Process Safety Management of Highly Hazardous & Explosive Chemicals

Process Safety Information & Toxicity
1910.119(d)(1)

In accordance with the schedule set forth in paragraph (e)(1) of this section, the employer shall complete a compilation of written process safety information before conducting any process hazard analysis required by the standard. The compilation of written process safety information is to enable the employer and the employees involved in operating the process to identify and understand the hazards posed by those processes involving highly hazardous chemicals. This process safety information shall include information pertaining to the hazards of the highly hazardous chemicals used or produced by the process, information pertaining to the technology of the process, and information pertaining to the equipment in the process.
Hazard Determination

- Single Process
- Any group of vessels which are interconnected, and
- Separate vessels which are located such that a highly hazardous chemical could be involved in a potential release
Hazard Determination

Determine:

- Chemicals in Your Process
- Process Chemistry
- Quantity of Chemicals in lbs
- Compare to Appendix A List with Threshold Quantities (TQ’s)
Hazard Determination

- How to Calculate from Gallons to lbs?

Multiply the gallons of Liquid
\[ \times 8.33 \text{ (How much a gallon of water weighs)} \times \text{Specific Gravity of Liquid} = \text{lbs of Liquid} \]

Example: Wt of 10,000 gallons of gasoline
\[ 10,000 \times 8.33 \times 0.739 = 61,559 \text{ lbs} \]
Hazard Determination

- Compare the lbs of Liquid or Gas to the Threshold Quantity in Appendix A of the Standard

Example: Anhydrous Ammonia
  TQ = 10,000 lbs

If You Exceed the Threshold Quantity, You Have a "Covered Process" & Are Required to Comply
Hazard Determination-Examples

The Threshold Quantity (TQ) for chlorine is 1500 lbs.

These cylinders will likely exceed the chlorine TQ.
Hazard Determination-Examples

- Food Processing & Cold Storage
- Anhydrous Ammonia Plants
- Typically involve Quantities of over 10,000 lbs in a single system or in close proximity to adjacent anhydrous systems
Hazard Determination-Examples

49 CFR Department of Transportation Hazardous Materials Act:

Gives OSHA authority to regulate worker safety in hazardous materials transportation (called a “reverse federal preemption provision”)

Hazardous material cargo would not be exempted by DOT Hazmat rules or from OSHA regulation including PSM (e.g., loading and unloading facilities)
Toxicity Information

1910.119(d)(1)(i)

Information pertaining to the hazards of the highly hazardous chemicals in the process. This information shall consist of at least the following: 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.

Note: Material Safety Data Sheets meeting the requirements of 29 CFR 1910.1200(g) may be used to comply with this requirement to the extent they contain the information required by this subparagraph.
Toxicity Information

- Obtain Toxicity Information on the Chemical(s) in the Process
- MSDS are Typical Resource
- You May Need Other References, NIOSH Pocket Guide, ACGIH TLV’s
Toxicity Information

- Additional References
  - Dangerous Properties of Industrial Materials by Irving Sax
  - NFPA Handbook, [www.nfpa.org](http://www.nfpa.org)
  - Patty’s Industrial Toxicology
MATERIAL SAFETY DATA SHEET

Recapture Metals, Inc. Gallium Mineral Water
High Point-Gallium
1877 E. Harris Lane (102-7) Revision Date: February 19, 2004
Blanding, Utah 84511 Emergency Phone:
(435) 678-2734 CHEMTREC: (800) 424-9300
FAX: (435) 678-3276

SECTION 1 - IDENTIFICATION

Substance: Gallium Nitrate Solution
Trade Names/Synonyms: Gallium Nitrate Solution; Gallium (III) Nitrate; Nitric Acid, Gallium (III) Salt; Gallium (III) Nitrate (3+); Nitric Acid, Gallium (3+); Oil810600
Chemical Family: Metal Salt
CAS#: 13494-90-1
Molecular Formula: Ga(NO3)3
Molecular Weight: 255.75

SECTION 2 - INGREDIENTS

Chemical: Gallium Nitrate
Gallium Nitrate 13494-90-1 10-15 Not established Not established
Nitric Acid 7697-37-2 0-1 2 ppm 2 ppm
Water 85-90 N/A N/A

SECTION 3 - PHYSICAL DATA

Description: Colorless solution
Boiling Point: 105-110°C, decomposes
Melting Point: No data
% Volatiles (by wt): 85-90
Solubility in Water: Very soluble

SECTION 4 - FIRE AND EXPLOSION HAZARD DATA

Flash Point: N/A
Auto Ignition Temperature: N/A
Extinguishing Media: Concentrated gallium nitrate (>40%) is a strong oxidizer whose heat of reaction with reducing agents or combustibles may cause ignition. Use water, carbon dioxide, dry chemical extinguishing agents, dry sand, or ground dolomite.
Special Fire Fighting Procedures: No special fire fighting procedures needed. Use normal procedures, which include wearing NIOSH/MSHA approved self-contained breathing apparatus, flame and chemical resistant clothing, hoes, boots, and gloves. If in contact with the skin, remove all material from the fire area. Cool container with water from maximum distance.

SECTION 5 - HEALTH DATA

OSHA (PEL): None
ACGIH (TLV): None

A. ANIMAL TOXICITY
Half the mice ingesting 4360 mg/kg (solid nitrate/body weight) died, with symptoms of paralysis, somnolence, and changes in their food intake. For animal dosage, do not administer internally in concentrations greater than 1% gallium nitrate; topical applications no greater than 7% gallium nitrate.

B. EFFECTS OF EXPOSURE

ACUTE EFFECTS - Ingestion: Large amounts of concentrated nitrate taken by mouth may have serious or even fatal results. The symptoms are dizziness, abdominal cramps, vomiting, a metallic taste, itching, bone marrow depression leading to anemia, bloody diarrhea, blood damage with subsequent renal damage, weakness, convulsions, and collapse. May damage the mouth and gastrointestinal tract.
Skin Contact: Will cause irritation with prolonged contact or if highly concentrated.
Eye Contact: Will cause irritation of the cornea and the conjunctiva.
Inhalation: May cause irritation of mucous membranes and respiratory passages.
Medical Conditions Aggravated by the Chemical: None known

SECTION 5 - HEALTH DATA (cont.)

Other Medical Hazards: None known
Most Likely Route of Entry: Ingestion

C. EMERGENCY AND FIRST-AID PROCEDURES

Ingestion: Treat symptomatically and supportively. Obtain medical attention immediately. If vomiting occurs, keep head lower than hips to prevent aspiration.
Skin Contact: Remove contaminated clothing, flood skin with large amounts of water. If irritation persists seek medical attention. In case of chemical burns, cover area with sterile, dry dressing.
Eye Contact: Immediately flush eyes, including under eyelids, with large amounts of water for at least 15 minutes. Cover with sterile bandage. Call a physician immediately.
Inhalation: Remove from exposure area to fresh air. If breathing has stopped, perform artificial respiration. Keep the person warm and at rest. Treat symptomatically and supportively. Get medical attention immediately.

SECTION 6 - REACTIVITY

Incompatibility: Reducing agents, oxidizable material, combustibles. Mixtures with Boron Phosphide, Cyanides, Esters, Phosphor, Phosphorus, Sodium Hypophosphite, Sodium Chloride, and Thiooxanates may be explosive. Avoid contact of Gallium metal and strongly acidic Gallium solutions with aluminum structures (plates). Metallic Gallium will dissolve the metal, resulting in a substantial reduction of the construction. However, these dilute solutions of gallium nitrate (15% or less) have no discernable effect on aluminum during 24-hour exposure testing.

Hazardous Decomposition Products: NOx, Ga2O3
Conditions to Avoid: Thermal decomposition.
Stability: Stable under normal temperatures and pressures.
Hazardous Polymerization: Will not occur

SECTION 7 - ENVIRONMENTAL INFORMATION

RCRA Code: D001: TSCA Registration: Yes
Spill and Leak Procedure: Keep unnecessary personnel away. Isolate hazard area and deny entry. Wear protective equipment. Cover spill with dry sand or vermiculite. Mix well to ensure all liquid is absorbed, carefully transfer to a container for later disposal.
Waste Disposal: Consult state, local, or federal EPA regulations for proper disposal procedures.

SECTION 8 - PROTECTION INFORMATION

Ventilation: Provide local exhaust or general dilution ventilation system.
Respiratory Protection: High efficiency particle respirator or self contained breathing apparatuses depending upon contamination levels present. Both of the positive pressure mode type with a full face piece.

SECTION 9 - SPECIAL PRECAUTIONS

Handling/Storage: Keep container tightly closed. Store in a cool, dry, ventilated area. Wash thoroughly after use.
Other Precautions: Lab coat, apron, or coveralls; eyewash capable of sustaining flushing, and facilities for washing.

SECTION 10 - TRANSPORTATION INFORMATION - U. S. D. O. T.
Per IATA regulations special provisions A85, this material is NON REGULATED

SECTION 11 - COMMENTS

Gallium nitrate solutions at the concentration specified in Section 2, pose minimal health and safety risks as long as handled responsibly. Generally, the above hazards and warnings pertain to highly concentrated solutions or solid nitrate salts.

Employers should use this information only as a supplement to other information gathered by them, and should make independent judgment of suitability of this information to sustain proper use and protect the health and safety of employees. This information is furnished without warranty, and any use of the product not in accordance of this Material Safety Date Sheet, or in combination with any other product or process, is the responsibility of the user.
Permissible Exposure Limits

- OSHA Establishes PEL’s
- Listed in 1910.1000 Table Z-1
Physical Data

- Physical Data of Chemical - Example - Xylene
- Physical state and appearance:
  - Liquid. (Liquid.) **Odor:** Not available.
  - **Taste:** Not available.
  - **Molecular Weight:** 106.17 g/mole
  - **Color:** Colorless.
  - **pH (1% soln/water):** Not applicable.
  - **Boiling Point:** 138°C (280.4°F)
  - **Melting Point:** 12°C (53.6°F)
Critical Temperature: Not available.
Specific Gravity: 0.86 (Water = 1)
Vapor Pressure: 9 mm of Hg (@ 20°C)
Vapor Density: 3.7 (Air = 1)
Odor Threshold: 0.62 ppm
Dispersion Properties: See solubility in water, methanol, diethyl ether.
Solubility: Easily soluble in methanol, diethyl ether. Insoluble in cold water, hot water.
Reactivity Data

- Reactivity Data of Chemical-Example - Anhydrous Ammonia

- **STABILITY**: Stable at room temperature. Ammonia will react exothermically with acids and water.

- **CONDITIONS TO AVOID**: Avoid mixing with sulfuric acid or other strong mineral acids. Avoid mixing with hypochlorites (chlorine bleach) or other halogens and sodium hydroxide. Avoid contact with galvanized surfaces, copper, brass, bronze, aluminum alloys, mercury, gold, silver, and strong oxidizers. Avoid heating.

- **HAZARDOUS DECOMPOSITION PRODUCTS**: Hydrogen and nitrogen gases above 450°C (842°F)
Corrosivity Data

- **Example - Sulfuric Acid**
- Corrosive. Swallowing can cause severe burns of the mouth, throat, and stomach, leading to death. Can cause sore throat, vomiting, diarrhea. Circulatory collapse with clammy skin, weak and rapid pulse, shallow respirations, and scanty urine may follow ingestion or skin contact. Circulatory shock is often the immediate cause of death.
- Toxic fumes of oxides of sulfur when heated to decomposition. Will react with water or steam to produce toxic and corrosive fumes. Reacts with carbonates to generate carbon dioxide gas, and with cyanides and sulfides to form poisonous hydrogen cyanide and hydrogen sulfide respectively.
Thermal & Chemical Stability

- **Example - Sulfur Dioxide**
- **General Behavior**: React with moisture to give very corrosive sulfurous acid.
- **Aluminum**: Satisfactory
- **Brass**: Satisfactory but corrosive in presence of moisture.
- **Copper**: Satisfactory but corrosive in presence of moisture.
- **Ferrite Steels (e.g. Carbon steels)**: Satisfactory but corrosive in presence of moisture.
- **Stainless Steel**: Satisfactory but corrosive in presence of moisture except for high quality stainless steel
High Pressure Hydrogen Plant
Team Exercise

- With the Information to Follow in The NASA Case Study Video, Presentation & Notebook,

- With Your Team Members, Answer the Following Questions:
Case Study Facts

Remember:

- The High Pressure Gas Plant Uses
  - Helium
  - Nitrogen
  - Hydrogen

- The Nitrogen & Helium Plant is one Section of the Plant
- The Hydrogen Plant is remotely located from the Nitrogen & Helium Plant
- The Hydrogen is Piped from the Hydrogen Plant to the Engine Test Stands through a valved system
- There are approximately 100 miles of pipe at the NASA Stennis Space Center
Case Study Exploration

1. What is the Appearance & State of Hydrogen in the Gas Plant?
2. What is the Specific Gravity of Hydrogen?
3. What are the Physical Hazards related to Liquid & Gaseous Hydrogen?
4. What is the Toxicity or Health Hazard of Liquid & Gaseous Hydrogen?
5. Are there incompatibilities with Hydrogen Gas?

We will Discuss Team Findings
What’s Next

- Technology of the Process &
- Equipment in the Process