

Hydrogen Chloride Gas Generators Associated with Clandestine Drug Labs



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**Hydrogen Chloride Gas Generators
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HCl, CAMEO RIDS printout

Field Ballistics Testing

Ecology is an equal opportunity agency. If you have special accommodation needs, contact Amy Krause (360) 407-6370 (Voice) or (360) 407-6006 (TDD).

Ecology or CADRE do not intend to endorse any particular method outlined in this report. Nor do Ecology or CADRE assume any liability for any injuries that may result from the use of any particular method outlined in this report. Each responder must make his or her own judgment regarding the safety of any particular field response method based on actual field conditions as well as the responders level of training and experience.

Executive Summary

The Washington State Department of Ecology (“Ecology”) requires practical field methods to assess and render safe hydrogen chloride (HCl) gas generators. Ecology is responsible under Washington State law (RCW 69.50.511) to dispose of these generators along with other chemical wastes associated with clandestine labs encountered in Washington State.



Ecology responder with waste from typical clandestine lab

This report discusses the hazards of HCl generators, provides a description of generators encountered in the field and details methods used to date for assessing and rendering them safe.

CADRE, Inc. of Woodinville, Washington, was contracted by Ecology to compile and prepare this report. Related reports, describing 5 gallon propane tanks, valves, ammonia gas and field-tested methods for handling ammonia tanks associated with clandestine labs, have been prepared for Ecology by CADRE, Inc. For copies contact:

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The methods discussed in this report are intended to be conducted by trained and equipped responders who are complying with OSHA and State regulations and following their employer’s standard operating guidelines. In addition, the following seven steps should be considered:

1. management and control of the scene (IC, backup, site control, notifications, etc..)
2. identify hazard (assess generators carefully, review other potential hazards, etc..)
3. analyze hazard (potential for uncontrolled, airborne release, explosions, etc..)
4. select appropriate personal protective gear (consider respiratory and skin hazards, etc..)
5. control and contain (release pressure, disposal, transportation, etc..)
6. decontaminate (personnel and equipment, etc..)
7. terminate (on-site debriefing, follow up notifications, lessons learned, restock, etc..)

HCl gas is a common component used for the illegal production of methamphetamine. Pure sources of HCl can be used and cylinders of commercial HCl gas have been observed in the field. More commonly however, HCl gas is obtained by mixing sulfuric acid (e.g., commercial drain cleaner) or hydrochloric acid (muriatic acid) and salt (e.g., rock or table salt) in a reaction container, referred to as an HCl generator.

Hazards likely to be encountered by responders handling HCl generators include gases, liquids and solids that are toxic, corrosive and flammable. Corrosive gases likely to be encountered in HCl generators are hygroscopic (will absorb water). HCl gas is a strong respiratory and eye irritant and exposure can cause permanent injury or death. Respiratory and skin protection equipment is mandatory for responders who intend to handle HCl generators.

HCl gas corrodes most of the containers encountered at clandestine labs. This creates the additional hazard of container failure with the potential sudden violent release of pressurized contents. The hazards these generators pose may increase with time as the generator degrades and becomes potentially more unstable.

HCl generators associated with clandestine labs are typically not labeled or identified according to regulatory standards and may appear disguised as common household items intended for non-hazardous purposes.

HCl generators encountered in the field have included:

- propane tanks
- plastic gasoline containers
- 2 liter pop bottles
- soda syrup cylinders
- medical oxygen cylinders
- freon and helium cylinders
- ketchup dispensers
- ziploc or plastic bags
- glass vacuum flasks
- fire extinguisher bottles
- acetylene cylinders
- dive bottles
- self-contained breathing apparatus bottles
- baby bottles
- various other containers

Many of the items encountered at labs may not be modified, hazardous or even associated with illegal clandestine lab activities, yet still require assessment and disposal by Ecology.

It is critical that a proper assessment be conducted on any HCl generator found in the field prior to handling for any purpose. Field assessments should initially include a thorough visual examination to determine the general condition of the generator including:

- type and condition of any installed valves or connections
- presence of burn marks or staining on the outside of the generator
- apparent degradation of the generator itself
- identification of the clandestine lab recipe being used
- how the generator has been stored (vertical vs. horizontal, possibly plugging valves)

These generators could contain HCl, ammonia, propane, hydrogen, air or a variety of wastes from the illicit lab process. Simple testing with wetted pH paper (with an observed pH of 0-1) is typically the first step to determine if a container is an HCl generator. Additional tests may include

the use of portable combustible gas monitors prior to initial venting or final opening for disposal.

The following methods have been used or considered by Ecology to render HCl generators safe for disposal and are listed in no order of preference. Each method has pros and cons. Experienced responders are likely to encounter field scenarios where a combination of one or more methods is/are preferable.

1. transportation for temporary storage, treatment or disposal
2. air release using a hand-operated valve
3. remote drilling with hardware store equipment
4. remote opening by law enforcement shooter
5. remote opening by bomb squad technician
6. sparging into water then neutralizing
7. specialized contractor with specialized equipment
8. cutting open a vented generator for disposal purposes

These methods are currently considered by Ecology to be the best that are practically available given the budgetary and time constraints they are working under. So far these methods have proven safe and effective. However, Ecology recognizes that they are not state of the art and continues to consider additional options. If your organization has additional information or has developed field techniques that are not listed in this report, please contact Ecology at the address listed above, so that in the interest of safety, they can review it and potentially share it with others.

As a response community, we require practical and available solutions. CADRE recommends that a variety of tested options be made available for trained and experienced field responders.

Credits:

Photos supplied by Ecology, SW Regional Office staff (Jim Oberlander, Eric Heinitz, Brett Manning, Ron Holcomb, Doug Stoltz, Mike Osweiler) and CADRE.

Thanks to Ecology's SW Regional Office staff for their sincerity and willful interest in sharing what they've learned through considerable field experience.

Thanks also to technical reviewers: Dale Mann, Washington State Patrol Crime Lab; Pamela Johnson, DEA Missouri Crime Lab; Wendy Phippen, University of Washington; Roger Ely, DEA San Francisco Crime Lab; and Rob Turkington, HazTech Inc.

Field notes used in the preparation of this report are in CADRE's project file.

History

Responses to clandestine drug laboratories by Ecology have increased during the period of 1990 (38 labs) to 1997 (203 labs)¹. The trend continues in 1998. Increasing numbers of clandestine lab responses have also been reported in the States of California, Missouri, Arizona and Hawaii.

Typically, each lab cleanup conducted by Ecology involves at least one HCl generator.



*assortment of containers confiscated at clandestine lab
(the propane tank in the rear is an HCl generator)*

Additional chemical and other hazards commonly encountered at labs include:

- acetone
- toluene
- alcohols (methyl and ethyl)
- ether
- white gasoline
- muriatic acid
- sulfuric acid (battery acid or selected drain cleaners)
- anhydrous ammonia or ammonia cleaning solution
- propane
- table or rock salt
- debris from batteries (lithium, carbon, flammable solvent, metal jackets, etc..)
- residue and 'binders' from precursor extraction
- sodium metal
- iodine
- red phosphorous
- hydriodic acid
- Drano or Red Devil Lye
- unstable and violent suspects
- unknowns (booby traps, explosives, chemical mixtures, etc..)

¹ Focus, publication # 98-1119-SPPR, Washington State Department of Ecology, August 1998

Types of generators encountered:

As observed at clandestine labs, an HCl generator typically has the following operational design elements:

1. ability to add acid and salt together in small quantities, then be sealed
2. ability to contain pressurized HCl gas
3. ability to valve off the generator
4. ability to transfer the HCl gas through a hose
5. portability
6. inexpensive
7. considered by the clandestine lab operator to be disposable
8. ability to disguise as a common household item (e.g. propane tank, etc.)

Although a simple plastic generator would most likely serve the purpose, many illegal cooks utilize metal generators often fabricated with elaborate valving.

The following photos depict a variety of HCl generators encountered by Ecology, beginning with the one of the most common types, propane cylinders. Propane cylinders, from 1 to 10 gallon in size, are the most common ones Ecology has seen to date. The Washington State Patrol Crime Lab reports finding plastic containers (gas carriers, pop bottles, etc..) as the most common type they have encountered.

Propane cylinders:



5 gallon cylinder



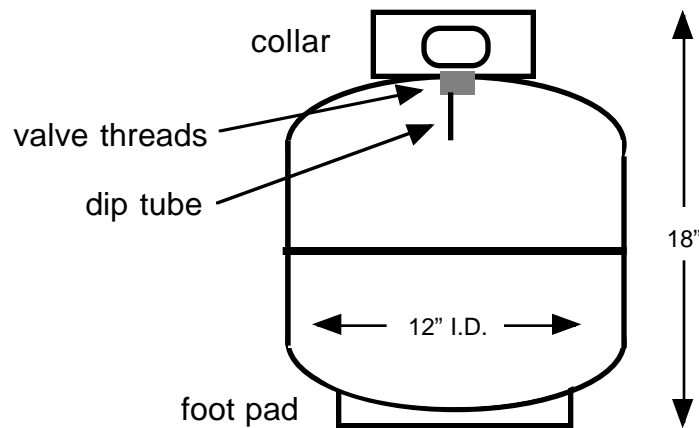
generator w/ hose

Five gallon propane tanks are made of fine-grain, high-strength, low-alloy steel with a wall thickness of 0.078". They have the following rated pressures for propane service:

- 240 psi, working pressure
- 480 psi, test pressure (hydrostatic testing)
- 960 psi, burst pressure (they cannot burst below this pressure)
- 1200 to 2000 psi, typical observed burst pressures

Identification markings will be found on the tanks, typically on the collar at the top or “valve” end of the tank:

<u>Tank Marking</u>	<u>Description</u>
TW	Tare Weight (5 gallon empty tank w/valve installed will typically be around 18 lbs.)
DT	Dip Tube (length of the dip tube in the tank, typically 4”)
WC	Water Capacity (amount of water the tank could hold)
LP	Liquefied Petroleum
LPG	Liquefied Petroleum Gas
DOT-4BA240	DOT specification that the tank was built to
WCW, WCG, WII, WORTHJ, Worthington or Manchester	the manufacturers identification marking



A dip tube, which aids in filling, may be present. It typically extends 4 inches down from the propane valve into the tank. When properly filled, a valve is opened allowing gas to escape up through this dip tube. When the liquid level in the tank reaches the dip tube level, liquid will begin escaping the dip tube opening, indicating the tank is full.

These tanks are intended for use with propane, not the acids, ammonia and other products typically encountered at clandestine labs.

Valves

Tanks used as HCl generators typically do not have a properly-rated valve installed. They often have a home-made arrangement of brass, galvanized copper and stainless steel fittings. Brass, galvanized steel and copper are quickly corroded by acids and ammonia. Although stainless steel valves may be rated for HCl, all valves on HCl generators should be considered highly suspect due to their illegal and questionable origin.



..home-made stainless steel valve assembly on 10 gallon propane tank



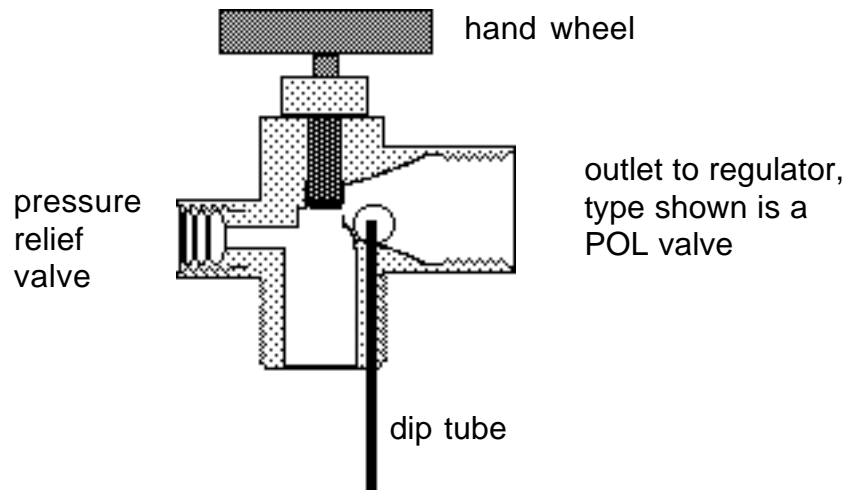
..home made brass and ..galvanized valve on 5 gallon propane tank



..valve handle that ...broke off whenbeing turned

Propane tanks are commonly used as HCl generators. Often, standard brass propane valves are observed in the field. There are 3 primary types of standard brass propane valves on the market today:

1. POL (CGA 510), about 90% of the market, with internal left-hand threads:



typical brass POL propane valve found on 5 gallon propane tanks



.....Brass POL propane valve
(note the tool marks, indicating
it has been improperly removed
.....from a cylinder



Brass POL valve, cutaway



corroded POL valve

2. ACME or Type 1 (1 5/16" M. ACME and CGA 510), external right hand threads and internal left hand threads (POL valve)



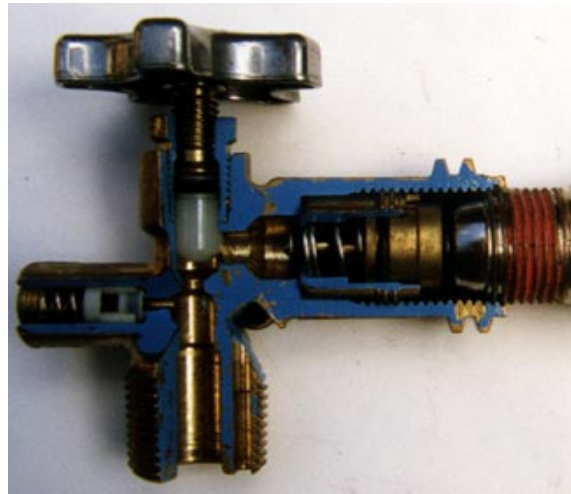
.Type 1 valve



.....Type 1 valve, cutaway



corroded Type 1 valve



Type 1 valve depicting how internal plunger is normally depressed by female fitting to allow the release of propane

3. Quick Connect or Type 2, similar to fittings on air hoses, no threads



Type 2 valve



Type 2 valve, sleeve pulled back



Type 2 valve with adaptor from hardware store that depresses internal fitting allowing propane to flow

All three of these standard propane tank valves have a pressure-relief valve that actuates at about 375 psi. At that pressure, it is designed to automatically open, decreasing the pressure in the tank. It is designed to release either gas or liquid from the tank. The rated pressure of the safety-relief valve is typically stamped on the side of the tank valve. Again, this well-engineered valve is not typically found on HCl generators, and if it is, it is probably corroded or damaged. There may be no pressure relief device at all!

Additional types of HCl generators that are commonly encountered in the field:



plastic gas cans



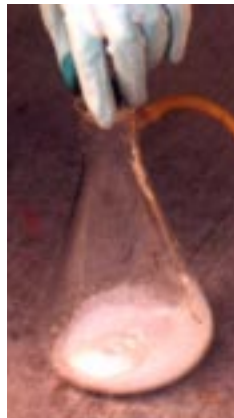
*CO2 fire extinguisher
with modified valve*



*medical oxygen bottles
(the manufacturer's valve has
been illegally replaced with a
POL brass propane tank valve)*



*freon tank w/attached
hose*



*glassware
(e.g., vacuum flask)*



*Carbon Dioxide (CO2)
cylinder*



commercial HCl cylinder with home-made



commercial HCl cylinder being loaded for transport



freon tank with home-made valve and hose connection



.....
....baby bottle with hose



mustard dispenser with hose

Chemistry of HCl generators

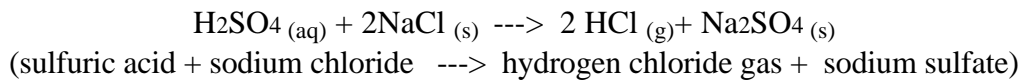
HCl gas is typically produced in an HCl generator when acid is mixed with salt. The 2 most common acids used for this purpose are hydrochloric (muriatic) and sulfuric. Either or both may be encountered in the same generator and, as observed in the field, the hazards are relatively similar.

A common source of hydrochloric acid is hardware store “muriatic” acid, usually sold in plastic jugs intended for masonry work. It is typically yellow in color due to impurities that include iron.

Common sources of sulfuric acid include battery acid or sulfuric acid-based commercial drain cleaner which is sold in hardware stores and often packaged in plastic 1 qt. jugs.

Sodium chloride is simply table or rock salt and therefore readily available at grocery stores.

The production of HCl gas by combining sulfuric acid and salt is a well-understood and commonly-referenced chemical reaction:



This reaction generates heat and pressure as the HCl is produced. Typically, clandestine lab chemists simply combine enough acid and salt to make some HCl gas. They are not interested in balancing out measured quantities to maximize their yield for this step of the illicit drug-manufacturing process. By-products can therefore be expected to contain unreacted salt, sulfuric acid, impurities (water, hydrochloric acid, previous contents of the generator, etc.) and sulfate compounds.

By-products and wastes found in HCl generators have typically been found to contain semi-solid crystalline-like materials. They have been described as wet, sludgy, congealed, dirty, rock salt in a “crusty ball residue.” Chemical analysis performed on the waste material left over in an HCl generator indicated the presence of sulfate, chloride and sodium ions². The sample had a pH less than 1.0. These results are consistent with the chemical reaction described above.



*waste material described as “dirty wet rock salt” found in
5 gallon propane tank HCl generator*

This HCl generator was relatively easy to cut in half by first venting it, releasing all pressure, testing to confirm all pressure was released, then drilling a pilot hole and using a sawzall with a metal blade.

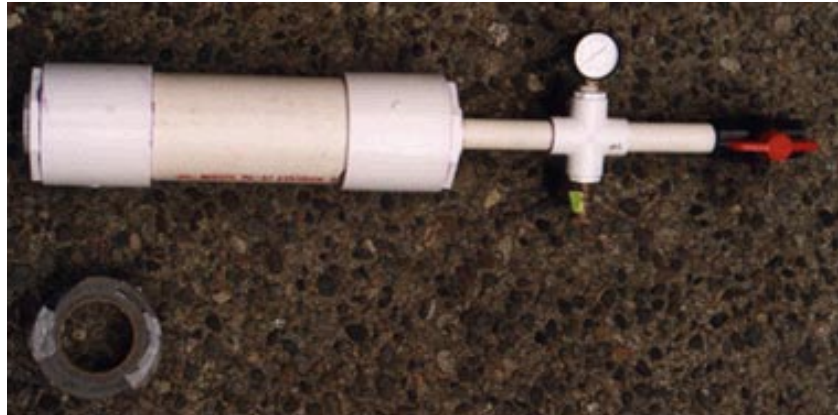
Hazards of HCl generators (pressure, corrosion, unknown contents)

The standard pressure found inside commercially prepared and packaged cylinders of HCl gas is 630 psi at room temperature. While experiments suggest that pressures developed inside typical drug lab HCl generators are around 10% of this level, it is possible that jury rigged vessels have been filled to much higher pressures using commercially prepared cylinders as the source.

Two separate field tests conducted by CADRE indicate that an HCl generator under the listed conditions reached a maximum internal pressure of 57 psi. The tests were completed at both 50 °F

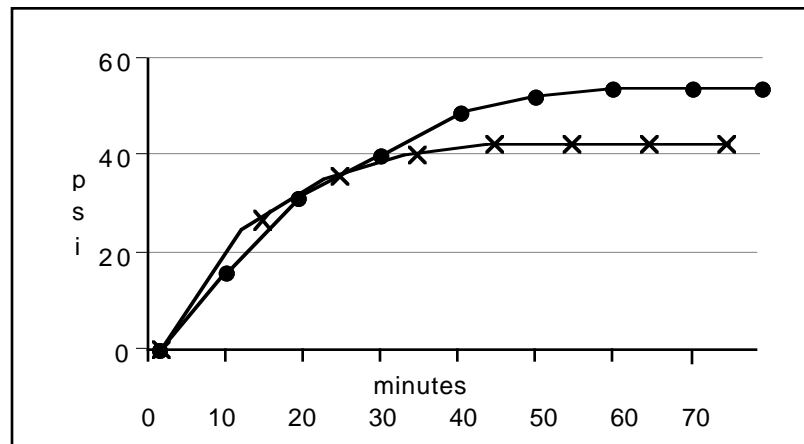
² Case Narrative #124598, Manchester Environmental Laboratory, Port Orchard, WA, 4/8/98

and 100 °F. However, the unknown and illegal nature of suspected HCl generators could pose situations where internal pressures were higher than 57 psi.



CADRE HCl generator testing unit with pressure gauge and 75 psi pressure safety valve

Test procedure: 2 cups of sulfuric acid (95%) drain cleaner were mixed with 2 cups of grocery store rock salt and mixed inside the CADRE test HCl generator. For each of the 2 tests conducted the generator was shaken vigorously for 10-15 seconds every 5 minutes and pressure readings were recorded. Shaking had minimal effect on the pressure rise, approximately 1-2 psi each time.



pressure buildup at 100 °F = ●
pressure buildup at 50 °F = X

As expected, the pressure generated was higher at the higher temperature. This is a good reminder that lowering the temperature of an HCl generator will have the effect of lowering the internal pressure. This has been accomplished in the field using ice and carbon dioxide fire extinguishers. Care should be taken not to quickly freeze components of the HCl generator causing them to become brittle and prone to failure.

After both tests the test unit was vented after 90 minutes. The HCl gas was sparged into water for neutralization and disposal. It took approximately 10 minutes to initially sparge the unit. The outlet valve was then closed and the unit was allowed to sit for 1 hour. Residual pressure of less

than 5 psi had built back up, most likely due to a small amount of reactive materials left in the generator. This residual pressure was sparged off and the unit was then flushed with water.

Ecology staff have observed 5 gallon propane tanks used as HCl generators with burn or torch marks on their side. This is likely due to clandestine lab operators attempting to warm up the contents of their generator to produce additional HCl gas after the pressure has dropped and the reaction neared completion. Higher temperatures of any gas typically result in higher pressures. Compressed gas cylinders are not designed to be heated and reused in this manner. Metal fatigue is likely to occur and the structural integrity of the cylinder is unpredictable. A sudden release of corrosive gas and/or liquid is possible.



Burn marks on lower portion of tank are most likely caused by a torch. The collar at the top of the cylinder has been removed by the clandestine lab operator to provide better access to the valve ,which is also severely corroded



Burn marks on HCl generator created with propane torch.

HCl generators are by design a home made manufacturing device for the production of a toxic, corrosive gas. Appropriate industry standards are not followed for the selection of the materials used in the construction of these devices. Brass (e.g., propane valves) quickly corrodes in the presence of acids and ammonia. The types of steel used in most of these cylinders corrodes in the presence of water mixed with sulfuric or hydrochloric acid. Plastic components can be degraded by solvents and exposure to the sun. None of the HCl generators observed to date in the field has been designed to contain all of the following potential contents:

- HCl gas
- propane gas
- ammonia
- hydrogen gas
- water (the presence of water greatly increases the corrosivity of any acid)
- sulfuric acid
- hydrochloric acid (muriatic acid)
- sodium sulfate
- salt
- waste solvents (gasoline, toluene, ether, alcohols)
- a mixture of the above
- unknowns

Impurities and unknown storage conditions require responders to consider all HCl generators as hazardous and unpredictable. These containers should not be considered acceptable for anything more than on-site remediation or secure transport for remediation. Again, plugged valves from 'rocky sludge' may be blocking valves preventing venting.

Field assessment of HCl generators

Field response techniques used to assess an HCl generator include, but are not limited to, the following:

1. Note original manufacturers intended use:
 - low-pressure welded metal compressed gas cylinder (propane, etc..)
 - high-pressure metal compressed gas cylinder (oxygen, CO₂, hydrogen, etc..)
 - plastic container (gasoline, pop bottle, ketchup dispenser, etc..)
 - glassware (laboratory, kitchen, etc.)

Note: Responders can contact the original manufacturer of a pressurized cylinder to obtain engineering specifications by obtaining the manufacturers name or identification markings from the cylinder and either calling them directly or working through ChemTrec 1-800-424-9300.

2. Valve: (Warning, unseen corrosion may be present, consider all valves highly suspect)
 - original manufacturers valve (brass, other metals, plastic, etc.)
 - home-made valve

- condition of valve (blue or green corrosion may be evident)



modified valve using galvanized and brass components including a standard brass propane valve (corroded to a blue color) this tank contained ammonia

3. Visual Observations:

- identifying marks (see the report “Initial Considerations for Handling 5 Gallon Pressurized Tanks of Ammonia Gas Associated with Clandestine Drug Labs”, 6/30/96, for a description of 5 gallon propane tanks and valves. (This report is available from the Ecology contact listed on the cover page.)
- rust, burn marks, stains, shape, tool marks indicating removal of valves



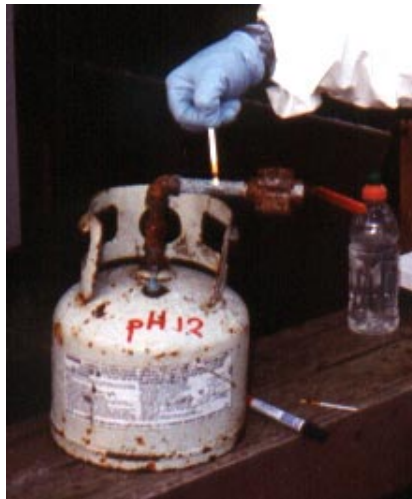
commonly encountered blue stain on clandestine lab cylinder, typically associated with ammonia



bulging cylinder that has been exposed to fire

4. Sampling without opening up valve:

- pH - place wetted pH paper on the neck around the valve, or flush a small amount of water around the neck of the valve using a squirt bottle of water
- low pH (0-1) most likely HCl generator
- high pH (12+) most likely ammonia cylinder neutral pH (5-9) most likely propane



*Suspected HCl generator with modified valve. pH was 12+.
It contained ammonia.*

5. Test for leaks without opening up valve:

- Liquid soap solution can be placed on and around the valve. This can be done during both the initial assessment and during removal of the valve to insure that no residual pressure remains.



testing with soap for leaks around the valve neck

6) Sample contents using valve that appears functional. (Warning, be prepared for valve failure with release of generator contents.)

- When possible, install a second valve (in good condition) onto the generator and use it to control the release of contents. Generator valves may fail upon opening and responders may not be able to close them. Having a backup valve will require obtaining an assortment of fittings and valves, commonly available at hardware stores. These backup valves should be considered disposable.
- Place a wetted piece of pH paper in a clear plastic resealable sampling bag. Using a functioning valve, release a small amount of the contents of the generator into the bag.
 - gas release with low pH, most likely an HCl generator
 - gas release with high pH, most likely an ammonia cylinder
 - gas release with no pH change, most likely propane or air (further testing using CGI/O₂ meter can confirm propane)
 - no gas release (spent HCl generator, waste container, plugged or inoperative valve, empty, etc.)
- Colorimetric indicator tubes can be used to confirm the presence of HCl or ammonia. Samples can be taken from the sampling bag.
- Small leaks of hydrogen chloride may also be detected by holding an open bottle of concentrated ammonium hydroxide solution near the site of the suspected leak (formation of dense white ammonium chloride fumes, $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl}$.)



sampling bag with pH paper inside

7. Intended use by the clandestine lab operator:

- Was this a clandestine lab operation? (Are there associated chemicals and hardware present)

- Does it appear that this was intended for use as an HCl generator? (Attached hoses are typically used to transfer the HCl gas.)

8) Weight of the generator:

- Propane cylinders have the tare weight stamped on the collar. This weight can be compared to the weight of the generator to assist in determining if the generator has any contents (see page 7).
- The weight of the generator cannot be reliably used to evaluate the amount of HCl gas (if any) present, due to the impurities and solids that may be present. However, field experience has shown that relatively heavy generators typically contain a corresponding amount of 'rock salt sludge'.

9. X-ray:

- Law enforcement bomb technicians often have portable x-ray equipment available for use in the field. It is reported to be able to depict clumps of rock salt inside a suspected generator.

Options for rendering HCl generators safe:

These methods are currently considered by Ecology to be the best that are practically available given the budgetary and time constraints they are working under. So far these methods have proven safe and effective. However, Ecology recognizes that they are not state of the art and continues to consider additional options. If your organization has additional information or has developed field techniques that are not listed in this report, please contact Ecology at the address listed above, so that in the interest of safety, they can review it and potentially share it with others.

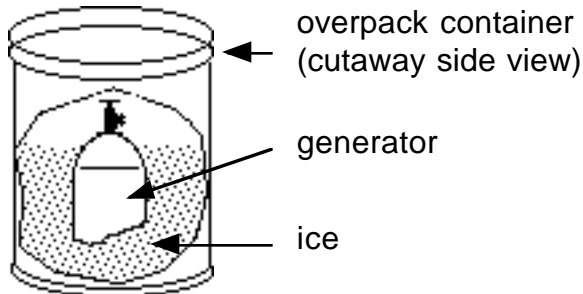
As a response community, we require practical and available solutions. CADRE recommends that a variety of tested options be made available for trained and experienced field responders

1. Transportation to secure location for remediation:

The hazards inherent in transporting an HCl generator can be decreased by cooling the generator. (This will effectively lower internal pressure.) Cooling can be accomplished by moving the generator into the shade, preferably away from responders.

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

If warranted, cooling can also be accomplished by placing the generator inside an unsealed overpack container and packing ice around it. This will of course have the most effect when the weather is warm and generator temperatures are higher. If the overpack container has a bunged lid, the bungs should be left off to prevent pressure buildup from leaks or a pressure release bung vent should be installed.



a cooling option

PROS:

- Cooling the generator will lower internal pressure, making it safer for transport.
- Transportation provides a method for moving the generator to a more secure or remote location to be rendered safe.
- Authorized officials may have regulatory approval for transporting generators under their emergency response laws. Ecology reports such an exemption for their staff.

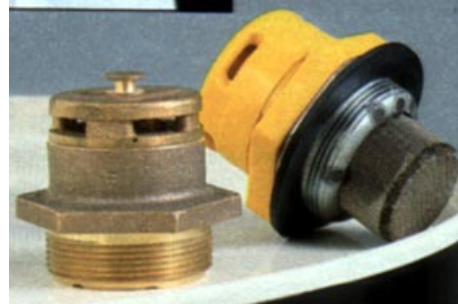
CONS:

- Responders must handle the generator.
- The generator should be kept in an upright position. This may require “packaging.”
- If not properly secured in the overpack container, the generator may “float” when the ice melts. (The tendency to “float” can be minimized by keeping the ice level low, and securing the generator in the overpack container with clamps, rope, etc.)
- The overpack container should not be sealed in order to prevent pressure buildup due to leaks from the HCl generator. This may allow HCl gas to leak out and be detectable, pose a health threat or corrode exposed equipment.
- The overpack container should be monitored for leakage of HCl. Colorimetric indicator tubes or wet pH paper can be used for this purpose.
- Transportation of potentially unstable HCl generators may not be allowed under shipping regulations by unauthorized officials.
- Proper labeling and manifesting of the package is required.
- Storage for any length of time in an enclosed unvented vehicle is not recommended. Heat from the sun can quickly raise internal temperature of the vehicle, increasing the temperature of the generator, which will increase its internal pressure. Also, hazardous fumes may be trapped inside the vehicle.

Note: A related special exemption (#12009) for ammonia cylinders has been prepared by the U.S. DOT. For information contact the Associate Administrator for Hazardous Materials Safety, Research and Special Programs Administration, Department of Transportation, Washington, D.C., 20590.

2. Air release using a hand operated valve:

This option requires the responder to manually operate a valve and vent the HCl generator to air in a suitable location.



5 psi drum vents

Requirements:

- Trained responders with appropriate protective equipment and backup personnel
- Remote location, escaping gas cloud has been observed to travel up to approximately 100 yards downwind. (Air modeling programs do not accurately model this small of an amount of HCl gas, over this short a distance.)

PROS:

- Simple.
- Relatively quick way to reduce generator gas pressure.
- Inexpensive.

CONS:

- **Requires manual manipulation of potentially unstable HCl generator.**
- **Potential for valve to fail, which could spray responder with contents and/or limit control over escaping gas.**
- Backup valve is recommended to be installed and used when practical. Many times the installed valve is stripped or unstable.
- Remote location required.
- Escaping gas cloud will be toxic and corrosive.
- Responders may need to obtain permission from local air pollution authorities.
- Responders will have little control over escaping gas cloud. (It can be “knocked down” somewhat with water spray. HCl is water soluble.)
- Valve may become plugged with solid contents from generator and stop venting at an acceptable rate.
- Contents of generator may spray into the air. Ecology has had this occur on three occasions, when the valve stem broke completely off, resulting in a “geyser” of HCl gas.
- Solid “sludge” inside the generator remains. Disposal typically requires removing and neutralizing this sludge. The generator may have to be sawed in half or rinsed with water.



*valve removal techniques
(done only after generator pressure has been released)*

Comments:

There is a good potential for the valve to fail. The responder could be exposed.

The air release method has been used by Ecology.

Ecology has observed valves fail in the open position and valves that were completely frozen and unable to be opened.

It is common to have the valve become obstructed by “sludge” inside the generator. Steps taken to clear those obstructions include:

1. A thin diameter object (e.g., coat hanger, nail, ice pick, etc..) pushed down the throat of the valve, relatively ineffective and potentially dangerous as the object could be propelled back towards the responder
2. Low air or nitrogen pressure (less than 10 psi) sprayed down the throat of the valve used to “blow back” obstructions.

Responders can attach a functioning, closed backup valve to the generator prior to operating the installed valve. If the installed valve fails, and can no longer be closed, the backup valve can then be used to control the pressure. Another benefit of installing a backup valve is that the responder only has to manipulate the installed valve once, to open it. Cons of this method include increased time and equipment, and the tank valve may be plugged and inoperative (a common occurrence) rendering a backup valve useless.

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, and downwind observer or air monitoring, etc.



air release from HCl cylinder



nearly spent HCl generator being manipulated by hand to try and clear blockage in the valve and neck from "sludge" in the generator

3. Sparging into water then neutralizing:



*sparging into water while monitoring temperature
(A parts list of the hardware used for this sparging setup is in earlier reports prepared for Ecology on NH₃ cylinders. Contact them for a copy.)*



Ecology responder conducting sparging using the hose that was found on the generator.

Releasing the contents of the HCl generator into a container of water is called “sparging.” This technique will result in a solution of hydrochloric acid (muriatic acid), which can then be disposed of as a corrosive liquid, or neutralized using a suitable base (e.g., baking soda, soda ash, etc.).

Hydrogen Chloride gas is soluble in water, 67% at 86 °F. A common solution of HCl in water is called muriatic acid, found in hardware stores at around 30% concentrations.

Note: quickly bubbling HCl gas into water (sparging) may not allow all of the HCl to go immediately into solution. Some may escape to the surface as bubbles and vent into the air as HCl gas. A slow rate of release will minimize this off-gassing. Responders should plan on HCl gas being present during sparging and monitor for it's presence. Fire Departments in California have reported incidents where responders without appropriate protective gear were exposed to HCl gas during sparging attempts.

The concentration, amount and strength of acids used in an HCl generator will typically be impossible to estimate prior to beginning a sparging operation. Unlike NH₃ cylinders, HCl generators have too many potential impurities and solids to make weighing them a practical field option for this purpose.

Sparging, and the addition of any neutralization materials, should be conducted slowly and only by responders trained and experienced in field-neutralization techniques.

Recommendations:

- Do not use the generator itself as a container for neutralization. All HCl generators should be considered suspect and prone to failure. Pour the contents into a heavy plastic or poly container that is at least 2 times the volume of the generator. This will allow for some head space. Neutralization reactions typically produce foaming and toxic gases. Available head space on a neutralization container is required to keep product from spilling out.

- As a coarse rule of thumb, for every gallon of HCl generator waste present, have a minimum of 18 lbs. of soda ash or 20 lbs. of baking soda available for neutralization purposes. Add it slowly with stirring and monitor the pH during the neutralization process. In most cases, these amounts of soda ash or baking soda are more than what has been required in the field.
- Neutralization can typically only take place in the presence of water. Dry materials found inside generators may need to be washed out with water and wetted to effectively neutralize them.

PROS:

- Can be done on site.
- May lead to inexpensive waste-disposal process.

CONS:

- Requires responder to manipulate potentially dangerous valve.
- Requires specialized (although inexpensive) equipment.
- Valve could become inoperative and need to be removed.
- If neutralization is conducted improperly, it can result in considerable amounts of foam being generated, which can spill out and create a mess. The use of secondary containment can limit this.
- Neutralization is typically a slow process.
- It may be easier to simply handle the acidic liquid as a corrosive waste and dispose of it as such. (Ecology has utilized a household hazardous waste facility and hazwaste disposal facilities.)
- Neutralization reaction can generate gases and heat.
- Responders may become exposed to contents of generator other than acids.

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

4. Remote opening by law enforcement shooter.

This method has been used effectively by Ecology on over 100 HCl generators under the strict guidance of law enforcement officials and is used by law enforcement officials in and around Missouri.



Law enforcement and safety officials conducting ballistics testing.

This method may not be allowed under the standard operating guidelines for your organization. It is considered an option by Ecology for use on 5 gallon propane tanks or similar HCl generators where the valve is suspect or contents are unknown. Ecology reports similar success with 1 to 10 gallon consumer-grade propane tanks, soda syrup tanks, SCBA tanks, fire extinguishers, freon tanks and some thicker-walled cylinders. Shooting has never been recommended or intended for use by CADRE or Ecology on rail cars, trucks, fixed storage tanks, etc.

A ballistics report has been prepared by Bruce Jackson, Chief Criminal Investigator, Pierce County Sheriffs Office, Tacoma, Washington, detailing testing that was conducted on 5 gallon propane tanks. It is available through the Ecology contact listed at the front of this document.

PROS:

- Law enforcement shooter can stay 100+ yards from HCl generator.
- Remote technique with immediate venting of generator.
- Ballistics testing report by law enforcement officer refers officials to tested techniques.
- Methods were documented that penetrated the tank, but did not perforate it. The bullet remained in the tank.
- Testing was conducted on 5 gallon propane tanks that were empty, filled with ammonia and filled with propane. (No explosions or fireballs, simply vented gas.)
- Ballistics testing indicated that deflection did not occur if the tip of the bullet hit the tank.
- Relatively inexpensive.
- Does not require manipulation of potentially unstable valves.
- May be the safest method as it allows responders to remain a safe distance from the suspect generator as it's being vented.
- A suitable staging area with liquid containment can be prepared and used. Ecology has prepared a sand and plastic lined area for this purpose.

CONS:

- Responders must still assess the generator and most likely transport it to a secure appropriate location.
- Requires law enforcement official to conduct shooting. (May be some cost and coordination involved.)

- Requires remote location with backstop and standard range safety protocols.
- Requires a minimum recommended downwind evacuated area of 200 yds.
- May not be addressed by standard operating procedures, and therefore not allowed in your jurisdiction. (Some law enforcement officials report being unable to discharge any weapon for this intended purpose.)
- Training may need to be conducted prior to considering this option. Some officials have expressed serious concern about the method, yet when queried typically admit no training or field experience with it. To date, on over 100 cylinders (including propane, ammonia and HCl generators) the release of pressure been relatively uneventful.
- Some responders are reluctant to discuss this option. (CADRE recommends that all available options be considered and responders allowed to use the method they feel is safest for responders, the public and the environment.)
- If the 5 gallon propane tank is not vented thoroughly, the potential for semi-solid particles inside an HCl generator plugging up bullet holes exists. These particles can be shaken loose with a resulting “popping” of gas out of the hole when the tank is later moved. (This has been observed by Ecology on two occasions.)
- Ballistics testing was conducted only on 5 gallon propane tanks.
- Does not eliminate the need to clean out the tank of spent acid and other wastes.
- Tank may become difficult to handle due to the holes. It will leak through them as it is being washed out.
- Holes created by bullets can create sharp edges, which might tear protective gear.

On two occasions to date, Ecology has had generators “pop” after being shot. The generators were clearly penetrated 1-3 times by a law enforcement shooter and venting was observed to have stopped within several minutes. Believing the generator pressure to be expended, Ecology responders then approached and manually began to handle the generators in preparation for disposal. The 2 generators then “popped” a jet of HCl gas out of one of the bullet holes. Ecology responders were properly protected and no injuries occurred. However, this “popping” was unexpected. It is believed that semi-solid sludge inside the generator ended up plugging up the bullet holes after the generators were shot. When the generators were moved, the semi-solid sludge was dislodged and a jet of HCl gas escaped. The production of HCl gas inside the generator may be stimulated by the shock wave from the bullet as it penetrates the generator. Ecology now requires that each generator be penetrated a minimum of 3-5 times in order to minimize the chance of this “popping” from occurring again.

Some containment of materials that might be released during this potential “popping” can be provided by placing a clear plastic garbage bag or drum liner over the generator prior to shooting it or by covering it with plastic prior to handling it after it is shot.

On one occasion to date, Ecology experienced a dense white plume that slowly developed and covered an area approximately 50 yards wide and high. This was most likely caused by a mixture of ammonia and hydrogen chloride gas from cylinders of both types that had been staged next to each other and shot a few seconds apart. The mixture of ammonia and hydrogen chloride gases creates ammonium chloride ‘fume’, a highly visible white airborne compound. This technique is commonly used in industry as a detection device for leaks on chlorine systems. Ammonium chloride fume is reported to be clearly visible at concentrations as low as 5-50 ppm depending upon ambient temperature and humidity. The OSHA 8 hr. airborne exposure limit for ammonium

chloride fume is 10 mg/m^3 (5 ppm). It is suggested that to minimize the mixing of ammonia with HCl that cylinders expected to contain one type of gas be vented completely prior to venting cylinders of another gas in the immediate vicinity.

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

Generators should be placed on a plastic tarp to help with containment of product after being shot.



*The top cylinders (on their side) contained ammonia.
The bottom two are suspected HCl generators. They are wrapped in heavy clear plastic bags.
pH test paper is being used to monitor their discharge.*

5. Remote opening by law enforcement bomb squad technician.



*Shape charge applied to empty tank
Before and after photos.*

Bomb squad technicians have the capability to vent an HCl generator, as depicted in the above photos. Pros and cons of this technique are similar to those of the shooting option. During testing in October of 1998, the Army EOD Unit at Ft. Lewis WA used shape charges to vent cylinders containing propane, ammonia and HCl gas. All three containers were vented as depicted above. There were no fireballs or secondary explosions.

Testing indicated that commercial and military linear shape charges effectively opened up 5 gallon propane bottles. These same shape charges can be used to cut those bottles completely in half, allowing for easier removal of any 'salty sludge' left in the bottle. With care, bomb technicians have indicated this is a relatively easy procedure for them to conduct.

Costs for commercial linear shape charge are approximately \$40 per foot which includes shipping. A typical 5 gallon propane tank will require 3 ft. 3 inches of charge to vent and separate the tank into two halves. Total materials cost for a 5 gallon propane tank including blasting cap are therefore in the \$120 to \$150 range.

Additional considerations include:

- The potential for dispersal of contents should the charge fragment the generator.
- The ability to clearly open up the generator insuring complete venting.
- Purchased explosives will require special storage, transportation and handling.
- Qualified and licensed explosives technicians will be required

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

6. Remote drilling with hardware-store equipment.

The use of portable, relatively inexpensive hardware store equipment allows responders to vent HCl generators in the field by drilling a small hole in them. A list of equipment which has been used successfully over 50 times on 5 gallon propane tanks containing ammonia is provided at the end of this report. A similar setup has been used successfully by Ecology on an HCl generator. Remote drilling can be conducted to allow for either air release or under water, allowing the generator contents to “sparge” or dissolve in water.



*Remote drill setup and remote drilling under water.
(A parts list of the hardware used for this setup is in earlier reports prepared for Ecology on NH₃ cylinders. Contact them for a copy.)*

Air release using remote drilling has essentially the same pros and cons as the method of air release using a hand-operated valve discussed above. Additional factors include the need for relatively specialized, but inexpensive, equipment and setup time.

Remote drilling under water (to sparge generator contents) minimizes air release. HCl gas is soluble in water. Additional factors include the need for a disposal method for the water.

Hydrogen Chloride gas is soluble in water, 67% at 86 °F. A common solution of HCl in water is called “muriatic acid,” which is available in hardware stores at around 30% concentrations.

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

Note: quickly bubbling HCl gas into water (sparging) may not allow all of the HCl to go immediately into solution. Some may escape to the surface as bubbles and vent into the air as HCl gas. A slow rate of release will minimize this off-gassing. Responders should plan on HCl gas being present during sparging and monitor for it's presence. Fire Departments in California have reported incidents where responders without appropriate protective gear were exposed to HCl gas during sparging attempts.



Close up of remote drilling hardware. Note circular magnet to keep drill bit from “walking.”

7. Contractor with specialized equipment.

Specialized contractors are available to handle unknown or potentially unstable pressurized cylinders. They can provide overpack cylinders referred to as “coffins,” specially-designed remote-operated drills and fume hood/scrubber boxes designed for field use. The availability of a coffin designed to handle the typical size of propane tank encountered in the field has not been confirmed.

The cost for mobilizing and using the services of these contractors is approximately \$4,000 to \$8,000 per day.

Ecology has not to-date used a specialized contractor for handling HCl generators. They have elected to use the methods discussed earlier in this report.



DOT rated salvage cylinders (“coffins”) designed for

low-pressure chlorine (under 250 psi).



specialized contractor setup with remote drilling unit, scrubber unit and containment hood

7. Cutting open a vented generator for disposal purposes

Ecology has determined that final disposal of generators requires them to be opened completely up to flush out and remove any remaining residue after all internal pressure has been relieved by one of the previous methods and confirmed with portable monitoring instruments and pH paper. All cylinders should be checked for the presence of flammable gases prior to the use of power tools.

Tools used for this purpose include a 'sawzall' and 'chop or cut saw'. Both are available through rental outfits for approximately \$40 per day. The sawzall with a metal blade is effective, but relatively slow. The 'chop or cut saw' has been found to be much quicker but creates a considerable amount of sparks. The use of welding chaps over protective gear may be required.

Ecology has used a simple wooden brace to hold the cylinder steady while being sawed upon. A pipe fitters vice has been suggested.



chop or 'cut' saw being used, note the sparks being produced

Responders are encouraged to follow standard site safety protocols including the use of site control, PPE, decon, tell tales for wind direction, designated escape routes, decon, backup, etc.

Remote Drill Device, parts list

- Model 6011DWE-2, 12V cordless Makita w/ spare battery and charger
- Vermont American part # 17192 drill press stand
- Assorted drill bits (cobalt, 1/8" and less)
- 5/16" hardened steel bit X 12" length
- 1/2" hardened steel bit, to drill drum rim for pipe clamp assembly
- Speedbor 2000, 12" X 1/4" power drill bit extension
- Assorted hose clamps
- Assorted self-tapping screws
- 1/2" pipe nipple X 48"
- "Pony" pipe clamp part # 5203 for 1/2" threaded pipe
- 2" x 4" x 12" lumber, ripped in half at a 45 degree angle and mounted on 1/2" plywood to support Propane tank in horizontal position.
- 50' of nylon line
- Contico 24" deluxe "Tuff-E" tool box
- 2 10" lengths of 1/4" round solid black steel rods for securing pipe to foot pad
- Hand socket driver for hose clamps
- Adjustable wrench for drill press
- Circular magnet with a hole in the center, to be applied to the top of the tank for the purpose of keeping the drill bit from "walking"

Costs totaled \$350 including 8% sales tax. The cost of the drill was \$160.

Remote operating device designed and tested by Dave Jackson, CADRE.