CHEMICAL AND PHYSICAL FACTORS THAT INFLUENCE NO$_x$ PRODUCTION DURING BLASTING - EXPLORATORY STUDY

by Michael Sapko, James Rowland, Richard Mainiero, and Isaac Zlochower

ABSTRACT

The National Institute for Occupational Safety and Health (NIOSH) carried out exploratory laboratory-scale studies to identify factors that may contribute to nitrogen oxides (NO$_x$) production associated with non-ideal detonation of blasting agents. Explosive admixture with drill cuttings, loss of fuel oil in ammonium nitrate and fuel oil (ANFO) from wicking, ammonium nitrate dissolution with water, degree of explosive confinement, ANFO density, and critical diameter were identified as contributing factors to increased NO$_x$ production under the laboratory test conditions. Experiments were also conducted to examine the effectiveness of various additives in reducing the NO$_x$ production from ANFO, emulsion, and ANFO/emulsion blends. Aluminum powder, coal dust, urea, and excess fuel oil in ANFO formulations were tested and were found to reduce both the nitric oxide (NO) and nitrogen dioxide (NO$_2$) production. Fumes measurements were obtained in the NIOSH underground closed chamber from the detonation of 4.5-kg (10 lbs) charges in schedule 80 seamless steel pipe and from detonations in light weight galvanized steel stove pipe. Some exploratory tests were also conducted with 0.8-kg (1.8 lbs) charges of pulverized ANFO initiated with 0.08-kg (0.18 lbs), 50/50 (Pentolite) boosters (in the NIOSH 12-ft (3.7-m) diameter steel sphere) to measure the degree of fumes production associated with post-detonation oxidation. Ammonium nitrate, emulsion and Pentolite boosters were also detonated in an oxygen-poor environment.

INTRODUCTION

The generation of orange post-blast NO_2 clouds, more commonly referred to as yellow or orange smoke, is not uncommon in the commercial explosives' industry. The occurrence of such post-detonation fumes has historically been associated with wet conditions and has generally not been viewed with alarm due to the rapid dispersion of the gas into the air. Current cast-blasting in some surface coal mining operations have resulted in the use of millions of pounds of ANFO and ANFO/emulsion agents in a single blast. While NO_2 dissipation into the atmosphere from relatively small shots is generally achieved in a matter of seconds, comparable NO_2 dissipation from huge casting operations may take minutes. Faced with the noticeable levels of NO_2 in the form of orange/red clouds which may drift off the mine property, the mining industry has requested assistance from NIOSH to identify potential causes for generation of these orange clouds, and to recommend ways to minimize their occurrence.

The orange/red coloration is caused by the presence of NO_2 which is a direct product of the detonation process, and is also produced in the after burning reactions and by the secondary oxidation of NO to NO_2 as the cloud mixes with air. Both NO and NO_2 are toxic gases, as indicated by the NIOSH recommended exposure limits (REL) for a 10-hour work day of 25 ppm and 2 ppm respectively[1]. The cloud due to NO_2 is both more noticeable and potentially more toxic.

Several factors have been identified as contributing to the non-ideal detonation behavior observed in some large cast blasts: A weak overburden, which significantly reduces the necessary explosive confinement; significant water infiltration during long intervals between loading and firing, which changes the explosive composition; long explosive columns, which produce bottom hole hydrostatic pressures that decrease the probability of successful detonation propagation; and explosive pre-compression caused by hole-to-hole shock propagation due to wet overburden and clay veins. Research has shown that the degree of confinement of an explosive charge and the material being blasted both have a significant impact on fumes production[1,4,5]. As a result, measurements of fumes produced by blasts in one mine tells us little about the fumes that would be produced for a different blast pattern in different material at another mine. Tests on a smaller scale, with better control over the variables are therefore required in order to delineate causal factors and to indicate means of minimizing this problem.

Over the years, extensive explosive testing research has been done on the toxic fumes generated by the detonation of high explosives, and many countries have test procedures and formal requirements in place as to the maximum permitted fumes production in the mandated tests [2,3]. Typically, 100 grams or so of high explosives are detonated in a chamber and the fumes collected for analysis. Measuring the fumes produced by the detonation of blasting agents is much more difficult. Any test to measure the fumes produced by blasting agents must take into account the fact that most blasting agents require boosters, larger charge sizes, and heavy confinement to detonate well and to simulate the conditions used in actual practice. In addressing this issue, NIOSH developed tests that report fumes production under a well defined set of conditions[6,7,8] in a large mine room and in a large steel sphere.

It must be understood, however, that it is not generally possible to extrapolate quantitative toxic fumes data to mine site conditions. First, it is difficult to achieve consistent detonations of ANFO in small diameter pipes without pulverizing the prills and thereby introducing a grain-size variable. Second, the degree of confinement plays an important role in determining the detonation conditions and the composition of the expanded detonation products. The actual degree of explosive confinement in the field

can not be duplicated in the laboratory. Laboratory studies, however, provide a useful, inexpensive approach for comparing the relative effectiveness of various techniques for reducing the production of toxic fumes.

This paper describes results from the series of detonation tests with blasting agents conducted in the mine chamber and in a smaller scale 12-ft (3.7-m) diameter sphere to identify factors contributing to fumes production, and to evaluate the potential of various additives or stemming techniques to reduce the formation of NO_2 when blasting under non-ideal conditions primarily caused by low confinement. Most blasting agents are formulated to be near stoichiometrically balanced in fuel vs oxygen content to maximize energy output while minimizing carbon monoxide (CO), NO, and NO_2 production when properly boosted, shot in large diameters, and shot under heavy borehole confinement. In many blasting operations, the ground conditions do not provide good confinement, resulting in non-ideal detonations. This study focuses on the potential use of inexpensive additives to blasting agents to reduce the formation of NO and NO_2 generated under these non-ideal conditions. Various stemming materials were also evaluated to determine their potential to reduce the NO_2 concentration through absorption by water and/or alkaline materials. ANFO additives included, aluminum, coal dust, urea, and diesel fuel. Stemming materials included water, $NaHCO_3$, Na_2CO_3, coal dust, trona, and wet drill cuttings. The most important consideration is safety when considering modification to any explosive formulation through the incorporation of additives. Any non-proven modifications to explosive formulation should be approached with extreme caution and only by qualified explosive manufacturers. Preliminary results will be presented, but further full-scale field research under controlled field conditions must be conducted to evaluate the validity of these potential remedial measures.

EXPERIMENTAL APPROACH

Underground Chamber

A facility for detonating large, confined charges in a controlled volume has been constructed at the Pittsburgh Research Laboratory=s Experimental Mine and has been used for measuring fumes production as a function of various additives in 4.5-kg (10 lbs) explosive charges[8]. Tests are conducted in thin-wall 4-in (10-cm) diameter galvanized pipe to simulate light confinement, and in nominal 4-in (10-cm) schedule 80 seamless steel pipe to simulate heavier confinement. The facility, illustrated in Figure 1, consists of a portion of mine entry enclosed between two explosion proof bulkheads. Total volume of the chamber is 9,667 ft (274 m3). The chamber is equipped with an air circulating system and is vented by opening the vent ports to the mine's airflow. Up to 4.5-kg (10 lbs) charges can be detonated in the chamber using a variety of confinements. For a typical test, the blasting agent is confined in a 4-in (10-cm) schedule 80 seamless steel pipe and is initiated by a 2-in (5.1-cm) diameter, 2-in (5.1-cm) thick Pentolite booster. This combination of confinement and initiation yields a detonation velocity of about 4,000 m/s for a 26-in (66-cm) column of ANFO prills. Twenty-four 2-in (5.1-cm) thick steel plates are suspended around the pipe, which is itself suspended vertically above a heavy steel plate on the mine floor, to form a cage which stops shrapnel that would otherwise seriously damage the chamber. Following detonation of an explosive in the chamber, a circulating fan is run for about 10 minutes to uniformly mix the chamber atmosphere. Fumes samples are taken out of the chamber through 0.25-in (6-mm) Teflon tubes via sampling pumps for analysis. Vacutainer gas samples are taken and sent to our analytical laboratory for gas chromatographic analysis. The latter technique is appropriate for components that are stable in the Vacutainer, namely

hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), and methane (CH_4). NO and NO_2 are measured with an on-line chemiluminescence analyzer and ammonia (NH_3) is measured with a MSA Chilguard[*] analyzer[8]. A minimum of 2 and a maximum of 6 experiments were conducted with each explosive mixture and the average concentration reported. The reproducibility for most tests was within10% with the largest difference being 20%.

12-ft (3.7-m) Diameter Sphere

Smaller scale studies were conducted in NIOSH=s 12-ft (3.7-m) diameter sphere shown in Figure 2. The preparation of ANFO mixtures involves blending of No. 2 diesel fuel (with red dye) with pulverized ammonium nitrate (AN). The AN had passed through a 60-mesh screen, corresponding to AN particles that are less than 250 microns. For a typical test, the pulverized ANFO mixture is placed in a glass tube with a 1.75-in (4.45-cm) inner diameter, 0.06-in (0.15-cm) wall thickness and 24-in (61-cm) long. Glass was chosen because it is inert and would not contribute to the fumes production. A cast Pentolite booster that is 1-in (2.5-cm) thick (about 80 grams) was taped with masking tape to one end of the tube. Prior to loading the pipe with explosive, a continuous velocity probe of the type described by Lon Santis[9] is taped to the inner surface of the pipe along its length. The glass tube filled with ANFO is suspended vertically in the geometric center of the 12-ft (3.7-m) sphere and initiated with a No. 8 copper blasting cap.

Ten minutes after detonation, gas samples are withdrawn at about 1.2 L/min through an MSA[*] Ultra-Filter with Type H cartridge via Teflon tubing and introduced into the flow controlled electrochemical cells in a Testo 350 analyzer[*]. The Testo provides an on-line readout of NO, NO_2, and CO concentrations. The Testo 350 has a time constant of about 2 minutes and was calibrated before each test with calibration quality mixtures of each of the sensed gases (CO, NO, and NO_2) in nitrogen. Vacutainer samples were also taken at 5, 10, 30, and 60 minutes after the detonation for subsequent GC analysis for H_2, CO_2 and the hydrocarbons (C_1-C_5). Overpressure in the sphere following the detonation was less than 3 kPa (20 torr). Continuous and batch sampling results showed a relatively constant concentration of CO from 5 minutes to 60 minutes after detonation. Some detonation tests were also conducted in mostly argon atmospheres containing less than 1% oxygen.

RESULTS AND DISCUSSION

ANFO Particle Size

Several chamber tests were conducted to compare the fumes production from the detonation of prilled and pulverized ANFO. 10 lbs (4.5 kg) of prilled and pulverized ANFO was loaded and shot in 4-in (10-cm) galvanized steel pipe. The bulk loading density of the prills was 0.86 g/cc and the bulk (non tamped) loading density of the pulverized ANFO (< 200 microns) averaged 0.82 g/cc. The average measured detonation velocity (VOD) was 3927 m/s for the pulverized ANFO and 2738 m/s for prilled ANFO. The resulting fumes from the detonations were collected and measured. With the same degree of light confinement, the NO_2 production from pulverized AN was a factor of 4 lower than that produced from standard prills. Both CO and H_2 from the detonation of pulverized AN were

about factor of 2 lower, and the NO was 30% lower than with pills. No significant difference in CO_2 production was detected between the pulverized and prilled AN. With pulverized AN, the ammonium nitrate is presumably more intimately mixed with the fuel than in the case of the prills. The more intimate contact between the ammonium nitrate and fuel may cause a more complete reaction to take place. With prills, the decomposition reactions in the grains of nitrate may take place further behind the detonation front to yield more NO. Studies continue in the mine chamber and in the 12-ft (3.7-m) sphere in argon to better understand the causes for the NO_x reduction with decreasing AN particle size.

ANFO Prills vs Emulsion and Confinement

It has been proposed that the reduced confinement provided by a soft overburden present at some surface mines may promote the generation of NO from the explosive composition within the borehole due to thermal reaction of the nitrates (and fuel) contained in the explosives. As the NO is released from the muck pile following the detonation of the blast pattern, the gas is further oxidized in air to form the colorful after-blast fumes of NO_2. NIOSH's underground chamber was used to examine the relative NO_x production as a function of simulated levels of explosive confinement. Three explosive compositions with different detonation velocities were examined. Compositions of ANFO, a 50/50 blend of emulsion with ANFO, and straight emulsion were detonated in both schedule 80 steel pipe and in light weight galvanized pipe. The emulsified explosive used in this study was the Apex 1220 emulsion donated by Energetic Solutions Inc[*], and the AN prills were from the Seneca[*] plant in Pennsylvania. Post-detonation products were analyzed and the results are presented in Figures 3 and 4.

The oxidation of NO to NO_2 in air depends on the initial NO concentration and time. Concentrations of both NO and NO_2 are added and the sum is given as NO_x concentration. The NO_x concentration shows significant increases with decreasing confinement for all three explosives. Furthermore, the ANFO and 50/50 ANFO/emulsion blend produced much more NO_x than the emulsion. Grain size of the explosive is probably most important in this connection, too. Explosives like ANFO contain rather large grains of AN which tend to decompose and yield NO_x. In emulsion explosives, the nitrate is mainly found in solution and more intimately in contact with the emulsified fuel droplets. As a result the NO_x produced from the thermal decomposition of AN will tend to react with hydrocarbons to yield nitrogen and water rather than remaining as NO after the detonation.

Critical Diameter of the Emulsified Explosive

To determine the critical diameter, the emulsion was detonated in various diameter schedule 40 steel pipe from nominally 1 to 4-in (2.5 to10-cm) diameters. The length of the pipe was 2-ft (61- cm). The velocity of detonation (VOD) was measured and the degree of pipe fragmentation was noted. The VOD results shown in Table 1 indicate that the emulsion detonated about 6600 m/s in 4-in (10-cm) pipe to slightly over 5300 m/s in 1 in pipe (inside diameter of 1.05-in or 2.67-cm). The critical diameter for this emulsion appears to be less than 1-in (2.5-cm) and the detonations using heavy confinement are relatively ideal, thus producing much less $_{Nox}$.

Table 1.- VOD as a function of pipe diameter.

Nominal Size Schedule 40 Pipe	VOD (m/s)
4-inch[1]	6604
3-inch	6634
1.5-inch	5862
1-inch	5346
[1]Nominal size Schedule 80 steel pipe	

ANFO Additives

The generation of post-blast NO_2 is hypothesized to be the result of thermal reactions (in addition to the ideal products of detonation), which result in the enhanced formation of NO_x. The NO component readily oxidizes to the visual orangish cloud characteristic of NO_2 when introduced into the atmosphere. Modification of the explosives' composition was considered as a remedial method for reducing the probability of forming NO_x in the reaction zone following the detonation front. Detonation tests with blasting agents were conducted in the mine chamber and in the 12-ft (3.7-m) diameter sphere to evaluate the potential for various additive or stemming techniques to reduce the formation of NO_2 when blasting under low confinement. Coal dust, urea, excess diesel fuel, WR Conditioner 260* additive, and aluminum were mixed in various proportions with the emulsion, ANFO, and blends, followed by detonation in light weight 4-in (10-cm) galvanized steel pipe. These additives had been alleged to reduce NO_x in blasting operations. The WR Conditioner also forms a gel in contact with water to provide protection against AN dissolution. Figure 5 compares the NO and NO_2 produced from ANFO with that produced using various additives. Excess diesel fuel (8%), reduces the NO_2 production by a factor of 3 with only a slight reduction in NO. The addition of 3% Pittsburgh Pulverized Coal (PPC) dust to the 6% fuel oil (FO) was just as effective. The 3% FO plus 3% PPC produced less NO_2 than 6% FO, with an increase in NO. Making the explosives fuel rich thus leads to a reduction of NO_x, but at the expense of an increase in CO. The benefit of any additive with low confinement will be lost if some of the explosive column is compromised during the long interval between borehole loading and firing from water influx dissolving the AN or to the loss of fuel oil due to wicking action of the borehole walls. In such cases the explosive column composition would have to be protected against water influx and against oil absorption by the surrounding overburden material. This is the intended function of the WR additive.

50/50-ANFO/Emulsion Blends with Additives

Figure 6 compares the NO and NO_2 production for 50/50 blends of emulsion with ANFO shot in galvanized steel pipe with and without additives. The additive is mixed with ANFO and then mixed with the emulsion. Pittsburgh Pulverized Coal (PPC) (mean particle size 74 microns) had little effect

on the NO and NO_2 production. Even 5% PPC produced only a slight reduction in NO_2. Addition of 3% urea also had little effect on NO_2 production. When 3% aluminum was added to the 6% FO - 91% AN the NO_2 decreased by a factor of 2.5. Added aluminum powder was expected to increase the temperature, reaction rate and the completeness of the thermal reaction of the fuels and the oxidizer. Studies continue with blends to evaluate the effectiveness of higher aluminum concentrations.

Stemming Materials

In addition to the additives, stemming with water was considered a potential mitigation technique to reduce NO_2 production by dissolution of the soluble acidic gas in water augmented by a basic material such as sodium carbonate (Na_2CO_3). One liter of water mixed with 10 grams of Na_2CO_3 reduced the detectable NO_2 by 48% with little reduction in NO. Practical stemming with water may, however, be somewhat difficult to accomplish in the field. One would need to ensure that water does not leak into a lower explosive column during the long period between loading and firing. Adding a gelling agent to the bagged water could minimize such concerns. Wetting down the blast area prior to firing was considered as a way to help absorb the NO_2 on damp dust dispersed during the blast.

Oil Wicking and AN Dissolution

A common explanation for post-detonation NO_2 fumes from ANFO is that the mix was under-fueled (positive oxygen balance) or the boreholes were wet. If under-fueling occurred, the production of oxides of nitrogen may be expected due to incomplete reduction of the nitrates to nitrogen. The possibility exists that a balanced ANFO formulation could become fuel-poor if fuel oil is lost to the borehole wall by wicking. Several experiments were conducted to assess the amount of fuel oil loss due to wicking of the fuel oil in ANFO. AN prills were mixed with No. 2 diesel fuel and set for 24 hours. They were then placed in simulated boreholes consisting of cylindrical holes in porous cement blocks. The cement was made with 12 parts sand and 1 part cement, plus enough water to yield a workable mix and set in 1-gal metal paint cans. The 'boreholes' were 1, 2, and 2.5- in (2.5, 5, and 6-cm) in diameter. Larger, 4.5-in (11-cm) diameter boreholes were fabricated in 6-gal sealable plastic cans. All of the cement blocks were dried in an oven at 110ºC for 7 days before loading. The ANFO was weighed, placed in a hole, sealed, and kept at 55ºC during testing. The ANFO was removed from the boreholes and weighed at 1, 2, 6, 8, 9, and 13 day intervals. The mass loss was found to be relatively constant at 0.0048 g/in²/day. Using this average loss rate, the fuel oil content as a function of borehole diameter for 7, 14, and 30 days was calculated and is shown in Figure 7. For 3-in (7.6-cm) diameter boreholes, after 30 days the average fuel oil concentration in the mixture decreases from 6% to 4.5%. Such a loss of fuel oil would result in under-fueled explosives in blasting situations, leading to an increase in NO and NO_2 production.

Similar tests were conducted as above except that 8% moisture was added to the dried cementitious borehole. Eight percent was chosen since the drill cuttings from a mine in Wyoming that had experienced red cloud formation after blasting, contained from 7% to 8% water. The drill cuttings, with 8% bound moisture, seemed dry to the touch. The can with the added water set for about 24 hours while the moisture was drawn into the walls of the simulated cementitious borehole. ANFO was weighed and added to the empty 2-in (5-cm) diameter borehole and sealed. In these tests, the

hygroscopic AN, drew the water from the cement, which dissolved some AN, and the column height decreased as the AN solution was drawn into the cementitious walls. The height of the column was recorded and the mass loss was calculated from the change in prill height and initial density. Shown in figure 8 is AN loss as a function of time. Note that in 10 days about 50% (½ the column height) was lost to the cementitious borehole. Similar tests were also conducted with the borehole cased with 12 parts drill cuttings and 1 part cement. There was no significant difference in loss rate between the sand/cement borehole and the one fabricated with drill cuttings of similar particle size. Without borehole liners, there can be a significant loss of AN. Even with holes that appear dry to the touch, a significant loss of AN can result with time.

Thickening Agents

Two additives were evaluated, one added to the fuel oil and one to the AN, to help reduce the fuel oil and AN loss. Two percent Cabosil[*] (fumed silica) was added to the fuel oil component and rapidly mixed with the AN prills. The mixture was then placed in the pre-dried 2-in (5.1 cm) diameter boreholes and the oil loss measured. The Cabosil prevented the wicking away of the fuel oil from the prills. However, under these conditions the Cabosil may have also prevented the oil from effectively migrating into the prill pores. Adding the Cabosil to the prills first, then mixing in the red-dyed fuel oil, appeared to restrict the oil absorption by the prills and prevented uniform distribution of the oil on the outside of the prills. Work continues to identify other liquid gelling agents that permit oil distribution throughout the prills before gelling occurs. The thickened fuel oil significantly reduced the loss of oil wicking but did not reduce the AN loss when placed in the simulated borehole containing 8% water.

WR Conditioner 260, an ANFO gelling agent, was also evaluated. The conditioner was added to the ANFO and placed in a simulated 2-in (5.1-cm) diameter cement-sand borehole containing 8% moisture. When compared with results from straight ANFO, the conditioner delayed the AN loss as shown in figure 9. As the AN draws water from the walls of the borehole, the WR Conditioner gels the water near the wall of the borehole, thereby reducing the rate of AN dissolution. The performance of WR Conditioner, under damp conditions, is expected to improve with an increase in borehole diameter. As the gelled water boundary layer between the explosive column and the borehole wall thickens, the better the center explosive core is protected from further erosion. These observations were based on a 2-in (5.1 cm) diameter simulated borehole and would have to be evaluated in the field in larger and deeper holes where hydrostatic effects may become important.

Emulsion Admixture with Drill Cuttings

Cast blasting is used extensively in large surface coal mines. Angled holes, 12.25 in (31 cm) in diameter, 170-ft (53 m) long are commonly used to cast overburden into the pit, thereby reducing drag line time and providing a more stable highwall. As the drill is withdrawn from the hole, the weak overburden from the walls of the hole falls down and accumulates at the bottom of the hole, as illustrated in figure 10. When drilling in soft overburden, the angled drill holes often become elliptical in cross-section. In some cases the angle holes are slightly sub-drilled into the coal, and backfilled with drill cuttings. Loading emulsion explosives on top of drill cuttings will tend to produce a mix of emulsion and drill cuttings near the bottom of the boreholes. The hydrostatic head produced by the

emulsion will tend to force it into the interstitial void within the drill cuttings. Some mixing of drill cuttings and emulsion will also occur at the top of the column when drill cuttings are piled on top for stemming.

NIOSH conducted a series of tests to examine the potential impact of emulsion admixture by Wyoming drill cuttings on the toxic fumes production. Shown in figure 11 is a 4-in (10 cm) diameter glass pipe with drill cuttings placed on top of the emulsion column and dead weight loaded at 10 psi (69 KPa) to simulate a 20-ft (6.1 m) high column of stemming. The drill cuttings sink into the emulsion filling the interstitial spaces. To measure the relative production of toxic fumes associated with this type of emulsion dilution, 5 lbs (2.3 Kg) of drill cuttings were mixed with 5 lbs (2.3 Kg) of emulsion and this mixture was shot atop of 5 lbs (2.3 Kg) of straight emulsion in a galvanized pipe in the mine fumes chamber. The explosive was initiated at the emulsion end and the detonation propagated into and through the mixture. VOD probes, along with a schedule 80 seamless steel witness pipe, were placed outside and parallel to the galvanized pipe. Shown in figure 12, is the NO and NO_x produced from the 50/50 blend of emulsion and drill cuttings. The average VOD measured through the emulsion was 6000 m/s while the average VOD through the drill cutting/emulsion mix was 3500 m/s. The witness pipe was completely collapsed near the straight emulsion and about 75% collapsed over the section containing the 50/50 emulsion/drill cuttings. The NO and NO_2 produced was about 6 to 8 times greater than with the straight emulsion. A mixture of 25% emulsion and 75% drill cuttings was also tested. The emulsion detonated but the 25/75 mixture failed to propagate the detonation. Consequently, there was little increase in NO_x production. Tests were also conducted using 1/8 in (0.32 cm) coal chips from a surface coal mine in place of the overburden drill cuttings. The fumes production with coal chips was about the same as with the inert drill cuttings, indicating little chemical reaction. Additionally, both drill cuttings and coal seem to serve as a thermal sink in cooling the reaction front. These results indicate that inadvertent admixture of solids in a emulsified explosive may be a significant contributing factor to NO_x production.

Argon Atmosphere in 12-ft (3.7-m) Sphere

Exploratory tests were conducted in the 12-ft (3.7-m) sphere in which the air was displaced with argon in order to minimize the influence of air on post-detonation reactions. The 80 g Pentolite boosters (2-in (5.1-cm) diameter by 1-in (2.5-cm) thick) when detonated in argon produced an average of 257 L/kg of CO, 2.5 L/kg of NO, 250 L/kg of CO_2, and no NO_2, as compared to 35 L/kg of CO, 8 L/kg of NO, 680 L/kg of CO_2 and no NO_2, when detonated in air. This indicates significant post-detonation air oxidation reactions even with the high-explosive fuel rich booster. A significant amount of carbon was deposited on the absolute filter in the sampling line in for the argon detonations. Figure 13 compares the NO and NO_2 production from the detonation of 750 g of finely pulverized ANFO (AN particles < 250 microns, density-0.75 g/cm^3) in air and in argon with a max oxygen concentration of 0.4%. Detonated in air, 6.8 L/kg of NO and 3.7 L/kg of NO_2 were measured. When detonated in argon, 23.2 L/kg of NO and zero NO_2 was produced. The CO production in air was 25.8 L/kg and decreased to 15.3 L/kg when detonated in argon. The results for ANFO in air and argon are obtained once the corresponding CO and NO contribution from the booster is removed from the data (Also in figures 13 and 14). Figure 14 compares the production of NO, NO_2 and CO from the detonation of 1.65 lbs (750 g) of emulsion detonated in air with that produced when detonated in argon. In the presence of air, 2.8 L/kg of NO and 18.2 L/kg of CO are

produced. In argon, the detonation produced an average of 6.8 L/kg of NO and 8.5 L/kg of CO with no NO_2 detected in either the air or argon atmosphere. These results indicate significant post-detonation reactions, particularly for the booster explosive and ANFO. Studies continue in argon atmospheres to better understand the mechanism of fumes formation and results will be reported at a later date.

SUMMARY

Generally, the heavier the explosive confinement the more ideal the detonation and the lower the NO and NO_2 production for all blasting agents tested. NO and NO_2 production from the emulsion explosive is less sensitive to degree of confinement when compared to ANFO and to a 50/50 blend of the emulsion and ANFO. At the same confinement, the NO production was about the same for ANFO and the 50/50 blend with both about 3 times higher than that of the more ideal emulsion.

Additives like coal dust and excess fuel oil when mixed with ANFO slightly reduced the NO production whereas urea and WR Conditioner 260 showed a slight increase over that of 6% ANFO. All ANFO additives tested reduced the NO_2 production. These small scale laboratory tests indicate that excess fuel (8%) in AN reduces NO_2 formation as much as any other additive including coal dust. The same additives when mixed with the ANFO component of the 50/50 blend showed little to no benefit in reducing NO or NO_2.

The NO production, from the detonation of pulverized 6% FO/94% AN in argon, was about 3.4 times higher than in air. The NO_2 decreased from about 3.7 l/kg in air to zero when detonated in argon. Studies continue in the 12-ft (3.7-m) sphere in the presence of argon to better understand the formation of NO and NO_2 and the role of post-detonation fumes production.

Lab results indicate that dry, soft, and porous overburden may wick away significant amount of fuel oil from ANFO during long intervals between explosive loading and firing ("sleep times"). The degree of wicking was more pronounced with smaller diameter holes. In addition, ANFO in the presence of overburden containing only 8% bound moisture will cause significant AN dissolution over time. If practical for field use, borehole liners should reduce the wicking of fuel oil and AN dissolution during long sleep times.

Lab studies show that inadvertent emulsion admixture with drill cuttings can be a significant contributing factor to NO_x production. The NO production from the detonation of emulsion equally mixed (by mass) with drill cuttings increased by a factor of 2.7 over that of emulsion alone. The corresponding NO_2 production increased by a factor of 9 while propagating a steady VOD at 3500 m/s. Placing stemming plugs at the bottom of the hole and loading emulsion from the bottom up through flexible tubing, may help reduce borehole erosion caused by cascading emulsion falling through slanted holes; further study is warranted. Also, placing a stemming device at the top of the emulsion column should help reduce explosive admixture from drill cuttings.

ACKNOWLEDGMENTS

REFERENCES

1. NIOSH Pocket Guide to Chemical Hazards. Cincinnati: Department of Health and Human Services, Public Health Service, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 94-116. pp. 54-55 (1994).

2. Streng, A.G. Evaluation of Toxic After-Detonation Gases Formed by Industrial Explosives. Explosivstoffe, Vol. 19, No. 3/4, 1971, pp. 58-64.

3. Karmakar, N.C. and S.P. Banerjee. A Review of Laboratory and Field Test Methods for Studying Fume Characteristics of Explosives. Journal of Mines, Metal and Fuels, Vol. 32, No. ½, Jan-Feb, 1984, pp. 398-402.

4. Roberts, W., P.D. Katsabanis, E.M. de Souze. Experimental Investigation of the Fumes Produced by Modern Commercial Explosives. Proceedings of the 8th Annual Symposium on Explosives and Blasting Research, Orlando, FL, January 22-23, 1992, pp. 53-62.

5. Persson, G. and P.A. Persson. Estimation of Toxic Fume Characteristics of Explosives from Steel Tube Blasting. Propellants and Explosives, Vol. 5, No. 2/3, 1980, pp. 75-78.

6. Mainiero RJ [1997]. A technique for measuring toxic gases produced by blasting agents. In: Proceedings of the 23rd Annual Conference on Explosives and Blasting Technique. Cleveland, OH: International Society of Explosives Engineers, pp. 595-604.

7.   Rowland JH, Mainiero, RJ [2000]. Factors affecting ANFO fumes production. In: Proceedings of the 26th Annual Conference on Explosives and Blasting Technique. Anaheim, CA: International Society of Explosives Engineers, pp. 163-174.

8.   Rowland JH, Mainiero RJ, and DA Hurd [2001]. Factors affecting fumes production of an emulsion and ANFO/emulsion blends. In: Proceedings of the 27th Annual Conference on Explosives and Blasting Technique. Orlando, FL: International Society of Explosives Engineers, pp. 133-141.

9. Santis LD, and RA Cortese. A method of measuring continuous detonation rates using off-the-shelf items. In: Proceedings of the 22nd Annual Conference on Explosives and Blasting Technique. Orlando, FL: International Society of Explosives Engineers, February 4-8, 1996, 11pp.
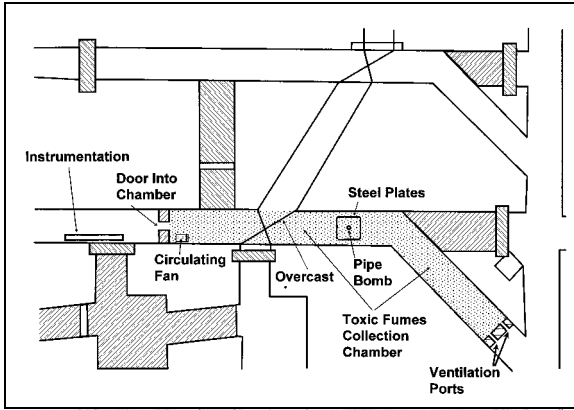
Figure 1. Chamber in the underground mine at the NIOSH Pittsburgh Research Lab in which the gaseous products of a 10-lb explosive detonation are confined and analyzed.

Figure 2. Twelve-foot sphere in which the gaseous products of 2-lb explosive charges are confined for analysis.
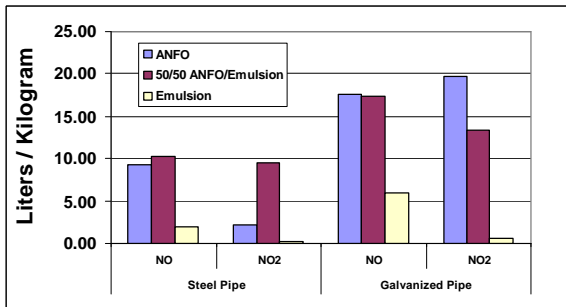

Figure 3. The effect of relative confinement on the NO and NO_2 production from the detonation of ANFO, Emulsion, and 50/50 blend.
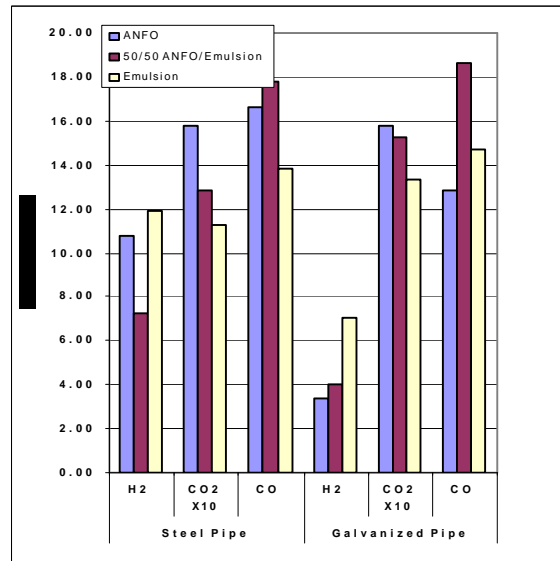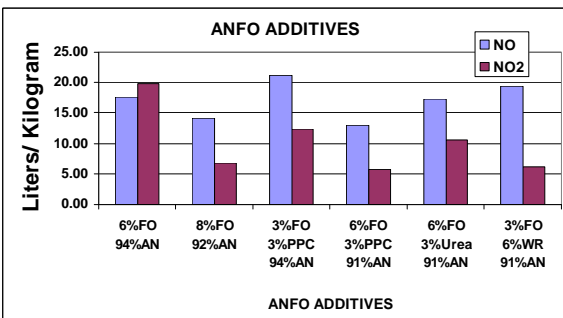

Figure 4. The effect of relative confinement on the CO, CO_2, and H_2 production from detonation of ANFO, Emulsion, and 50/50 blend.

Figure 5. The effect of ANFO additives on the production of NO and NO_2.
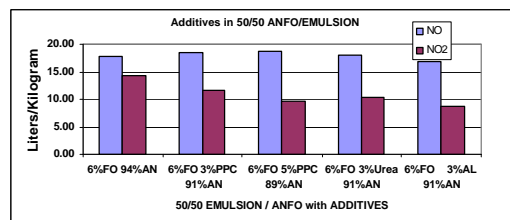
Figure 6. The effect of ANFO additives with a 50/50 blend of Emulsion/ANFO on the production of NO and NO_2.
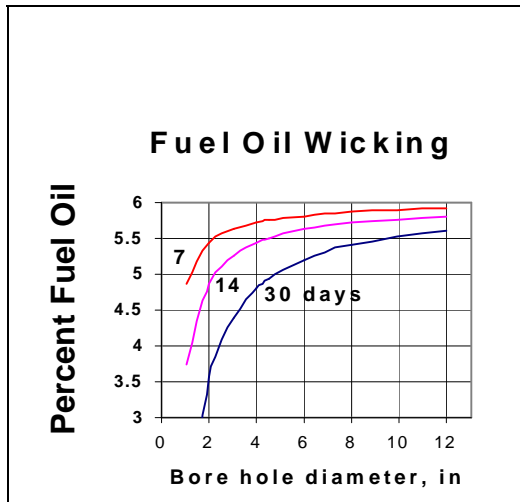
Figure 7. Calculated loss of fuel oil, due to wicking, from
6 % FO-94%AN mixture as a function of borehole diameter.
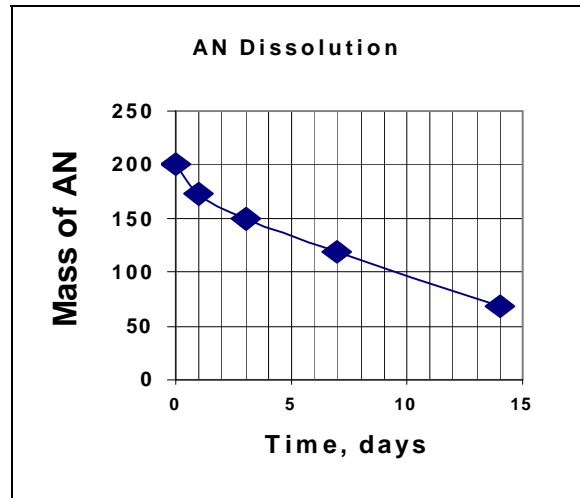
Figure 8. The dissolution of ammonium nitrate as a function of time when exposed to 8 % moisture in a simulated cementitious borehole.
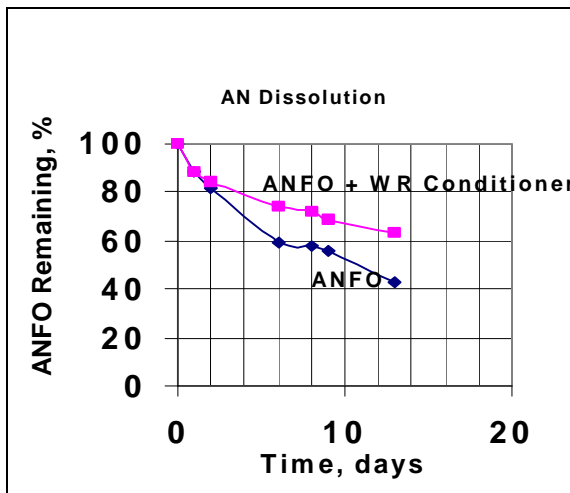

Figure 9. Comparison of ANFO dissolution with and without WR 260 Conditioner in 2-inch diameter cementitious borehole.
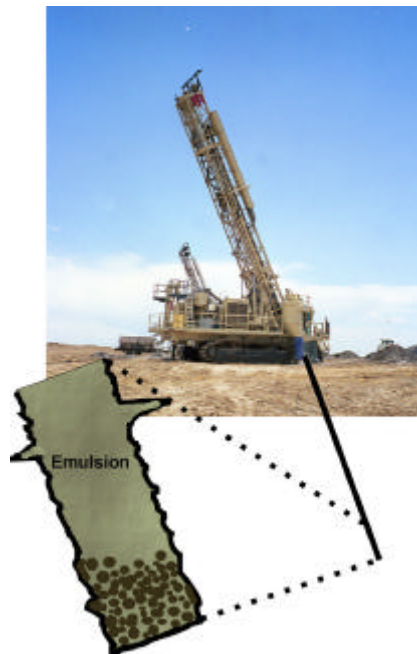

Figure 10. Schematic showing potential emulsion dilution with drill cuttings.

Figure 11. Photo showing the emulsion permeating the interstitial spaces of drill cuttings when loaded at 10 psi.
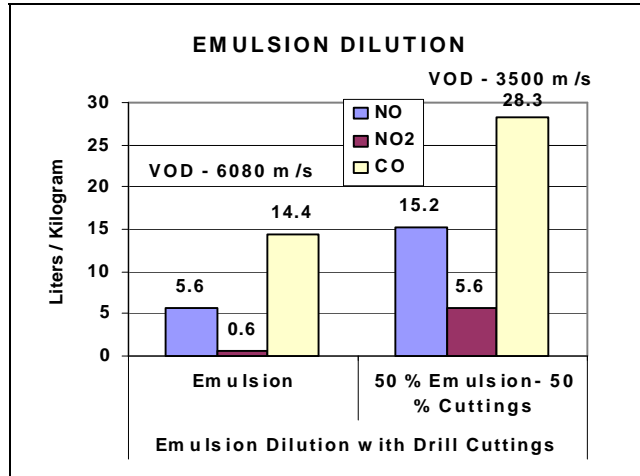

Figure 12. Comparison of NO, NO_2, and CO formed from the detonation of emulsion and a 50/50 blend of emulsion and drill cuttings.
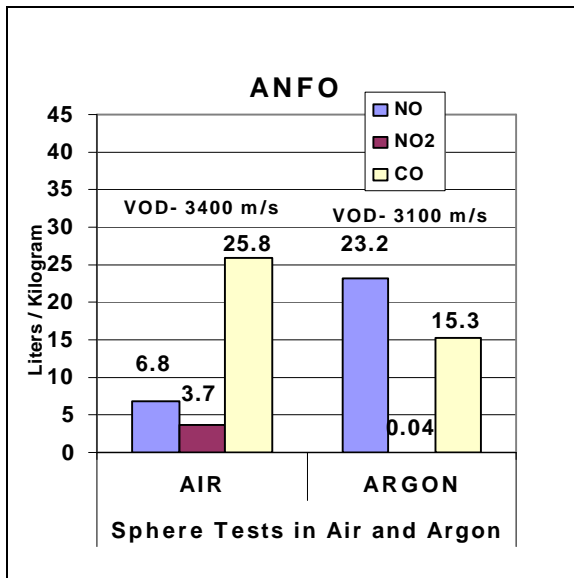

Figure 13. Comparison of NO, NO_2, and CO formed from the detonation of pulverized ANFO in air and in argon.
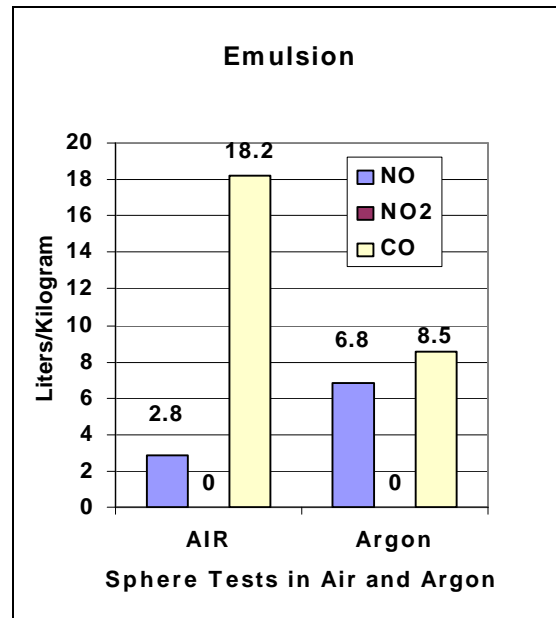

Figure 14. Comparison of NO, NO_2, and CO formed from the detonation of emulsion in air and in argon.