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Revision Memo

12/02 Additional information added to current applications section
 Sub-sections added to materials of construction
 Added dosage rules of thumb for hydrogen peroxide



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PROPRIETARY INFORMATION - For Authorized Company Use Only

SCOPE

This subsection presents guidelines for preparing duty specifications for facilities that utilize one of several forms of chemical oxidation for the removal of contaminants from wastewater. Process and design conditions are not specified in the Practice as they vary greatly with technology and from application to application. At this point in time, all major new applications of chemical oxidation should be piloted tested in the field to define treatment performance and to provide information to size facilities.. Standard applications of reducing odors due to H₂S, or trim treating COD for short term applications can be done in small scale laboratory tests.

This subsection does not address the use of chemical oxidants to produce useful products, nor does it attempt to show applications of the oxidants in non-wastewater service.

REFERENCES

DESIGN PRACTICES

- [Section XIX-A](#) Guidelines for Selecting Wastewater Treatment Systems
- [Section XIX-A5](#) Biological Treatment of Wastewater
- [Section XIX-A9](#) Water/Wastewater Chemical Feed Systems

EMRE WATER AND WASTEWATER DESIGN GUIDE (TMEE 080)

- DG 11-6-1 Chemical Feeders for Boilers and Deaerators
- DG 11-6-3 Chemical Feeders for Wastewater Treating

OTHER REFERENCES

1. Bigda, R. J., Fenton's Chemistry, Environmental Technology May/June 1996 (p. 34).
2. Eckenfelder, W. W., Industrial Water Pollution Control, (2nd ed.), McGraw-Hill, New York, 1989.
3. Eckenfelder, W. W., et al. ed., Chemical Oxidation Technologies for the Nineties, Technomic Publishing Co., Lancaster PA, 1992.
4. Malley Jr., J. P., et al, The Performance and Microbiology of Ozone-enhanced Biological Filtration, J.A.W.W.A., December 1993 (p. 47).
5. Metcalf and Eddy, Inc., Wastewater Engineering Treatment, Disposal, and Reuse (3rd ed.), McGraw-Hill, New York 1991.
6. Scherer, G., et al., Practical Environmental Applications of Hydrogen Peroxide in the Petroleum Industry, Proceedings of AIChE 1995 Spring Meeting, Houston TX, 1995.
7. Intertech Conferences, Osicative Treatment of Pollutants in Wastewater, Conference Proceedings, March 12-22, 1994, Philadelphia, PA.

DEFINITIONS

Oxidation - The chemical reaction of a material with an oxidizing substance.

Oxidant/Oxidizer - A chemical that can easily accept electrons from another substance in an oxidation/reduction reaction. The valence state of the oxidizer is decreased and the valence state of the oxidizable wastewater contaminant is increased (oxidation).

Oxidation Potential - A scale of the oxidizing potential of substances expressed in the voltage generated by a standard electrode (units are typically measured in millivolts). Higher values indicate more powerful oxidants.

BACKGROUND

Chemical oxidation (Chem Ox) is a collective term for a number of related technologies for the destruction or change in oxidation state of contaminants in wastewater. In general, the processes work by combining an oxidizing agent (chemical) with the contaminant and reacting the two compounds to make a third more desirable compound. There are a number of potential oxidizing agents ranging in strength (oxidation potential) from air to ozone (O₃). There are also some notable non-oxygen oxidizers, the primary one being chlorine (Cl₂).

During oxidation the oxidizer removes one or more electrons (oxidizes) increasing the valence state of the target contaminant. This action can be accomplished on both organic and inorganic materials. For instance, an organic contaminant could be oxidized from an aromatic ring (C in the +1 state) to CO₂ (C in the +4 state). Sulfides (H₂S, S = -2) can be converted to SO₂ (S = +4).

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- Temperature, pH, salt and the presence of other contaminants can have an impact on the oxidation reaction and dramatically change the reaction time and dosages needed, and the end product formed. For example, a typical application of reducing odors due to H₂S (actually NaS or NaHS forms in most cases) in wastewater with hydrogen peroxide can yield either a sulfate or an elemental sulfur end product. At pH >8, the predominant form will be Na₂SO₄, and at pH < 7 the predominant form will be solid sulfur particles (suspended in water) of elemental S.

The oxidant generally reacts with all the oxidizable material in the wastewater in proportion to the relative reaction rates. Typically large "excess" quantities of oxidant may be required to ensure that an adequate amount is "left over" to decompose the target contaminant.

- Chemical oxidation is an exothermic reaction meaning heat is released by the operation. For wastewater treatment applications, this is rarely an issue, except that addition facilities need to be designed to ensure oxidant chemical cutoff in pipelines when wastewater flow is diverted or stopped, during maintenance for example. The contaminants are in solution at parts per million levels and the heat of reaction may not raise the water temperature by a noticeable amount. This must always be confirmed however by calculation and by laboratory analysis. Some oxidation processes on concentrated waste streams can generate sufficient heat to be a problem if not anticipated.

ADVANTAGES AND DISADVANTAGES

- The major advantages of chemical oxidation of wastewater is that the equipment required is usually small and inexpensive, and rapidly deployed. Also, some contaminants in the wastewater can be oxidized where they would normally be resistant to biological removal. These advantages can be utilized, for instance, by operating facilities that have a short term issue with a contaminant, perhaps because of a unit turnaround or malfunction. A peroxide storage tank and injection skid can be rented from a vendor, be installed on site, and treating the problem within a few days (the skid may have to be modified to meet site equipment requirements).

The other major advantage is that some compounds are resistant to biological wastewater treatment, and can inhibit the operation of the main plant waste treatment system. In these cases, it may be advantageous to oxidize the contaminant in a small concentrated stream. The treated stream might either meet discharge criteria as is, or else be sufficiently non-inhibitory to be treated in the main biological treatment system.

The most common disadvantage of chemical oxidation is the operating cost of the oxidants compared to biological treatment. If the wastewater can be biologically treated, it is very unusual for chemical oxidation to be a long term preferred option. In one study, the cost per mole of delivered oxygen was three times higher for hydrogen peroxide than it was for compressed air. Operating and capital cost can be traded-off during the process selection process; often a more capital intensive ozone process can be substituted for a more operating cost intensive peroxide system.

MAJOR OXIDANTS

- The most common oxidation systems in use in wastewater treatment are hydrogen peroxide, Fenton's Reagent, ozone, chlorine in the preferred hypochlorite (bleach) form, chlorine dioxide, and air/oxygen. Sometimes, ultraviolet light (UV) is used to catalyze the peroxide and ozone reactions to speed conversion.

CURRENT APPLICATIONS WITHIN EXXON

- There are relatively few chemical oxidation wastewater treatment systems within Exxon. The systems that are used are primarily peroxide addition systems. Campana Refinery has used hydrogen peroxide injection to remove phenols from stripped sour water prior to commingling the stream in the general wastewater. Ingolstadt Refinery and the former Karlsruhe Refinery periodically add peroxide to the treated effluent to ensure adequate COD (Chemical Oxygen Demand) removal. Sriracha Refinery has installed peroxide on their tank bottom water drawoffs to reduce odors of the wastewater going to and in the oxidation pond biological treatment system. Sakai Refinery has used sodium hypochlorite bleach for treatment of sulfides in desalter washwaters. Other sites have investigated Chem Ox as a treatment option for individual problematic streams, but it has not been the least cost alternative. Hydrogen peroxide has also been used occasionally at some Exxon plants that have biological treatment plants for filamentous bacteria control (poor settling biomass).

PRODUCTS OF CHEMICAL OXIDATION

The primary goal of many Chem Ox systems is to pretreat the wastewater to make further treatment more effective. In these situations, it is not necessary to react the material all the way to complete removal. Partial reaction to change the undesirable contaminant into one less toxic is often sufficient.

Oxidation of organic molecules can lead to many compounds, in addition to carbon dioxide (CO₂). Most written descriptions simplistically indicate that organics are decomposed to CO₂ and water. While this is true, each potential application should be checked for the possible formation of undesirable compounds through partial oxidation of the contaminants. This is especially true if chlorine is used. With a few materials, the partially oxidized material is less biodegradable than the original compound. Ozone and peroxide can lead to the formation of aldehydes and organic acids in the treated water.