonated approximately 1,000 litres of gas are produced. These reaction gases principally consist of carbon dioxide (CO₂), nitrogen (N) and water vapour (H₂O). However, as such detonations do not occur under ideal conditions, other toxic gases may also be formed, such as carbon monoxide (CO), nitrogen monoxide (NO) and nitrogen dioxide (NO₂).**

The degree of toxic fume production depends upon a number of factors including:

- **Oxygen balance**
  An ANFO mixture containing 5.6% diesel by weight is said to be oxygen balanced and will produce the minimum quantity of toxic fumes when detonated. Mixtures with too much fuel tend to produce increased levels of CO and those with too little fuel produce increased levels of oxides of nitrogen (collectively known as NOx).

- **Homogeneity**
  If an oxygen-balanced ANFO mixture is used but is not well mixed then this explosive will contain both oxygen-positive and oxygen-negative portions. The detonation of such a product will therefore produce increased levels of both CO and NOx.

- **Presence of water**
  It is well known that if ANFO is contaminated with water there is a likelihood of increased levels of NOx and CO. It is thought that the addition of water to the mixture both adds oxygen and reduces the reaction temperature.

### Exposure limits

The Health and Safety Executive publication ‘EH40’ gives occupational exposure limits. This paper examines the effect of prill type and mixing technique.
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(OELs) for many hazardous substances. Separate limits are given for short- and long-term exposure. The short-term limits for CO, NO and NO₂ are all quoted over 15min exposure periods, as listed in table 1.

Additional information on exposure levels is given in documents published by the United States Environmental Protection Agency. These documents, currently in draft form, give guideline values related to three levels of impact known as AEGL-1, AEGL-2 and AEGL-3, as outlined below:

- AEGL-1 is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long-lasting adverse health effects, or an impaired ability to escape.
- AEGL-2 is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.
- AEGL-3 is the airborne concentration (expressed as ppm or mg/m³) of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening health effects or death.

The AEGL levels relating to CO, NO and NO₂ are also listed in table 1. There does not appear to be any information available on maximum instantaneous levels, irrespective of exposure time, for these three gases.

Gas-monitoring equipment

All the monitoring detailed in this paper has been carried out using standard Crowcon gas-monitoring equipment. The units used had the following gas sensors fitted:
- carbon monoxide: 0–500ppm
- nitrogen monoxide: 0–100ppm
- nitrogen dioxide: 0–17ppm

One particular advantage of the system chosen was that gas levels could be logged at 1s intervals for periods of up to 100min.

Ammonium nitrate prills

In general, there are two basic types of ammonium nitrate prills used to produce ANFO explosives. These are porous (also known as explosive grade) and dense (also known as agricultural grade). The essential difference between the two products is their porosity and therefore also their density.

It is worth noting that ammonium nitrate prills are available with densities ranging from 0.6 to 1.0 and therefore with a similarly wide range of porosities. Other products are available that consist of a blend of prill types or may even include microspheres inside the prills.

Figure 1 shows two samples of ANFO mixed under laboratory conditions, each with a mass of 1kg and containing 5.6% diesel fuel. The diesel used in this case had a red dye added to it to increase the colour contrast. It can be seen that the porous-prill mixture has an even colour and reaches well up the sample tube. The dense-prill mixture does not fill as much of the tube, due to the higher density of the prill, and it is also very noticeable that much of the diesel has free-drained to the bottom of the sample. The densities of the two samples were measured at 0.85 for the porous-prill product and 1.0 for the dense-prill product.

Subsequent analysis of the dense-prill mixture showed that the bulk of the sample had only 2% diesel by weight. This finding was later confirmed by field sampling of a similar product. It was concluded that while the porous-prill could easily absorb 5.6% diesel, the dense prill could only retain 2%. It is also suspected that in the dense-prill mixture the fuel is mainly to be found on the outside of the prill.

Outline of test work at Camborne School of Mines

In order to be able to carry out gas-monitoring work under

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Table 1: Exposure limits from EH40 and from AEGL documentation

<table>
<thead>
<tr>
<th>Gas</th>
<th>Occupational Exposure Limit, 15min</th>
<th>Acute Exposure Guidance Levels, 10min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>AEGL-1 Non-disabling</td>
<td>AEGL-2 Disabling</td>
</tr>
<tr>
<td>Carbon Monoxide</td>
<td>200ppm</td>
<td>420ppm</td>
</tr>
<tr>
<td>Nitrogen Monoxide</td>
<td>35ppm</td>
<td>80ppm</td>
</tr>
<tr>
<td>Nitrogen Dioxide</td>
<td>5ppm</td>
<td>0.5ppm</td>
</tr>
</tbody>
</table>

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Fig. 2. Plan of underground test area
controlled conditions it was decided to undertake a series of test blasts at the underground test mine facility at Camborne School of Mines in Cornwall.

The part of the mine employed for this work is shown on the plan in figure 2. It can be seen that the blast area was in a dead end with a forced-ventilation system. This meant that all the after-blast fumes had to pass through the monitoring station and at a constant air velocity. The tunnel profile at the gas-monitoring station was square with dimensions of 2.9m x 2.9m, giving a cross-sectional area of 8.4 m². The average air velocity through this location was 0.12m/s.

Two Crowcon gas monitors were used at the monitoring station with one positioned 1m below the roof and the other 1m above the floor.

Each test blast consisted of three 32mm diameter blastholes drilled at a shallow angle into the sidewall to a depth of 1.2m. The holes were spaced 0.8m apart and each contained 0.75kg of ANFO.

The explosives used for each blast were:

1. **Laboratory-mixed ANFO** (porous)
   - Prill type: standard porous
   - Fuel: diesel at 6% by weight
   - This is the standard factory-mixed product and was made under laboratory conditions using weighed ingredients.

2. **Site-mixed ANFO** (porous)
   - Prill type: standard porous
   - Fuel: diesel at 6% by weight
   - This was mixed on site by adding 6% diesel, waiting 30min and then gently mixing. The final product, as poured in the holes, did not look well mixed.

3. **Laboratory-mixed ANFO** (dense)
   - Prill type: dense
   - Fuel: diesel at 2% by weight
   - This product was mixed in the laboratory. Only 2% diesel was added as it is known from previous work that dense prill is only capable of retaining this amount and that any additional diesel simply free drains.

   Each blasthole was primed with a 20g Pentolite primer and fired with a non-electric detonator. The three holes were fired at 25ms intervals with the centre hole being fired first in each case.

**Velocity of detonation**

In order to examine the relative performance of each sample of explosive, a velocity of detonation (VoD) measurement was undertaken in the first hole to fire in each blast. The results were:

1. Laboratory-mixed with porous AN — 2,300m/s
2. Site-mixed with porous AN — 2,200m/s
3. Laboratory-mixed with dense AN — 410m/s

The results for tests 1 and 2 are in line with expectations for ANFO in small-diameter holes, however the dense-prill ANFO is seen to have deflagrated.

**Near-field acceleration**

As an additional performance indicator, acceleration readings were taken at the location indicated in figure 2. The acceleration recordings are shown in figures 3, 4, and 5. It can be seen that these recordings consist of a series of three pulses in each case. It is apparent from the...
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Traces that individual holes give an approximate acceleration of either 5g or 1g. It is reasonable to assume that the low-acceleration pulses correspond to holes that have deflagrated while the high-acceleration pulses correspond to those that have detonated. These results correspond to those collected via the VoD recordings for the first hole in each test.

From a combination of the acceleration and velocity of detonation readings it can therefore be determined that each hole performed as outlined in table 2.

Gas monitoring

Figure 6 shows the gas-monitoring data for nitrogen monoxide recorded both close to the roof and close to the floor of the mine. The illustrated traces are from test blast 3 and clearly show how the levels of gas are substantially higher close to the mine roof. All remaining results given in this paper are from the roof monitoring location. Figures 7, 8, and 9 show the monitoring results for the test blasts grouped by gas type.

The NO₂ results for test blast 3 give a clear indication that the gas sensor has been saturated/overloaded, thereby limiting the maximum recorded level to 17ppm. It can be shown from other monitoring data that for each blast event there is a relatively constant ratio between NO and NO₂. For this recording a ratio of 0.79 can be determined from the data recorded before the overload period. Application of this ratio to the NO data gives a predicted NO₂ trace as shown in figure 9. The predicted maximum level for NO₂ is 35.5 ppm.

Peak levels for each blast and gas type are shown in table 3.

Carbon monoxide

It can be seen from figure 7 that all three test blasts gave broadly similar levels of CO with peak levels of 60–70ppm. This level is well below the 15 min occupational exposure limit (OEL) of 300ppm.

Nitrogen monoxide

The levels of NO from the test blast series showed large variations between the various explosive types. ANFO made from dense prills resulted in levels five times higher than the product made with porous prills and mixed in the laboratory, while the peak level for dense prills just exceeded the permitted 15 min OEL level of 35ppm.

Nitrogen dioxide

For NO₂ there was a very stark contrast between the various explosive types. The product made from porous prills and mixed in the laboratory gave a maximum value of 0.6ppm, which is well below the 15min OEL of 5ppm. The comparable product mixed on site gave a peak level of 10.3ppm, which is well above the 15min OEL, although this level was not exceeded for a full 15min. The product made from dense prills produced a predicted maximum level of 35.5ppm, which is

<table>
<thead>
<tr>
<th>Explosive Type</th>
<th>Prill Type</th>
<th>Hole 1 VoD m/s</th>
<th>Detonation or Deflagration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Lab. mixed</td>
<td>Porous</td>
<td>2,300</td>
<td>Detonation, Detonation, Deflagration</td>
</tr>
<tr>
<td>2. Site mixed</td>
<td>Porous</td>
<td>2,200</td>
<td>Detonation, Deflagration, Deflagration</td>
</tr>
<tr>
<td>3. Lab. mixed</td>
<td>Dense</td>
<td>410</td>
<td>Deflagration, Detonation, Detonation</td>
</tr>
</tbody>
</table>

Table 2: Detonation data for each hole
59 times higher than the product made with porous prills and mixed in the laboratory. Test blast 3 was above the 15min OEL for almost exactly 15min and also exceeded the AEGL-3 level of 34ppm.

Conclusions

Although the tests described in this paper are small in scale they do highlight a number of important points regarding the level of toxic fume that can be produced by ANFO mixtures. Of particular importance is the degree of control that can be achieved regarding the production of nitrogen monoxide and especially nitrogen dioxide.

The key actions that can be taken to minimize the production of toxic after-blast fumes from ANFO are:

- Only use ammonium nitrate prills that are designed for explosive manufacture, i.e. capable of absorbing 5.6% diesel.
- Add the correct amount of diesel fuel to achieve an oxygen-balanced mixture.
- Mix the ANFO thoroughly to ensure even distribution of the fuel throughout the explosive.

The UK minerals industry is currently taking part in a series of excellent safety initiatives under various banners such as ‘Hard Target’. One relatively easy target is to minimize the production of toxic after-blast fumes by the correct use of ANFO mixtures.

Table 3: Maximum recorded gas levels

<table>
<thead>
<tr>
<th>Explosive Type</th>
<th>Prill Type</th>
<th>Carbon Monoxide</th>
<th>Nitrogen Monoxide</th>
<th>Nitrogen Dioxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Laboratory mixed</td>
<td>Porous</td>
<td>70.1</td>
<td>8.1</td>
<td>0.6</td>
</tr>
<tr>
<td>2. Site mixed</td>
<td>Porous</td>
<td>62.3</td>
<td>29.4</td>
<td>10.8</td>
</tr>
<tr>
<td>3. Laboratory mixed</td>
<td>Dense</td>
<td>62.3</td>
<td>42.6</td>
<td>17 (35.5)</td>
</tr>
</tbody>
</table>

References


Fig. 9. Nitrogen dioxide data for the three test blasts