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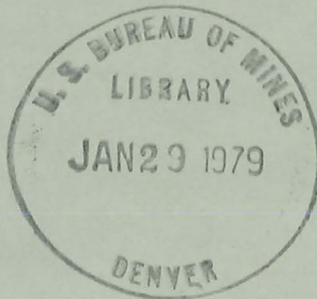
ANALYSIS OF TOXIC FUMES GENERATED
DURING SHOT FIRING

Prepared for

United States
Department of the Interior
Bureau of Mines

by

MSA Research Corporation
Division of Mine Safety Appliances Company
Evans City, Pennsylvania 16033



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Final Report

on

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FOREWORD

This report was prepared by MSA Research Corporation, Evans City, Pennsylvania under USBM Contract J0166092. The contract was initiated under the Metal and Nonmetal Health and Safety Research Program. The contract was administered under the technical direction of the Pittsburgh Mining and Safety Research Center with Mr. Theodore Christos acting as the Technical Project Officer. Mr. A. C. Young was the Contract Administrator for the Bureau of Mines.

The program was under the technical direction of Mr. Sheridan Rodgers of MSA Research Corporation. Other MSAR personnel who assisted in the study were Messrs. Eugene Polite and James Mangold. Special recognition must be given to mine management, ventilation engineers and mining personnel of Cominco American, Inc. whose cooperation made this program possible.

This report is a summary of the work completed under Contract J0166092 during the period 10 June 1976 to 5 November 1976. This report was initially submitted on 17 December 1976.

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ABSTRACT

Toxic fumes generated during shot firing under actual mining conditions were measured. Eight shots with Gelodyn-2X and seven shots with Tovex-100 4VT were monitored. Average CO values for Gelodyn-2X and Tovex-100 4VT were 0.20 ft³/lb and 0.09 ft³/lb, respectively. Average NO_x values for Gelodyn-2X and Tovex-100 4VT were 0.049 ft³/lb and 0.026 ft³/lb, respectively. The results obtained with these in-mine tests will be used by the U.S. Bureau of Mines in the development of a large chamber method of measuring fumes from shotfiring of explosives.

FINAL REPORT

to

U.S. Department of the Interior
Bureau of Mines
Washington, D. C.

on

ANALYSIS OF TOXIC FUMES GENERATED DURING SHOT FIRING (Contract J0166092)

INTRODUCTION

Toxic fumes generated during shot firing in metal and nonmetal (noncoal) mines may result in hazardous conditions to mining personnel. Ventilation is the method most commonly employed to prevent exposure of mining personnel to toxic fume concentrations exceeding the Threshold Limit Values (TLV) set by the American Conference of Governmental Industrial Hygienists (ACGIH). The toxic fume concentrations at any given time after shot firing are dependent upon the ventilation rate, the type of explosive used and the size of the charge which is shot. These factors must be considered by mine management when specifying time limits for reentry of personnel to work places.

Carbon monoxide (CO) and the oxides of nitrogen (NO and NO₂) are the major toxic fumes generated during shot firing. Sulfur dioxide (SO₂) is produced by certain explosives and when shot firing is conducted in high sulfur ore bodies. Ammonia can be produced by the decomposition of ammonium compounds and amines and the odor of ammonia has been reported on occasions by shot firers. Carbon dioxide (CO₂) is generally considered as a simple asphyxiant rather than a toxic fume, but a TLV has been specified for CO₂. The ACGIH has set the following TLVs for toxic fumes of interest:

<u>Contaminant</u>	<u>Threshold Limit Value (ppm)</u>
CO	50
NO	25
NO ₂	5
SO ₂	5
NH ₃	5
CO ₂	5000

Peak toxic fume concentrations and the time required to reduce these concentrations to acceptable levels will depend upon the type and quantity of toxic fumes generated and the ventilation rate. Manufacturers of explosives currently formulate their products for underground usage in noncoal mines to meet the Institute of Makers of Explosives Fume Class I (~ 0.16 ft³ poisonous gases/200 grams of explosive).¹ The U.S. Bureau of Mines has been continuously testing toxic fume release from various explosives using the Bichel-gage² and Crawshaw-Jones³ methods, and is at present conducting research on the use of a 1350 ft³ chamber for this purpose.

The purpose of this study was to provide data on the quantities of toxic fumes which are generated by explosives under actual mining conditions. The results obtained from these in-mine studies will be used by the U.S. Bureau of Mines in the development of a large chamber method of measuring toxic fumes from shot firing of explosives.

BACKGROUND

MSA Research Corporation has conducted a U.S. Bureau of Mines study entitled "The Analysis of Noncoal Mine Atmospheres: Toxic Fumes From Shot Firing" (Contract No. S0231057, Modification No. 5)⁴. During this previous program, the drift in which the studies were conducted was ventilated with the existing mine ventilation system. Outputs from the various toxic fume monitors were continuously recorded, and the quantity of toxic fumes which were generated were determined using the area under the curve and the ventilation air flowrate. The instrumentation was the same as that used in earlier phases of Contract No. S0231056 (Analysis of Noncoal Mine Atmospheres)⁵.

Two nitroglycerin based explosives (Gelex-2 and Gelodyn-2X), three water gels (Tovex-100, Tovex-105 and Iremite-40) and an ammonium nitrate-fuel oil explosive were evaluated. Summary results from references 4 and 5 are presented in Table 1 and are a condensation of results from two different mines and four different working sections. The results indicated that the nitroglycerin-based explosives produced a greater amount of toxic fumes than either the water gels or ANFO. The water gels produced the lowest amount of CO and oxides of nitrogen.

In the earlier work (4,5), the quantity of toxic fumes generated during shot firing was calculated using the area under the curve and the air velocity and cross sectional area of the drift at the point of measurement. It was recognized that the method possessed certain inherent errors. These included:

1. Errors in tracing the curves onto vellum
2. Errors in weighing the vellum
3. Errors in measuring the cross section of the drift
4. Errors in measuring air velocity in the drift
5. Possible losses of toxic fumes to the walls of the drift.

TABLE 1 - TOXIC FUMES GENERATED BY NITROGLYCERIN
BASED EXPLOSIVES, WATER GELS AND ANFO

<u>Type of Explosive</u>	Toxic Fumes Generated (ft ³ /lb)				
	<u>CO</u>	<u>NO</u>	<u>NO_x</u>	<u>SO₂</u>	<u>CO₂</u>
Gelex-2(a)	0.91	0.082	0.095	0.054	3.75
Gelodyn-2X(b)	0.95	0.086	0.161	0.050	4.11
Tovex-100 & 105(a)	0.32	0.045	0.054	0.009	3.04
Iremite-40(b)	0.41	0.045	0.045	0.020	2.95
ANFO(c)	0.54	0.061	0.061	0.004	1.87

- (a) Average value for four shots
 (b) Average value for five shots
 (c) Average value for ten shots

The method used for measuring the quantity of toxic fumes generated during shot firing was modified in the current study. This modification entailed enclosing a known volume of air within the drift, mixing the toxic fumes within this enclosed volume, measuring the toxic fume concentration within the volume and calculating the quantity of toxic fumes from the concentration and volume of the enclosure. This modification served a twofold purpose. First, it eliminated the potential errors inherent in the method used previously, except possible wall losses. Second, it simulated the Bureau's large chamber method which is an enclosed volume technique thus providing a basis for determining whether the large volume method can accurately predict the quantity of toxic fumes which are generated under actual shot firing conditions.

EXPERIMENTAL PROGRAM

Selection of Test Site

Since one of the major modifications to the test procedures was to allow the toxic fumes to expand into an enclosed volume, selection of the test site was of major importance. This modification dictated that:

1. The test site would not be occupied after the shot
2. That no other source of toxic fumes existed.

As a result of these considerations, a development drift at the Cominco American Incorporated, Warm Springs Operation, phosphate rock mine in Garrison, Montana was selected.

A development drift on the 6000 ft level was chosen since it was the only operation being conducted on that level. The mine was working only one shift in this drift so it was not necessary to ventilate the drift after shot firing. This permitted sealing the drift, mixing the toxic fumes within the enclosed volume and observing the behavior of the toxic fumes as a function of time.

Schematic diagrams of the drift are shown in Figures 1 and 2. A PVC-coated brattice seal was located approximately 60 ft from the face. The brattice was secured to existing mine timbers, and the spaces between the timbers and rib were sealed with polyurethane foam (Figure 3). The brattice was maintained in an open position during the normal work day to permit movement of personnel, materials, equipment and mine cars. The brattice was then dropped and secured when the spitter cord was lit.

During the course of the program, work was terminated at the 6000 ft development drift. This necessitated selecting a new test site at the mine, moving all of the equipment to the new site and reinstalling the brattice. The new site was a development drift on the 5800 ft level (Figure 4). The temperature in the drift was 54°F and the relative humidity was 75-80%. Figure 5 shows the 2000 cfm mixing fan which was used, and the instrument station.

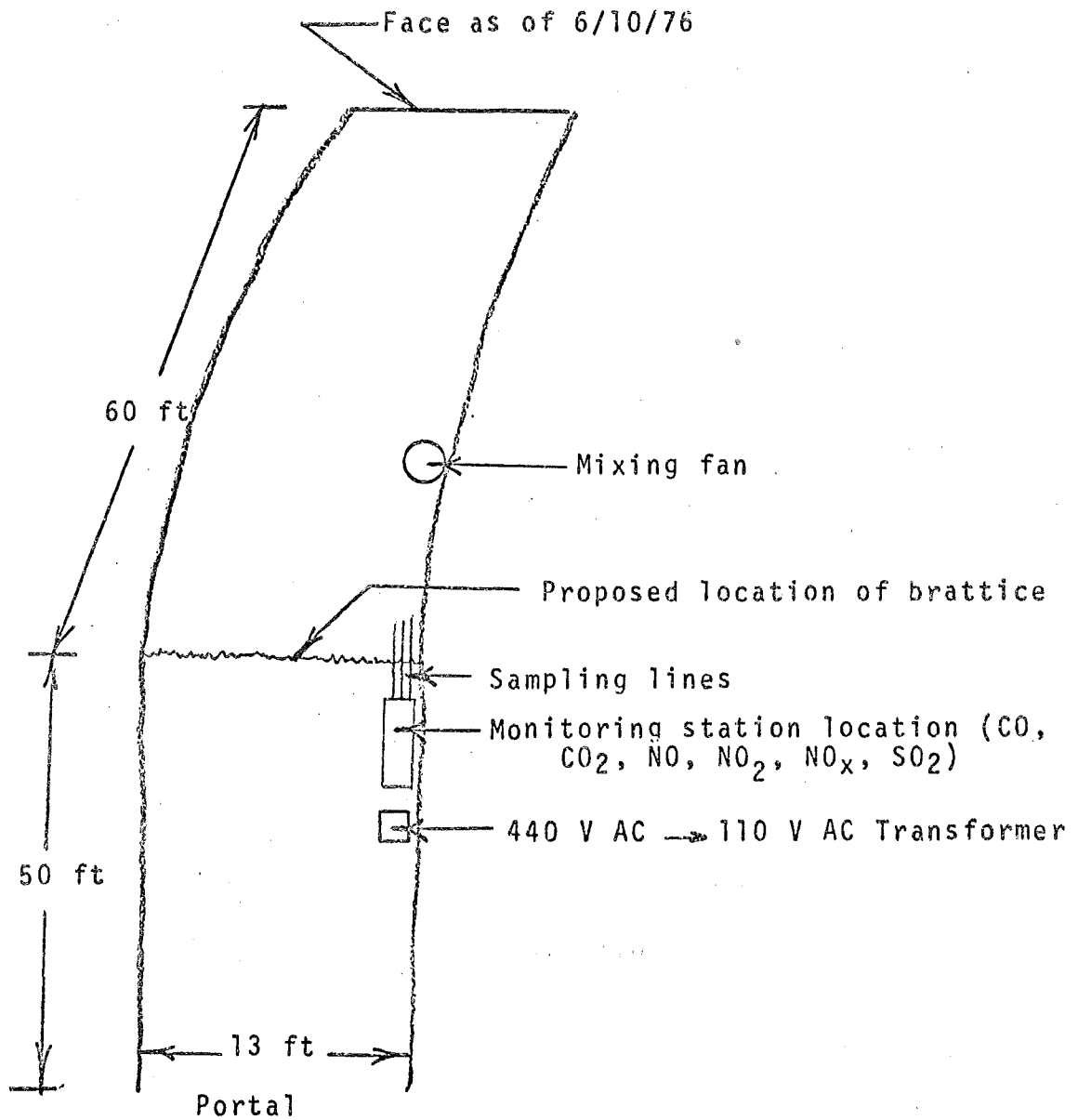


FIGURE 1 - DIAGRAM OF THE 6000' DEVELOPMENT DRIFT, COMINCO AMERICAN, INC.

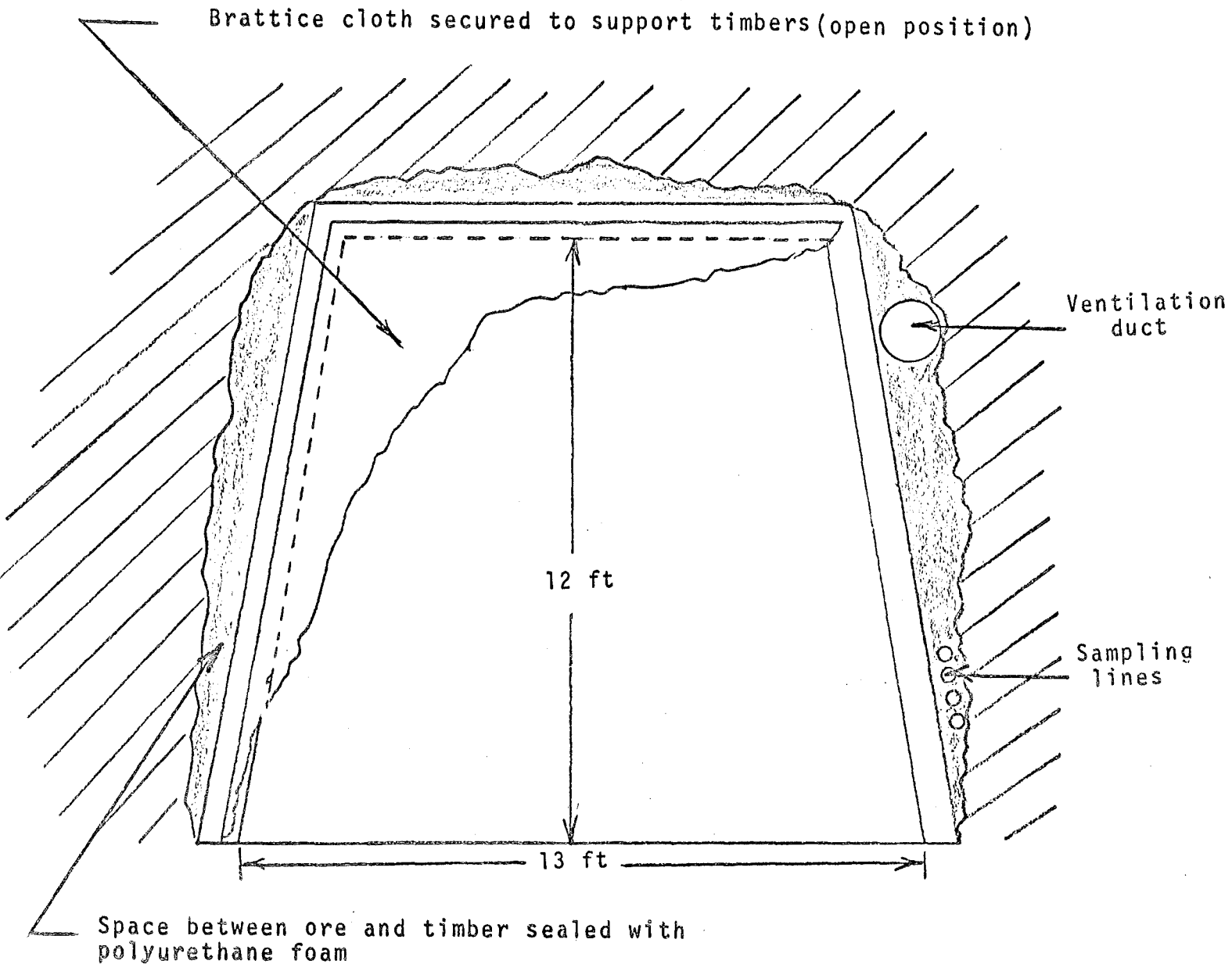
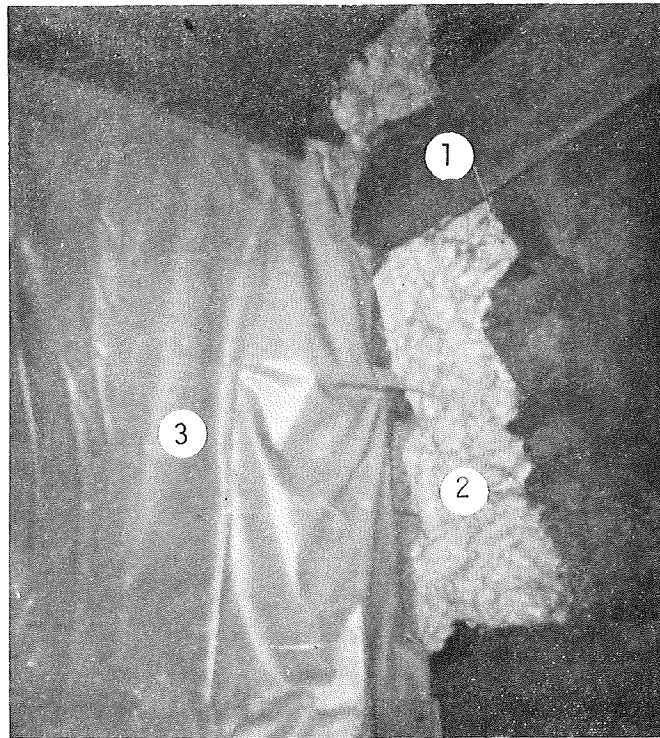
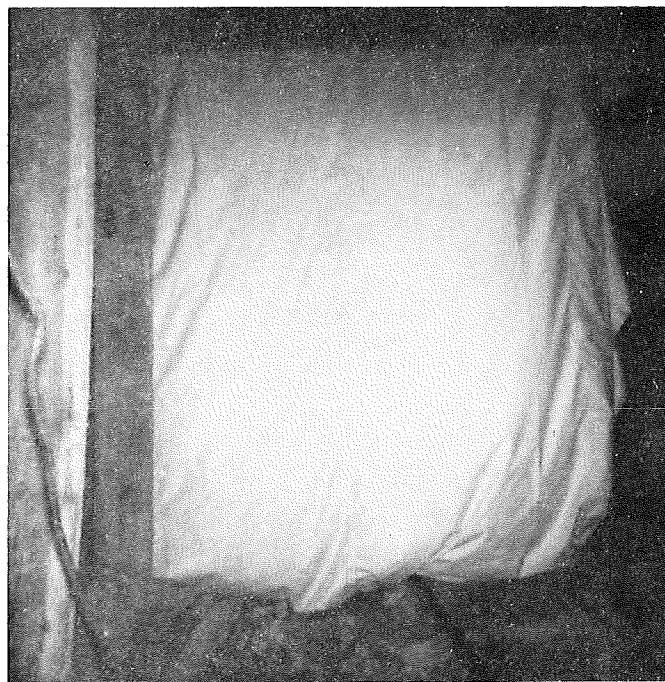


FIGURE 2 - SCHEMATIC DIAGRAM OF THE PROPOSED BRATTICE CLOTH LOCATION



- ① Existing Timber
- ② Polyurethane Seal
- ③ Brattice

Inby the Brattice



Outby the Brattice

FIGURE 3 - PVC BRATTICE SEAL

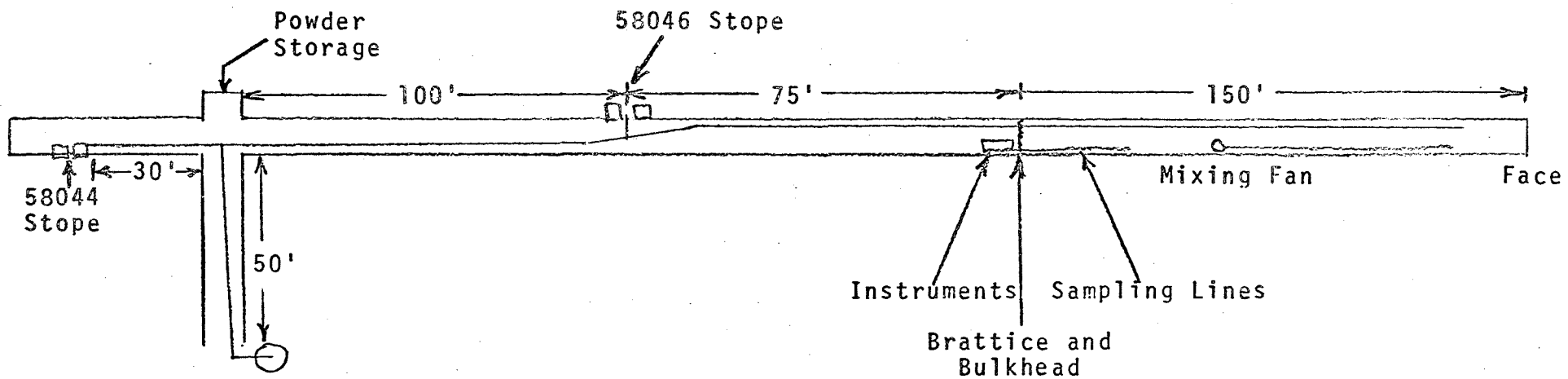
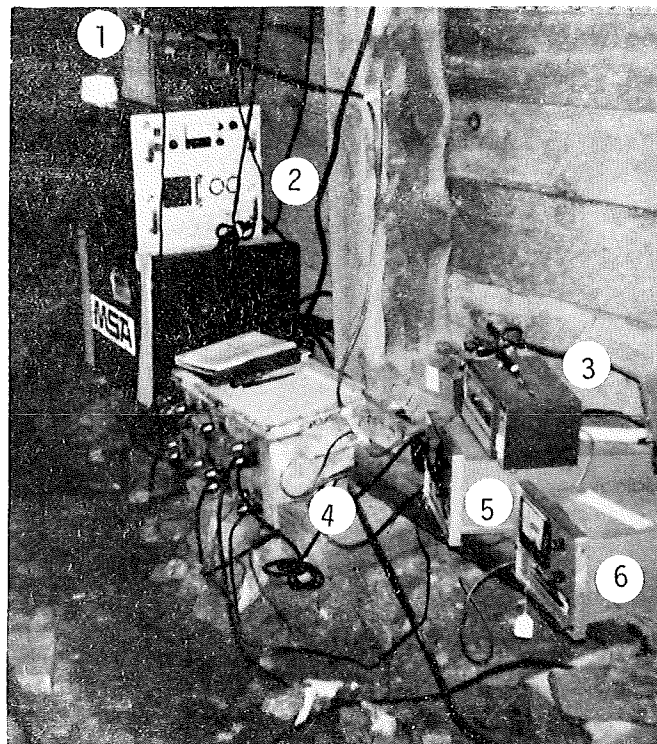


FIGURE 4 - DIAGRAM OF 5800' DRIFT, COMINCO AMERICAN INC. MINE



- ① Ductwork to Face
- ② 2000 cfm Fan



- ① Molybdenum Converter
- ② NO-NO₂-NO_x Analyzer
- ③ Recorder
- ④ Transformer
- ⑤ CO₂ Analyzer
- ⑥ CO Analyzer

FIGURE 5 - MIXING FAN AND INSTRUMENT STATION

Toxic Fume Monitoring

Selection of Instrumentation - Table 2 lists the instruments which were used to monitor toxic fumes. The instruments used for monitoring CO, CO₂, and SO₂ were the same as those used on Contract No. S0231057, Modification No. 5. The U.S. Bureau of Mines uses an MSA LIRA for monitoring CO in the 1350 ft³ chamber tests. A Thermo Electron Model 14D was selected for monitoring NO-NO₂-NO_x since this is also the same instrument used by the Bureau. Multirange capabilities for each of the instruments were necessary since the amount of toxic fumes released by the water gels were lower than that released by the nitroglycerin explosives.

A glass wool plug was used in each sample line to remove large particulates from the sample stream. A 5 micrometer vinyl membrane filter was used at the sample inlet to each instrument to prevent contamination of the instruments.

An attempt was made to determine the amount of ammonia generated during shot firing. A sample was drawn through fritted glass filters at a flow rate of 2 liters per minute. Two bubblers filled with 0.1N H₂SO₄ were used in series to assure that all of the ammonia was collected. A membrane filter (0.8 μ) was used upstream of the bubblers to remove particulate material from the air stream. The solutions were analyzed using a selective ion electrode. Ammonia results of the various shots showed a wide scatter, so bubblers were run for varying lengths of time. Duplicate sets of bubblers were run, one set for one minute and one set for 10 minutes. The amount of ammonia found in the two sets of bubblers was essentially the same. It is believed that ammonia was absorbed rather quickly on the wet walls of the mine, and that the time required for complete mixing (~25 min) resulted in essentially complete sorption of ammonia. The technique used for measuring ammonia was obviously not applicable to the conditions existing in the mine, therefore the results of the ammonia analyses were obviously incorrect and are not reported.

Calibration - The instruments were zeroed and calibrated each day using zero gas and standard gas mixtures (±3% accuracy) purchased from Linde Corporation. The calibration gases and the concentrations are listed on the following page:

TABLE 2 - INSTRUMENTATION USED FOR MONITORING TOXIC FUMES

<u>Toxic Fume</u>	<u>Instrument</u>	<u>Range (ppm)</u>
Carbon Monoxide (CO)	MSA LIRA	0-2500 (Tovex-100); 0-5000 (Gelodyn-2X)
Carbon Dioxide (CO ₂)	MSA LIRA	0-5000 (Tovex-100); 0-14,000 (Gelodyn-2X)
Sulfur Dioxide (SO ₂)	Theta Sensors	0-100
Nitric Oxide (NO)	Thermo Electron Model 14D	0-100; 0-500; 0-1000
Nitrogen Dioxide (NO ₂)	Thermo Electron Model 14D	0-50; 0-100; 0-500
Oxides of Nitrogen (NO _x)	Thermo Electron Model 14D	0-100; 0-500; 0-1000

<u>Calibration Gas</u>	<u>Concentration (ppm)</u>
Carbon Monoxide in Nitrogen	1063 48
Carbon Dioxide in Nitrogen	1400
Nitric Oxide in Nitrogen	94 367
Nitrogen Dioxide in Nitrogen	45
Sulfur Dioxide in Nitrogen	40

The calibration cylinders were transported into the mine each day. Normal calibration procedures involved filling Tedlar bags with the calibration gas and attaching the bag outlet to the sample inlet. The use of Tedlar bags eliminated any calibration errors due to back pressure.

The volume of the enclosure was also calibrated. This was accomplished by passing a measured volume of pure CO₂ through a dry test meter, mixing the CO₂ with the fan and reading the concentration with the CO₂ instrument (Figure 6). The volume of the enclosure was then calculated as follows:

$$V_E = \frac{V_{CO_2}}{C_f - C_i}$$

where V_E = volume of the enclosure (ft³)

V_{CO_2} = volume of pure CO₂ added (ft³)

C_f = final CO₂ concentration (%)

C_i = initial CO₂ concentration (%)

The volume determined by this method agreed within 10% of the estimated value based on the cross section of the drift and the length of the enclosed volume.

The volume of the drift was calibrated twice using this method. In the first case, the volume was approximately 10,000 ft³ and in the second case it was approximately 17,000 ft³. Each shot resulted in the removal of approximately 400 ft³ of rock. This resulted in a 4% increase in the 10,000 ft³ volume and a 2.4% increase in the 17,000 ft³ volume. These increases were factored into calculation of the quantity of toxic fumes which were generated.

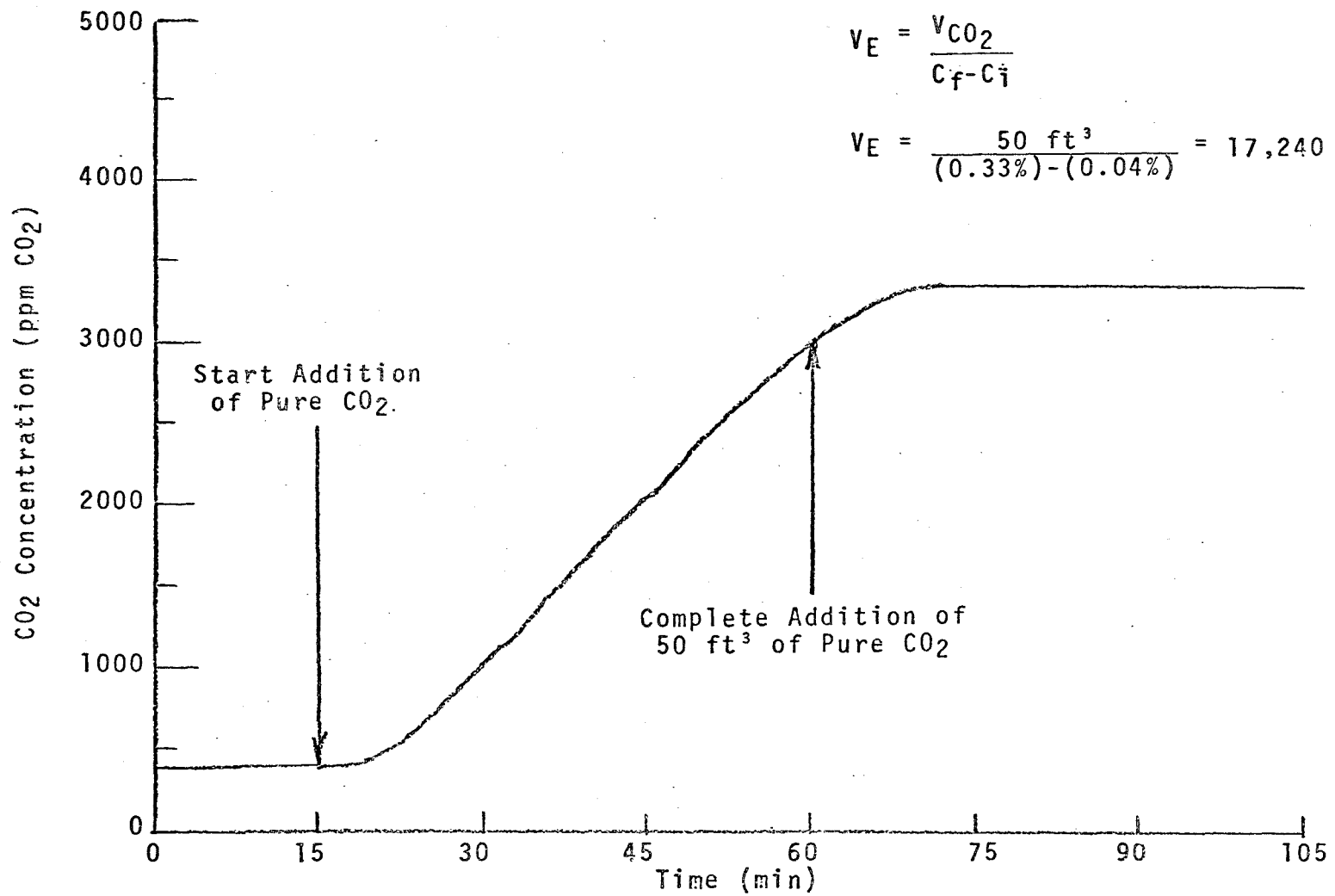


FIGURE 6 - CALIBRATION OF THE ENCLOSURE USING A MEASURED VOLUME OF CO₂

The concentration of toxic fumes in the enclosed volume varied according to the size of the enclosure and the type and quantity of explosive which was shot. The ranges of the CO, NO_x, CO₂ and SO₂ concentrations are shown in Table 3.

Selection of Explosives

Two types of explosives were selected to represent modern shot firing operations in underground noncoal mines. Gelodyn-2X (Atlas Powder Company) was selected to represent the nitroglycerin-based explosives and Tovex-100 (DuPont) was selected to represent the water-gel explosives. These selections were made as a compromise of three separate factors:

1. Previous work, in Contract No. S0231057, had shown some differences in the types and quantities of toxic fumes generated from these two basic formulations.
2. These two candidates were considered as representative of each type of explosive.
3. The Bureau of Mines had previously measured toxic fumes from these explosives in their 1350 ft³ experimental test chamber.

Experimental Procedures

Prior to initiation of the experimental program, standard procedures were developed to assure that all systems were functioning properly and that all the necessary data were acquired. The experimental plan is presented in Table 4.

TABLE 3 - CONCENTRATION RANGES OF CO, NO_x, CO₂ AND SO₂
 IN THE 10,000 ft³ and 17,000 ft³ ENCLOSED VOLUMES (ppm)

<u>Contaminant</u>	<u>10,000 ft³ Enclosure</u>	<u>17,000 ft³ Enclosure</u>
	<u>Gelodyn-2X</u>	
CO	1400-1900	650-1150
NO _x	140-240	210-370
CO ₂	5400-8000	2200-3300
SO ₂	90-100	22-100
	<u>Tovex-100 4VT</u>	
CO	700-1000	200-725
NO _x	125-145	80-210
CO ₂	2200-4300	1500-2900
SO ₂	12-14	3-12

Note: Quantities of explosives shot ranged from 58-83
 pounds of Gelodyn-2X and 53-100 pounds of Tovex-100 4VT

TABLE 4 - TYPICAL CHRONOLOGY OF AN EXPERIMENT

1. Check with mine supervisor; get key for powder magazine; procure two 50 pound boxes of explosives.
2. Return key to mine office.
3.
 - a. Drive to development drift
 - b. Unload and store powder
4. Check instruments and recorders for malfunction and power failure.
5. Zero and calibrate CO monitor; change chart and mark time.
6. Zero and calibrate CO₂ monitor; change chart and mark time.
7. Zero and calibrate NO-NO₂-NO_x monitor; check Drierite; change chart and mark time.
8. Zero and calibrate SO₂ monitor; change chart and mark time.
9. Fill ammonia scrubbers; replace filter; check pump flow.
10. Count number of holes; count number of sticks not used.
11. Drop brattice and secure to timbers.
12. Shoot
13. Activate mixing fan.
14. Observe instruments; record data and/or remove charts when traces show that mixing is complete; turn off ammonia scrubber; turn molybdenum converter to NO position.
15. Roll up brattice (wear self-contained respiratory protection).
16. Turn off mixing fan.
17. Turn on ventilation fan.
18. Turn off ventilation fan after 1/2 hr.
19. Return unused explosive to powder magazine.

EXPERIMENTAL RESULTS

Initial Tests (6000 ft Development Drift)

The initial test series was beset with an unusual number of start-up problems. These included equipment malfunctions, mine power failures and interferences between test and mine operating schedules, in addition to the normal problems associated with establishing new test procedures. The major problems occurred with the NO-NO₂-NO_x analyzer. These problems included:

1. Inoperative voltage accumulator
2. Defective optical board
3. A 10 volt output from the instrument coupled with a 5 volt three channel recorder
4. A broken ozonator tube.

Because of these problems, no data were obtained at the 6000 ft development drift on the oxides of nitrogen. While attempts were being made to repair the NO-NO₂-NO_x analyzer in the field, measurements were made on the other toxic fumes. This provided preliminary data on toxic fume generation during shot firing, but more importantly it provided for refining the experimental program.

The results of testing at the 6000 ft development drift are presented in Table 5. These preliminary results indicated that the amount of CO generated was less with the water gel than with the nitroglycerin-based explosive.

One of the operational problems encountered during this series of tests was that the Tovex-100 was not easily tappable, and misfires occurred frequently. This problem had not been encountered in the earlier studies⁴, and it was learned that the manufacturer had changed the type of wrapper. Tovex-100 was originally packaged in a 2 mil thick Mylar wrapper which was friable and the sticks could be easily tamped. The manufacturer subsequently changed to a 4 mil thick polyethylene wrapper and it was learned that similar

TABLE 5 - SUMMARY OF RESULTS AT COMINCO AMERICAN, INC. (1)

Date	Type of Explosive	No. of Holes (3)	No. of Sticks	Weight (lbs)	Toxic Fumes Generated (2)						
					CO		CO ₂		SO ₂		NH ₃ (4)
					ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /200 g
7/13	Tovex-100 (5)	19	188	69.6	0.12	0.052	0.52	0.23	<0.001	<0.0005	N.D.
7/19	Tovex-100 (5)	21	158	58.5	0.16	0.069	0.70	0.31	<0.001	<0.0005	N.D.
7/20	Tovex-100 (5)	22	189	69.9	0.18	0.080	0.75	0.33	<0.001	<0.0005	N.D.
7/15	Gelodyn-2X (6)	21	251	69.7	0.30	0.13	1.29	0.57	0.011	0.005	N.D.
7/16	Gelodyn-2X (6)	20	246	68.4	0.32	0.14	1.48	0.65	0.011	0.005	N.D.

(1) Tests conducted at the 6000 ft development drift, Warm Springs Mine

(2) Volume of enclosed gases = ~18,000 ft³

(3) Depth of holes = 6 ft; no stemming

(4) N.D. = not detected. Lower limit of detection = 0.1 ppm in air (0.0001 ft³/200 g; 0.003 ft³/lb)

(5) DuPont, 1"x12" sticks, 0.370 lbs per stick

(6) Atlas, 1"x8" sticks, 0.278 lbs per stick

complaints regarding tampability had been expressed by the mining industry. It was learned that the manufacturer had modified the wrapper to enhance tampability and this explosive (Tovex-100 4VT) was ordered for subsequent tests.

Complete Monitoring Tests (5800 ft Development Drift)

Complete monitoring tests are defined as those tests in which all of the toxic fumes of interest (CO, NO, NO₂, NO_x, CO₂ and SO₂) were measured. Complete monitoring of eight shot firings with Gelodyn-2X and seven shot firings with Tovex-100 4VT was accomplished at the 5800 ft development drift. A tabulation of these results is shown in Table 6. Average values and mean deviations are shown for CO, NO_x, CO₂ and SO₂. Average values are not given for NO and NO₂ since, as will be discussed later, a reduction in the NO concentration and an increase in the NO₂ concentration with time were observed.

SO₂ Behavior - During the course of the program, the mine shot an explosive which it normally uses (Hercules Powder Company's Unigel, 1 in. x 16 in.). This offered a unique opportunity to evaluate SO₂ generation from various explosives, and as was found later, to observe the behavior of SO₂ in the mine atmosphere. Figure 7 shows the SO₂ traces for Unigel, Gelodyn-2X and Tovex-100 4VT.

The traces show that significantly more SO₂ is generated with the nitroglycerin-based explosives than with the water gel. The fact that SO₂ concentration appears to decrease with time suggests that SO₂ is being sorbed onto the wet walls of the mine. If SO₂, an acid gas, exhibits this behavior, then one would expect ammonia, an alkaline and much more water-soluble gas, to be sorbed even more rapidly in the acid mine water. As stated before, it is doubtful that a reliable ammonia value can be acquired under the constraints of the experimental procedure.

Behavior of Other Toxic Fumes - Figures 8 and 9 show the CO, CO₂, NO, NO₂ and NO_x traces of a Gelodyn-2X and Tovex-100 4VT shot, respectively. Figure 8 shows that mixing was attained in 20-25 min, as indicated by the steady state readings of the CO and CO₂ curves.

TABLE 6 - SUMMARY OF RESULTS, COMINCO AMERICAN, INC. (1)

Date	Sticks	lbs	Gelodyn-2X(2)											
			CO		NO		NO ₂		NO _x		CO ₂		SO ₂	
			ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g
9/20(4)	299	83.1	0.14	0.06	0.004	0.002	0.018	0.008	0.025	0.011	0.55	0.24	>0.003	>0.003
9/21(4)	278	77.3	0.20	0.09	0.009	0.004	0.017	0.007	0.025	0.011	0.87	0.38	0.010	0.004
9/22(4)	296	82.3	0.20	0.09	0.004	0.002	0.011	0.004	0.015	0.006	0.77	0.33	0.010	0.004
10/22(5)	278	77.3	0.29	0.13	0.031	0.014	0.039	0.017	0.072	0.032	0.64	0.28	>0.020	>0.009
10/25(5)	266	73.9	0.16	0.07	0.024	0.011	0.020	0.009	0.045	0.019	0.67	0.30	0.011	0.005
10/27(5)	211	58.7	0.17	0.07	0.020	0.009	0.031	0.013	0.054	0.024	0.56	0.25	0.005	0.003
10/28(5)	245	68.1	0.20	0.09	0.028	0.012	0.016	0.007	0.047	0.020	0.70	0.31	0.008	0.004
10/29(5)	45	12.5	0.21	0.10	0.058	0.026	0.055	0.025	0.108	0.048	0.55	0.26	0.008	0.004
Avg.	--	--	0.20	0.09	--	--	--	--	0.049	0.021	0.66	0.29	0.009	0.004
Std. Deviation			±0.045	±0.022	--	--	--	--	±0.030	±0.013	±0.12	±0.05	±0.002	±0.0006

Date	Sticks	lbs	Tovex-100 4VT(3)											
			CO		NO		NO ₂		NO _x		CO ₂		SO ₂	
			ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g	ft ³ /lb	ft ³ /200 g
9/27(4)	188	100.0	0.09	0.04	0.004	0.002	0.005	0.003	0.011	0.006	0.38	0.17	0.0011	0.0004
9/28(4)	146	77.7	0.08	0.04	0.003	0.001	0.013	0.006	0.017	0.007	0.34	0.15	0.0013	0.0006
10/21(5)	103	54.8	0.08	0.04	0.005	0.003	0.026	0.012	0.034	0.015	0.61	0.26	0.0035	0.0016
10/26(5)	100	53.2	0.05	0.03	0.006	0.003	0.023	0.010	0.030	0.013	0.42	0.18	0.0026	0.0011
11/2(5)	147	78.2	0.14	0.06	0.009	0.004	0.004	0.003	0.015	0.007	0.55	0.25	0.0018	0.0008
11/3(5)	162	86.2	0.11	0.04	0.009	0.004	0.028	0.012	0.036	0.016	0.36	0.16	0.0026	0.0011
11/4(5)	150	79.8	0.11	0.04	0.008	0.004	0.030	0.013	0.040	0.018	0.43	0.19	0.0005	0.0003
Avg.	--	--	0.09	0.04	--	--	--	--	0.026	0.012	0.44	0.19	0.0019	0.0008
Std. Deviation			±0.020	±0.010	--	--	--	--	±0.011	±0.005	±0.10	±0.004	±0.0003	±0.0001

- (1) Tests conducted at the 5800 ft development drift; results corrected to 760 mm, 25°C.
 (2) Atlas Powder Co., 1"x8" sticks, 0.278 lb/stick
 (3) DuPont Co., 1"x16" sticks, 0.532 lb/stick
 (4) Shot in hard rock
 (5) Shot in soft rock and mud seams

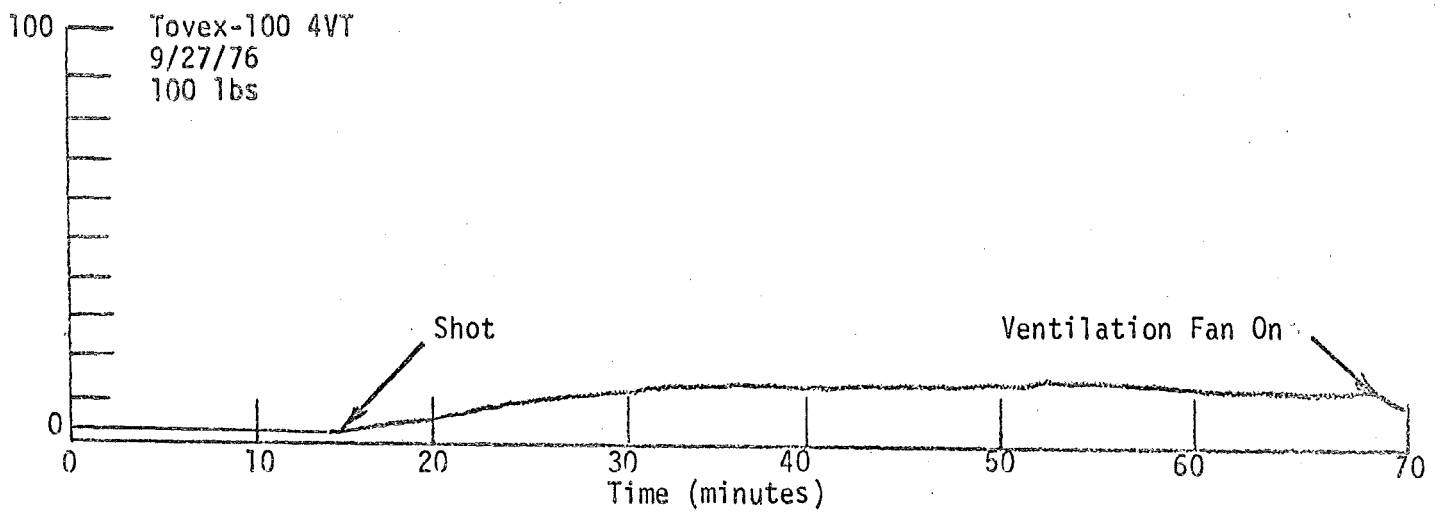
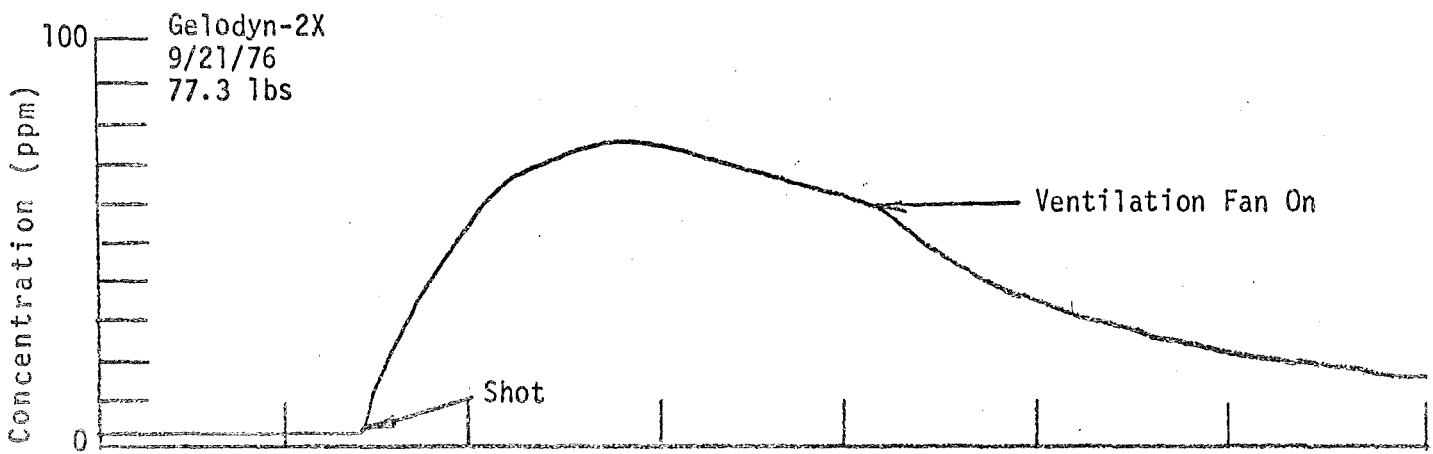
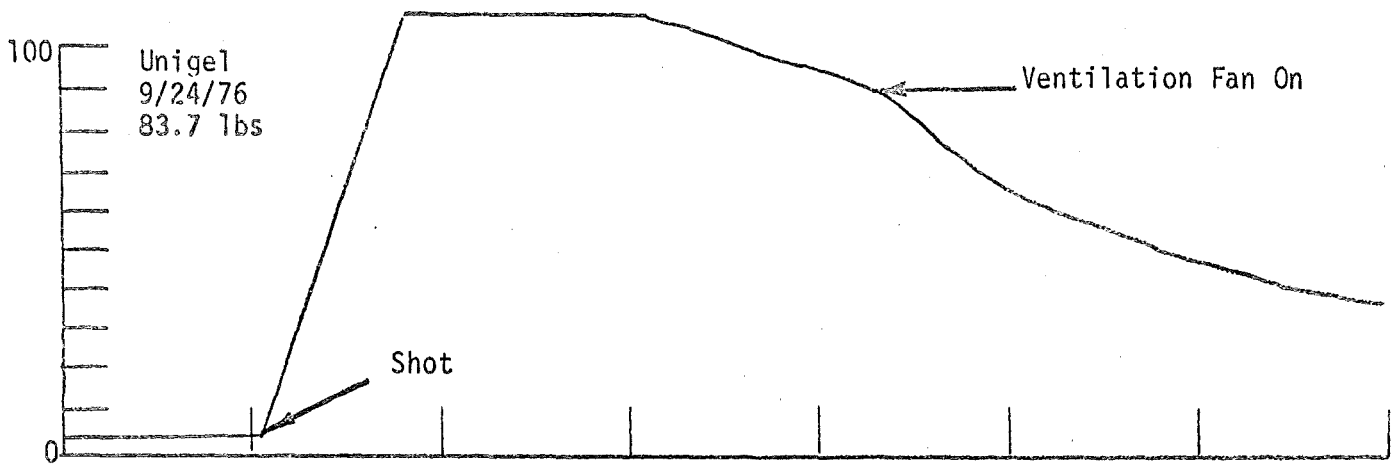


FIGURE 7 - SO₂ TRACES (Unigel, Gelodyn-2X, Tovex-100 4VT)

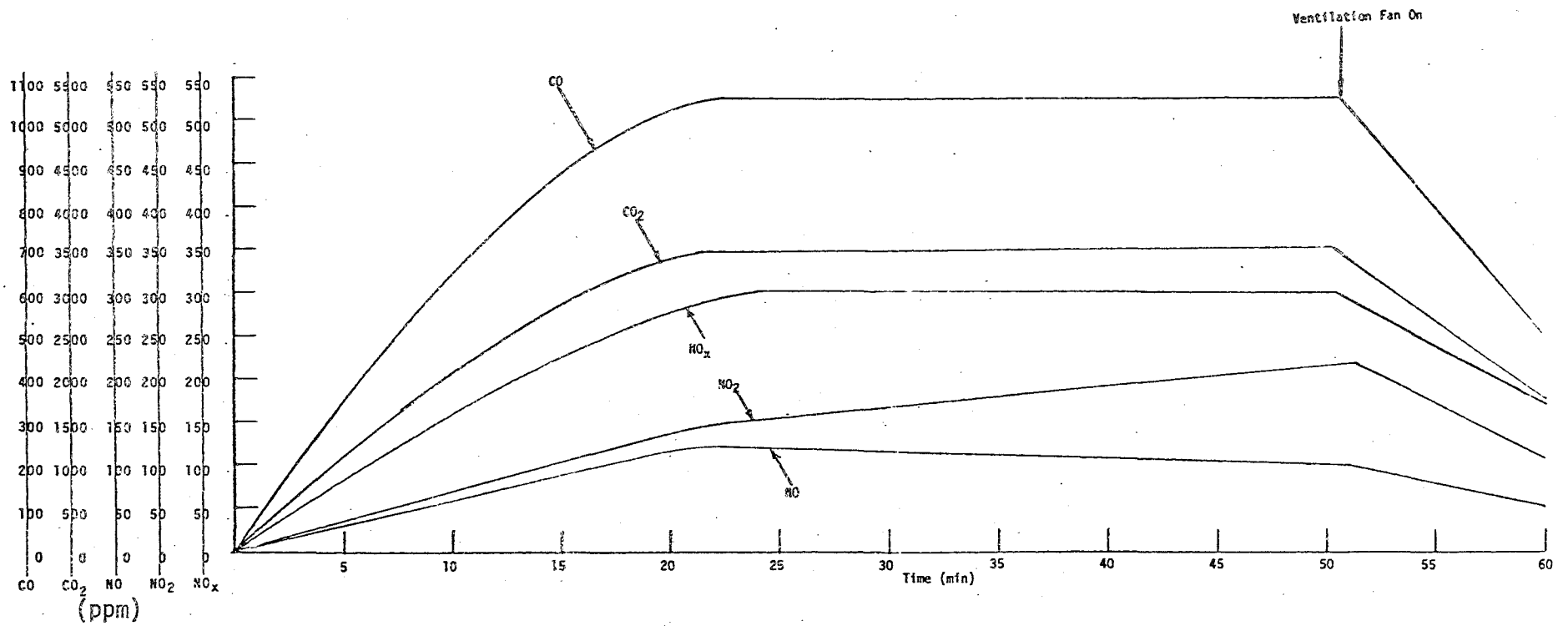


FIGURE 8 - CO, CO₂, NO, NO₂, and NO_x TRACES, GELODYN-2X (10/22/76)

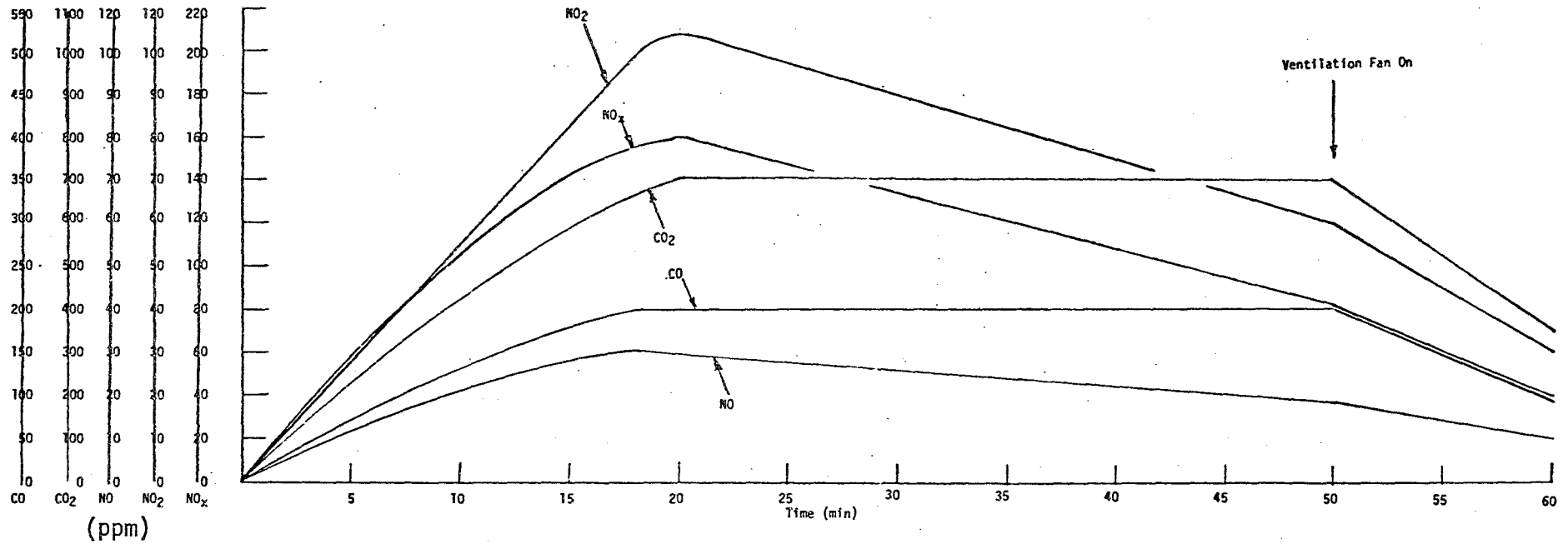


FIGURE 9 - CO, CO₂, NO, NO₂ and NO_x TRACES, TOVEX-100 4VT (10/26/76)

The decrease in NO concentration and the increase in NO₂ concentration are shown in Figure 8. This behavior has also been observed in tests conducted by the U. S. Bureau of Mines in the 1350 ft³ chamber.⁶ It should be noted, however, that this behavior was not observed in all cases, although it appeared to be more prevalent with Gelodyn-2X than with Tovex-100 4VT. The reason for this phenomenon occurring in some cases but not in others is not immediately apparent. Temperature has an effect on the reaction rate of NO, but the temperature of the mine air was essentially the same each day. Other factors which may affect the reaction rate of NO include moisture and possible catalytic effects produced by dust and/or other gas present in the atmosphere.

Figure 9 shows the behavior of CO, CO₂, NO, NO₂ and NO_x for one of the Tovex-100 4VT shots. These curves are presented to show that, in this particular shot, the NO, NO₂ and NO_x concentration decreased with time. This behavior was not observed to this degree in any of the other shots. It does, however, demonstrate that these gases can be sorbed onto wet walls, as was the case with SO₂. Therefore, the length of time between shot firing and measurement of toxic fume concentration can be of importance.

DISCUSSION

Toxic fumes generated from eight shots of Gelodyn-2X and seven shots of Tovex-100 4VT were monitored. The quantity of toxic fumes generated per unit weight of each explosive was calculated. Average values for CO, NO_x, CO and SO₂ were determined.

Toxic Fume Generation

The average amount of CO generated during shot firing of Gelodyn-2X, a typical nitroglycerin-based explosive, was 0.20 ft³/lb. Tovex-100 4VT, a typical water gel, produced an average CO value of 0.09 ft³/lb. The average amount of NO_x generated during shot firing of Gelodyn-2X was 0.049 ft³/lb. Tovex-100 4VT produced an average NO_x value of 0.026 ft³/lb. Previous in-mine tests and U.S. Bureau of Mines tests indicate that 70-80% of the NO_x produced is in the form of NO. These current tests did not corroborate this fact, however, it must be noted that complete mixing in the mine required 20-25 minutes and during that time it is likely that a portion of the NO was oxidized to NO₂. Indeed, the strip chart traces indicated that NO was being oxidized to NO₂.

The amount of SO₂ produced by Gelodyn-2X (0.009 ft³/lb) was greater than that produced by Tovex-100 4VT (0.0019 ft³/lb). Previous in-mine tests showed that nitroglycerin-based explosives produced larger amounts of SO₂ than did the water gels.

An attempt was made to measure the amount of ammonia during shot firing. However, due to the length of time required for mixing, it was concluded that most of the ammonia was probably sorbed into the water in the mine and that the results were invalid.

Relationship of In-Mine and Large Chamber Tests

Significant differences exist between in-mine and large chamber tests. In-mine conditions and probable large chamber conditions are listed on the following page.

<u>Variable</u>	<u>In-Mine</u>	<u>Chamber</u>
1. Size of charge	1 in. dia	1-1/8 in. dia
2. Weight of charge	70-100 lb	1 lb
3. Confinement of charge	Tightly tamped	Loose fit in mortar
4. Rock hardness	Variable	Not applicable
5. Mixing time	20-25 min	3-5 min
6. Moisture	Wet walls (70-90% RH)	Near ambient RH

Other variables may exist which are not immediately apparent.

The weight of the charge may have a significant effect on the toxic fumes generated. The highest NO_x value with Gelodyn-2X was observed when a small charge of 12.5 lbs was shot. This shot produced 0.108 ft³/lb of NO_x compared to the average of 0.049 ft³/lb. Similar behavior was noted in the earlier studies which were conducted on toxic fume generation.

Rock hardness may have a significant effect, also. Shots conducted in September were in hard rock seams while those conducted in October were in soft rock or mud seams. The shots conducted in hard rock seams appeared to produce lower NO_x values than the shots conducted in soft rock seams.

As large chamber test data become available, any differences between the in-mine and large chamber results should be evaluated with respect to these variables.

RECOMMENDATIONS

The results of these studies indicated that the general procedure used to measure toxic fumes from shot firing was a viable method. These studies have resulted in some observations which should be considered in any future studies:

1. An air door type stopping would probably be more practical than the currently used brattice type stopping. The door could be left open during shot firing, thus avoiding blast damage to the stopping. The door could be located at various distances from the face; this would permit changing the size of the enclosed volume to accommodate the measurement of smaller charges.
2. The possibility of paying the difference between normal day rate and contract rate for the miners should be given consideration. This would permit greater flexibility in selecting the type of explosives to be used.
3. Rock hardness, type of rock and water content should be used as criteria for test site selection.
4. Storage conditions and age of the explosive may affect toxic fume generation characteristics.

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