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Test Report for Enclosure/Static Mixer Testing for Future Investigation/Exploitation of Phosgene Munitions

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Chemical Biological Application and Risk Reduction$,CBARR; U.S. Army Combat Capabilities Development Command Chemical Biological Center; Aberdeen Proving Ground, MD) programs require investigation, assessment, and recovery operations of phosgene (CG) munitions ranging in size from 250 lb. light case bombs to 1000 lb. CG bombs. The operations are conducted under engineering controls (environmental enclosures interfaced to multiple filter units) to eliminate or minimize the release of CG into the atmosphere. There is significant concern that release of high concentrations of CG into an environmental enclosure and then adsorbed onto carbon beds could cause filter units to catch on fire. A CBARR team investigated options to reduce CG concentrations introduced to carbon filters.

15. SUBJECT TERMS

Phosgene (CG)	Filtration units	Static mixer
Ignition	Enclosure	Carbon

Activated carbon, impregnated with copper, silver, zinc, molybdenum, and triethlyenediamine (ASZM-TEDA)

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PREFACE

The work described in this report was authorized under CBC Flex 4 Funding. The work was started in November 2020 and completed in August 2023.

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TEST REPORT FOR ENCLOSURE/STATIC MIXER TESTING FOR FUTURE INVESTIGATION/EXPLOITATION OF PHOSGENE MUNITIONS

1. BACKGROUND

CBARR has programs requiring investigation, assessment, and recovery operations of phosgene (CG) munitions ranging in size from 250 lb. light case bombs to 1,000 lb. CG bombs. The operations are conducted under engineering controls (environmental enclosures interfaced to multiple filter units) to eliminate/minimize the release of CG into the atmosphere. There is significant concern high concentrations of CG being released into the environmental enclosure, and then adsorbed onto the carbon beds, could cause the filter units to catch on fire. High concentrations of phosgene cause the filters to ignite due to the rapid and repeated exothermic reactions between the phosgene molecules and the carbon filter impregnates. Lower concentrations of phosgene provide more time in between each reaction allowing the temperature to decrease enough to mitigate ignition by the next reaction.

One option to reduce the concentration of CG before it enters the filter is by using a scrubber. Scrubbers are extremely effective against phosgene. The combination of phosgene with water creates hydrochloric acid, a much easier chemical to dispose of. However, due to the austere environment of the work site, wet scrubbers are much more difficult to implement due to their need for large amounts of water. Needing a constant supply of water causes enormous operational impact. Additionally, scrubbers are not effective in defeating all other type of chemical warfare agents (CWA). Therefore, a filter system is still required in case any other agents are encountered. Due to these challenges, CBARR is investigating the following options to reduce CG concentrations introduced to the carbon filters:

a. Increase the enclosure size. Increasing the size of the enclosure (tent) provides more air to dilute the CG should it be released into the enclosure, thus lowering the CG concentration seen by the carbon.
b. Use an in-line static air mixer. An in-line static mixer mixes outside air with enclosure air, reducing the concentration of CG seen by the filter. This solution is the most cost-effective and has a small operational footprint which is beneficial for operations on difficult terrain.
c. Increase the number of filter units attached to the enclosure.

With more filter units drawing air out of the enclosure, the concentration of CG going into each filter unit is reduced. Adding additional filters is not the best option because of cost and the terrain challenges.

With site terrain presenting operational challenges, the options for mitigating CG concentrations on the filters narrow. This includes increasing the size of the environmental enclosure, as some operations could be on a steep slope. To overcome this challenge, CBARR proposes use of a larger “dilution” enclosure ducted to a smaller “operation” enclosure. This approach allows for a more agile operations posture, as the dilution enclosure remains in place and the operational tent is relocated as needed to interrogate multiple targets. In addition, a smaller enclosure as the operational enclosure reduces project cost regarding devegetation and ground leveling for enclosure placement.

To determine a path forward, CBARR took a two-pronged approach:

a. Request the assistance of the Research & Technology (R&T) Directorate to determine the ignition concentration of CG on impregnated filters.
b. Procure and test in-line static air mixers in various enclosure configurations to determine their effectiveness in reducing the concentration of phosgene going into a filter unit without effecting enclosure pressure differential.

2. R&T EFFORT SUMMARY

2.1 Background

The team at the Research and Technology Directorate at the Chemical Biological Center has performed testing in the past to challenge filter systems. The team constructed an apparatus, like ones used in previous testing to ensure repeatability. The apparatus consists of instrumentation placed up and downstream of the carbon to monitor for signs of ignition. Instrumentation upstream established the humidity and phosgene concentration feed conditions. A gas chromatograph measures for phosgene breakthrough downstream of the filter media. An inlet HEPA filter on the system is used to mimic the Chemical Agent Filtration System (CAFS) operation on the large scale. The carbon bed depth and superficial velocity is established to mimic operating conditions of a 5600 CFM CAFS unit. The testing set-up shown in Figure 1 is tested and compared to historical data to ensure repeatable data is collected.

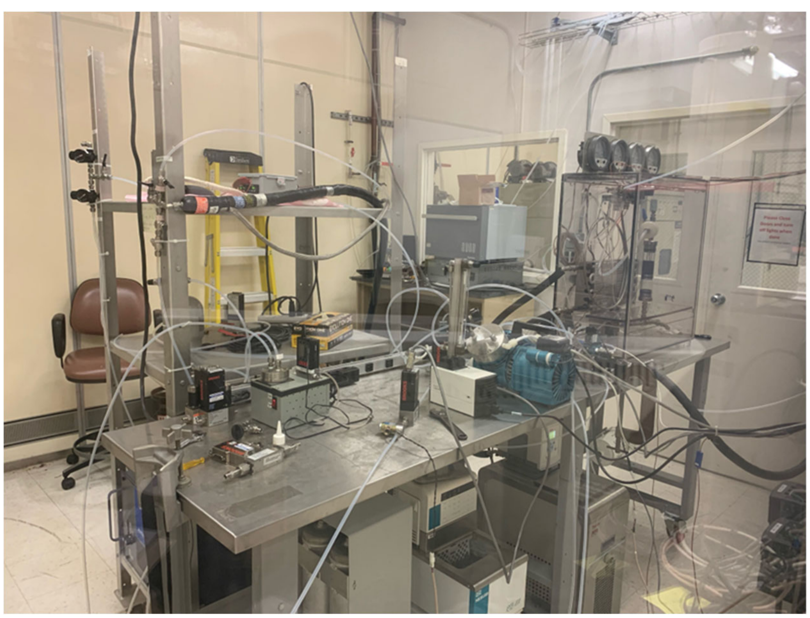

Figure 1. The testing space for the testing performed on the interaction of ASZM TEDA carbon filter and phosgene.

2.2 Test Procedure

The test operator begins by establishing a feed condition of concentration and humidity, and monitoring the outlet for temperature, phosgene concentration, and CO2 levels. The test is stopped if the phosgene breaks through the filter, the ignition point is observed, or if a pre-determined maximum dose of phosgene is delivered to the filter element located inside of the containment box shown in Figure 2. A series of tests are conducted where the carbon is equilibrated at the lowest test humidity, 15% relative humidity (RH), and then challenged with the lowest phosgene concentration. The same procedure is then performed at the next temperature and humidity condition.

2.3 Test Conditions

Humidity Levels: 15, 40, 60, 80% RH
Temperatures: 25C and 35C
Concentrations: 30,000; 40,000; 60,000; 80,000; and 100,000 mg/m3

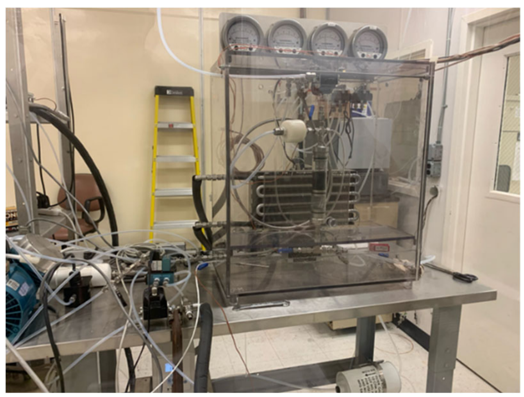

Figure 2. An image of the test apparatus used by R&T.

2.4 Results

Comparison of temperature values before and after the filter media is the best way to determine if the carbon filter media ignited or is considered an "ignitable condition". Below is a table which shows the maximum temperature seen during the duration of each of the below tests at both the inlet and outlet of the carbon bed. Tests where the carbon filter media ignited are represented by highlighted red values. Other higher temperature values are "ignitable conditions", so they are not included in the acceptable range of concentrations. Ultimately, the results shown in Table 1 display the conclusions of the study of safe operating concentrations for phosgene interaction with ASZM TEDA carbon filters. Note: part of the R&T report defines breakthrough times for the challenge concentrations against the filter media. This table depicts the breakthrough results for a constant challenge at a given concentration, which is not representative of reality. The number of filter systems is selected to ensure there is enough carbon to adsorb all potential CG, so breakthrough is not a concern.

- Tests at ≤80,000 mg/m^3, at 25 °C, at any humidity level, do not pose ignitable conditions.
- Tests at ≤60,000 mg/m^3, at 35 °C, at any humidity level, do not pose ignitable conditions.

Table 1. Temperature Results of the R&T Study which Tested Interaction of Phosgene with ASZM TEDA Carbon Filters

	Inlet Temp (C)				Effluent Temp (C)			
25C								
RH/Conc	15	40	60	80	15	40	60	80
30,000	28	34	101	35	41	41	51	26
40,000	38	38	106	28	42	40	62	37
60,000	37	41	107	34	47	40	86	31
80,000	42	40	87	95	51	53	88	89
100,000	30	40	97	103	115	140	95	92
	Inlet Temp (C)				Effluent Temp (C)			
35C								
RH/Conc	15	40	60	80	15	40	60	80
60,000	71	60			71	110		
70,000	86	180			146	80		
80,000	87	ignition	35		ignition	155	47	
90,000		176				84		
100,000	ignition		43	105	149		42	99
120,000		180	49	102		90	44	103

3. CBARR STATIC MIXER TESTING

3.1 Static Air Mixer Design

The CBARR team found a vendor to design and build the custom static air mixer shown in Figure 3 to meet our defined parameters. To meet residence time across the filter media, the actual calculated CFM of a 5600 CFM Chemical Agent Filtration System (CAFS) is 5337 CFM. The in-line static air mixer is designed to ensure proper mixing of the enclosure air with outside air using the predicted required flow to maintain negative pressure inside of the enclosure. The static mixer is designed using the total CAFS unit airflow (5337 CFM) and the estimated airflow required to maintain negative pressure in the enclosure (1800 CFM, assuming two filter systems). According to the manufacturer, the minimum length of ductwork after the mixing unit must be 6 diameters past the outlet of the mixing unit to allow for complete mixing. The mixer ensures the contaminated enclosure air is thoroughly blended with outside air to avoid hotspots of higher concentrations of phosgene.

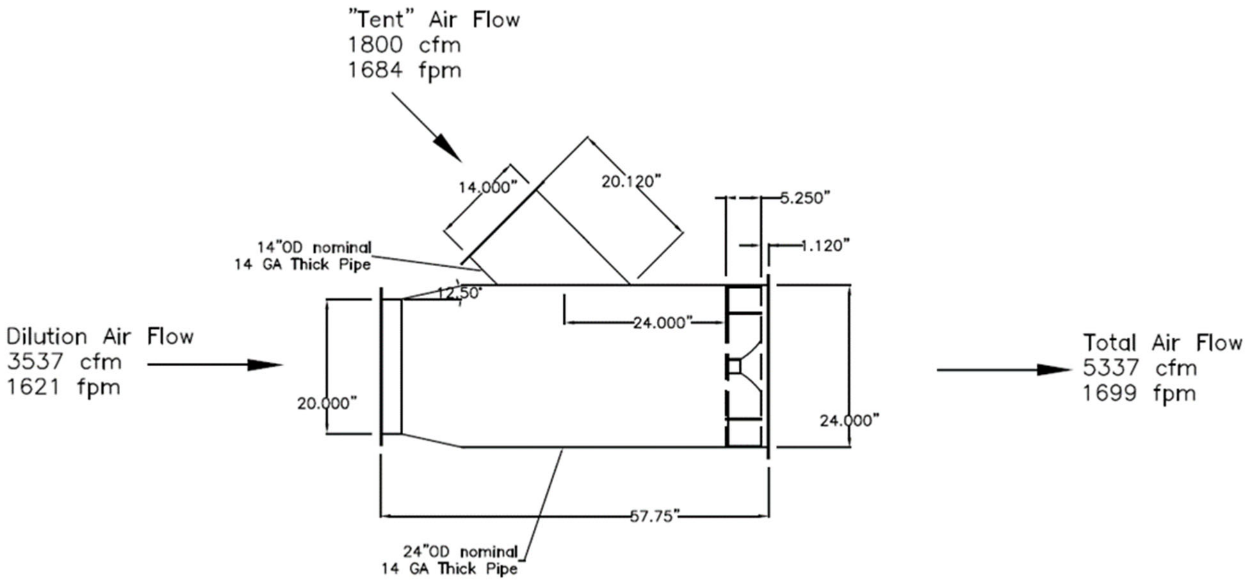

Figure 3. An image of the static air mixer as designed by the vendor to meet parameters provided by the CBARR team.

3.2 Testing Setup

To accomplish the two connected enclosures setup, the team places two identical filter systems side by side. The filter systems are connected to a 15' section of metal ductwork so the static mixer properly blends the air before entering the filter housing. The metal ductwork is connected to two identical inline static mixers. On both the outside air and enclosure air sides of the mixer, there are dampers so flow can be controlled to allow more or less outside or enclosure air. These dampers, named outside damper (OD) and enclosure damper (ED) are labeled by their percentage openness throughout the study (ED66=enclosure damper 66% open). The enclosure side of the mixer is ducted to the medium enclosure. On the opposite side of the enclosure, inside of the enclosure, an inline blower is placed to assist in pulling air through the long length of ductwork connecting the medium enclosure to the small. A smoke generator is introduced into the small enclosure to simulate phosgene. There are only two variables changing during the testing: the static mixer damper settings and the length of ductwork between the medium and small enclosures. Both variables are changed to determine how flow affects negative pressure and dilution. A diagram of the testing setup can be seen in Figure 4.

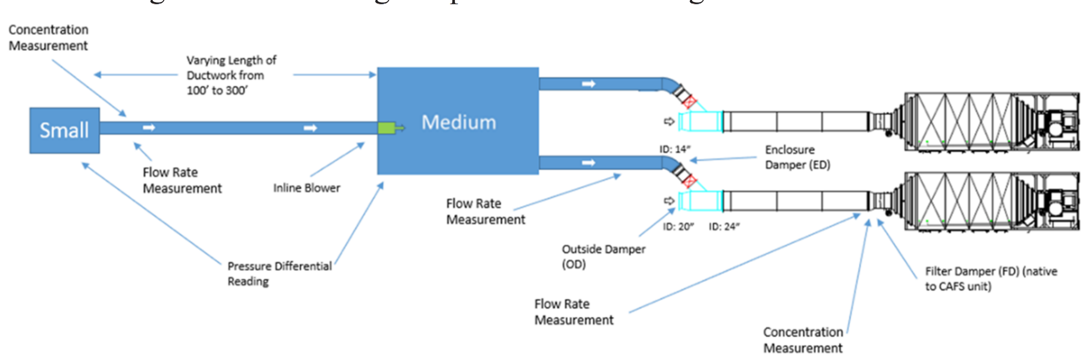

Figure 4. A schematic of the test plan.

3.3 Test Procedure

At the beginning of the test, the damper of the filter systems is set so the flow entering the filter system is roughly 5337 CFM to mimic a fully loaded 5600 CFM filter system. Once the length of ductwork between the medium and small enclosures is set, the beginning of each trial of the test begins by configuring the dampers. The dampers are varied throughout the testing to determine how it effects dilution and negative pressure. After the dampers are set, flow measurements and negative pressure values are read and recorded. Next, the smoke particle counters begin to collect data and an operator enters the enclosure, turns on the smoke generator, and exits the enclosure. Then, when the smoke reaches a constant concentration in the small enclosure, the operator enters and turns off the smoke. The smoke follows the path outlined in Figure 5 below:

1. Smoke is introduced at the far end of the enclosure.
2. Smoke is exhausted out of the small enclosure.
3. Smoke enters the medium enclosure because of the inline blower's fan, located just inside the medium enclosure.
4. Outside air enters the static air mixers where it dilutes the smoke with outside air prior to the filter.
5. Smoke enters the filter system.

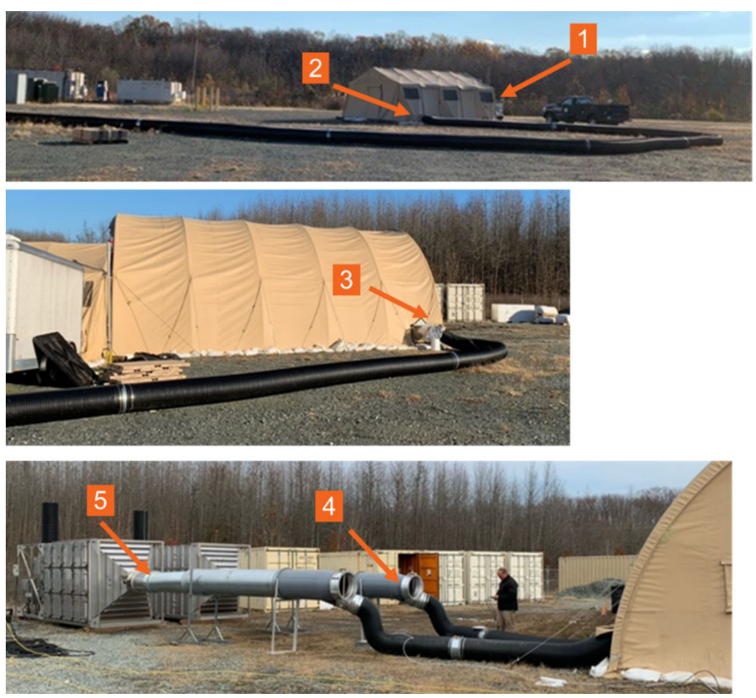

Figure 5. Photos from the setup and testing of the static mixers.

3.4 Calculation of estimated phosgene release

The most important step to understanding if this configuration provides enough dilution is to calculate an estimated peak dilution. This calculation is complicated and involves many factors and variables. Please see the Table 2below for inputs and outputs of the calculation. The estimation is for the peak concentration seen in the small enclosure. The mass used for this example is the total mass of phosgene in a 250 lb. light case munition. The enclosure volume is the volume of the small enclosure. One piece of data collected during testing is the flow rate on the exhaust from the small enclosure. This data is analyzed to allow for a minimum expected exhaust flow to be calculated. This number is important because it determines the number of air changes in the small enclosure. Temperature and pressure are estimated environmental conditions. The evaporation surface area is a key assumption because the calculation of phosgene release rate considers the total surface area from which the phosgene can release from. So, assuming the 250 lb. light case munition is in vertical orientation, the surface area is derived as 95.03 inches squared. Finally, taken from the results of the R&T testing performed, the input of 60,000 mg/m^3 is used in the calculation of the dilution percentage.

Table 2. Inputs and Output of the Estimated Phosgene Release Calculation

CG Mass (lb)	Enclosure Volume (m^3)	Min Enclosure Exhaust Flow (CFM)	Temperature (F)	Barometric Pressure (Torr)	Evaporation Surface Area (in^2)	Maximum Allowable Concentration at Filter System (mg/m^3)
130	84	463	75	750	95.03*	60,000

Key Assumption: Surface area calculated as if the bomb is in vertical orientation.

⬇

Peak Concentration in Small Enclosure (mg/m^3)	Min Required Dilution (%)	Phosgene Evaporation Time
88555.18	32.25	3048.55s (50.81min)

The results of the calculation are the expected peak concentration inside of the small enclosure and the total release time expected. From the data, we calculate required dilution as a ratio of the expected peak concentration to the maximum allowable concentration into the filters. 32.25% is the amount of dilution required to dilute the contaminated air to an acceptable CG concentration. This value is used to compare to dilution test data to determine if the system in this configuration dilutes the phosgene concentration enough to avoid ignition of the ASZM TEDA filters.

3.5 System Configuration Smoke Testing Results

With an estimated phosgene release calculated, the dilution required is a known value. The smoke testing data is collected by two particle counting photometers capturing data in unison. An “upstream” and a “downstream” photometer captures concentration values of the smoke just after leaving the small enclosure and just before entering the filter banks. These collection points allow for the overall system dilution to be captured. From these two time-series data plots shown in Figure 6, a dilution value for each second of the test is calculated. The below plot is a representative example of this data collection displayed graphically. There are no units on the plot because both concentration and dilution values are shown, rather units are shown on the legend. In orange section one, the light grey plot represents the upstream concentration values in mg/m^3. The curve quickly climbs at the beginning of data collection as the smoke fills the small enclosure. The yellow curve, the downstream smoke concentration in mg/m^3, slowly rises as the concentration is diluted before making it to the filter system. The dark gray plot, dilution percentage, starts at around 100% because the system is seeing a non-zero concentration upstream and a zero concentration upstream, which equates to perfect dilution. As the filter system starts to see a concentration of smoke, the dilution values naturally decrease. In section 2, the upstream curve reaches a "steady state" where the concentration remains relatively constant, this is either due to the enclosure filling with smoke or due to operator intervention. This mimics the predicted release of a phosgene munition; it is believed this will be a constant release. The downstream concentration continues to slowly rise as the smoke makes its way through the system but tapers off to a constant concentration by the end of section two. Since the upstream concentration is relatively constant, the dilution values follow the downstream concentration values. The values decrease slightly at the beginning and then taper off to be constant dilution. In section three, the smoke source is turned off. Therefore, both the upstream and downstream concentrations begin to fall. Similarly, the dilution values decrease, however, at the point when the source is turned off, the dilution values are not representative of what the system requires at this point because the downstream concentration (what the filters will be exposed to) is starting to decrease. At the steady state of the dilution, this is the minimum dilution expected by that system under the parameters utilized during the test.

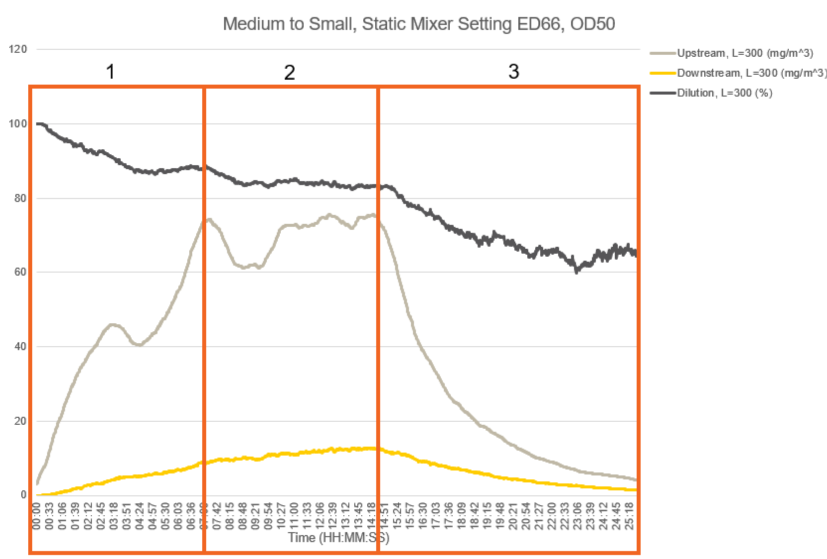

Figure 6. A representative plot of upstream concentration, downstream concentration, and dilution for the parameters ED66, OD50 and Length 300ft.

For Figure 7 below, the three systems that displayed the lowest dilution at steady state are shown in comparison to the predicted required dilution. Proving the lowest diluting systems meet required dilution gives flexibility to parameters in the field setup of the equipment. That said, the following chart shows the dilution plots from three different system configurations. Again, the dilution results after the time the smoke is turned off are not factored in as minimum dilution values. From the chart, the lowest calculated dilution value at steady state is 78.71%. Referring back to the estimated phosgene release, 32.25% is the amount of dilution required to prevent filter ignition. Because the minimum expected dilution value is greater than the required dilution value, these configurations are predicted to provide enough dilution to prevent filter ignition.

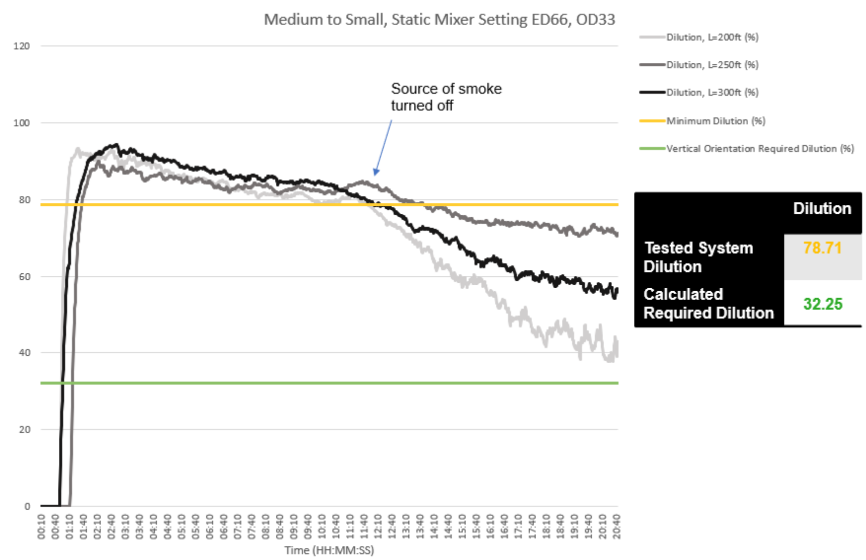

Figure 7. Dilution plots from three configurations, as well as the predicted required dilution plot.

Based on the data collected during testing, the configurations shown in Table 3 below will be successful in diluting the phosgene concentration to the required level, while maintaining negative pressure in both enclosures and would be viable configurations for the variables provided.

Table 3. Display of Configurations that Provide the Necessary Dilution to Minimize the Likelihood of Filter Ignition

Larger Enclosure Size	Smaller Enclosure Size	Length (ft)	Enclosure Air Damper Setting	Outside Air Damper Setting
Medium (29.5'Wx32.5'Lx15'H)	Small (18'Wx25'Lx8.25'H)	200	66% open	33% open
			66% open	50% open
			83% open	50% open
		250	66% open	33% open
			66% open	50% open
			83% open	50% open
		300	66% open	33% open
			66% open	50% open
			83% open	50% open

The phosgene release rate is calculated using variables predicted for field operations. Table 4 depicts conditions that would provide additional reduction in the likelihood of ignition. Reduction in ambient temperature would benefit in two respects, (1) cooling the exothermic reaction between phosgene and the ASZM TEDA carbon filters, and (2) reduction the vapor pressure of phosgene. Similarly, increasing the barometric pressure of the environment reduces the rate of phosgene off gassing. If possible, the bomb being exploited should be in the orientation leading to the least amount of surface area of phosgene being exposed for off gassing (typically the vertical orientation). Finally, from test data, it is determined that having a larger exhaust flow being drawn from the small enclosure leads to more dilution air being drawn into, and mixing with the contaminated air, right at the source.

Table 4. Variables that would Further Decrease the Likelihood of Ignition

Temperature	Barometric Pressure	Bomb Orientation	Small Enclosure Exhaust Flow
<75 F	>750 Torr	Vertical	>463 CFM

3.6 Testing Observations/Recommendations for Field Operations

There are a few important recommendations to ensure the filters systems do not get overloaded with phosgene. The enclosure should be placed so the filter inlet is as far as possible from the anomaly, this allows for more mixing to occur with the enclosure air, therefore reducing the concentration going into the filter units. Additionally, phosgene is heavier than air, so, if possible, it is beneficial to place the filter inlet in the enclosure higher than ground level. This way the phosgene will slowly draw into the filter system, allowing for more outside air to be mixed in with the phosgene via leakage.

3.7 Conclusions

In conclusion, using in-line static air mixers to dilute phosgene before entering filter units is a practical way to reduce the concentration without adding additional filter systems. These operational configurations require a delicate balance between minimizing contaminated flow exhausting from the enclosure, while maintaining negative pressure in the enclosures. More flow being pulled from the enclosure both increases negative pressure and the amount of contaminant being sent to the filters. There are other ways to handle phosgene interrogation options, such as scrubbers, larger enclosures, additional filter systems, but those options come with substantial financial burdens and operational difficulties. Under the guidance of this study, enormous cost savings and operational flexibility are realized.

ACRONYMS AND ABBREVIATIONS

APG	Aberdeen Proving Ground
ASZM	Activated Carbon, Impregnated with Copper, Silver, Zinc, Molybdenum
CAFS	Chemical Agent Filtration System
CBARR	Chemical Biological Application in Risk Reduction
CG	Chemical Symbol for Phosgene
CWA	Chemical Warfare Agent
ED	Enclosure Damper
OD	Outside Damper
R&T	Research and Testing Directorate
RH	Relative Humidity
TEDA	Triethylene di-amine

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