ER Gas Scrubbing

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Chemically Speaking LLC

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Gas Scrubiing

- Gases can be chemically scrubbed via
  - Wet Liquid Reaction
  - Dry Media Reaction
  - Combustion
  - Combination of the above
- Wet is the most common method due to lower operating cost

Wet Scrubber

- Air contaminated with the gas is brought into contact with a liquid chemical media which will react and form a non reactive byproduct.
- Efficiency is gained by improving the gas to liquid contact (interface). The most efficient type is packed bed

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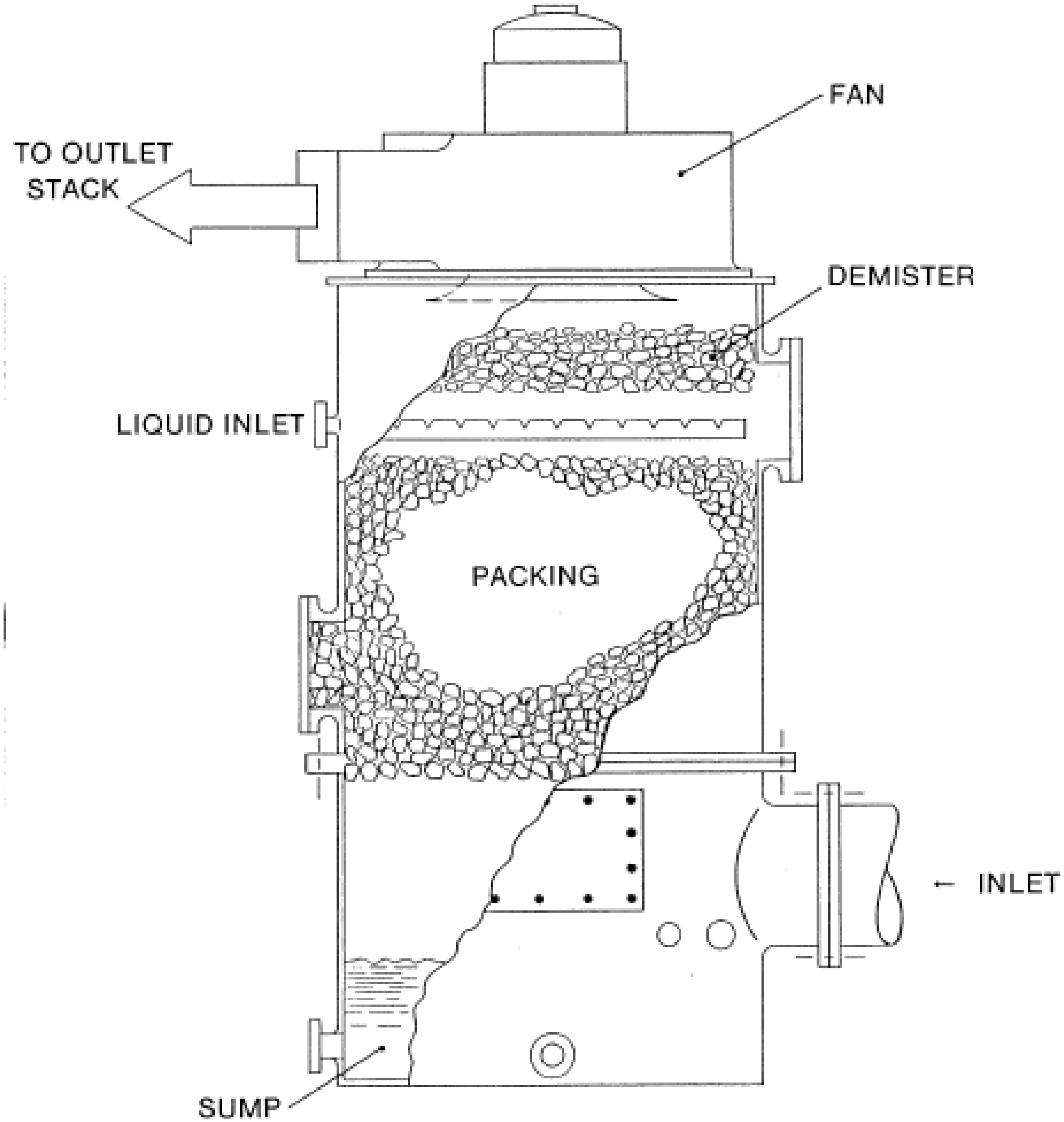

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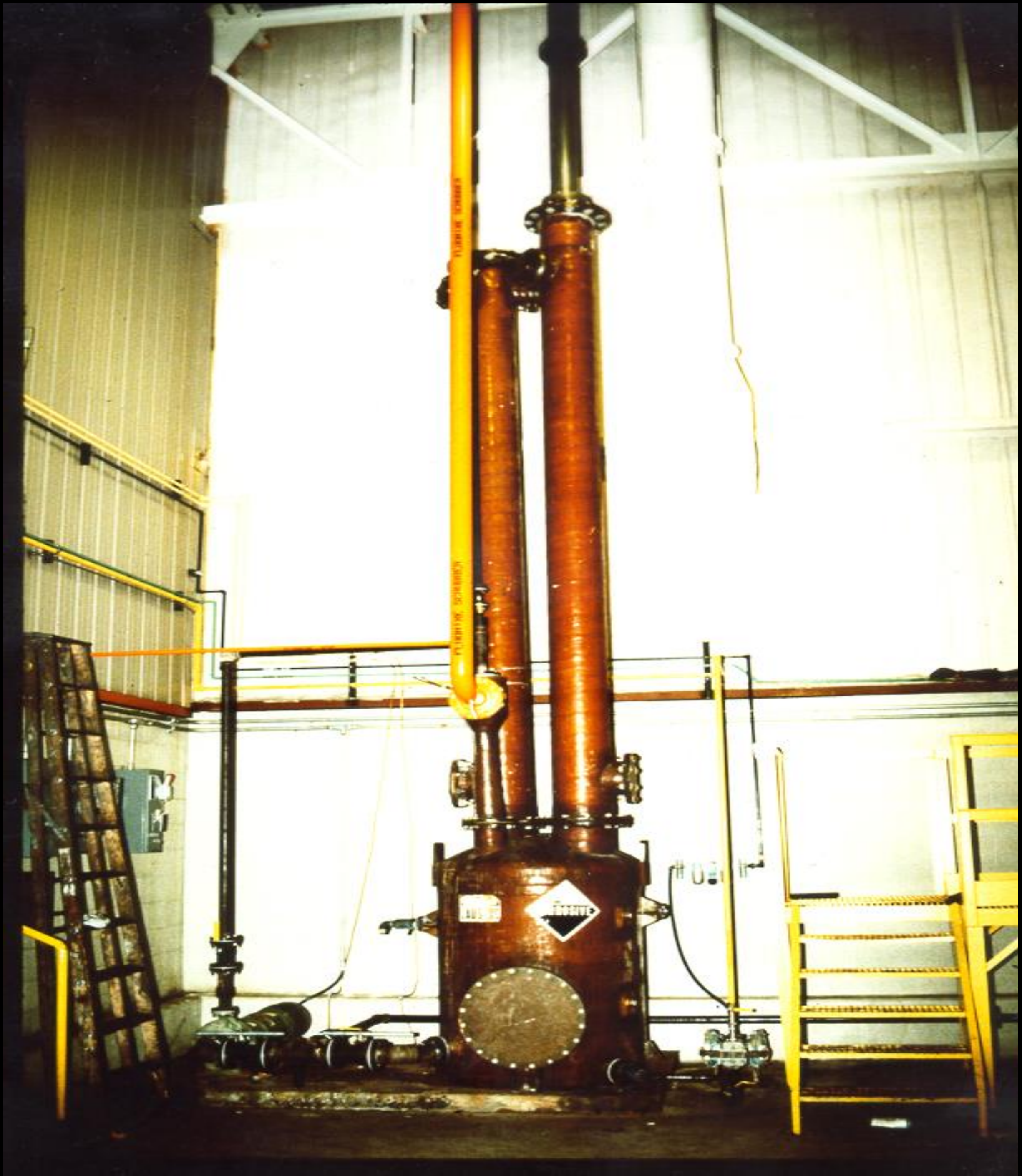

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Matheson Mobile Emeregncy Scrubber Apparatus (MESA)

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ER Scrubbing of Gases Overview

- Field Scrubbing of Specialty Gases during an Emergency sometimes are conducted under less than ideal conditions and under public scrutiny.
- Scrubbing is the deliberate Chemical Reaction of the gas into a form that is easily contained, less reactive and less toxic. To maximize efficiency very strong chemical solutions have been selected. As a result, proper precautions and PPE must be followed.
- The ER Scrubbers try to emulate the function of very large facility scrubbers in a compact, portable design. To do this, we sacrifice system flow rates. This is noticeable with the gases that are difficult to scrub such as Arsine, which has low solubility and low TLV’s.
- The primary scrubbing systems are the Bubbler and Portable Scrubber. Both rely on physical absorption followed by chemical reaction. The Bubbler is a wet system while the Portable Scrubber is a dry system.

ER Scrubbing of Gases Safety

- All the reactions are exothermic, releasing considerable heat. This will affect the flow rates into the system.
- Charcoal based media (e.g. FCA Charcoal) is no longer used due to flammability. Ignitions have occurred in the Portable Scrubber
- Some gases are highly soluble in water (Hydrogen Chloride, Ammonia) and could potentially suckback the scrubbing solution into the cylinder causing a violent reaction or explosion.
- The scrubbing solutions are strong acids, bases or oxidizers and must be handled with appropriate PPE.
- The scrubbing solutions also have high solution heats. The diluting must be done carefully and only pour the concentrated solution into water not water into concentrated solution!
- Some reaction products can also be hazardous; i.e., hydrogen is flammable and sodium fluoride is highly toxic.
- Liquefied gases are never to be introduced as liquids into the scrubbers. without proper guidance.

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ER Scrubbing of Gases Operational Notes

- Rapid discharge of gas could subcool contents of a liquefied gas cylinder.
- Moisture or the scrubbing solution can form solids, plugging the system; i.e., Boron Trichloride.
- Gas could have polymerized in the cylinder; i.e., Ethylene Oxide.
- Valves can be plugged with polymer or rust.
- The solid scrubbing materials could require some residual moisture for reaction.
- At 0 psig, the cylinder is not empty. Successive fill and venting with and inert gas is required to dilute the gas and discharge it from the cylinder.
- Many gases, such as H_2S and Amines, have an odor threshold at ppb levels and will be a nuisance rather than a safety problem.

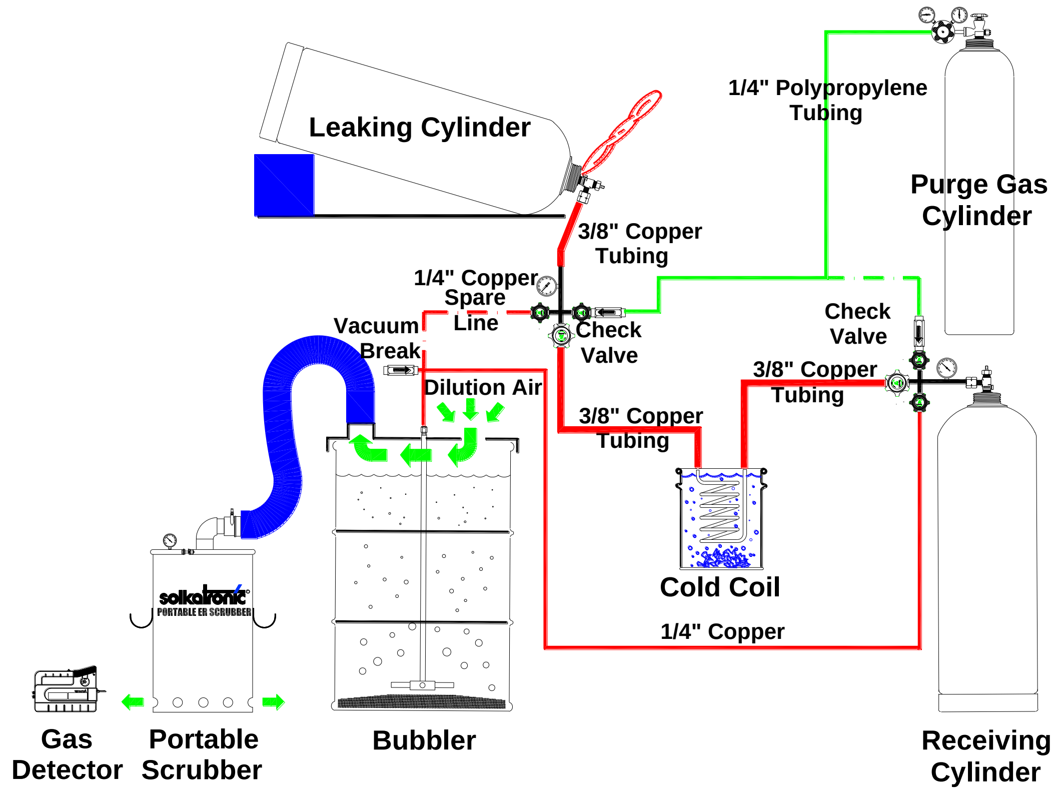
ER Scrubbing of Gases
Wet Scrubbing

- Wet scrubbing efficiency is largely a function of the gas solubility in that solution. Even if there is a fast reaction, if the gas cannot diffuse into the solution, it will not be scrubbed. In some rare cases the reaction rate constant is high enough that this becomes insignificant. The primary ER tool is the Bubbler
- Effective scrubbing is defined by the system mass transfer and reaction rate
- Gas mass transfer will be the critical factor. All of the reaction solutions listed have very fast reactions
- The hotter the solution, the faster the reaction rate however this is not critical since it is already fast
- The hotter solution however lowers the solubility of the gases therefore lowering the mass transfer. Cooling of the solution is critical.

ER Scrubbing of Gases
Typical Setup

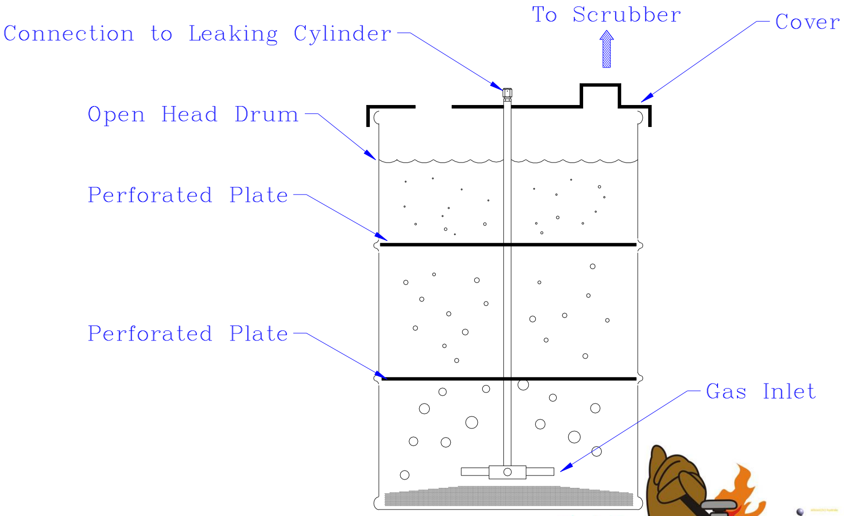
For ER the Bubbler and Portable Scrubber is setup to support the venting and purging of residue gas remaining in the leaking cylinder after a Cold Coil or Cascade.

In some cases, the team may elect to dispose of the entire contents of the leaking cylinder through the scrubber rather than transfer the product

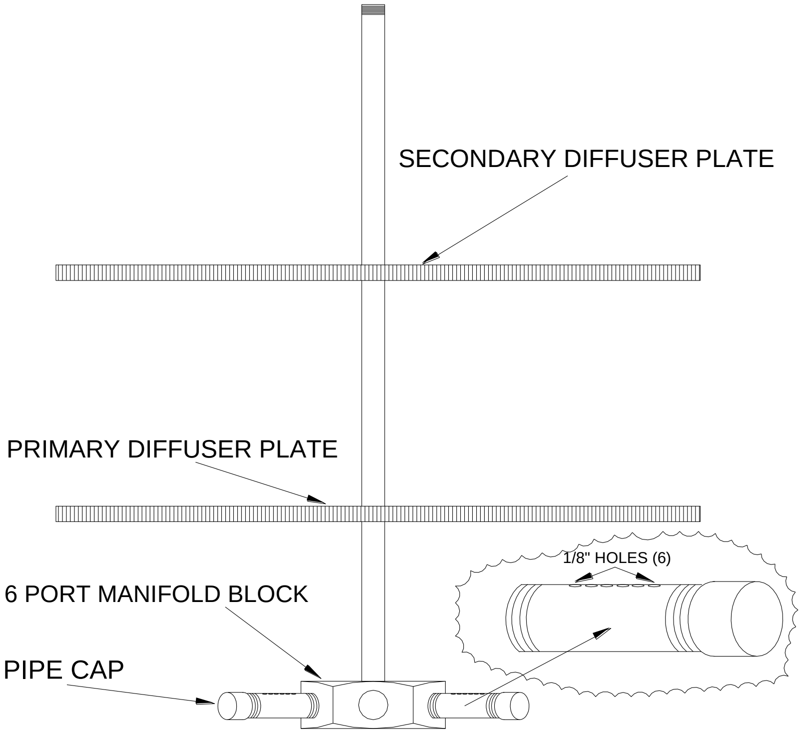


Bubbler

- Crude Scrubbing Unit to knock out the bulk of the problem gas
- Open Head 55 Gal Drum
- Gas Distribution Assembly With 2 Perforated Plates To Enhance Mass Transfer
- Premeasured Chemical Reactants
- Addition Of Ice To Cool Solution
- Cover To Exhaust Into Portable Scrubber to polish the exhaust



Bubbler



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Bubbler Dispersion

ER Scrubbing of Gases Theory

Bubbles

Gas bubble size is critical for efficiency. A bubble ½ the dia of another has only 12.5% of the volume and 25% of the surface area. This results in a bubble with 2 times the mass to volume ratio which helps mass transfer.

The gas in the bubble is static, limited mixing occurs and boundary layers are created. The center will be pure unreacted gas

The diffuser in the Bubbler breaks the gas into smaller bubbles and spreads it across the cross section of the Bubbler

The perforated plates breaks any large bubbles and redistributes the bubbles. Also helps to mix the gas inside the bubble

Ice on top helps to breakup the bubbles

Gas flow too fast into the liquid will create larger bubbles as they are released from the sparger or combine with each other

Residence time is the time it takes for the bubble to travel to the top. The longer the time, the more efficient the scrubbing.

An increase in the volume of the bubble increases the buoyancy. Diffusers and spargers are used to break the gas flow

Higher bouyancy decreases the residence time since it floats upward quicker.

The purge gas used during cylinder purging will typically make a bubble more bouyant and will not be solubilized.

ER Scrubbing of Gases
Bubbler/Portable Scrubber Combinations

Bubbler with Straight Tube

Examples: Trichlorosilane, Dichlorosilane, Boron Trichloride, Silicon Tetrachloride

Water soluble/reactive gases which form solids as by products must use a open inlet into the Bubbler to minimize plugging. This system must be capable of being physically cleaned.

Bubbler with Portable Scrubber

Examples: Chlorine, Hydrogen Sulfide

Less soluble gases may require secondary scrubbing. The reaction rate is fast and if the sparging/diffusion is good enough, the Bubbler will be sufficient. Good steady control of the flow rate in will also eliminate the need for secondary scrubbing

Bubbler with Sparger

Examples: Ammonia, Hydrogen Fluoride, Hydrogen Chloride, Hydrogen Bromide

Water soluble gases do not require secondary scrubbing. Hydrogen Chloride and Ammonia are so soluble that no bubbles float to the top. You only hear the bubbler rattling or rumbling. Mass transfer is very quick at the gas/liquid interface (Bubble surface) The bubble gets smaller as it rises. To increase the overall flow rate, a sparger or diffuser is used

Bubbler with Portable Scrubber

Examples: Arsine, Germane, Hydrogen Selenide, Phosphine

Low solublility gases which also have a low TLV's must have secondary scrubbing. Many of these are also Flammable and their byproducts are Flammable

Trichlorosilane

- **Alkaline conc is critical. When it is close to pH 7, alot of foaming**

Suckback

Disposing of highly soluble gases this can occur when the flow is stopped. Very dangerous

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Silicon Tetrachloride

- Liquid phase disposal of $SiCl_4$ into the Bubbler filled with KOH. As expected the solution got very hot during the reaction and had a gel like consistency. Very thick.
- When it cooled overnight the solids precipitated out
- Chlorosilanes are so water reactive that no bubblers come up from the Bubbler even when we introduced liquid through just a ½" pipe opening in the Bubbler.

Bubbler Test Results

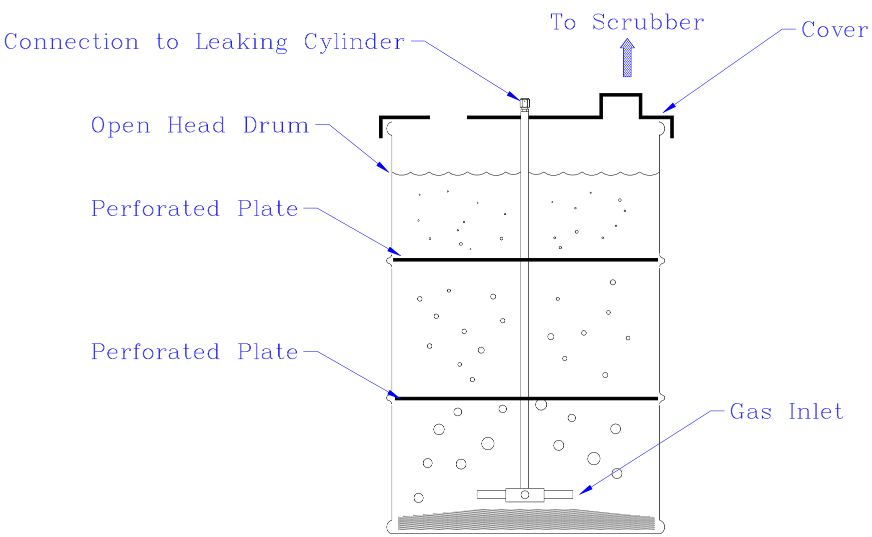
- Tests have shown that the Bubbler can react 0.5 lbs of HCl per min without any detectable emission in a 1% NaOH solution
- Flow is at regulator setting of 20-25 psig and produces a low roar with no bubbles at surface
- Heat gain is estimated at 1460 BTU/lb HCl
- For a 60 lb cylinder 60 lbs of NaOH and 83 lbs of Ice will be required
- The flow rate will be limited to the amount of heat transferred into the cylinder for the last half

Whoops! Shouldn't have used that all in one Bleach!

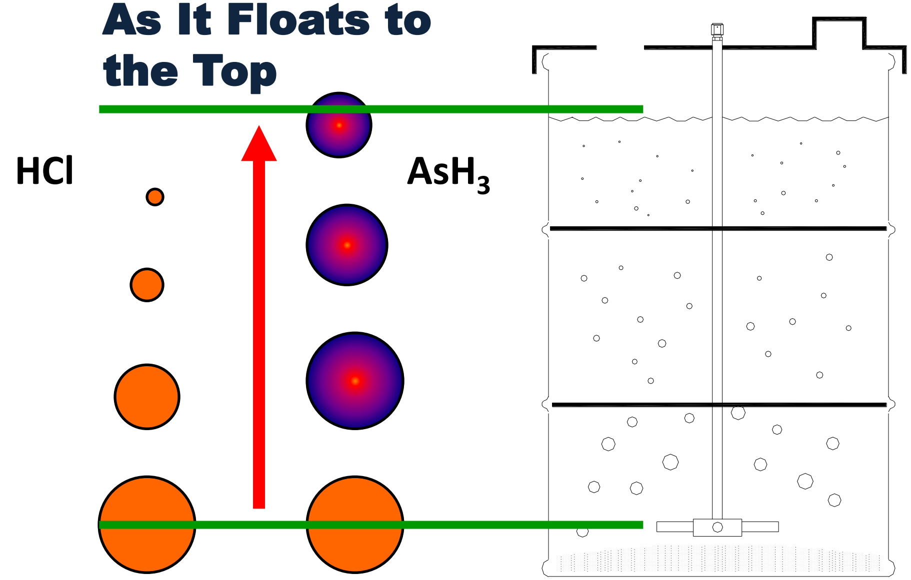
ER Scrubbing of Gases Liquid

The Bubbler is a open head 55 gal (210 liter) metal drum with a removable metal gas inlet inserted

Solutions and reactions are summarized in the following slides



Life of a Bubble As It Floats to the Top



The HCl bubble will steadily decrease until it disappears while the AsH_3 bubble will only have surface reaction

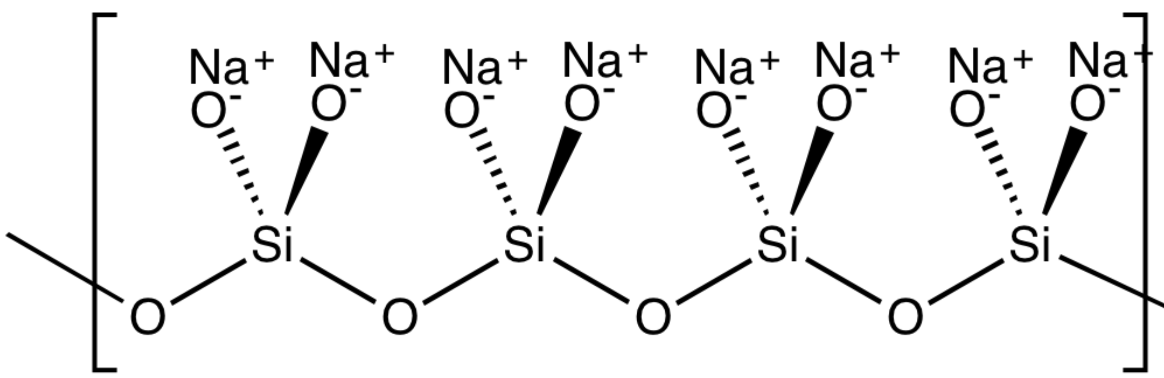
Emergency Scrubbing
Sodium Hydroxide Solution

- ***Boron Trichloride*** (1.7 lbs BCl_3 /lb NaOH)
  $BCl_3 + 3H_2O \longrightarrow H_2BO_3 + 3\,HCl$
  $H_2BO_3 + 3HCl + 5NaOH \longrightarrow Na_2B_4O_7$ ◆ $10H_2O + NaCl$
  or $NaBO_2$ ◆ $4H_2O$ (Borax)
  Boron Trichloride + Sodium Hydroxide ⟶ Sodium Borates + Sodium Chloride
- ***Chlorine*** (1.13 lbs Cl_2 /lb NaOH)
  $Cl_2 + 2\,NaOH \longrightarrow NaOCl + NaCl + H_2O$
  Chlorine + Sodium Hydroxide ⟶ Sodium Hypochlorite (bleach) + Sodium Chloride (salt) + Water
- ***Dichlorosilane*** (1.27 lbs DCS/lb NaOH)
  $SiH_2Cl_2 + 2\,NaOH \longrightarrow SiH_2O + 2NaCl + H_2O$
  $SiH_2O + O_2 \longrightarrow SiO_2 + H_2O$
  Dichlorosilane + Sodium Hydroxide + Oxygen ⟶ Silicon Dioxide (sand) + Sodium Chloride (salt) + Water

Note: Some of the intermediate Siloxanes may contain trapped Hydrogen and are highly flammable.

TCS Reaction

The reaction of TCS is vigorous in a NaOH solution in the absence of air will form a soup of sodium silicates $(Na_2O)x(SiO_2)_y$ typically $Na_2Si\ O_3$, Na_4SiO_4, $Na_6Si_2O_7$ that are stable in neutral and alkaline solutions. In acidic solutions, the silicate ions react with hydrogen ions to form silicic acids, which tend to decompose into hydrated silicon dioxide gel. If heated to drive off the water it forms silica gel.



Emergency Scrubbing
Sodium Hydroxide Solution

- ***Hydrogen Bromide*** (2.02 lbs. HBr/lb NaOH)

  $HBr + NaOH \longrightarrow NaBr + H_2O$

  Hydrogen Bromide + Sodium Hydroxide → odium Bromide + Water

- ***Hydrogen Chloride*** (1.1 lbs. HCl/lb NaOH)

  $HCl + NaOH \longrightarrow NaCl + H_2O$

  Hydrogen Chloride + Sodium Hydroxide → Sodium Chloride + Water

- ***Hydrogen Selenide*** (1.01 lbs H_2Se/lb NaOH)

  $H_2Se + NaOH \longrightarrow NaHSe + H_2O$ & $NaHSe + NaOH \longrightarrow Na_2HSe + H_2O$

  $Na_2HSe + 4\ NaOCl \longrightarrow Na_2SeO_4 + 4NaCl$

  Overall

  $H_2Se + 2\ NaOH + 4NaOCl \longrightarrow Na_2SeO_4 + 4NaCl + 2\ H_2O$

  Hydrogen Selenide+ Sodium Hydroxide + Sodium Hypochlorite (bleach) → Sodium Selenate + Sodium Chloride (salt) + Water

Emergency Scrubbing
Calcium Hydroxide Solution

Calcium Hydroxide is the preferred scrubbing solution for the Fluoride Gases since it doesn't generate toxic Sodium Fluoride, reacts to a solid Calcium Fluoride. In addition, contact times of <1 sec and Sodium Hydroxide concentrations of <2 wt% will generate highly toxic and reactive Oxygen Difluoride. gas

- ***Boron Trifluoride*** (0.61 lbs. BF_3/lb Ca $(OH)_2$)

  $2BF_3 + 3Ca(OH)_2 \longrightarrow 3CaF_2 + B_2O_3$

  Boron Trifluoride + Calcium Hydroxide $\longrightarrow$ Calcium Fluoride + Boric Oxide (insoluble)

- ***Hydrogen Fluoride*** (0.54 lbs. HF/lb $Ca(OH)_2$)

  $2HF + Ca(OH)_2 \longrightarrow CaF_2 + 2H_2O$

  Hydrogen Fluoride + Calcium Hydroxide $\longrightarrow$ Calcium Fluoride + Water

- ***Tungsten Hexafluoride*** (4.02 lbs. WF_6/lb $Ca(OH)_2$)

  $WF_6 + Ca(OH)_2 \longrightarrow 3CaF_2 + WO_2$

  Tungsten Hexafluoride + Calcium Hydroxide $\longrightarrow$ Calcium Fluoride + Tungsten Oxides

- ***Silicon Tetrafluoride*** (0.70 lbs. SiF_4/lb $Ca(OH)_2$)

  $SiF_4 + 2Ca(OH)_2 \longrightarrow 2CaF_2 + SiH_2O$

  Silicon Tetrafluoride + Calcium Hydroxide $\longrightarrow$ Calcium Fluoride + Siloxane

Acid Gas Scrubbing
lb Scrubbing Media/lb Gas

	Sodium Hydroxide	Potassium Hydroxide	Calcium Hydroxide	Baking Soda	Calcium Carbonate
Boron Trichloride	1.8	2.4	2.6	3.6	3.5
Boron Trifluoride	1.7	2.5 [1]	1.7	3.7	2.2
Bromine Trifluoride	1.2	1.7 [1]	1.1	2.5	1.5
Chlorine	1.2	1.6	1.1	2.4	1.5
Dichlorosilane	0.8	1.2	0.8	1.7	1.0
Fluorine Mixtures [3]	2.2	3.0	2.0	4.5	2.7
Hydrogen Bromide	0.5	0.7	0.5	1.1	0.7
Hydrogen Chloride	1.1	1.6	1.1	2.3	1.4
Hydrogen Fluoride	2.0	2.8 [1]	1.9	4.2	2.5

Acid Gas Scrubbing
lb Scrubbing Media/lb Gas

	Sodium Hydroxide	Potassium Hydroxide	Calcium Hydroxide	Baking Soda	Calcium Carbonate
Hydrogen Selenide [2]	1.0 (plus 8.5 gal. of bleach/lb)	1.4 (plus 8.5 gal. of bleach/lb)	1.0 (plus 8.5 gal. of bleach/lb)	2.1 (plus 8.5 gal. of bleach/lb)	1.3 (plus 8.5 gal. of bleach/lb)
Hydrogen Sulfide [2]	2.4 (plus 20 gal of bleach/ lb.)	3.3 (plus 20 gal of bleach/ lb.)	2.2 (plus 20 gal of bleach/ lb.)	5.0 (plus 20 gal of bleach/ lb.)	3.0 (plus 20 gal of bleach/ lb.)
Silicon Tetrachloride	1.0	1.4	0.9	2.0	1.2
Silicon Tetrafluoride	1.6	2.2 [1]	1.5	3.3	2.0
Sulfur Dioxide	1.3	1.8	1.2	2.7	1.6
Sulfur Tetrafluoride	2.3	3.2 [1]	2.1	4.7	2.8
Trichlorosilan e	0.9	1.3	0.9	1.9	1.2
Tungsten Hexafluoride	0.9	1.2 [1]	0.8	1.7	1.1

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Acid Gas Scrubbing Notes:

- Potassium Hydroxide is the preferred scrubbing solution for the fluorides since it does not generate slightly toxic sodium fluoride. Instead it generates potassium fluoride. Sodium fluoride and calcium fluoride will also precipitate out of solution that may cause plugging.
- These gases need to use bleach as their scrubbing solution to help oxidize/neutralize the disposal gas.
- Need to figure out fluorine mass of mixture.

Emergency Scrubbing Phosphoric Acid Solution

While Ammonia is highly soluble in water (33wt%), it has a high equilibrium pressure. At 0.01 wt% in water, the vapor above the liquid has a concentration of 100 ppm in Air.

Ammonia **(0.70 lbs NH_3/lb H_3PO_4)**

$$4NH_3 + H_3PO_4 + 2H_2O \longrightarrow (NH_4)H_2PO_4 + (NH_4)_2HPO_4$$

The Ammonium Phosphates are primarily mono-Ammonium Phosphate and Diammonium Phosphate, both of which are highly soluble and stable (22.7 gms/cc and 37.5cc respectively)

NH_3 Heat of Hydrolysis

100 lbs NH_3

55 gal (210 liter) drum of water @ 70ºF

Reaction heat of liquid ammonia dissolving into water = -348 BTU/lb Specific Heat of 10% solution = 1.0 Btu/lbºF @ 60ºF

144 BTU to melt 1 lb of ice

1 gal of water = 8.35 lbs

Basis:

While NH3 has a very high solubility 89% @ 32ºF for ER only 10% will be used

Calculation:

100 lbs of NH3 requires 1,000 lbs of water

55 gal of water = 459 lbs

Therefore 348 BTU/lb x 1,000 lbs = 348,000 BTU

348,000 BTU / 144 BTU = 2,416 lbs of ice

Alkaline Gas Scrubbing lb Scrubbing Media/lb Gas

	Hydrochloric Acid	Sulfuric Acid	Acetic Acid	Phosphoric Acid
Ammonia	2.2	2.9	3.5	1.5
Dimethylamine	0.8	1.1	1.3	1.5
Monomethylamine	1.2	1.6	1.9	2.1
Trimethylamine	0.6	0.9	1.0	1.1

Weights for the neutralizer are based on 100% acid concentration. For diluted solutions of acid mixtures, use the following equation: Amount of neutralizer in the chart / % of acid solution (100) = amount of mixture needed by weight

Emergency Scrubbing
Potassium Permanganate Solution

Maximum solubility is 4 wt% at 70ºF. Purple in color with change to brown. Also generates insoluble Manganese Oxides which settles out as a precipitate.

- ***Arsine*** **(0.25 lbs AsH_3/lb $KMnO_4$)**

  $AsH_3 + 2KMnO_4 \longrightarrow MnO_2 + K_3AsO_4 + H_2O$

  Manganese Oxide, Potassium Arsenate, Water

- ***Diborane*** **(0.18 lbs B_2H_6/lb $KMnO_4$)**

  $B_2H_6 + KMnO_4 \longrightarrow MnO_2 + K_2B_2O_4 + H_2O$

  Manganese Oxides, Potassium Metaborate, Water

Caution:

High concentration mixtures and pure may be scrubbed inefficiently creating high concentrations above the scrubbing fluid which can react explosively

- ***Germane*** **(0.48 lbs. GeH_4/lb $KMnO_4$)**

  $2GeH_4 + 2KMnO_4 \longrightarrow MnO_2 + K_2Ge_2O_3 + 2H_2O$

  K_2GeO_3

  $K_2Ge_4O_9$

  Manganese Oxides, Potassium Germanates, Water

Emergency Scrubbing
Potassium Permanganate Solution

- ***Phosphine*** (0.11 lbs PH_3/lb $KMnO_4$)

  $PH_3 + 2KMnO_4 \longrightarrow MnO_2 + K_2HPO_4 + H_2O$

  KH_2PO_2

  K_3PO_4

  KH_2PO_4

  Manganese Oxide, Potassium Phosphites or Phosphates

Caution:

High concentration mixtures and pure may be scrubbed inefficiently creating high concentrations above the scrubbing fluid which can react explosively

Hydride Gas Scrubbing
lb Scrubbing Media/lb Gas

	Potassium Permanganate [1]	Sodium Hypochlorite
Arsine	6.1	3.9 (8.9 gal chlorox) [2]
Diborane	11.5	16.2 (36.9 gal chlorox)
Germane	2.1	2.0 (4.6 gal chlorox)
Hydrogen Selenide	3.9	3.7 (8.4 gal chlorox)
Nitric Oxide	5.3	3.7 (8.4 gal chlorox)
Phosphine [3]	12.4	6.6 (15 gal chlorox)

1) Potassium Permanganate is purple in color and it changes to brown in reaction with a hydride.
Potassium Permanganate will stain the body and equipment; it can be removed with a solution of acetic acid and hydrogen peroxide.
2) Chlorox bleach has 5.24% sodium hypochlorite which equates to 0.44 lbs/gal.
3) Chlorox bleach has a pH of 10.5. It needs to be lowered to a pH 9.0 to increase the reaction rate.

Emergency Scrubbing Water

Silane is a pyrophoric gas which can explode with violent force when confined. No chemicals reactants shall be used and the cover on the Bubbler shall be removed

- ***Silane***

  $SiH_4 + 2O_2 \longrightarrow SiO_2$

- ***Disilane***

  $Si_2H_4 + 31/20_2 \longrightarrow 2SiO_2 + 3H_2O$

- ***Phosphine/Silane Mixture***

  $2PH_3 + 4O_2 \longrightarrow P_2O_3 + 3H_2O$

  $SiH_4 + 2O_2 \longrightarrow SiO_2 + 2H_2O$

Note: Exhaust must go to scrubber for removal of trace amounts of Phosphine.

Potassium Permanganate

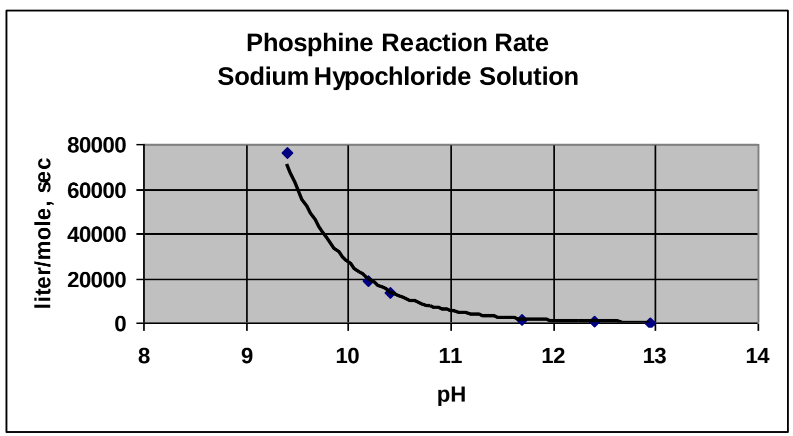
- $KMnO_4$
- Solubility in water up to 6.51 wt% @ 20^{0}C (68^{0}F) 2.78% @ 0^{0}C (32^{0}F)
- Will stain body and equipment, remove with solution of Acetic acid and Hydrogen Peroxide
- Is not corrosive to carbon steel if alkaline
- Normally deep purple in color. Will turn dark brown with Hydride reaction. Creates solid precipitate Manganese Oxide
- Improved reaction via addition of 0.1 wt% Sodium Tetraborate (Borax). Preferred pH of 8-9.
- Addition of 3.5 lbs of Ferric Sulfate (($Fe_3(SO_2)_4$ $6H_2O$) will precipitate out 1 lb of Arsenic

Scrubbing Solution
Sodium Hypochlorite

- **Chlorox Bleach has 5.24% Sodium Hypochlorite. 0.44 lbs/gal.**
- **When open to air becomes sodium bicarbonate, as carbon dioxide in air replaces the chlorine**
- **Has pH of 10.5 need to lower to 9.0 to increase reaction rate. Typically an addition of 3.6 wt% of HCl to 5% solution will lower.**
- **Oxidation is primarily by Hypochlorous acid (HOCl) which exists in equilibrium with OCl^-. At pH of 7.3 each is 50 mole%.**

$$2NaOCl + 2H2O \Leftrightarrow NaOH + HOCl + OCl^- + H^+$$

- **Reaction better for Phosphine due to higher solubility which improves mass transfer**



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Acid Gas Scrubbing Notes:

1. **Potassium Hydroxide is the preferred scrubbing solution for the fluorides since it does not generate slightly toxic sodium fluoride. Instead it generates potassium fluoride. Sodium fluoride and calcium fluoride will also precipitate out of solution that may cause plugging.**
2. **These gases need to use bleach as their scrubbing solution to help oxidize/neutralize the disposal gas.**
3. **Need to figure out fluorine mass of mixture.**

Fluorine Wet Scrubbing

The nature and concentration of by-products formed by the reaction between water and F_2 depend on a combination of competing reactions and physical conditions. Reported by-products of this reaction include HF, O_2, and H_2O_2, along with small concentrations of OF_2. Fundamental studies have identified HOF as a reaction intermediate3 and determined the mechanisms causing the formation of oxygen difluoride,4 which is a stable, colorless, poisonous gas that can produce high yields under any of the following three exceptional conditions.

Adding electric energy (electrolysis) to an aqueous HF solution:5

$2\ HF(aq) + 6\ H_2O(l)$ — $OF_2(g) + O_3(g) + 7\ H_2(g)$

Passing fluorine through an aqueous alkaline solution (60% maximum yield using 0.5 to 1-molar alkali concentrations):2

$2\ F_2(g) + 2\ H\text{-}(aq)$ — $OF_2(g) + 2\ F\text{-}(aq) + 7\ H_2O(l)$

Passing F2 over cooled ice.4 (Reactions took place at the surface of ice and did not occur in liquid water):

$F_2(g) + H_2O(s)$ — $HF(g) + OF_2(g)$

Oxygen difluoride was also reported to be formed when fluorine gas was passed through 60% $HClO_4$, H_5IO_6, and hydrated alkali fluorides. Under normal scrubber operating conditions, without the use of caustic injection, the concentration of OF_2 generated from the reaction of F_2 and water was insignificant.

Potassium Hydroxide

- Potassium hydroxide bubbler

  Must keep caustic above 5% concentration to avoid forming HOF (Hypofluorous acid, oxidation of water) (capriciously explosive) and OF_2 (very toxic gas)

  KOH is best- KF is most soluble product, avoids scrubber plugging
- Charcoal burner

  Small units have the same issues as the caustic scrubber

  Require special training

  Harder to acquire

	Sodium Hydroxide	Potassium Hydroxide	Calcium Hydroxide	Baking Soda
Fluorine/F2 Mixes	2.2	3.0	2.0	N/A
Boron Trifluoride	1.7	2.5[1]	1.7	3.7
Bromine Trifluoride	1.2	1.7[1]	1.1	2.5
Chlorine Trifluoride	1.8	2.4	1.6	3.7
Hydrogen Fluoride	2.0	2.8	1.9	4.2
Silicon Tetrafluoride	1.6	2.2	1.5	3.3
Sulfur Tetrafluoride	2.3	3.2	2.1	4.7
Tungsten Hexafluoride	0.9	1.2	0.8	1.7

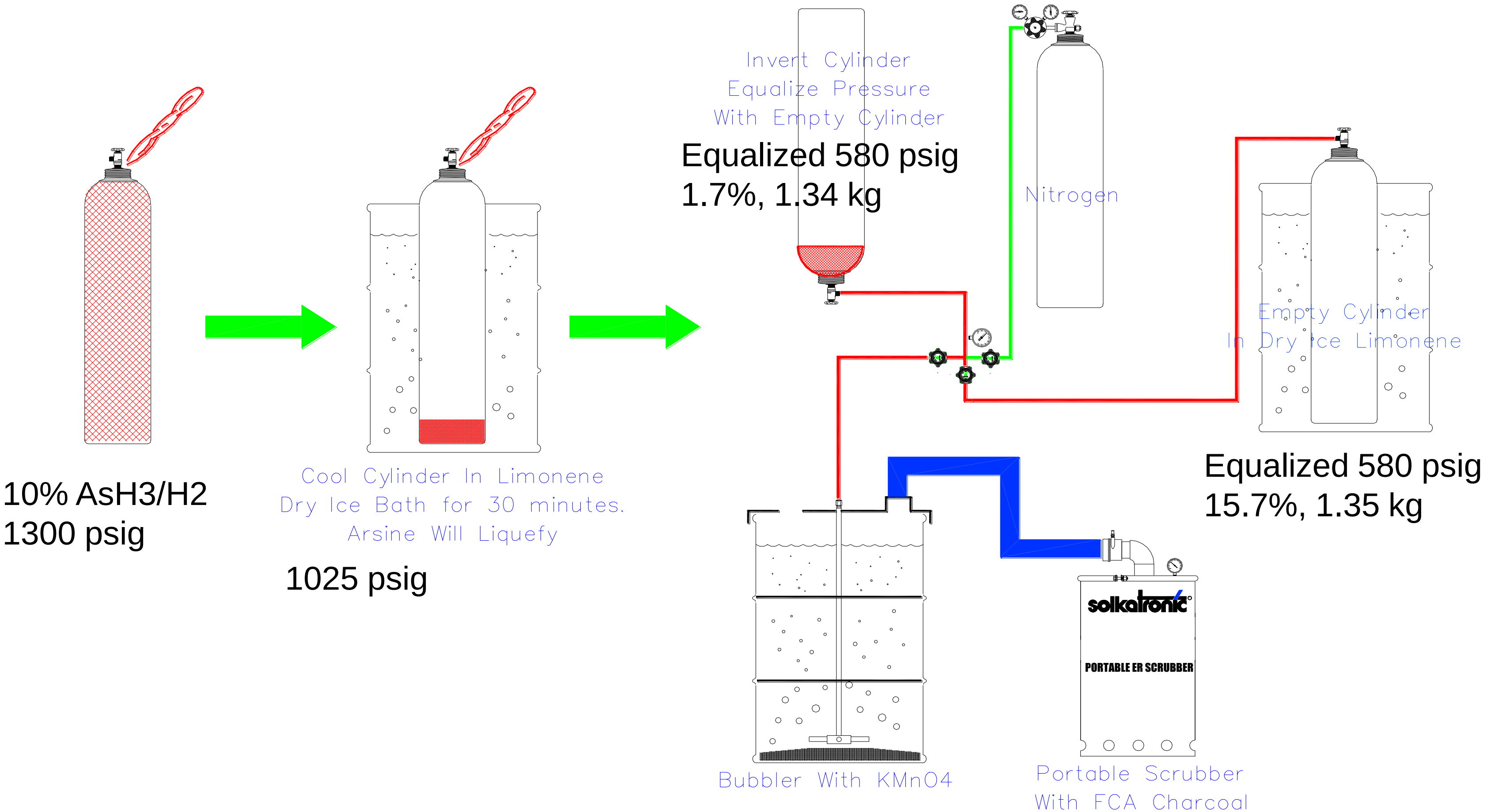
Nitrogen Oxides

- Nitrogen Dioxide is scrubbed very effectively by Sodium Hypochlorite, while Nitric Oxide is not. Sodium Hydroxide does not work as evidenced by the brown fumes.
- Nitric Oxide at 15 psig or less can be converted quickly into Nitrogen Dioxide by pressurizing with Air to 45 psig. Heat increase is 20 C. For safety reasons this is the maximum pressure of Nitric Oxide to treat. Any pressures higher than this can be handled by cascading into empty cylinders first. The system must be O_2 cleaned.

ER Disposal of Arsine Mixture

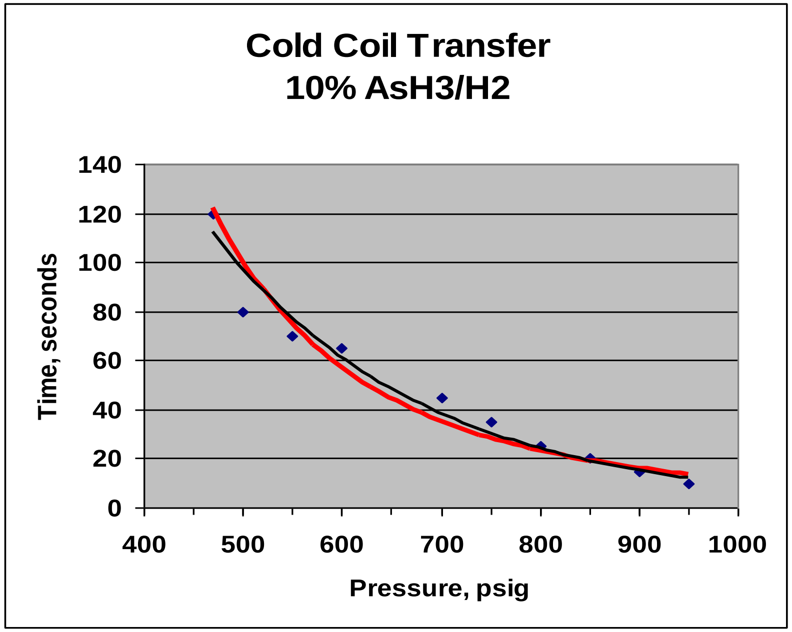
- High concentration mixtures >5% of Arsine can be liquefied at low temperatures and the liquid transferred into an empty cylinder and the gas pressure equalized. This will concentrate more of the Arsine into the empty cylinder and the leaking cylinder would have a much lower concentration to dispose of.
- For example the transfer done in Jan 2002 concentrated the Arsine into the empty cylinder. This reduced the concentration in the leaking cylinder from 10% to 1.7%. The lower concentration will be easier to dispose.
- This method only works with liquefied gases and high pressures

Arsine Mixture Disposal, Jan 18, 2002



Transfer Information

Pressure, psig	Time, sec
950	10
900	15
850	20
800	25
750	35
700	45
600	65
550	70
500	80



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Small Fluorine Scrubber Data
Note: Not for Acid Gases

- Aluminum Oxide scrubber media will react 118% by wt of F_2 in the following reaction

$$Al_2O_3 + 3\,F_2 \;\text{--->}\; 2\,AlF_3\,\text{(solid)} + 1.5\,O_2$$

- The Fluorine Gas Scrubber contains 5.5 lbs (2.5 kgs) of Aluminum Oxide.
- It will react > 5 lbs of F_2 (1398 liters)
- At a leak rate of 50 cc/min this will last 139,832 minutes (97 days) for a 20% Mixture
- A full 40’ tube contains 220 lbs of F_2 and cannot be fully disposed of using these scrubbers.

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Fluorine Solid Scrubber

- Reaction: Al_2O_3 + 3 F_2 ---> 2 AlF_3 (solid) + 1.5 O_2

- For 100% Al_2O_3 reaction, 1.118 kg of F_2 would react or 0.89 kg Al_2O_3 per kg F_2. We have never measured the efficiency of the reaction, particularly relative to breakthrough of some low concentration of F_2.
- Packed bulk density of Alcoa F-200 alumina 7x14 mesh size = 0.77 kg / liter.
- Thus 20.2 / 0.77 = 26.2 L x 0.2642 gal/L = 6.9 gal vessel (2.8 gal for 25% efficiency).
- The heat generated from the reaction is 107 kcal / mole of F_2 or 2,816 kcal / kg of F_2 or 11,174 BTU / kg of F_2.

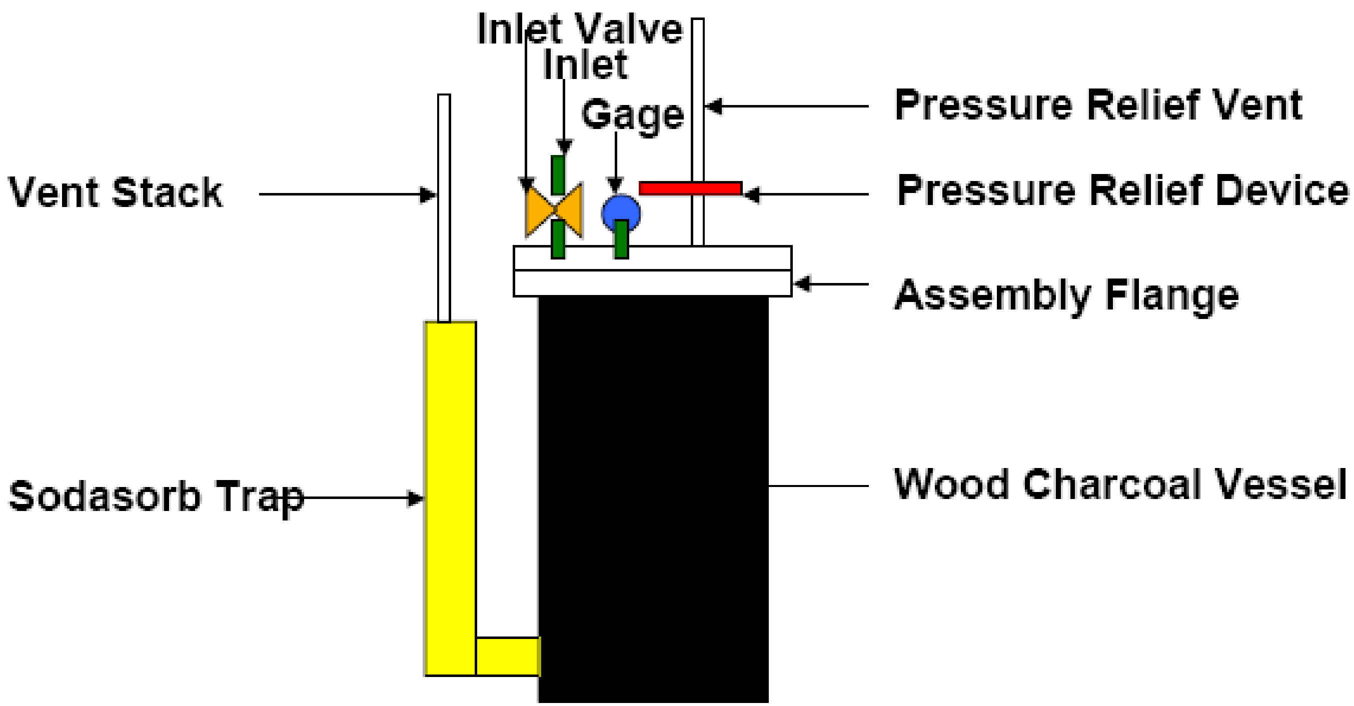
Small Acid Scrubber Data
Note: Not for Fluorine

- Puracarb acid scrubber media will react 2-8 wt% HCl
- Puracarb contains up to 10% activated carbon which can react violently with Fluorine under certain conditions
- The Acid Gas Scrubber contains 3.92 lbs of Puracarb.
- It will react 0.2 lbs of HCl (59.67 liters)
- At a leak rate of 50 cc/min this will last 1193 minutes (19 hours)
- A full 40’ tube contains 3000 lbs of HCl and cannot be fully disposed of using these scrubbers.

Fluorine Disposal

- Disposal is via wood charcoal at the rate of 5.7 lbs. F_2 per lb. of charcoal to Carbon Tetrafluoride. A 6 ft.$_3$ barrel has been subjected to a flow rate of 0.5 lbs. – 21.1 lbs. per hour at concentrations of 6.5-100% F_2 . Concentration must be kept at a minimum of 6.5% and the reactor walls must be kept hot.
- Water reaction to O_2, HF, small amounts of O_3, H_2O_2, OF. It will burn with flame or without (uninhibited and inhibited). Violent explosions will occur when it shifts from inhibited to uninhibited and vice versa

Charcoal Burn Unit in Place of Liquid Scrubber



F_2 Scrubber

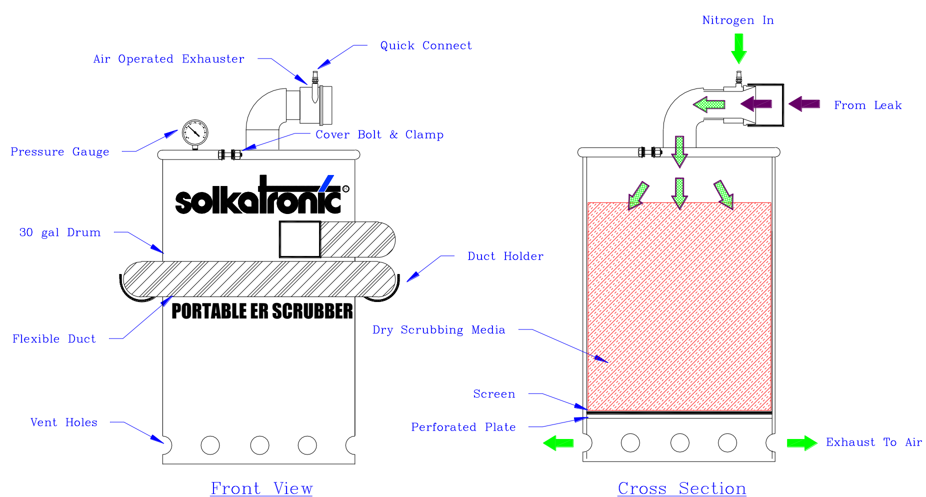
- Packed with natural charcoal without binders
- Concentration of F_2 must be > 6.5%
- Immersed in water bath
- Sodasorb trap at outlet

Portable ER Scrubber

- US Patent #5,482,536
- Powered by Nitrogen or Compressed Air
- Explosion Proof
- Exhaust flow rate can be varied
- Dry Scrubbing Media to Chemically React Hydride, Acid or Alkaline Gases.
- The Portable ER Scrubber contains enough dry media to effectively scrub a few pounds of the leaking gas. It is not designed to scrub the entire contents of a cylinder. A bubbler leak (10 cc per minute), for example, will require 10 days to release 1 pound of Arsine.

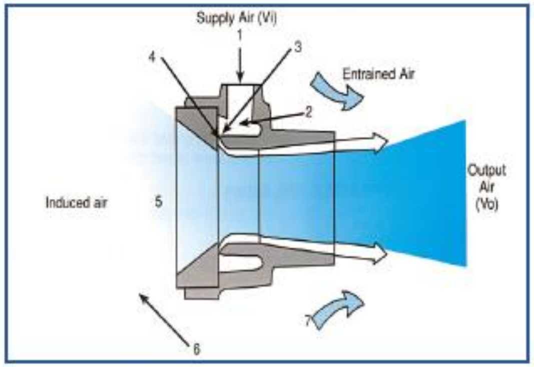
Portable ER Scrubber

- Designed to quick isolate and capture a gas leak from a cylinder or system
- It can be filled immediately prior to use with the appropriate scrubbing media.
- The leaking gas will be passed through the appropriate chemical media which will react/neutralize it



Portable ER Scrubber

- 2 sizes, standard (30 gallon) and large (55 gallon)
- Gas pressure can be supplied from a house Nitrogen or Compressed Air line, Nitrogen cylinders, dewars, etc. A high flow air compressor can also be used
- To save on air or nitrogen, use a pressure as low as possible that will still capture the leak
- Can be staged through the facility for immediate use



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Portable ER Scrubber

Note: Pressure Gauge is in inches of water and is used to determine whether the dry media has plugged during use

Pressure Gauge

Top Lid and Bolt

Nitrogen Quick Connect

Venturi Eductor

Scrubbing Media

- Hydride Gas Scrubbing (Purafil SP)
  - Arsine
  - Diborane
  - Diethyltelluride
  - Dimethylzinc
  - Germane
  - Hydrogen Selenide
  - Hydrogen Sulfide
  - Hydrogen Telluride
  - Phosphine
  - Note: Do not use for Silane or Disilane. Violent reaction can occur

- Acid Gas Scrubbing (Puracarb)
  - Boron Trichloride
  - Boron Trifluoride
  - Chlorine
  - Dichlorosilane
  - Hydrogen Bromide
  - Hydrogen Chloride
  - Hydrogen Fluoride
  - Silicon Tetrafluoride
  - Silicon Tetrachloride
  - Trichlorosilane
  - Tungsten Hexafluoride

Alkaline Gas Scrubbing (Puracarb AM)
  - Ammonia
  - Amines

Scrubbing Media from Purafil Corp.

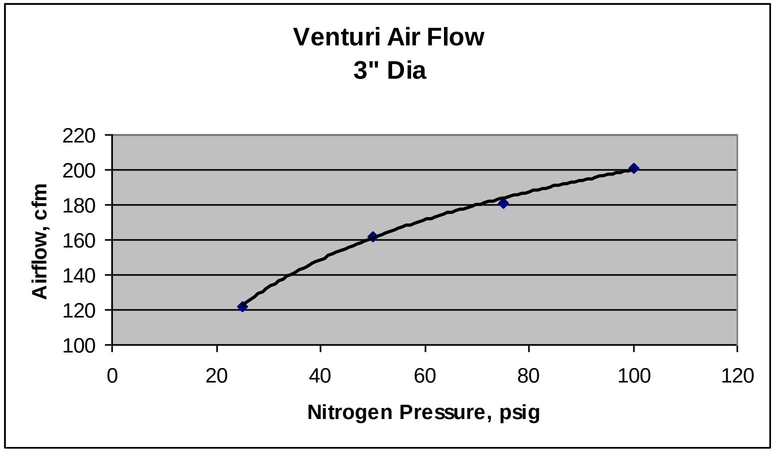
- Hydride Gas Scrubbing (Purafil SP)
  - Sodium permanganate impregnated alumina that will oxidize the metal hydride gases such as phosphine or diborane (1/8” pellets, 50 lbs/ft^3)
- Acid Gas Scrubbing (Puracarb)
  - Potassium carbonate (potash) impregnated mixture of activated charcoal and alumina pellets that will absorb and neutralize acid gases such as hydrogen chloride or chlorine (1/8” pellets, 45 lbs/ft^3)
- Alkaline Gas Scrubbing (Puracarb AM)
  - Phosphoric acid impregnated mixture of activated charcoal and alumina pellets that will absorb and neutralize alkaline gases such as ammonia or amines (1/8” pellets, 45 lbs/ft^3)

Scrubber Capacity

- Small Scrubber filled with 2 boxes of media (2 ft^3)
- Leak at 10 cc/min
  - Germane – 5 days
  - Hydrogen Chloride – 103 days
  - Ammonia – 237 days

Portable ER Scrubber

- For effective scrubbing, the dry media bed must not exceed a cross sectional velocity of 200 ft/min (61 m/min) . Purafil claims that their media is effective from 60-500 ft/min (18.3 – 152.4 m/min)
- The bed depth must be greater than 6”.(15.24 cm) A box of Purafil Media is approx 1 cubic foot in volume. It will fill the standard scrubber to a depth of 5 ½” (14 cm). The typical Mass Transfer Zone for a dry chemical reacting media is 3-4” (7.6 – 10.2 cm) and for good efficiency with gases like Arsine, two boxes should be used.
- The deeper the bed, the higher the pressure drop which will reduce the exhaust flow developed by the venturi.



Nitrogen or Air Supply

- A 49 liter (Size "A") cylinder of Nitrogen at 2400 psig will supply ~20 minutes of exhaust at 80 psig use pressure
- Extended use should be a dewar or house Nitrogen

Procedure

- Open the scrubber lid by removing the bolt and top lid.
- Remove any debris or spent media from the inside.
- Inspect the screen for any tears.
- Select the appropriate dry media and empty the contents on top of the screen. Note: appropriate PPE must be worn to protect from dust generated
- Gently level the dry media
- Reinstall the lid and tighten the bolt
- Connect the 3” dia flexible hose to the venturi eductor by sliding one end over the opening. Tighten the ring clamp to secure the duct.

Procedure

- Connect the regulator (CGA 580) to a cylinder of Nitrogen and back off the regulator by turning knob counterclockwise or connect to a N_2 or air supply..
- Open the Nitrogen cylinder valve and turn up the pressure on the regulator or open valve on the N_2 or air supply. This will start the exhaust flow in the flexible hose.
- Position the flexible duct opening by the leak point and secure it in place.
- Check to see if the exhaust flow is adequate by using a gas specific leak detector to sample the area around the duct opening
- Use the gas specific leak detector to also sample the outlet of the scrubber to insure that it is scrubbing effectively. Note: Some Hydride Leak Detectors are sensitive to Hydrogen and will give a false reading

Procedure

- If using high pressure N_2 cylinder periodically check the cylinder pressure. Change when it reaches 100 psig.
- With the leak now temporarily contained, the ER Team can proceed to bring in the appropriate ER Equipment such a Emergency Response Containment Vessel (ERCV) to encapsulate the cylinder.
- After the Portable ER Scrubber has been used, it should be purged for 5 minutes by running the Nitrogen pressure with the flexible duct exposed to open air.
- Empty the portable scrubber of dry Media and dispose as Hazardous Waste

Safety

- The Portable ER Scrubber is designed to effectively scrub low concentrations of leaking gases if the proper dry media is used. These leaks are captured by positioning the flexible duct by the leak point and are diluted to low concentrations by the exhaust air flow. At no time should pure gas be introduced directly into the Portable ER Scrubber without the Venturi Eductor operating, this could generate considerable reaction heat and reaction
- If the Portable ER Scrubber is used with the ER Bubbler system the reaction byproducts from the metal Hydride Gases (i.e. Arsine) will be hydrogen, which can reach explosive concentrations if not diluted enough. Flow of these gases into the ER Bubbler must be controlled and the Portable ER Scrubber must be operated at a high exhaust rate.
- The Portable ER Scrubber is not to be used on cylinders that are on fire. Besides the danger of a possible cylinder rupture, the scrubber will not be effective in reacting the combustion byproducts

Sept 2021

ER Gas Scrubbing

Drum Sizing

- 30 gal (115 liter) drum
  - Cross sectional area 2.02 ft^2 (0.187 m^2)
  - Flow rate of 200 cfm (5.67 m^3/min), the velocity is 92 ft/min (28.0 m/min)
  - 2 ft^3 (57 liters) of media will create a 15.5” (39.37 cm) depth
- 55 gal (210 liter) drum
  - Cross sectional area of 2.64 ft^2 (0.245 m^2)
  - Flow rate of 200 cfm, (5.67 m^3/min), the velocity is 75 ft/min (22.9 m/min)
  - 3 ft^3 (85 liters) of media will create a 13.5” (34.29 cm) depth

Challenge Testing HCl Cylinder Cracked Valve (2-3 liters/min), 13 minutes 0.5 ppm at outlet

Thank You

http://www.chemicallyspeakingllc.com