Chlorination/Dechlorination of Wastewater

General
The effectiveness and efficiency of the disinfection process is of concern. The benefits of disinfection are in the destruction of a wide variety of waterborne diseases and viruses. The use of chlorine must minimize the need for additional treatment. Removal of excess chlorine (the amount of chlorine exceeding discharge limitations) is accomplished by the addition of chemicals such as sulfur dioxide (dechlorination) after the disinfection process is completed.

Chlorination
Disinfection is the process of destroying pathogenic micro-organisms by physical means. This bulletin is directed toward chlorine, the most widely used chemical for disinfection, and sulfur dioxide for dechlorination.

Proper disinfection ensures removal of pathogens from wastewater before it is discharged to the environment. The importance of proper disinfection must not be minimized even with imposed discharge limitations on chlorine residuals as low as 0.02 ppm, or no detectable limit.

There are six factors that influence effective disinfection with chlorine.

1. pH
The initial reaction when chlorine is dissolved in water is the formation of a mixture of hypochlorous (HOCl) and hydrochloric (HCl) acids.

\[ \text{Cl}_2 + \text{H}_2\text{O} \leftrightarrow \text{HOCl} + \text{H}^+ + \text{Cl}^- \]

This reaction is pH dependent. At pH levels above 7, the equilibrium shown above is shifted far to the right. Hypochlorous acid is a weak acid and dissociates according to Figure 1.

\[ \text{HOCl} \leftrightarrow \text{H}^+ + \text{OCl}^- \]

At pH levels between 4.0 and 6.0, chlorine exists predominately as HOCl. At pH levels above 8, hypochlorite ions (OCl\(^-\)) predominate. Hypochlorite ions exists almost exclusively at pH levels of 9 and above.

2. Temperature
Temperature also effects the disinfection process, although it is rarely controlled in wastewater treatment. Wastewater is treated most efficiently at higher temperatures.

3. Turbidity
The turbidity level of wastewater has been reduced considerably by the time it reaches the disinfection process. Excessive turbidity will create demand although chlorine is forgiving in the disinfecting process. When wastewater is filtered to a turbidity of one unit or less, most of the bacteria has been removed. Suspended matter may also change the chemical nature of the water when the disinfectant is added.
4. Mixing/Induction
An efficient diffusion device to assure rapid initial mixing of chlorine and wastewater is essential.
The most effective way of assuring rapid mixing and improving safety is to use the gas induction unit, CHLOR-A-VAC®.
This unit replaces the conventional diffuser, mixer, ejector, booster pump and long water solution line. CHLOR-A-VAC is a
submerged gas induction unit that generates vacuum, reduces chemical consumption, and improves mixing.

5. Contact Time
Contact time is important after rapid mixing, to reduce the bacteria count. Most states require a minimum contact time
of 30 minutes at peak flows for effective disinfection.

6. Control Systems
The control method impacts the system’s effectiveness and chemical consumption. Manual control does not
compensate for increases or decreases in chlorine demand nor variation in flow. The use of automatic gas feeders is
justified by the savings in chemical usage and the improved environment.
The choice of a control method should be based upon the best method to meet the conditions.

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Dechlorination
Dechlorination is a practice used to reduce or remove the chlorine discharge levels. Free and combined chlorine
residuals are reduced by sulfur dioxide, sulfites and other dechlorinating agents.

Figure 2 - Typical Cylinder Mounted Dechlorination System
The most cost effective dechlorinating agent is sulfur dioxide. Stoichiometrically, 0.9 parts of sulfur dioxide are required to remove one part chlorine. In actual practice, at least 10% excess may be required for complete dechlorination.

**Sulfur Dioxide**

Sulfur dioxide is the most common dechlorinating agent for the following reasons:
1. Removes free or combined chlorine residual
2. Cost effective
3. Similar to chlorine feeding apparatus design
4. Simple to control

**Chemistry of Dechlorination**

Sulfur dioxide dissolves in water rapidly, forming sulfuric acid as shown in the following reaction:

$$\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$$

The sulfite radical formed in this solution reacts with free and combined chlorine as shown in the following equations:

$$\text{H}_2\text{SO}_3 + \text{NH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4 + \text{HCl}$$

$$\text{H}_2\text{SO}_3 + \text{NH}_3\text{Cl} + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 + \text{HCl}$$

Each reaction is rapid and complete.

See Figures 2 and 3 for examples of chlorination/dechlorination systems.

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**Figure 3 - Typical Ton Container Mounted Dechlorination System**
Factors Influencing Effective Dechlorination

Mixing/Induction
Since sulfur dioxide is more soluble in water than chlorine (11 times greater solubility), the use of CHLOR-A-VAC™ as a gas induction and mixing device has proved very effective. Normally, dechlorination must be accomplished quickly and completely since the luxury of a contact tank may not be available. CHLOR-A-VAC effectively provides the mixing required.

Contact Time
Contact chambers may not be needed for sulfur dioxide feed. The chemical reaction between the sulfur dioxide solution and the chlorine residual is practically instantaneous at the pH and temperature levels usually encountered.

Sizing
For any control system to operate efficiently, the equipment must be sized to satisfy the requirements of the process. The formula used to determine sulfur dioxide feed is as follows:

\[ \text{PPD} = 0.012 \times \text{GPM} \times \text{ppm} \]

Where:
- PPD = pound per day of sulfur dioxide
- GPM = wastewater flow in gallons per minute
- ppm = sulfur dioxide dosage

Sulfur dioxide dosage = (chlorine residual)

It is important to know the maximum water flow rate when sizing the sulfonation equipment. The system demand for sulfur dioxide is variable based upon the chlorine residual. The sulfur dioxide demand is indicated by an excess chlorine residual after adequate contact time.

Dechlorination Control
After the size of the unit is determined, the type of control (manual or automatic) can be selected. Since over-sulfonation results in wasted chemical and decreases both the water’s dissolved oxygen content and pH, accurate control the feed rate is necessary. Automatic control systems are used due to discharge requirements that require more accurate control of the chlorine residual. The automatic control systems most frequently used are: flow proportioning; residual control, compound loop and feed forward.

The type of automatic system utilized will depend upon the characteristics of the treatment plant and effluent quality.
Feed Forward System (Figure 4)

Feed forward systems use a flow signal representing plant flow at the chemical injection point and a chlorine residual signal measured upstream of the sulfur dioxide injection point. These signals are directed to a controller that proportions the feed rate of sulfur dioxide to the amount of residual chlorine to be removed from the water supply. The controller compensates for process changes in response to the input signal it receives. Similar to a compound loop system, a feed forward control system requires accurate flow and residual signals.
Flow Proportioning (Figure 5)

Flow proportioning (open loop) control is a simple, effective means of providing accurate control in a system experiencing wide flow variations and a fairly constant chemical demand. The dechlorination controller provides linear, proportional sulfur dioxides gas feed control in response to a signal from a water flow meter. The system accuracy is dependent upon the flow signal.

Figure 5 - Flow Proportioning System
Residual Control (Figure 6)
Residual control (closed loop) should be limited to dechlorination systems which have a constant flow rate but a varying chlorine demand. When the chlorine residual is to be controlled to a level greater than or equal to 0.1 ppm, a dechlorination residual control system will work effectively. For treatment systems requiring chlorine residuals below 0.1 mg/l, use a sulfite analyzer in lieu of the chlorine residual analyzer to control to a positive sulfite level.

A dechlorination controller responds to the chlorine residual analyzer signal. Rapid flow changes or excessive lag time will have a detrimental effect on the total system response. The total system lag time must be minimized. To avoid excessive lag time: 1) Locate the automatic valve close to the point of application; 2) Use a CHLOR-A-VAC for mixing; 3) Locate the sample point near the sulfur dioxide fed point; 4) Locate the chlorine residual analyzer as close as possible to the point of sampling.

![Figure 6 - Residual Control System](image-url)
Compound Loop System (Figure 7)

A compound loop system combines flow proportioning and residual control so that sulfur dioxide is fed to the point of application in proportion to the flow and residual signals.

The compound loop controller responds mainly to the flow signal to control the sulfur dioxide feed rate while the residual portion of the controller automatically adjusts the dosage level to maintain the desired effluent residual. Since the compound loop system combines both flow proportioning and residual systems, cycling caused by flow rate variations and changing chlorine levels are minimized. As in the residual system, a compound loop controlled sulfonation system using a chlorine residual analyzer should not be used when the chlorine residual must be less than 0.1 ppm. In this instance, a sulfite analyzer is called for to maintain a minimum sulfite level.