

Drinking Water Plant Operator Certification Training



Module 25: Hypochlorite

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MSDS for sodium hypochlorite

Unit 1 – Background and Properties

Learning Objectives

- Outline the history of hypochlorite use.
- List the uses of hypochlorite.
- Explain how hypochlorite is produced.
- List and explain six properties of hypochlorite.

History of Use

- During the early history of water chlorination, the only sources of chlorine were dry chlorine-containing compounds and sodium hypochlorite bleach solutions. Initially, the following problems occurred:
 - ▶ The poor stability and variable effective chlorine content resulted in operating difficulties.
 - ▶ Feeder equipment was crude, therefore, yielding erratic results.
- In 1909, liquid chlorine became commercially available and the use of hypochlorite for water chlorination gradually decreased in popularity.
- In 1928, the commercial availability of calcium hypochlorite resulted in renewed use.

Uses



Hypochlorite refers to the various salts of hypochlorous acid commonly used in water treatment for disinfection, oxidation, and taste and odor control. This term is commonly used interchangeably to refer to the liquid form, sodium hypochlorite, and the solid form, calcium hypochlorite.

Disinfection

- Chlorine compounds are added to water to destroy or inactivate disease-producing (pathogenic) organisms.
- Disinfection differs from sterilization, which is the destruction of all living organisms.

Oxidation

- Hypochlorites are commonly used to oxidize iron, manganese, organic matter, cyanide, and sulfide for subsequent removal.

Taste and Odor Control

- Removal (oxidization) of chemicals and organic matter helps to control tastes and odors in the treated water supply.

Hypochlorite Production

Manufactured Products

- There are two types of hypochlorites that are manufactured: liquid sodium hypochlorite and granular calcium hypochlorite. These will be discussed in more detail later in this unit.

On-Site Generation

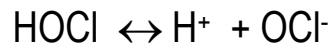
- Hypochlorites can be generated on-site. This will be discussed in greater detail in Unit 3 of this module.

AWWA Standard Product Specification

The American Water Works Association (AWWA) has established Standard ANSI / AWWA B300-99, covering the hypochlorite chemicals for use in the treatment of water supplies. The standard provides the minimum requirements for hypochlorites, including physical, chemical, packaging, shipping and testing requirements. Plant operators should verify that the chemicals used comply with this standard.

Chemistry

- Hypochlorites have the same equilibrium in water as gaseous chlorine.
- Hypochlorous acid (HOCl) dissociates into hydrogen (H⁺) and hypochlorite (OCl⁻) ions.
 - ▶ The reaction is almost instantaneous.
 - ▶ The reaction is dependent on temperature and pH.
 - ▶ The reaction is reversible:



- At pH below 6, hypochlorous acid is weak and dissociates poorly.
- Between pH 6 and 8.5, a sharp change from undissociated HOCl to almost complete dissociation occurs.
 - ▶ At 20° C above pH 7.5 and at 0°C above pH 7.8, hypochlorite ions (OCl⁻) predominate.
- Above pH 9.5, OCl⁻ exists almost exclusively.
- The normal pH of water supplies is within the range where both hypochlorous acid and hypochlorite ion exist as indicated in the following figure.
 - ▶ Solutions of hypochlorites contain excess alkali, which tends to increase pH.
- The disinfection effectiveness of liquid chlorine will increase with temperature and decrease with pH.

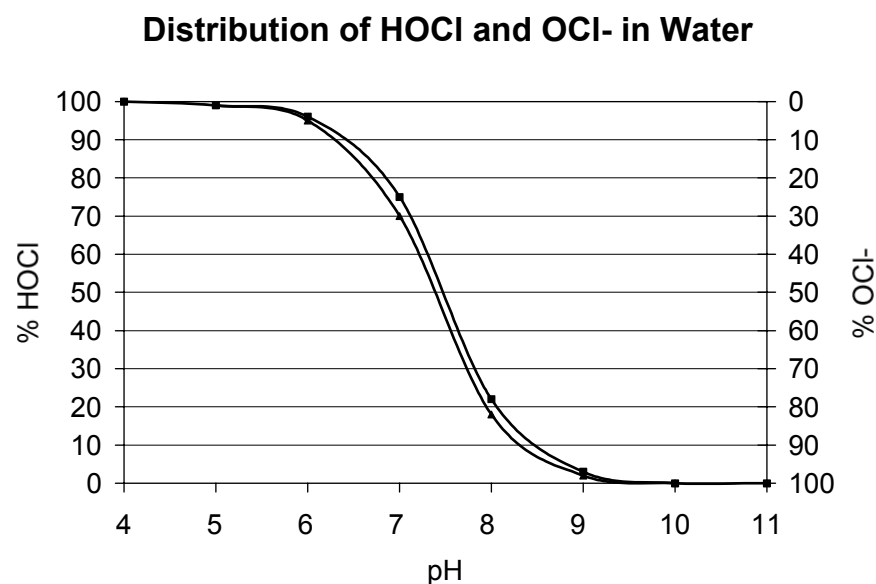


Figure 25.1 The Distribution of HOCl and OCl⁻ in Water



Free available chlorine is chlorine existing in water as hypochlorous acid and hypochlorite ions.

Sodium Hypochlorite

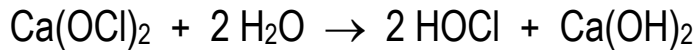
- Sodium hypochlorite is a clear, light yellow-green liquid and is supplied in various strengths.
 - ▶ Common household laundry bleach is 5.25% available chlorine by weight.
 - ▶ Commercial strength used for water disinfection is 12 – 15% available chlorine by weight.
- It is strongly alkaline and corrosive.
- Sodium hypochlorite has a strong chlorine odor.
- The chemical formula for sodium hypochlorite is NaOCl.
- The properties of sodium hypochlorite are:
 - ▶ Boiling point: 110° C (230° F)
 - ▶ Specific Gravity: 1.19 (Specific Gravity of Water = 1.0)
 - ▶ pH: 9.0 to 12.0
- Reaction in water:



Calcium Hypochlorite

- Calcium hypochlorite is a white free-flowing granular powder or solid cake.
 - ▶ Its common name is high test hypochlorite (HTH), which is commonly used for swimming pool chlorination.
 - ▶ Available chlorine content is 65 to 70%.
 - ▶ It is stable and can be stored for long periods of time with only a small loss of strength.
 - ▶ It should be stored in cool, dry places, isolated from other chemicals since moisture contributes to its deterioration and spontaneous reactions may occur with organic materials and other oxidizable materials.
- It is readily soluble in either warm or cold water.
 - ▶ Very concentrated solutions can be prepared.
 - ▶ Solutions are strongly alkaline and corrosive.
- Calcium hypochlorite has a strong chlorine odor.

- The chemical formula for calcium hypochlorite is $\text{Ca}(\text{OCl})_2$.
- The properties of calcium hypochlorite are as follows:
 - ▶ Specific Gravity: 2.35 at 20° C (S.G. of Water = 1.0)
 - ▶ pH: 11.5 (5% solution)
- Reaction in water:



Concentration of Available Free Chlorine

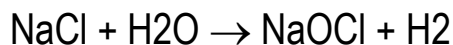
Manufactured Liquid Sodium Hypochlorite

- Usually available in 12 to 15% solution strength.
- 12.5% solution strength is common.
 - ▶ 1.04 gallons of 12.5% solution is equivalent to 1 pound of chlorine gas.

On-Site Generated Liquid Sodium Hypochlorite

A weak solution of liquid sodium hypochlorite can be generated on-site.

- An electrical charge is applied to a salt brine solution to generate a weak sodium hypochlorite solution. This reaction produces hydrogen gas, which dissipates into the atmosphere.



- The following requirements must be met to generate hypochlorite on-site:
 - ▶ Power: 2.5 KWH/lb Cl
 - ▶ Salt: 3 lb/lb Cl
 - ▶ Water: 15 gal/lb Cl, softened to less than 17 mg/L total hardness
- The properties of on-site generated hypochlorite are:
 - ▶ 0.7 to 0.9% available chlorine
 - ▶ Solution pH: 9.1 to 9.3

Calcium Hypochlorite

- Calcium Hypochlorite has 65 to 70% available chlorine.
 - ▶ Every 100 pounds of $\text{Ca}(\text{OCl})_2$ contains 65 – 70 pounds of available chlorine.
 - ▶ It is readily soluble in either warm or cold water.
 - ▶ Very strong (concentrated) solutions can be prepared. Usually a solution containing 1 to 3 % of available chlorine is prepared. 125 pounds per 1000 gallons of water makes a 1% solution.

Stability

Liquid Sodium Hypochlorite

- The stability of hypochlorite solutions is greatly affected by concentration, heat, light, and the presence of heavy metals.
 - ▶ The higher the concentration, the faster the rate of deterioration.
 - ▶ The most stable solutions are of low concentration. On-site generated solution at 1% is more stable than bulk purchased solution at 12%.
 - ▶ The higher the temperature, the faster the rate of deterioration.

Table 25.1 The Effects of Temperature of Various Concentrations

Percent Available Chlorine	Half-life (days)		
	140 °F	77 °F	59 °F
10.0	3.5	220	800
5.0	13.0	790	5000
2.5	28.0	1800	--
0.5	100.0	6000	--

- To maintain a somewhat constant solution concentration, quantities should be used within 30 days and stored at 60 to 70 °F.
- Solutions exposed to light deteriorate faster than those kept in darkness. The half-life of 10 to 15 percent solution will be reduced about 3 or 4 times when exposed to light.

- The presence of iron, copper, nickel, or cobalt catalyzes the rate of deterioration; therefore, piping systems should be plastic or other non-metallic material to prevent active corrosion of iron, copper or brass materials.
- The most stable hypochlorite solutions are those with low hypochlorite concentration, a pH of 11 and low iron, copper, or nickel content, stored in the dark at low temperature.

Calcium Hypochlorite

- Dry material is relatively stable under normal atmospheric conditions and will lose 3 to 5 percent available chlorine per year.
 - ▶ Reduce deterioration by maintaining a 30 to 60 day stock supply of dry material and mixing fresh solution daily.
- Decomposition is exothermic, meaning it gives off heat. Decomposition proceeds rapidly if heated to 350° F.
 - ▶ Many fires of spontaneous origin have been caused by improperly stored calcium hypochlorite.
- Never store calcium hypochlorite where it may be subject to heat or allowed to contact organic material.
- Calcium hypochlorite releases chlorine fumes when exposed to heat. It may build up pressure in sealed storage containers if containers are exposed to sunlight or other heat sources.

Vapor Pressure

- All hypochlorite solutions, whether purchased liquid sodium hypochlorite or plant prepared solutions of calcium hypochlorite, will release oxygen gas as the solution decomposes.
- Provisions must be included in the chemical feed system to vent this gas to prevent air binding of the feed lines.
- Care must be taken to prevent trapping the solution between two closed valves since the build up of pressure may rupture the piping system.



Key points for Unit 1 – Background and Properties

- ✚ Chlorine compounds are added to water to destroy or inactivate pathogenic organisms.
- ✚ Hypochlorites can be used to oxidize dissolved metals and to help control taste and odor problems.
- ✚ Hypochlorites are provided as liquid sodium hypochlorite or granular calcium hypochlorite.
- ✚ Sodium hypochlorite is a clear light yellow-green liquid with a chlorine odor.
- ✚ Sodium hypochlorite can be purchased as a liquid or it can be generated on site.
- ✚ Concentration, heat, light, and the presence of dissolved heavy metals can affect the stability of hypochlorite solutions.
- ✚ Calcium hypochlorite is a white free-flowing granular powder or a solid cake.
- ✚ Calcium hypochlorite is readily soluble in either warm or cold water. However, if it is kept dry and cool, it can be stored for long periods of time.
- ✚ Calcium hypochlorite will lose 3 to 5 percent of available chlorine per year. A 30 to 60 day stock supply is often recommended to keep chlorine losses within acceptable limits.



Exercise for Unit 1 – Background and Properties

1. List and explain two uses of hypochlorite.
 - a.

 - b.

2. Two gallons of a 12% solution of liquid sodium hypochlorite are equivalent to how many pounds of chlorine gas?
 - a. 1 pound
 - b. 2 pounds
 - c. 3 pounds
 - d. 4 pounds

3. Assume that calcium hypochlorite has 65% available chlorine. How many pounds of calcium hypochlorite is needed to provide the equivalent of 2.6 pounds of chlorine gas?
 - a. 1 pound
 - b. 2 pounds
 - c. 3 pounds
 - d. 4 pounds

4. Dry calcium hypochlorite will lose _____ to _____ percent available chlorine per year.

5. All hypochlorite solutions will release oxygen gas as the solution decomposes.
 - a. True _____
 - b. False _____

Unit 2 – Chemical Handling, Storage and Safety

Learning Objectives

- Describe how to properly handle bulk liquid and containerized shipments of hypochlorite.
- List and explain four considerations of hypochlorite storage vessels.
- Explain the importance of temperature, ventilation and light on the storage of hypochlorite.
- Utilize the MSDS to locate information about hazard classification, environmental hazards and health hazards of hypochlorite solutions.
- List safety equipment required for hypochlorite handling and explain the importance of each type of equipment.
- Describe how to properly handle hypochlorite spills.

Quantities

- Provide storage in separate rooms to avoid contact with organic material.
- Storage for a 30- day supply should be available.
- Sodium hypochlorite should not be stored longer than 45 days since its strength decomposes in storage.
- Store in a cool, dry atmosphere.

Types of Storage Containers

Sodium Hypochlorite

- Storage is available in 5, 15, 30 and 55 gallon drums.
- Bulk liquid should be stored in on-site bulk liquid storage tanks.

Calcium Hypochlorite

- Storage is available in 5, 15, 100, and 300 pound cans, and 415 and 800 pound barrels.
- It should be stored in shipping containers until it is used.
- After a container is opened, loss of chlorine will occur, particularly if exposed to moisture in the air.

Storage Rooms

Temperature

- Maintain temperature of storage rooms between 60 and 70° F.

Ventilation

- Forced air ventilation should be provided.
- Operate fans when the room is occupied.

Light

- Prevent exposure to sunlight.

Materials of Construction

Hypochlorites are caustic; therefore, rubber, glass, PVC and other similar materials should be used when contact with hypochlorite solutions is necessary.

Containment

- Provide spill containment for bulk liquid storage facilities.
- Provide containment volume of 110% of the largest liquid vessel to be stored.

Material Safety Data Sheets

A Material Safety Data Sheet, or MSDS, is available from the chemical Manufacturer/Supplier for every chemical. You should read and understand the MSDS for each chemical used in the plant. You should also maintain a personal copy for all hazardous chemicals that are used.

An MSDS contains detailed assessment of chemical characteristics, hazards and other information relative to health, safety and the environment. Typical information present in an MSDS includes:

- The product name and its synonyms.
- The Chemical Abstracts Service (CAS) registry number.
- The manufacturer's address and telephone number.
- Components and contaminants.
- Physical data.
- Fire and explosion hazard data.
- Toxicity data.
- Health hazard data, including exposure limits, effects of exposure and emergency and first aid procedures.
- Reactivity data, including storage and disposal recommendations and conditions to avoid.
- Spill or leak procedures.
- Protective equipment.
- First aid procedures.

A sample MSDS is located in the Appendix.

Hypochlorite Hazards

- Hypochlorite does not present the same hazards as gaseous chlorine, so it is safer to handle.
- All forms of chlorine can give off chlorine gas and fumes.
 - ▶ Chlorine gas is released when hypochlorite is exposed to high heat.
 - ▶ Chlorine fumes have a distinct chlorine smell, which can result in respiratory problems similar to those experienced with chlorine gas.

Spills

- Hypochlorite spills should be washed with large volumes of water to dilute it.

Health

- Hypochlorite can irritate both skin and eyes. It will cause discomfort and/or a rash.
- Immediately wash affected areas thoroughly with water, and flush eyes if hypochlorite has come into contact with them.

Environmental

- The effects of hypochlorite on animals are similar to the health effects it has on humans. It is toxic to aquatic life.
- Hypochlorite will spontaneously react with organic materials. As a result, it should be stored separate from all organic materials such as:
 - ▶ Turpentine.
 - ▶ Oils.
 - ▶ Sugar.
 - ▶ Fats.
 - ▶ Other oxidizable materials.
- Hypochlorite should be handled with clean, dry implements that are free of organic materials.

Personnel Safety Protection

Basic Equipment

- Safety protection equipment for hypochlorite is similar to equipment used for other corrosive chemicals.
- Equipment must be used and maintained in strict accordance with manufacturers' recommendations and instructions.
- Protective clothing includes:
 - ▶ Eye protection.
 - ▶ Gloves.
 - ▶ Rubber aprons.
- Emergency showers and eye-wash stations should be provided.



Figure 2.1 An Emergency Shower



Figure 2.2 An Eye Wash Station

First Aid

Inhalation

- Remove the injured party and take person(s) to an uncontaminated outdoor area.
- Call for medical assistance.

Skin Contact

- Immediately shower with large quantities of water.
- Remove protective clothing and equipment while in the shower.
- Flush the skin with water for at least 5 minutes.
- Call for medical assistance.
- Keep the affected area cool.

Eye Contact

- Immediately shower with large quantities of water while holding eyes open.
- Call a physician immediately.
- Transfer person(s) promptly to a medical facility.

Ingestion

- Do not induce vomiting.
- Give large quantities of water.
- Call a physician immediately.
- Transfer person(s) promptly to a medical facility.

OSHA

The Occupational Safety and Health Administration (OSHA), in the U.S. Department of Labor, has the primary responsibility for administering the Occupation Safety and Health Act of 1970 which assures safe and healthful working conditions for men and women working throughout the U.S. Employers must comply with applicable OSHA regulations and supply adequate employee training, appropriate protective and safety equipment, and prompt correction of unsafe conditions discovered in workplace inspections or reported by employees. Additional regulations may apply depending upon the actual workplace conditions. Further information about particular workplace requirements can be obtained by contacting OSHA.¹ The OSHA website contains a wealth of information and the regional office in Philadelphia will respond to phone requests for information and advice.

In addition to getting information directly from OSHA, industry specific manuals such as *Safety Practices for Water Utilities*² which is an American Water Works Association publication can be very helpful. It is written for the drinking water industry and contains numerous explanations of OSHA regulations.



Key points for Unit 2 – Chemical Handling, Storage and Safety.

- ✚ Temperature, ventilation, and light are important considerations when storing hypochlorite.
- ✚ Storage rooms should be kept separate and avoid contact with organic material.
- ✚ Storage for a 30 day supply is usually recommended.
- ✚ Don't store for more than 45 days since hypochlorite decomposes and loses potency.
- ✚ Hypochlorites are caustic. Use rubber, glass, PVC and other similar materials when contact with hypochlorite is necessary.
- ✚ Provide spill containment for bulk liquid storage.
- ✚ Material Safety Data Sheets, or MSDS, should be readily available at the work site and reviewed by each worker.
- ✚ Hypochlorite should be handled with clean, dry implements that are free of organic materials.
- ✚ Appropriate protective clothing includes eye protection, gloves, and rubber aprons. An emergency shower and an eye wash station should also be available.
- ✚ Each worker should thoroughly review and/or receive training in first aid procedures for hypochlorite accidents.
- ✚ Employers and employees should follow appropriate OSHA regulations for hypochlorite workplace situations.

**Exercise for Unit 2 – Storage, Handling and Safety**

1. Sodium hypochlorite should not be stored longer than _____ days since its strength decomposes in storage.
2. Calcium hypochlorite should be stored in its _____ containers until it is used.
3. Hypochlorites decompose and release _____ into the air.
4. Forced air ventilation should be turned on whenever workers enter the hypochlorite storage or work area.
5. MSDS is an abbreviation for _____
_____.
6. Typical information in a MSDS includes:
 - a. The product name and its synonyms.
 - b. Fire and explosion hazard data.
 - c. Toxicity data.
 - d. First aid procedures.
 - e. All of the above.
7. Hypochlorite spills should be washed with large amounts of _____ to dilute it.
8. Hypochlorite will react spontaneously with organic material and should be kept separate from all organic compounds such as: fats, sugar, oils, turpentine, and other oxidizable materials.
 - a. True _____
 - b. False _____
9. First aid procedures for skin contact with hypochlorite include showering with large quantities of _____ and calling for medical assistance.
10. Hypochlorite should be stored so that it does not get direct exposure to _____.

References

1 Further information about OSHA requirements can be obtained from:

www.osha.gov

or by phoning the

OSHA regional office in Philadelphia 215-861-4900

2 *Safety Practices for Water Utilities*, AWWA Manual of Water Supply Practices, M3, Sixth Edition, 2002.

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Unit 3 – Chemical Feed

Learning Objectives

- Explain breakpoint chlorination.
- Identify the chemical feed equipment required for hypochlorite chemical addition.
- Perform basic hypochlorite chemical feed calculations.
- Explain the important maintenance considerations for calcium hypochlorite.
- List and explain the system components required for on-site generation of sodium hypochlorite.
- List and explain methods for controlling chemical feed.

Regulatory Requirements

Continuous disinfection is required of all public water systems.

Surface Water Supplies

- The disinfection process must achieve 99.9 percent (3 log) inactivation of Giardia cysts and 99.99 percent (4 log) inactivation of enteric viruses. Chlorination equipment must be capable of maintaining a chlorine residual, which achieves a minimum of 1 log Giardia cyst inactivation following filtration.
- This must be determined by CT factors and measurement methods established by EPA. Refer to EPA's *Guidance Manual for Compliance with the Filtration and Disinfection Requirements for Public Water Systems Using Surface Water Sources*.

Groundwater Supplies

- This applies to groundwater supplies not under the influence of surface water intrusion.
- A minimum of 20 minutes of contact time must be provided.

Chlorine Residual Requirements

- Minimum free, combined or chlorine dioxide residual entering the distribution system must exceed 0.2 mg/l, and be maintained at a measurable level at the most distant points in the system.
- Chlorine added to water containing organic and inorganic chemicals reacts with these materials to form chlorine compounds. Maximum Contaminant Levels (MCLs) have been established for these compounds

Maximum Contaminant Levels



Maximum contaminant levels (MCLs) regulations are issued by the USEPA and in Pennsylvania by the DEP. The MCLs list a variety of organic and inorganic chemicals, disinfection by products (DBPs), radionuclides, microbiological contaminants, and turbidity levels that pertain to drinking water. Some example MCLs are listed below.

■	Total Trihalomethanes (TTHMs), a DBP	0.080 mg/l
■	Haloacetic Acids (HAA5), a DBP	0.060 mg/l
■	Bromate, a DBP	0.010 mg/l
■	Benzene	0.005 mg/l
■	Diquat	0.02 mg/l
■	Chlorine (as Cl ₂)	4.0 mg/l as maximum residual disinfectant level (MRDL)

Secondary contaminant levels are also included since these may affect taste and odor. Some examples are shown below.

 Sulfate	250 mg/l
 Iron	0.3 mg/l
 pH	6.5 – 8.5

Chlorination Mechanics and Terminology

- The exact mechanism of chlorine disinfection action is not fully known.
 - ▶ One theory is that chlorine directly destroys the bacterial cell.
 - ▶ Another theory is that chlorine inactivates the enzymes which enable the cells to use food, thus starving the organisms.



Chlorine demand is the amount of chlorine required to react with all the organic and inorganic material.

- In practice, the chlorine demand is the difference between the amount of chlorine added and the amount remaining after a given contact time.
- Some reactive compounds have disinfecting properties while others do not.



Chlorine residual is the total of all compounds with disinfecting properties and any remaining free chlorine.

$$\text{Chlorine Residual (mg/l)} = \text{Combined Chlorine Forms (mg/l)} + \text{Free Chlorine (mg/l)}$$

- The presence of measurable chlorine residual indicates that all chemical reactions have been satisfied and that sufficient chlorine is present to kill or inactivate the microorganisms.



Chlorine dose is the amount of chlorine needed to satisfy the chlorine demand plus the amount of chlorine residual needed for disinfection:

$$\text{Chlorine Dose (mg/l)} = \text{Chlorine Demand (mg/l)} + \text{Chlorine Residual (mg/l)}$$

Breakpoint Chlorination



Breakpoint chlorination is the addition of chlorine until all chlorine demand has been satisfied. It is used to determine how much chlorine is required for disinfection.

- A residual in the form of free available residual chlorine needs to be provided. This has the highest disinfecting ability.

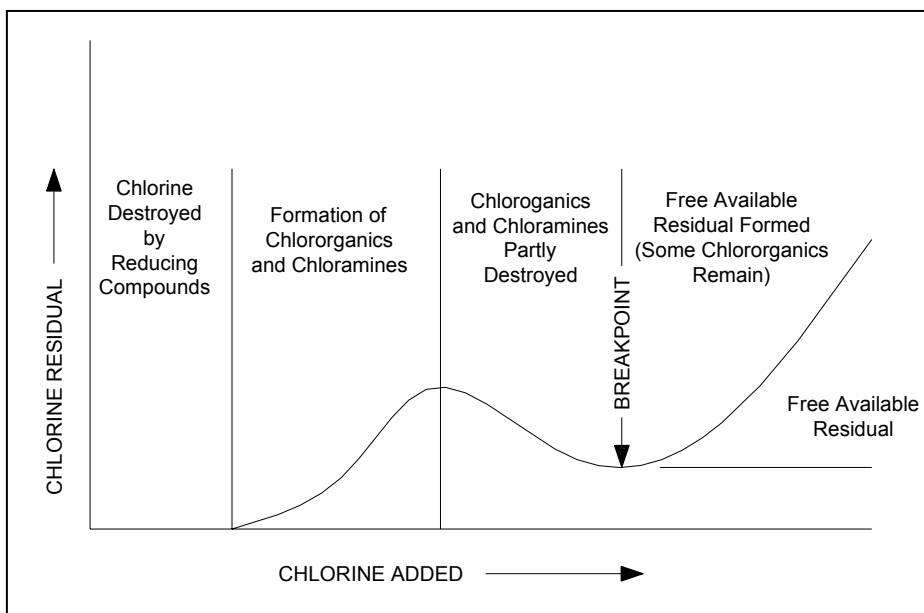


Figure 3.1 Breakpoint Chlorination Curve

Process Calculations

There are two basic chlorination process calculations: chlorine dosage and chlorine demand.

Chlorine Dosage Calculation

- To perform the calculation, you will need to know the amount of chlorine being added and the amount of water being treated.

$$\text{Chlorine Dosage (mg/l)} = \frac{\text{Chlorine Feed (lb/day)}}{[\text{Flow (mgd)} \times 8.34 \text{ (lb/gal)}]}$$

Chlorine Demand Calculation

- A sufficient amount of chlorine must be added so that the chlorine demand is met and the desired chlorine residual is provided.

$$\text{Chlorine Demand (mg/l)} = \text{Chlorine Dose (mg/l)} - \text{Chlorine Residual (mg/l)}$$



Sample Calculations

The hypochlorinator at a water treatment plant operating at a flow rate of 1.0 million gallons per day is set to feed 20 gallons of 12.5% sodium hypochlorite in a 24 hour period. The chlorine residual in the finished water leaving the plant after a 20 minute contact period is 0.5 mg/l. Calculate the chlorine demand of the water.

Known: Flow, (mgd) = 1.0 MGD
 Chlorinator setting = 20 gallons/day
 12.5% Sodium Hypochlorite = 1.04 pounds Cl/gal
 Finished water chlorine residual = 0.5 mg/l

Find: Equivalent Chlorine Feed rate (lb/day)
 Equivalent Chlorine Dosage (mg/l)
 Chlorine Demand (mg/l)

Step 1: Calculate equivalent chlorine feed rate (ECF) in lb/day

$$\begin{aligned} \text{ECF (lb/day)} &= (20 \text{ gal/day}) (1.04 \text{ lb/gal}) \\ &= 20.8 \text{ lb Cl/day} \end{aligned}$$

Step 2: Calculate equivalent chlorine dosage (ECD) in mg/l

$$\begin{aligned} \text{ECD (mg/l)} &= \frac{\text{ECF (lb/day)}}{\text{Flow (mgd)} \times 8.34 \text{ (lb/gal)}} \\ &= \frac{20.8 \text{ lb/day}}{[1.0 \text{ (mgd)} \times 8.34 \text{ (lb/gal)}]} \\ &= \frac{20.8 \text{ lbs CL/day}}{[1.0 \text{ (mgd)} \times 8.34 \text{ (lb/gal)}]} \\ &= \frac{20.8 \text{ lb Cl/day}}{8.34 \text{ (million lb water/day)}} \\ &= 2.49 \text{ lb Cl/million lb water} \\ &= 2.49 \text{ Parts Per Million (ppm)} \\ &= 2.49 \text{ mg/l} \end{aligned}$$

Step 3: Calculate Chlorine Demand in mg/l

$$\text{Chlorine Demand (mg/l)} = \text{Chlorine Dose (mg/l)} - \text{Chlorine Residual (mg/l)}$$

$$\begin{aligned} \text{Chlorine Demand (mg/l)} &= 2.49 \text{ (mg/l)} - 0.5 \text{ (mg/l)} \\ &= 1.99 \text{ mg/l} \end{aligned}$$



Exercise.

1. Explain what breakpoint chlorination is.

2. A water treatment plant operating at 750,000 gallons per day adds 33.6 gallons of 12.5% sodium hypochlorite each day for disinfection. After a 30 minute contact period, the chlorine residual is measured at 1.35 mg/l. Compute the chlorine demand of this water.

3. A water plant treating 1.5 million gallons per day uses 185 gallons of a 2% solution of Calcium Hypochlorite (70%) each day as the disinfectant. Compute the quantity of HTH that must be mixed with 200 gallons of water (1+ days supply) to obtain the proper strength batch. After a 30 minute contact period, the chlorine residual is measured at 1.05 mg/l. Compute the chlorine demand of this water.

Sodium Hypochlorite

- Sodium hypochlorite is supplied only in solution form.
- It is ready for use as received.
- Sodium hypochlorite is usually fed neat (i.e., at the strength received) if 12.5% strength or less. If the solution strength is greater than 12.5%, it may need to be diluted.

Figure 3.1 shows a typical bulk sodium hypochlorite feed system schematic diagram.

Figure 3.2 depicts a schematic diagram of a typical sodium hypochlorite drum feed system.

HYPOCHLORITE FEED EQUIPMENT, OPERATION AND MAINTENANCE

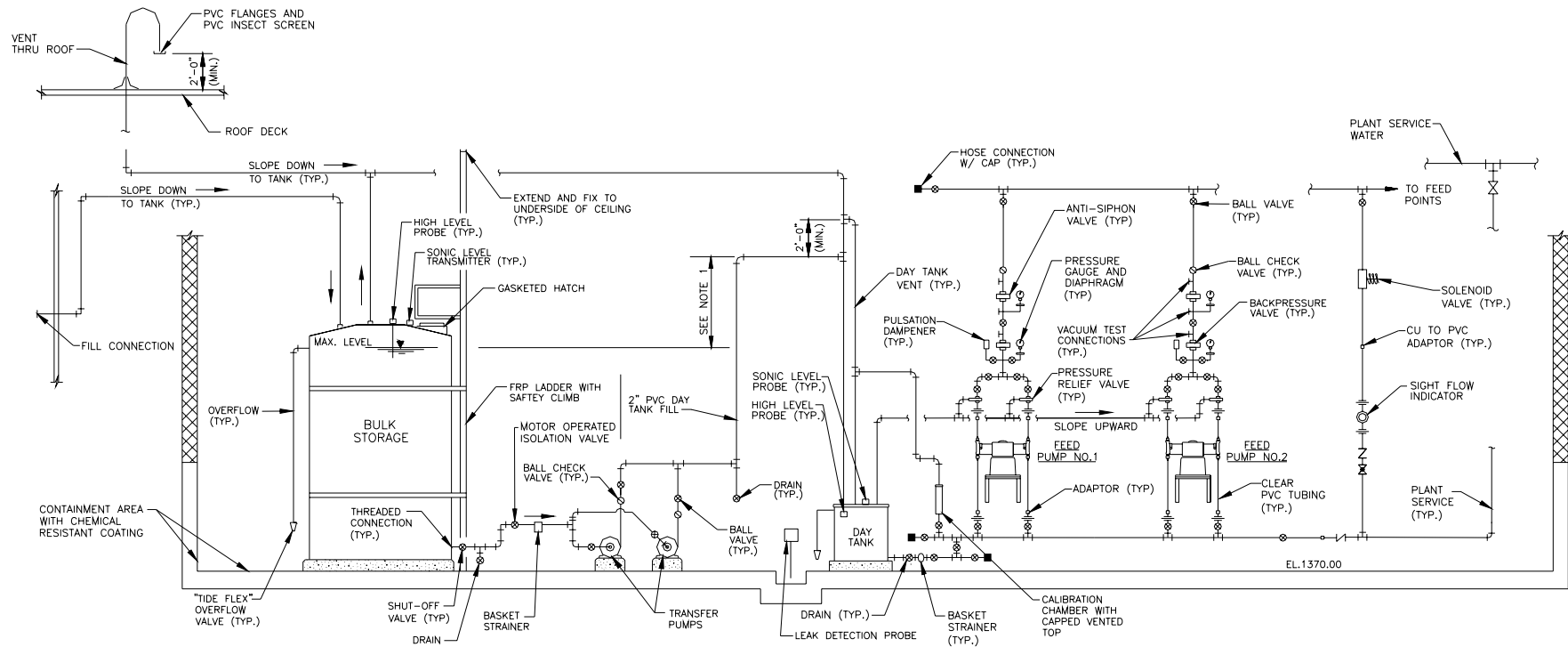


Figure 3.1 Typical Bulk Sodium Hypochlorite Feed System Schematic

HYPOCHLORITE FEED EQUIPMENT, OPERATION AND MAINTENANCE

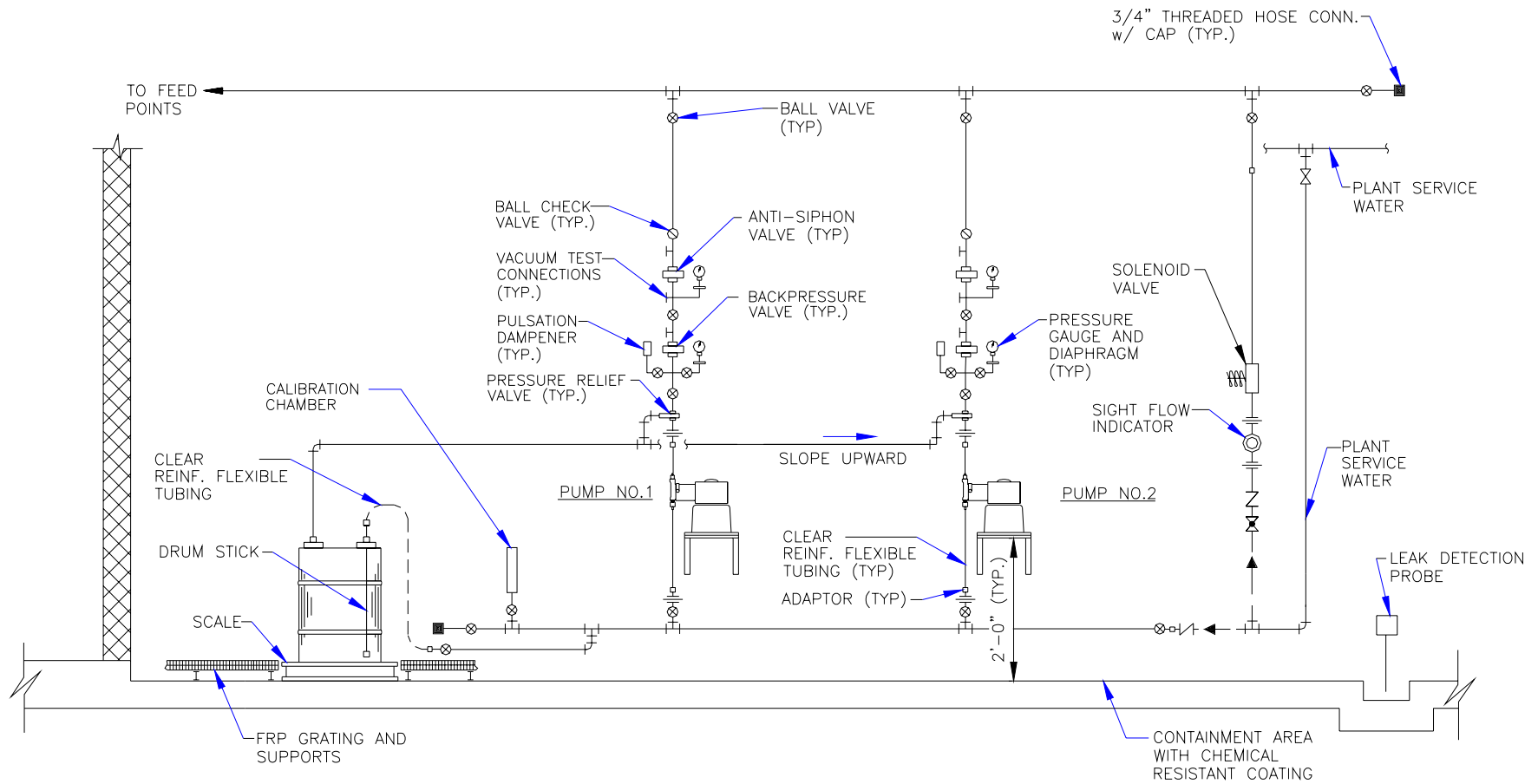


Figure 3.2 Typical Sodium Hypochlorite Drum Feed System Schematic

Hypochlorite Feed Equipment

With the exception of the type of chemical storage/solution preparation, the equipment for feeding the two forms of hypochlorite is similar. The major components and the purpose of each follow.

Storage/Solution Preparation

- The bulk storage tank provides a container for the storage of a 30-day minimum supply of sodium hypochlorite solution. The bulk storage tank should provide a minimum volume of 110% of the maximum chemical delivery quantity to minimize the potential for overflowing the tank during chemical deliveries.
- The solution preparation tank provides containers for preparation of a minimum 1-day supply of calcium hypochlorite solution. Two containers are suggested: one in service and one with solution aging to facilitate settling of insoluble compounds.

Scales

- Scales provide an indication of the quantity of chemical remaining, which is useful for chemical inventory control.

Transfer Pumps

- Transfer pumps are used for the transfer of sodium hypochlorite from the bulk storage tank to day tanks.

Day Tank

- The day tank stores daily chemical required for delivery by feeders, and also monitors chemical usage and provides inventory control.

Chemical Feeder

- The chemical feeder uses positive displacement diaphragm pumps such as the mechanical diaphragm type, the hydraulic diaphragm type, or an electronic solenoid pump. Some chemical feeders are vacuum eductor-type feeders.

Chemical Feed Piping

- The backpressure valve maintains a constant backpressure on the feed pump discharge.
- The antisiphon valve prevents backsiphonage of process water into the chemical feed system.
- The pressure relief valve limits the discharge pressure of the feed pump and protects the feed piping.
- The isolation valves permit maintenance of various system components without the need to remove the entire feed system from operation.

Calcium Hypochlorite

Most plants manually prepare stock batch solutions. Figure 3.3 depicts a typical Calcium Hypochlorite Feed System.

- Usually a one-day supply of 1 to 3 % strength is prepared.
- The proper quantity of HTH is dissolved in a sufficient quantity of water.
- The batch solution should be prepared in a separate container.
 - ▶ Allow the solution to stand for 8 to 24 hours before actual use.
 - ▶ Pour or siphon the clear solution into the day tank supplying the feeder.

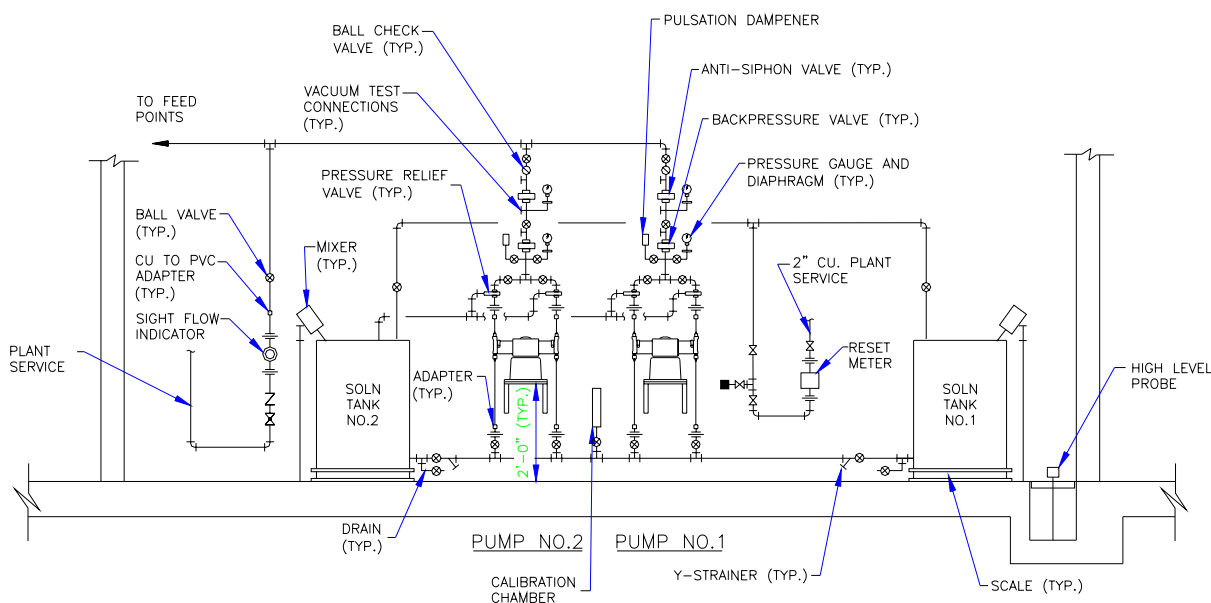


Figure 3.3 Typical Calcium Hypochlorite Feed System

On-Site Generated Sodium Hypochlorite

Typical sodium hypochlorite generation process layout is shown in the following figure.

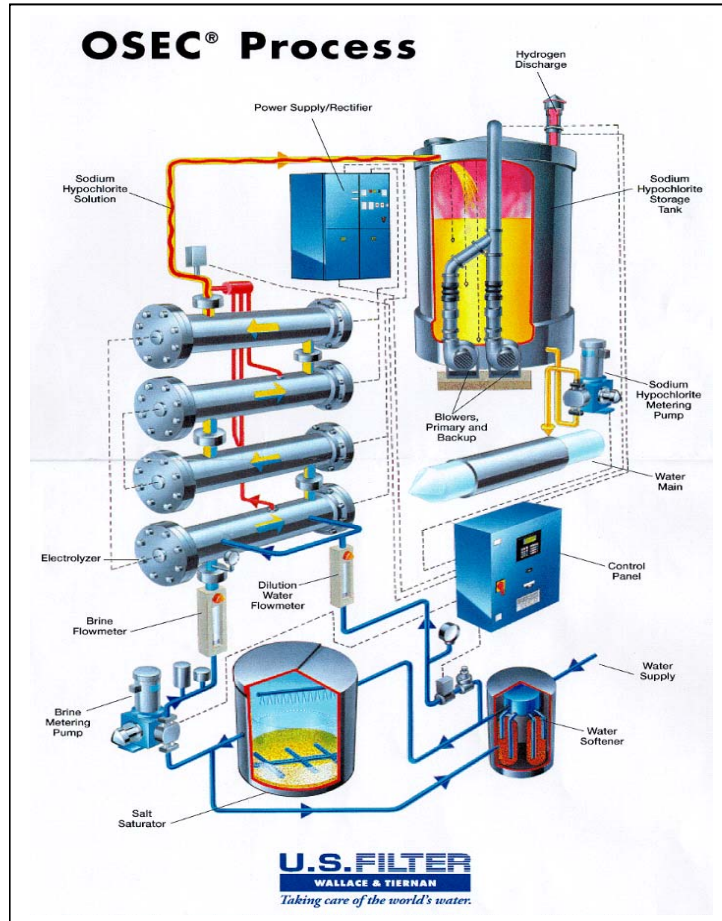


Figure 3.4 On-Site Hypochlorite Generation Process¹

System Components

- The brine storage vessel stores salt and softened water where concentrated brine solution is made and stored. (Noted as Salt Saturator in Figure 3.4.)
- The water softener reduces the hardness of the water supply to less than 17 mg/l total hardness.
- The hypochlorite generators are reaction vessels where electrical charge is applied to the brine solution, resulting in the formation of sodium hypochlorite. (Noted as Electrolyzer in Figure 3.4.)
- The control system or panel controls the hypochlorite production cycle.
- The storage tanks store hypochlorite solution. Hydrogen is released from the process.

Chemical Feed Control

There are five basic methods of controlling the operation of chlorine gas feeders: manual, start-stop, flow proportional, chlorine residual and compound loop.

Manual

- The operator places the equipment into operation and shuts down the equipment manually.
- The operator manually adjusts the chlorine feed rate at the chlorinator. This provides satisfactory control where chlorine demand and flow remain reasonably constant. However, the operator must manually adjust the feed rate when demand of flow changes.

Start-Stop

- The chlorinator is activated in response to a control signal from other equipment.
- Usually the feed rate adjustment is manual.
- Control is based on time parameters, or pump or other mechanical equipment operation.
- Start-stop is typical for the chlorination of well supplies where the well pump does not operate continuously.

Flow Proportional

- The chlorinator feed rate is automatically adjusted proportional to a water flow signal in this method.
- It maintains constant chlorine feed rate proportional to the metered flow.
- This method is typical for chlorination at a plant where the chlorine demand remains relatively constant but the treated water flow rate varies.

Chlorine Residual

- The chlorinator feed rate is automatically adjusted proportional to a measured chlorine residual signal.
- It maintains a constant chlorine residual by varying the chlorine feed rate.

Compound Loop

- This method combines flow proportional and chlorine residual control.
- The chlorinator is automatically adjusted based on the flow signal, and the feed rate is automatically trimmed in accordance with the measured chlorine residual.

Hypochlorite Feed System Operation

Normal Operation

Normal operation of the hypochlorite feed system requires regular observation of the facilities and equipment, and a regular preventative maintenance program. Exact operating procedures will depend on the type of hypochlorite in use at the facility and on the equipment that is installed at the facility.

The general procedure is as follows:

Daily

- Visually inspect the storage and feed areas.
- Verify operation of chemical transfer pumps.
- Read scales, charts or meters at same time each day to determine actual chemical usage. Be sure to record readings for water pumped and actual chemical usage.

HYPOCHLORITE FEED EQUIPMENT, OPERATION AND MAINTENANCE

- Check chlorine residual in the system and adjust chlorine feed rate as necessary. Verify the proper operation of chemical feed pumps.
- Prepare calcium hypochlorite solution as necessary.
- Look for leaks.

Weekly

- Check the chemical dose by verifying proper pump calibration and computing the actual weekly chemical dosage.
- Check the entire system for problems.
- Clean the area.
- Verify the chemical supply on-hand and order as necessary.

Monthly

- Clean and lubricate equipment in accordance with manufacturer's recommendations.

Abnormal Operation

In the event of an abnormal operation, be sure to inform your supervisor of the problem.

Low Chlorine Residual

- Determine the actual chlorine residual in the laboratory and compare with the residual analyzer reading. Then recalibrate the analyzer appropriately.
- If the analyzer is properly calibrated, check the following:
 - ▶ The sample pump operation.
 - ▶ The feed pump operation.
 - ▶ The control system, if it is on automatic control. Operate in manual control mode if necessary.
 - ▶ The water chlorine demand. Increase the feed rate if necessary. Add additional feed pumps on line if demand is higher than can be provided by a single unit.

Chemical Pump Not Operating

- Verify the hypochlorite supply availability.
- Start the spare pump to maintain system chlorination.
- Check the electrical supply equipment, such as electrical connections, circuit breakers and control equipment.
- Check for blockages:
 - ▶ In the solution tank.
 - ▶ In the valves, both manual and electrically controlled.
 - ▶ In feed lines such as the feed pump suction lines and feed pump discharge lines.



Key points for Unit 3 – Chemical Feed.

- ✚ Chlorine demand is the amount of chlorine required to react with all the organic and inorganic material.
- ✚ Chlorine residual is the total of all chlorine compounds with disinfecting properties and any remaining free chlorine.
- ✚ Chlorine dose is the amount of chlorine needed to satisfy the chlorine demand plus the amount of chlorine residual needed for disinfection.
- ✚ Breakpoint chlorination is the addition of chlorine until all chlorine demand has been satisfied. It is used to determine how much chlorine is required for disinfection.
- ✚ Sodium hypochlorite is supplied in solution form and typically it is used as received.
- ✚ Sodium hypochlorite can be generated on site by using special equipment to supply an electric charge to a brine solution.
- ✚ The five basic methods of controlling the operation of chlorine gas feeders are manual, start-stop, flow proportional, chlorine residual and compound loop.
- ✚ Hypochlorite feed system equipment should be inspected daily for proper operation.
- ✚ Check the chlorine residual in the system daily and adjust chlorine feed rate as necessary.



Exercise for Unit 3 – Chemical Feed

1. The _____ chlorination curve can be used to determine how much chlorine is required for disinfection.
2. The disinfection process for surface water supplies must achieve _____ percent (3 log) inactivation of Giardia cysts and _____ percent (4 log) inactivation of enteric viruses.
3. Chlorine dose = _____ (mg/l) + _____ (mg/l).
4. A _____ tank stores daily amounts of chemical required for delivery by feeders.
5. In the event of an abnormal operation, be sure to inform your _____ about the problem.
6. Calcium hypochlorite solutions are typically prepared with a _____ to _____ % strength.

¹ Courtesy of U.S. Filter, Wallace & Tiernan Products (18 June 2003).

A Typical Chlorine MSDS Sheet

OLIN CORPORATION -- SODIUM HYPOCHLORITE, 7-15 %, CPE 622680

MSDS Safety Information

FSC: 6810
NIIN: 01-029-5565
MSDS Date: 04/23/1997
MSDS Num: BVFLX
Product ID: SODIUM HYPOCHLORITE, 7-15 %, CPE 622680
MFN: 02
Responsible Party
Cage: 99530
Name: OLIN CORPORATION
Address: 501 MERRITT 7
Box: 4500
City: NORWALK (FORMALLY IN STAMFORD, CT) CT 06856-4500
Info Phone Number: 203-750-3000/203-750-3543
Emergency Phone Number: 800-654-6911/203-356-2000
Preparer's Name: UNKNOWN
Review Ind: Y
Published: Y

Contractor Summary

Cage: 03JX8
Name: ENVIROTROL INC (504-736-9041)
Address: UNKNOWN
Box: UNKNOWN
City: UNKNOWN NK 00000
Phone: UNKNOWN
Cage: 99530
Name: OLIN CORPORATION
Address: 501 MERRITT 7
Box: 4500
City: NORWALK CT 06856-4500
Phone: 203-750-3000/800-511-MSDS
Cage: 0STM5
Name: VOPAK USA INC
Address: 6100 CARILLON POINT
City: KIRKLAND WA 98033-7357
Phone: 425-889-3400/425-889-3617

Item Description Information

Item Manager: S9G
Item Name: SODIUM HYPOCHLORITE SOLUTION
Specification Number: NONE
Type/Grade/Class: NONE
Unit of Issue: DR
Quantitative Expression: 00000000055GL
UI Container Qty: 0
Type of Container: DRUM

=====

Ingredients

=====

Cas: 7681-52-9
RTECS #: NH3486300
Name: SODIUM HYPOCHLORITE (CERCLA); AVAILABLE CHLORINE 5%
% Wt: 7 - 15
Other REC Limits: NONE RECOMMENDED
OSHA PEL: NOT ESTABLISHED
ACGIH TLV: NOT ESTABLISHED
EPA Rpt Qty: 100 LBS
DOT Rpt Qty: 100 LBS

Cas: 1310-73-2
RTECS #: WB4900000
Name: SODIUM HYDROXIDE (CERCLA)
% Wt: 0.5-2.5
Other REC Limits: NONE RECOMMENDED
OSHA PEL: 2 MG/M3
ACGIH TLV: C 2 MG/M3; 9596
EPA Rpt Qty: 1000 LBS
DOT Rpt Qty: 1000 LBS

Cas: 7647-14-5
RTECS #: VZ4725000
Name: SODIUM CHLORIDE
% Wt: 5 - 11
Other REC Limits: NONE RECOMMENDED
OSHA PEL: NOT ESTABLISHED
ACGIH TLV: NOT ESTABLISHED

Cas: 7732-18-5
RTECS #: ZC0110000
Name: WATER
% Wt: BALANCE
Other REC Limits: NONE RECOMMENDED
OSHA PEL: NOT RELEVANT
ACGIH TLV: NOT RELEVANT

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 Health Hazards Data
 =====

LD50 LC50 Mixture: LD50 (ORAL, RAT) 3000-5000 MG/KG
 Route Of Entry Inds - Inhalation: YES
 Skin: NO
 Ingestion: YES
 Carcinogenicity Inds - NTP: NO
 IARC: NO
 OSHA: NO
 Effects of Exposure: TARGET ORGANS:EYES, SKIN, RESPIRATORY AND
 GASTROINTESTINAL TRACTS. ACUTE- CORROSIVE. MAY CAUSE EYE AND SKIN IRRITATION &
 BURNS. VAPORS ARE IRRITATING TO UPPER RESPIRATORY TRACT. MAY CAUSE BURNS.
 HARMFUL IF INHALED/SWALLOWED. MAY CAUSE GASTROINTESTINAL TRACT BURNS. CHRONIC-
 MAY CAUSE LUNG DAMAGE, SKIN ULCERATION.
 Explanation Of Carcinogenicity: NONE
 Signs And Symptions Of Overexposure: SEVERE IRRITATION, TEARING, NAUSEA,
 VOMITING, WHEEZING, SHORTNESS OF BREATH, CHEST PAIN, CORNEAL DAMAGE, TISSUE
 DESTRUCCTION, SWELLING
 Medical Cond Aggravated By Exposure: ASTHMA, RESPIRATORY AND CARDIOVASCULR
 DISEASES
 First Aid: GET MEDICAL HELP IF SYMPTOMS PERSIST. INHALED:MOVE TO FRESH AIR.
 PROVIDE CPR/OXYGEN IF NEEDED. EYES/SKIN:IMMEDIATELY FLUSH WITH WATER FOR 15
 MINUTES. HOLD EYELIDS OPEN. ORAL:DO NOT INDUCE VOMITING. IF CONSCIOUS, DRINK
 PLENTY OF WATER. SEEK IMMEDIATE MEDICAL ATTENTION. IF VOMITING OCCURS, KEEP
 HEAD BELOW HIPS. DO NOT GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS PERSON.

=====
 Handling and Disposal
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Spill Release Procedures: FLUSH TO SEWER WITH LARGE AMOUNT OF WATER IF
 PERMITTED. OTHERWISE, ABSORB SPILL WITH INERT MATERIAL SUCH AS VERMICULITE.
 PLACE IN A CONTAINER FOR DISPOSAL. CLEAN AREA THOROUGHLY TO REMOVE RESIDUAL
 CONTAMINATION.
 Neutralizing Agent: WEAK ACIDS
 Waste Disposal Methods: DISCHARGE, TREATMENT OR DISPOSAL IS SUBJECT TO
 FEDERAL, STATE OR LOCAL REGULATIONS. FLUSH TO SEWER WITH LARGE AMOUNT OF
 WATER, IF ALLOWED. SINCE EMPTIED CONTAINERS RETAIN PRODUCT RESIDUE, FOLLOW
 LABEL WARNINGS EVEN AFTER CONTAINER IS EMPTIED.
 Handling And Storage Precautions: STORE IN A COOL PLACE AWAY FROM DIRECT
 SUNLIGHT AND INCOMPATIBLE MATERIALS.
 Other Precautions: DO NOT GET IN EYES, ON SKIN OR ON CLOTHING. AVOID
 INHALATION OF VAPORS OR MISTS. KEEP OUT OF REACH OF CHILDREN. OBEY HAZARD
 WARNING LABEL. USE WITH ADEQUATE VENTILATION. DO NOT CONTAMINATE ENVIRONMENT.

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Fire and Explosion Hazard Information
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Flash Point Text: NONE
Lower Limits: NOT RELEVANT
Upper Limits: NOT RELEVANT
Extinguishing Media: SMALL FIRE: DRY CHEMICAL, CARBON DIOXIDE, WATER SPRAY.
LARGE FIRE: WATER FOG IN FLOODING AMOUNT.
Fire Fighting Procedures: WEAR PROTECTIVE CLOTHING AND NIOSH-APPROVED SELF-CONTAINED BREATHING APPARATUS. COOL FIRE - EXPOSED CONTAINER WITH WATER SPRAY.
Unusual Fire/Explosion Hazard: MAY EMIT CHLORINE GAS.

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Control Measures
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Respiratory Protection: NONE NORMALLY NEEDED. IF WORKING IN CONFINED AREAS, IF EXCESSIVE MISTING IS EXPECTED, WEAR NIOSH-APPROVED RESPIRATOR (REFER TO 29 CFR 1910.134)
Ventilation: MECHANICAL (GENERAL/LOCAL EXHAUST)
Protective Gloves: RUBBER
Eye Protection: SAFETY GLASSES WITH SIDE SHIELD/GOGGLES
Other Protective Equipment: EYE WASH STATION, QUICK DRENCH SHOWER AND IMPERVIOUS CLOTHING
Work Hygienic Practices: OBSERVE GOOD INDUSTRIAL HYGIENE PRACTICES AND RECOMMENDED PROCEDURES. WASH AFTER HANDLING AND BEFORE EATING OR DRINKING.
Supplemental Safety and Health: FORMULA CHANGED. FOR PREVIOUS FORMULATION, SEE PNI A, SAME NSN.

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Physical/Chemical Properties
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HCC: B1
NRC/State LIC No: NOT RELEVANT
Vapor Pres: UNKNOWN
Vapor Density: UNKNOWN
Spec Gravity: 1.08 - 1.26
PH: >11
Viscosity: UNKNOWN
Evaporation Rate & Reference: UNKNOWN
Solubility in Water: MISCIBLE
Appearance and Odor: GREENISH-YELLOW LIQUID; CHLORINE ODOR
Percent Volatiles by Volume: 88- 95
Corrosion Rate: UNKNOWN

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Reactivity Data
=====

Stability Indicator: YES
Stability Condition To Avoid: HIGH HEAT, SUNLIGHT, ULTRA-VIOLET LIGHT
Materials To Avoid: ACIDS, OXIDIZING AGENTS, IRON, COPPER, AMMONIUM COMPOUNDS, ORGANICS
Hazardous Decomposition Products: CHLORINE GAS
Hazardous Polymerization Indicator: NO
Conditions To Avoid Polymerization: NOT RELEVANT

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Toxicological Information
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 Ecological Information
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 MSDS Transport Information
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 Regulatory Information
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 Other Information
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 Transportation Information
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Responsible Party Cage: 99530
 Trans ID NO: 100231
 Product ID: SODIUM HYPOCHLORITE, 7-15 %, CPE 622680
 MSDS Prepared Date: 04/23/1997
 Review Date: 01/27/1998
 MFN: 2
 Radioactivity: NOT RELEVANT
 Net Unit Weight: 468-546 LBS
 Multiple KIT Number: 0
 Review IND: Y
 Unit Of Issue: DR
 Container QTY: 0
 Type Of Container: DRUM
 Additional Data: PROPER SHIPPING NAME, HAZARD CLASS, UN ID NUMBER AND
 PACKAGING GROUP PER MSDS. REPORTABLE QUANTITY (RQ) 100 LBS
 =====

=====
 Detail DOT Information
 =====

DOT PSN Code: HNU
 DOT Proper Shipping Name: HYPOCHLORITE SOLUTION
 Hazard Class: 8
 UN ID Num: UN1791
 DOT Packaging Group: III
 Label: 8
 Special Provision: B104,N34,T7
 Packaging Exception: 154
 Non Bulk Pack: 203
 Bulk Pack: 241
 Max Qty Pass: 5 L
 Max Qty Cargo: 60 L
 Vessel Stow Req: B
 Water/Ship/Other Req: 26

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Detail IMO Information

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IMO PSN Code: IKL
IMO Proper Shipping Name: HYPOCHLORITE SOLUTION
IMDG Page Number: 8186
UN Number: 1791
UN Hazard Class: 8
IMO Packaging Group: II/III
Subsidiary Risk Label: -
EMS Number: 8-08
MED First Aid Guide NUM: 741

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Detail IATA Information

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IATA PSN Code: NYC
IATA UN ID Num: 1791
IATA Proper Shipping Name: HYPOCHLORITE SOLUTION +
IATA UN Class: 8
IATA Label: CORROSIVE
UN Packing Group: III
Packing Note Passenger: 819
Max Quant Pass: 5L
Max Quant Cargo: 60L
Packaging Note Cargo: 821

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Detail AFI Information

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AFI PSN Code: NYC
AFI Proper Shipping Name: HYPOCHLORITE SOLUTIONS
AFI PSN Modifier: WITH MORE THAN 5% BUT LESS THAN 16% AVAILABLE CHLORINE
AFI Hazard Class: 8
AFI UN ID NUM: UN1791
AFI Packing Group: III
Special Provisions: P5, N34
Back Pack Reference: A12.3

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HAZCOM Label

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Product ID: SODIUM HYPOCHLORITE, 7-15 %, CPE 622680
Cage: 99530
Company Name: OLIN CORPORATION
Street: 501 MERRITT 7
PO Box: 4500
City: NORWALK CT
Zipcode: 06856-4500
Health Emergency Phone: 800-654-6911/203-356-2000
Label Required IND: Y
Date Of Label Review: 12/09/1997
Status Code: C
MFG Label NO: UNKNOWN
Label Date: 12/09/1997
Year Procured: 1998
Origination Code: G
Eye Protection IND: YES
Skin Protection IND: YES
Signal Word: WARNING
Respiratory Protection IND: YES
Health Hazard: Moderate
Contact Hazard: Moderate
Fire Hazard: None
Reactivity Hazard: None
Hazard And Precautions: TARGET ORGANS: EYES, SKIN, RESPIRATORY & GI TRACTS.
ACUTE- CORROSIVE. MAY CAUSE EYE & SKIN IRRITATION & BURNS. VAPORS IRRITATING
TO RESPIRATORY TRACT. HARMFUL IF INHALED/SWALLOWED. MAY CAUSE GI TRACT BURNS.
CHRONIC- MAY CAUSE LUNG DAMAGE. STORE AWAY FROM INCOMPATIBLES. ABSORB SPILL
WITH VERMICULITE. PLACE IN A CONTAINER FOR DISPOSAL. CLEAN AREA TO REMOVE
RESIDUAL CONTAMINATION. FIRST AID- GET MEDICAL HELP IF SYMPTOMS PERSIST.
INHALED: MOVE TO FRESH AIR. PROVIDE CPR/OXYGEN IF NEEDED. EYES/SKIN: IMMEDIATELY
FLUSH WITH WATER FOR 15 MINUTES. HOLD EYELIDS OPEN. ORAL: DO NOT INDUCE
VOMITING. IF CONSCIOUS, DRINK PLENTY OF WATER. CALL PHYSICIAN AT ONCE.

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