

Disinfection with Liquid Sodium Hypochlorite: Principles, Methods, and Lessons Learned

Frank A. Miller

As the water and wastewater industries continue to transition away from gaseous chlorine due to risk management issues, use of liquid sodium hypochlorite as a disinfectant is becoming more common. Gaseous chlorine has been a staple method of disinfection for water and wastewater treatment facilities in the United States for over one hundred years. Gaseous chlorine technology is proven and inexpensive in terms of capital cost relative to other disinfection technologies. However, increasing emphasis on risk management issues involved with storing and handling toxic, pressurized chlorine cylinders has prompted utilities nationwide to search for alternatives.

One such alternative is the use of liquid sodium hypochlorite (NaOCl). Sodium hypochlorite, commonly known as bleach, is gaining increasing acceptance by virtue of its safety relative to gaseous chlorine, ability to maintain a residual, flexibility in application, storage and delivery methods, and low cost compared to most other disinfection technologies.

Sodium Hypochlorite Chemistry

Disinfection Chemistry

Sodium hypochlorite (NaOCl) is encountered in the water and wastewater industry as a greenish-yellow liquid solution containing 0.5 percent to 15 percent NaOCl by weight in an aqueous solution, depending on the source or generation technology used to produce NaOCl. Sodium hypochlorite has a molecular weight of 74.5 grams per mole. The specific gravity of NaOCl solution varies with the strength of the solution, as well as the quantities of impurities present, but is typically around 1.157 to 1.168. At 12.5 percent "trade strength", NaOCl solution will weigh around 9.72 pounds per gallon and will have 1 pound of free chlorine available per gallon.

When NaOCl is dissolved into an aqueous solution, it disassociates into its constituent ions according to the following equation:



Note that one of the products of this reaction is hypochlorous acid (HOCl). For comparison, when gaseous chlorine is dissolved in water, it reacts according to the following equation:



Equation 2 shows that elemental chlorine dissolved in water will produce hydrochloric acid (HCl), which is a strong acid, but takes no part in disinfection. Equation 2 also produces HOCl in the same molar ratio as the sodium hypochlorite reaction in Equation 1. Thus, one mole of sodium hypochlorite provides the same oxidation capability as one mole of chlorine gas.

Equation 1 also shows that the other product of NaOCl dissociation is sodium hydroxide (NaOH). This is a strong base, so depending on the solution strength, NaOCl solution will have a pH of 11 to 13.

Degradation Chemistry

Sodium hypochlorite solution will degrade in strength over time. Degradation results in loss of available chlorine, the formation of byproducts and impurities, and the generation of gaseous products, mainly oxygen. Degradation is accelerated due to higher temperatures, the presence of light (UV), contamination with transition metals and bromine compounds, low pH (below 8), very high pH (13 or above), and higher initial concentration of HOCl. The HOCl will decompose into chlorate (ClO_3^-) according to the following stoichiometric equation:



Since HOCl predominates over OCl^- at pH values at or below 7.6, lower pH will increase the rate of degradation. The degradation reaction is second order with respect to HOCl, so doubling the initial concentration of HOCl will quadruple the rate of chlorate formation and accompanying rate of HOCl degradation.

At pH values of 13 or above, the degradation reaction follows a different pathway. Since virtually no HOCl is present at this pH, hypochlorite ion (OCl^-) will degrade into

Frank A. Miller, P.E., is supervising engineer with Brown and Caldwell Inc. in Maitland.

chlorate by the stoichiometric equation:



Thus, the rate of sodium hypochlorite degradation has two maxima: at pH = 8 and at pH = 13. Since the dissolution of NaOCl in water will result in a basic solution due to the formation of NaOH per equation 1, manufacturers of NaOCl will maximize the stability of the solution by providing a limited excess of NaOH between 0.10 percent to 0.40 percent by weight. In higher temperature climates such as Florida, the minimum excess NaOH will be increased to 0.15 percent to compensate for the increased degradation rate due to temperature. For each 10oF increase in solution, temperatures above 70°F will double the rate of degradation. Typical degradation rates will result in a loss of about 20 percent of available chlorine within 14 days, given a starting concentration of 12.5 percent and a temperature of 80°F.

A third degradation pathway results in the formation of oxygen from the degradation of OCl^- per the following reaction:



In pure sodium hypochlorite solutions, equation 5 is a minor degradation pathway with a very slow rate of oxygen formation. However, the presence of transition metals (such as nickel, copper, and iron) contaminating the hypochlorite solution will catalyze the reaction and greatly increase the rate of oxygen formation. Heat and sunlight will also increase the rate of oxygen formation. Along with the formation of oxygen, transition metals and other metals such as Ca^{+2} and Mn^{+2} can result in the formation of sludge and scaling within the sodium hypochlorite system tanks and piping.

Bromate contamination is also a potential problem with sodium hypochlorite solutions. Bromide is present in the salts used in

Continued on page 6

Continued from page 4

NaOCl generation and can be found in some raw water supplies. Oxidation of bromide ions will form sodium bromate (NaBrO_3). Sodium bromate is a suspected carcinogen and is regulated by the U.S. Environmental Protection Agency with a maximum contaminant level of 10 $\mu\text{g/L}$.

Use of Sodium Hypochlorite in the Water and Wastewater Industry

Sodium hypochlorite can be used in water and wastewater utilities wherever chlorine gas is used. Disinfection is the primary use for both water and wastewater facilities. Oxidation processes for odor control, return activated sludge (RAS) chlorination for filamentous bacteria control, and prechlorination for algae and other biological control for water treatment are all possible applications of sodium hypochlorite.

Both large and small facilities commonly employ sodium hypochlorite systems for the uses stated above. Small water treatment systems will commonly have sodium hypochlorite delivered in drums or totes, and injected into the finished water with a metering pump. Larger facilities may use sodium hypochlorite delivered in bulk quantities by tanker truck or generate their own supply on-site.

A major driver for the adoption of sodium hypochlorite is the reduced risk compared to the use of chlorine gas. Chlorine is typically supplied in pressurized containers where the chlorine is compressed to liquid form. Rupture or leakage of these containers can result in the discharge of toxic gas that is hazardous to both plant staff and the surrounding community. As a result, utilities are obligated to invest in risk management strategies, including the installation of emergency chlorine scrubbers, automated shut-off and ventilation systems, and other safety precautions.

Sodium Hypochlorite System Equipment

Bulk Deliveries and On-Site Generation

NaOCl can be delivered in bulk by tanker truck, or in drums or totes. A full tanker truck contains 4,000 to 5,500 gallons of NaOCl, while smaller facilities may receive NaOCl in quantities as small as individual 55-gallon drums. Typical bulk-delivered NaOCl is usually at least 10 percent, but commonly delivered at 12.5 percent NaOCl.

An alternative to bulk deliveries is on-site generation (OSG) of sodium hypochlorite. Sodium hypochlorite generated on-site is any-

where from 0.5-0.8 percent for low-strength generation systems, and up to 12 to 15 percent for high-strength on-site generation systems. The OSG systems vary by manufacturer, but require a softened water supply, a salt (NaCl) supply, and electricity. The NaOCl is produced by electrolyzing a brine solution per the following equation:



Equation 6 is used in low-strength (0.5-0.8 percent) OSG systems. High-strength OSG systems use a two-step process described by equations 7 and 8:



Typical consumption rates of these raw materials for OSG are about 2 kg salt per kg Cl_2 , 8 liters of water per kg Cl_2 , and 4 to 7 kWh of electricity per kg of Cl_2 generated. In both low- and high-strength OSG systems, hydrogen gas is generated and must be vented to the atmosphere. A variation of the high-strength OSG system foregoes the step described in equation 8, and the chlorine gas produced in equation 7 is used in an on-demand basis and fed directly to chlorine injectors in a manner similar to conventional gas chlorination. This allows the recovery of the NaOH as a usable by-product if desired.

Storage

On-site storage can be in tanks constructed of fiberglass reinforced plastic (FRP), high-density polyethylene (HDPE), or lined steel tanks. Storage quantities for bulk-delivered and high-strength OSG systems are similar due to the comparable concentration of sodium hypochlorite, while low-strength OSG systems would require significantly greater volumes due to the low concentration. The trade-off benefit resulting from the low-strength OSG system is lower degradation rates due to the more dilute solution. Higher concentration NaOCl from either bulk delivery or high-strength OSG may also be diluted to reduce degradation, but a softened water supply must be used to prevent scaling of calcium carbonate within the system.

Pumping

In order to deliver the sodium hypochlorite to application points, metering pumps are typically used; hydraulic diaphragm metering pumps or peristaltic (hose) pumps are the most common. Each has its benefits and drawbacks as described in the "Design Issues" section.

If the storage facility is located remotely from the application point(s), a transfer pump system feeding day tanks can be used as well; magnetically driven sealless pumps are often used for this. Pumps using mechanical seals or packing are unsuitable for sodium hypochlorite due to the aggressive nature of the chemical. Wetted parts must be non-metallic or otherwise suitable for sodium hypochlorite service.

Conveyance

Sodium hypochlorite conveyance (piping) systems are usually constructed of PVC, HDPE, or Teflon tubing. The CPVC can be used, but the only advantage is a higher temperature rating. Titanium piping is also mentioned in literature, but is uncommon outside of NaOCl manufacturing facilities due to the cost. Double containment is commonly used to prevent accidental leakage from escaping into the environment. The conveyance piping can be either direct-buried or routed through pipe trenches in a manner similar to other chemical systems.

Application

In many smaller systems, the sodium hypochlorite is introduced via a simple drip tube or chemical injection quill or diffuser. For larger systems, or systems with low-flow periods where mixing could be an issue, flash or induction mixers may be used to disperse the sodium hypochlorite into the process flow. Installing a vacuum breaker upstream of the induction mixer will help to stabilize the flow of sodium hypochlorite by preventing its gas-liquid separation. Materials of construction for the mixers should be compatible with sodium hypochlorite.

Control

Proper control of the sodium hypochlorite dosing is critical for public health and permit compliance, particularly with disinfection applications. Sodium hypochlorite metering pumps can be paced using control strategies similar to conventional chlorination. Typically, these control systems are flow-paced (feed forward), residual-paced (feedback) or a combination (PID loop). In any case, the metering pumps should have the capacity to provide for proper dosing at peak flow conditions, as well as having sufficient turn-down to avoid overdosing during low-flow periods. In all disinfection applications, process reliability must be assured by providing at least one standby pump, along with the duty pump, for each application point.

Sodium Hypochlorite System Engineering and Design Issues

Storage

Whether a sodium hypochlorite system uses bulk deliveries or OSG, proper selection of storage tanks materials is important for system reliability and longevity. The two most common materials used in NaOCl storage tanks are FRP and HDPE, as mentioned previously. Steel tanks lined with an elastomeric interior coating are also used. However, frequent inspection of the liner is required, and replacement every two to three years is usually typical. Failure of the lining will result in tank corrosion and possible failure. Iron contamination of the sodium hypochlorite will lead to accelerated degradation and off-gassing, along with iron deposits in the system, leading to operational and maintenance difficulties.

The FRP tanks, when properly specified, can last for 10 or more years. The tanks should be hand laid-up or have orthogonally wound construction. Filament wound tanks should be avoided since a minor flaw in the corrosion liner will result in 'wicking' of the sodium hypochlorite along the glass fibers, leading to rapid failure of the tank. Vinyl resin should be used for both the corrosion barrier and the structural layers of the tank, starting with two nexus veils. The corrosion barrier should use a benzoyl peroxide/dimethylaniline (BPO/DMA) cure system with a four-hour minimum post cure. Care should be taken in specifying a tank manufacturer to ensure that it has sufficient experience in fabricating FRP tanks for sodium hypochlorite service.

The HDPE tanks are also common, especially for smaller tanks. The tanks typically last four to seven years in outdoor service, and six to nine years indoors, or when painted or coated for ultraviolet (UV) protection. The tanks should be opaque to minimize NaOCl degradation due to UV exposure. Care must also be taken when installing penetration fittings. This is the most common leak location, and the best solution is to provide tanks with molded fittings instead of bulkhead type fittings.

For both FRP and HDPE tanks, allowance for tank expansion when full of liquid ("squatting") is extremely important. Rigid piping connections or inadequately supported piping will apply stress to the tank fittings and adjacent piping, leading to leaks. Flexible expansion joints at the tank penetration will prevent stress-induced leaks. All fitting flanges should use Viton gaskets. Pipe supports should be FRP. Stainless steel is to be avoided in sodium hypochlorite applications due to corrosion.

Containment

Spill containment will usually be required for both Florida Department of Environmental Protection (FDEP) and fire marshal permitting. Containment volume should be a minimum of 110 percent of the largest tank volume. An epoxy-based chemically resistant coating on the interior surfaces of the containment structure will minimize leakage. For smaller installations, HDPE containment vessels can house the tanks instead of concrete containment structures. Finally, double wall tanks can be specified for containment as well.

Degradation

As described, sodium hypochlorite degradation is a function of product concentration, temperature, pH, light, and contamination. At 80oF, 12.5 percent sodium hypochlorite will degrade about 20 percent within two weeks, leaving only a 10 percent solution. Pump and system design should take this degradation into account when determining NaOCl feed rates. Degradation can also be minimized by providing filters for suspended solids removal at the unloading stations, and by minimizing the volume stored on-site. Storage tanks should be located out of direct sunlight and heat as well.

Mitigation of Off-Gassing

Along with the degradation issues addressed, system design should incorporate measures to mitigate the effects of off-gassing of oxygen. Metallic components should be scrupulously avoided; even small items like ball check valve springs and hose fittings can lead to metal-catalyzed off-gassing. Off-gassing can lead to serious operational problems such as air binding of pumps and instruments, uneven pumping rates, and dangerous pressure buildup in isolated piping and closed valves. Piping runs that are isolated for extended periods should be drained and flushed. Valves for sodium hypochlorite service should be diaphragm-type valves. Ball valves should only be used when provided with drilled vent holes in the ball to the upstream side. Unvented ball valves can trap oxygen in the valve, leading to explosive rupture due to the gas pressure build up.

Air binding of pumps can be avoided by providing a suction-side vent or standpipe to act as a bubble trap prior to entering the pump. Pumps should be installed to have a flooded suction, and caution should be exercised when depending on the catalog values for suction lift of metering pumps. Suction piping should be sloped upward from the pump to the tank to allow oxygen to migrate back to the tank wherever possible.

Pumps and Piping

The most common types of metering pumps used for sodium hypochlorite service are hydraulic diaphragm metering pumps and peristaltic hose pumps. Each type has advantages and drawbacks, and neither is suitable for all applications.

Hydraulic diaphragm metering pumps use a reciprocating piston in a hydraulic fluid to flex a diaphragm back and forth in conjunction with suction and discharge ball valves. The diaphragm and all wetted parts need to be carefully specified to ensure compatibility with sodium hypochlorite. These pumps are common to the water and wastewater industry for a wide variety of chemical applications, so they have the advantage of familiarity on the part of plant staff. Hydraulic diaphragm pumps also have the ability to adjust both the pump speed and stroke length, which allows a larger turn-down ratio and thus larger operating range over an equal-sized hose pump. Hydraulic diaphragm pumps are generally better suited for larger flows due to the frequent need to replace the hose on peristaltic pumps, and thus have a lower overall life-cycle cost than hose pumps in the larger sizes.

Hydraulic diaphragm pumps can be subject to vapor lock (air binding) due to off-gassing, unless the measures described are taken to mitigate this effect. Some models of hydraulic diaphragm pumps can also be equipped with automatic "degassing" vents on the pump head to discharge accumulated oxygen in the pump head. Operation of these pumps should avoid the combination of high speed and short stroke to avoid off-gassing by rapid churning of the sodium hypochlorite. Control strategies can be programmed to avoid this combination by regulating the minimum stroke allowed for a given speed range. Particulate contamination of the sodium hypochlorite can also lead to jamming or leak-by of the suction and discharge ball check valves.

Peristaltic, or hose, pumps operate by rotating a set of rollers in a circular pattern in contact with the hose tubing that carries the product. As the roller travels, it compresses the hose between it and the housing and pushes the product through the hose in front of the roller. Hose pumps have the advantages of simplicity, can be run dry, are self-priming, and thus are not susceptible to vapor lock like the hydraulic diaphragm pumps. Also, no parts of the pump except the hose are in contact with the sodium hypochlorite, which makes material compatibility less of a concern. For smaller peristaltic pumps, replacement hose is very inexpensive and easily changed.

Disadvantages of peristaltic pumps include the difficulty and expense of frequent

Continued on page 8

Continued from page 7

hose replacement in larger-sized pumps. Hose replacement will vary depending on the average speed at which the pumps operate. Some installations require weekly or biweekly hose replacement due to the aggressive nature of sodium hypochlorite weakening the hose material, while operating the pumps at a high, sustained speed increases the wear on the hose. Particulate contamination is also an issue with hose pumps due to abrasive damage to the hose when the roller can grind particulate matter into the hose, causing damage with each rotation. Hose pumps also do not generally have as great a turn-down capability compared to hydraulic diaphragm pumps, so they may not be suitable to facilities that experience large flow variations.

Sodium hypochlorite system piping is another area where care should be taken in the design and construction of the feed system. While PVC is the most common material for sodium hypochlorite piping, solvent welding (glue) joints must be made in accordance with ASTM D2855-96. This standard specifies the technique for joining solvent-welded piping. The standard also specifies that only silica-free glue is allowed for joining sodium hypochlorite piping; sodium hypochlorite will dissolve silica present in conventional PVC cements, leading to leaks and joint failure. Threaded joints and unions should be avoided due to the likelihood of leakage past the threads. Where threaded joints are unavoidable, Mil Spec P-27730A Teflon tape should be used.

The HDPE tubing has also been successfully used for sodium hypochlorite service. Small diameter (< 2") HDPE tubing is available in spools that provide several hundred feet of tubing, depending on the diameter. This minimizes the number of joints needed and avoids the complications of proper joining of PVC pipe. The drawback to HDPE tubing is that the welding apparatus for making the connections is not equipment that utility plant maintenance staff typically possesses, thus leaving the plant at the mercy of an installation contractor should repairs be necessary.

Some utilities have used Teflon or flexible PVC tubing pulled through a conduit pipe in a manner similar to pulling electrical cable through a conduit such as a 4-in. to 6-in. PVC pipe. Manholes and pull boxes are located at changes in direction to allow pulling of the tubing through the conduit. This arrangement shows promise, although it has been reported that the tubing can be very difficult to pull when other tubes are located in the same conduit due to the friction between the tubing and along the conduit. As more experience is

gained with this approach, techniques for installation will invariably be improved.

Other aspects of system piping design and layout that ensure a properly functioning system also deserve attention. One of the most important points is to minimize the distance between the metering pump and the application point to the extent possible. Piping runs greater than 500 feet, or having hydraulic detention times greater than about four hours should be avoided due to off-gassing. Bends and obstructions such as valves and reducers should be minimized as well in order to avoid locations for scale or contaminant deposition. Unless a softened water supply is available, sodium hypochlorite should be pumped undiluted to avoid scaling and clogging. Fluid velocities in piping should be as high as possible, but under five to seven feet per second. The high velocity will serve to sweep oxygen bubbles along to minimize gas accumulation, but going higher can result in shearing of the sodium hypochlorite into separate slugs of gas and liquid.

Safety

While sodium hypochlorite is inherently safer than gaseous chlorine, safety is still a matter of concern when working around and with sodium hypochlorite. Emergency eye-wash and shower facilities should be provided at unloading stations, pump and storage facilities, and other locations where sodium hypochlorite is stored or handled.

When working on sodium hypochlorite systems, face and eye protection should be worn, and piping systems isolated, drained, and flushed prior to work. Obviously, all established lockout/tagout procedures will need to be adhered to as well.

Permitting

Permitting of sodium hypochlorite systems also contains some challenges to design and operation. The National Fire Protection Association code, NFPA 704, contains some ambiguity regarding sodium hypochlorite; it is not specifically named in NFPA 704, leading to a large amount of latitude for interpretation on the part of the local fire marshal at any given location. Some agencies interpret the code such that only very limited quantities of sodium hypochlorite can be stored inside a building. Others will allow unlimited quantities to be stored indoors, but will require fire sprinklers and alarm systems. However, sodium hypochlorite is a strong oxidizer and is thus usually classified as a high-hazard class H-4. This classification will require more stringent egress and other life safety requirements to be met. In any case, early communication with the local authority having

jurisdiction is recommended to ascertain the local interpretation to be enforced.

There is also a need to communicate early and often with the FDEP district office having jurisdiction. The main reason is that FDEP will often require 30 days of storage for chemicals at treatment facilities in accordance with design standards adopted by reference in the regulations (e.g., Ten States Standards). However, thirty days of storage for sodium hypochlorite is unnecessary and indeed undesirable due to the degradation issues. Proper communication with FDEP can usually result in negotiation of storage volumes of 10 to 14 days on an average flow basis, or three days of peak day flow chemical storage.

Conclusions

Liquid sodium hypochlorite can be an attractive alternative for utilities looking to transition away from gaseous chlorine. Sodium hypochlorite systems can range from simple bulk-delivered, tank-and-pump systems with little automation, to large, sophisticated systems using on-site generation technology and transfer pumps and day tanks, with metering pumps controlled by flow, residual, and oxidation reduction potential (ORP), or combinations of thereof.

Sodium hypochlorite can replace gaseous chlorine in all relevant applications of chlorine in the water and wastewater industry. However, hazards and complications do exist, which require that designers, operators, and regulators apply this technology using sound practices and principles.

References

- White Paper on Disinfection with Hypochlorites, AWWA Ohio Section Technology Committee, 2007.
- Water Quality and Treatment—A Handbook of Community Water Supplies, 4th edition, AWWA, 1990.
- Sodium Hypochlorite General Information for the Consumer, Odyssey Manufacturing Co., 2007.
- Bleach Stability and Filtration, Powell Fabrication and Manufacturing Inc., 1996.
- Hypochlorite Heaven—A Sodium Hypochlorite System that Solves Hypochlorite Problems, Rob Baur, Unified Sewerage Agency, 2000.
- On-Site Generation Systems Feasibility and Design for the MDWASD John E. Preston Water and Hialeah Water Treatment Plants, Ralph Terrero, P.E., et al., 2009.
- Design of Municipal Wastewater Treatment Plants, 4th Edition (MOP 8), WEF, 1998. ◊