



Wastewater Technology Fact Sheet Dechlorination

DESCRIPTION

Dechlorination is the process of removing residual chlorine from disinfected wastewater prior to discharge into the environment. Sulfur dioxide is most commonly used for dechlorination and is the major focus of this fact sheet. Some dechlorination alternatives include carbon adsorption, sodium metabisulfite, sodium bisulfite, and hydrogen peroxide. Sodium metabisulfite and sodium bisulfite are mainly used in small facilities because these materials are more difficult to control compared to sulfur dioxide. Hydrogen peroxide is not frequently used because it is dangerous to handle (WEF, 1996).

APPLICABILITY

Chlorination has been used widely to disinfect wastewater prior to discharge since passage of the 1972 Federal Water Pollution Control Act (WPCA), (Finger et al., 1985). In the first years following the WPCA, disinfected wastewater with significant levels of residual chlorine was routinely discharged into the receiving waters. It became clear, however, that residual chlorine is toxic to many kinds of aquatic life (see, for example, Mattice and Zittel, 1976, and Brungs, 1973). Moreover, the reaction of chlorine with organic materials in the water formed carcinogenic trihalomethanes and organochlorines (WEF and ASCE, 1991). As a result, dechlorination was instituted to remove residual chlorine from wastewater prior to discharge into sensitive aquatic waters.

Dechlorination minimizes the effect of potentially toxic disinfection byproducts by removing the free

or total combined chlorine residual remaining after chlorination. Typically, dechlorination is accomplished by adding sulfur dioxide or sulfite salts (i.e., sodium sulfite, sodium bisulfite, or sodium metabisulfite). Carbon adsorption is also an effective dechlorination method, but is expensive compared to other methods. Carbon adsorption is usually implemented when total dechlorination is desired.

Specific design criteria and monitoring requirements for a particular region are determined by the state regulatory agency. Typically, the treatment plant's National Pollutant Discharge Elimination System (NPDES) permit limits effluent chlorine residual and toxicity. Currently, many permits require very low or "non-detect" chlorine residuals, making dechlorination critical.

One important alternative to dechlorination is to achieve disinfection without the use of chlorine. Other means of disinfection, such as ozone or ultraviolet disinfection, have also become increasingly prevalent (U.S. EPA, 1986; Blatchley, E.R. III, *et al.*, 1996).

ADVANTAGES AND DISADVANTAGES

Advantages

- Protects aquatic life from toxic effects of residual chlorine.
- Prevents formation of harmful chlorinated compounds in drinking water through reaction of residual chlorine with water-born organic materials.

Disadvantages

- Chemical dechlorination can be difficult to control when near zero levels of residual chlorine are required.
- Significant overdosing of sulfite can lead to sulfate formation, suppressed dissolved oxygen content, and lower pH of the finished effluent.

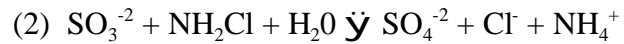
DESIGN CRITERIA

Chemistry of Dechlorination by Sulfonation

Sulfur dioxide (SO_2) is a corrosive, nonflammable gas with a characteristic pungent odor. At atmospheric temperature and pressure, it is a colorless vapor. When compressed and cooled, it forms a colorless liquid. Sulfur dioxide is supplied as liquefied gas under pressure in 100 or 150 pound containers and one-ton cylinders. As an alternative to sulfur dioxide gas, various dry chemicals are available which form sulfur dioxide in solution. These include sodium sulfite (Na_2SO_3), sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$), sodium bisulfite (NaHSO_3), a 38 percent aqueous solution of sodium metabisulfite, and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), among others (Lind, 1995).

When dissolved in water, chlorine hydrolyzes to form hypochlorous acid (HOCl) and hypochlorite ions (OCl⁻) which, taken together, are referred to as "free chlorine." (Free, uncombined chlorine, Cl_2 , is rarely found in wastewater since the conditions of formation are relatively extreme [Lind, 1995]). Once formed, the free chlorine reacts with natural organic matter in water and wastewater to form chlorinated organic compounds. The free chlorine also combines with ammonia to form mono-, di-, and trichloramines in quantities dependent on the ratio of chlorine to ammonia nitrogen (Lind, 1995).

When either sulfur dioxide or sulfite salts are dissolved in water, aqueous sulfur compounds in the +4 oxidation state are produced, often notated S(IV) (Helz and Nweke, 1995). The S(IV) species, such as the sulfite ion (SO_3^{2-}), reacts with both free and combined forms of chlorine, as illustrated in equations (1) and (2) (WEF, 1996):



Since free chlorine and inorganic chloramines react rapidly with S(IV) (Helz, 1998), a short contact time of one to five minutes is considered to be sufficient; nevertheless, complete blending at the point of application is essential for effective dechlorination (WEF and ASCE, 1992).

Proper dosage is critical to produce a non-detectable chlorine residual. On a mass basis, 0.9 parts sulfur dioxide (or 1.46 parts NaHSO_3 or 1.34 parts $\text{Na}_2\text{S}_2\text{O}_5$) is required to dechlorinate 1.0 part residual chlorine. In practice, approximately a one-to-one ratio is used (WEF, 1996). Dosing in excess must be avoided because excess sulfite can react with dissolved oxygen (four parts sulfite to one part oxygen) in the wastewater to produce sulfates, potentially leading to reduced dissolved oxygen concentrations and low pH levels in the finished effluent for high levels of overdose (WEF, 1996). Careful process control will help prevent overdosing.

Equipment for gaseous sulfonation

Equipment required for gaseous sulfonation using SO_2 is similar in design to that used for chlorination, except that the materials are chosen for their application-specific chemical resistance (WEF, 1996). The four basic components of the system include: sufficient gas supply with automatic switch-over between cylinders; a metering system, usually consisting of a vacuum regulator and a rotameter for feed rate control; one or more injectors with check valves; and a residual analyzer to measure and transmit a continuous signal proportional to the chlorine residual in the sample stream.

In small concentrations, exposure to SO_2 can cause eye and throat irritation. In high concentrations, exposure can produce a suffocating effect caused by irritation to the upper respiratory tract. Therefore, facility design should include features for safe storage, handling, and use of sulfur dioxide. The chlorine and sulfur dioxide cylinders should be located in separate rooms and stored in a well-

ventilated, temperature-controlled area so that their temperature never drops below 18 or exceeds 70 degrees Celsius. Gas leak detectors are necessary in the storage area and the sulfonator area. An emergency eyewash shower and self-contained breathing apparatus should also be provided. All personnel should receive emergency response training. Facilities with more than 1,000 pounds of SO₂ stored on-site must abide by the Process Management Safety Standard in the OSHA regulations (OSHA, 1998).

Effect of Temperature on Gas Withdrawal Rate

The room temperature where the gas supply is located should be maintained around 70 degrees F to ensure optimal gas withdrawal rates (WEF, 1996). At this temperature, the maximum safe sulfur dioxide gas withdrawal rate is approximately 2 lb/hr for a 150 lb container, or 25 lb/hr for a ton container. Higher temperatures are required to achieve higher continuous gas withdrawal rates. Strip heaters or liquid baths may be used for this purpose.

Injector Selection

Proper selection of the injector is critical for proper system operation. The injector produces a vacuum that draws sulfur dioxide gas through the sulfonator. It then mixes the gas with dilution water supply and injects the solution into the wastewater. To properly size the injector, the back pressure on the injector at the point of application and the water supply pressure required at the injector must be determined. The injector can either be installed in a pipe or an open channel. As an alternative to the typical vacuum regulator with injector system, a chemical induction system may be used to introduce the sulfur dioxide directly as a gas.

Control

At present, few options exist for reliable long-term measurement of sulfite salts or close-to-zero levels of residual chlorine in the finished effluent (ASCE and WEF, 1991). In recent practice, the only viable method for continuous residual chlorine measurement has been the amperometric technique,

but this suffers from loss of accurate calibration at low concentrations (Finger et al., 1985). Though some sources claim to have developed process control methods employing oxidation reduction potential (ORP) as an effective stand-in for direct chlorine measurement (Bossard et al., 1995), other sources assert that ORP is an inappropriate technique for this purpose (WEF, 1996). For these reasons, control of dechlorination—particularly dechlorination to zero residual—has been problematic. Treatment plant operators have had to work around this limitation using various control strategies.

One commonly used strategy is the use of a “zero-shifted” or “biased” analyzer (WEF, 1996; Nagel, 1994). In this scheme, a residual chlorine analyzer is used and a known concentration, X, of chlorine is added to the effluent sample to be analyzed. In this technique, the “zero” point is shifted by the value of X, and residual chlorine or sulfur dioxide can be inferred from the result of sample analysis.

Two types of control systems are often used for dechlorination (WEF, 1996). A “feed-back” control system can be used at treatment plants that are not required to dechlorinate their effluents to zero levels. With feed-back control, an analyzer measures the chlorine residual at a point downstream of the sulfur dioxide addition. This signal, along with flow rate data, is relayed back to the sulfonator and the dosage is automatically adjusted accordingly. Though there is a lag time between the injection point and the sample point, the lag is deemed to be minimal since the dechlorination reaction occurs almost instantaneously.

For treatment plants that must discharge a zero concentration or undetectable residual chlorine but are not equipped with biased or direct reading analyzers, feed-back control is typically not feasible (WEF, 1996). Therefore, such dechlorination systems often use a “feed-forward” control that measures the chlorine residual after disinfection but *prior to* the addition of sulfur dioxide. A mass flow signal is sent to the sulfonator from the in-line analyzer and the sulfur dioxide delivery rate is automatically calculated and adjusted to the ratio required for proper dechlorination of the effluent.

Instrumentation combining feed forward control with biased analysis may provide an effective method to dechlorinate the effluent to low-level residuals. Another useful design feature involves using an automated chlorine flush of the sample line (with sulfonator response temporarily locked). This procedure prevents the buildup of slime and algae in the sample line, thus eliminating chlorine demand in the line which can suppress residual chlorine analyzer results (Nagel, 1994).

Sample Calculation

Given: Peak flow = 20 mgd. Measured chlorine residual is approximately 1.5 mg/L.

Calculate: Maximum dosage of sulfur dioxide needed per day. Assume a 1:1 ratio of SO₂ to Cl₂.

Capacity = (flow rate) x (Cl₂ residual) x (dosage ratio) = (20 mgd) x (1.5 mg/L Cl₂) x (8.34 lb/Mgal.mg/L)x(1 mg/L SO₂ per mg/L Cl₂) = 250 lb SO₂ per day maximum.

Using Sulfite Salts

Upon dissolution, sulfite salts produce the same sulfite ion as sulfur dioxide gas (WEF, 1996). While the gas has the highest dechlorinating efficiency per net pound of the product added, many smaller facilities choose to use one of the sulfite salts because of the storage, handling, feeding, and safety problems associated with using gaseous sulfur dioxide on a large scale. Of all the sulfite salts available, sodium metabisulfite has the lowest addition rate required for dechlorination (Lind, 1995).

PERFORMANCE

Sulfonation has been widely considered effective for removal of chlorine compounds in disinfected wastewater and reduction of toxicity for aquatic life. Nevertheless, two studies have suggested that disinfected/sulfonated wastewater poses a hazard to some sensitive aquatic species (Hall *et al.*, 1982;

Rein *et al.*, 1992). Furthermore, one estimation of chlorine removal efficiency is from 87 to 98 percent (Helz and Nweke, 1995), leaving the actual residual chlorine following sulfonation above most regulatory limits.

Chloramines tend to be longer lived and less reactive than other chlorinated species in wastewater (Lind, 1995). While hydrophilic organic chloramines have been thought of as generally nontoxic, Helz and Nweke have found that the S(IV) fraction resistant to dechlorination may be composed of hydrophobic secondary amines and peptides, including chloramines, suggesting possible toxicity for aquatic organisms in receiving streams. The authors note that this fraction of S(IV)-resistant chlorine has been overlooked because the dechlorinating agent interferes with standard analytical methods for total chlorine (Helz and Nweke, 1995). Continued testing is underway to further characterize the dechlorination-resistant fraction and its effects on aquatic organisms (Helz, 1998).

OPERATION AND MAINTENANCE

Components of the pressure manifold—especially flexible connectors, valves, and the injector and solution system—are the most likely to need repair (WEF, 1996). In view of this, these components should be inspected at least every six months. Additionally, diaphragms and injector gaskets should be replaced every two years. The gasket should be replaced each time the joint is broken in a gasketed pressure connection. Asbestos fiber gaskets are not recommended because they often do not seal properly. Used gaskets should *never* be re-used. Springs should be replaced according to the manufacturer's instructions.

Spare parts—especially parts for the pressure manifold—and standby equipment, should be kept on hand to prevent significant down time in the event of equipment problems. Because sulfonators are configured with the same components as chlorinators, some plant engineers tend to treat sulfonators as standby chlorinators (WEF, 1996), but this practice should be avoided. Chlorinators and sulfonators are composed of different polymeric materials (sulfonators typically of PVC and

chlorinators of ABS plastic), each chosen for application-specific chemical resistance. Use of non-chemical resistant materials with chlorine or sulfur dioxide gases can lead to equipment failure. Moreover, equipment misuse leading to accidental mixing of chlorine and sulfur dioxide gases can lead to an exothermic chemical reaction and equipment failure.

Water can be used to clean most component surfaces. For buildup of impurities or for stains, a dilute hydrochloric (muriatic) acid solution may be necessary (WEF, 1996). Following cleaning, the components must be thoroughly dried before they are reassembled. Drying is best done using compressed dry air or nitrogen.

COSTS

Costs for a dechlorination system vary widely depending on particular site conditions. Detailed estimates are not included here because they may be misleading. One of the largest overall cost variables is whether an existing facility is being upgraded to accommodate dechlorination or whether the chlorination/ dechlorination system is a component of new plant construction. Site-specific construction costs can vary by hundreds of thousands of dollars, depending on the type of project.

Table 1 gives a cost example of a 2,800 ppd gas sulfur dioxide system installed in 1994 in Florida. Cost considerations must also include the cost of equipment, installation, labor, and operation and maintenance. The type of dechlorination agent to be used will affect both the equipment and chemical costs. For large plants, sulfur dioxide gas is typically the agent of choice because of its dechlorinating efficiency on a per pound basis. However, as previously mentioned, many smaller plants may find that storage, handling, and safety issues offset whatever gains in efficiency can be obtained by using compressed gas.

Effective process control will help prevent chemical overdosing and allow for chemical cost savings. One 40-mgd facility has reported a savings of \$7,000 per month—a greater than 1,000 pound per day reduction in SO₂ use (>50%) and a greater than

TABLE 1 COST OF A 2,800 PPD GAS SULFUR DIOXIDE SYSTEM IN 1994

Component	Cost (\$)
Sulfonator and ancillary mechanical equipment	100,000
Gas Scrubber	150,000
Ventilation System	45,000
Miscellaneous piping and valves	30,000
Building & Architectural items	250,000
Electrical	75,000
Instrumentation	30,000
<i>Subtotal</i>	<i>680,000</i>
Contractor Overhead (@6.5%)	44,200
Total (In 1993 dollars)	724,200

Source: Parsons Engineering Science, Inc., 2000.

one-third reduction in chlorine use—resulting from the purchase of a new automatic process control system (Bossard *et al.*, 1995). The savings represented a three month payback period on the new equipment.

REFERENCES

Other Fact Sheets

Chlorine Disinfection
EPA 832-X-99-062
September 1999

Other EPA Fact Sheets can be found at the following web address:
<http://www.epa.gov/owmitnet/mtbfact.htm>

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ADDITIONAL INFORMATION

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