Chlorine

How to use it – not abuse it.

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Chlorine and Chlor-Alkali Chemicals

- Chlorine: Discovered 1774.
- Hypochlorite: Discovered 1787.
- Caustic soda: (NaOH approximately late 1700's) lye earlier.
- Hydrochloric (muriatic) acid: Known to alchemists.
- Salt (NaCl): Used for over 6000 years.
- Phosgene: Discovered 1812.
- Chloramine

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Chlorine

- Originally discovered by Scheele in 1774 who reacted pyrolucite (MnO_2) with HCl to produce chlorine. (Confirmed as an element in 1810)
- Takes its name from Greek *chloros* meaning pale green
- Used in 1915 as the first chemical weapon in the modern era. (Killed about 3,000 people before being replaced by lewisite)

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Chlorine *(cont'd)*

- Chlorine was available from the 1850's but not used significantly until 20th Century
- Reduction in waterborne diseases like typhoid, cholera, and dysentery.
- Typhoid fever in the U.S.
  - 100 per 100,000 in 1900
  - 33.8 per 100,000 in 1920
  - 0.1 per 100,000 in 2006

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Water chlorination history

- 1854 - Dr. John Snow (England) disinfect the Broad Street Pump water supply in London, identified as a cause of a cholera outbreak from sewage contamination.
- 1879 - William Soper (England) chlorinated lime to treat feces of typhoid patients before disposal into the sewer.
- 1893 - Chlorine was used on a plant scale basis for drinking water disinfection in Hamburg, Germany.

Water chlorination history *(cont'd)*

- 1897 - Sims Woodhead temporarily sterilized the potable water distribution mains at Maidstone, Kent, using a bleach solution.
- 1903 - ***First use of chlorine gas*** disinfection drinking water in Middlekerke, Belgium. (Previous chlorination was with hydrated lime, chloride of lime or bleaching powder.)
- 1908 - Jersey City, NJ first water utility (US) to use full scale water chlorination, using sodium hypochlorite.

Water chlorination history *(cont'd)*

- 1908 - Union Stockyards Chicago, IL, Bubbly Creek Filter Plant began chlorinating water supply using chloride of lime.
- 1910 - Youngstown, Ohio, first use ***compressed chlorine gas from a steel cylinder*** for water system.
- 1914 - U.S. Department of the Treasury enacted a set of standards calling for a maximum bacterial concentration of 2 coliforms per 100 ml in drinking water

Chlorine Production and Usage

- Approximately 50 Million Tons produced (2007)
  - Used in 85% of pharmaceuticals.
  - Used in 96% of agricultural chemicals.
  - Approximately 5% used in water disinfection.
  - Market for chlorine equipment estimated at $ 150 M/year.
  - Three largest industrial users: China, India, US.
- 12 Million Tons produced in US (2010).

Chlorine Properties

- Boiling point -30°F (-34°C)
- Density (2.5 times heavier than air)
  - Liquid 91.6 lb/ft^3
  - Gas 0.2006 lb/ft^3 (5 ft^3/lb)
  - Expands 456 times
- Specific Heat
  - Heat of Vaporization 123 BTU/lb
  - Specific Heat .113 BTU/lb/°F (-30 to 80°F)
    - 12.4 BTU/lb to cool gas from 80°F to -30°F)

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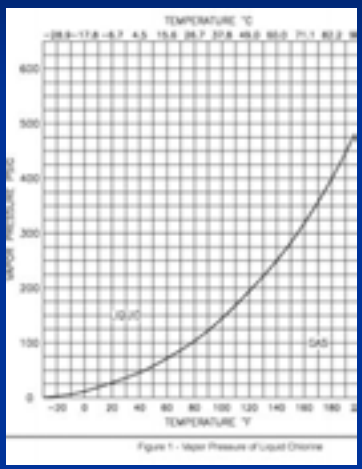
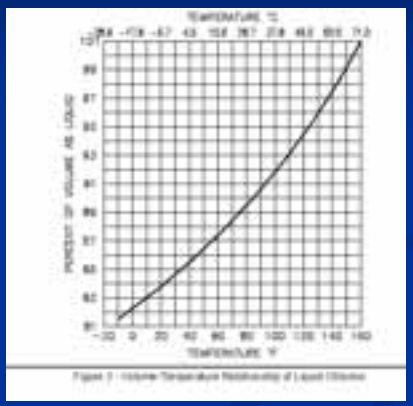
Chlorine Properties *(cont'd)*





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Chlorine Hazards - Physical

- Chlorine is not combustible but it supports combustion
- Chlorine is reactive with some materials such as aluminum, iron, and copper. Reactions are usually exothermic.

Chlorine Hazards - Human

- Four means of entry for a chemical into the human body:
  - Injection – not a likely means of entry for chlorine.
  - Ingestion – not a likely means of entry for chlorine.
  - Absorption – chlorine will react with skin and outer tissue and form acid when it comes into contact with water. Acid coagulates tissue. This can cause blindness. 4500 ppm of chlorine on skin will react to form a pH of 4 the same pH as soda water.
  - Inhalation – Low levels can maim and higher levels of chlorine will kill.

Chlorine Hazards - Stupidity

Main Hazard of Chlorine

- Inhalation
- Chlorine Institute RAGAGEP recommends full faced APR for work around cylinders where concentration is less than IDLH. SCBA otherwise.

Chlorine Hazards – Inhalation Hazard

Conc (ppm)	Symptom
0.08	Readily Detectable odor
0.5 – 7	Acute Conditions: EENT irritation, sneezing, salivation, general excitement, restlessness,. LIQUID EXPOSURE MAY CAUSE FROSTBITE. dermatitis.
	Chronic Conditions: Low levels may result in chloracne, tooth enamel corrosion, coughing, severe chest pain, sore throat, hemoptysis, susceptibility to tuberculosis.
5-15	Irritation to respiratory tract
30	Immediate chest pain, vomiting, dyspnea, cough
40-60	Toxic pneumonitis, pulmonary edema
430	Potentially fatal within 30 minutes
1000	Fatal within a few breaths

0.5 ppm Cal / OSHA PEL ERPG 1

1.0 ppm OSHA PEL and STEL

3 ppm ERPG 2

10 ppm IDLH (1999)

20 ppm ERPG 3

30 ppm IDLH (1976) (no longer valid)

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Chlorine – How much does it take?

Conc (ppm)	Condition	Room 12'x10'x10' 1,200 cf (lb)	Size 15'x50'x14' 10,500 cf (lb)
0.5	Cal / OSHA PEL ERPG 1	0.00012	0.0010
1.0	OSHA PEL & STEL	0.00024	0.0021
3.0	ERPG 2	0.00072	0.0063
10	IDLH	0.0024	0.021
20	ERPG 3	0.0048	0.042
30	IDLH (1976) (no longer valid)	0.0072	0.063
430	Potentially fatal within 30 min	0.104	0.907
1000	Rapidly fatal	0.241	2.11

- Conditions exaggerated as calculations assume equal amount of chlorine instead of heavy gas with higher concentration at ground level. Concentration at wall monitor may *not* be concentration where person is breathing.

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Federal, State, and Local Agencies and Their Programs

- Federal Regulators
  - EPA – Accidental Release Prevention (ARP) or Risk Management Program
  - OSHA – Process Safety Management (PSM)
- California
  - EPA – CalARP (RMP) regulated through the CUPA
  - DTSC – Partly regulated through the CUPA
  - Cal / OSHA - Various Safety Orders: LOTO, IIPP, Respiratory Protection, Emergency Action Plan, Emergency Response Plan, Hot Work, HazWOPER, HazCom, Eyewash/ Showers, Heat Illness, Confined Space, Unfired Pressure Vessels (liquid systems only)
- Emergency Planning
  - CUPA – Hazardous Materials Business Plan, Consolidated Contingency Plan
  - LEPC – Coordination with Local Emergency Response Plans
- Fire Departments
  - HazMat Response – Are they capable and is it physically possible?
- Building Departments – CBC, CMC, and CFC, Life Science

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Codes and Standards Applicable to Chlorine Systems

- Chlorine Institute
  - Pamphlet 65 Personal Protective Equipment for Chlor-Alkali Chemicals Edition 5 February 2009
  - Pamphlet 73 Atmospheric Monitoring Equipment for Chlorine Edition 7 June 2003
  - Pamphlet 89 Chlorine Scrubbing Systems Edition 3 Revision 1 October 2008
  - Pamphlet 137 Guidelines: Asbestos Handling for the Chlor-Alkali Industry Edition 5 October 2005
  - Pamphlet 155 Water and Wastewater Operators Handbook Edition 2 January 2008
  - Pamphlet 164 Reactivity and Compatibility of Chlorine and Sodium Hydroxide with various Materials Edition 2 August 2007
  - Pamphlet 165 Instrumentation for Chlorine Service Edition 2 July 2009
  - Pamphlet 167 Learning from Experience Edition 1 March 2002
- California Fire Code
- California Building Code
- California Mechanical Code 2010 –NFPA
  - 70 - National Electrical Code
  - 497A - Recommended Practice for Classification of Class I Hazardous Locations for Electrical Installations in Chemical Process Areas
- 8 CCR Division of Industrial Relations
  - GISO 3220 Emergency Action Plan
  - GISO 5143 Ventilation
  - GISO 5144 Respiratory Protection

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What facility is better?

Chlorination Systems - Disinfection

- Chlorine delivered
  - Standard Sizes:
    - 100 lb cylinders
    - 150 lb cylinders
    - 1 Ton containers
    - 55 or 90 Ton rail cars
  - Bulk delivery into facility tank

Chlorination Systems - Feed

- 100 and 150 lb cylinders
  - Almost always under vacuum from vacuum reducing valve
  - Occasionally multiple tanks manifolded together to vacuum reducer.

- Ton containers
  - Mostly under vacuum with vacuum reducing valve on container.
  - Sometimes gas pressure withdrawal.
  - Occasionally liquid withdrawal if higher dosing rates needed.

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Chlorination Systems – Feed *(cont'd)*

- Rail cars
  - May start out with gas withdrawal.
  - Almost always switches over to liquid withdrawal.

- Bulk Tanks
  - Feed system varies.

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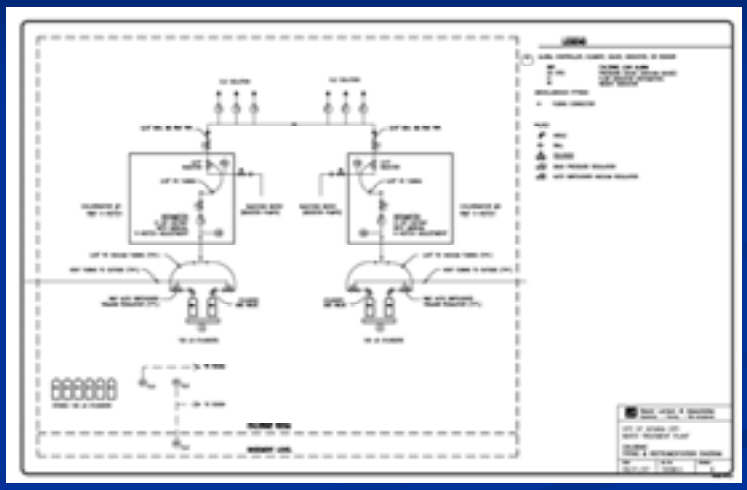
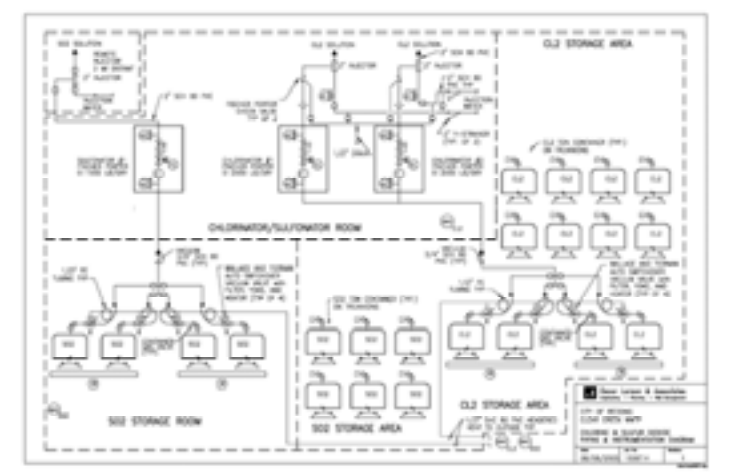
Chlorine Systems – 100 & 150 lb



Chlorine Systems – 100 & 150 lb

Chlorine Systems – Ton Containers



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Chlorine Systems – Ton Containers

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Chlorine Systems – Ton Containers

How It All Fits Together

- OSHA and Cal / OSHA do not write specific standards for chlorination, but instead rely on manufacturers' recommendations and codes and standards written by industry leaders (Chlorine Institute).
- Recognized and Generally Accepted Good Engineering Practice (RAGAGEP).
- General Duty Clause – A fallback when specific regulations do not specify compliance requirements. This is not enforced by the CUPA or Cal / OSHA but is by Region 9 EPA and Fed OSHA.

Maintenance and Mechanical Integrity

- RAGAGEP maintenance and mechanical integrity of system components.
  - Not specifically listed in codes and standards.
  - Often part of equipment manufacturers' recommendations or part of predictive maintenance program.
    - Yearly maintenance of most equipment.
    - Bump testing perimeter monitors.
    - Calibrating perimeter monitors and individual read monitors.

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Eyewash Shower

- 8 CCR 5162 requires that a unit be placed within 10 seconds of an exposure (injured person). Cal/OSHA figures between 4.5 and 5. 5 feet per second
- Obstructions are not allowed.

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Eyewash / Shower

Alternatives to hard plumbed units, but do they provide 15 minutes of flushing time with large amounts of water as the MSDS recommends?

Alternative to having hard plumbed units in remote locations.

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How are different codes and standards that conflict with each other interpreted?

- Laws
  - Chaptered into Code
    - Regulations developed by agencies
      - Performance specifications
      - RAGAGEP from authoritative groups
    - Regulations administered by different agencies
- RAGAGEP (Recognized and Generally Accepted Good Engineering Practices)
- General Duty Clause

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Application Difficulties

- How are facilities designed under earlier codes dealt with – grandfathered in?
- Revision calendars for applicable codes and standards differ – which code should be followed, especially when doing upgrades?
- Lag time between issuance of Codes and Standards and consistent use by industry. - "Communication"

What happens if excrement hits the rotary oscillator?

- OSHA 170 logs for chlorine
  - 45 Accidents reported between 5/13/2003 and 5/30/2012
  - 8 fatalities
    - 1 fall from roof weakened by chlorine vapors
    - 1 train car derailment
    - 2 exposure delayed deaths
    - 2 mixing chemicals that produced chlorine

Inhalation in processing plant.

- On August 21, 2011, Forty seven employees, … were sent to hospitals … after being exposed to chlorine dioxide released inside a tomato processing plant. Three employees were admitted for further treatment. The chlorine dioxide release was due to equipment failure … after a similar incident in 2007, which resulted in exposure of employees to chlorine dioxide.

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Chlorine Exposure

- At approximately 2:30 p.m. on March 2, 2011, six workers were employed as milling or planing machine operators at a corn and flour milling facility in Lincoln, NE. A chlorine leak was detected in the chlorine room, so the milling superintendent and a miller/operator entered the chlorine storage room and closed a manual valve on a manifold. The facility was evacuated, and members of the local fire department and hazmat team responded. …

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Chlorine Exposure

- The expanding cloud of chlorine gas seeped from the storage area on the east side of the facility. It entered the negative pressure mill and surrounding outside area. Employees working in the immediate area and in the mill were exposed. Employees were also exposed as they were evacuating their work areas. … It was later determined that a vacuum regulator in the chlorine process piping system had ruptured.

Chlorine Exposure Fatality

- At approximately 7:00 p.m. on November 15, 2006, Employee #1 was a process operator … He was preparing to bleed off chlorine on a process line, to clear the line for maintenance work. The valve handle indicated that it was in a closed position. …, the bleed valve was not completely closed, and the pressure on the chlorine line caused the cap to blow off, releasing chlorine.

Chlorine Exposure Fatality

- Employee #1 was exposed to the inhalation hazard of chlorine gas when his airline became caught on a nearby pipe and his mask was pulled away. He continued to work until his shift was over. He went to a coworker's home after leaving the plant because he was too tired to go home. Employee #1 was hospitalized approximately one hour later. He was pronounced dead at 10:00 a.m. …

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Farm Fatality

- … 2003, a maintenance employee went to the chlorine house to turn on the chlorination system. The chlorine house measured 3 feet, 10-inches wide by 5 feet, 10-inches long and was approximately 10-feet high. The water lines ran through a hole in the block wall. The hole in the block wall lead directly from the chlorine house into the chemical room. The hole was approximately 12 inches wide by 10-inches high.

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Farm Fatality

- The maintenance employee stated that when he cracked the chlorine valve, he noticed the seal was leaking. He ran out of the chlorine house, about 20 feet away, caught his breath, collected his thoughts, and then went to the maintenance shop to get a respirator. He returned to the chlorine house, entering an unknown released concentration of chlorine, and shut the valve off.

Farm Fatality

- The maintenance employee fixed the seal and a lead washer and turned the chlorine valve back on. … He then saw Employee #1 approximately 30 feet away, acting very bizarre. The maintenance employee then went to the picking room where he felt chlorine gas burning his eyes. … Employee #1 then asked for someone to summon emergency personnel because he needed oxygen. As he was being helped outside, he collapsed. … He was pronounced dead.

Are we safe if we get rid of chlorine gas?

Fatal accident chemical mixing

- At approximately 12:00 p.m. on July 13, 2010, an employee was working by himself … the employee moved and set up a 300 gallon tote and tank of **32% Hydrochloric Acid** for transfer ... These were not the location or process tanks used for hydrochloric acid. One of these tanks was **12.5% sodium hypochlorite** and the other 38 sodium bisulfite. The hydrochloric acid process tank was located outside. All the tanks were clearly labeled

Fatal accident

- At approximately 12:00 p.m. on July 13, 2010, an employee was working by himself … the employee moved and set up a 300 gallon tote and tank of 32 Hydrochloric Acid for transfer ... These were not the location or process tanks used for hydrochloric acid. One of these tanks was 12.5 sodium hypochlorite and the other 38 sodium bisulfite. The hydrochloric acid process tank was located outside. All the tanks were clearly labeled.

Fatal accident

- When the hydrochloric acid tote was connected, a reaction began between the sodium hypochlorite and hydrochloric acid that released chlorine gas. It was not known yet if the transfer pump was started. The employee exited the connex and was met by a coworker of the gas well company. The morning foreman returned to the location and transported the employee to the hospital.

Fatal accident

- The employee passed out on the way to the hospital. The morning foreman was then involved in a vehicle wreck as he was taking the employee to the hospital. The employee was placed on a respirator at the hospital and declared brain dead at about 8:30 p.m. He was then removed from life support around midnight.

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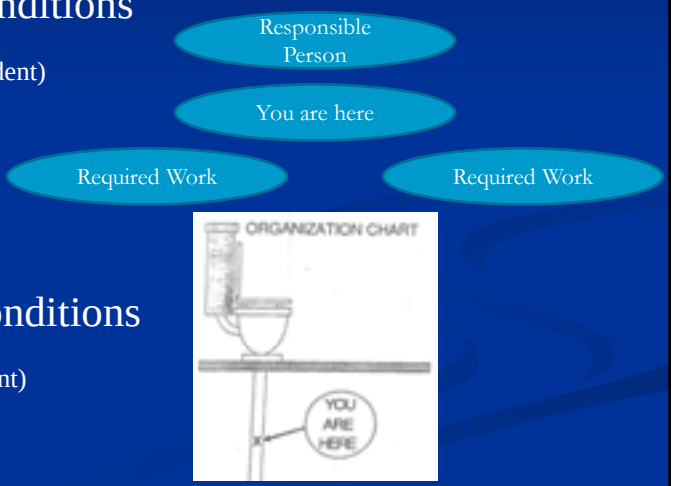
Take Away

- Normal Conditions

(before accident)



- Revised Conditions

(after accident)

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Questions

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