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TECHNICAL BULLETIN Phosphorous Removal

With the enactment of the Clean Water Act in the United States, came a focus to remedy the detrimental effects of nutrient addition to the common waterways of the United States and Canada. The Joint Great Lakes Commission was established and soon developed a plan to limit the amount of phosphorous and nitrogen entering the Great Lakes. The plan began with banning the use of phosphate detergents. Soon phosphorous limits were established for discharges from industrial and publicly owned wastewater treatment facilities.

Although there are a number of ways to treat and remove phosphorous from wastewater, the primary and most employed method has been through the chemical treatment of wastewater with iron salts such as ferric chloride and ferrous chloride.

Ferric Chloride and Ferrous Chloride both react with phosphorous to form phosphate precipitates. However, there are some major differences in application procedures between the two. The major difference is that ferrous chloride requires an oxidation step to convert the ferrous ions into ferric ions to provide effective phosphorous removal. In practice, this usually translates into a requirement in the wastewater treatment plant for conventional biological treatment capability, with the aeration step providing the necessary oxidation of ferrous to ferric ions.

Ferric Chloride, on the other hand, has none of the constraints of ferrous chloride and can be applied without an oxidation step. Therefore, ferric chloride functions in either the primary or secondary area of a WWTP. An additional benefit of using ferric chloride is that once the demand for phosphate and hydrogen sulfide is met by the initial concentrations of ferric chloride, any additional ferric ions will react with the alkalinity in the water to form ferric hydroxide. This ferric hydroxide acts as both a coagulant and a flocculant. As such, it works to settle out not only the ferric phosphate and sulfide compounds just formed, but also any other suspended solids in the waste stream. Ferrous Chloride on the other hand must be subjected to the oxidation of a conventional secondary treatment system to achieve the settling properties of ferric chloride, and then it will only marginally improve the performance of secondary clarification.

In the past few years a relatively new approach to phosphorous removal has appeared that focuses on a biological removal method. This method manipulates the biomass to metabolize phosphorous and achieves moderate levels of phosphorous removal. Although effective in certain situations, the method can be limited with regard to removing enough phosphorous to meet many current government standards. Additionally, these operations are sensitive to changes in sewage quality.

Many facilities that employ this technology supplement the operation with additions of ferric or ferrous chloride to provide operational reliability.

Establishing Ferric or Ferrous Chloride Dosages for Phosphate Removal in Wastewater Treatment Plants

The following chart is a quick guide for matching iron dosages to soluble phosphorous/phosphate removal. The dosages represent stoichiometric parts per million relationships or ratios:

Ratios of Ferric Chloride to Soluble Phosphorous and Phosphate		
Iron/Phosphorous (ppm)	Phosphorous	Phosphate
Fe ⁺³ (Iron)	1.80	0.59
FeCl ₃ (dry, 100% basis)	5.23	1.71
Liquid Ferric Chloride (38%)	13.75	4.49

Ratios of Ferrous Chloride to Soluble Phosphorous and Phosphate		
Iron/Phosphorous (ppm)	Phosphorous	Phosphate
Fe ⁺² (Iron)	2.70	0.89
FeCl ₂ (dry, 100% basis)	6.19	2.03
Liquid Ferrous Chloride (22%)	28.2	9.23

Determining the ferric or ferrous chloride dosage level begins by establishing the soluble phosphate level in the sewage to be removed. The ferric or ferrous chloride dosage rate is then calculated from the above chart (i.e. 2 ppm phosphate would require 2 x 1.71 ppm or 3.42 ppm FeCl₃). This is the base dosage rate.

From this point, additional ferric chloride is added to enhance solids removal. This normally takes an additional quantity (i.e. 3 – 15 ppm of ferric chloride), the amount being proportionate to the total suspended solids concentration of the wastewater and the presence of any competing anions, such as sulfides, which increase the demand for the ferric chloride.

Troubleshooting begins with an analysis of soluble and insoluble phosphorous in the system effluent. The presence of soluble phosphorous would indicate insufficient ferric or ferrous chloride dosage. The presence of insoluble phosphorous would point to poor settling conditions, which are normally addressed through the adjustment of hydraulic loading rates, mixing adjustments, polymer dosage adjustment or, in the worst case, providing additional flow capacity.

It is important to note that ferric chloride, as compared to ferrous chloride, actually performs three functions in wastewater treatment. The first is its reaction with and precipitation of soluble phosphate compounds. The second and third functions come from the reaction of ferric chloride with alkalinity in the water to form ferric hydroxide which functions as both a coagulant and flocculant. As such ferric hydroxide enhances sedimentation and aids in the removal of suspended solids, including the ferric phosphate precipitates. The flocculant step is often facilitated with a subsequent application of an anionic polymer (polyelectrolyte).