22. Chlorination

- Treated wastewater effluent is disinfected prior to its discharge into a water body inorder to destroy pathogens primarily to prevent spread of waterborne disease and minimize public health problems
- Chlorine is a very effective disinfectant and is the most widely used disinfectant for wastewater
- Chlorine disinfection is a practical and economical means for disinfecting large quantities of wastewaters which have been treated to various degrees.
- However, due to its toxicity, associated risk factors and its rising cost, use of ultraviolet light and ozone for wastewater disinfection is on the rise

22.1 Forms of Chlorine

- Due to safety issues related to the use of chlorine gas, **hypochlorites** are often used in lieu of chlorine
- Types of hypochlorites
  - Sodium hypochlorite (NaOCl) comes in a liquid form which contains up to 12.5% chlorine
  - Calcium hypochlorite ($Ca(OCl)_2$), also known as HTH, is a solid which is mixed with water to form a hypochlorite solution. Calcium hypochlorite is 65-70% concentrated.
- Hypochlorites decompose in strength over time while in storage. Temperature, light, and physical energy can all break down hypochlorites before they are able to react with pathogens in water.

22.2 Chlorine Properties

- Chlorine is a yellowish-green gas at room temperature and atmosphric pressure
- Chlorine gas can be pressurized and cooled to its liquid form for making it easy to ship and store.
- When liquid chlorine is released, it quickly turns into a gas that stays close to the ground (being heavier than air) and spreads rapidly.
- While it is not explosive or flammable, as a liquid or gas it can react violently with many substances
- Chlorine is only slightly soluble in water (0.3 to 0.7% by weight.)
- Chlorine gas has a greenish-yellow color
- It has a characteristic disagreeable and pungent odor, similar to chlorine-based laundry bleaches, and is detectable by smell at concentrations as low as 0.2 to 0.4 ppm
- It is about two and a half times as heavy as air

- One volume of liquid chlorine yields about 460 volumes of chlorine gas.
- Liquid chlorine is amber in color and is about one and a half times as heavy as water
- Chlorine is an irritant to the eyes, skin, mucous membranes, and the respiratory system

22.3 Chlorine Storage and Safety

22.3.1 Chlorine Delivery

- Typically for smaller plants chlorine gas is shipped in pressurized steel cylinders - 150 lb or 2000 lb (ton cylinder) size
- Larger plants may get their chlorine supply in rail tank cars
- The daily chlorine usage is typically established based upon the weighing of the chlorine containers.

22.3.2 Chlorine Leak Response

- Typically for smaller plants chlorine gas is shipped in pressurized steel cylinders - 150 lb or 2000 lb (ton cylinder) size. Larger plants may get their chlorine supply in rail tank cars.
- The daily chlorine usage is typically established based upon the weighing of the chlorine containers.
- The withdrawal rates from a chlorine cylinder is based on the temperature of the liquid in the cylinder, and thus the pressure of the gas.
- As chlorine gas is withdrawn from the cylinder, it absorbs the heat from the surroundings.
- For low withdrawal rates, heat will be able to be transferred from the surrounding air to the container in time so that there is no drop in temperature or pressure,
- If the chlorine withdrawal is larger, the air will not be able to transfer the heat quickly enough and the temperature (and pressure) of the chlorine will drop, thus resulting in a lower feed rate.
- If high enough and prolonged enough, this can even result in ice formation around the outside of the container, further decreasing the withdrawal rate.
- The most effective way to increase withdrawal rate from a single container is to circulate the surrounding air with a fan. Again, never apply heat to the containers.
- If chlorine gas escapes from a container or system, being heavier than air, it will seek the lowest level in the building or area
- Only trained staff with access to proper personal protection equipment (PPE) including self-contained breathing apparatus, should handle the chlorine cylinders and address chlorine leak issues
- When a leak is suspected, it is recommended that ammonia vapors be used to find the source. When ammonia vapor using a rag or brush, is directed at a leak, a white cloud will form. To produce ammonia vapor, a plastic squeeze bottle containing about 5 % ammonia, aqua ammonia (ammonium hydroxide solution) should be used. A weaker solution such as household ammonia may not be concentrated enough to detect minor leaks
- All safety equipment should be located outside of the chlorine room and be easily accessed by all personnel
- Small leaks around valve stems can usually be corrected by tightening the packing nut or closing the valve. A leak can also be reduced by removing the chlorine as rapidly as possible
- If it cannot be added to the process there are several chemicals which can be used to absorb the chlorine gas. For example, chlorine can be absorbed by using $1 frac 14$ pounds of caustic soda or hydrated line, or 3 pounds of soda ash per pound of chlorine.
- If the leaking container can be moved, it should be transported to an outdoors area where minimal harm will occur. Keep the leaking part the most elevated so that gaseous chlorine will leak rather than liquid chlorine.
- If the leak is large, all persons in the adjacent area must be warned and evacuated. Only authorized persons equipped with the proper breathing apparatus, and protective measures to the eyes and body should investigate.
- As water is not an efficient absorbent for chlorine and the fact that chlorine reacts with water to form very corrosive hydrochloric acid, never apply water to a leak or consider submerging a chlorine cylinder (for example, in a pond or tank), since it will probably float.

- Remember to keep windward of the leak.
- As chlorine cylinders pressure increases with temperature, as a safety measure the chlorine cylinders are fitted with fusible plug which melts between 158^o and 165^o F.
- Keep chlorine cylinder or container emergency repair kits available. Be familiar with their use and location.
- Leaks at fusible plugs and cylinder valves requires special handling and emergency equipment. The chlorine supplier must be notified immediately
- Pin hole leaks in cylinder walls or ton tanks can usually be stopped by mechanical pressure applications (clamps, turnbuckles, etc.). This only temporary and may require your ingenuity.
- Leaking containers cannot be shipped.
- In general, daily inspection of all chlorine cylinders will avoid major problems

22.3.3 Chlorine Reactions Related to Disinfection

Chlorine reacts with water to form hypochlorous and hydrochloric acids

Cl_2	+	H_2O	$\Longleftrightarrow$	HOCl	+	HCl
chlorine		water		hypochlorous acid		hydrochloric acid

- Hypochlorous acid dissociates in water to form the hydrogen and hypochlorite ions

HOCl	$\Longleftrightarrow$	H^+	+	OCl^-
hypochlorous acid		hydrogen ion		hypochlorite ion

  - Hypochlorous acid is the most effective form of chlorine available to kill microorganisms
  - Hypochlorite ions is much less efficient disinfectant
- The concentration of hypochlorous acid and hypochlorite ions in chlorinated water will depend on the water's pH
  - A higher pH facilitates the formation of more hypochlorite ions and results in less hypochlorous acid in the water
- A significant percentage of the chlorine is still in the form of hypochlorous acid even between pH 8 and pH 9

22.4 Chlorine Disinfection

- When chlorine is added to a wastewater flow, it will first react or combine with certain organic and inorganic substances present, prior to acting on pathogens. The amount of chlorine used up as part of these reactions is referred to as the **chlorine demand**
- The **free chlorine** remaining after the chlorine demand is satisfied, is the strongest form of chlorine available for disinfection.
- Chlorine combined with ammonia (as chloramines) and organic compounds (as chloroorganic compounds), known as **combined chlorine** also exhibit disinfecting properties - albeit weaker than the free chlorine.
- Total residual chlorine is the sum of free chlorine and combined chlorine and it is the residual chlorine concentration which represents the amount of chlorine available for disinfection
- **Chlorine Demand = Applied Chlorine Dose - Chlorine Residual**
  Chlorine residual should be the basis of measuring the effectiveness of chlorine disinfection
- Chlorine residuals are measured in the field using a colorimeteric method. In the laboratory, chlorine residuals are measured typically using: 1) Amperometric Titration, or 2) Iodometric Titration
- Chlorine dosage is typically established from either bench scale laboratory testing, or actual measurement of field results.
- Since field conditions, particularly the mixing element, are not as well controlled as laboratory tests, the actual dosage is expected to be generally higher than from that established in the laboratory.
- Even though residual chlorine concentration can be used for establishing the effectiveness of disinfection, the ultimate effectiveness of disinfection can be monitored by conducting bacteriological testing.

22.5 Factors Affecting Chlorine Disinfection Efficiency

The disinfection efficiency of chlorine depends on the following factors:

- pH: Disinfection is more efficient at a low pH when large quantities of hypochlorous acid are present than at a high pH when hypochlorite ions is the dominant species in the water
- Concentration: Contact Time Ratio (CT): For effective chlorine disinfection both sufficient chlorine dosages – concentration (C) as well as contact time (T) are necessary. There may be a substantial residual but if CT factor is not adequate, disinfection may not be effective. Generally both of these factors must be worked out experimentally for a given system
- Temperature: Colder temperatures are less favorable for disinfection. Proper contacting or mixing or agitation: This is necessary to make sure that the chlorine applied contacts or reaches the microbial cells
- Organic and inorganic material present: The chlorine used by these organic and inorganic reducing substances including metal ions, organic matter and ammonia, is defined as the chlorine demand. So that the amount of chlorine that has to be added to wastewater for different purposes will also vary.
- Even though residual chlorine concentration can be used for establishing the effectiveness of disinfection, the ultimate effectiveness of disinfection can be monitored by conducting bacteriological testing.

22.6 Dechlorination

- Dechlorination is the process of removing residual chlorine from disinfected wastewater prior to discharge into the environment
- Dehlorination is necessary to mitigate the toxic effect of chlorine on the receiving waters.
- Sulfur dioxide is most commonly used for dechlorination.
- Other chemicals used for sodium bisulfite, sodium sulfite and sodium thiosulfate.

22.7 Math Problems

22.7.1 Establishing Chlorine Dosage

Example Problems:

1. Calculate how many pounds per day of chlorine should be used to maintain a dosage of 12 mg/l at a 5.0 MGD flow.
   Solution:
   $lbs/day = conc.(mg/l) * flow(MGD) * 8.34$
   $lbs/day = 12 * 5 * 8.34 = \boxed{500.4 lbs/day}$

22.7.2 Calculating Dosage/Residual/Demand Concentrations

Example Problems:

2. If 80 pounds of chlorine are applied each day to a flow of 1.5 MGD, what is the dosage in mg/l?
   Solution:
   Applying the pounds formula:
   $lbs/day = conc.(mg/l) * flow(MGD) * 8.34$
   $\implies conc.(mg/l) = \frac{lbs/day}{flow(MGD) * 8.34} = \frac{80}{1.5 * 8.34} = \boxed{6.4 mg/l}$
3. How many pounds per day of chlorine will be required to disinfect a secondary effluent flow of 1.68 MGD if the chlorine demand is found to be 8.5 mg/l and a residual of 3 mg/l is desired? Chlorine dosage = chlorine demand + chlorine residual
   $chlorine\ \ dosage = 8.5 + 3 = 11.5 mg/l$
   $lbs/day = conc.(mg/l) * flow(MGD) * 8.34 = 1.68 * 11.5 * 8.34 = \boxed{161.2 lbs/day}$