Wastewater treatment - sulphide control with chlorine dioxide

Chlorine dioxide (ClO_2) is effective as both a disinfectant and an oxidant in water and wastewater treatment. Its selective reactivity makes it a powerful non-chlorinating oxidizing agent useful in many water treatment applications for which chlorine and other oxidizing agents are unsuitable. Unlike most oxidants, it may be used over a broad pH range to oxidize sulphide without the formation of colloidal sulphur, which can cause equipment blockages.

Application description

Sulphide exists in wastewater in three forms; hydrogen sulphide gas (H_2S), non-volatile ionic species hydrogen sulphide (HS^-) and sulphide (S^{2-}). The ratio of each of the three species H^2S, HS and S^{2-} is dependent on the pH. At pH 6, 90% of the sulphide will be present as H_2S, and the higher the H^2S concentration the greater the tendency for it to volatilise. Conversely at pH 10, 100% of the sulphide will be present as S^{2-}.

Sulphides are produced by both biological and chemical action. They are produced biologically by anaerobic bacteria, and chemically by many industries including the chemical, petroleum, paper, and textile industries.

H^2S occurs naturally through the anaerobic decay of organic matter and is easily recognized by its characteristic rotten egg odour. In the absence of dissolved oxygen and in the presence of soluble Biological Oxygen Demand (BOD), *Desulfovibrio desulfuricans* and other sulphate-reducing bacteria (SRB's) convert the sulphate ion to sulphide.

$$SO_4^{2-} + \text{Organic matter} \xrightarrow[\text{(no D.O.)}]{\text{Anaerobic micro-organisms}} H_2S + CO_2$$

Many systems provide an environment that promotes the growth of a healthy biological community. H^2S formation in wastewater systems occurs primarily in the gelatinous slime layer (biofilm) that accumulates on pipe walls and in the sludge blankets of clarifiers and other solids processing units. The rate of sulphide production is dependent upon the concentrations of sulphate ions, organic matter, and dissolved oxygen, as well as other factors such as pH, temperature, retention time, stream velocity, and surface area.

Many industrial processes produce sulphide-containing gases and waste products. These are generated, for example, during petroleum refining, coal coking, black liquor evaporation in Kraft pulping, viscose rayon manufacture and natural gas purification. In addition to their disagreeable "*rotten egg*" odour, sulphides are corrosive to concrete and are extremely toxic. These gases and wastes are frequently scrubbed with alkaline solutions and require treatment before discharge.

Treatment Alternatives

Sulphide can be removed from a system by precipitation with iron or by oxidization. Various oxidizers including chlorine, hydrogen peroxide, and potassium permanganate are commonly used for oxidation of sulphide. Different treatment strategies are required depending on the application.

Chlorine Dioxide

ClO_2 is effective where alternative oxidants don't work, such as when rapid destruction of sulphide is important or the formation of halogenated by-products prevents treatment with chlorine.

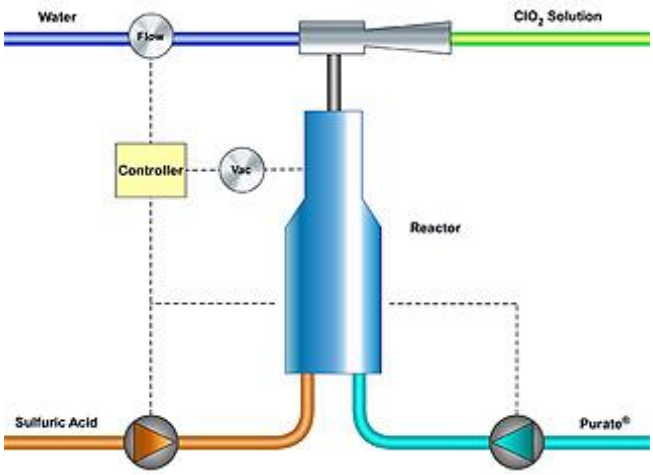
ClO_2 reacts very rapidly with hydrogen sulphide gas or the sulphide ion. Between pH 5-9, minimum 3.36ppm of chlorine dioxide should be used to instantly oxidize 1ppm of sulphide to sulphate.

$$5H_2S + 8ClO_2 + 4H_2O \longrightarrow 5SO_4^{2-} + 8Cl^- + 18H^+$$

In wastewater systems where the odour causing sulphides are produced from colonies of bacteria metabolizing sulphate, ClO_2 is an effective control strategy. ClO_2, when fed at somewhat higher dosages than those required to destroy the sulphide, will remove the biofilm that contains the bacteria creating the sulphide.

Purate® technology and SVP-Pure® ClO_2 generators set the industry standard for quality, reliability, ease of operation and overall cost effectiveness.

The benefits of Purate® compared to chlorite / hydrochloric acid generation of chlorine dioxide:



- Less corrosion due to chloride free operation
  - (2 to 3g Chlorides per kg ClO_2 are added with the chlorite / hydrochloric acid process) - an important factor in many industrial applications
- Totally Chorine free
  - Purate® provides the most pure chlorine dioxide
- Less volume of chemicals to transport and handle
  - at least 44% less precursor chemicals
- In most cases operating costs are significantly lower
  - ClO_2 production rates rapidly adjusted to demand
- High conversion efficiency to chlorine dioxide
  - greater than 95%
- Low service costs

Advantages of CLO2 for odour control:

- **it reacts more rapidly and completely than other available oxidizers**
- **it does not require pH adjustment or increase solids loading**
  - It won't form colloidal sulphur[1].
  - Hydrogen peroxide, potassium permanganate and chlorine all require excess oxidizer and a basic pH to avoid colloidal sulphur formation[2].
- **it doesn't form chlorinated by-products**
  - While chlorine is the least expensive oxidizer available, it cannot be used when organic compounds are present due to the formation of chlorinated organic by-products.
- **it forms soluble by-products**
  - Potassium permanganate and catalyzed hydrogen peroxide (*Fenton's chemistry*) result in high solids loading and significant disposal costs.

Method of generation

Purate® is a stabilized aqueous solution of 40% sodium chlorate and 7 to 10% hydrogen peroxide. Purate® is a precursor chemical for the production of chlorine dioxide in an SVP-Pure® Chlorine Dioxide Generator. It may be used as an oxidant for phenol destruction, iron and manganese oxidation, hydrogen sulphide removal, and many other applications. It also may be used in pesticide applications where it is FIFRA registered for use as a disinfectant, biocide, slimicide, algaecide, fungicide, and molluscicide in drinking water, wastewater, and process water systems. It has FDA approval for disinfection of processed fruits, vegetables and poultry. It must be used in conjunction with sulphuric acid to produce ClO_2 .

At *Scotmas* we strive to deliver the highest quality products, services and support to our customers. Our strategic partners *Eka Chemicals* developed the Purate® process to meet the needs of high-volume water treatment and speciality bleaching customers. Purate® chlorine dioxide technology is the product of more than 35 years of experience designing safe and reliable chlorine dioxide systems.

References

1. Synan, J.F., Malley, H.A., "Chlorine dioxide as an alternative for Disinfection in Water Systems", *Engineering Panel of the Campden Foold Preservation Research Assoc., Chipping Campden, Glos., England,* Oct 21, (1975)
2. Bowker et. al., "Odour and corrosion control in Sanitary Sewerage systems and treatment plants", Design Manual, EPA-625/1-85-018, US EPA Washington, D.C.

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