## Wastewater Dechlorination – A Survey of Alternatives

PAULA A. RILEY Industrial Waste Officer, Marshall. Texas

HLORINE has been used for many years to treat both municipal and industrial wastewaters. The main reason for using chlorine is to destroy pathogenic organisms, bacteria, and viruses, thereby preventing the spread of disease by water borne agents. However, there is increasing concern that the levels of residual chlorine in wastewaters being discharged to streams, rivers, lakes, or bays may be having an adverse effect on the biological integrity of the receiving waters. To compound the problem, some organic chemicals often present in wastewaters may be converted to other toxic materials by chlorination. A number of studies have been made relating the residual chlorine in treatment plant effluent to a drop in aquatic population and diversity in the receiving water.

The threat to human health and welfare posed by surface water pollution is multifaceted. There are direct effects, which may result from the consumption of contaminated water supplies and food. There are indirect effects, which may result from the impact of pollutants on the quantity and quality of aquatic organisms used for human food, the recreational use of water, the esthetic quality of the environment, and the integrity of the biosphere. These effects can include

death, disease, behavior abnormalities, physiological malfunctions, physical deformities and birth defects, mutations, and cancer. Toxicity, therefore, is defined in terms of the adverse effects on all types of organisms.

The determination of the effects of pollution on aquatic life is done through a biological monitoring process that measures the integrity of the ecosystem. In the biomonitoring test, one or more species of minnows and/or water fleas are introduced into an observation area containing a sample of the effluent diluted to the appropriate concentration found in the receiving stream water. This sample is monitored simultaneously with a control group of organisms over a given amount of time. Significant differences in the life cycles of the two groups are calculated to determine if the discharge has any lethal or sublethal effects.

The EPA has proposed to require all facilities with Federal NPDES Permits, and some with state permits, to conduct biomonitoring tests to determine if the effluent discharge is toxic and/or sublethal to living organisms in the receiving waters. If the discharge is found to be toxic, follow-up testing will be required to determine what pollutant is causing the toxicity.

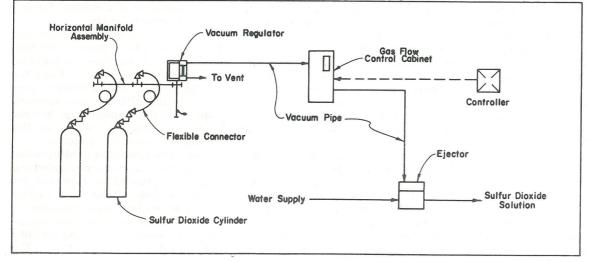
If follow-up testing shows chlorine to be toxic in the receiving stream (and research studies have shown that it probably will be), the facility must take action to eliminate it. This article discusses two primary methods currently being studied to accomplish this: 1) dechlorinating chemicals and techniques and 2) alternate disinfection methods.

It is generally believed that dechlorination is beneficial, especially since it reduces acute toxicity and on occasion, mutagenicity. However, some questions still remain about the environmental effects of the general use of dechlorination chemicals.

Very little research has been done on the kinetics of halocarbon production from wastewater chlorination. Thus, it is not possible to determine how short the period between chlorination and dechlorination must be to significantly reduce halocarbon yields. One study suggests that this period must be substantially shorter than the 20 minutes often used at treatment plants. However, wastewater treatment operators, who need a contact time long enough to meet disinfection objectives, may not have the flexibility to control these halocarbon yields prior to dechlorination.

Because of differences in stoichiometry, not all dechlorinating agents react in the same ratio with chlorine. Table 1 gives some of the approximate cost ratio data on some commonly used dechlorinating agents. Treatment costs are determined by multiplying the use ratio

## COMPONENTS of a sulfer dioxide system for wastewater dechlorination. Reprinted courtesy Capitol Controls.



times the cost per pound of dechlorinating agent. The result is the relative dechlorination cost per pound of chlorine taken out of the system.

The dechlorinating chemicals most currently in use today include sodium thiosulfate and, from the sulfur (IV) series, sulfur dioxide.

Sodium thiosulfate is non-toxic and does not present any difficult handling problems. It has a favorable use factor in determining the treatment cost per pound of product, and thus the relative dechlorination cost per pound of chlorine is low in comparison with other dechlorinating agents. However, studies have suggested the presence of toxic material other than chlorine in wastewater dechlorinated with sodium thiosulfate. It is not known if these effects were created by the dechlorinating agent directly, by subsequent reactions of the dechlorinating agent, or by chlorine by-products generated before the dechlorinating agent was added.

Sulfur dioxide is a colorless gas with a very pungent odor. Of the sulfur (IV) compounds, sulfur dioxide gas is generally preferred as a dechlorinating agent because it can be applied with the same type of equipment and techniques that are used to apply chlorine. Some disadvantages of sulfur dioxide include its extreme corrosiveness, its ability to irritate the eves and mucous membranes, and its freezing action upon contact with skin. Although overdosing is frequently necessary to meet residual chlorine discharge standards, sulfur dioxide appears to leave less residual toxicity than some of the other dechlorinating methods.

The dechlorinating agents with more limited applications include the rest of the sulfur (IV) series — ammonium bisulfite, ammonium thiosulfate — and hydrogen peroxide. Several other methods being explored include the use of activated carbon, aeration techniques, ion exchange, and storage ponds. In addition, research is currently underway to develop other dechlorination techniques that are more efficient and less costly.

In conducting bioassays to determine the effects of dechlorination on certain aquatic organisms, studies indicate that the halogenated compounds formed during chlorination cause repressed sexual activity and slowed growth rates in some organisms. This leads to the conclusion that dechlorinating prior to discharge does not necessarily make an effluent nontoxic. Many unalterable and still unknown reactions occur, and un-

known compounds are formed. As a result, many treatment professionals are exploring alternate disinfection methods. The most common of these include chlorine dioxide, UV light, ozone, and combinations of these.

Ozone is a strong oxidizing agent that is invariably generated where needed by an electrical discharge in dry air or oxygen. Dissolved ozone is an excellent disinfectant with an effective dosage less than that required by chlorine. Ozone does not react with hydrocarbons to form carcinogens. It effects a faster and more complete bacterial kill and viral inactivation than is possible with chlorine. The ozonated effluent is less toxic than chlorinated effluent largely as a result of its more rapid dissipation in wastewater. The major drawbacks in the use of ozone include its initial cost.

disinfection by UV are relatively high compared with chlorination, but these costs might be reduced significantly in a facility operating at its design rate with gravity flow. In smaller plants, UV is generally the more cost-effective in comparison with ozone.

Ozone/Ultraviolet light systems used in combination have been proposed to reduce disinfection costs. Studies have indicated that in plants with flows greater than 10 mgd, the costs of ozone/UV in sequence become less than those of ozone or UV alone.

**Hydrogen Peroxide/Ozone** is another innovative hybrid being developed. This holds promise for solving microbiological and complex organics problems at half the cost of ozone alone. However, the economics

Table 1 — Use Ratios

(Parts Dechlorinating Agent per Part Chlorine Residual)

Dechlorinating Agent	Formula	Use Ratio
Sodium Thiosulfate	Na <sub>2</sub> S <sub>2</sub> O <sub>3</sub>	0.556
Sulfur Dioxide	SO <sub>2</sub>	0.903
Sodium Metabisulfite	Na <sub>2</sub> S <sub>2</sub> O <sub>5</sub>	. 1.338
Sodium Bisulfite	NaHSO <sub>3</sub>	1.465
Sodium Sulfite	Na <sub>2</sub> SO <sub>3</sub>	1.775
Hydrogen Peroxide	H <sub>2</sub> O <sub>2</sub>	0.488

the cost of generator maintenance, and the cost of electricity in running it.

Chlorine dioxide has chemical reactions that resemble ozone more than chlorine, and it is not a halogenating agent in most cases. The germicidal action of chlorine dioxide is less potent than that of chlorine, but since it exerts its bactericidal effect by becoming concentrated by adsorption on the cell wall, it is more effective than chlorine against bacterial spores. In a comparison of chlorine vs. chlorine dioxide, studies have been developed into a disinfection model that can serve as a guideline in designing disinfection facilities using chlorine dioxide.

Ultraviolet light disinfection is more effective in clear water because absorption by suspended matter or dissolved organics can severely limit the effective disinfection range. Therefore, a good UV disinfection system needs a detector that will monitor the intensity of the radiation after it has passed through the water. UV disinfection is recognized as a viable alternative to chlorination because there is little evidence that UV disinfection produces potentially hazardous by-products and improved technology has made the process increasingly reliable. The unit costs of of the process are highly dependent on water quality. Pilot-scale evaluations of the water to be treated are recommended to estimate the true cost.

Comparisons of the toxicity of chlorinated vs. dechlorinated waters uniformly show that dechlorination reduces acute toxicity to aquatic organisms. However, sublethal biological effects were noted in dechlorinated waters, and sometimes in waters treated only with dechlorinating agents. This makes pilot plant studies including biomonitoring tests critical in the selection of a method for any given treatment facility.

As a rule, alternate disinfection methods tend to be more costly than dechlorination, but they also leave little or no residual toxicity. Since the biomonitoring requirements proposed by the EPA are also extremely expensive, these options may become more economically feasible as this regulation comes into practice.

The chlorination/dechlorination issue appears to be a complicated and expensive proposition. However, the threat to human health and welfare posed by surface water pollution is one that must be addressed aggressively to assure a safe and plentiful water supply for us all.