CHLORINATION

Disinfection and Oxidation

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Chlorination/Disinfection Glossary

1. Bacteria: living single-celled microscopic organism having both characteristics of plant & animals; often useful but may also cause disease

2. Chloramines: chemical compounds formed from the reaction of chlorine with ammonia (NH_3); also called combined chlorine

3. Chlorination: application of chlorine to water generally for the purpose of disinfection, but also for other purposes such as odor control

Chlorination/Disinfection Glossary

4. Coliform Bacteria: bacteria that is used as an indicator of pollution; divided into two groups - Total Coliform (TC) & Fecal Coliform (E. coli. - found in the intestinal track of warm-blooded animals); FC is an indication of pollution

5. Chlorine Demand: the difference between the amount of Cl2 added to H2O (Cl2 dose) and the amount of Cl2 remaining after a period of contact time (Cl2 residual)

   Cl2 demand (mg/L) = Cl2 dose (mg/L) – Cl2 residual (mg/L)

Chlorination/Disinfection Glossary

6. Disinfection: the addition of chlorine to water in order to kill or inactivate disease causing organisms; the effectiveness of disinfection is measured using the Coliform test

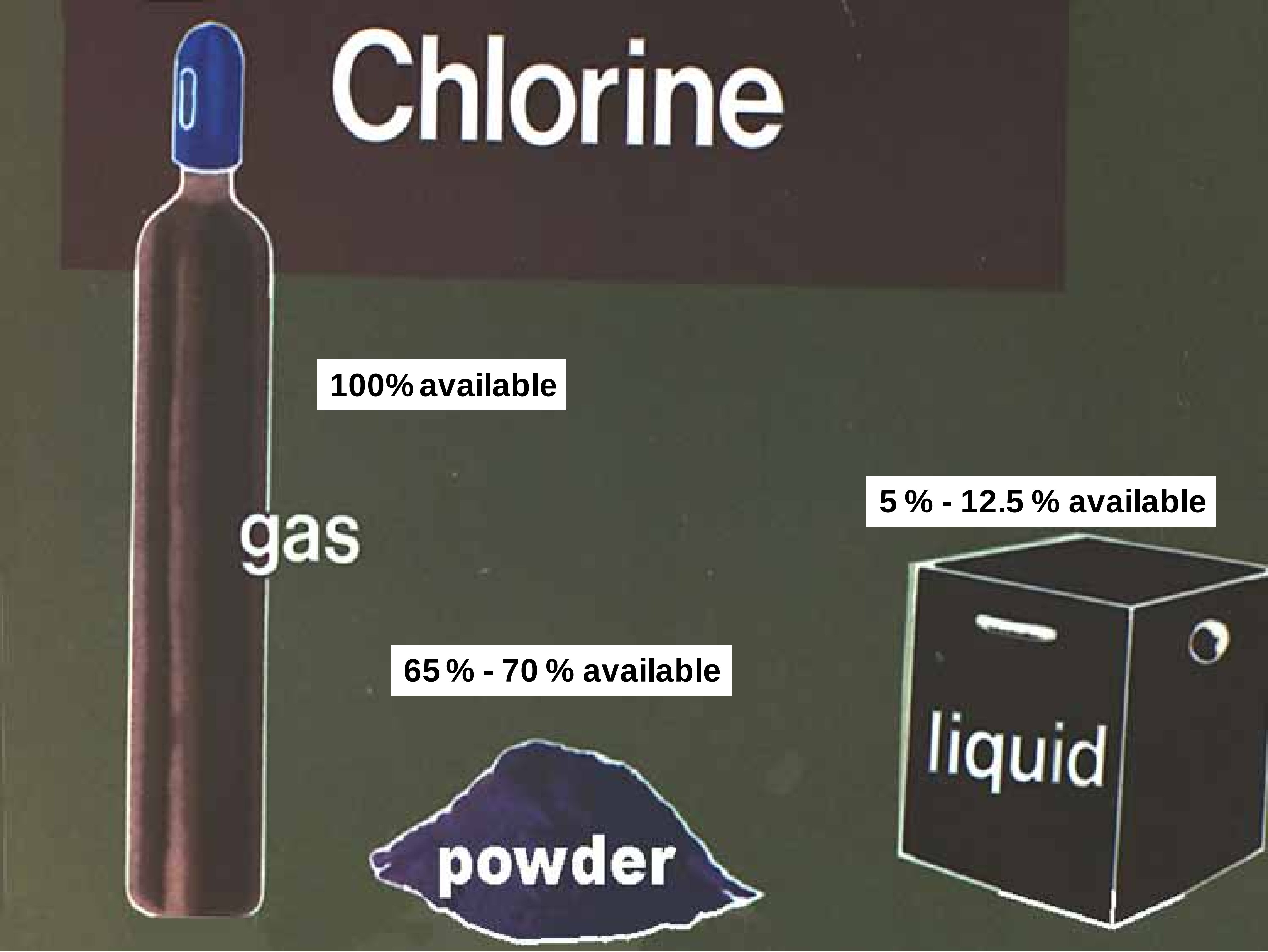
7. Free available Cl_2: that portion of total Cl_2 residual not combined with ammonia (NH_3); free Cl_2 includes Hypochlorous acid (HOCL) and Hypochlorite ion (OCL-)

8. Pathogens: disease causing organisms such as bacteria, viruses, & protozoa; examples are typhoid, cholera, dysentery, poliomyelitis, giardiosis & cryptosporidiosis

9. Sterilization: to be free from all living organisms

Introduction to Chlorine (Cl_2)

- Disease causing organisms can be found in surface water and some in ground water, some can be removed by preliminary, primary and secondary treatments processes. But not all are removed.
- The addition of a chemical disinfectant is necessary if a water treatment processes is to meet the coliform MCL, preventing any water borne diseases.
- Cl_2, due to it relatively low cost & ease with which it be obtained is the most commonly used chemical for this purpose.
- Chlorine is available in 3 forms:
  1. Chlorine Gas
  2. Calcium or Sodium Hypochlorite solution
  3. Calcium or Sodium Hypochlorite powder (HTH)


Chlorine
100% available
gas
5 % - 12.5 % available
65 % - 70 % available
liquid
powder

Chlorine Strength, Storage and Aging

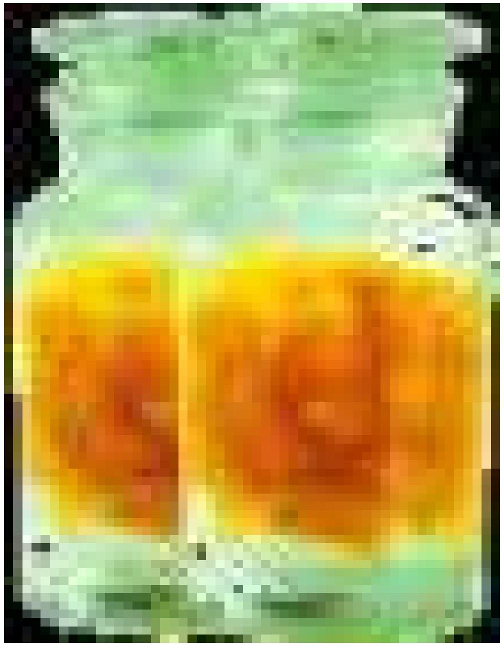
Sodium Hypochlorite Concentrations vs Specific Gravity
(USA BlueBook #119, page 612)

Trade %	Sp Gr	Trade %	Sp Gr
1.0	1.020	9.0	1.129
2.0	1.034	10.0	1.142
3.0	1.048	11.0	1.155
4.0	1.062	12.0	1.168
5.0	1.076	13.0	1.181
6.0	1.089	14.0	1.193
7.0	1.103	15.0	1.206
8.0	1.116		

Properties of Cl_2

Cl_2 Gas

- Amber-Yellow in color
- Containing 99.5% pure Cl_2
- Has a penetrating and distinctive odor
- Slightly heavier than water
- 2½ heavier than air
- Has very high coefficient of expansion; i.e., a temperature change from 50 F to 85 F will cause a volume increase from 84% to 89%
- No Cl_2 cylinder should be filled over 85% capacity (see above characteristic)
- One liter of liquid Cl_2 can evaporate to produce 450 liters Cl_2 gas
- Cl_2 is non-flammable & non-explosive but it will support combustion



The Reaction of Chlorine with H_2O

- Cl_2 + H_2O → HOCl + HCl

  chlorine + water → Hypochlorous acid + hydrochloric acid
- HOCl is one of two free available Cl_2 forms & due to the ease which it penetrates into & kills bacteria it is the most effective form of Cl_2 for disinfecting.
- However some of the HOCl dissociates to form a weak acid.
- HOCl → H^+ + OCl^-

  Hypochlorous acid → hydrogen + hypochlorite ion
- Hypochlorite ion the second type of free available Cl_2 residual and is a relatively poor disinfectant, primarily because of its inability to penetrate into the bacteria.
- It also dissociates, forming hydrogen which neutralizes alkalinity or lowers the pH.

The effectiveness of Cl_2 is based on 5 important factors

1. pH
2. Temperature
3. Concentration
4. Contact time
5. Demand

The Effectiveness of Cl_2 Based on pH

1. pH strongly influences the ratio of HOCl to OCl-
   - Low pH values favor the formation of HOCl, the more effective free residual
   - High pH values favor the formation of OCl-, the less effective free residual
   - As pH increases from 7 to 10 the OCl- begins to predominate & the time required for free residual to effectively disinfect increases

The Effectiveness of Cl_2 Based on Temperature

2. Temperature
   - The higher the temperature the more effective chlorination
   - Lower temps slightly favor the formation of HOCl
   - Lower temps allow Cl2 residuals to persist somewhat longer
   - chemical & biological reaction rates increase as the temperature increases making Cl2 more effective at higher temps

The Effectiveness of Cl_2 Based on Dose and Contact Time

3. Concentration of Cl_2
    - time dependent for different organisms
    - providing conditions remain constant, as the contact time is increased, less concentration is needed to accomplish the same level of disinfection
    - as dosage concentration is increased contact time can be decreased

4. Contact Time
    - the destruction or inactivation of an organism is directly related to the contact time

The effectiveness of Cl_2 Based on Demand

5. The inorganic & organic material in raw and finished water take part in the reactions with Cl_2
   - Reaction with Ammonia (NH_3) is one of the most common
     - NH_3 can result from decaying vegetation or from domestic & industrial waste
     - Cl_2 reacts with NH_3 to form chloramines, or combined chlorine residual
   - Uses the chlorine that would otherwise be available for disinfection
   - Other demand-causing reactions include Fe, Mn, S compounds, turbidity, TOC/DOC, biofilm

Formation of Chloramines

- NH_3 + $HOCl$ → <u>*NH_2Cl*</u> + H_2O

Ammonia + Hypochlorous acid→ <u>*Monochloramine*</u> + Water

- NH_2Cl + $HOCl$ → <u>*$NHCl_2$*</u> + H_2O

Monochloramine + Hypochlorous acid→ <u>*Dichloramine*</u> + Water

- $NHCl_2$ + $HOCl$ → <u>*NCl_3*</u> + H_2O

Dichloramine + Hypochlorous acid → <u>*Trichloramine*</u> + Water

Formation of Chloramines

The formation of chloramine compounds depends on the pH of the water & the presence of ammonia.

- Chloramines are a combined available chlorine which is a less active oxidizing agent than free available chlorine, but it has a longer lasting residual

- 25 times the amount of *combined available chlorine* is needed to be as effective as *free available chlorine*

Mechanism of Disinfection

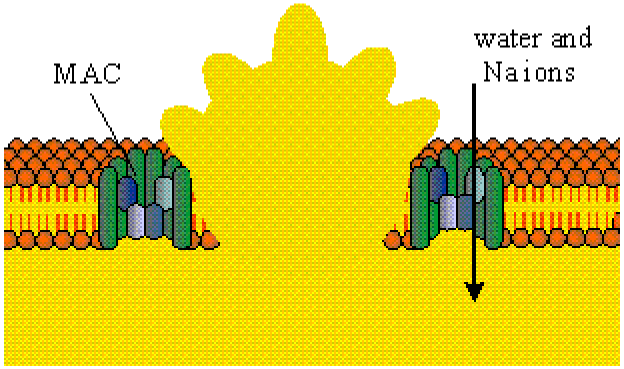
Four mechanisms have been proposed to explain the action of disinfectants:

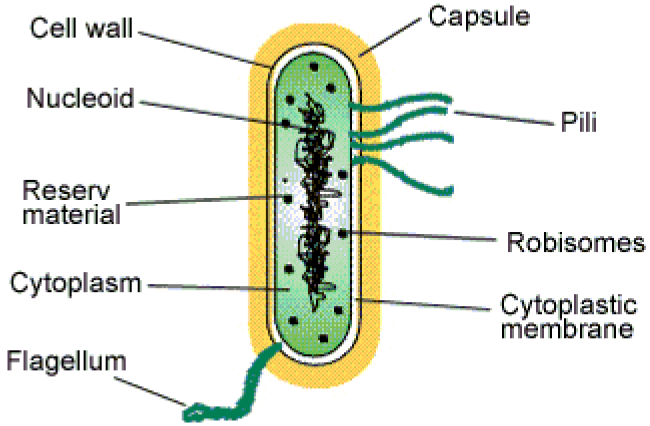
- (1) **Damage to the cell wall** Damage or destruction of the cell wall will result in cell disintegration and death. Some agents, such as penicillin, inhibit the synthesis of the bacteria cell wall.

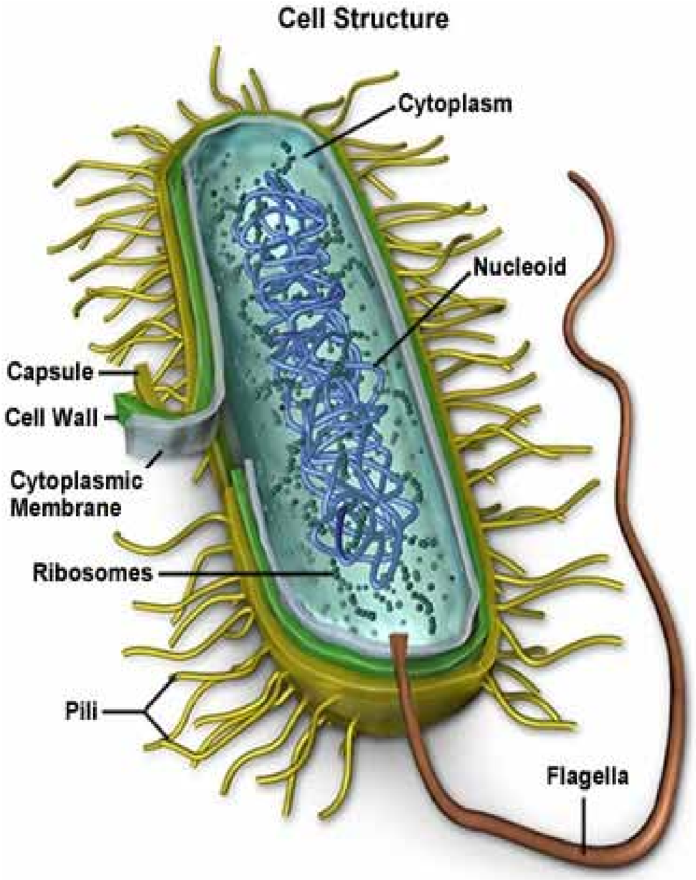
- (2) **Alteration of cell permeability** Agents such as phenolic compounds and detergents alter the permeability of the cytoplasmic membrane. These substances destroy the selective permeability of the membrane and allow vital nutrients, such as N and P, to escape.) Similar to alcohols

- (3) **Alteration of the colloidal nature of the protoplasm** Heat, radiation, and highly acidic or alkaline agents alter the colloidal nature of the protoplasm. Heat will coagulate the cell protein and acids or bases will denature proteins, producing a lethal effect.

- (4) **Inhibition of enzyme activity** Oxidizing agents such as chlorine can alter the chemical arrangements of enzymes and deactivate the enzymes.


MAC
water and
Naions


Cell wall
Capsule
Nucleoid
Pili
Reserv
material
Robisomes
Cytoplasm
Cytoplastic
membrane
Flagellum


Cell Structure
Cytoplasm
Nucleoid
Capsule
Cell Wall
Cytoplasmic
Membrane
Ribosomes
Pili
Flagella

Breakpoint Chlorination

Chlorine Demand

What is added		What is used		What remains
Dosage	–	**Demand**	=	**Residual**

Organics

Microorganisms

Ammonia-Nitrogen

Nitrate

Iron

Silt

Reaction with Iron (Fe)

- Iron is an undesirable element in water often found in GW, is easily oxidized and precipitated by chlorine, causes red strains, red water and can plug well screens; aeration may be an effective treatment

- The chemistry:

$$2Fe(HCO_3)_2 + Cl_2 + Ca(HCO_3)_2 \rightarrow 2Fe(OH)_3\downarrow + CaCl_2 + 6CO_2$$

ferrous carbonate	chlorine	calcium bicarbonate	ferric hydroxide	calcium chlorite	carbon dioxide

- Ferric hydroxide precipitates almost immediately to form a fluffy, rust-color sludge

- Calcium bicarbonate represents the alkalinity in the water

- Each mg/L of iron removed requires 0.64 mg/L of Cl_2

Reaction with Manganese (Mn)

- It’s an undesirable constituent often found in ground water supplies
- Causes brown or black water, stains on fixtures
- Normally in the form of a soluble salt, manganous sulfate ($MnSO_4$)
- Cl_2 forms the precipitate manganese dioxide (MnO_2)
- Reaction time is relatively slow, about 2 hours
- **DO NOT** want this to occur in Distribution System

Reaction with Manganese (Mn)

- Each mg/L of Mn removed requires 1.3 mg/L of free available Cl_2. Combined available Cl_2 is not effective.

$$MnSO_4 + Cl_2 + 4NaOH \rightarrow MnO_2\downarrow + 2NaCl + Na_2SO_4 + 2H_2O$$

Manganous sulfate	Chlorine	Sodium hydroxide	Manganese dioxide	Sodium chlorite	Sodium sulfate	Water

Reaction with Hydrogen Sulfide (H_2S)

- H_2S is found in ground water supplies and rarely in surface waters
- At 0.05 mg/L H_2S can give water an unpleasant taste
- At 0.5 mg/L H_2S gives off an odor of rotten eggs
- At > 0.1 – 0.2 mg/L H2S can be fatal in minutes if inhaled
- At concentrations > 4.3 % by volume in the air, H_2S is flammable

Reaction with Hydrogen Sulfide (H_2S)

When Cl_2 is used to remove H_2S, one of two reactions can occur, depending on Cl_2 dosage & pH values:

1. 2.2mg/L Cl_2 @ pH 6.4 will convert 1mg/L of H_2S to sulfur, forming a fine colloidal particle that causes a milky-blue turbidity.

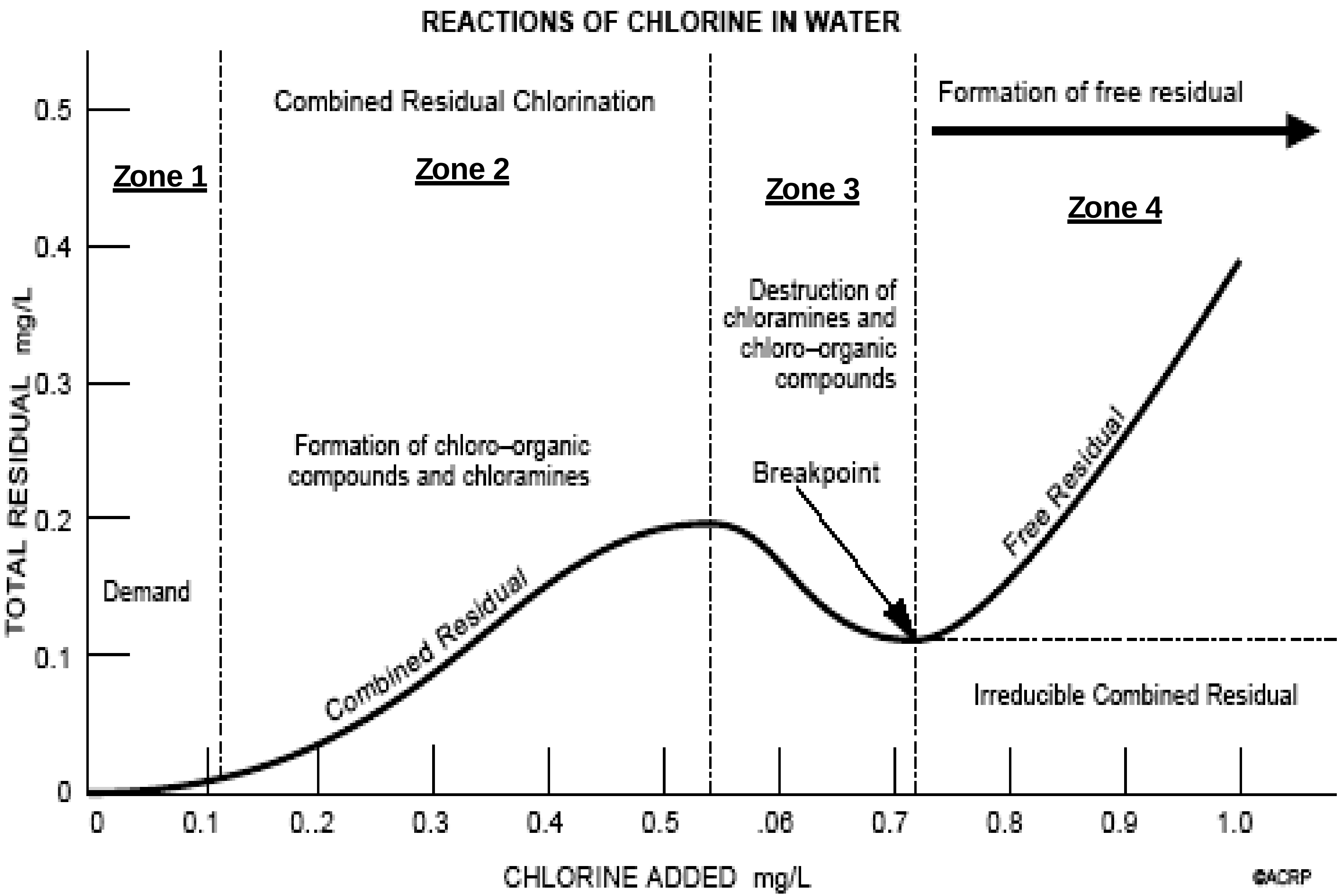
$$Cl_2 + H_2S \rightarrow 2HCl + S$$

chlorine + hydrogen sulfide → hydrochloric acid + sulfur

2. The second reaction is operationally preferred.
   - 8.9 mg/L of Cl_2 @ pH 6.4 will convert 1 mg/L of H_2S to sulfuric acid.

$$4Cl_2 + H_2S + 4H_2O \rightarrow 8HCl + H_2SO_4$$

Chlorine + hydrogen sulfide + water → hydrochloric acid + Sulfuric acid



Breakpoint Chlorination Curve

Taste & Odor Thresholds

Compound	Taste/Odor Threshold
Free HOCl	20 mg/L
Monochloramine	5 mg/L
Dichloramine	0.8 mg/L
Nitrogen trichloride	0.02 mg/L

Operational Considerations

- There may be times when chlorine taste and odor complaints become a problem in the distribution system

- This problem is generally related to high combined residuals and inadequate free residual

- The solution to this problem may be to increase the chlorine dose rate to get past the breakpoint

Operational Considerations

- As a rule of thumb, the free residual should be at least 85% of the total residual in order to prevent chlorine taste and odor problems and insure an adequate free residual for effective disinfection

- A sudden increase in combined chlorine may signify the presence of organic contaminants such as dirt and debris

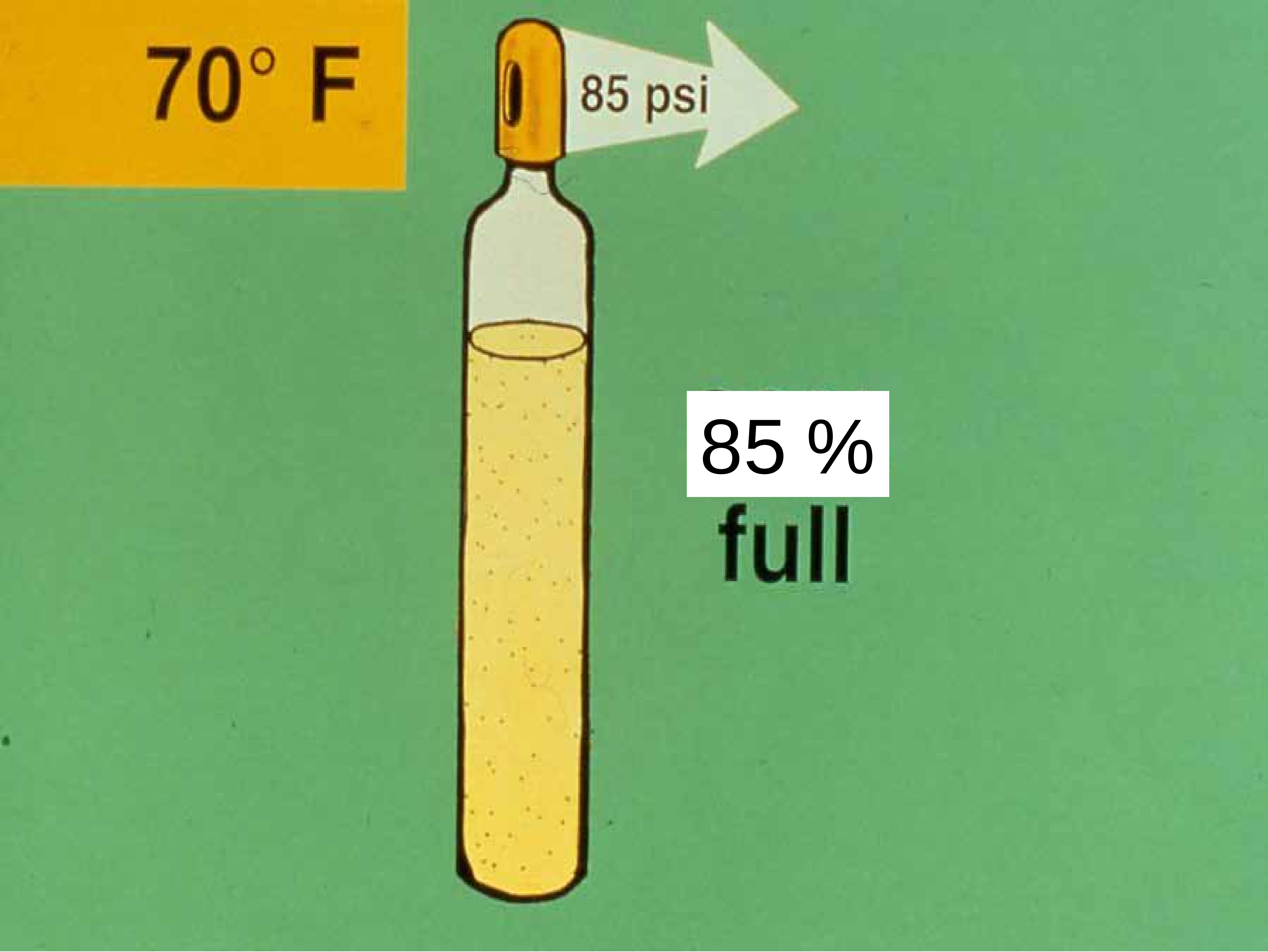
- The sudden presence of organic material may result from a line break, loss of pressure or unprotected cross connection such as lawn irrigation, etc.

Chlorine Residual Testing
DPD Colorimetric

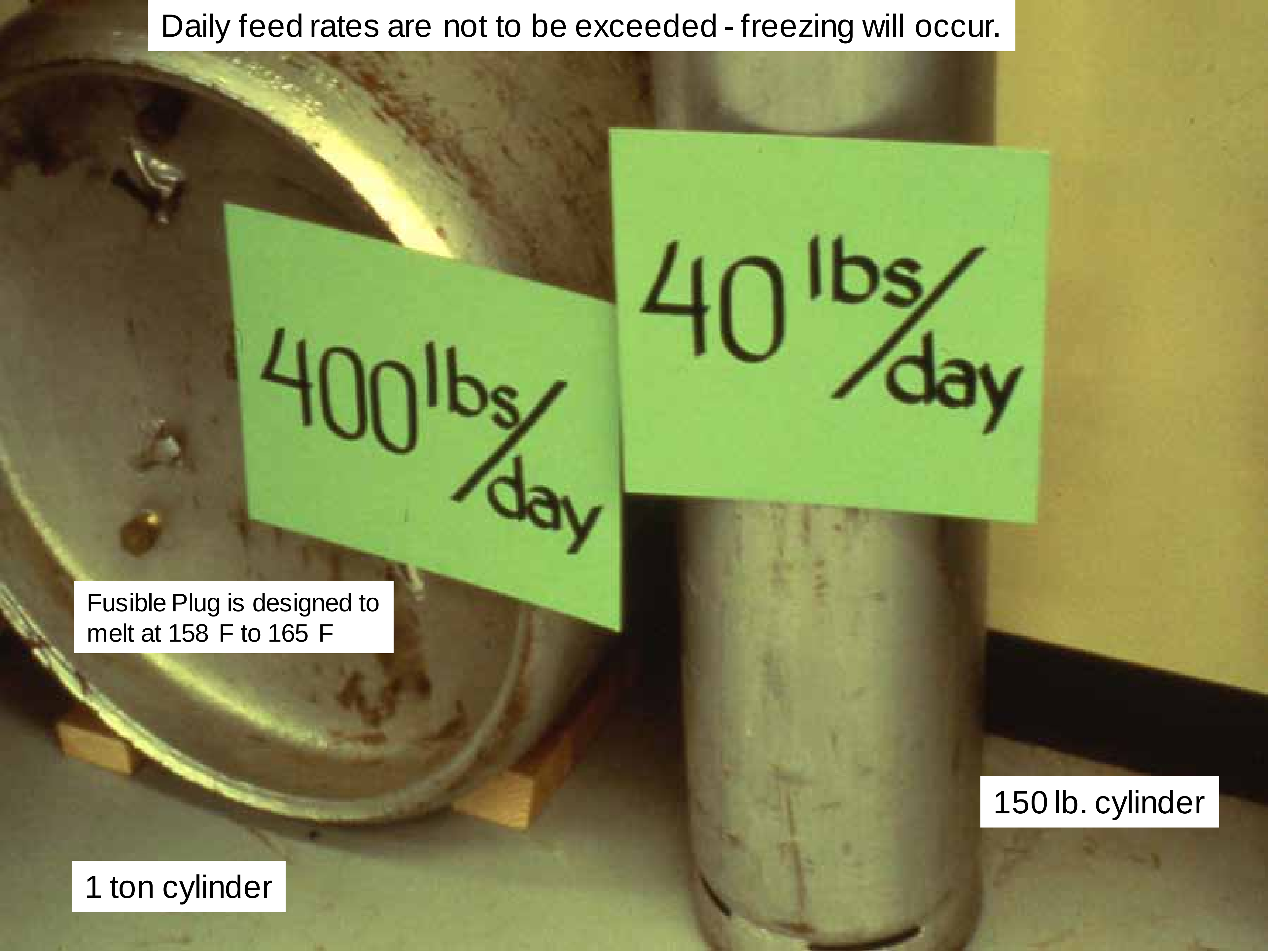
Chlorine Residual Testing

- Typically based on a contact time of 30 minutes
- Looking for target residual between 0.4 mg/L and 2.0 mg/L after 30 minutes (at pH 8.0)
  - Regulatory minimum 0.4 mg/L at EP (SW)
  - Looking for residual ≥ 0.2 mg/L after 24 hours (SW)
- **DO NOT** exceed the MRDL – Maximum Residual Disinfectant Level
  - 4 mg/L for chlorine, chloramines – CWS, NTNCWS
  - 0.8 mg/L for chlorine dioxide - TNCWS

Chlorine Operation and Maintenance


70° F
85 psi
85 %
full

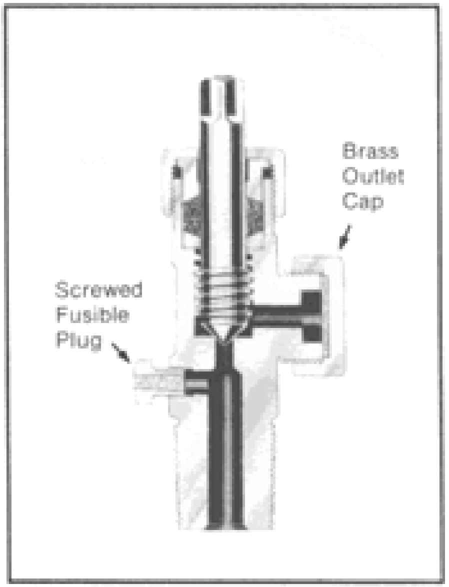
Daily feed rates are not to be exceeded - freezing will occur.



Fusible Plug is designed to melt at 158 F to 165 F

1 ton cylinder

150 lb. cylinder

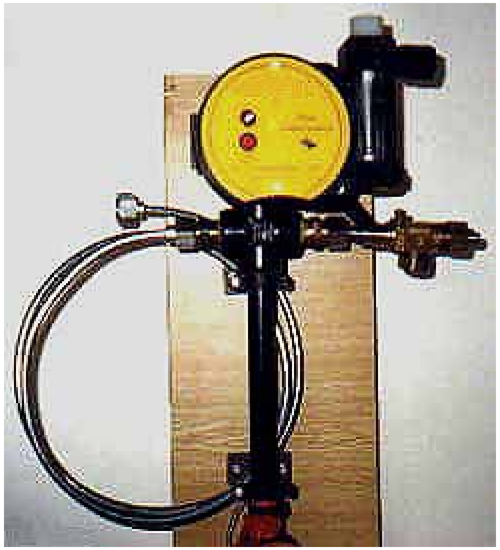

Brass
Outlet
Cap
Screwed
Fusible
Plug

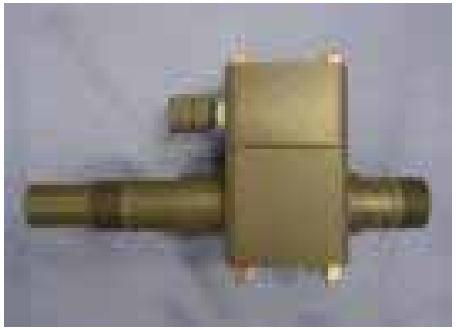
Chlorine / Sulfur Dioxide Leak Indicator Bottles

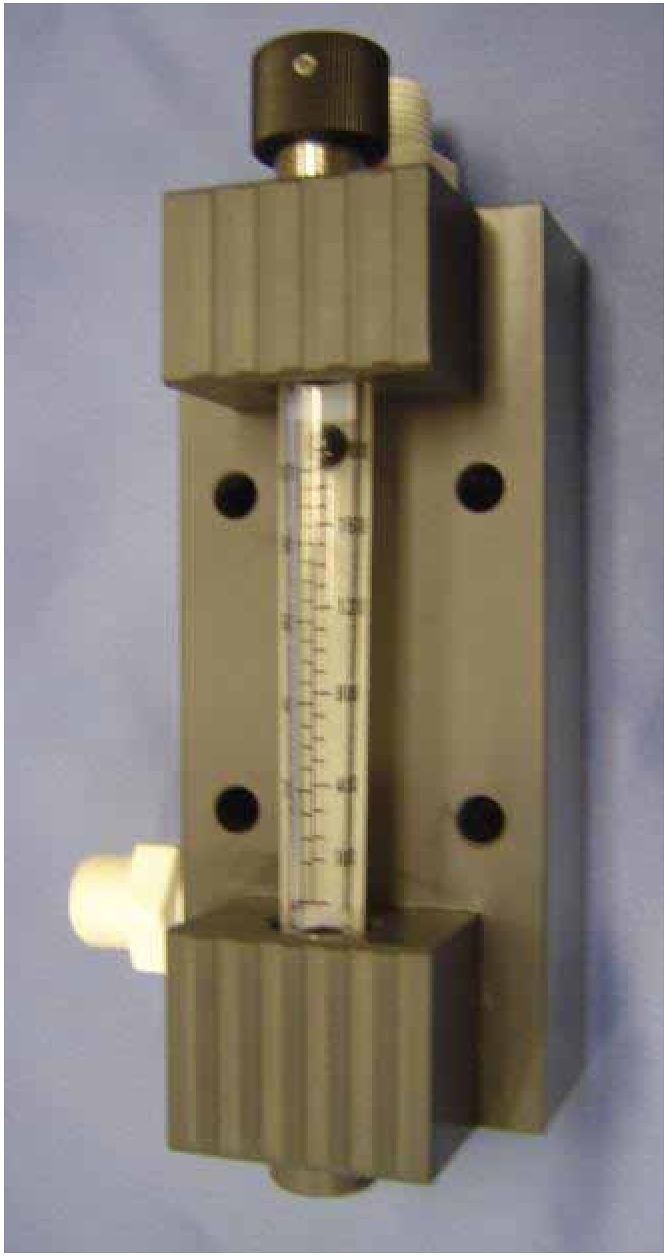
Chlorine and sulfur dioxide gas leaks can be easily & safely identified with ***aqua ammonia vapors.*** Chlorine and sulfur dioxide safely react with ***aqua ammonia vapors*** to form a visible white cloud that identifies the source of the chemical leak.

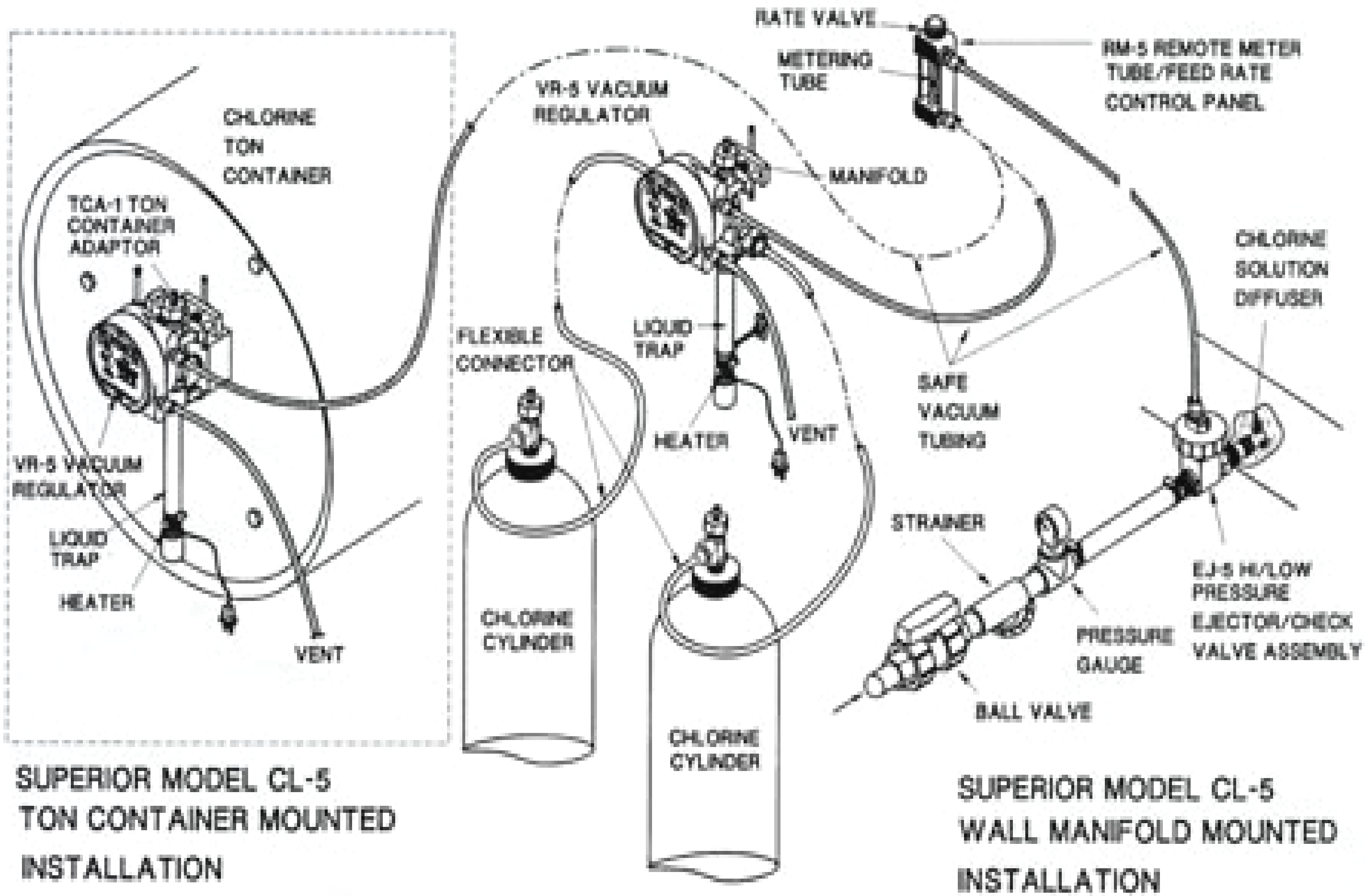
Ammonia may cause problems with metal alloys. Anyone testing for chlorine leaks with ammonia water (ammonia hydroxide solutions) on brass or copper alloys must take care ***that only the ammonia vapor and not the liquid solution comes into contact with the alloy.***


REGAL



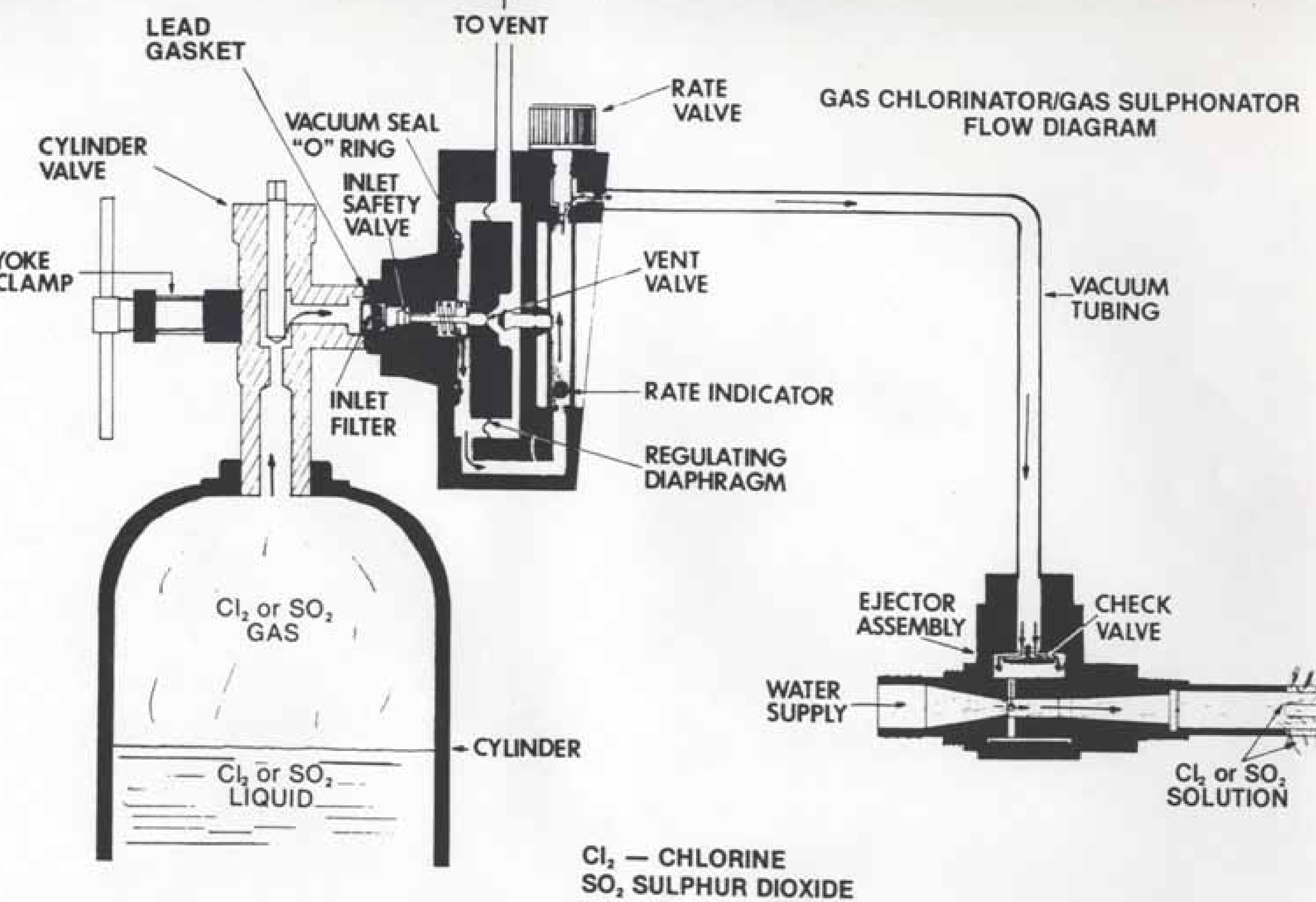






TYPICAL INSTALLATION

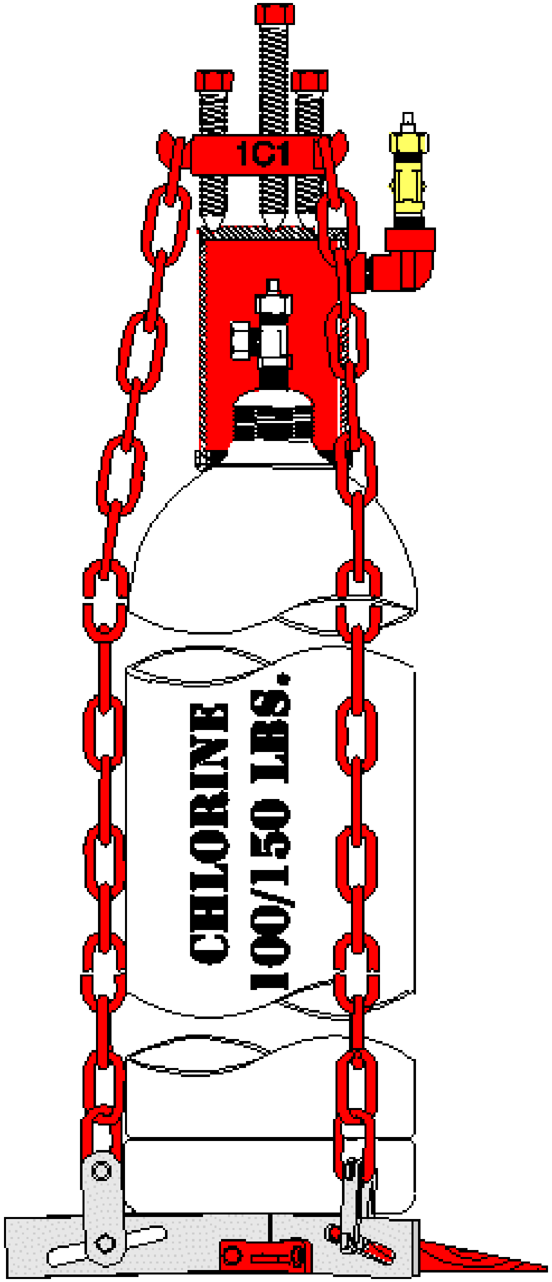
GAS CHLORINATOR/GAS SULPHONATOR FLOW DIAGRAM



TROUBLESHOOTING GAS CHLORINATORS

Symptom	Probable Cause
•Low Feed Rate and Low Vacuum	Clogged Injector/Ejector
•Low Feed Rate and High Vacuum	Clogged Gas Feed Line Closed Cylinder Valve Empty Cylinder
•Feed Rate Jumps	Clogged Flow Controller/Needle Valve
•Feed Rate Won't "Zero"	Dirty Flow Indicator/Rotameter
•Chlorine Gas at Vent	Dirty Pressure Regulating Valve
•No Vacuum	No Supply Water Vacuum Leak

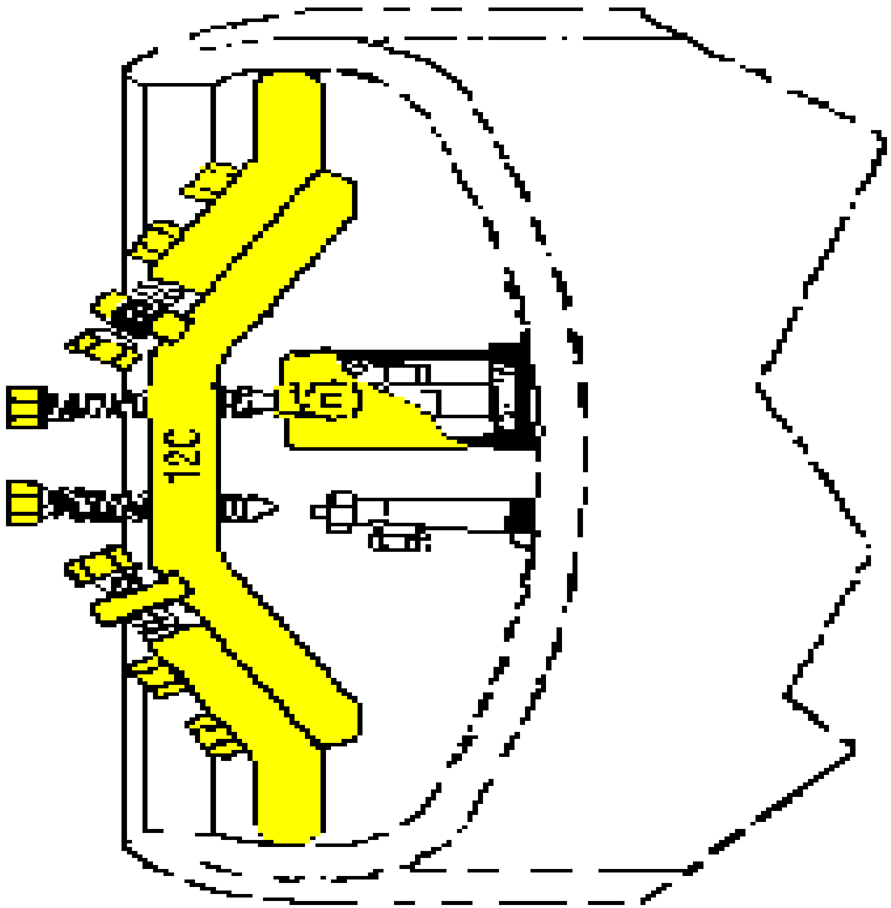
Emergency Kit “A”
For 100 lb. & 150 lb. Chlorine Cylinders



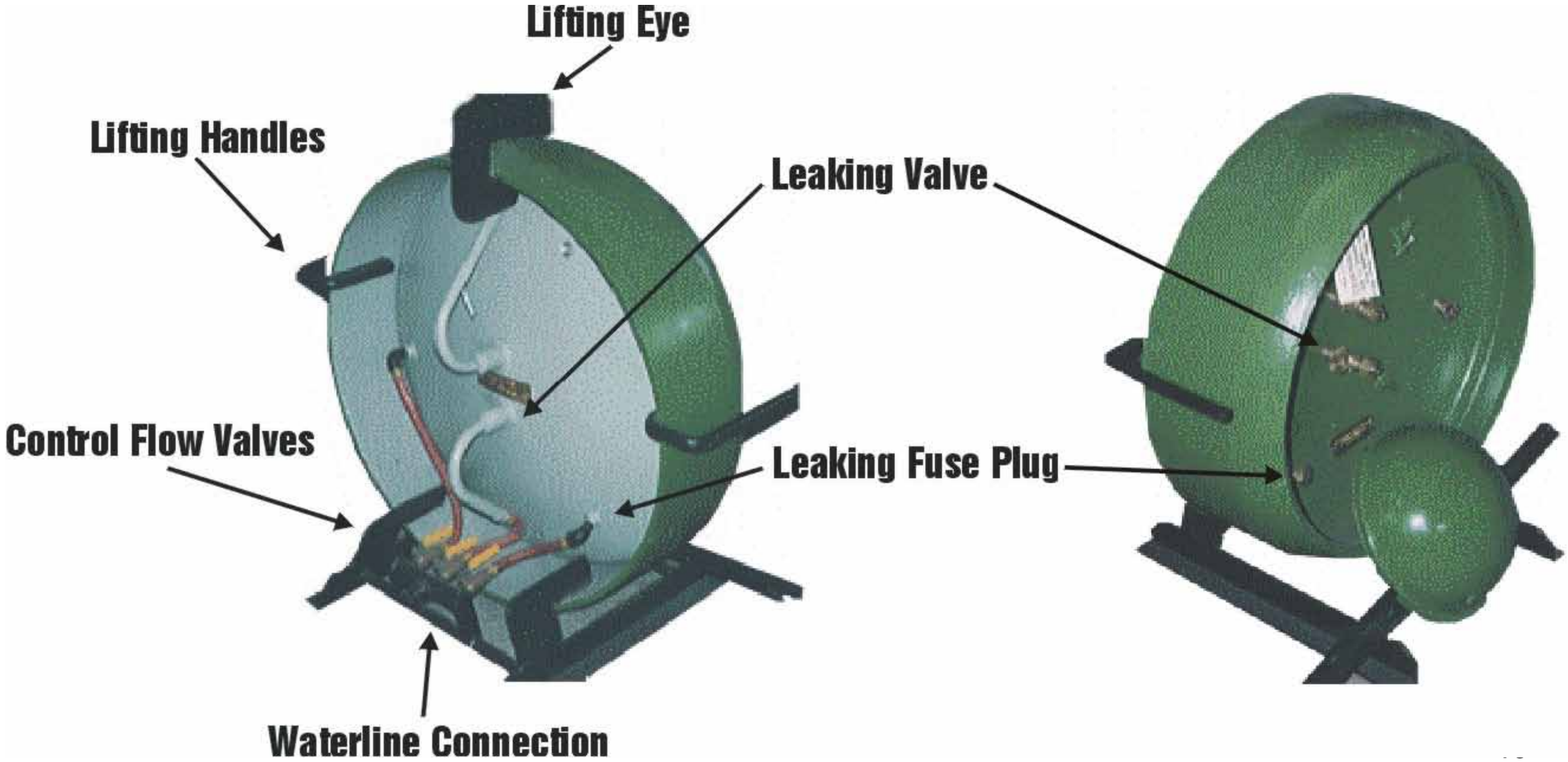
CHLORINE
100/150 LBS.

DOT E 9781
SALVAGE CYLINDER

Emergency Kit "B"
For Chlorine 1 Ton Containers


12C

One Ton Cylinder



Powder Chlorine (Calcium Hypochlorite)

1. Calcium Hypochlorite $Ca(OCl)_2$

- dry loose granular material
- Also comes in tablet form
- White or yellow-white in color
- Contains 65% - 70% available Cl2 by weight
- Other 35% - 30% are binding compounds of lime
- Supports combustion

Liquid Chlorine (Sodium Hypochlorite Solution))

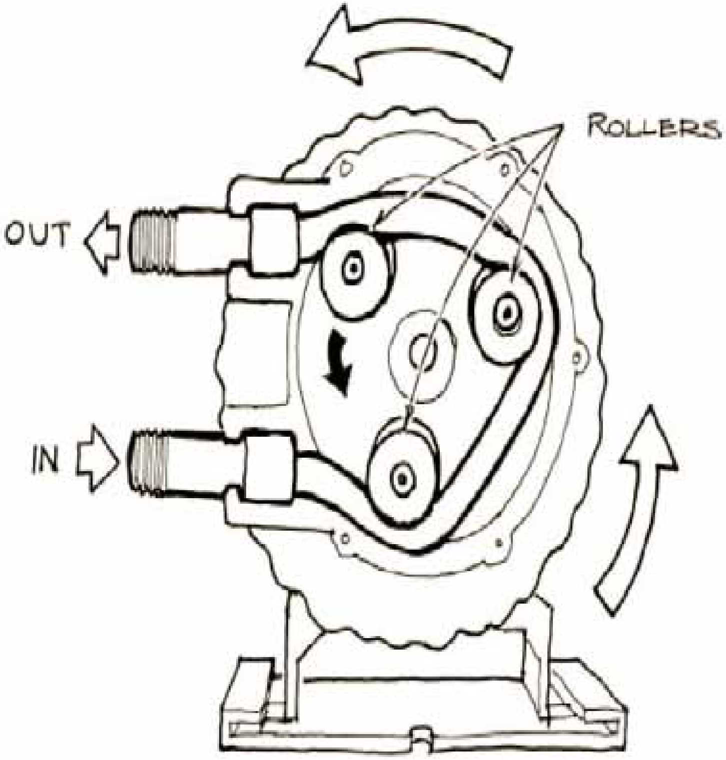
1. Sodium Hypochlorite (NaOCl)

- Clear to greenish-yellow liquid solution
- 9% - 15% available Cl2
- No fire hazards are connected to NaOCl
- quite corrosive
- Reactive with other chemicals

Sodium hypochlorite generating unit, 0.8% available produced “Clor-Tec”

MIOX System

PERISTALTIC TYPE CHEMICAL FEED PUMP



Series 45 M – Adjustable Low Pressure: 0 to 25 psi (1.72 bar) Maximum Discharge Pressure

MODEL TUBE FEED RATE CONTROL SETTING: Outputs per day in U.S. Gallons @ 60Hz (black, left) & Liters @ 50Hz (green, right)

MODEL	TUBE	L		1		2		3		4		5		6		7		8		9		10	
45M1	#1	0.2	0.6	0.3	0.9	0.6	1.8	0.9	2.7	1.2	3.6	1.5	4.5	1.8	5.5	2.1	6.4	2.4	7.3	2.7	8.2	3.0	9.1
45M2	#2	0.5	1.5	1.0	3.0	2.0	6.1	3.0	9.1	4.0	12.1	5.0	15.1	6.0	18.2	7.0	21.2	8.0	24.2	9.0	27.3	10.0	30.3
45M3	#3	1.1	3.3	2.2	6.6	4.4	13.3	6.6	20.0	8.8	26.6	11.0	33.3	13.2	40.0	15.4	46.6	17.6	53.3	19.8	60.0	22.0	66.6
45M4	#4	1.7	5.1	3.5	10.6	7.0	21.2	10.5	31.8	14.0	42.4	17.5	53.0	21.0	63.6	24.5	74.2	28.0	84.8	31.5	95.4	35.0	106.0
45M5	#5	2.5	7.6	5.0	15.1	10.0	30.3	15.0	45.4	20.0	60.6	25.0	75.7	30.0	90.8	35.0	106.0	40.0	121.1	45.0	136.3	50.0	151.4

Series 45 MHP – Adjustable High Pressure: 0 to 100 psi (6.9 bar) Maximum Discharge Pressure

MODEL TUBE FEED RATE CONTROL SETTING: Outputs per day in U.S. Gallons @ 60Hz (black, left) & Liters @ 50Hz (green, right)

MODEL	TUBE	L		1		2		3		4		5		6		7		8		9		10	
45MHP2	#1	0.2	0.6	0.3	0.9	0.6	1.8	0.9	2.7	1.2	3.6	1.5	4.5	1.8	5.5	2.1	6.4	2.4	7.3	2.7	8.2	3.0	9.1
45MHP10	#2	0.5	1.5	1.0	3.0	2.0	6.1	3.0	9.1	4.0	12.1	5.0	15.1	6.0	18.2	7.0	21.2	8.0	24.2	9.0	7.3	10.0	30.3
45MHP22	#7	1.1	3.3	2.2	6.6	4.4	13.3	6.6	20.0	8.8	26.6	11.0	33.3	13.2	40.0	15.4	46.6	17.6	53.3	19.8	60.0	22.0	66.6

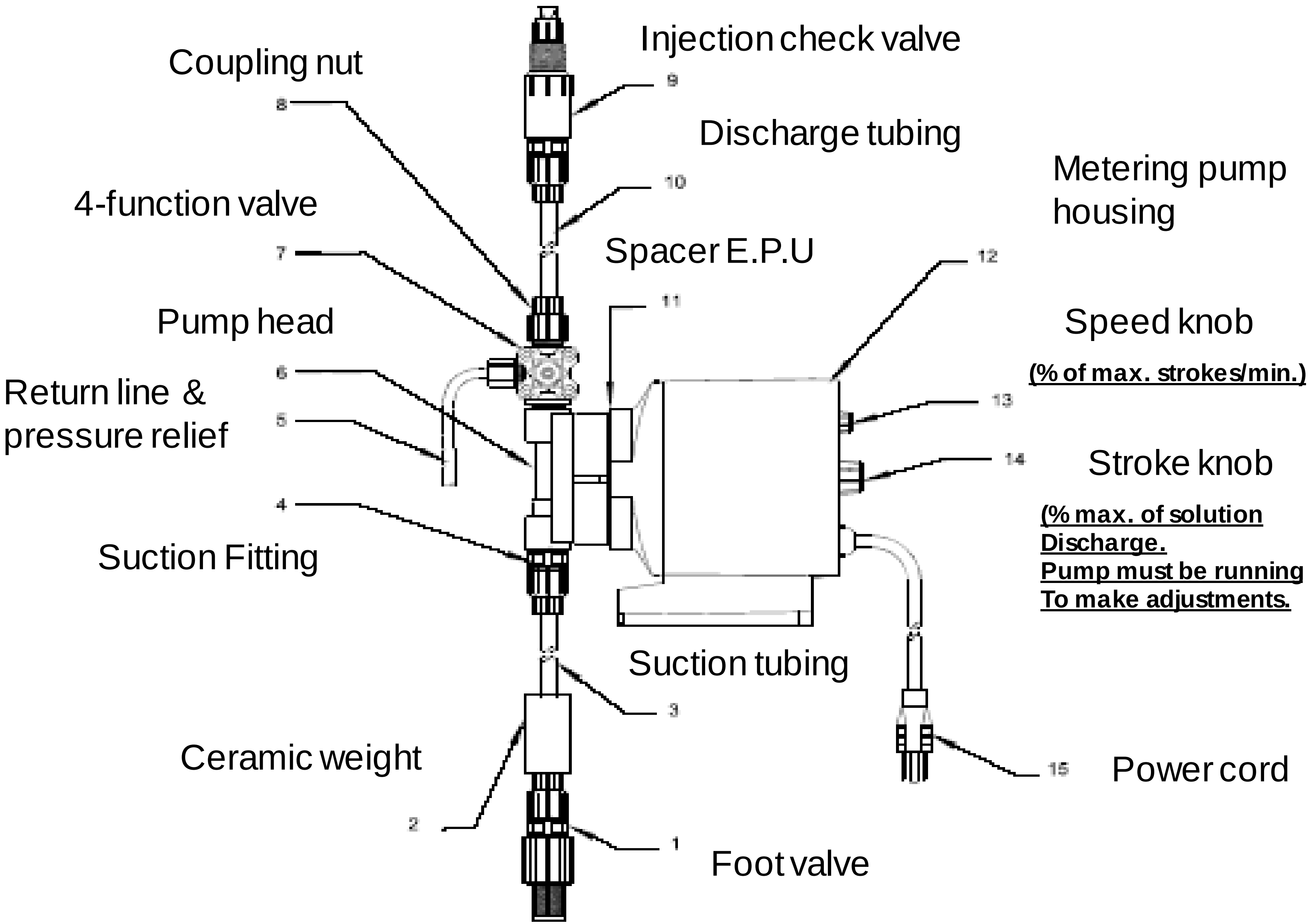
Series 45 MP – Fixed Rate Low Pressure: 0 to 25 psi (1.72 bar) Maximum Discharge Pressure

MODEL	PUMP TUBE	FIXED OUTPUT: U.S. Gals - Liters	
45MP1	#1	3.0	9.1
45MP2	#2	10.0	30.3
45MP3	#3	22.0	66.6
45MP4	#4	35.0	106.0
45MP5	#5	50.0	151.4

Series 45 MPHP – Fixed Rate High Pressure: 0 to 100 psi (6.9 bar) Maximum Discharge Pressure

MODEL	PUMP TUBE	FIXED OUTPUT: U.S. Gals – Liters	
45MPHP2	#1	3.0	9.1
45MPHP10	#2	10.0	30.3
45MPHP22	#7	22.0	66.6

Diaphragm Chemical Feed Pump Type



LMI Calculating Required Output

- Set-up & Installation

$$\frac{\text{Desired (mg/L) X GPM (Max Flow of Well Pump)}}{\text{\% Concentration of Chemical (Use \% Whole Number)}} \text{ X .006 (Conversion to GPH)}$$

= Required Pump Output in GPH

- Calculating output %

$$\frac{\text{Required Pump Output}}{\text{Maximum Output of Pump}}$$

= % Output Required from Pump

- Calculating % Speed & % Stoke

$$\sqrt{\text{\% Output Required from Pump}} \text{ (Square Root)}$$

= % Speed & % Stroke