Dechlorination with INTEROX® Hydrogen Peroxide

Industries and municipalities historically looked to chlorine to disinfect drinking water and wastewater effluents. However, while chlorine effectively kills microorganisms and oxidizes a number of industrial wastes, further treatment may be required prior to discharge.

Environmental authorities now require dechlorination of waste streams previously considered acceptable, and upper limits for chlorine content may be in the parts-per-billion (ppb) range.

INTEROX® Hydrogen Peroxide offers many benefits as a dechlorinating agent. Under the right conditions, the reaction occurs instantaneously and removes chlorine concentrations that range from parts-per-billion up to 1% and more. Unlike dechlorination methods based on sulfur dioxide or its salts, hydrogen peroxide leaves behind no additional salts to further contaminate the effluent.

Dechlorination alternatives

Two basic approaches apply to dechlorination, one approach based on sulfur dioxide, the other on hydrogen peroxide.

Sulfur dioxide. This approach includes the use of sulfur dioxide (SO₂) gas or its salts which include sodium thiosulfate (Na₂S₂O₃), sodium bisulfite (NaHSO₃), and sodium sulfite (Na₂SO₃). Any of these will reduce all forms of active chlorine (chlorine gas, hypochlorites and the chloramines) to chloride. The method works but has several drawbacks.

- Sulfur dioxide presents some of the same problems that chlorine gas presents. Requirements for special storage and handling equipment make initial capital costs very high.
- The sulfur dioxide salts are solids that must be dissolved before use. The solutions may freeze in cold weather, and some are corrosive or require a high use ratio.
- An excess of some form of sulfur dioxide must be present to destroy all the chlorine. This excess sulfur dioxide not only creates an oxygen demand, but it also threatens various forms of aquatic life.

- Sulfur in any form adds sulfate ion, nontoxic but still undesirable. Some manufacturing facilities cannot tolerate sulfate as a contaminant. In addition, some plants must dechlorinate waste streams for recycling back into the production process. Sulfate ions may make recycling impossible.

A comparison of these technologies is shown in Table One (see page 2).

INTEROX Hydrogen Peroxide. INTEROX Hydrogen Peroxide offers a far superior method of removing chlorine in alkaline effluents where no ammonia is present.

The INTEROX Hydrogen Peroxide advantage

INTEROX Hydrogen Peroxide offers the ideal solution for many industrial dechlorination applications. When the pH is above 8.5 and no ammonia is present, hydrogen peroxide reduces hypochlorite to chloride ions, producing oxygen as a byproduct. Advantages of the system include:

- Safe and stable. Hydrogen peroxide is a ready-to-use, easily transportable liquid that produces no toxic fumes. It requires minimum capital investment. Handled properly, the concentrated commercial product is quite stable, with decomposition at less than 1% per year.
- Nontoxic. Residual peroxide degrades to water and oxygen, which is beneficial (rather than toxic) to receiving waters.
• **Effective over a wide range of concentrations.** Hydrogen peroxide reacts with hypochlorite instantaneously in stoichiometric ratios over concentrations that range from ppb to percentages. Slightly less than one pound of hydrogen peroxide will destroy two pounds of chlorine as hypochlorite ions.

• **No salts produced.** Hydrogen peroxide does not contaminate treated water with sulfate salts. This makes it possible for plants to dechlorinate and recycle side streams instead of creating waste disposal problems. It also means that products ready for market can be dechlorinated without contamination.

• **Minimum reaction heat generated.** The reaction between chlorine and hydrogen peroxide releases 37 kcal per mole, compared to the sulfur dioxide reaction which liberates 119 kcal per mole.

### Table One: A comparison of dechlorination technologies

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>Advantage</th>
<th>Disadvantage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium Thiosulfate</td>
<td>Easy to use.</td>
<td>Subject to freezing.</td>
</tr>
<tr>
<td>Sodium Bisulfite</td>
<td>Easy to use.</td>
<td>May be corrosive.</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>Easy to use.</td>
<td>Inefficient usage ratio.</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>Inexpensive for larger uses.</td>
<td>Corrosive. High capital cost.</td>
</tr>
</tbody>
</table>

### Table Two: A comparison of dechlorination chemistry

<table>
<thead>
<tr>
<th>Reducing Agent</th>
<th>Reaction</th>
<th>Ratio w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen Peroxide</td>
<td>(H_2O_2 + Cl_2 \rightarrow 2HCl + O_2)†</td>
<td>0.488</td>
</tr>
<tr>
<td>Sulfur Dioxide</td>
<td>(SO_2 + Cl_2 + 2H_2O \rightarrow H_2SO_4 + 2HCl)</td>
<td>0.903</td>
</tr>
<tr>
<td>Sodium Thiosulfate</td>
<td>(Na_2S_2O_3 + 4Cl_2 + 5H_2O \rightarrow 2NaHSO_4 + 8HCl)</td>
<td>0.556</td>
</tr>
<tr>
<td>Sodium Bisulfite</td>
<td>(NaHSO_3 + Cl_2 + H_2O \rightarrow NaHSO_4 + 2HCl)</td>
<td>1.465</td>
</tr>
<tr>
<td>Sodium Sulfite</td>
<td>(Na_2SO_3 + Cl_2 + 8H_2O \rightarrow Na_2SO_4 + 2HCl)</td>
<td>1.775</td>
</tr>
</tbody>
</table>

The ratios given are theoretical. Observed ratios are often higher, depending on the stream to be treated. Past experience with peroxide has shown that usage is quite close to theoretical.

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The speciation graph in Figure One is important because while peroxide reacts instantaneously with hypochlorite (\(OCl^-\)), it reacts very slowly with the other two species, hypochlorous acid (\(HOCI\)) and chlorine gas (\(Cl_2\)). For the most effective use of hydrogen peroxide, the pH should be above 8.5 so that the majority of chlorine exists as hypochlorite. There is no upper limit to alkalinity.

Hydrogen peroxide reacts with hypochlorite as follows:

\[ OCl^- + H_2O_2 \rightarrow Cl^- + H_2O + O_2 \]

Effective dechlorination also requires the absence of ammonia. Chlorine reacts quickly with ammonia to form monochloramine (\(NH_2Cl\)), dichloramine (\(NHCl_2\)), and trichloramine (\(NCI_3\)), which are not degraded by hydrogen peroxide. Since one part of ammonia can react with eight to ten parts of chlorine, even small amounts of ammonia will result in significant amounts of chlorine remaining after the peroxide reaction. This explains why hydrogen peroxide is not always practical for dechlorination of municipal wastes.

The reaction between hydrogen peroxide and hypochlorite takes place so rapidly that other organic or inorganic compounds, including peroxide decomposition catalysts like iron, have no negative effect. Although oxygen is produced, bubbles will not generally form at low chlorine concentrations because water dissolves almost 10 ppm of oxygen at room temperature. Oxygen may effervesce in more concentrated solutions, where venting space must be provided.

A comparison of dechlorination chemistry is given in Table Two.

Hydrogen peroxide eliminates chlorine by reacting with hypochlorite instantaneously and quantitatively at any pH above 8.5. Any active chlorine that can be converted into hypochlorite can be treated. At the end of the treatment, chlorine levels will be below detection limits.

The reaction produces only chloride ions, water, and oxygen, so the treated solution remains free of other contamination. The treated solution is ready to be sold, recycled back to the process stream, or discharged as chlorine-free wastewater.

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The chemistry of hydrogen peroxide and chlorine

Chlorine gas in water rapidly hydrolyzes to hypochlorous acid (\(HOCI\)), which in turn ionizes to the hypochlorite ion (\(OCl^-\)):

\[ \text{Cl}_2 + H_2O \rightleftharpoons HOCI + H^+ + Cl^- \]

\[ HOCI \rightleftharpoons H^+ + OCl^- \]

The amount of each ion present depends upon the pH, as shown by Figure One (see page 3).
**Typical application:**
**Dechlorination from a scrubber effluent**

An organic chemical manufacturer was issued a new NPDES permit that would force it to reduce residual chlorine levels from 15,000 mg/L to less than 1 mg/L. The manufacturer evaluated several different dechlorination methods, including bisulfite, sulfur dioxide and hydrogen peroxide.

Solvay Chemicals conducted a feasibility study to assist in the evaluation of hydrogen peroxide. Hydrogen peroxide was evaluated at ambient temperature as well as at the actual wastewater temperature of 57°C. No pH adjustment was necessary since the waste stream was naturally alkaline. After 5 minutes, residual chlorine and hydrogen peroxide were measured. More than 98% of the residual chlorine was removed using a dose equivalent to 0.5 lbs. of H₂O₂ per pound of OCI⁻. A 0.75:1 H₂O₂:OCI⁻ dose removed all traces of residual chlorine. Similar results occurred at both reaction temperatures. A field trial was conducted which further verified the cost-effective method for treating their wastewater.

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**Safety**

When properly handled, hydrogen peroxide and peroxygen compounds are safe, easy-to-use chemicals. However, as with the most powerful chemicals, improper application or handling could create hazardous conditions or cause injuries to personnel. We strongly recommend you contact Solvay Chemicals before experimenting with, designing, installing or modifying an application system, or otherwise using these chemicals.

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**Delivery**

Solvay Chemicals ships product from two North American plant sites and a number of strategically located distribution terminals. We operate a fleet of high-purity aluminum and stainless steel railcars, as well as stainless steel tank trucks dedicated to hydrogen peroxide transport.

We also can provide stainless steel ISO containers to deliver, store and dose liquid hydrogen peroxide. These “isotainers” are ideal for environmental applications at remote sites, and especially suitable for seasonal or short-term needs. In emergency situations, we can use our Quick Response program to get isotainers of hydrogen peroxide to your site right away. For the information you need, call 1-800-SOLVAY-C (1-800-765-8292).

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**Quality**

Solvay Chemicals strives to bring you the best in peroxygen products, service and technology. Exceeding, not just meeting, your expectations is the basis for our pursuit of continual improvement.

To demonstrate our commitment, Solvay Chemicals’ Quality Management System is registered to the ISO 9001:2000 International Quality Management System Standard. Our registration encompasses the production and distribution of hydrogen peroxide at both of our manufacturing facilities in Deer Park, Texas and Longview, Washington, as well as administrative activities at our Houston headquarters.

Solvay Chemicals will continue to pursue excellence in everything we do. We dedicate ourselves to this effort because we know that our success depends on satisfying you.
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