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A Primer on Chlorine Gas Disinfection

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The disinfection of water using chlorine gas has been practiced in the United States for over a century. It is one of the most effective and reliable disinfection agent and although its use has decreased in recent years owing to safety concerns and regulatory constraints, it remains a widely used disinfection technique. This article summarizes the principal issues to be considered in the selection of chlorine gas disinfection.

What is it?

The element Chlorine was first isolated by Carl W. Scheele a Swedish chemist in 1774. The greenish tint of the gas caused Sir Humphry Davy in 1810 to name it chlorine from “chloros” meaning “pale green” in Greek. German physician Robert Koch in 1881 demonstrated that bacterial cultures were destroyed by hypochlorites, an aqueous form of chlorine, thereby proving the effectiveness of chlorine as a disinfectant.

Chlorine has an atomic number of 17 and a molecular weight of 71 . It is in the halogen group of elements. It exists as a gas at standard temperatures and pressures with a specific gravity of 2.486. It is heavier than air and will pool in low lying areas.

It is a strong oxidizer and personal protection is mandated for exposure to concentrations above 0.5 ppm.

Its CAS number is 7782-50-5.

Historical Practice in the Water Industry

Its first use as a disinfection agent dates from 1897 when the water supply of Maidstone, England was disinfected by the addition of a concentrated solution of chloride of lime. Chlorine gas for disinfection was first demonstrated in the United States in 1910, it was followed by the invention of the Chlorinator by Charles Wallace in 1913 at the Belmont filter plant in Philadelphia, Pennsylvania. The Chlorinator has been in production by Wallace & Tiernan since that time.

Why does it work so well?

As a strong oxidizing agent, chlorine reacts with a wide range of organic (alive or dead) and inorganic material. It is able to kill microorganisms by disintegrating the lipids that form the cell walls and react with enzymes and proteins found within the cell.

When dissolved in water, chlorine forms hypochlorous acid (HOCL), hypochlorite ion (OCL-) and elemental chlorine (Cl2). The distribution of these three chlorine compounds is highly dependent on the pH of water. For a pH from 6.5 to 8.5, typical values for drinking water, HOCL and OCL- are the prevailing species and their concentration in water is called free available chlorine. It is these compounds that provide the disinfection action on organic material. For a more complete description of the chemistry of chlorine disinfection see WATER TREATMENT PLANT DESIGN, 5th Edition, published jointly by the American Water Works Association (AWWA) and the American Society of Civil Engineers, for example.

Current Practice in US

The best snapshot of Chlorine disinfectant use in the US is found in the AWWA's 4th survey of drinking water utility disinfection practices issued in October 2008[1)]. The AWWA Report summarizes responses to a survey received from 312 water providers ranging in size from <10,000 population served to >500,000 served. The results of the survey are instructive and the findings summarized below:

- 98% reported providing disinfection of some kind.

- Chlorine gas was used by 63%, bulk liquid hypochlorite use was 31%, on-site generated chlorine/hypochlorite was used by 8%, and 8% used some dry forms of hypochlorite. The percentages total more than 100% because some systems used multiple forms of chlorine as a disinfection agent.

- Replacement of chlorine gas with bulk liquid hypochlorite was the most frequently reported disinfection related change since the previous survey of drinking water utility disinfection practices performed by AWWA in 1998, safety being the main reason for converting away from gas chlorination.

- However, chlorine gas remains the preferred disinfection technique by far for the following reasons given in survey responses:
    - Reliability
    - Cost effectiveness
    - Ease of operation
    - Provides a "residual disinfection" in the distribution system that prevents the regrowth of microbes

[1] Committee Report: Disinfection Survey, Part 1 – Recent Changes, Current Practices, and Water Quality (PDF); Volume 100, Number 10; October 2008

The California Experience

The Cities of Benecia and Huntington Beach currently operate gas chlorine disinfection systems at their respective Water Treatment Plants. Each houses the active chlorine cylinders in a containment vessel. Some particulars from the Benecia plant:

- 12-MGD rated Water Treatment Plan
- Dosing rate of 0.6 mg/L for pre-chlorination and 1.5 to 1.8 mg/L for post-chlorination
- A 1-ton cylinder is emptied every 3 weeks, on average. Yearly usage is approximately 18 1-ton cylinders
- Cylinders are stored in a separate room that is adjacent to the Operations Building
- Switch over from an empty cylinder to a full, spare cylinder is done manually, demonstrating full operator control

Both are required to prepare a Risk Management Study (RMP) – see discussion below – that is approved by the local Certified Uniform Program Administrator (CUPA), usually the County environmental health department and reviewed by the US Environmental Protection Agency (EPA). Although this effort was qualified as time consuming, the consensus was that the effort was manageable.

Huntington Beach notes that it would not operate a gas chlorine system without containment vessels as these offer significant public and operator safety protection as well as additional security from tampering or vandalism.

Finally, the operating staff at both plants would recommend the use of gas chlorine as a disinfectant because it is:

- Efficient
- Easiest to use and handle
- Cost Effective; it provides the most disinfection for the least cost

What are the Safety Issues?

Chlorine has been designated as an Extremely Hazardous Substance (EHS) in 40 CFR 355 and, as such, is highly regulated by federal, state and local agencies. Leaks are of great concern and rules have been promulgated by the US Environmental Protection Agency (USEPA) and OSHA, among others requiring the preparation of emergency planning activities known as Risk Management Studies (RMP) when chlorine is stored above a certain threshold quantity (TQ). Additionally, the method of storing chlorine will influence the scope and extent of the emergency plan preparation that is required by the RPM regulations. It is recommended that state and local regulations be reviewed when preparing emergency plan preparations for additional requirements.

How to Control Leaks

The water treatment industry uses two techniques for the control of chlorine leaks. These are scrubbing or containment.

- Scrubbing is a treatment system that neutralizes the accidental release of chlorine gas by drawing contaminated air through a chemical absorption system. The treated air is discharged to the atmosphere.

- Containment systems employ a self-contained vessel within which the chlorine gas cylinder is housed. Accidental leaks of chlorine are kept within the containment vessel, an ASME rated pressure tank, for recycling to the injection system at a normal flow rate. No atmospheric venting is generated because the leaked gas is kept within the containment vessel. TGO Technologies, Inc., of Santa Rosa, California, has developed self-containment vessels for both 150-pound and 1-ton cylinders that perform this function and provides for total containment that keeps our communities safe. See photo.

Risk Management Studies (RPM) are Required

Both scrubbing and containment technologies for chlorine gas are subject to the requirement of an RMP, as stipulated in Section 112 (r) of the Clean Air Act and Article 80 of the Uniform Fire Code. In Section 112 (r), the USEPA developed a list of 77 toxic and 63 flammable substances for which TQs were established. The TQ for chlorine is 2,500 pounds.[2)] Facilities storing chlorine gas in quantities that equal, or exceed 2,500 pounds are required by statute to prepare an RMP in accordance with 40 CFR Part 68, Subpart G.

It is important for Plant Managers to accurately inventory the quantities of stored chlorine gas cylinders at the plant site. Stored quantities of less than 2,500 pounds do not trigger the preparation of a Federal RMP, an activity that requires significant administrative time and effort which diverts scarce resources from plant operation and system monitoring.

A further consideration when determining whether a facility must prepare an RMP is the method used to control chlorine leaks. A self-contained, total containment vessel of the type available from TGO Technologies, as described above, is considered a separate process if not manifolded or interconnected to other vessels. That is, a single, unconnected 1-ton cylinder housed in a total containment vessel would be below the exempt TQ of 2,500 pounds and an RMP would not be required. Up to sixteen (16) 150-pound gas cylinders may be interconnected and not meet the TQ of 2,500 pounds (i.e. 150x16 = 2,400 pounds). However, the manifolding of a seventeenth 150-pound cylinder triggers the requirement for a Federal RMP. It is recommended that treatment facilities review their gas chlorine system storage and delivery designs to determine if these designs can be modified to separate, currently connected 1-ton cylinders, resulting in a stored quantity of 2,000 pounds, a quantity below the threshold 2,500-pound TQ amount, and thereby avoid the preparation of an RMP.

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[2] From EPA 550-B-15-001; Lists of Lists, Page 31; March 2015

We have been discussing the specific TQ amounts that trigger the preparation of a Federal RMP as presented in Section 112 (r) of the Clean Air Act. The use and storage of gaseous chlorine triggers other safety and reporting requirements as mandated by the Emergency Planning and Community Right to Know Act (EPCRA), the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and others such as OSHA's Section 1910.119[3)] that must be prepared by the facility. We also note that state RMP TQs may be more stringent than the federal regulation identified in Section 112 (r); for example, California's TQ for chlorine is only 100 pounds. It is strongly recommended that your state's TQ requirements for chlorine be checked when assessing the need to perform an RMP.

What does the Future Hold for Gas Chlorination ?

There continues to be concern regarding the safety for use of chlorine base disinfection technology and gas chlorine system in particular. Improved containment and detection technologies in recent years have mitigated some of this concern by providing a reliable and redundant spill control technology that is growing in its application.

The use of chlorine as a disinfectant has proven to be cost effective. A December 2008 study performed by Whitfield & Associates for the Chlorine Chemistry Division of the American Chemistry Council[4)] determined the estimated annual cost of constructing and operating a small water system (treating 0.4 million gallons per day for a population of less than 10,000) to be as follows:

- Ozone $0.44 per gallon
- Nanofiltration $0.35 per gallon
- Anodic Oxidation $0.11 per gallon
- Chlorine Dioxide $0.075 per gallon
- Chlorine $0.06 per gallon
- Hypochlorites $0.035 per gallon

The report concludes that the costs of disinfection using chlorine chemistry are significantly lower than for other non-chlorine technologies for water systems of all sizes. Of additional benefit is the residual chlorinated species that remain in the water when using chlorine based disinfection technology, providing additional safeguards in controlling microbiological contamination in distribution systems.

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[3] 29 CFR Ch. XVII (7-1-12 Edition). This regulation governs the preparation of a Process Safety Management Program (PSM). The storage of 1,500 lbs or more of chlorine triggers a Federal PSM.
[4] The Benefits of Chlorine Chemistry in Water Treatment; Whitfield & Associates, December 2008; American Chemistry Council.
[5)] Shah, Jeny and Qureschi, Naem; "Chlorine Gas vs. Sodium Hypochlorite: What's the Best Option?" OPFLOW, July 2008; Table 4. The authors recommend the use of the on-site generation of Sodium Hypochlorite because of the safety issues with the use of gas chlorine. It is not clear if containment or scrubbing of gas chlorine cylinders was considered in their comparison.

A cost comparison study of the use of gas chlorine versus on site sodium hypochlorite disinfection was presented in an OPFLOW article[5)]. The authors calculated the expected costs of installation, operation and maintenance of each process for a 20-MGD system including chemical costs. The present value of the cost of implementing and operating a gas chlorine system was found to be approximately one-third that of a commercially available Sodium Hypochlorite system. Note that local conditions and regulatory requirements must be factored into any comparative analysis of any disinfection technology.

Summary

This article has provided a short summary of the chemical characteristics of chlorine, its implementation history and use in the United States. Because of the safety concerns of using gaseous chlorine as a disinfectant, the benefits of secondary containment for leak control when compared with the use of scrubbers was discussed. It was noted that passive secondary containment can successfully address the safety and regulatory concerns by providing a reliable, secure and cost effective leak protection technology to keep our communities safe. The article also outlined the requirements for the preparation of a Federal RPM as is necessary for any facility storing gaseous chlorine.

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