AlTRET Industries Private Limited

Chemical Oxidation with CHLORINE

In the field of Waste Water treatment, chemical oxidants such as chlorine, ozone & hydrogen peroxide are widely used for disinfections, removing organic materials that are resistance to biological & other treatment processes & conversion of Cyanides to innocuous products. Use of chlorine as a disinfectant destroys or inactivates bacteria present in waste water before it is discharged into receiving streams. Chlorine rapidly penetrates bacterial cells & kills the bacteria. However, the effectiveness of chlorine is influenced greatly by the physical & chemical characteristics of wastewater.

Initially when chlorine is added to water, it forms by chlorous acid HOCl $Cl_2 + H_2O$

$HOC + H^+ + Cl^- \longrightarrow$

Hypochlorous acid is the disinfecting agent & is referred to us free residual or free available chlorine. If any reducing agents such as ferrous ions or hydrogen sulphide are present in waste water, chlorine reacts with them & the concentration of chlorine available to destroy pathogenic bacteria is reduced. The reduction reaction with hydrogen sulphide may be represented as:

$$H_2S + 4Cl_2 + H_2O \longrightarrow H_2SO_4 + 8\ HCl$$

Waste water usually contain ammonia. In the presence of ammonia, HOCl reacts to form sequentially, monochloroamine (NH_2Cl) dichloramine ($NHCl_2$) & Trichloramine according to the following:

$$NH_3 + HOCl \longrightarrow H_2O + NH_2Cl$$
$$HOCl + NH_2Cl \longrightarrow H_2O + NHCl_2$$
$$HOCl + NHCl_2 \longrightarrow H_2O + NCl_3$$

Monochloramine & Dichloramine are referred to as combined residuals & are more stable then free residual but less effective as disinfectants. Once all ammonia has reacted, further addition of chlorine converts the combined residuals into a free residual, the conversion being proportional to the dose at the "break point". This is the limit beyond which all the residual chlorine is available as free chlorine.

Chlorination is used to oxidize cyanide in industrial waste water to harmless carbon & nitrogen compounds. This is done in alkaline media at pH greater than 8.5 to prevent the generation of poisonous hydrogen cyanide gas.

$$2CN + 5\,Cl_2 + 8OH^- \longrightarrow 10\,Cl^- + 2CO_2 + N_2 + 4H_2O$$

The residual cyanide concentration after a reasonable reaction time, is very small.

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Method of Testing of CHLORIDE

Method: - Argentometric Method

For Chloride as ppm: - Method of calculation of Chloride as ppm. Method given in Alfloc.

Our previous calculation for chloride method is given below:

Calculation: -

$$\text{Chloride } [Cl-] = \frac{\{\text{ml of N/50 (0.02N) } AgNO_3 \text{ / B.R. in ml}\} * 1000}{\text{sample taken for titration in ml}} \text{ Mg /L (ppm)}$$

Or

$$\text{Cl- mg /L (in ppm)} = \frac{1000 \times \text{B.R.}}{\text{Sample taken for titration}}$$

Note:-

1) In this method the calculation for chloride is expressed in ppm as $CaCO_3$.
2) In this calculation Normality of $AgNO_3$ solution considered as Std 0.02N

Conclusion: - ppm of Chloride in this calculation consider Equivalent weight of calcium chloride [E.W.- 50]. SO ppm of Chloride is expressed in ppm as $CaCO_3$.

Modified calculation method consider Eq.Wt of Chloride (Cl^-) and in this method Normality is not considered as 0.02N, but we standardize $AgNO_3$ solution & take the Normality whatever it is in the modified calculation method.

Calculation of this method is given below:

$$\text{Cl- mg/L In ppm} = \frac{\text{B.R. x N x Eq.wt (35.45) x } 10^6}{\text{ml sample taken x 1000}}$$

$$= \frac{\text{B.R. x N x Eq.wt (35.45) x } 10^3}{\text{ml sample taken x 1000}}$$

$$= \frac{\text{B.R. x N x Eq.wt 35.450}}{\text{ml sample taken x 1000}}$$

Where,

B.R. = titration reading in ml

N = Normality of $AgNO_3$ solution

Eq. wt = equivalent weight of chloride (Cl^-) =35.450

One example for both calculation method Ex: -

Sample taken for titration is 10 ml

B.R. {Titration reading} is 5.0 ml

Normality of $AgNO_3$ solution = 0.02N and observed chloride in ppm from both methods

PREVIOUS METHOD: -

$$Cl^- \text{ in ppm} = \frac{\text{1000 x B.R.}}{\text{Sample taken}}$$

$$= \frac{\text{1000 x 5.0}}{10.0}$$

=500 ppm

Where, B.R. = 5.0 ml

Sample taken: - 10.0 ml

MODIFIED METHOD:-

$$Cl^- \text{ in ppm} = \frac{\text{B.R. x N x 35450}}{\text{Sample taken}}$$

$$= \frac{5.0 \times 0.02 \times 35450}{10.0}$$

$$= \frac{354.5}{10}$$

$$= 35.45 \text{ ppm}$$

The chloride difference from both method is:

Difference = previous chloride method - modified chloride method
= 500 – 354.5
= 145.5 ppm Difference in
% is 29.1

Conclusion: -

In this calculation, consider equivalent weight of chloride [E.W. – 35.45]

Difference between both the method: -

Previous method gives 29.1% more ppm chloride because it is expressed as Calcium Carbonate. Hence we determine chloride as per modified method.

Ref : -**1.** ***This calculation method is based on "ALFLOC" Water Treatment Service.***
2. Amended method of calculation for Chloride as ppm is given in American Std.