Sulfur Dioxide – Use and Safety.

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Sulfur Dioxide

- Known and used since antiquity
  - Homer describes burning sulfur in Odyssey as a way to fumigate houses.
  - Romans used to burn sulfur candles inside empty wine barrels to preserve wine.
    - Germany rejoiced in 1497 when the Prussians officially allowed sulfur dioxide as a preservative in wine making.
  - Used as chemical warfare agent in Greece Peloponnesian War, around 429 B.C and Syria against the Romans

Sulfur Dioxide Production and Usage

- Approximately 24 Million Tons / yr produced in US (1979)
  - Mostly used for producing Sulfuric Acid by producing SO_3 which is used to make Oleum and diluted to Sulfuric Acid.
  - 150 Thousand Tons / yr produced for other applications.

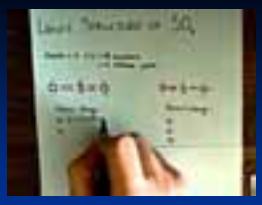
Sulfur Dioxide *(cont'd)*

- Non sulfuric acid uses include:
  - Preservative for dried apricots, figs other fruits.
  - Added to sulfured molasses.
  - Winemaking. (Unsulfurated wine can have a concentration of up to 10 mg/L. Upper limit of total SO_2 in wine 350 ppm (US) 160 ppm (EU) for red wines 210 ppm for white and rosé wines).
  - Important sanitizing agent in wineries. (Do not use bleach to avoid cork taint).

Sulfur Dioxide *(cont'd)*

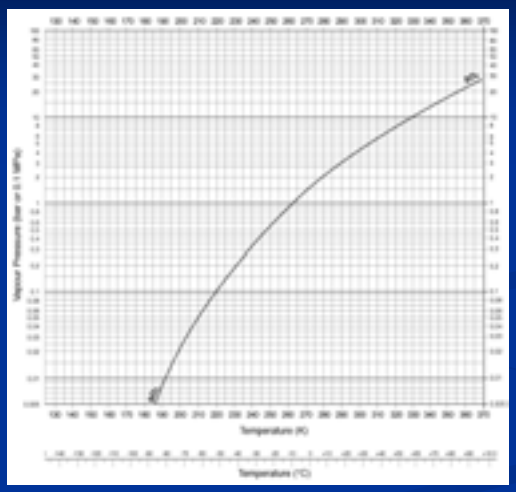
- Used in wastewater industry to dechlorinate effluent.

Sulfur Dioxide Properties



- Boiling point 14°F (-10°C)
- Density (2.2 times heavier than air)
  - Liquid 89.9 lb/ft^3
  - Gas 0.168 lb/ft^3 (5.26 ft^3/lb)
  - Expands 535 times
- Specific Heat
  - Heat of Vaporization 171 BTU/lb
  - Specific Heat .146 BTU/lb/°F (14 to 80°F)
    - 9.34 BTU/lb to cool gas from 80°F to 14°F)

Sulfur Dioxide Properties *(cont'd)*



Sulfur Dioxide Hazards - Physical

- Sulfur dioxide is not combustible and does not support combustion.
- Sulfur dioxide will combine with water to form sulfurous acid.
- Sulfuric acid is a strongly dissociated acid and can strongly oxidize materials.

Sulfur Dioxide Hazards - Human

- Four means of entry for a chemical into the human body:
  - Injection – not a likely means of entry.
  - Ingestion – not a likely means of entry.
  - Absorption – Sulfur dioxide will react with skin and outer tissue and form acid when it comes into contact with water. Acid coagulates tissue. This can cause blindness.
  - Inhalation – Chronic low levels can maim and acute higher levels will kill.

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Sulfur Dioxide Hazards – Stupidity

SO_2 in orange juice manufacturing

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Main Hazard of Sulfur Dioxide

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

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Sulfur Dioxide– Inhalation Hazard

Conc (ppm)	Symptom
0.3-1	Odor Threshold
0.075 – 0.5	Acute Conditions: Constriction of the respiratory tract amongst people suffering from asthma.
	Chronic Conditions: Reduced pulmonary function in children. Increased mortality elderly.
20	Severe, extremely unpleasant irritation symptoms including coughing, etc.
50	Severe irritation of mucous membranes, pulmonary hemorrhage and edema, laryngospasms with danger of asphyxiation

0.3 ppm ERPG 1

2 ppm Cal / OSHA PEL

3 ppm OSHA PEL ERPG 2

5 ppm Cal / OSHA STEL

25 ppm ERPG 3

100 ppm IDLH

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Sulfur Dioxide– How much does it take?

Conc (ppm)	Condition	Room 12'x10'x10' 1,200 cf (lb)	Size 15'x50'x14' 10,500 cf (lb)
0.3	ERPG 1	0.000068	0.00060
2	Cal / OSHA PEL	0.00046	0.0040
3	ERPG 2	0.00068	0.0060
5	STEL	0.0011	0.010
25	ERPG 3	0.0057	0.050
50	Potential Laryngospasms	0.0114	0.0998
100	IDLH	0.0228	0.199

- 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~~ Sulfur Dioxide 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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Sulfur Dioxide Systems - Disinfection

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

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Dechlorination Systems - Feed

- 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.
  - Occasionally gas pressure withdrawal.
  - Also liquid withdrawal if higher dosing rates needed.

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Sulfur Dioxide Systems – Feed *(cont'd)*

- Rail cars
  - Liquid withdrawal.

- Bulk Tanks
  - Liquid withdrawal.

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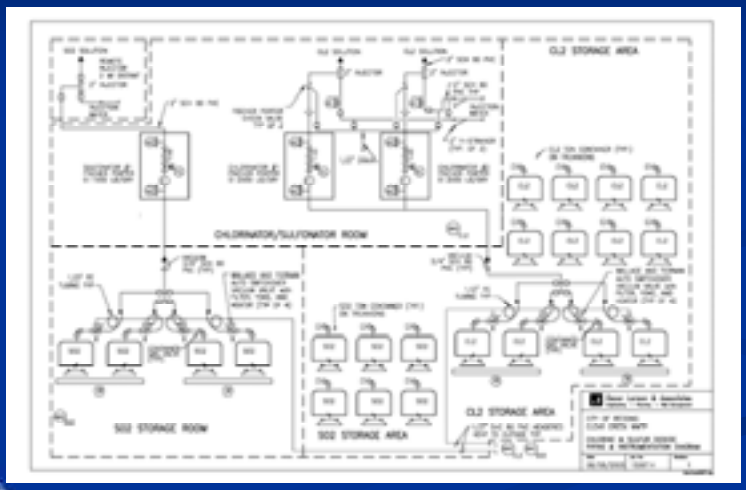
Sulfur Dioxide Systems – Ton Containers



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Sulfur Dioxide Systems – Ton Containers

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Sulfur Dioxide Systems – Ton Containers

How It All Fits Together

- OSHA and Cal / OSHA do not write specific standards for chlorination or dechlorination, but instead rely on manufacturers' recommendations and codes and standards written by industry leaders (Chlorine Institute).
- Recognized and Generally Accepted Good Engineering Practice (RAGAGEP).
  - Some industries / chemicals do not have RAGAGEPs so nearby industries or chemicals are used.
- 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.

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.

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 sulfur dioxide
  - 3 Accidents reported between 11/13/2002 and 11/13/2012
    - 1 Winery
    - 1 Wastewater Treatment Plant
    - 1 Refinery
  - 0 Fatalities

Inhalation in a winery.

- On September 23, 2011, Employee #1 was transferring sulfur dioxide from a 1-ton cylinder to a 6-pound gun. A hose, with a clamp attached, was used to transfer the chemical from the cylinder to the gun. As Employee #1 was tightening the clamp screw, it broke. This caused the hose to detach from the gun and release sulfur dioxide.

Sulfur Dioxide Exposure

- Employee #1 backed away and raised his arms, knocking his respirator off. He then inhaled the sulfur dioxide, suffering a decrease in lung function. Employee #1 was taken to a nearby medical facility, where he was hospitalized and treated for sulfur dioxide exposure.

Chlorine / Sulfur Dioxide Exposure

- On February 27, 2004, Employee #1 a water/waste operator for the Cottonwood treatment facility, she believed all the necessary valves were shut off on the cylinders and manifold. Employee #1 loosened the connections on the right cylinder of the two-cylinder pair. Chlorine gas rapidly escaped from the manifold connection and exposed her face to the gas.

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Chlorine / Sulfur Dioxide Exposure

- She received chemical burns to her eyes, nasal passages, and facial skin. She was taken by paramedic to Mercy Hospital, Redding and released later in the day.

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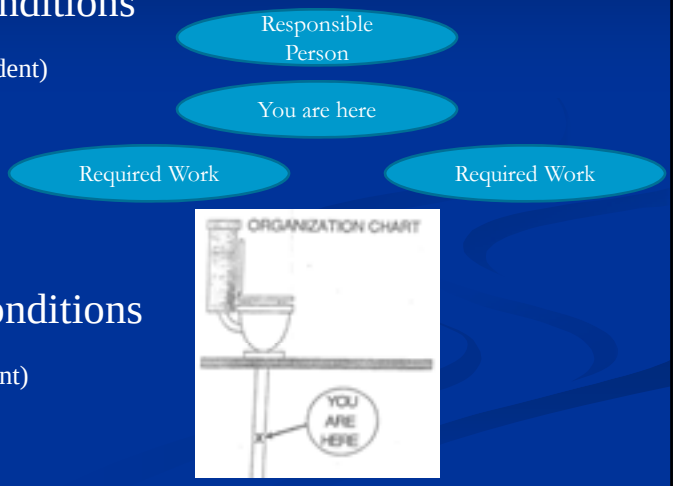
Take Away

- Normal Conditions

  (before accident)

- Revised Conditions

  (after accident)



Questions

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