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Not Just Your Father's Chlorine Safety: A Lesson in Modern Chemical Safety Techniques

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Gary M. Lohse, P.E.

WATER MADE EASY

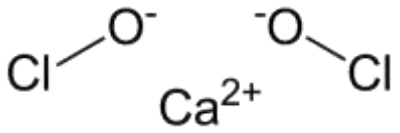
MARINE | ENERGY | MUNICIPAL | INDUSTRIAL

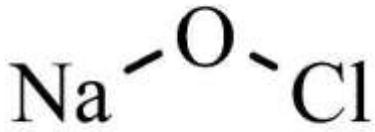
Topics to Be Covered

- Background
- Solid Chlorine
  - Calcium hypochlorite
- Liquid Chlorine
  - Commercial (Bulk)Sodium Hypochlorite
  - On-Site Hypochlorite Generation
- Gas Chlorine
  - Gas Basics
  - Your Father's Chlorine Safety
  - Containment Systems
  - Automatic Shut Off Valves
  - Emergency Scrubber Systems
- Summary

Water / Wastewater Disinfection

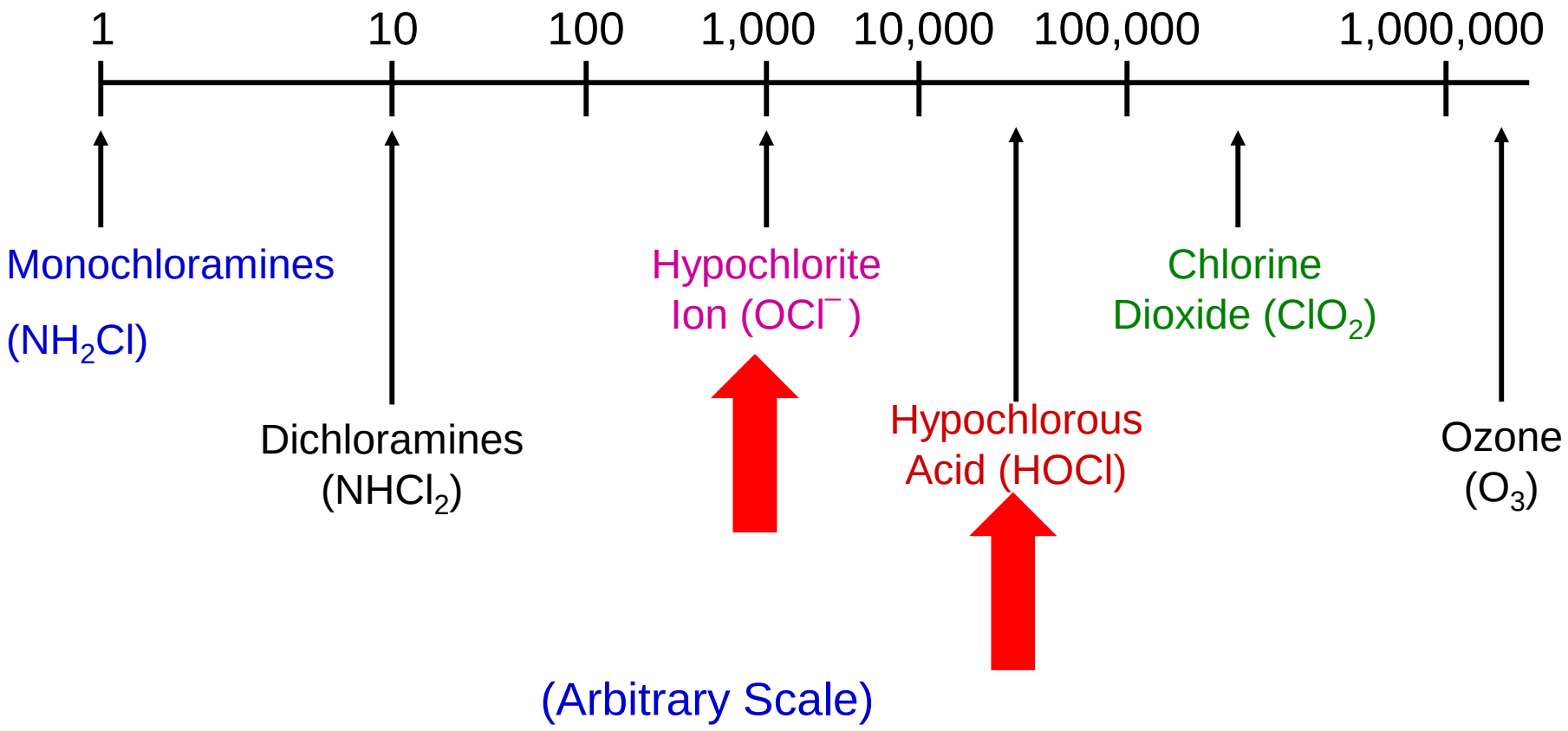
- Chlorine Based
  - Calcium hypochlorite
  - Commercial hypochlorite (bulk/bleach)
  - On-site hypochlorite generation
  - Gas chlorination
  - Chlorination-De-chlorination
  - Chloramines
  - Chlorine dioxide
- Alternate
  - UV disinfection
  - Ozone
  - Peracetic Acid





DISINFECTION EFFECTIVENESS

EPA ESTIMATE



C hlorine Chemistry

- Definitions - 2

  HOCL & OCL^- = Free Residual Chlorine

  +

  Chloramines = Combined Chlorine Residual

  Total Chlorine Residual

- Analytical methods can measure Free or Total Chlorine Residual
- Combined Chlorine Residual must be determined arithmetically

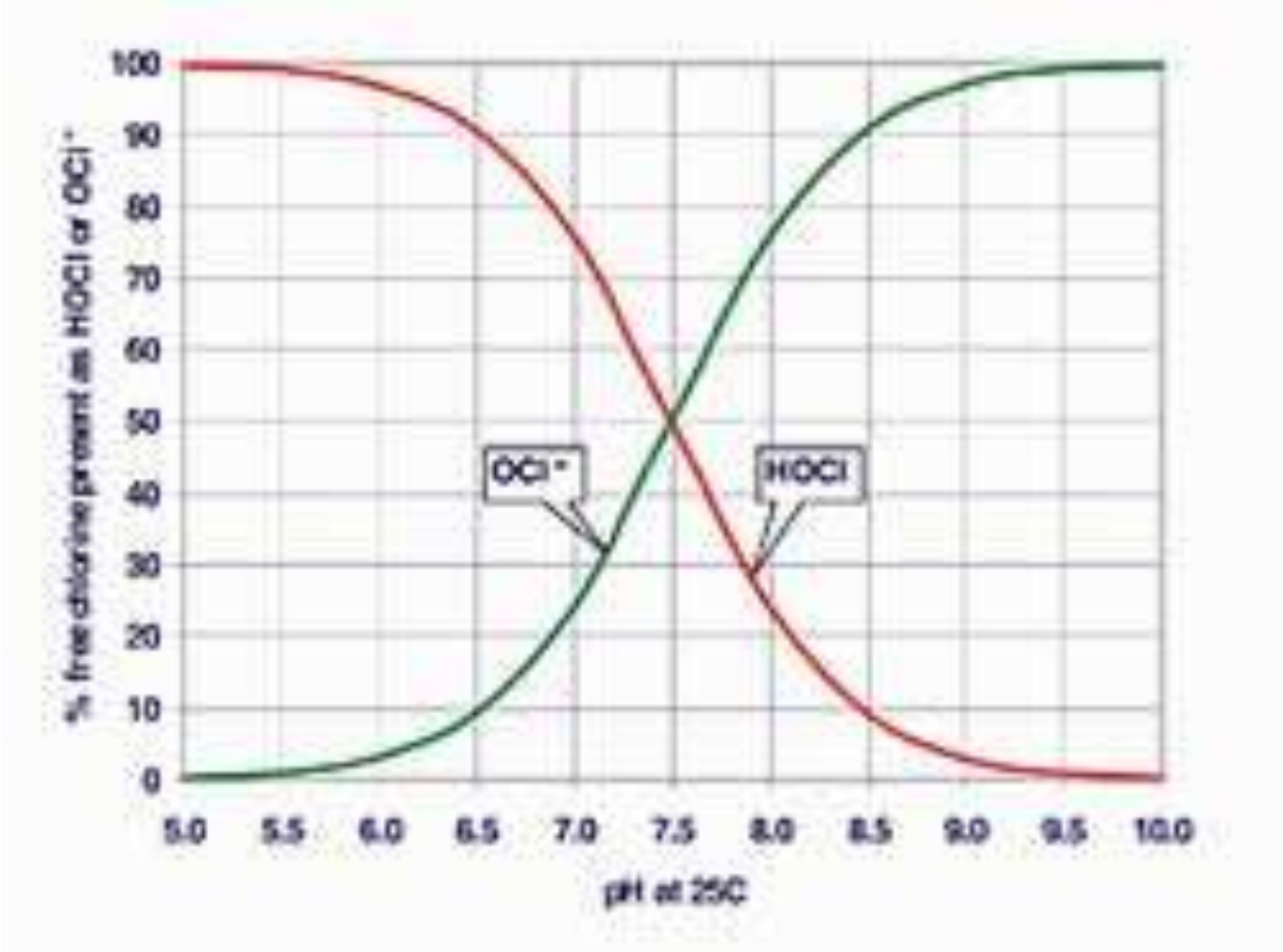
Chlorine Reactions in Water

- Chlorine + Water → Hypochlorous Acid + Hydrochloric Acid
  - **$Cl_2 + H_2O \rightarrow HOCl + HCl$**

- Dissociation Reaction
  - **$HOCl \rightarrow H^+ + OCl^-$**

Disinfection Distribution

- Relationship between HOCL and OCL^- at various pH values



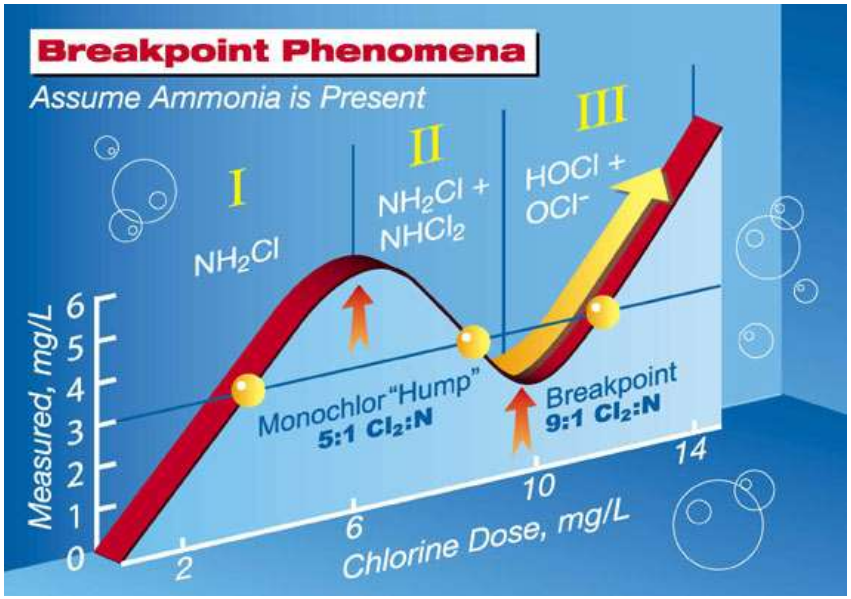
Chlorine Reactions

- $Cl_2 + NH_3 \rightarrow NH_2Cl$ (Monochloramine)
- $NH_2Cl + Cl_2 \rightarrow NHCl_2$ (Dichloramine)
- $NHCl_2 + Cl_2 \rightarrow NCl_3$ (Trichloramine, Nitrogen Trichloride)

Dechlorination Reactions

- $SO_2 + H_2O \rightarrow H_2SO_3$
- $H_2SO_3 + HOCl \rightarrow H_2SO_4 + HCl$
  (Free)
- $H_2SO_3 + NH2Cl + H2O \rightarrow NH4Cl + H2SO4$
  (Monochloramine)

Chemistry



Breakpoint Chlorination

- Ammonia destruction reactions:

  $2NH_2CL + HOCL \rightarrow N_2 + H_2O + 3HCL$

  $NH_2CL + NHCL_2 \rightarrow N_2 + 3HCL$

- When dosage reaches approximately 8 to 10 times the ammonia concentration (theoretical ratio is 7.6) the "breakpoint" is reached.

- Complete destruction of ammonia seldom occurs at breakpoint and some chloramines persist beyond it.

Other Forms of Chlorine

- Calcium Hypochlorite + Water → Hypochlorous Acid + Alkali
  - **$Ca(OCl)_2 + H_2O \rightarrow 2HOCl + Ca(OH)_2$**
- Sodium Hypochlorite + Water → Hypochlorous Acid + Alkali
  - **$NaOCl + H_2O \rightarrow HOCl + NaOH$**

Equivalent Chlorine Forms

- 1 Pound (0.4536 kg) of chlorine gas

  equals

- 1 Gallon (3.785 liters) 12% sodium hypochlorite solution

  equals

- 15 Gallons (56.8 liters) 0.8% on-site generated sodium hypochlorite solution

  equals

- 1.55 Pounds (0.676 kg) calcium hypochlorite (65%)

Calcium Hypochlorite

Advantages	Disadvantages
Very effective at typical pH	Difficult to dose unless dissolved first
Proven & reliable (Swimming pools)	Leaves a residual – potential for declor
Leaves a residual – potable water	Often used for small wastewater plants
	Reacts with ammonia
	Effectiveness decreases at high pH
Safety	**Safety**
• Easily stored	• Dust concerns
• Stable as solid	• Incompatibility with solvents
• Not highly regulated	• Safety issues often overlooked

Calcium Hypochlorite Safety Lesson

Spontaneous fire in SUV cause by calcium hypochlorite mixing with a solvent which caused the death of two children

Commercial Sodium Hypochlorite

Typical Sodium Hypochlorite Dosing Station

Commercial Sodium Hypochlorite Highlights

- Delivered to site in usable liquid form
- Delivered as 12-15% chlorine
- Major system components include 1) storage tanks, 2) metering pumps 3) analytical instrumentation
- Use analyzer & flow meter to pace based on flow and demand

Commercial Sodium Hypochlorite

Advantages	Disadvantages
Very effective at typical pH	Reacts with ammonia
Proven & reliable	Effectiveness decreases at high pH
Widely used for water & wastewater	Concentration decays quickly
Leaves a residual	Chlorine by-product formation
Simple chemical feed system	Leaves a residual - potential for declor
Low capital cost	High cost per pound
Safety	**Safety**
• Liquid safer/more familiar than gas	• Can cause severe burns
• No make down required	• Potential for off gassing
• Not highly regulated	• Hazardous material - secondary containment required
	• Safety issues often overlooked

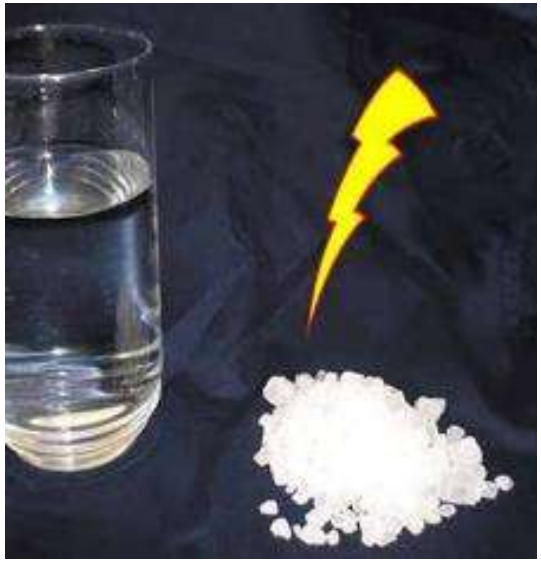
On-Site Sodium Hypochlorite Generation

Typical 24 lb On-Site Hypochlorite Generation System

On-site Sodium Hypochlorite Highlights
• Delivered to site as salt
• Sodium hypochlorite produced on-demand with minimum storage
• 0.8 % sodium hypochlorite solution produced (Clorox 6%, Bulk 12.5%)
• Utilizes DC current, salt, water
• Storage tank and metered feed pumps (flow or residual paced)
• 3-5 days storage typical

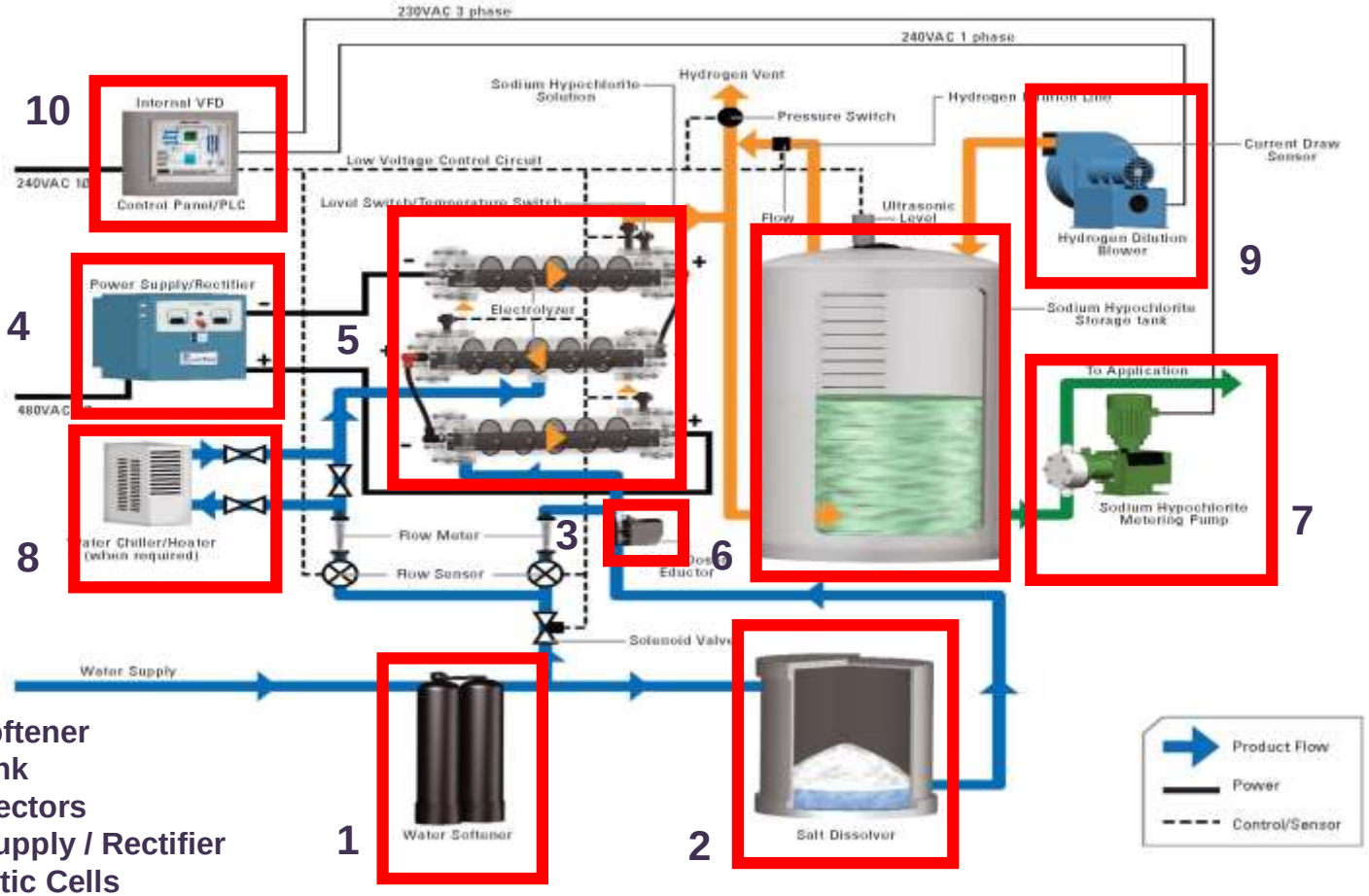
On Site Sodium Hypochlorite Generation

$$NaCl + H_2O + 2E = NaOCl + H_2$$



- For each lb. equivalent of Cl2:
  - Salt (NaCl) 3.0 lbs
  - Softened Water 15 gal
  - Electrical energy 2 kWh DC
- For each pound of Cl2 equivalent produced:
  - (15 gallons of 0.8% concentration Sodium Hypochlorite)
  - 1/35 lb. of H2 gas produced (5.6 ft3)
- H2 gas Immediately diluted upon production with air blower 100:1 to reduce H2 to 25% of LFL

On-site Sodium Hypochlorite Generation



1. Water Softener
2. Brine Tank
3. Brine Injectors
4. Power Supply / Rectifier
5. Electrolytic Cells
6. NaOCl Tank
7. NaOCl Dosing System
8. Water Chiller / Heater
9. Hydrogen Dilution system
10. Control Panel

On-Site Hypochlorite Generation System Schematic

On-site Sodium Hypochlorite Generation

On-Site Generated Sodium Hypochlorite

Advantages	Disadvantages
• Very effective at typical pH	• Reacts with ammonia
• Proven & reliable	• Effectiveness decreases-high pH
• Often used for water & wastewater	• THM Formation
• Leaves a residual	• Leaves residual - potential declor
• Minimal concentration decay	• More complex process than bulk
• Low cost per pound	• Higher capital cost than bulk
Safety	**Safety**
• 0.8% liquid safer than bulk	• Generates H2 gas which is vented to atmosphere
• Deliver & store salt. Small quantity of chlorine on-site	• Larger volume required
• Not highly regulated	• Can cause eye irritation and burns
• Secondary containment not required	• pH lower than 12% hypochlorite

Chlorine Gas Feed Systems

Typical Chlorine Gas Feed System

Chlorine Gas System Highlights
• Delivered to site as gas in cylinders or containers or rail cars
• Stored on-site in original containers
• Chlorine removed form containers as liquid or gas
• Mixed with water prior to injection
• Automatic control valve controlled by residual analyzer or flow meter or compound loop

Gas Properties Comparisons

	Chlorine (Cl_2)	Sulfur Dioxide (SO_2)	Ammonia (NH_3)
Detectable Odor:	1.0 PPM	3 - 5 PPM	5 PPM
Throat Irritation:	5.0 PPM	8 - 12 PPM	400 PPM
Coughing:	20 PPM	20 PPM	1700 PPM
Dangerous in 30 - 60 Min.:	40 - 60 PPM	400 - 500 PPM	2500 - 4500 PPM
Specific Gravity (Air=1.0):	2.49:1	2.26:1	0.596:1
Color:	Yellow-Green	Colorless	Colorless
Solubility in Water (Lbs/Gal) :	0.1216	1.9	4.417
Expansion Factor (Liquid/Gas):	1:457	1:73	1:146

- Of the three gases, Chlorine (Cl_2) is the most commonly used in the water and wastewater industry, followed by Sulfur Dioxide (SO_2), and Ammonia (NH_3).

Recent Newspaper Headlines

If you have a gas leak, it will make the news

"Chlorine leak at Elm Bank contained"

"Chlorine gas leak controlled at water treatment plant"

"Chlorine Gas Leak in Arkansas Plant Prompts Evacuation of Workers June 28"

"Chlorine gas leak prompts late-night panic"

"Rogersville sewer plant gas leak contained"

"Chlorine gas leak at Wis. pool sickens 22"

"173 hospitalized in chlorine gas leak at Tyson plant"

Gas is Not Always Gas

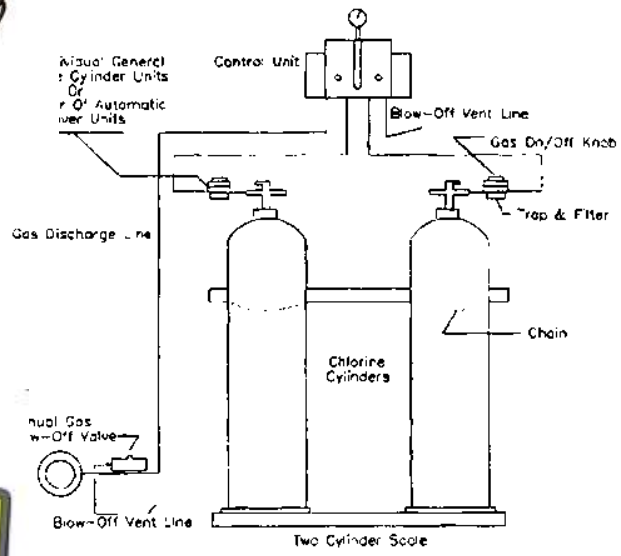
Tyson disputes findings on chlorine gas accident in 2011

Submitted by The City Wire Staff on Fri, 12/07/2012 - 9:20am

A language barrier is being blamed for the June 2011 chemical accident at Tyson Foods' Berry Street chicken processing plant in Springdale. Tyson Foods disputes the findings of a federal report by the Centers for Disease Control and Prevention's National Institute for Occupational Safety and Health report on the chlorine gas release that sickened nearly 200 workers, hospitalized 152 people last year. The CDC reported that the employee who poured sodium hypochlorite into a drum with residual acidic antimicrobial solution could only read Spanish, while the drum was labeled in English. The drum in question was a sample drum left near the sodium hypochlorite inadvertently, the CDC reported, and the acidic solution was normally stored in larger, square containers. The employee, who the CDC says required a Spanish translator for interviews, knew the chemical combination was dangerous but said he could not read the label. Tyson spokesman Worth Sparkman said Friday the worker responsible is not Hispanic and his primary language is English and had been properly trained about the hazardous chemicals.

Your Father's Chlorine Gas Safety

- Pressurized systems
- Danger Signs
- Ammonia bottle to find leaks
- Cylinders vertical, containers horizontal
- Chain cylinders together
- Keep cool and away from combustibles
- Eye wash



Modern Chlorine Gas Safety

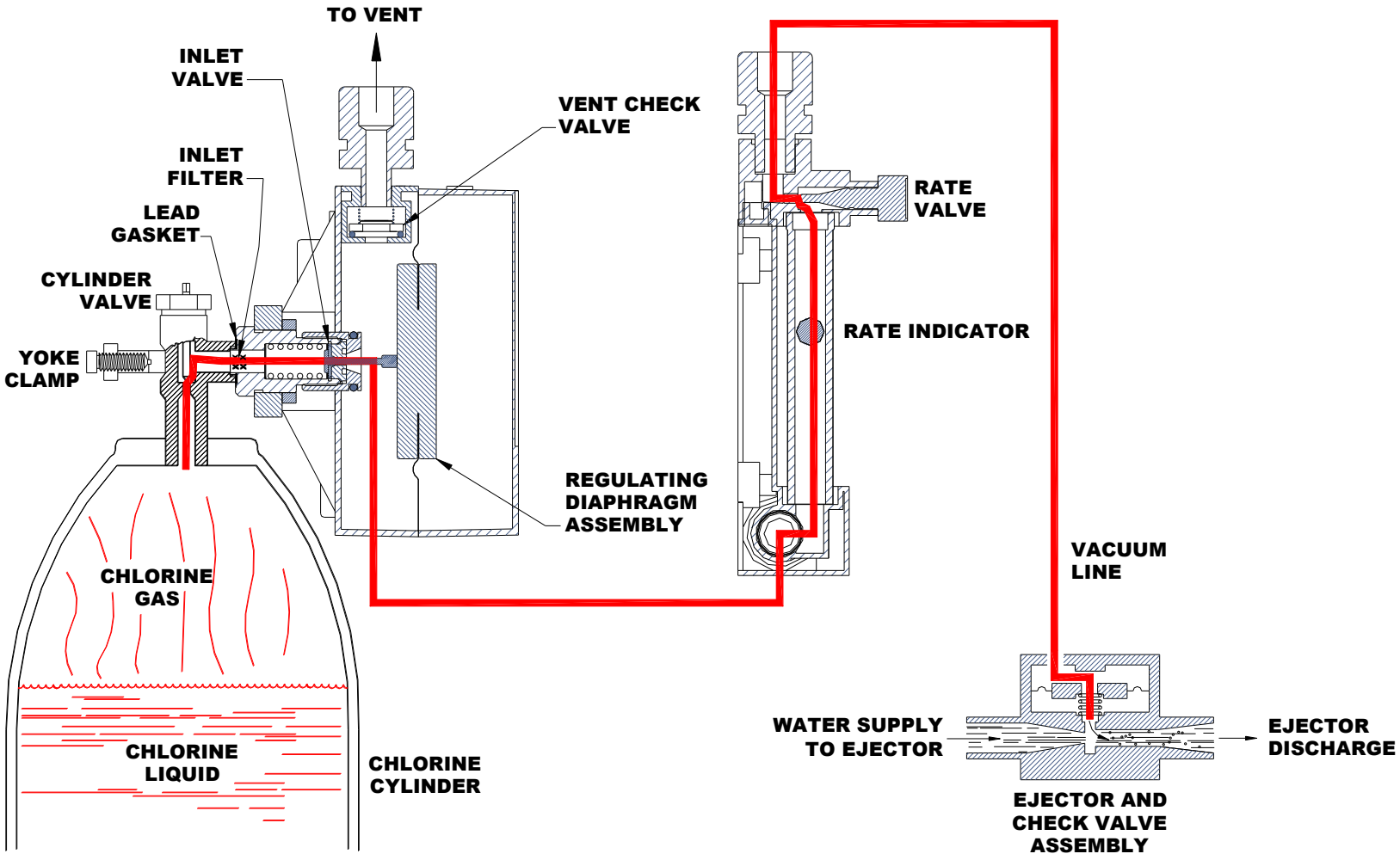
- Significant technical advances
- Residual analyzer with feedback loop
- Non-pressurized vacuum systems
- Chlorine gas leak detector
- Alarm Systems / SCADA
- Automatic shut off valve
- Vega scrubber system for small leaks
- Scrubber system for gas containment
- Positive pressure breathing apparatus
- Specialized chlorine safety kits
- Fully automated system to contain leaks
- Federal, state and local regulations
- Written Emergency Procedures



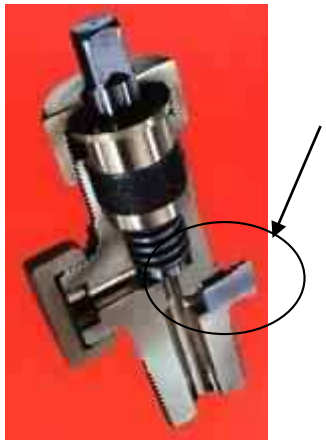


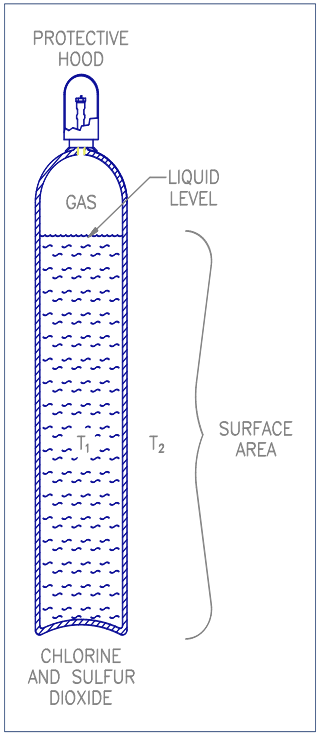



How Gas Vacuum Feeders Work



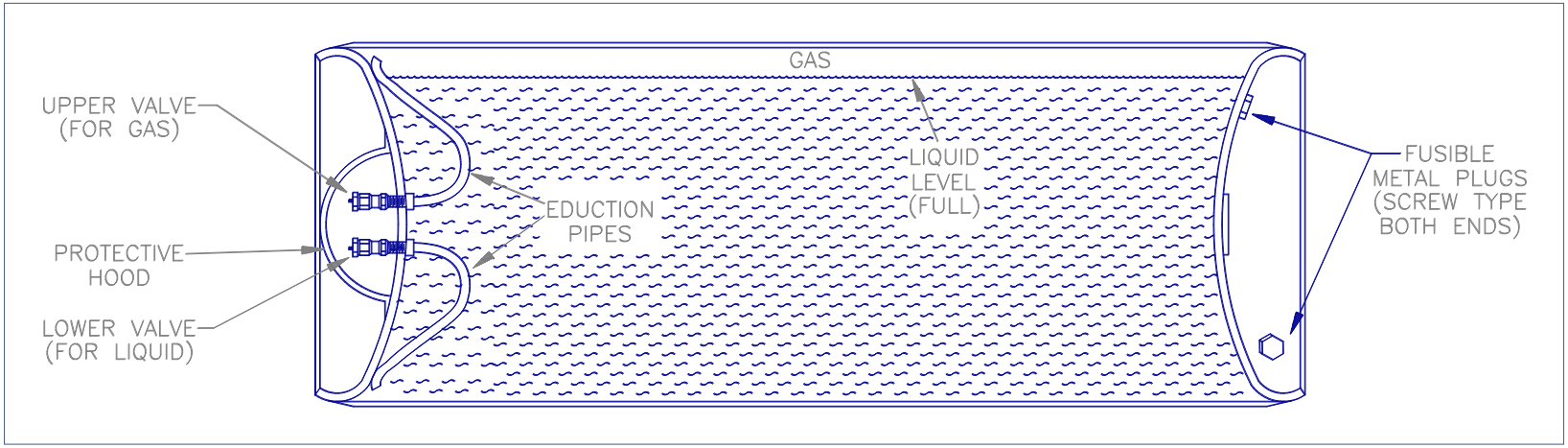
Chlorine Gas Storage Cylinders





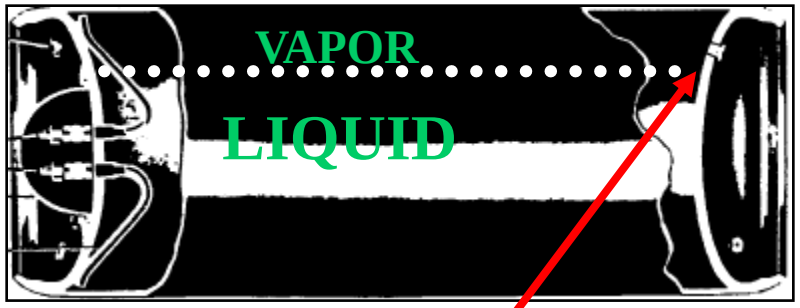
Chlorine Gas Cylinders
Capacity 1 to 150 lb
150 lb. predominate
One opening - valve connection
Standard cylinder valve with pressure relief device &fusible metal plug
Fusible plug melts at 158-165°F

One - Ton Containers

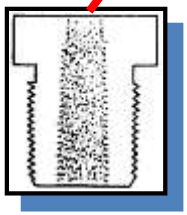


- Capacity - 2000 lb.
- Two identical valves
- Can use as gas feed (upper valve)
- Can use as liquid feed with vaporizer (lower valve)
- Six (6) fusible plugs - three (3) in each end, melt at 158-165°F

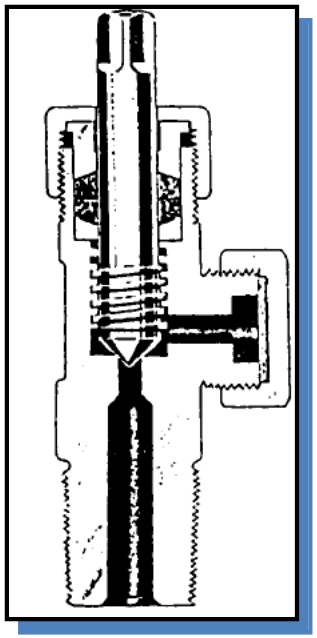
ONE-TON CONTAINER LEAK SOURCES



Sides and Heads of Container
Fusible Plugs and Feed Valves



Fusible Plug Core
Fusible Plug Threads



Valve Packing
Valve Seat
Valve Threads – In & Out & Nut
Broken Valve – usually at container thread

Chlorine Gas

Advantages	Disadvantages
• Very effective at typical pH	• Reacts with ammonia
• Proven & reliable	• Effectiveness decreases-high pH
• Widely used for water & wastewater	• THM Formation
• Leaves a residual	• Leaves residual - potential declor
• Low capital cost	
• Low cost per pound	
Safety	**Safety**
• Smaller room area required	• Gas phase dangers
• Widely used in industry	• Higher risk -catastrophic accident
• Significant advances in safety systems decrease risk	• Highly regulated – OSHA, NFPA.USEPA, USDHS –
	• More training & reporting required • Risk management Plan

Chlorine Containment Systems

Typical Chlorine Containment Systems for Ton Container

Chlorine Containment Highlights
Steel shell containment system
Available for 150 lb. cylinders or one ton containers
Put in place – anchor bolt to floor
Gas connections on outside
Hinged door seals shut

Chlorine Containment Systems -150# Cylinder

Typical 150 Lb Cylinder Containment System

Chlorine Containment Systems

Advantages	Disadvantages
Used for water or wastewater	Very expensive especially on large systems
Proven & reliable	One containment system required for each connection (cylinder or container)
Can reuse any chlorine captured	Extra time to change out cylinders or containers required
Does not shut feed system down upon leak	
Safety	**Safety**
• Effective for leaks at tank	• No protection from leaks in line
• No release of chlorine at all for leaks at tank	• Room not cleared of Chlorine
• Can enter room after leak	

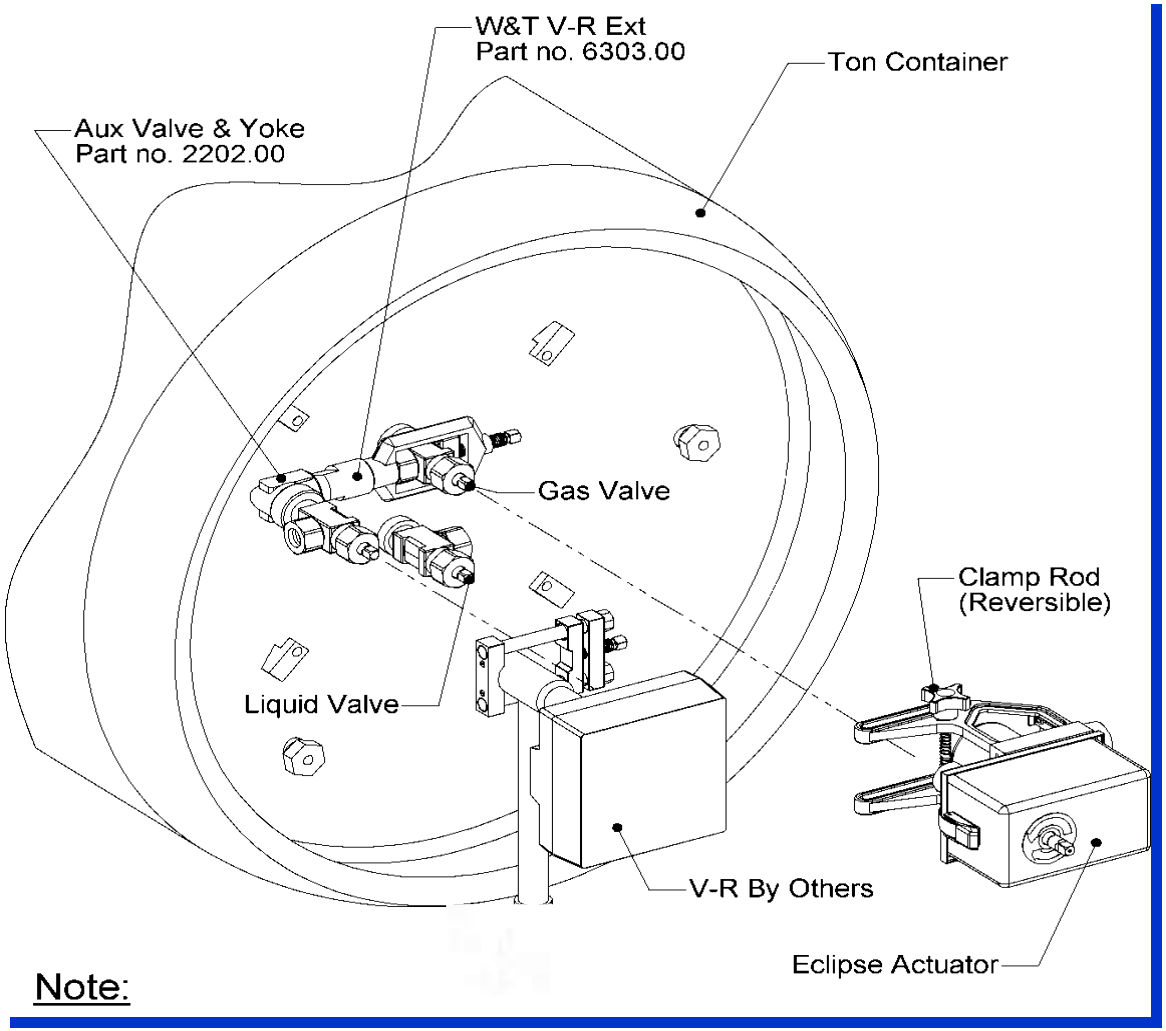
Automatic Valve Shut Off Systems

Automatic Actuator - 150 Lb Cylinder

Automatic Valve Shut off System Highlights
• Actuators mount directly to standard valve assemblies on ton containers and cylinders
• Fully automated system to automatically close the valves

• Can be activated by
  • Leak Detector
  • Panic or Emergency Button
  • SCADA and Fire Alarm System

Mounting the Emergency Actuator

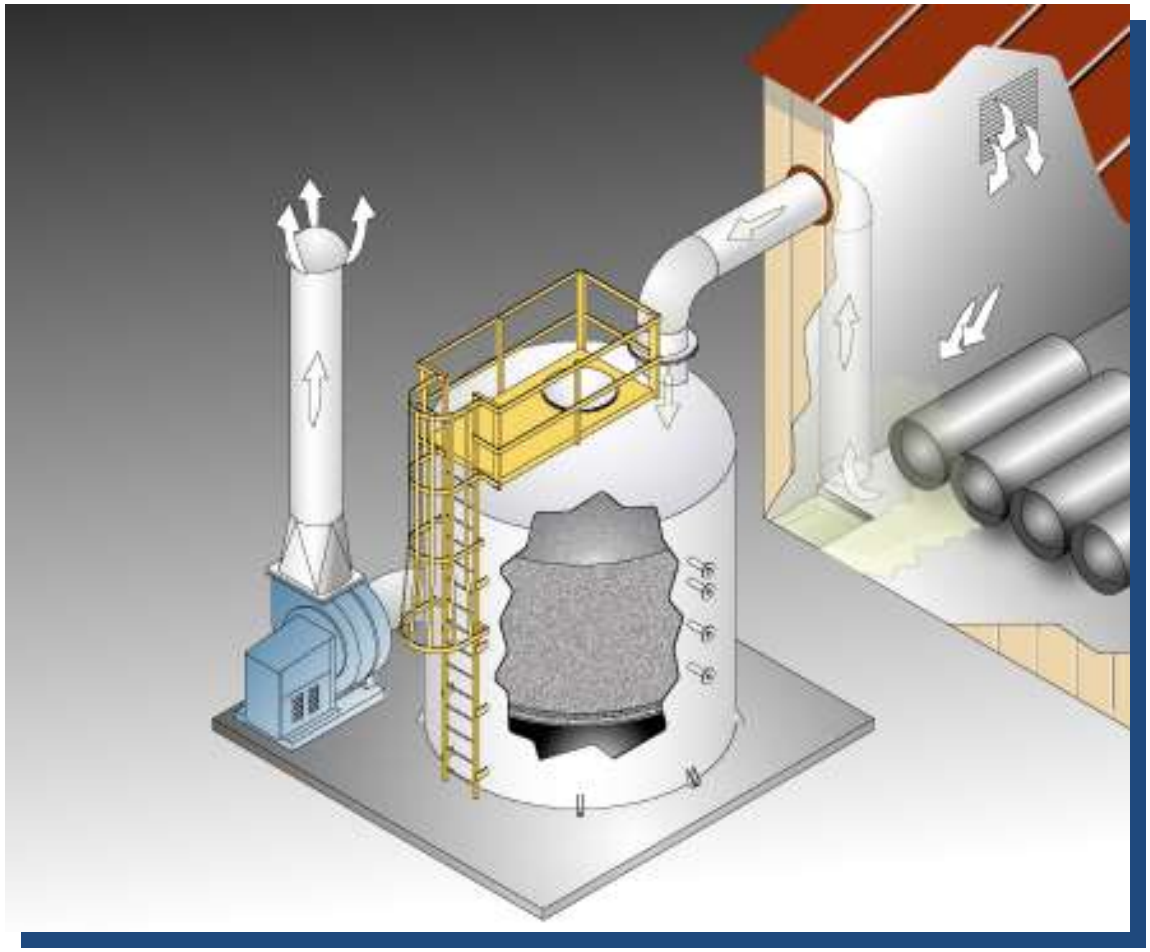


Multi Tank System Automatic Shutoff System

Automatic Valve Shutoff Systems

Advantages	Disadvantages
• Fully automatic system	• One system required for each tank in service
• Simple to operate and maintain	• Increases time to change out tank
• Available for cylinders and containers	
Safety	**Safety**
• Protect against line leaks	• Does not protect against plug or tank failure
• Completely automated	• Some gas leaks in room prior to automatic closure
• Battery operated – will operate in power outage	• Does not empty room of Chlorine

Emergency Chlorine Scrubbers



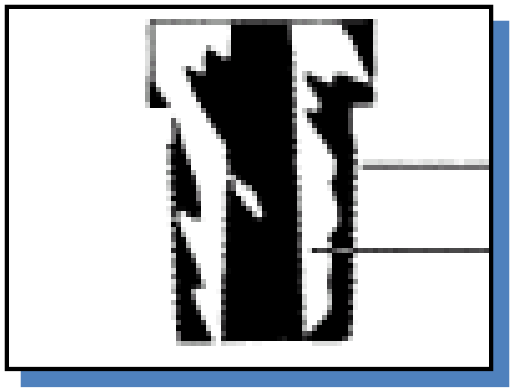
Typical Emergency Chlorine Scrubbers System

Emergency Chlorine Scrubber Highlights
Wet or Dry Scrubbers Available
Major Components: 1) Instrumentation for activation 2) Exhaust Blower, 3) Treatment System 4) Vents to Atmosphere
Fully automatic – Start and stop based
Chlorine Room Design Very Important

Emergency Chlorine Scrubber Design

FUSIBLE PLUG WORST-CASE

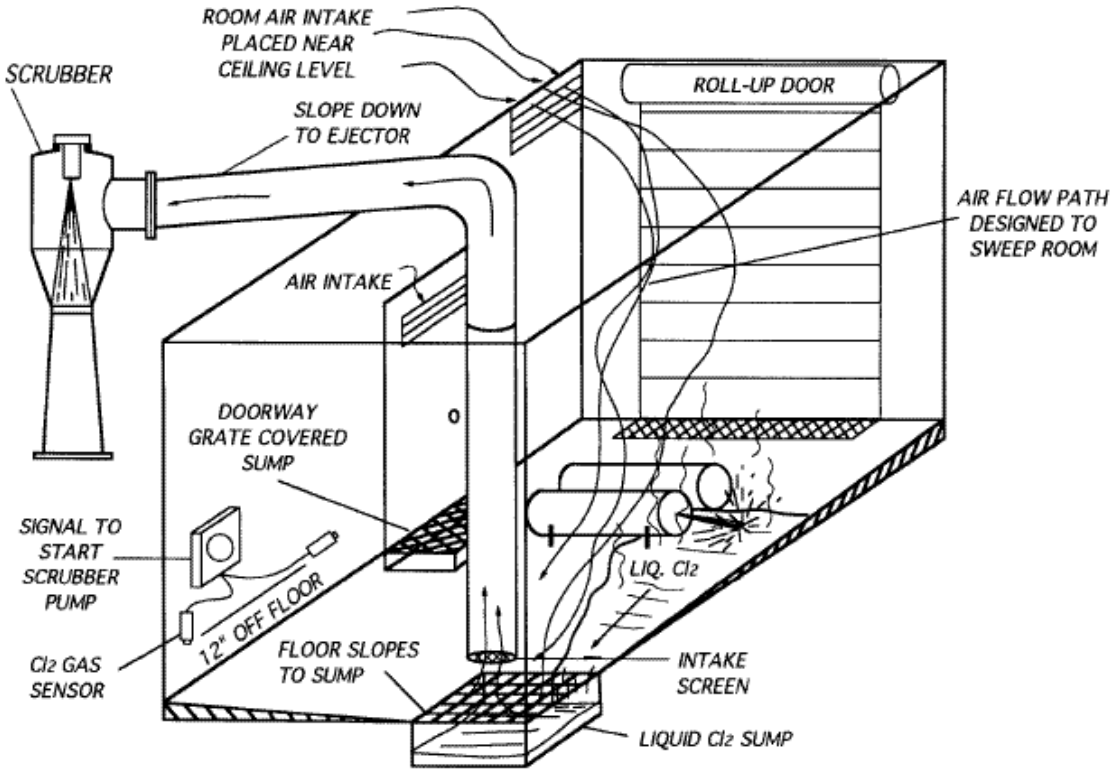
- Melts at approximately 160 ºF
- Cl_2 at 80 ºF = 117 psia vapor pressure
- Cl_2 at 160 ºF = 325 psia vapor pressure
- 0.34” diameter orifice = 437 lbs/min at 160 ºF
- Ton Container liquid plug empties ~ 5 minutes
- Design for release of 5 PPM chlorine



Keep room at negative pressure

- 437 lbs/min = 2380 scfm
- Trend is to specify 3,000 scfm systems for one-ton containers.
- 150 lb Cylinders: Gas Leak Rate is 20 lbs/min = 110 scfm
- Scrubber Rate: Typically 250 cfm

Gas Chlorine Room Containment Design



Typical Gas Chlorine Room

Room Containment Design Considerations
Chlorine gas is heavier than air
Must Contain gas and Liquid Chlorine
Pick up duct should be 12-18 inches above floor
Slope floors – confined corner sump
Step down doorways, gratings covered
Flood room to check for liquid escape routes
Gas Detector 12 inches off floor
Dual Rooms – Dual Intakes

Emergency Chlorine Scrubbers - Types

Types of Emergency Chlorine Scrubber Systems

1. **Wet Packed Emergency Chlorine Scrubber Systems**
   - Utilizes caustic to neutralize chlorine
   - $Cl_2 + 2\ NaOH \Rightarrow NaOCl + NaCl + H_2O + 628\ BTU/lb\ Cl_2(g)$
   - Upwards airflow, downwards chemical flow
   - Produces hazardous waste material

2. **Wet Pack-less Emergency Chlorine Scrubber Systems**
   - Same chemical reaction as packed tower
   - $Cl_2 + 2\ NaOH \Rightarrow NaOCl + NaCl + H_2O + 628\ BTU/lb\ Cl_2(g)$
   - Utilizes ejector venturi
   - Produces hazardous waste material

EJECTOR VENTURI SCRUBBER

SCRUBBING LIQUID INLET
Water or other liquid under pressure.

SPRAY (MOTIVE) NOZZLE
Breaks the scrubbing liquid into a high velocity spray for maximum entrainment of gases and impaction of particulates.

GAS INLET
Contaminated gases are drawn into the ejector by the action of the spray liquid.

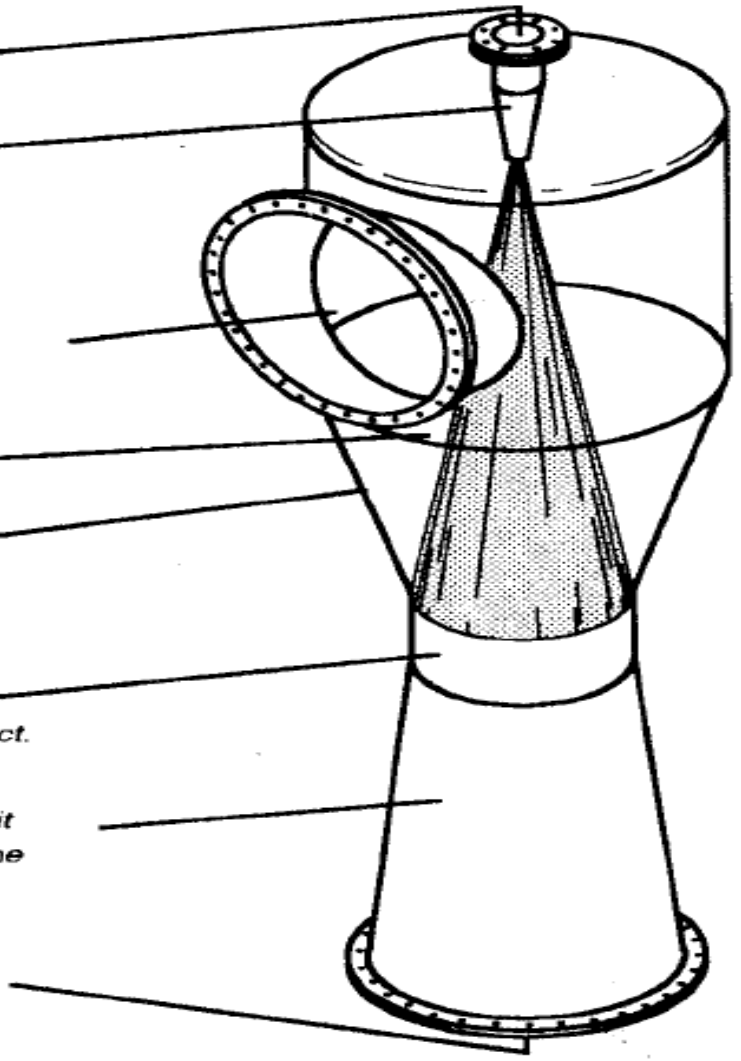
BODY
Expanded chamber for the uniform distribution of gases.

CONVERGING SECTION
Designed to reduce internal pressure losses and assure uniform distribution of gases.

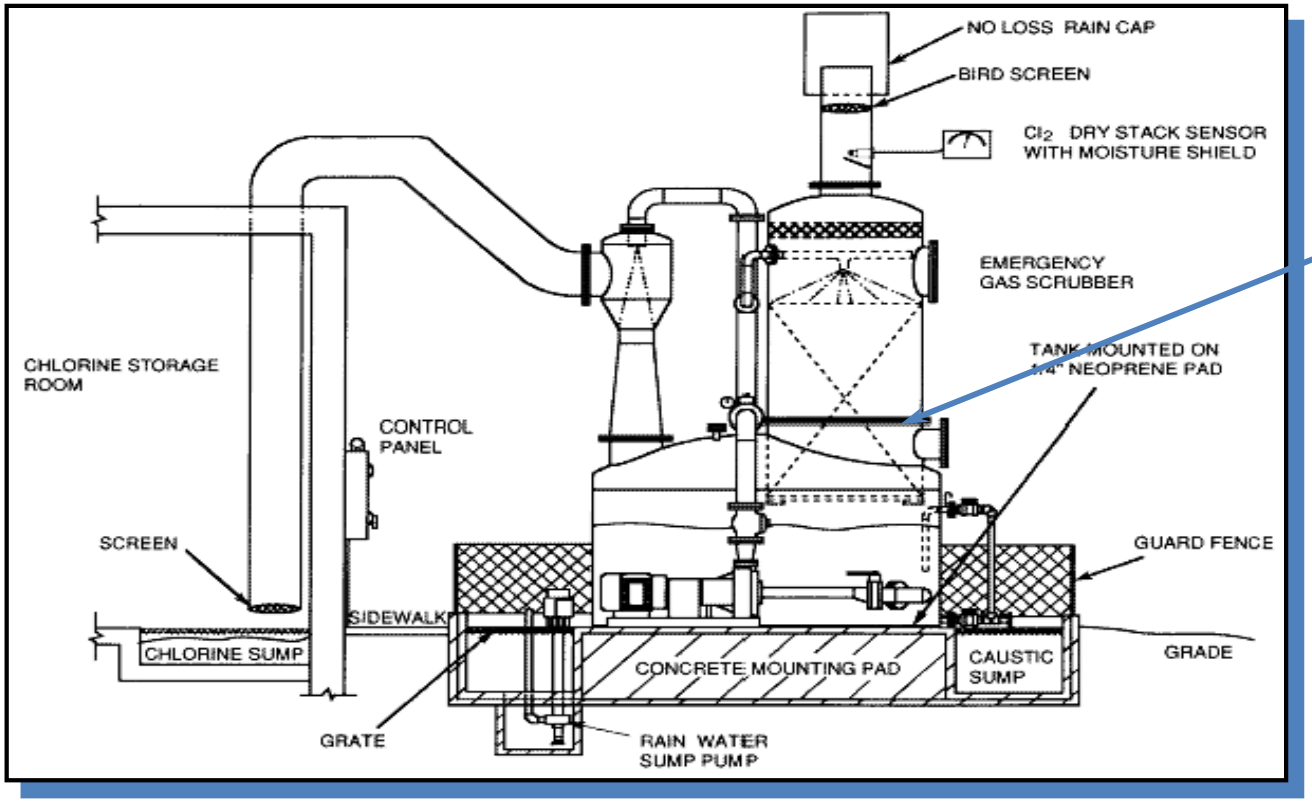
VENTURI THROAT
Designed for maximum gas-liquid contact.

DIVERGING SECTION
Designed for the maximum regain of unit pressure and for the agglomeration of the scrubbing liquid spray.

GAS DISCHARGE
Cleaned gases and scrubbing liquid discharge to a gas-liquid separator.



Emergency Chlorine Scrubbers



High Performance Packing Media

Typical Wet Ejector Venturi / Packed Tower

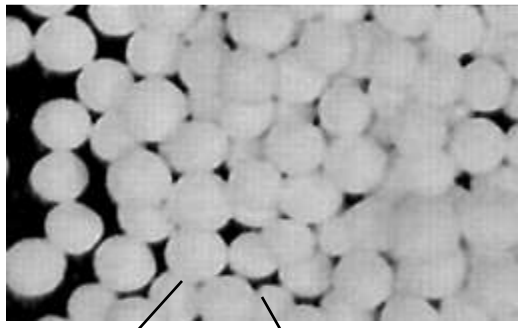
Emergency Chlorine Scrubbers - Types

3. Dry Emergency Chlorine Scrubber Systems

- Latest innovation in emergency scrubbers
- Utilize dry 4 mm impregnated activated alumina beads
- **Cl_2 + STS media $\Rightarrow$ NaCl (Salt)**
  - No liquid chemicals required –media lasts forever
  - Produces non-hazardous waste material – landfill
  - Automatic operation - minimum maintenance

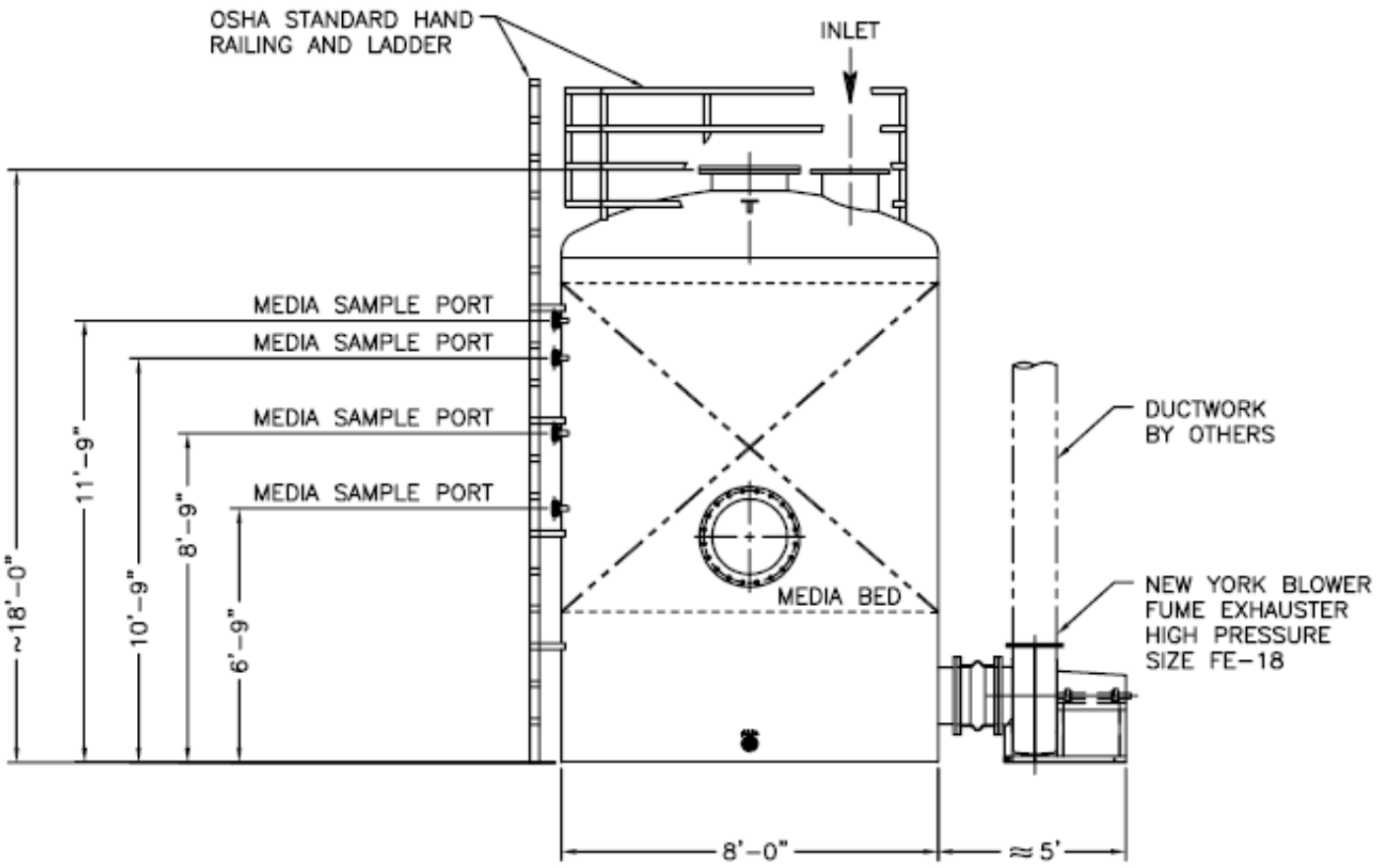
Dry Media Scrubber Features & Benefits as Compared to Traditional Caustic Scrubbers

- No chemical maintenance
- New as well as exhausted media is non-hazardous
- One moving part - blower
- No chemical pumps
- Chemical leak containment is not required
- No heaters required in cold climates
- Safe
- User-friendly
- Dependable operation
- Tested and certified
- Low cost of ownership

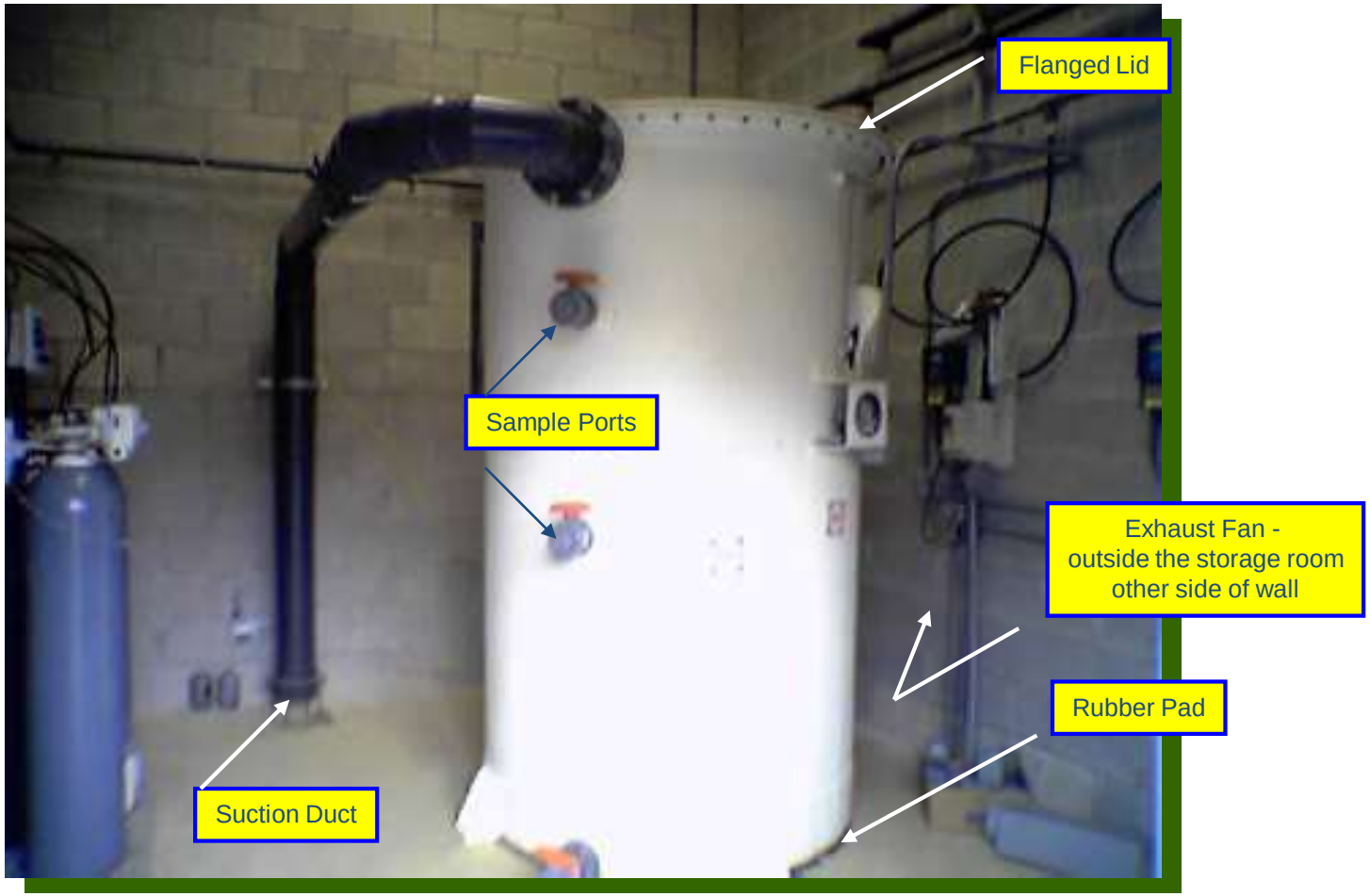


Type "STS" 4 mm impregnated activated alumina beads

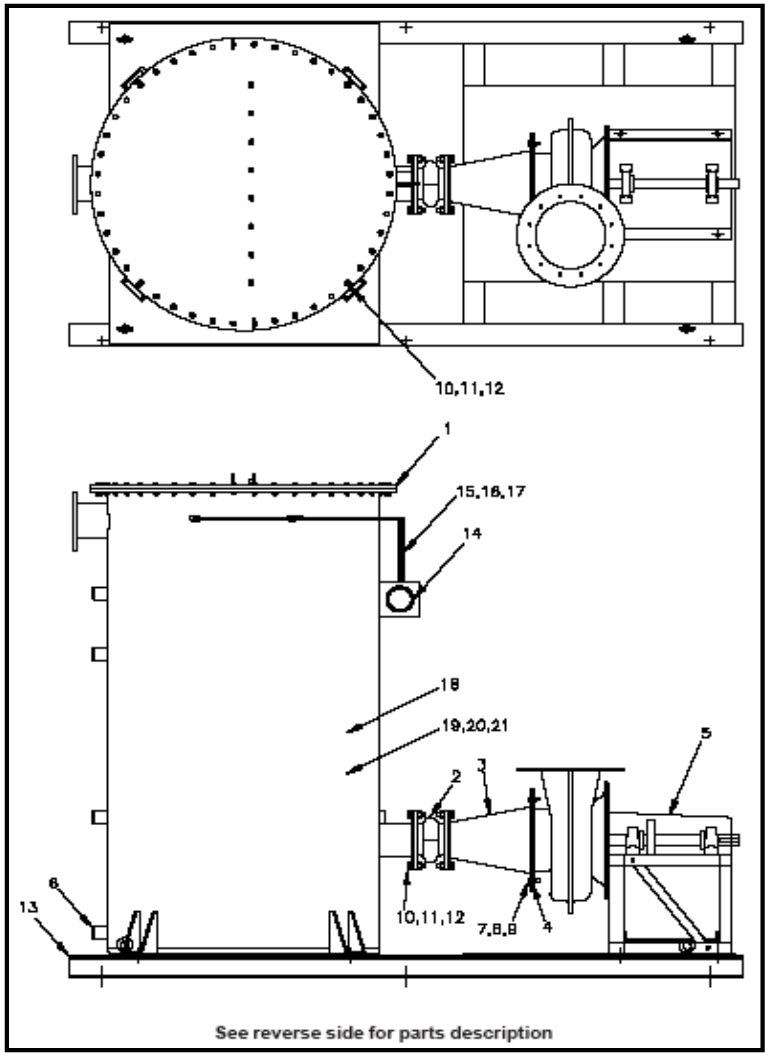
Dry Media Scrubber (one ton container)



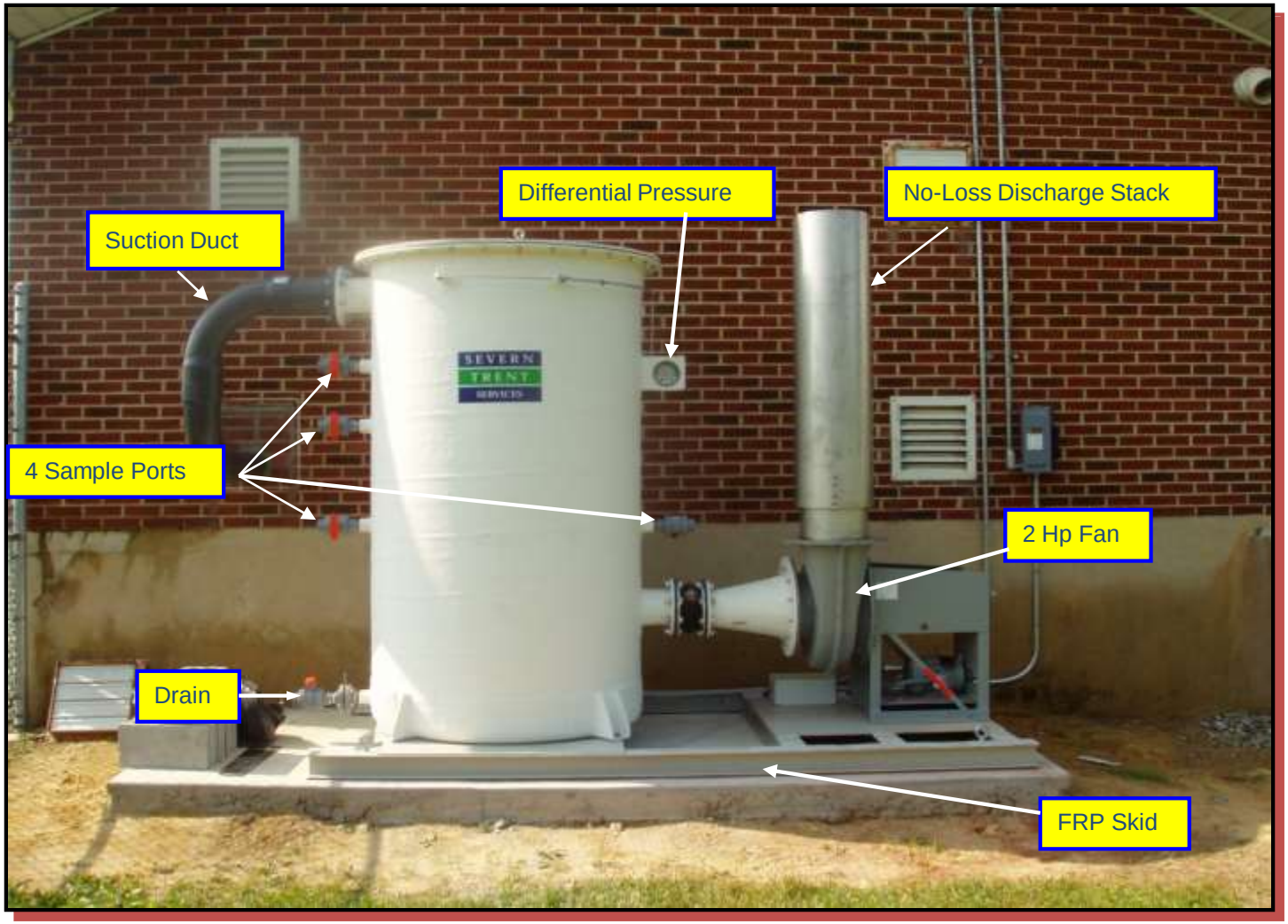
150 # Cylinder Scrubber Installed Inside Storage Room



Skid Mounted Dry Scrubber for 150 Lb Cylinder



Dry Scrubber Skidded Assembly



Scrubber Dry Media Refill

VENT EXHAUST GAS ARRESTOR

- Treat vacuum regulator vent line
- Reduces room corrosion and outside releases
- Five gallon HDPE disposable bucket
- Dimensions are 10” Square x 15” Tall
- Passive – No fans required
- Pressure loss is less than same length of tubing
- Weighs 35 pounds with ‘STS’ 4 mm media beads
- Scrubs over 3 pounds of chlorine
- Media is non-toxic in fresh or spent forms
- Stackable for gas-side series mounting
- Visible Exhaustion Indicating Strips

Emergency Chlorine Dry Scrubbers

Advantages	Disadvantages
• Fully automatic systems	• Like insurance – often are never used because not needed
• Dry media scrubbers require minimum maintenance	• Room design considerations
• Medium capital cost	
• Cost benefit to using gas significant	
Safety	Safety
• Suggested by Ten States	• Cannot enter room without safety equipment until cleared
• Reduce liability significantly	
• Proven safe and reliable • Completely empties room of Chlorine	

Safety Option Matrix – Cost vs Benefit

Safety Option	Description	Capital Cost	O&M Costs	Cost of Chlorine	Room Coverage	Ease of Operation	Operator Safety
1	Gas - Auto Value	Low	Low	Low	Valve Only	Easy	Medium
2	Gas – Container System	High	Low	Low	Cylinder	Medium	Medium
3	Gas- Wet Scrubber	High	High	Low	Full Room	Medium	High
4	Gas - Dry Scrubber	High	Low	Low	Full Room	Easy	High
5	Commercial Sodium Hypochlorite	Low	Low	High	None	Easy	High
6	On-site Hypochlorite Generation	High	Medium	Medium	None	Easy	High

Summary

- Chlorine gas, commercial hypochlorite and on-site hypochlorite are all very effective methods of disinfecting wastewater
- Commercial hypochlorite avoids many of the safety issues associated with chlorine gas but the cost is significantly more per pound of chlorine and has safety issues of it's own
- On-Site hypochlorite generation also avoids many of the safety issues associated with chlorine gas but with a lower cost per pound of chlorine than commercial hypochlorite
- There are various methods to improve chlorine gas safety including containment systems, automatic shutoff valves and emergency scrubbers
- Dry media emergency scrubbers have significantly less operation and maintenance costs compared to wet scrubbers
- A life cycle cost analysis should be completed to properly assess the costs and benefits of each safety solution

Questions?

Contact:
Gary M. Lohse, P.E.
Technical Sales Manager - Disinfection
De Nora Water Technologies
3000 Advance Lane
Colmar, Pa 18915
Cell: (215) 859 - 3814
Email: gary.lohse@denora.com