ESG Emergency Response Product Transfer

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Feel the Heat!

Chemically Speaking LLC

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Transfer

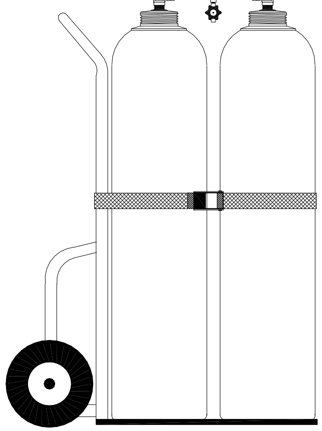
- **A variety of techniques are used to transfer the gas into empty cylinders**
  - **Cascade**
  - **Cold Coil**
  - **Vapor Condensation**
  - **Pressure Push**

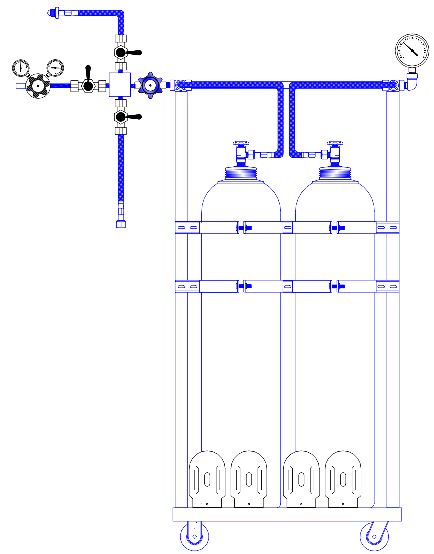
Cascade

Cascade System

- Empty cylinders used to equalize pressure from leaking cylinder
- Effective only with compressed gases or small quantities of liquefied gases
- Stored with slight positive pressure of inert gas. This eliminates the concern over air being sucked in during storage under vacuum
- Maximum effect is achieved by cascading rather than equalizing all cylinders at once
- Must be used in conjunction with scrubber to vent remaining gas in leaking cylinder
- Typically 4 cylinders manifolded together for immediate use
- Aluminum not authorized for corrosive gases
- After use must be disconnected and shipped with cylinder caps on and labeled for transportation

Cascade Systems

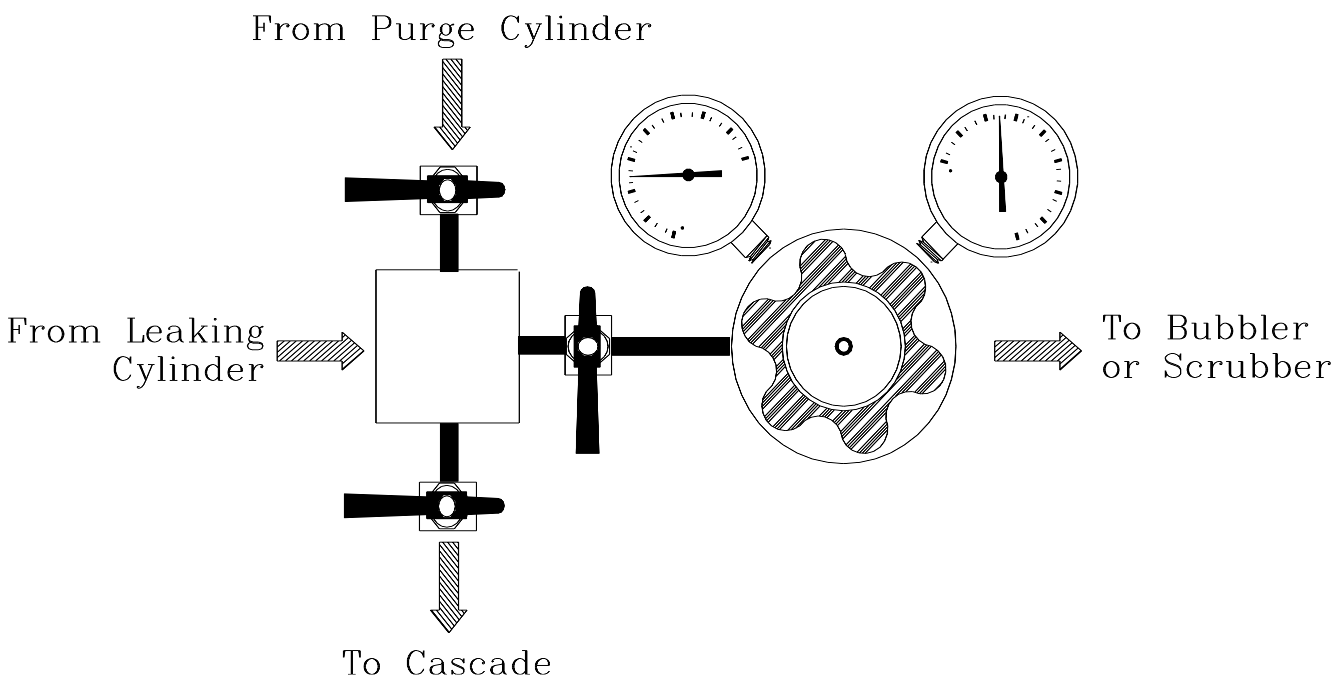




Aluminum Cylinders on Handcart

Steel Cylinders on Metalcart

Cross Purge Assembly



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Cascade

- Cascading is more effective than simply opening all the cylinders. For example a 15 kg Silane cylinder at 1345 psig with 4 empty cylinders assuming ideal gas
  – If all cylinders are opened at the same time, all would equalize at 229 psig of pressure
  – If cascaded sequentially the 1^{st} 673 psig, 2^{nd} 337 psig, 3^{rd} 169 psig, 4^{th} 85 psig
  – The leaking cylinder would be reduced by a significantly larger amount 85 psig vs. 229 psig
- Due to the compressibility of silane, the pressures would be much lower.
- It is better to have all the cylinders connected at the same time to save on the purging time

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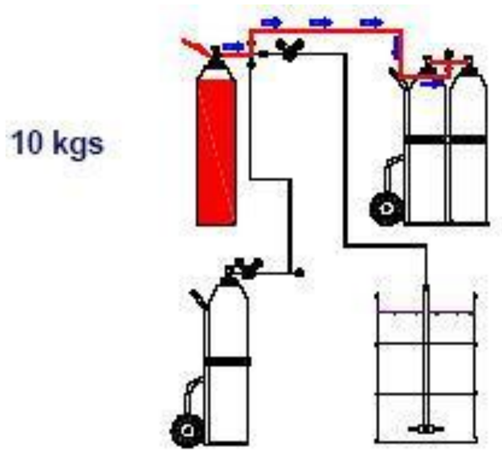
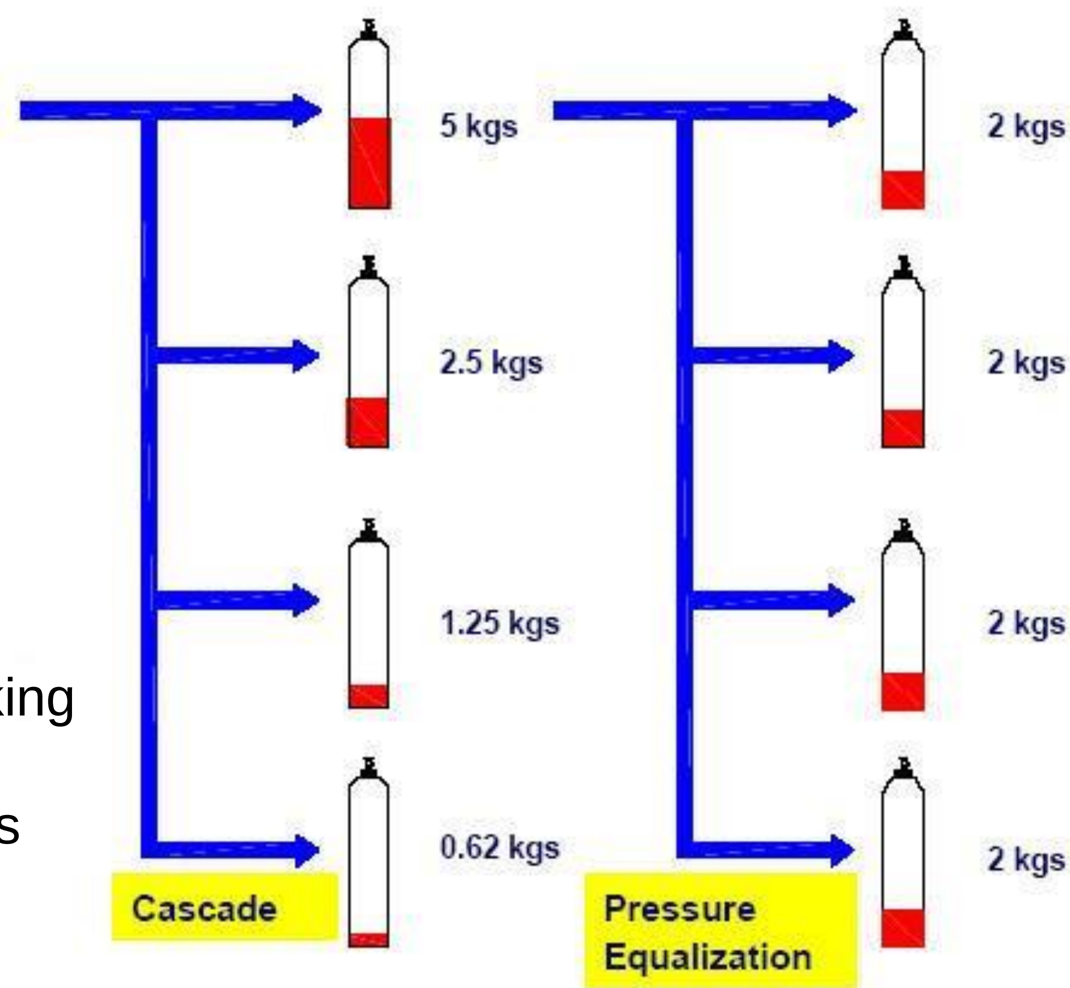
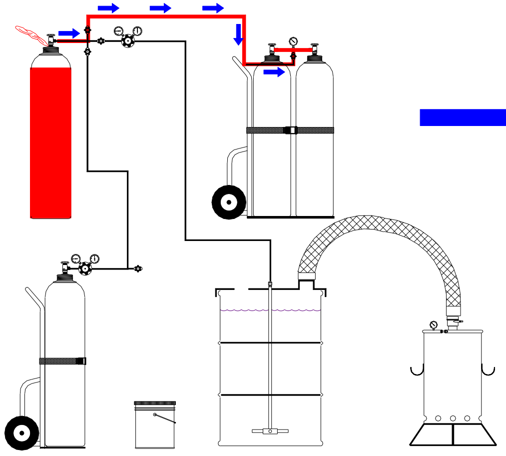
Comparison of Cascade vs Pressure Equalization of 10 kg Silane cylinder into 4 empty Cylinders





By cascading the leaking cylinder content was reduced to 0.62 kgs vs the 2 kg of pressure equalization

Disposal of 5% Arsine Mixture @ 1800 psig, 44 l Cylinder

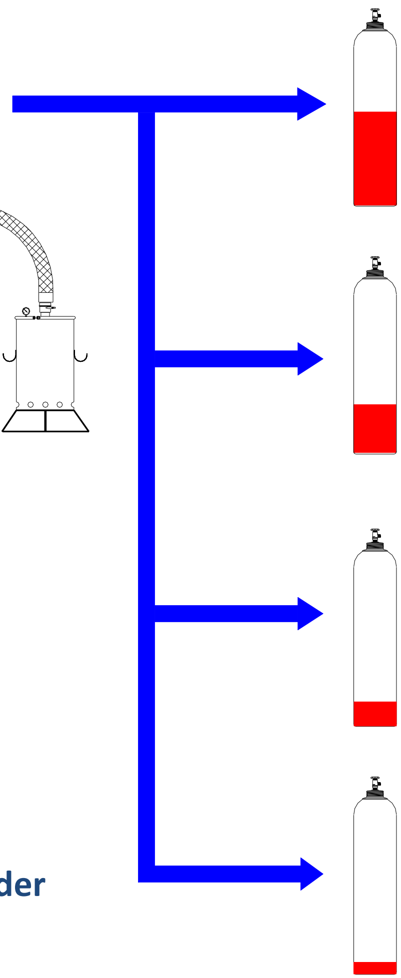


Connect Leaking Cylinder to System and Leak Check

Mix solution of $KMnO_4$

Vent pressure from Transfill Cylinders

Start Transfill into first Cylinder



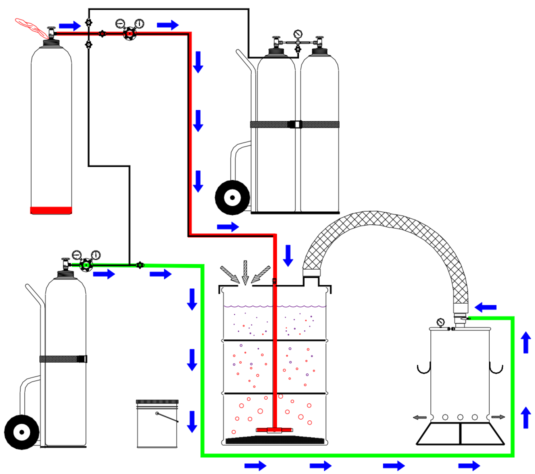
First Cylinder will Fill to 900 psig — Step 1

Second Cylinder will Fill to 450 psig — Step 2

Third Cylinder will Fill to 225 psig — Step 3

Fourth Cylinder will Fill to 112 psig — Step 4

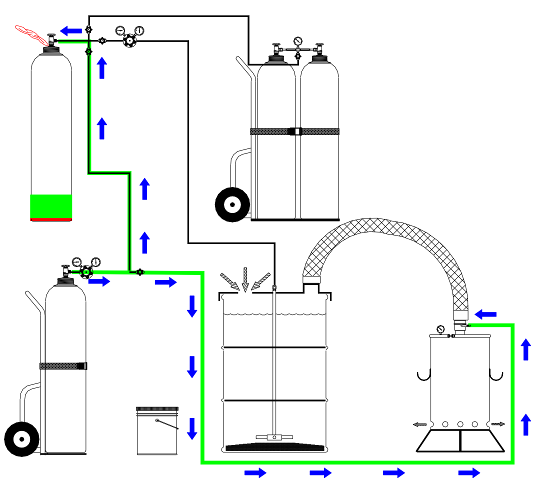
Disposal of 5% Arsine Mixture @ 1800 psig, 44 l Cylinder



Step 5

Start Nitrogen to Portable Scrubber

Vent Leaking Cylinder into Bubbler from 112 psig to 0 psig. Immediately Close Bubbler Valve. 53 gms of Arsine reacted & 7 gms. Remaining.



Step 6

Pressurize Leaking Cylinder with 100 psig Nitrogen

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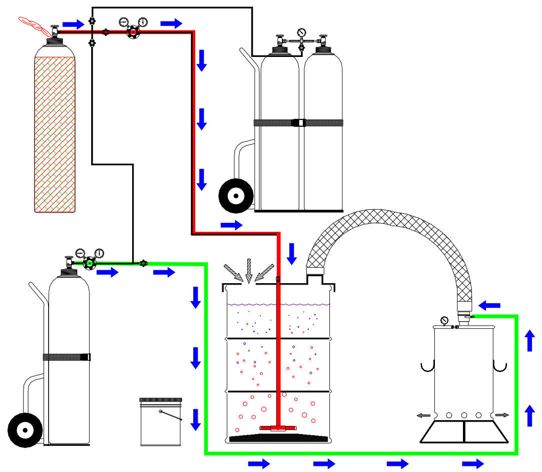
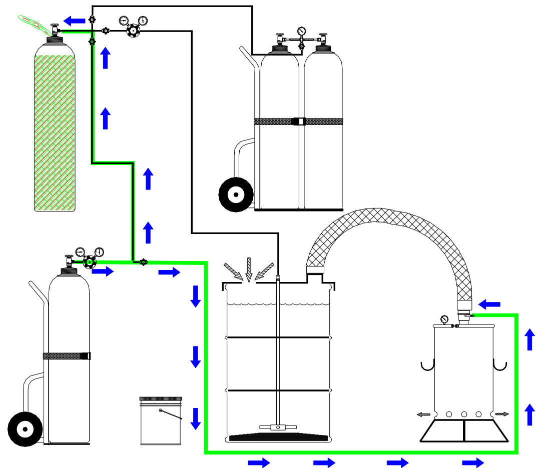
Disposal of 5% Arsine Mixture @ 1800 psig, 44 l Cylinder



Step 7

Arsine is diluted to 0.64% by Nitrogen

Vent Leaking Cylinder to Bubbler from 100 psig to 0 psig. Immediately Close Bubbler Valve



Step 8

Pressurize Leaking Cylinder with 100 psig Nitrogen

Disposal of 5% Arsine Mixture @ 1800 psig, 44 l Cylinder

Steps 9 - 13

Arsine is Diluted to 800 ppm by Nitrogen

Vent Leaking Cylinder into Bubbler from
100 psig to 0 psig. Immediately Close Bubbler Valve

Repeat Pressurization with Nitrogen and Venting 2 more times. Reducing Arsine to 12 ppm.

After final Vent leave Leaking Cylinder at 0 psig

Step 14

Purge Bubbler, Cascade & Portable Scrubber with Nitrogen for5 minutes. Disconnect system.

Step 15

Dispose of Bubbler Solution by Hazardous Waste Company. Total of 60 grams Arsine reacted.

Step 16

Remove Cascade Cylinders and Cap with Vaportight Cap and Cylinder Cap. Mark Contents and Pressure. Label with RMA Tag and Shipping Labels.

Step 17

Remove Leaking Cylinder and cap with vaportight cap and Cylinder Cap. Mark Contents and Pressure. Label with RMA Tag and Shipping Labels.

Step 18

Return Leaking and Cascade Cylinders with next shipment. Request additional Cascade Cylinders.

Cooling Cylinder Can Increase Cascade

Cascading Silane Bulk Systems

- **Y Containers or ISO Modules available for Cascade can be partially full**

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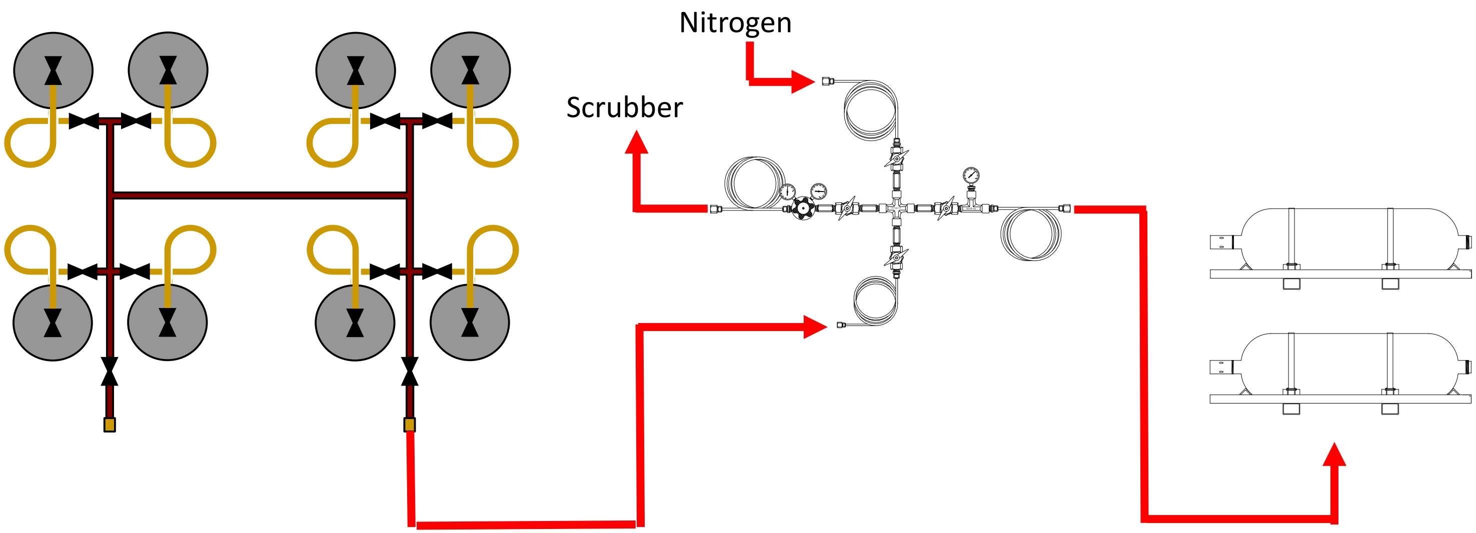
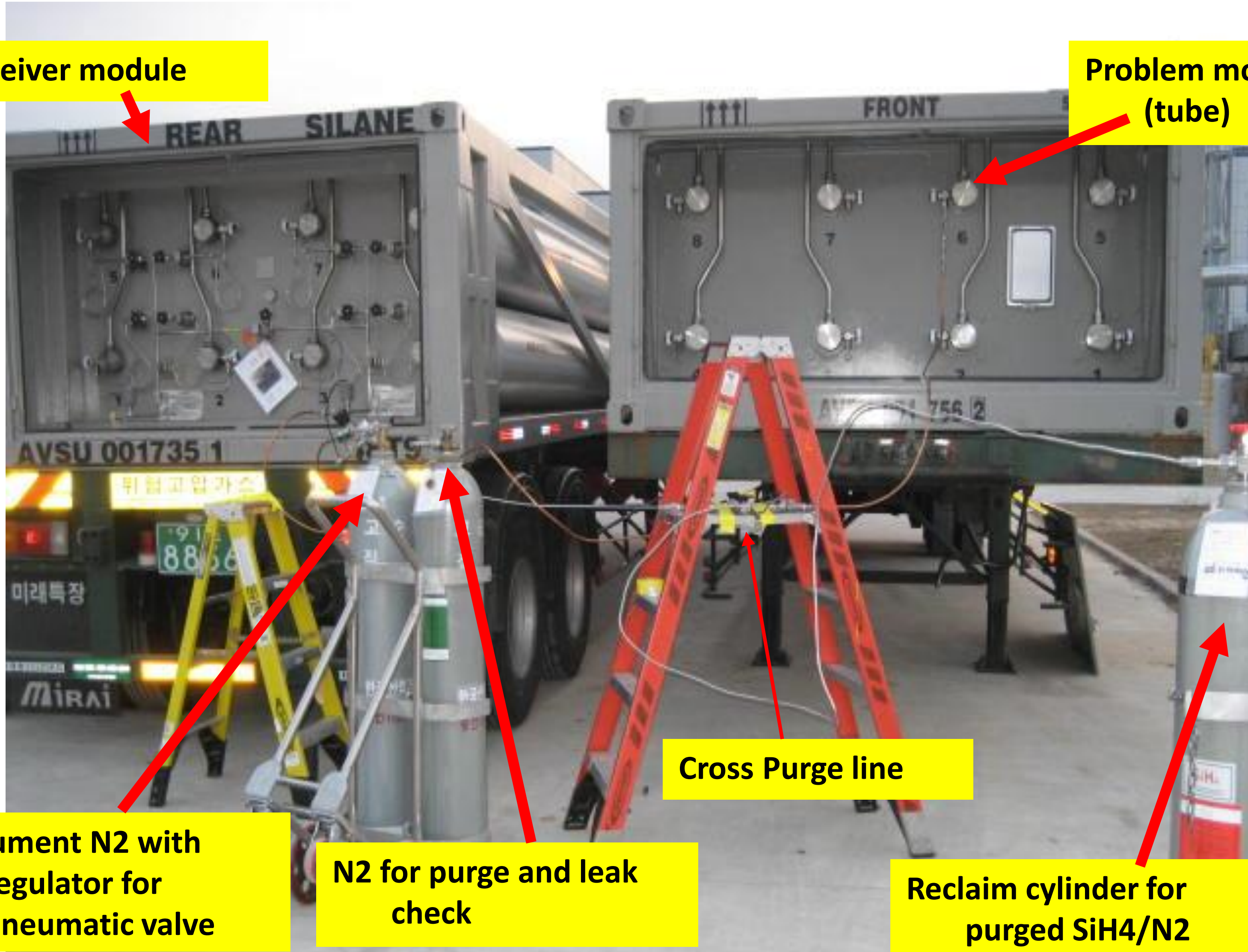
ISO Cascade to Y Cylinders



20’ ISO Tube Cascade into Empty Y’s

- A Y Container has 36.1% of the volume of a 20’ tube.
- Assuming a full tube at 1250 psig
  - 1st 913 psig
  - 2nd 666 psig
  - 3rd 486 psig
  - 4th 353 psig
  - At this pressure 40.7 kgs (89.5 lbs) Silane remaining to be scrubbed

Cascade from Front



ISO Tube Cascade into Other Tubes

- Cascade by equalizing the pressure with one then the next until you run out of tubes with a pressure lower than the leaking tube.
- For maximum effect start with the highest pressure tube.
- Vent the remaining pressure into a scrubber/vent stack
- Ideal case would be to cascade to "empty" tubes on the same trailer

Cold Coil

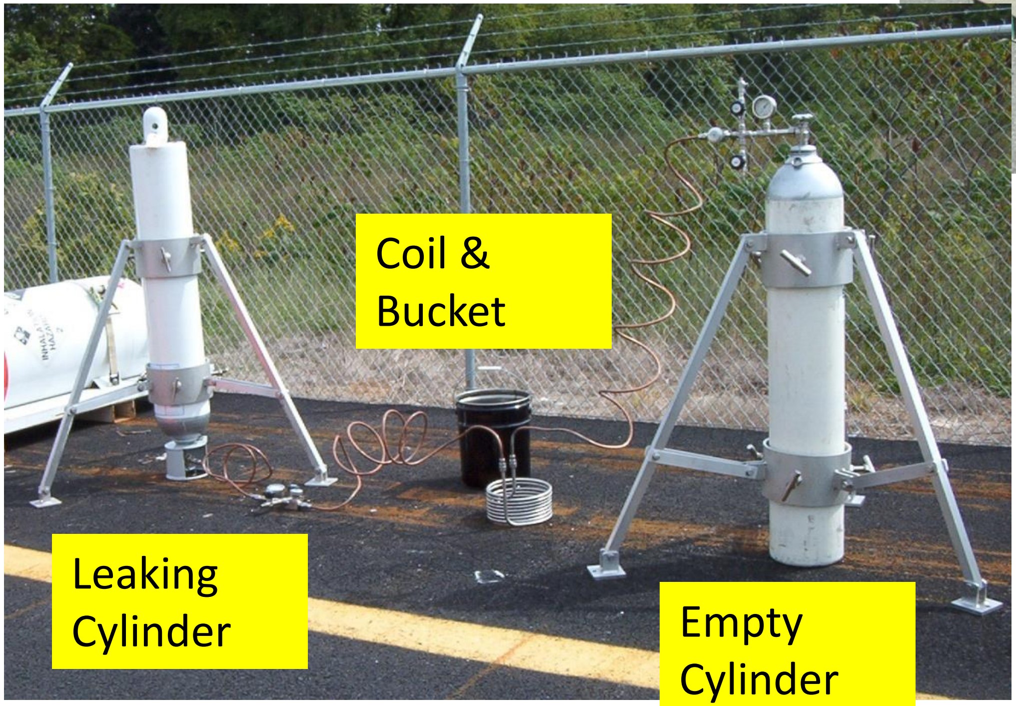
Cold Coil Transfer

- Cascading is ineffective for transfer of liquefied gases
- Transfer of liquid via pressure differential caused by temperature or gravity
- Transfer line valve must have Cv equal to or higher than cylinder valve. Ball valve is preferred to prevent vaporization cooling
- Receiving cylinder must be equal in size or larger than leaking cylinder
- Dry ice (-78^{o}C) is the coldest temperature allowed for seamless high pressure cylinders

Cold Coil

- Cooling occurs outside the cylinder to cool initial product to effect the transfer.
- Leaking cylinder must have good connections
- Cylinder to receive gas must be evacuated and ready

Cold Coil Setup



Collar to Invert Leaking Cylinder

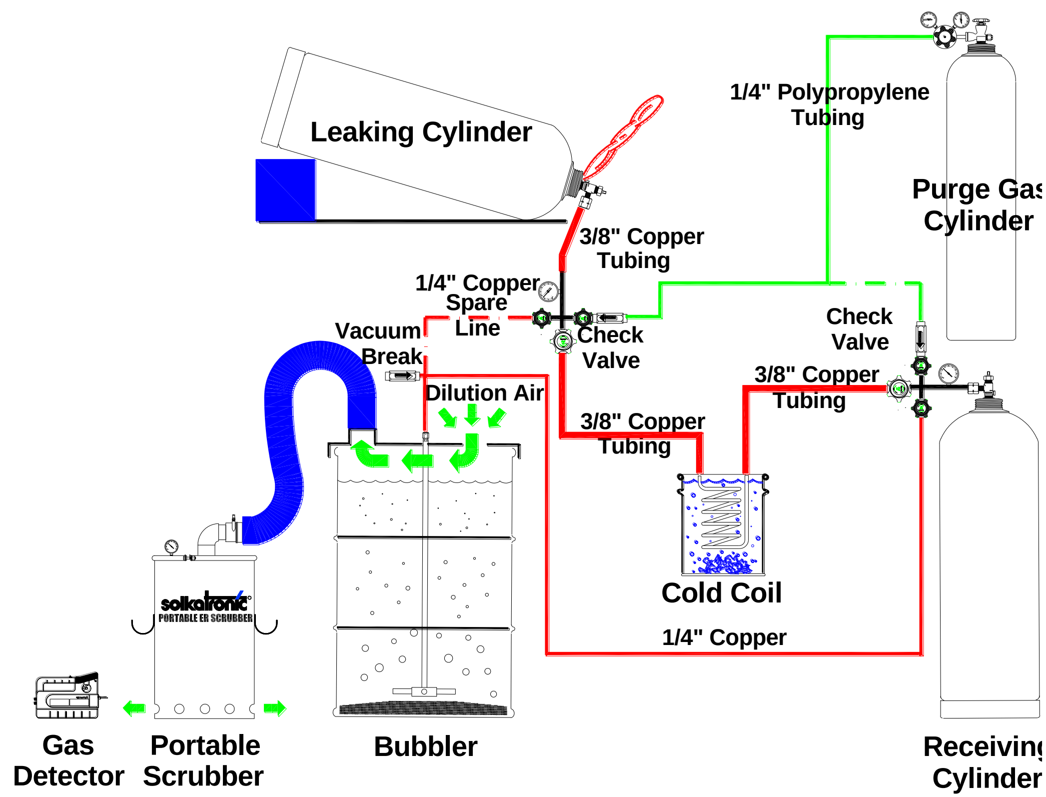
Typical Cylinder Cold Coil Transfer

The Leaking Cylinder can be bagged with MacGyver Bag to contain leak

The Leaking Cylinder should be secured from rolling and lifted high enough for valve handwheel to be turned

To prevent over fill, weigh both cylinders before and after.

If transfer stops, isolate coil and vent gas from receiving cylinder to cool



Three Stages of Cold Coil Transfer

Liquid Flow

Gas Flow from Heel

Flow Stopped

Cold Coil Notes

- Reversing Liquid Flow valve direction can cause lower stem assembly to not open due to pressure being greater than the spring force. Relieve the pressure and the valve will open
- Open valves in sequence from Leaking to Receiving Cylinder
- Never close two valves to trap liquid
- Add dry ice slowly into limonene to cool it. Will boil vigorously and could overflow the container. Wait for boiling to slow down before proceeding. This should become a fairly steady
- Open the leaking cylinder valve and then the coil valve valve slowly. The solution will start to boil vigorously.
- Watch the two pressure gauges. The leaking cylinder one should be higher than the receiving cylinder
- Make sure the two inline valves are fully opened. If the line from the leaking cylinder starts to frost immediately after the inline valve, the valve is not opened all the way.
- Orient coil so that the straight line is the outlet toward Receiving cylinder. The reverse will leave a lot of liquid in coil at end
- When purging the system, if the vent line starts to frost, liquid is being vaporized from coil

Cold Coil Facts

- A ½" x 20' coil with 0.065" wall thickness has a internal volume of 0.030 ft^3 (850 cc) can contain the following amount of liquid

  Arsine – 2.78 lbs

  Ammonia – 1.56 lbs

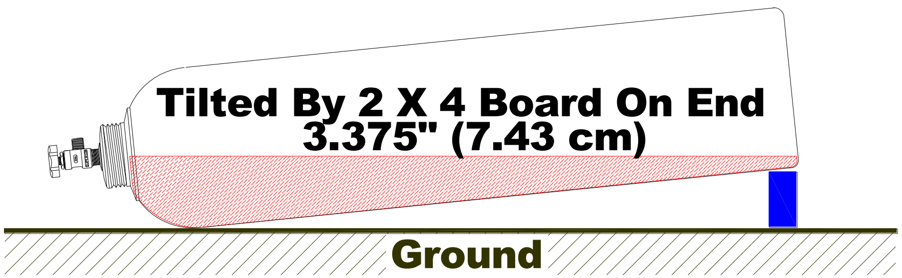
  Hydrogen Chloride – 2.16 lbs

  Phosphine – 1.06 lbs

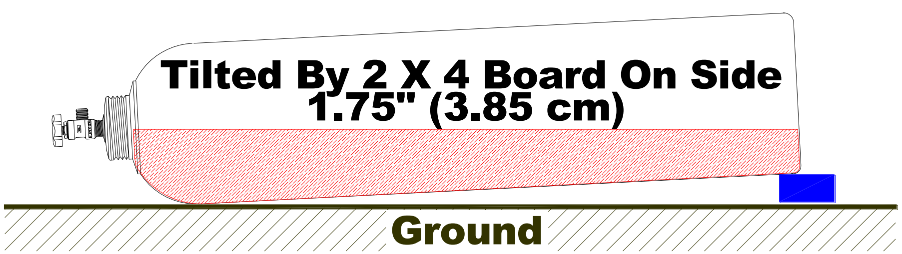
  This must be properly drained from the coil by closing the line valves in sequence from the leaking cylinder

  Note: This is only for the coil volume and does not include the connecting lines

Amount Remaining in Cylinder After Tilting



	49 liter (A)	44 liter (B)
Water	39.0 lbs	21.0 lbs
Ammonia	23.2 lbs	12.5 lbs
Hydrogen Chloride	32.2 lbs	17.3 lbs

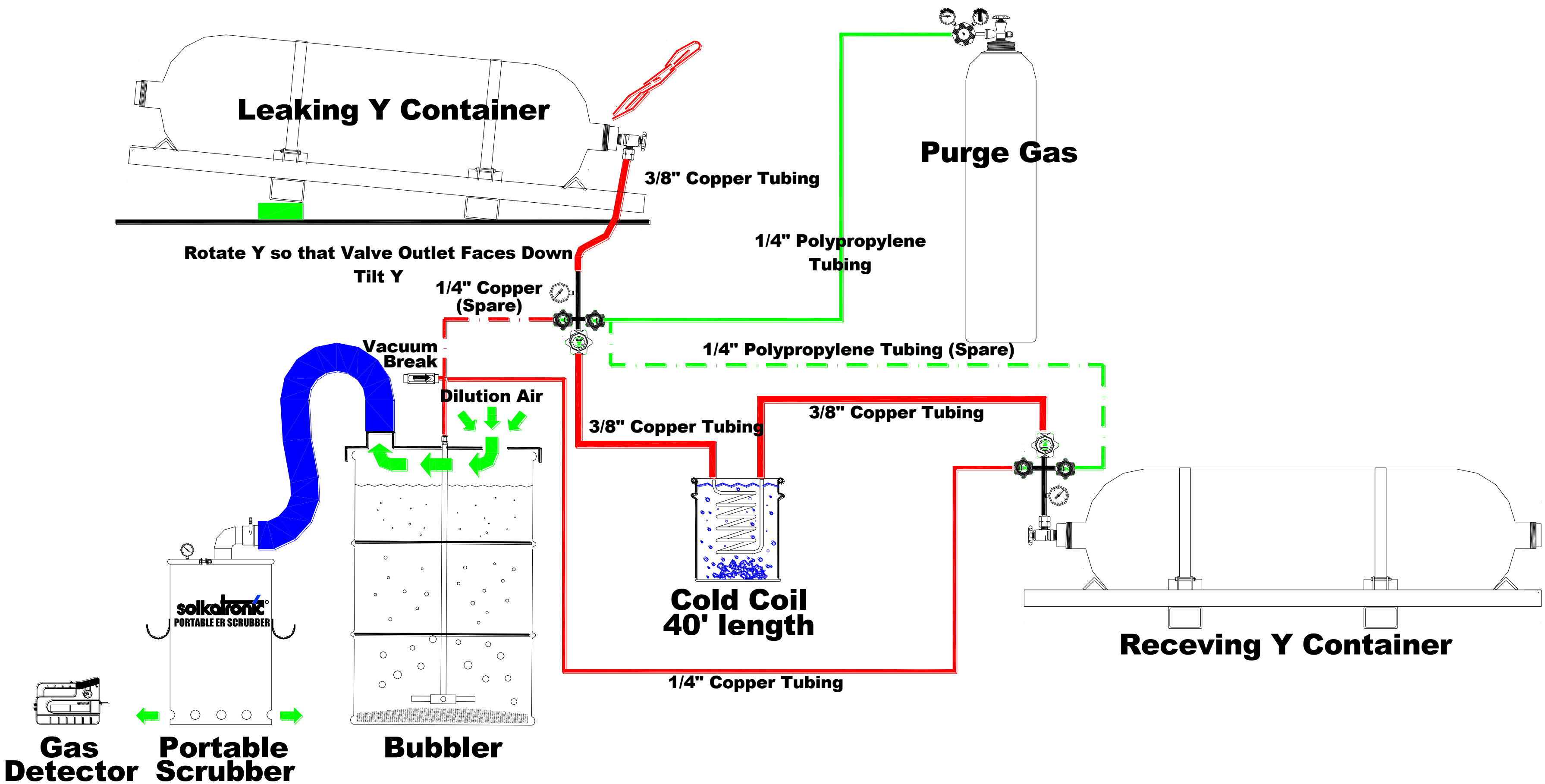


	49 liter (A)	44 liter (B)
Water	57.4 lbs	40.2 lbs
Ammonia	38.0 lbs	34.1 lbs
Hydrogen Chloride	52.7 lbs	47.3 lbs

Procedure

- After setting up system, start to add dry ice to coolant. Use care as the coolant will boil over quickly
- After the coolant bubbles start to calm down, start the transfer.
- Coolant bubbles will immediately start to be vigorous. The outlet line from the coil will start to frost up. There should be a lower pressure in the gauge for the receiving cylinder.
- Bubbling will slow down and the line from the leaking cylinder will start to frost. This is a sign that the liquid heel is vaporizing from the shoulder. Pick up cylinder to empty heel. Note this must be done quickly so as to not cool the liquid in the coil too much and cause the transfer to stop.
- Once pressure in the leaking cylinder drops to close to receiving cylinder, close the valve on the leaking cylinder and remove the coolant drum to warm the coil. This will bring up the pressure and vaporize into the receiving cylinder

Flow Schematic Y Container Cold Coil Transfer



Cold Cylinder Transfer

- Cooling the receiving cylinder will eliminate the need for a coil
- Insert cylinder into a cardboard tube and fill with dry ice
- Cannot use with welded cylinders
- Cannot be used with bulk cylinders

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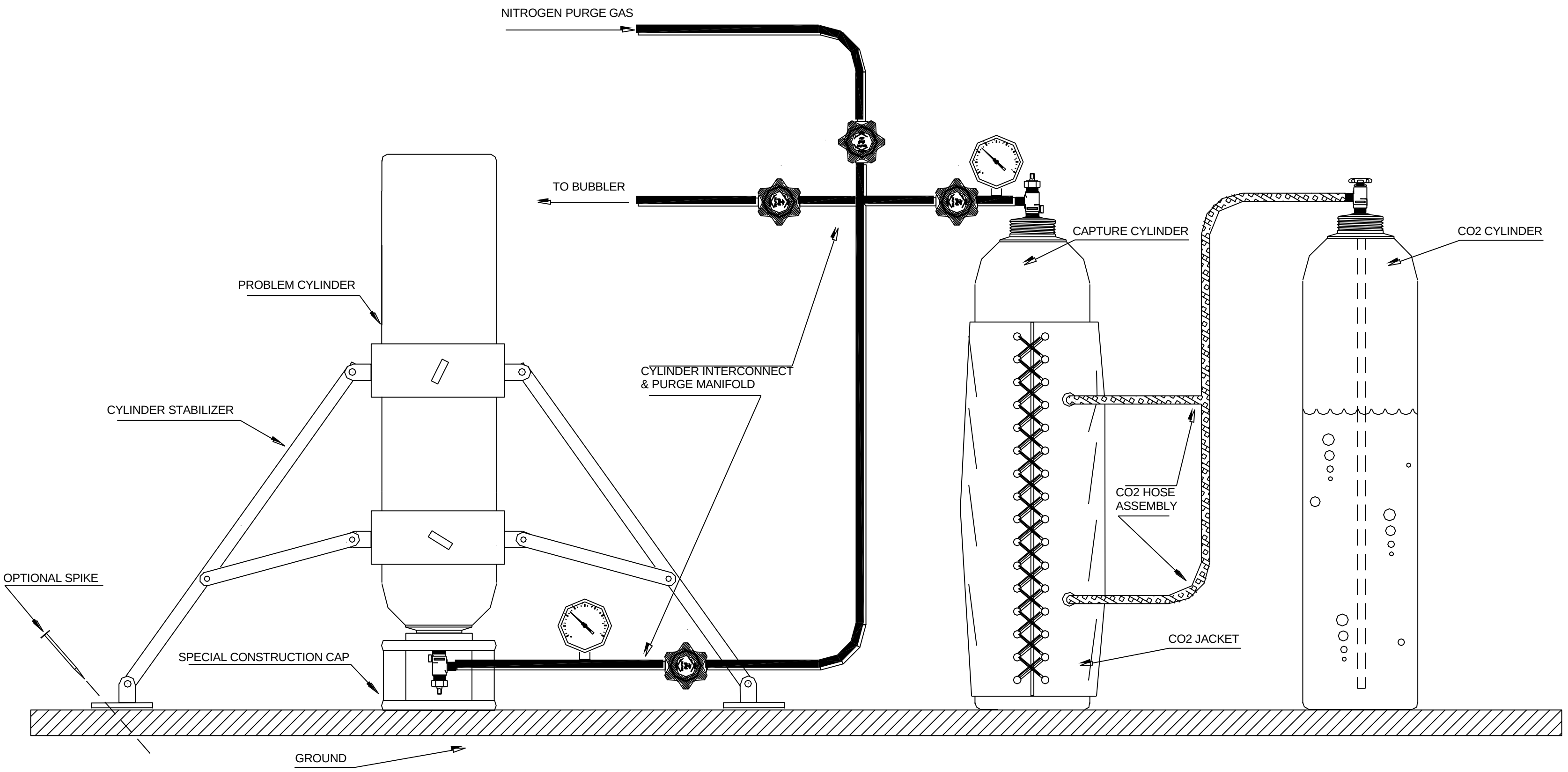
Cold Bag Transfer



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Cold Bag Transfer

- **Eliminates the cold coil and the use of Dry Ice**
- **Cooling media, Dry Ice is generated as needed**
- **Liquid CO_2 can be easily stored in cylinders**

Cold Jacket Transfer (Oct 29, 2004)

- Liquid CO_2 was throttled to maintain a -18F temperature
- Liquid Transfer of 35 lbs Ammonia using 34 lbs CO_2
- Difficult to tell that all the liquid was transferred (No sound)

Trimethylsilane Transfer

- Ambient temperature 90^{o}F. Cooled residue cylinders with ice
- Full cylinder, 35 lbs
- Transferred in 27 minutes
- All liquid was transferred into first cylinder. Second only got gas residue

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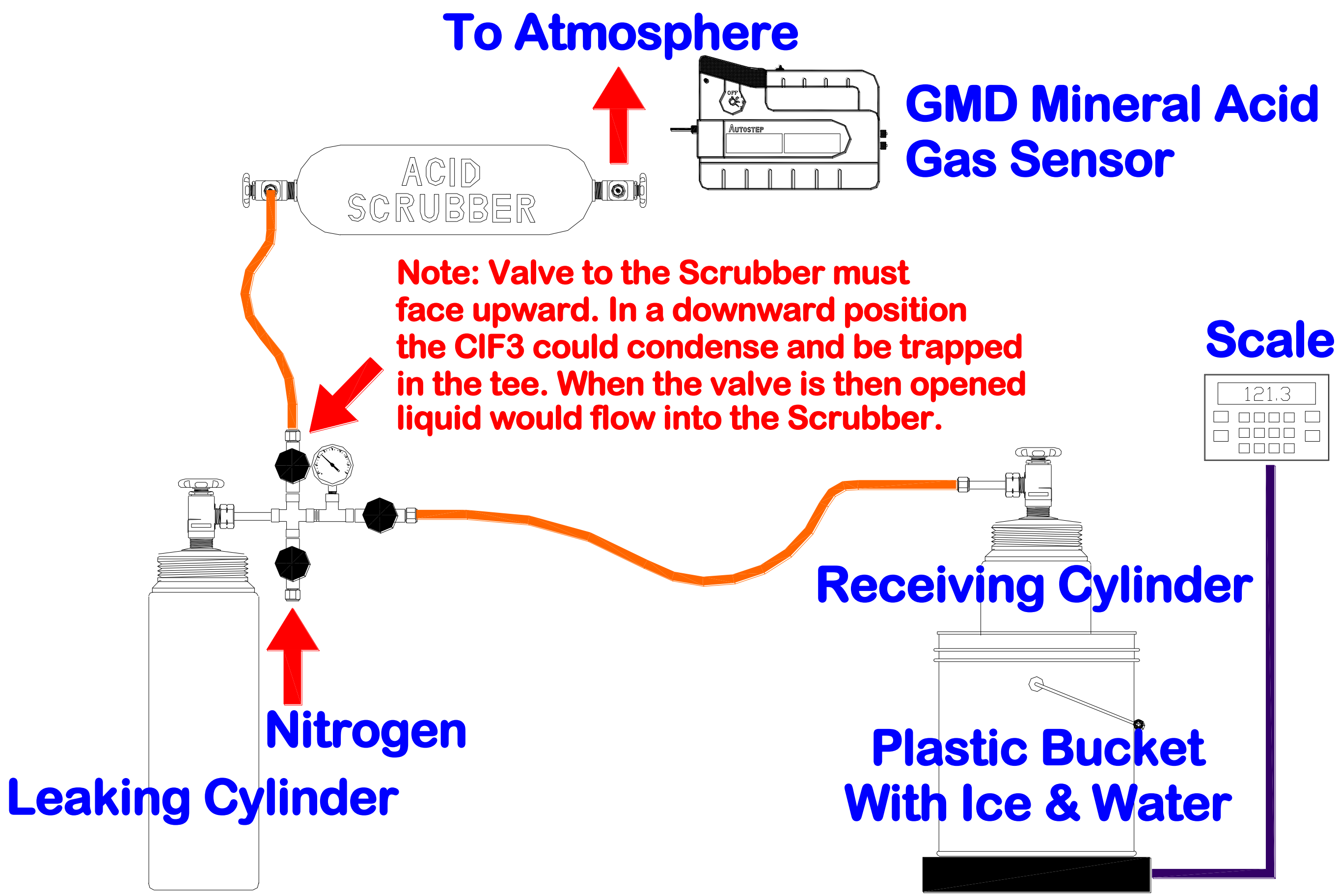
How do you safely transfill the low pressure toxic oxidizers?

Vapor Condensation

- Liquid ClF_3, BrF_3 and BrF_5 are very reactive
- Safer to handle vapor
- Dedicated oxidizer cleaned and Fluorine passivated system to vaporize and condense into cylinder

Vapor Condensation System, ClF_3



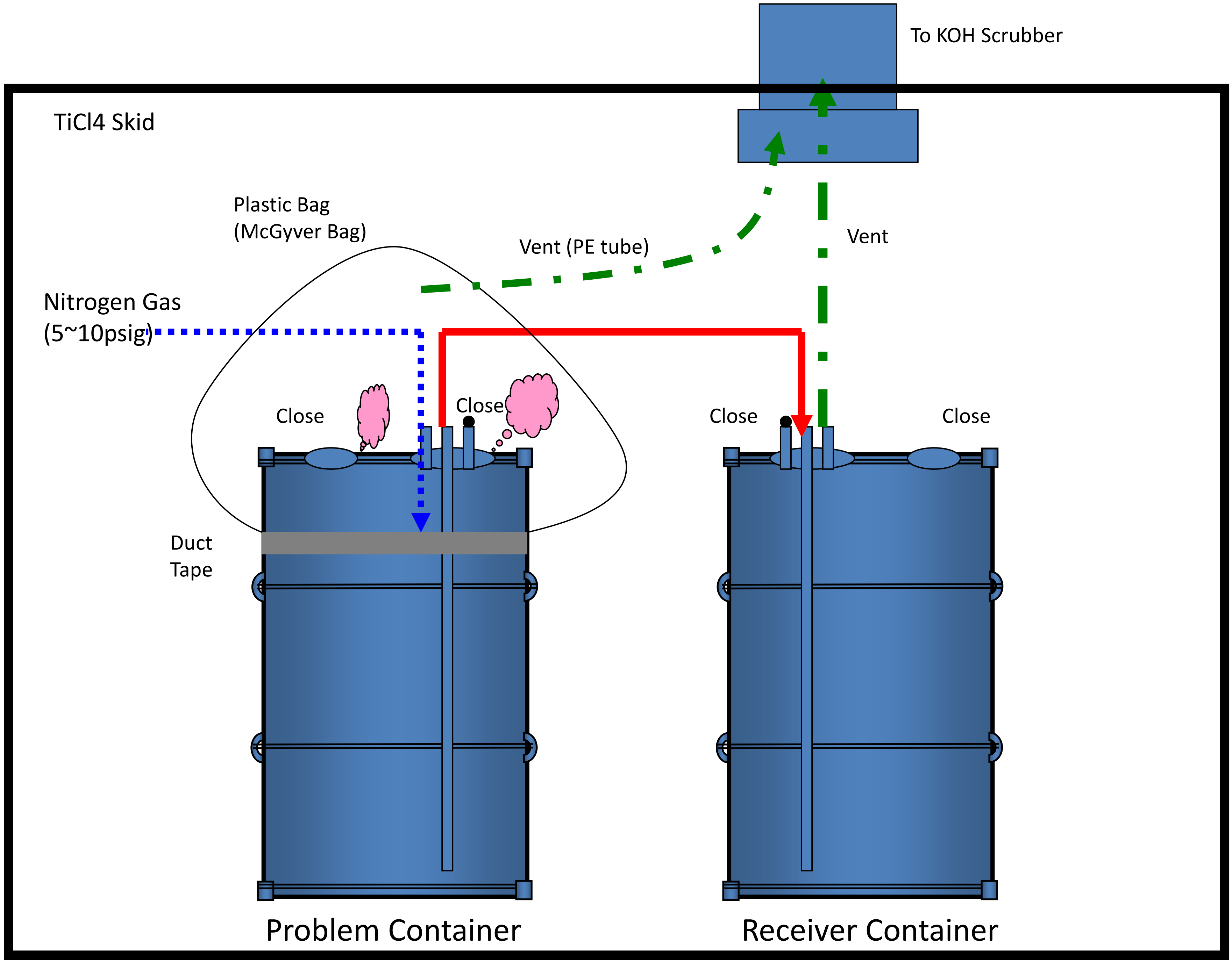
Place Cylinders and System on a Flat Non Combustible Surface. If on Asphalt, use flat metal pans under Scrubber and Cylinders to Catch any drips of liquid

How do you safely transfill liquids?

Liquid Transfer

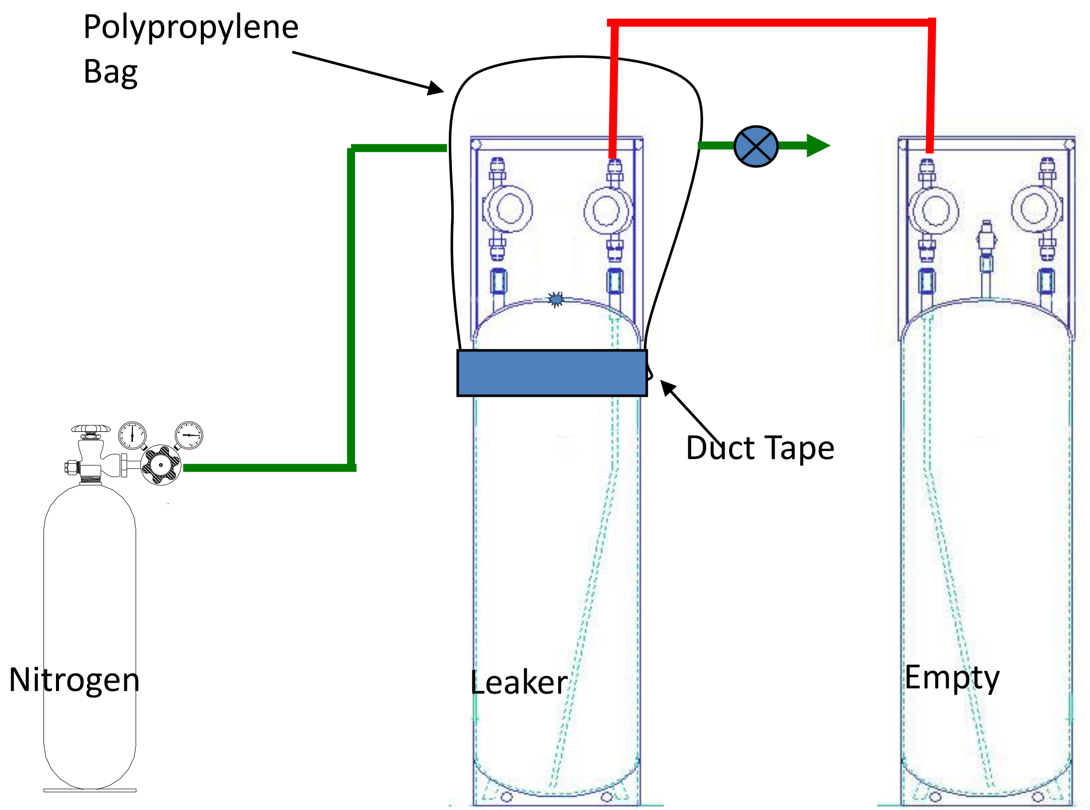
- No gas pressure to create differential
- Pressure push with inert gas
- Vacuum withdrawal

Pressure Push


To KOH Scrubber
TiCl4 Skid
Plastic Bag
(McGyver Bag)
Vent (PE tube)
Vent
Nitrogen Gas
(5~10psig)
Close
Close
Close
Close
Duct
Tape
Problem Container
Receiver Container

Venturi vacuum pull over

Vacuum Transfer of TMG



“Empty” Cylinder????

- You open the cylinder valve and nothing the pressure gauge shows 0 psig
- Empty?

“Empty” Cylinder????

- The valve might be plugged or damaged
- Always verify the operation of the valve by closing the valve and applying some gas pressure on the valve outlet. Then open the valve, the pressure should drop of the valve is open and not plugged

“Empty” Cylinder

- A cylinder is never empty until it is physically cleaned of its contents
- Even at 0 psig the cylinder will always contain 1 atm of the gas
- For a toxic, flammable or corrosive gas, 3 times 100 psig purge gas and vent. This will reduce concentration to 2000 ppm
- For highly toxic 5 times to reduce it to 30 ppm

“Empty” Cylinders

- Cylinder have proven to be hazards even with their valves removed.
- In 1960 in France a hydrogen cylinder had the valve removed and was open to the atmosphere for a week. A operator lowered a light into the cylinder to inspect the interior. The bulb broke against the side and a fire came out of the cylinder top, singeing the operators face

Oxygen Cylinder Fire After Devalving
Sept 7, 2004, Thunderbird Cylinders

- **On September 7, 2004, an experienced Thunderbird devalver had verified that pressure had been removed from a steel oxygen cylinder prior to removing its valve. He utilized a devalving machine with a lexan protective shield to safely remove the valve. He, then, numbered the valve and cylinder so that the valve could be rematched to the cylinder after hydrotest. When he turned back to the cylinder to use a wire brush on a drill to remove the Teflon thread and paste, an explosion occurred- see digital photos below. His hands were burnt, the drill's wire brushes fused, the drill's plastic housing singed and the operator frightened along with other personnel standing nearby. The cylinder was a steel 150cuft, ICC3A2015, Serial No. E67498, Mfr. 3H52 in oxygen service- at least, it had a 540 valve.**

Tried to tighten a Leaking Valve in Full Oxygen Cylinder

ER Transfer


NON-FLAMMABLE GAS

Thank You

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