PROCESS SAFETY MANAGEMENT (PSM)
CHLORINE HAZARDS IN WATER / WASTEWATER TREATMENT PROCESSES

Presented By

GERRY DIKE

MIOSHA DISASTER RESPONSE ADMINISTRATOR / PSM COORDINATOR

2013 WATER SECURITY SUMMIT

EAGLE EYE GOLF & CONFERENCE CENTER

15500 CHANDLER RD., BATH, MI 48808

NOVEMBER 12, 2008

OBJECTIVES

- IDENTIFY THE HAZARDS OF CHLORINE (CL_2)
- DESCRIBE CHLORINE WATER DISINFECTION PROCESSES AND OTHER EQUIPMENT COMMON IN CHLORINE SERVICES
- RECOGNIZE COMMON CAUSES AND SIGNS OF FAILURES IN CHLORINE SYSTEMS, AND PSM COMPLIANCE POLICY

PHYSICAL / CHEMICAL PROPERTIES OF CHLORINE

- Yellowish-green gas at room temperature
- Boiling Point -29 F
- Gas specific gravity 2.4 (at room temperature), ~2.9 at boiling point
- Pungent, irritating smell
- Sparingly soluble in water: 6.9 pounds / 100 gallons at 60°F
- Not flammable

PHYSICAL / CHEMICAL PROPERTIES OF CHLORINE

- A POWERFUL OXIDIZER – SUPPORTS COMBUSTION OF MANY MATERIALS
- GENERALLY STORED AND SHIPPED AS A LIQUID UNDER PRESSURE
- WET CHLORINE IS HIGHLY CORROSIVE

RELEASE PROPERTIES OF CHLORINE

- VAPOR HEAVIER THAN AIR – RELEASES TEND TO STAY NEAR THE GROUND, FILL LOW LYING AREAS, AND TO DISPERSE SLOWLY
- APPLYING WATER TO LIQUID CL_2 ADDS HEAT, INCREASES VAPORIZATION
- CHLORINEAND WATER FORM CORROSIVE HCL (HYDROCHLORIC) AND HOCL (HYPOCHLOROUS) ACIDS
- WATER SPRAY ON RELEASE POINTS CAN WORSEN RELEASES

Health Effects of Chlorine

- CHLORINE IS EXTREMELY IRRITATING AND CAN BURN THE SKIN AND EYES
- IF INHALED, CHLORINE CAUSES RESPIRATORY DISTRESS, AND CAN BE FATAL
- LIQUID CHLORINE RELEASES WILL FORM AN IMMEDIATE CLOUD (FLASH VAPOR) AND WILL COOL TO -29 F.
- EXPOSURE TO LIQUID CAN CAUSE FROSTBITE, AS WELL AS CHEMICAL BURNS.

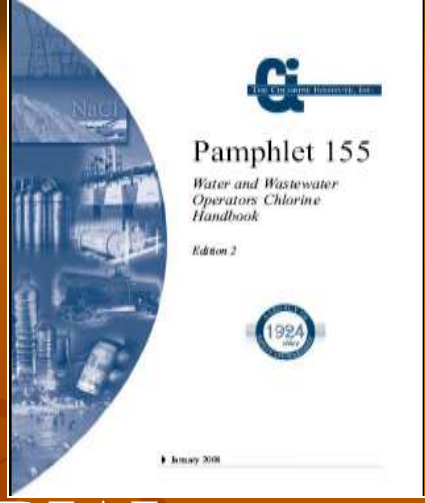
HEALTH EFFECTS OF CHLORINE EXPOSURE

- 1-3 PPM - MILD MUCOUS MEMBRANE IRRITATION
- 5-15 PPM - UPPER RESPIRATORY TRACT IRRITATION
- 30 PPM - IMMEDIATE CHEST PAIN, VOMITING, SHORTNESS OF BREATH (DYSPNEA) AND COUGH
- 40-60 PPM - INFLAMMATION OF LUNG TISSUES (TOXIC PNEUMONITIS) AND FLUID ACCUMULATION (PULMONARY EDEMA)
- 430 PPM - DEATH WITHIN 30 MINUTES
- 1,000 PPM - DEATH WITHIN A FEW MINUTES

EXPOSURE LIMITS FOR CHLORINE

- **OSHA /MIOSHA PEL - 1ppm**
- **NIOSH Recommended Exposure Limit(REL) - 0.5ppm**

CHLORINE IN WATER TREATMENT



- EXCELLENT SANITIZING AGENT
- FORMS HYPOCHLOROUS ACID IN SOLUTION – ACTIVE BIOCIDAL MATERIAL

  $CL_2 + H_2O \rightarrow HOCL + HCL$
- GOOD RESIDUAL ACTION – BACTERIOSTATIC AT 1-5 PPM CL_2 IN WATER
- ADVANCED TREATMENT MAY USE UV LIGHT WITH OZONE FOR SANITIZING, WITH SMALL DOSES OF CHLORINE TO ESTABLISH A BACTERIOSTATIC RESIDUAL
- CI PAMPHLET 155 – WATER & WASTEWATER OPERATORS CHLORINE HANDBOOK

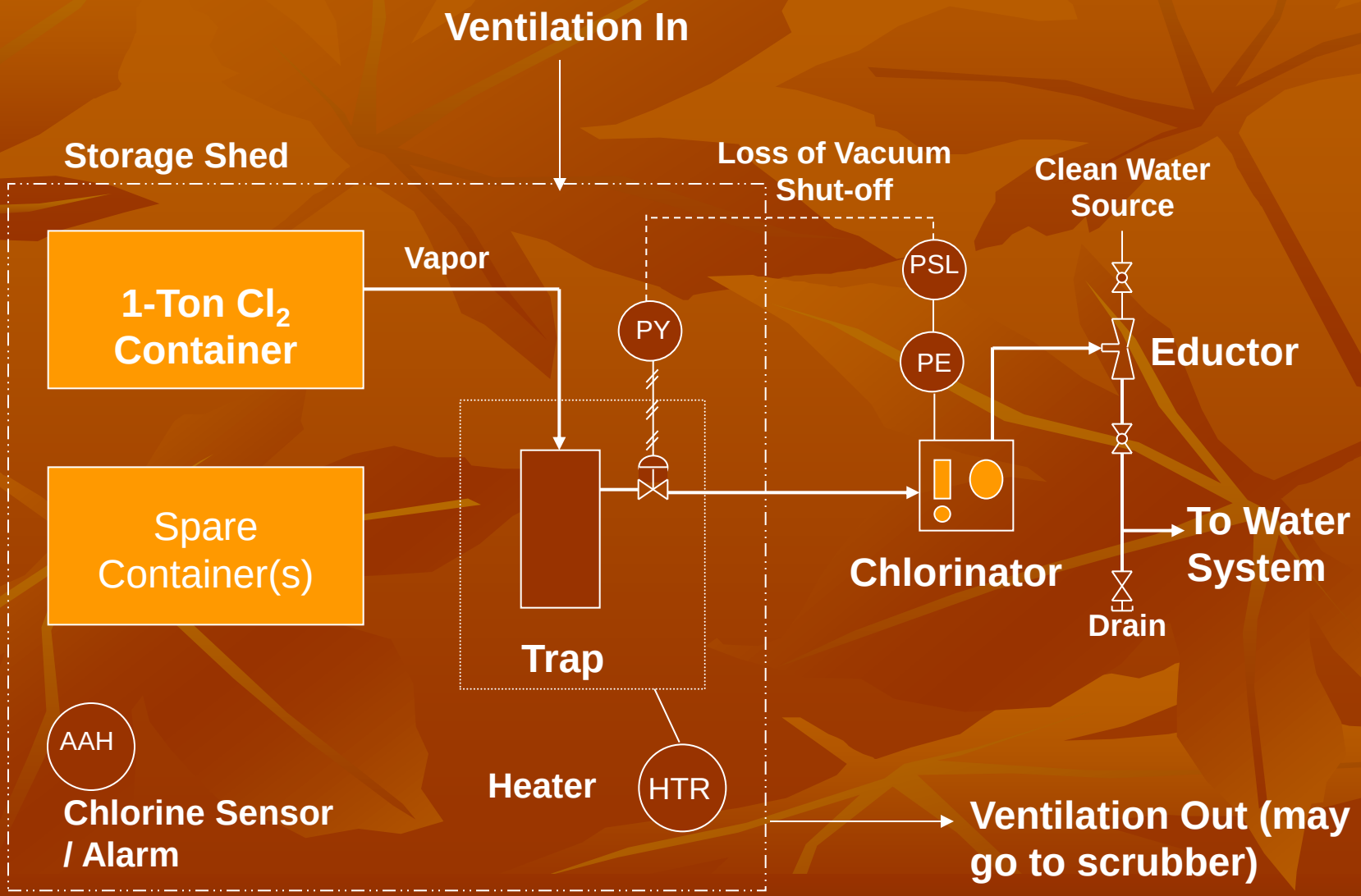
CHLORINE IN WATER TREATMENT

Chlorine Ton Containers in Water Treatment System (usually in separate building / room, with independent ventilation. May exhaust to scrubber)

Vacuum Chlorinator Cabinet

To injection point

CHLORINE IN WATER TREATMENT



PROCESS SAFETY MANAGEMENT (PSM)
PART 591 - SCOPE

- THESE RULES ESTABLISH THE MINIMUM REQUIREMENTS FOR PREVENTING OR MINIMIZING THE CONSEQUENCES OF CATASTROPHIC RELEASES OF TOXIC, REACTIVE, FLAMMABLE, OR EXPLOSIVE CHEMICALS.

PROCESS SAFETY MANAGEMENT (PSM)
1910.119(a) - APPLICATION

- A PROCESS WHICH INVOLVES A CHEMICAL AT OR ABOVE THE SPECIFIED THRESHOLD QUANTITIES (TQ) LISTED IN APPENDIX A TO THIS SECTION.

- Chlorine TQ = 1,500 pounds.
- Sulfur Dioxide TQ = 1,000 pounds.

ELEMENTS OF PSM STANDARD

- Employee participation
- Process safety information
- Process hazard analysis
- Operating procedures
- Training
- Contractors
- Pre-startup safety review

ELEMENTS OF PSM STANDARD

- Mechanical integrity
- Hot work permit
- Management of change
- Incident investigation
- Emergency planning and response
- Compliance audits
- Trade secrets

1910.119(c)
EMPLOYEE PARTICIPATION

- Employers shall develop a written plan of action regarding the implementation of the employee participation including information on how employees will be consulted on the development of ALL PSM standard elements
  - Process Hazard Analysis
  - Operating Procedures
  - Training
  - Management of Change
  - Emergency Action Plan
  - Compliance Audit

PSM - 1910.119(d) - Process Safety Information

- The employer shall complete a compilation of written process safety information before conducting any process hazard analysis required by the standard.

PSM -1910.119(d)(1)
Process Safety Information

- **Information pertaining to the hazards of the highly hazardous chemicals in the process:**
  - **Toxicity information**
  - **Permissible exposure limits**
  - **Physical data**
  - **Reactivity data**
  - **Corrosivity data**
  - **Thermal and chemical stability data**
  - **Hazardous effects of inadvertent mixing of different materials that could foreseeably occur**
- **Contained in MSDS**

PSM - 1910.119(d)(2)(i)
Process Safety Information

- Information pertaining to the technology of the process:
  - A block flow diagram or simplified process flow diagram
  - Process chemistry
  - Maximum intended inventory
  - Safe upper and lower limits for such items as temperatures, pressures, flows or compositions
  - An evaluation of the consequences of deviations, including those affecting the safety and health off employees

PSM - 1910.119(d)(2)(i)(B) Example of Process chemistry

- Chlorine gas, when exposed to water forms hypochlorous acid and hydrochloric acid (an oxidizing agent).
- It hydrolyzes rapidly according to the equation:

$$CL_2(g) + H_2O \Rightarrow HOCl\ (aq) + HCl\ (aq)$$

PSM - 1910.119(d)(2)(i)(C) Example Maximum intended inventory

- Maximum Intended Inventory = _____Tons.

- Just knowing how much chlorine is on-site does not meet the intent of the standard.

Examples for the means of maintaining- 1910.119(d)(2)(i)(D) and (E)- Safe Upper and Lower Limits , etc.

Equipment	Parameter	Nominal	Low	High	Consequence of deviation	Health & Safety Effects
Container	Temp F	Ambient	NA	150 F	Fusible plug melts, releasing chlorine	
Liquid line between ton container and evaporator	Pressure in psig	100 psig	30 psig	140 psig	At 400 psig, rupture disc blows, releasing liquid into liquid pressure relief system.	
Injector	Water pressure psig		20 psig		Minimum of 20 psig necessary to develop proper vacuum in chlorinator	

PSM - 1910.119(d)(3)(i)
Process safety information Information Pertaining to the Equipment in the Process

- Materials of Construction
- Piping and instrument diagrams (P&ID's)
- Electrical Classification
- Relief system design and design basis
- Ventilation system design
- Design codes and standards employed
- Material and energy balances for processes built after May 26, 1992
- Safety systems (e.g., interlocks, detection or suppression systems)

Process Safety Information 1910.119(d): Piping

- Do materials for piping and components comply with Ci recommendations – for metallurgy, schedule, and welding?

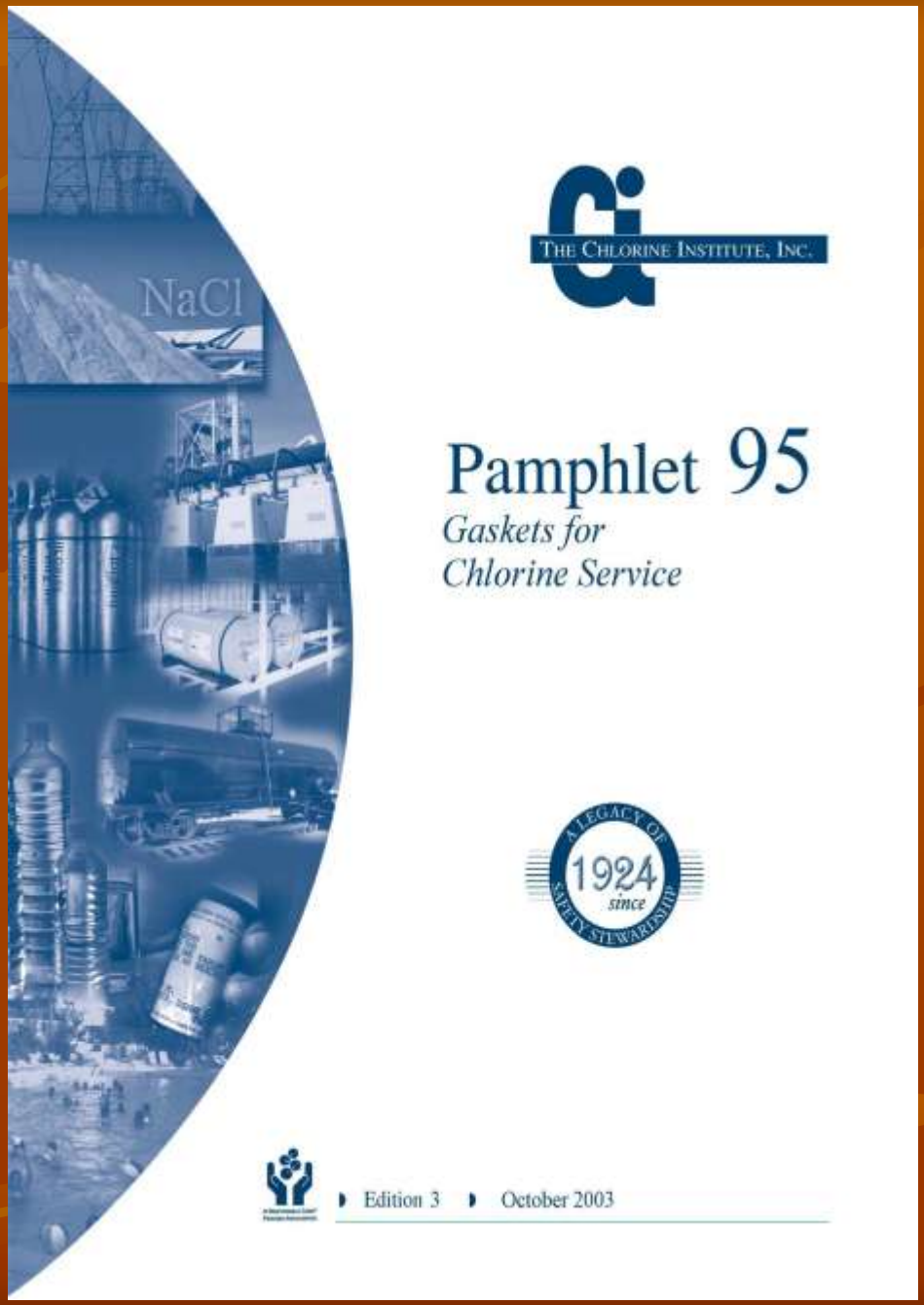
  – Ci 6 Sec 2

- Are materials for threaded connections PTFE tape or non-reactive pipe dope?
  - Ci 1 and 6 Sec. 3

Process Safety Information (d) (Piping) cont.

- Are gaskets compatible with liquid and gaseous chlorine?

CI Pamphlet 95 Sec 3



Process Safety Information (d) (piping) cont.

- Is piping adequately supported and braced? – Ci 6 Sec 10
- Are Cylinders and piping system protected from vehicular traffic?

  – Ci 6 Sec 10
- If piping is underground, is it monitored for leak?

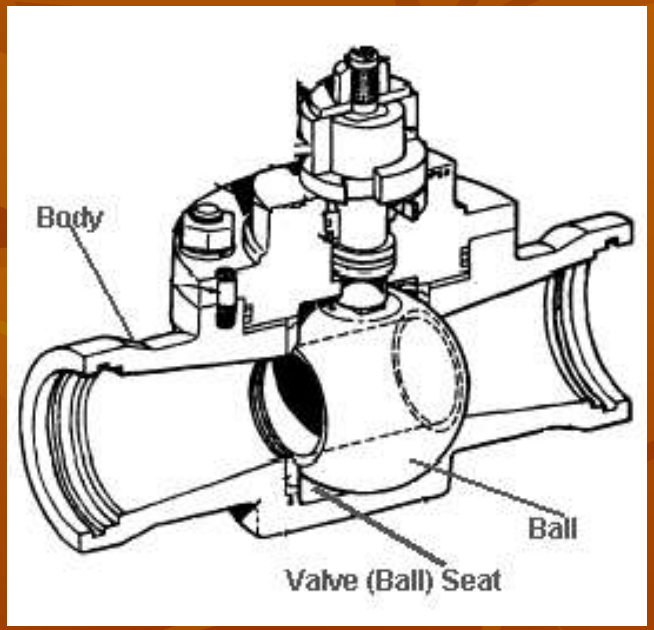
  – Ci 60 Sec 3

Process Safety Information (d) (Piping) cont.

- Are there expansion pots where liquid Cl_2 can be blocked in?
  - CI Pamphlet 5 Sec 5
- Is the expansion pot isolated by rupture disk and monitored?
  - CI Pamphlet 6 Sec 5

Process Safety Information (d) (Piping) cont.

- Are liquid valves designed to prevent trapping Cl_2 in the body? – Ci 6 Sec 4



- When Cl_2 pressure is lower than process pressure, is there backflow prevention? – Ci 9 Sec 4 and 5

Process Safety Information (d) (General Process)

- Are process areas monitored for chlorine?
  - Ci 1 Sec 7
- Are indoor chlorine areas properly ventilated?
  - Ci 1 Sec 7
- Are process vessels equipped with relief devices?
  - Ci 9 Sec 5

Process Safety Information (d) (Scrubbers) cont.

- Is there a means for chlorine gas to be vented from equipment and piping system?
  - Ci 89 Sec 1
- Is the scrubbing solution monitored to confirm continued capability?
  - Ci 89 Sec 2
- Is the scrubbing vent monitored? – Ci 89 Sec 4
- Is there adequate backflow prevention?
  - Ci 89 Sec 4

PSM - 1910.119(d)(3)(i)(A) Materials of Construction

Name/ID of Equipment	Design Codes	Materials of Construction
Chlorine piping	The Chlorine Manual	Schedule 80 seamless carbon steel pipe with 3,000 lb. forged steel fittings
Chlorine piping (vacuum) piping and fittings	Chlorine Institute, Pamphlet #6	Schedule 80 polyvinyl chloride pipe with solvent weld fittings; Dow lined pipe with Kynar (non vented)
Flexible connectors	The Chlorine Manual	Cadmium plated copper tubing

PSM - 1910.119(d)(3)(i)(C) Electrical Classification

- Since chlorine is neither classified as a flammable nor a combustible material, electrical classification is not applicable.

PSM - 1910.119(d)(3)(i)(E)
Relief system and Ventilation System

- Ton cylinder fusible plugs
- Rupture discs
- Pressure relief valves
- The Chlorine and Sulfur Dioxide buildings should be equipped with an automatically operated ventilation system. that operates when a building door is opened. A minimum of 30-40 air changes per hour is normally recommended for emergency ventilation

PSM - 1910.119(d)(3)(i)(F) Design Codes and Standards

- These codes and standards are published by organizations such as:
- The Chlorine Institute.
- American Water Works Association (AWWA).
- Chlorine Handling Manual - U.S. Filter Wallace & Tiernan.
- American National Standards Institute (ANSI).
- National Fire Prevention Association (NFPA).
- American Society for Testing and Materials (ASTM).

Examples for the means of maintaining 1910.119(d)(3)(i)(F)-Design Codes and Standards Employed

Name/ID of Equipment	Design Codes
Ton Containers	DOT Specifications
Piping and Valves (general)	ASTM Chlorine Institute Pamphlet #155
Vaporizer	Chlorine Institute Pamphlet #9

PSM - 1910.119(d)(3)(i)(H) Safety systems (e.g., interlocks, detection or suppression systems)

- Chlorine and Sulfur Dioxide buildings equipped with Chlorine and Sulfur Dioxide gas detectors
- Detectors interlocked with alarm system

PSM - 1910.119(d)(3)(ii) Recognized and generally accepted good engineering practices (RAGAGEPS).

- General: The Chlorine Institute, Manual, Fifth Edition, 1986.
- Piping: Chlorine Institute Pamphlet #6, Piping Systems for Dry Chlorine.
- Vaporizers: Chlorine Institute Pamphlet #9, Chlorine Vaporizing Equipment.
- Many Others

PSM - 1910.119(e)(1)
Process Hazard Analysis (PHA)

- Perform an initial process hazard analysis (PHA) on processes covered by the PSM standard.
- Perform PHA Revalidation every 5 years
- Select a PHA methodology that is appropriate to determine and evaluate the hazards of the process
- Use a PHA team with engineering and operations expertise, including one employee with experience in the process and one person knowledgeable in the PHA methodology
- Establish a system to promptly address the team's findings and recommendations

PSM - Process Hazard Analysis 1910.119 (e)

- Investigate the potential for nitrogen trichloride accumulation? – Ci 9 Sec 5, Ci 152 Sec 5
- Retain PHA reports and updates or revalidations, as well as documented resolutions of recommendations, for the life of the process.

PSM - 1910.119(e)(3)
PHA Shall Address…

- The hazards of the process;
- Identification of any previous incident which had a likely potential for catastrophic consequences in the workplace
- Engineering and administrative controls applicable to the hazards and their interrelationships
- Consequences of failure of engineering and administrative controls
- Facility siting
- Human factors
- A qualitative evaluation of a range of the possible safety and health effects of failure of controls on employees in the workplace.

http://www.osha.gov/pls/oshaweb/owadisp.show_document?p_table=INTERPRETATIONS&p_id=25051

PSM - 1910.119(f)(1) Operating procedures

- Initial startup
- Normal operations
- Temporary operations
- Emergency shutdown including the conditions under which emergency shutdown is required, and the assignment of shutdown responsibility to qualified operators to ensure that emergency shutdown is executed in a safe and timely manner;
- Emergency operations
- Normal shutdown
- Startup following a turnaround, or after an emergency shutdown

PSM - Operating Procedures (f)

- Also Establish Procedures for:
  - Appropriate steps for evacuating and filling cylinders and ton containers?
    - Ci 162 Sec 6
  - Leak testing containers before filling?
    - Ci 17 Sec 3
  - Proper evacuation of lines before disconnecting?
    - Ci 17 Sec 3
  - Appropriate torque setting of valves and packing nuts?
    - Ci 17 Sec 4

PSM - Training - 1910.119 (g) (employees and contractor)

- **Provide initial Training to employees presently involved in operating a process, and other employees before being involved in operating a PSM covered process**
- **Provide Refresher Training at least every three years, and more often if necessary to assure that employees understand and adhere to current operating procedures of the process.**
- **Consult with employees to determine appropriate frequency of refresher training**

PSM - Training - 1910.119 (g) (employees and contractor)

- Train Employees on:
  - Operation of chlorine equipment and container handling
  - Properties and physiological effects of chlorine
  - Equipment failure and leak reporting procedures
  - Emphasis on the specific safety and health hazards, emergency operations including shutdown, and safe work practices applicable to the employee's job tasks.

PSM - Training - 1910.119(g) (Employees and Contractor Cont.)

- Location, purpose and use of emergency equipment, fire fighting equipment, fire alarms, and shutdown equipment.
- Locations, purpose and use of safety equipment
- Location, purpose, and use of specialized first aid equipment.

PSM - 1910.119(g)(3) Training documentation.

- Prepare a record which contains the identity of the employee, the date of the training, and the means used to verify that the employee understood the training
- Acceptable means would included testing and/or on-the-job observation by experienced operator/supervisor

PSM - 1910.119(h)(1) Contractors.

- Applies to contractors performing maintenance or repair, turnaround, major renovation, or specialty work on or adjacent to a covered process.
- It does not apply to contractors providing incidental services which do not influence process safety, such as janitorial work, food and drink services, laundry, *delivery or other supply services*.

PSM - 1910.119(h)(1) Contractors Cont.

- Host Employer responsibilities.
  - When selecting a contractor, must obtain and evaluate information regarding the contract employer's safety performance and programs.
  - Inform contract employers of the known potential fire, explosion, or toxic release hazards related to the contractor's work and the process.
  - Explain to contract employers the applicable provisions of the facility's Emergency Action Plan.
  - Develop and implement safe work practices to control the entrance, presence and exit of contract employers and contract employees in PSM covered process areas.
  - Periodically evaluate the performance of contract employers in fulfilling their obligations.
  - Maintain a contract employee injury and illness log related to the contractor's work in process areas.

PSM - 1910.119(i)(1) Pre-startup safety review (PSSR).

- The employer shall perform a pre-startup safety review for new facilities and for modified facilities when the modification is significant enough to require a change in the process safety information

PSM - 1910.119(j) Mechanical integrity

- Applies to the following process equipment:
  - Pressure vessels and storage tanks
  - Piping systems (including piping components such as valves)
  - Relief and vent systems and devices
  - Emergency shutdown systems
  - Controls (including monitoring devices and sensors, alarms, and interlocks)
  - Pumps

PSM - Key Elements of a Mechanical Integrity Program

- Maintenance procedures (j)(2):
  - Inspections and tests to be performed.
  - Test and inspection frequencies.
  - Written procedures for maintenance tasks
  - Criteria for acceptable results.
  - Appropriate documentation of tests and inspections and their results.
  - Documentation of manufacturer recommendations for equipment and instrumentation.

PSM - Key Elements of a Mechanical Integrity Program

- Training for process maintenance activities
- Inspection and testing according to defined practices, codes and standards (RAGAGEPS)
- Correction of deficiencies in equipment that are outside acceptable limits
- Development of QA Program

PSM - 1910.119(j)(4) Inspection and testing.

- Performed Inspections and tests on process equipment.
- Inspection and testing procedures shall follow recognized and generally accepted good engineering practices (RAGAGEPS)
- The frequency of inspections and tests of process equipment shall be consistent with applicable manufacturers' recommendations and good engineering practices, and more frequently if determined to be necessary by prior operating experience
- The employer shall document each inspection and test and has been performed on process equipment. The documentation shall identify the date of the inspection or test, the name of the person who performed the inspection or test, the serial number or other identifier of the equipment on which the inspection or test was performed, a description of the inspection or test performed, and the results of the inspection or test

PSM - Mechanical Integrity Programs

Critical Equipment	Basis (i.e., manufacturer and RAGAEPS)	Frequency of testing (to be consistent with manufacturer's recommendations and good engineering practices)
Chlorine piping	Manufacturer and Chlorine Institutes Pamphlet 155	Visual inspections (manufacturer's recommendations), and; Chlorine Institutes Pamphlet 155 Water and Wastewater Operators Chlorine Handbook, Edition 1 1999, which states the following: *"Plastic piping can become brittle in chlorine service and has a limited service life. Periodic inspection and replacement is recommended."*
Chlorine Gas Leak Detectors (i.e., serious instruments and alarms)	Manufacturer	Testing (once per week) Zero and reset (Every 30 days) Calibrate (Every 60 days) Individual components of instrument loops may be grouped under a single instrument loop identification Functional test of each loop (every two years)

PSM - 1910.119 (j) Mechanical Integrity

- Do procedures require leaks to be repaired before allowing operations to begin or continue? – Ci 1 Sec 4, Ci 49 Sec 11, Ci 66 Sec 9
- Have lubricants been checked for compatibility (j(6))? – Ci 6 Sec 3
- Is the emergency shut-off system tested routinely? – Ci 57 Sec 3
- Are chlorine hoses tested and replaced on a preventive maintenance basis? – Ci 6 App A

PSM - Mechanical Integrity (j)

- Is the piping system routinely inspected? (Ci 6 Sec 12)
  - Flange bolt condition and tightness
  - Valve packing leaks
  - Valve operation
  - Insulation condition
  - Paint condition
  - Condition of supports
  - NDT for piping inspections

PSM - Mechanical Integrity (j)

- Are there procedures for inspection, testing and calibration of Cl2 / SO2 alarm systems?
- Are there procedures for inspection of valves? – Ci 17 Sec 4
- Are pressure relief valves scheduled for periodic inspection? – Ci 5 Sec 9
- Are chlorine storage tanks / cylinders scheduled for inspection? – Ci 5 Sec 8

PSM - Mechanical Integrity (j)

- Are there scheduled routine external and detailed internal inspections of the vaporizer? - Ci 9 Sec 8
  - Gaskets and valves for leaks
  - Damage and signs of leaks
  - Proper function of all instruments
  - Condition of supply equipment
  - General housekeeping to guarantee safe evacuation

PSM - 1910.119(k)(1) Hot Work Permit.

- The employer shall issue a hot work permit for hot work operations conducted on or near a covered process.

- The permit shall document that the fire prevention and protection requirements in 29 C.F.R. 1910.252(a) have been implemented prior to beginning the hot work operations; it shall indicate the date(s) authorized for hot work; and identify the object on which hot work is to be performed. The permit shall be kept on file until completion of the hot work operations.

PSM - 1910.119(l)(1) Management of change.

- Establish and implement written procedures to manage changes (except for "replacements in kind") to process chemicals, technology, equipment, and procedures; and, changes to facilities that affect a covered process.
- The procedures shall assure that the following considerations are addressed prior to any change:
  - The technical basis for the proposed change;
  - Impact of change on safety and health;
  - Modifications to operating procedures;
  - Necessary time period for the change; and,
  - Authorization requirements for the proposed change.

PSM - 1910.119(m)(1) Incident investigation

- The employer shall investigate each incident which resulted in, or could reasonably have resulted in a catastrophic release of highly hazardous chemical in the workplace
- Initiate Incident Investigation within 48 Hours of being Notified of the incident
- Develop and maintain written incident investigation report

PSM - 1910.119(n)
Emergency planning and response.

- Establish and implement an emergency action plan for the entire plant in accordance with the provisions of 29 C.F.R. 1910.38(a).
- In addition, the emergency action plan shall include procedures for handling small releases.
- Employers may also be subject to the hazardous waste and emergency response provisions contained in 29 C.F.R 1910.120(a), (p), and (q).

PSM - 1910.119(o)(1) Complaince Audits.

- Employers shall certify that they have evaluated compliance with the provisions of this section at least every three years to verify that the procedures and practices developed under the standard are adequate and are being followed.
- **Promptly** determine and document an appropriate response to each of the findings of the compliance audit, and document that deficiencies have been corrected.
- Maintain at least the two most recent compliance audit reports.

PSM - 1910.119(p)(1) Trade Secrets.

- Chlorination/De-chlorination processes utilizing chlorine and sulfur dioxide generally do not involve trade secrets.

References & Sources of Information

- Many key safety related publications are available for download free of charge from The Chlorine Institute (Ci), a major industry trade group, at http://www.cl2.org
- The Chlorine Institute also has RAGAGEPs on chlorine system design and operation(for purchase)
- OSHA's chlorine guidelines are at http://www.osha.gov/SLTC/healthguidelines/chlorine/recognition.html
- OSHA / MIOSHA PART 591 – PSM STANDARD

QUESTIONS

THANK YOU FOR YOUR ATTENTION