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## Dechlorination with Hydrogen Peroxide

### Introduction

Chlorine residuals are frequently present in industrial and municipal wastewaters. The growing concern that the presence of chlorine residuals are harmful to the ecology of receiving waters has resulted in their widespread regulation. Low concentrations are toxic to fish (Reference 1) and if discharged to a biological treatment system, desirable microorganisms may be adversely affected. In addition, free chlorine can react with organics present in the receiving waters leading to harmful chlorinated organic residuals such as halomethanes.

Hydrogen peroxide has found increasing use as an effective dechlorination agent for free chlorine (HOCl and  $\text{OCl}^-$ ). Unlike sulfur dioxide and its derivatives, which add sulfate and can create an oxygen deficiency in the receiving water, hydrogen peroxide adds only oxygen and water. This occurs during the dechlorination reaction and when excess hydrogen peroxide breaks down. Oxygen release results in environmental benefits to the receiving waters.

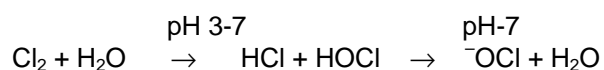
In contrast, sulfur dioxide and its bisulfite, metabisulfite and sulfite derivatives, used as dechlorination agents have inherent handling and environmental disadvantages. Sulfur dioxide is an irritating, toxic, liquidified gas requiring special handling equipment. The solid derivatives must be dissolved before use. Overdosing with sulfur dioxide or its derivatives is often required to meet residual chlorine standards, resulting in adverse effects on aquatic life and high oxygen demands in the receiving streams. In addition, a noticeable lowering of pH may occur. In cases where sulfur dioxide or its derivatives continue to be used, hydrogen peroxide addition will oxidize these species to sulfate and restore the dissolved oxygen balance.

Comparing chemical costs to treat one pound of chlorine, hydrogen peroxide has a \$0.073/lb advantage over dry sodium bisulfite. A bulk price of \$0.69 was used for  $\text{H}_2\text{O}_2$  (100% basis) and \$0.285 for dry sodium bisulfite. The destroy one pound of chlorine, 1.47 pounds of sodium bisulfite (100% basis) is needed compared to only 0.5 lb  $\text{H}_2\text{O}_2$  (100% basis).

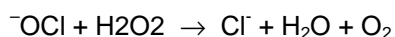
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## Chemistry

When elemental chlorine is dissolved in water, an equilibrium is established between  $\text{Cl}_2$ , HOCl and  $\text{OCl}^-$ . Chlorine predominates below pH 3, HOCl at pH 3-7 and  $\text{OCl}^-$  above pH 7.



Hydrogen peroxide reacts rapidly with free available chlorine at pH 7 and above.



The reaction still occurs below a pH 7 but at significantly slower rates. The equilibrium constant is expressed by

$$K = \frac{[\text{H}^+][\text{Cl}^-][\text{HOCl}]}{[\text{Cl}_2]}$$

The reaction is rapid at alkaline pH and the dechlorination rate is directly proportional to the concentrations of free chlorine and hydrogen peroxide e.g., at a starting pH 7 and 2 mg/L free chlorine, the reaction is over within 3 minutes using 5% excess hydrogen peroxide. The final pH was 6.7.

## Test Procedures

This simple test demonstrates the rapid destruction of free available chlorine by hydrogen peroxide. Determine the free available chlorine concentration in a liter of test wastewater. Adjust the pH to 7 or above and add one ml of a 0.1 wt%  $\text{H}_2\text{O}_2$  solution. This quantity may be approximated by adding one or two drops of a 3 wt%  $\text{H}_2\text{O}_2$  solution. The free chlorine should disappear within a few minutes as evidenced by the ortho-tolidine method. Unlike other chlorine test methods such as the Palin DPD method, the presence of excess hydrogen peroxide does not interfere with the ortho-tolidine method.

To determine the presence of free hydrogen peroxide without interference from chlorine, titanium sulfate reagent prepared from titanium sulfate and sulfuric acid can be used. (Titanium sulfate is available from GFS Chemical, PO Box 23214, Columbus, OH). This reagent reacts with  $\text{H}_2\text{O}_2$  to produce a yellow to red color with increasing  $\text{H}_2\text{O}_2$  concentration. The calibration with known concentrations of  $\text{H}_2\text{O}_2$  is determined at 400 nm using a spectrophotometer.

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## Applications

### Chlorine-Caustic Plants

Hydrogen peroxide is used to destroy free available chlorine in chlorine-caustic plants. At one plant using a membrane technology, hydrogen peroxide has replaced sodium bisulfite to:

- eliminate sulfate build-up
- obtain better control of dechlorination
- reduce acidity

At a second chlorine-caustic plant (diaphragm type), hydrogen peroxide has been used for dechlorination prior to the effluent waters entering the ocean. Tests showed 100% fish survival after 96 hours in the peroxide treated effluent. In a separate study, up to 40 mg/L hydrogen peroxide had no adverse effect on fingerling rainbow trout (Reference 2). In fact, hydrogen peroxide at low levels has produced weight gains of salmon in salmon rearing ponds (Reference 3).

### Chlorinated Cyanuric

At a chlorinated cyanuric acid plant, hydrogen peroxide has been used to destroy available chlorine permitting recovery of cyanuric acid from waste streams.

### Other Applications

Power plants using chlorine for once through cooling systems.

Municipal waste water effluents with high ratios of free to combined chlorine.

Abatement of exhaust Cl<sub>2</sub> gas by use of H<sub>2</sub>O<sub>2</sub> scrubbing.

Destroy sulfur dioxide or sulfate residuals after dechlorination when those sulfur compounds are used for dechlorination.

### References

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2. Eden, Freske and Melbourne, Chem & Ind 1105, December 15, 1951.
3. Sawyer, E.S., Sawyer, P.J., "A Solar Heated Fish Hatchery Recycling System Contract Number 14-34-0001-8811, July 1980 U.S. Department of the Interior Office of Water Research and Technology, Washington, D.C.

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