Measurement of Total Chlorine in Municipal Wastewater Effluent

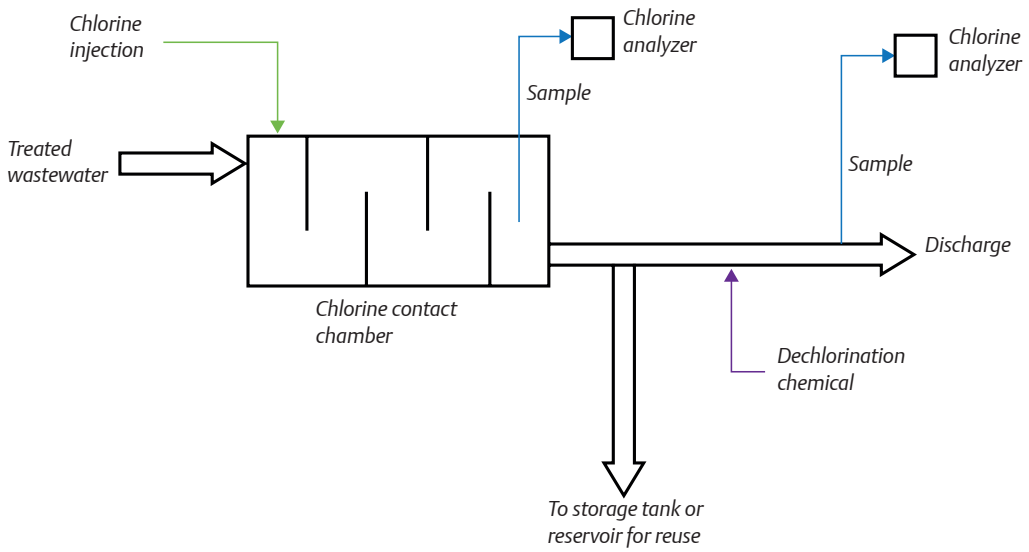
Background

Wastewater is any water that has been contaminated by human activity. Municipal wastewater is sanitary sewage from houses, offices, schools, and factories that is collected and treated at a central facility. It often includes process wastewater from small factories and businesses. Process wastewater from large factories, refineries, food processing facilities, and power plants is usually not discharged to a sanitary sewer. Instead, the water is treated onsite and discharged.

Municipal wastewater treatment involves several steps. At a minimum, treatment removes suspended solids and reduces the concentration of organic matter. Other steps may remove nutrients, such as nitrogen and phosphorus. Treatment must also kill disease-causing microorganisms. Chlorine gas and sodium hypochlorite are common disinfectants.

Treated wastewater can be discharged into another body of water or it can be reused. See Figure 1. Because chlorine is harmful to many aquatic and marine animals, including fish, discharged water must contain very low levels of chlorine. The discharge permit for the plant specifies the allowed concentration. To meet discharge limits, dechlorination using chemicals such as sulfur dioxide and sodium bisulfite is often necessary. Wastewater intended for reuse, that is for irrigation, injection into an aquifer, or injection into seawater barrier wells, is usually not dechlorinated.

Figure 1 - Chlorinated wastewater leaving the contact chamber can either be stored for subsequent reuse or discharged. Recycled wastewater is rarely dechlorinated. Discharged wastewater is almost always dechlorinated.



ROSEMOUNT® Analytical

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Properties of Chlorinated Wastewater

When chlorine is added to wastewater, a portion of it is consumed by reactions with chemicals in the water, making it unavailable for disinfection. Moreover, the chlorine that remains has often been converted to forms that are significantly poorer disinfectants than the sodium hypochlorite or chlorine gas originally added.
Only two forms of chlorine have disinfecting properties: free chlorine and combined chlorine. Free chlorine, which is by far the better disinfectant, is produced when sodium hypochlorite or chlorine gas is added to water. Combined chlorine is monochloramine and dichloramine, compounds formed by the reaction between free chlorine and ammonia. Because wastewater treatment seldom completely removes ammonia and organic amines, chlorinated wastewater typically contains combined chlorine, primarily monochloramine. Free chlorine will appear only if enough chlorine has been added to completely oxidize the chloramines, so-called breakpoint chlorination. Breakpoint chlorination is rarely practiced in municipal treatment plants.

The sum of free and combined chlorine is often called total chlorine. The term is misleading because standard analytical methods define total chlorine by the way it is measured, not as the aggregate of certain chemicals. Accordingly, total chlorine is all the oxidants, some of which may not contain chlorine, in the sample capable of oxidizing potassium iodide to iodine when the pH is between 3.5 and 4.5. The amount of iodine produced under these conditions is defined as total chlorine.

Applications

For chlorine, either free or combined, to be effective, the concentration and contact time must be controlled. Most treatment plants have a contact chamber where chlorine is injected, mixed, and allowed to remain in contact with the water for the required time. Flow rate into the chamber and the chlorine concentration at the outlet are used to control the chlorine injection rate.

If the wastewater requires dechlorination, chlorine is also measured after the dechlorinating chemical has been added. Typically, the chemical injection rate is controlled using the flow rate and the chlorine concentration at the outlet of the contact chamber. See Figure 1. A second contact chamber for dechlorination is not needed because dechlorination reactions are almost instantaneous.

Most wastewater applications require measuring total chlorine, although free chlorine might also be required. The chlorine concentration in reused wastewater can be as high as several ppm. In discharged wastewater, the allowed concentration is low, typically less than 0.05 ppm.

Direct measurement of trace chlorine is a challenge. If the discharge limit is close to the detection limit, the relative measurement error will be high. If the discharge limit is below the detection limit, the analyzer cannot be used at all. Many chlorine sensors, particularly amperometric ones, are calibrated against the results of a grab sample test. Because chlorine sensors cannot be accurately calibrated if the sample contains only a trace of chlorine, there must be a provision to interrupt the normal sample flow and replace it with chlorinated water. Chlorinated water is also needed for periodically checking the response of the analyzer to confirm that low chlorine readings are valid and not the result of a failed sensor.

Instrumentation: Free Chlorine

All Rosemount Analytical free chlorine sensors have some cross sensitivity to chloramines. If chloramines are present, the free chlorine measurement will have a positive bias, and may not be useful, particularly if the concentration of free chlorine is small and the concentration of chloramine is high and variable.

Instrumentation: Total Chlorine

The Rosemount Analytical total chlorine analyzer is a reagent-based system, which measures true total chlorine. It consists of the TCL sample conditioning system, the 499ACL-02 sensor, and any Rosemount Analytical chlorine analyzer. The sample conditioning system injects a solution of potassium iodide in vinegar into the sample. The vinegar adjusts the pH, and the iodide reacts with total chlorine to produce an equivalent amount of iodine, which the sensor measures. The sensor is a membrane-covered amperometric sensor with high sensitivity to iodine.

The TCL requires a sidestream sample. If the sample is not pressurized, a sample pump is required.

- 0 – 20 ppm linear range
- 0.02 ppm detection limit
- Reagent lasts two monthsHeavy Duty NEMA 4X (IP65)
- Easy sensor maintenance
- Low sample flow (0.25 gph minimum)
- Corrosion resistant construction

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