

Abstract

The San Diego Hazardous Incident Response Team (HIRT) conducted a chemical suicide study with the goal of determining the risk to the public and first responders. This study was designed to answer the following questions:

- Hydrogen sulfide is a flammable gas but can it reach the lower explosive limit with different volumes of reactants?
- How fast can it reach lethal levels and how long will it remain in an average sedan?
- What are the offsite consequences when a first responder or a good samaritan approaches or opens a door?
- How far will the gas travel once the door is opened?
- How long does it take to vent the gas to safe levels?
- What is the best instrumentation for first responders to use?
- What is the best personal protective equipment (PPE) to use?
- Is the remaining chemical mixture still a hazard to first responders?
- Will the bagged bodies be a hazard to the Medical Examiner staff?
- Is the remaining chemical mixture still a hazardous waste once neutralized?

Introduction

There are many types of chemical suicide; ingesting cyanide or pesticides, inhaling inert gases which are allegedly painful and not always successful. The most recent method is touted to be painless and 100% lethal. It is called “Detergent Suicide/Hydrogen Sulfide.” In the past couple of years chemical suicide by inhaling hydrogen sulfide gas has gained momentum as a method that is considered to be fast and painless.

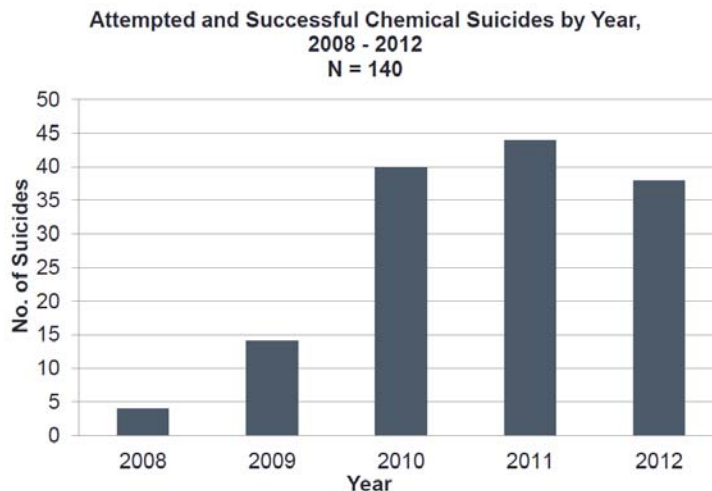
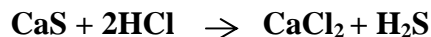


Figure 1. Source: CDC Morbidity and Mortality

Detergent Suicide originated in Japan using sulfur bath salts mixed with an acidic solution to generate hydrogen sulfide gas. Hydrogen sulfide gas is a toxic and flammable gas that is extremely lethal at low concentrations. This method was first recognized in the United States in Pasadena back in 2009. “The first sign that the technique was migrating to the United States came in August, when a 23-year-old California man was found dead in his car behind a Pasadena shopping center. The VW Beetle’s doors were locked, the windows rolled up and a warning sign had been posted in one of the windows. Police and firefighters evacuated the shopping center before a hazmat crew in chemical suits extracted the body and began cleaning up the grisly scene (www.wired.com)” Since this incident there have been numerous detergent suicides in the United States and in other countries.

Access to information via internet on how to commit this act has caused this to become a worldwide problem. With a few clicks you can figure out how to kill yourself with products easily obtained from a nursery, grocery or home improvement stores. The products that are commonly used are calcium polysulfide based fungicides or pesticides, and acidic liquids such as toilet cleaner (~20% Hydrogen Chloride). When these two chemicals are mixed there is an incompatibility reaction producing calcium chloride and hydrogen sulfide gas. The chemical reaction is demonstrated below.



Chemical reaction between calcium polysulfide and hydrochloric acid

There is as much danger to the public and first responders as there is to the person committing this act. In Canada there was a report of three police officers that were overcome by the hydrogen sulfide gas when opening a car door to assess an unresponsive person slumped over the wheel. There was also another report of firefighters who were relocating the bucket used to mix the chemicals and it generated more toxic, flammable hydrogen sulfide gas. This exposure caused several firefighters to be transported to the area hospital.

NIOSH Pocket Guide

Hydrogen Sulfide Chemical Profile

- CAS No. 7783-06-4
- Formula H₂S
- Exposure values
 - NIOSH REL C10 ppm
 - OSHA PEL 20 ppm
 - Immediately Dangerous to Life and Health (IDLH) 100 ppm
 - Rapid unconsciousness, cessation of respiration, and death 700 to 1000 ppm (Yant 1930)
- Physical Description: **Colorless gas with a strong odor of rotten eggs. [Note: Sense of smell becomes rapidly fatigued & can NOT be relied upon to warn of the continuous presence of H₂S]**
- Flammable range 4-44%
- Ionization Potential 10.46eV
- Solubility 0.4%
- Relative Gas Density 1.19

This type of incident is very dangerous for first responders and the public. The hazards and consequences resulting from the mixture of these reactants were relatively unknown. There is potential for a good samaritan or first responder to inhale a lethal dose, and/or innocent bystanders to be exposed to toxic levels of hydrogen sulfide gas. In certain concentrations hydrogen sulfide is a flammable gas. It was unknown if a car full of toxic flammable gas could ignite by opening a door, triggered by electronic locks or dome lights. Therefore, the San Diego HIRT set out to get some answers.

The logistics of creating live agent training requires a wide open space. This program was located at the Miramar Landfill in the city of San Diego. We had ample room to conduct this program in this location. To ensure there was a large enough space, plume modeling was conducted with 500 grams of hydrogen sulfide gas. This was considered to be greater than the worst case scenario that would be conducted in this study.

Chemical Suicide Risk Assessment for First Responders and the Public



Picture 1. The yellow outline represents 305 yards from the point source. At this border you can be at safe exposure levels of hydrogen sulfide gas. There was ample room at this location to conduct the study.

In this study we used a vehicle to simulate a real event. We were able to obtain a 1981 Nissan Maxima sedan from a local towing company. The vehicle was plumbed with tubing for real-time monitoring during the tests that were to be conducted.



Picture 2. Sedan with tubing plumbed into the breathing zones at all seats.

Chemical Suicide Risk Assessment for First Responders and the Public

The study was designed with safety being the number one priority. Operations were conducted using standardized Incident Command System. Two meteorological stations were set up to assess wind conditions for safety and downwind impacts.

The methodology was the same for each test in that we had two entry team personnel dressed out in firefighter turnouts and one designated mixer in a chemical protective hazmat suit, Level “B ” to provide splash protection when mixing the reactants. This person would mix the two reactants, close the sedan door and walk away. To monitor the hydrogen sulfide gas produced, the team used the following detection methods:

1. Combustible Gas Indicator (Lower explosion limit calibrated to hexane, oxygen %, carbon monoxide upper range 500 ppm, hydrogen sulfide upper range 100 ppm)
2. RAE 2000 & 3000 Photo Ionization Detectors (PID)
3. MSA Safe Site System (Remote detection-24 units with 4-gas detection, hydrogen cyanide and ammonia)
4. Drager Hydrogen Sulfide colorimetric tube, range 0.2-7%
5. PH paper
6. Lead Acetate paper (Detects sulfides)



Picture 3. Photo of the vehicle with all of the instrumentation plumbed into the car and the MSA Safesite on a barricade. The weather station is at the front of the car on a yellow tripod.

Results

Test 1

Reactants: 1. 32oz Calcium Polysulfide 28%
2. 32oz The Works Toilet Bowl Cleaner 20% Hydrogen Chloride

- Run time 31 minutes
- Lethal levels in 9 minutes (Lethal levels are 800-1,000 parts per million)
- Remains lethal for 20 minutes
- 15,000 parts per million hydrogen sulfide gas concentration
- 38% of the lower flammable limit
 - Not flammable based on PID calculations with correction factor
- Opened doors at ~300 parts per million and vented to zero in 15 min.

Test 2

Reactants: 1. 64oz Calcium Polysulfide 28%
2. 64oz The Works Toilet Bowl Cleaner 20% Hydrogen Chloride

- Run time 1.8 hours
- Lethal levels in 6 minutes (Lethal levels are 800-1,000 parts per million)
- Remains lethal for 20 minutes
- 11,000 parts per million hydrogen sulfide gas concentration
- 28% of the lower flammable limit
 - Not flammable based on PID calculations with correction factor
- Remained at Immediately Dangerous to Life and Health (IDLH) levels for >60 minutes
- Opened doors at 21 ppm and vented to zero in 15 min.

Test 3

Reactants: 1. 96oz Calcium Polysulfide 28%
2. 96oz The Works Toilet Bowl Cleaner 20% Hydrogen Chloride

- Run time 46 minutes
- Lethal levels in 4 minutes (Lethal levels are 800-1,000 parts per million)
- Remains at lethal levels for 30 minutes
- *5,500 parts per million hydrogen sulfide gas concentration
 - Equipment error due to reactants coating detection equipment (PID)
 - LEL% not calculated due to equipment errors
- Opened doors at 850 parts per million and vented to zero in 4 minutes

Test 4

- Reactants: 1. 128oz Calcium Polysulfide 28%
2. 128oz The Works Toilet Bowl Cleaner 20% Hydrogen Chloride

This test was run for a short duration with high volume of reactants (1 gal. each) to have the most impact downwind. The gas reached lethal levels in 4 min. and held until doors were opened at ~850 parts per million.

- Run time 16 minutes (Short run time for highest offsite consequence)
- Lethal levels in 4 minutes (Lethal levels are 800-1,000 parts per million)
- Remains at lethal levels for duration of the test, 15 minutes.
- 15,000 parts per million hydrogen sulfide gas concentration
- 38.5% of the lower flammable limit
 - LEL calculated using PID with correction factor and Drager tube 02.-7%.
- Opened doors at ~894 parts per million and vented to zero in 15 min.

Offsite Consequences

During all tests, the outside of the vehicle was monitored for hydrogen sulfide gas leaking from the door cracks. The MSA Safesite ® detectors were setup around the car, downwind up to 100'.



Picture 4. MSA Safesite Detector Setup

Doors Closed

It was found that the gas escaping from the vehicle was well above the IDLH levels (>100 ppm), within a few feet of the car.

Chemical Suicide Risk Assessment for First Responders and the Public

Doors Open

Test #4 showed that after ~15 min. hydrogen sulfide concentrations inside the car remained extremely high, ~4,300 ppm. If the doors are opened at these concentrations the exposure and downwind impacts can be significant. Concentrations were measured up to 75' downwind, but non detect at 100'

Table 1. Downwind concentrations:

Distance from car	Hydrogen Sulfide Gas Concentration
0-25 Feet	660 ppm
25 Feet	250 ppm
50 Feet	50 ppm
75 Feet	< 10 ppm
100 Feet	0 ppm

Answers to our questions:

1. Hydrogen sulfide is a toxic flammable gas but can the gas concentration reach the lower explosive limit with different volumes of reactants? Flammable range is 4-44% (40,000 ppm-440,000 ppm)

✓ Answer: No, not observed in this study. Through all the testing with different volumes of reactants the hydrogen sulfide gas did not reach flammable limits inside a standard sedan. The highest LEL% was 38.5%.

2. How fast can it reach lethal levels and how long will it remain in the car?

✓ Answer: According to our data, lethal levels could be reached in as little as 4 minutes after mixing and can remain at this lethal level for up to 30 minutes.

3. What are the consequences when a good samaritan or first responder opens a door to assist a detergent suicide victim?

✓ Answer: Potentially lethal if the door is opened within 30 minutes of mixing the reactants.

4. How far will the hydrogen sulfide gas travel when a door is opened and at what are the concentrations?

✓ Answer: According to the study, it has the potential to travel up to 75 feet. This data suggests a perimeter of 150 feet to be sufficient.

5. How long does it take to vent the gas to safe levels once the doors are opened?

✓ Answer: At lethal levels of the hydrogen sulfide gas remaining inside the sedan the hydrogen sulfide gas will vent to zero parts per million within 15 min.

6. What is the best instrumentation for first responders to use?

✓ Answer: Most first responding fire personnel do have a four gas meter (Flammable gas detection, % oxygen, carbon monoxide and hydrogen sulfide detection). These types of detectors have hydrogen sulfide sensors that will typically top out at 100-300 ppm. These will be good detectors for perimeter monitoring of the vehicle but are not the best choice for monitoring the cracks and crevices of a vehicle as the gas concentration may be too high. For monitoring high concentrations (>300ppm) a photo ionization detector is recommended as it can detect a higher concentration of the gas up to 10,000 ppm. There is a correction factor of 3.3 (RAE PID) that expands this detection capability up to 33,000 ppm. Typically photo ionization detectors do have less accuracy at very high levels but this detector will be very useful to determine lethality concentrations of ~800-1,000 ppm.



Picture 5. RKI Eagle2 combustibles gas indicator on the left and the RAE 3000 photo ionization detector (PID) on the right.

7. What is the best personal protective equipment to utilize for a detergent suicide incident?

- ✓ Answer: In our study the hydrogen sulfide gas does not concentrate enough to reach flammable limits inside a sedan. There may be other situations with different volumes of reactants and smaller spaces where this may occur. Therefore, it is recommended that fire fighter turnouts still be the PPE of choice to conduct a reconnaissance of the vehicle.



Picture 6. Entry team in fire fighter turnouts conducting reconnaissance at a real incident

- ✓ After the vehicle is vented the personal protective clothing should be changed to splash protection “Level B” to keep the responder from contaminating the firefighter turnouts during neutralization. This study determined that there is no flammability potential during this activity.



Picture 7. Level “B” ensemble for neutralizing the remaining solution.

8. Is the remaining chemical mixture still a hazard to first responders?

- ✓ Answer: YES. When the bucket is relocated for neutralization there is more hydrogen sulfide gas generated at almost lethal levels, ~800 ppm. Respiratory protection is required, such as a self-contained breathing apparatus with level “B” personal protective equipment.

9. Will the bagged bodies be a hazard to the Medical Examiner staff?

- ✓ Answer: The simulated mannequins with clothing used in the study were bagged after each test and stored for 24 hrs. They were monitored after 24 hrs. and the levels detected were safe for medical staff to proceed with their duties. Less than <10 ppm of hydrogen sulfide gas was detected. Also there were no significant acid residues on the clothing that could be determined using pH paper.



Picture 8. Mannequins used to simulate victims

10. Is the remaining chemical mixture still a “California Hazardous Waste” once neutralized?

- ✓ Answer: It depends on the neutralization method:
Yes, If the mixture is neutralized with soda ash, the neutralized mixture is still considered a hazardous waste as it fails toxicity and reactivity testing.
No, If the mixture is neutralized with fast set concrete it is NOT CONSIDERED a CA HAZARDOUS WASTE as it passes the toxicity (fish bioassay test) and reactivity testing. This mixture can be disposed of as solid waste saving a considerable amount of resources that is normally provided from state of California to dispose of the hazardous waste.

Summary

This program is aimed at saving lives, first responders and bystanders. The results have given all first responders the tools they need to safely and confidently approach the scene. The following are the recommended to mitigate a “Detergent Suicide.”

- Secure a perimeter of 150’
- Use fire fighter turnouts for reconnaissance and monitoring of the vehicle
 - Look for secondary devices
 - Look for yellow liquids and containers inside the vehicle
- The vehicle will not be at flammable limits and cannot catch fire
- Use the combustible gas indicator for perimeter monitoring and the photo ionization detector for monitoring cracks and crevices of the vehicle for higher concentrations.
- The vehicle can be vented with a 150’ perimeter and the gas will dissipate in 15 minutes
- Once vented ensure the Medical Examiner has provided approval to remove the chemical containers.
- Moving the mixing bucket can cause lethal levels of hydrogen sulfide gas to be generated and should be handled in full Level “B” chemical protective clothing
- Neutralizing with fast setting concrete will allow the agency to treat the solidified waste as a non-hazardous waste

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