AWWA Ohio Section
Technology Committee

White Paper on Disinfection with Hypochlorites

September 17, 2007

1.0 INTRODUCTION

Theoretically, hypochlorite chemicals can be used wherever gaseous chlorine is used for disinfection. In the water supply practice, it has achieved widespread acceptance since its initial uses in early water treatment history. Hypochlorites can be purchased or generated on site.

It is appropriate to use hypochlorites as a disinfectant in place of gaseous chlorine when operational, financial, availability or safety considerations show that it is more advantageous to the operational staff. If staff feels that the decision to switch to hypochlorites is difficult, it is strongly recommended that they seek advice from Ohio EPA, another utility that has already made the conversion, or an engineering consultant. The changeover will require Ohio EPA approval.

2.0 HYPOCHLORITE CHEMISTRY

2.1 Hypochlorite vs. Gaseous chlorine

Disinfection with chlorine products is aimed at the formation of hypochlorous acid, which is a strong disinfectant. Gaseous chlorine dissolves in water to form hypochlorous acid and hydrochloric acid. The chemical formula for this reaction is:

$$Cl_2 + H_2O \rightarrow HOCL + HCL$$

When hypochlorite compounds are used in place of gaseous chlorine, hypochlorous acid and sodium hydroxide are formed:

$$NaOCl + H_2O \rightarrow HOCl + NaOH$$

In either case, the HOCl that is formed dissociates into H^+ and OCl^-. The OCl^- portion of the dissociation determines the disinfectant power of the water in which it resides. At a pH of 7.3 there is roughly a 50-50 concentration of the HOCl and OCl^-. As pH increases, the OCl^- predominates and the result is less disinfectant power.

2.2 Demand Testing

Most waters will exert an oxidant demand, and so the operator needs to be able to meet the demand with sufficient dosage to overcome it before an excess of disinfectant (residual) can be maintained. Both inorganic (i.e., iron, manganese, hydrogen sulfide, etc.) and organic compounds (i.e., primarily natural organic matter) can contribute to chlorine demand. For general purposes, the chlorine demand of the water is defined as the dosage in mg/L of chlorine minus the amount of measurable chlorine residual that is left in the water after it has been dosed and mixed under treatment conditions for 30 minutes. Waters high in organic matter or other slowly reacting contaminants may continue to exert an appreciable demand for chlorine for hours or days, and the operator is encouraged to use good judgment as each source is unique.

To test for chlorine demand at the jar scale, the operator is directed to dose 2 Liter jars of raw water with 0.5 mg/L increments of available chlorine to bracket the expected demand requirements. The strength of the test solution should be determined by analysis. Other treatment processes and mixing energies will have an effect on the demand, so the operator should either include these steps in the jar test procedure, or estimate their effect on the demand calculation. Some steps, such as potassium permanganate, may cause erroneous readings if colorimetric analyses are employed.

2.3 Impurities

Sodium hypochlorite solutions contain varying levels of bromate that originate as a contaminant in the salt used to produce the product. The maximum contaminant level (MCL) for bromate is 10 μg/L. NSF approved sodium hypochlorite can contain up to 5 μg/L. Systems that utilize ozone (which also produces bromate) need to monitor and select hypochlorite products to help control bromate levels. Chlorates in finished water are not regulated with an MCL but should be considered as a possible issue for operational control. At least one state (CA) has limited its presence to 0.8 mg/L. Chlorates are formed as hypochlorite degrades, and so operators are encouraged to use a purchase and storage plan that minimizes this degradation. Operators should also institute an aggressive sampling plan which requires the manufacturer or deliverer to meet quality control standards. Procedures can be found in AWWA Standard for Hypochlorites (B300-04).

2.4 Degradation Issues

Sodium hypochlorite solutions tend to degrade over time. This degradation results in a decrease in available chlorine, the production of gases (off-gassing) and by-product formation that includes chlorate and perchlorate. The stability of these solutions is greatly affected by various conditions such as light, pH, temperature, storage time and the presence of impurities, such as heavy metals. Degradation must be considered during design of storage and feed equipment, and determination of feed rates during operation.

Effects that increase the rate of degradation are:

- Higher temperatures
- Presence of light
- Higher hypochlorite concentrations
- pH values below 11
- Presence of iron, copper, nickel or cobalt

2.5 Dosage Calculations

2.5.1 Strength of solution

Strength of solution is expressed in terms of available chlorine, either as trade percent (percent by volume), or as percent by weight of available chlorine. A table (Table 1) from the AWWA standard is provided at the end of this document.

The material will usually be delivered to the plant with a document that shows the strength of the solution as "trade strength". A 200 gram/Liter available chlorine solution is called "20 trade percent". Most operators will feed the chemical at 12.5 trade percent because this provides a solution that delivers 1 pound of chlorine per gallon of solution fed.

When operators dilute the hypochlorite solution to minimize degradation, they typically dilute to a 6 percent solution because this strength exhibits minimum degradation over time. At this strength, it takes a delivery of about 2 gallons of hypochlorite solution to yield 1 pound of chlorine fed.

2.5.2 Dosage equation

The equation for chlorine dosage needed is:

Dosage (mg/L) = Chlorine demand (mg/L) + Chlorine Residual (mg/L)

The general equations for dosage calculations are:

Feed rate (lb/day) = Flow rate (MGD) x Dosage (mg/L) x 8.34 lb/gal
Feed rate (gpd) = Feed rate (lb/day) ÷ Available chlorine (lb/gal)
or
Dosage (mg/L) = Feed rate (lb/day) ÷ [Flow rate (MGD) x 8.34 lb/gal]

2.5.3 AWWA Standard for Sodium Hypochlorite

The current AWWA Standard for Hypochlorites is AWWA B300-04, in which the discussion of Sodium Hypochlorite is found. It lists Sodium Hypochlorite as a 12 to 20 percent available chlorine chemical.

Calcium hypochlorites are used in water treatment for specialty cases such as swimming pools, or disinfection of new mains and water tanks. AWWA Standard B300-04 recommends that only sodium hypochlorite be used for ongoing disinfection and residual maintenance in drinking water supplies.

3.0 STORAGE

3.1 In treatment plant

Given the degradation issues stated previously, a strategy that minimizes amounts of hypochlorite purchased and stored will help to reduce degradation. Many operators have reported that hypochlorite solutions seem reasonably stable if 30 day supplies are maintained and carefully stored under proper conditions (absence of light, proper temperature, etc.). A strategy that allows for the purchase of small batches is desirable and will help the operator with these stability issues.

3.2 In distribution system

Storage of small amounts of hypochlorite solution at booster facilities (that feed hypochlorite) is important to minimize degradation, and because of safety factors and temperature regulation. Operators are urged to use a strategy that balances safety with reasonable logistical control of the hypochlorite especially where it is stored in residential areas.

3.3 Storage tank life

Hypochlorite storage tank life is estimated to be about 10 years, so operators should give thought to the need for replacement of facilities and the impact on future logistics.

4.0 DECISION TO CONVERT FROM GAS CHLORINE TO HYPOCHLORITE

4.1 Community considerations

Selection of satellite (or secondary) sites for hypochlorite application requires careful consideration and balancing of neighborhood impacts with operational needs. Considerations include the type of neighborhood (residential, commercial, etc.), size of the facility required, delivery frequency and scheduling, frequency of maintenance and seasonal usage and storage considerations along with other community specific concerns.

4.2 Financial considerations

The following items should be taken into collective consideration when determining whether sodium hypochlorite is the appropriate disinfection chemical:

- Chemical costs – hypochlorite is more expensive than chlorine gas in terms of available chlorine. Total system costs are more comparable when safety, regulatory and overall system capital costs are taken into consideration. The utility should consider the cost of a chlorine scrubbing system in the overall decision process.
- An attempt should be made to consider long term maintenance cost differences between gaseous chlorine and liquid hypochlorite feed.
- On-site generation vs. purchased hypochlorites should be considered.

4.3 Purchase vs. on-site generation

Systems will need to give consideration to either purchasing the hypochlorite they intend to use, or on-site generation. Each system has its advantages and the system operators are urged to choose carefully. In general, hypochlorite generation is an electrically intensive process. It yields a product at about 0.8% strength and so product degradation is not much of an issue, nor is safety when compared to purchased hypochlorite.

4.4 Safety factors that need consideration

Stored hypochlorite	Generated hypochlorite
Keep away from heat and fire	Electrical use precautions
Don't eat, drink or smoke near storage	Don't eat, drink or smoke near storage
Avoid contact with eyes and skin	Avoid contact with eyes and skin
Wash down spillage with water	Wash down spillage with water
Avoid contact with acids, organics, oils and greases, cleaning agents	Avoid contact with acids, organics, oils and greases, cleaning agents

5.0 DESIGN CONSIDERATIONS

5.1 Key components

The key system components for a sodium hypochlorite system are similar to many liquid chemical storage and feed systems, and include: delivery and dilution system (if diluted), storage tanks, mixing system, spill containment, day tanks and feed pumps.

5.2 Materials of construction (no metals except Titanium)

- Storage and day tanks – Linear and cross linked HDPE tanks are most commonly used (available from several manufacturers, standard sizes available). Rubber-lined steel tanks are also used (custom sizes available). Tank/liner life expectancy is up to 10 years.
- Piping – CPVC, vented for off-gassing.
- Solvent-cement – Standard PVC/CPVC solvent-cements typically contain fumed silica as a thickening agent. Hypochlorite is believed to dissolve silica over time, potentially resulting in leaks at fittings within the piping system. A solvent-cement specifically designed for sodium hypochlorite or caustic application which does not contain silica should be used. Installation should be in accordance with ASTM D 2855-96(2002), Standard Practice for Making Solvent-Cemented Joints with Poly(Vinyl Chloride) (PVC) Pipe and Fittings.

5.3 Connection types

- Tanks have tendency to flex with temperature; piping connections need to take this into consideration.

- Avoid threaded connections.

5.4 Off-gassing (valve types, line slopes, pumps, venting)

- When sodium hypochlorite degrades, it gives off gas bubbles. Since the chemical is relatively viscous and the bubbles are small, they tend to stay locked in suspension. Over time, this can produce vapor lock on the pumps.
- Diaphragm or vented/drilled full port ball valves – prevent vapor lock (or splitting of ball valve housings due to pressure build-up)
- Slope pump suction line up from pump to tank
- Provide a bubble-trap on the pump suction line and vent back to storage tank
- Provide vents on the calibration columns and on the high point of the pump discharge
- Peristaltic vs. diaphragm pumps
    - There is disagreement among operators as to the preferences between these two types of pumping systems. Peristaltic pumps may lessen the tendency for off-gassing, but need attention to tubing changes frequently as the hose does break down with use, sometimes weekly. Diaphragm pumps are more familiar to many operators and provide a comfort zone to them, but will produce more off-gassing in some situations.
- Sediment formation – Sediment can be present or form in hypochlorite during storage. Locate pump suction line a few inches above the bottom of the tank, to keep solids from accumulating in piping.

5.5 Storage location

- Store in a cool location, out of direct sunlight (basement or air conditioned room if practical, blinds on windows).

5.6 Storage – neat or diluted

- Neat – less volume required for storage, degradation potential higher, need to gauge degradation for dosing control.
- Dilute upon delivery – more storage volume required, dilution system necessary, dilution water characteristics need to be evaluated for potential scaling (may need to soften), less prone to degradation (reduces off-gassing and chlorate formation).
- Specific gravity and available chlorine concentration can vary with depth (both increasing w/ depth). Stratification is an issue in tanks where the hypochlorite solution does not move often, and so mixing may be necessary to keep solutions homogenous. Recirculation system may be considered to keep tank contents mixed or to transfer between multiple storage tanks.
- Sampling ports for applicable points of interested are highly recommended so that operators can obtain samples for percent strength analysis.
- Overflows on bulk storage tanks are recommended to include some method of trapping potential off-gases to minimize fugitive fumes within the chemical storage area. Suggested methods include submergence of the tank overflow in a bucket of water or inclusion of a goose-neck water trap with water connection to maintain water

in the low end of the overflow line. In both of these examples, the intent is for fugitive gas to dissolve in the water minimizing release into the room.

5.7 Mixing at point of addition

- Provide easy access to dispersion piping or diffuser nozzles for maintenance – (the high potential for scaling in this area dictates need for access)

5.8 Feed neat or use carrier water

- If chemical is diluted upon delivery or if carrier water is used, consideration should be given to softening (depending upon finished water characteristics) to prevent scaling in tanks, lines and diffusers at feed point
- Use of polyphosphates is indicated where softening costs are prohibited

5.9 Corrosion (of equipment in chemical feed room)

- Routine inspection of equipment should be made to ensure that it is not corroding. Operators should take steps to see that the piping and feed system components are corrosion-free. Keep equipment dry.

5.10 Safety

- An eye wash/shower is required, and operators should be trained in its use. When entering the room for any purpose other than routine rounds, aprons and gloves and eye protection should be used by each employee. Special care should be used when transferring chemical or when working on equipment as splashing can occur. No other chemicals should be allowed in the room with the hypochlorite.
- Proper signage – clearly label truck loading station with bold, visible signage (if delivered in bulk). Mixing acids or acidic chemicals with sodium hypochlorite may cause a violent reaction or the formation of chlorine gas
- Consider the use differently sized fill station connections or piping colors to help prevent accidental unloading of wrong chemical
- Consider a process of acknowledgement or sign-off by two plant staff members prior to unloading chemical
- Spill containment and separation of chemicals – provide proper spill containment and ensure proper separation from other WTP chemicals

6.0 SYSTEM OPERATION

6.1 Worker safety

Worker safety was covered previously but is reemphasized here for operations.

6.2 Chemical specification/delivery

Check strength and appearance upon delivery. It should look clean. If dirty, impurities can cause rapid degradation in storage. It is recommended that sodium hypochlorite shipments contain not less than 120 grams/Liter available chlorine (12 trade percent). As direct additives, they are required to meet NSF/ANSI 60 for Drinking Water Treatment Chemicals – Health Effects. Be sure to mix the solution thoroughly before sampling.

6.3 Off-gassing

Provisions for periodic flushing of chemical feed lines (also for sediment removal) are strongly recommended. Most operators report that they need to bleed the feed systems weekly, or even nightly if their operation is start/stop.

6.4 Dosage control

Dosage control was discussed previously but salient points are summarized here. See hypothetical SOP at end of document.

- Feed points – multiple in most plants – adequate to handle emergency needs.
- Compatibility with other treatment chemicals – should be stored by itself.
- Dosage calculation – operations needs to know strength of chemical, demand of water, and desired residual.
- Checking feed strength (as delivered, plus periodically in storage) is highly recommended. Staff usually gain experience and adapt their procedures to fit the season.

6.5 Other

- Scaling and precipitation can be an issue where feed lines are lengthy or bends in the piping are encountered. Preventive maintenance is a must and will help to forestall system failure.
- Troubleshooting the equipment is the domain of the trained maintenance staff or the equipment manufacturer representative. Schedule this maintenance on a routine basis to avoid emergencies or at least minimize them.
- Sample the stock chemical frequently to track its strength. Do so more frequently when degradation rate is likely to increase.
- Spare parts for the feeders and delivery points are important. Disinfection is a requirement in drinking water. If the hypochlorite system is the primary form of disinfection, the necessary spare parts must be stocked.
- Dosage pump rebuild kit is available from the pump and feeder manufacturer and is highly recommended. Because pump configurations tend to go through frequent iterations by the manufacturers, operators should know that parts may not be available when their system begins to age. It is a good idea to buy these kits at the time of initial pump purchase.

Table 1 – from AWWA Hypochlorite Standard B300-4 – shows the amount, in gallons of hypochlorite solution, needed to obtain 1 lb. of chlorine at various trade strengths in percent.

Available chlorine *(g/L)*	Trade percent available chlorine	Chlorine equivalent *(lb/gal)*	Chlorine equivalent *(kg/L)*	Gallons to obtain 1 lb chlorine	Liters to obtain 1 kg chlorine
200	20.0	1.630	0.200	0.61	5.0
160	16.0	1.333	0.160	0.752	6.25
150	15.0	1.250	0.150	0.800	6.667
120	*12.5*	*1.000*	0.120	*1.00*	8.333
50	5.0	0.417	0.050	2.40	20.0
10	1.0	0.083	0.010	12.00	100.0

The following is a hypothetical operational Standard Operating Procedure (SOP) for a utility receiving 12 percent chemical and diluting to and using it at 6 percent.

Step 1: Determine through laboratory demand testing or your own experience how much gaseous chlorine is needed in pounds per day.

Gas feed rate (lb/day) = Flow rate (MGD) x Dosage (mg/L) x 8.34 lb/gal

– Example: Operator wants to dose at 3 mg/L to treat a flow of 24 MGD. What is the chlorinator setting in lbs/day?

– 24 MGD × 3 mg/L × 8.34 lb/gal = 600 lbs/day

Step 2: Determine the amount of hypochlorite solution in milliliters per minute - you will need to feed that amount. You need to know the strength you are using.

1. Determine solution feed rate using hypochlorite solution at 6 percent:
   Solution feed rate (lb/day) = Gas feed rate (lb/day) ÷ Percent hypochlorite
   600 lb/day ÷ 0.06 = 10,000 lb/day (ppd)

2. Convert units:
   10,000 lb/day (ppd) ÷ 8.34 lb/gal = 1199 gal/day (gpd)
   1199 gal/day ÷ 24 hr/day = 49.95 gal/hr (gph)
   49.95 gal/hr ÷ 60 min/hr = 0.83 gal/min (gpm)
   0.83 gal/min × 3,785 mL/gal = 3,151 mL/min

Step 3: Set feed pumps to deliver the needed mLs/min

- Go to Chemical Feed Pump Control Panel in chlorine room
- Choose the pump that you will feed the chemical with at this time
- Input or otherwise dial in the mLs/min using the controls
- Start the pump – the pump readout will now indicate the desired mLs/min

Step 4: Check accuracy of pump delivery using the calibration column and adjust as necessary

- The calibration column must be isolated so that all of the feed to the pump comes from it and not from the storage tank
- Allow the feed pump to draw hypochlorite from the column and time the feed for several minutes to get an accurate account of mLs/minute fed
- Adjust pump if necessary

Quality Control Checks:

- Measure chlorine residual every two hours to determine if you are meeting goals
- Have laboratory check the strength of hypochlorite
- At each shift and at plant flow rate change, be sure to use the calibration tube to determine if the correct amount of hypochlorite is being fed.
- Cycle all of the pumps at your disposal to be certain that they get their fair share of work. In this way they will be available when needed. If SCADA is available operators should develop a list on the SCADA system that tracks the hours and the change times of each pump.
- Never allow a pump or feeder and equipment to sit idle with hypochlorite solution in it. If equipment is not to be used for awhile, flush it with water.

Laboratory Jar Testing Suggestion for Small System Operators

- For jar testing: Make 2000 mg/L chlorine stock solution
  Use bleach – 5.25%, or 52,500 mg/L NaOCl, or
  52,500 mg/L NaOCl X (71/74.5) = 50,034 mg/L as Cl_2
  Add 40 mLs bleach to DI water – make up to 1 L
  (40 mL)(50,034 mg/L) = (1,000 mL)(X), so
  X = 2,000 mg/L

- Check strength of stock
  - Add 1 mL 0f 2,000 mg/L stock to DI – make up to 1 L
  - Measure residual – this solution should be 2 mg/L
  - If using different starting strength, then factor it in.

As an alternative, the lab staff can use the hypochlorite from the daytank to make stock solutions, but as the material weakens over time, it will be more difficult to make predictions.

The above procedures can be used to determine hypochlorite strength, and this should be done when each load is delivered, and as frequently as needed is the hypochlorite is kept at full strength for more than a few weeks.

And easy way to check the strength is to use fresh Clorox as described above for your starting point, and then repeat the steps with the hypochlorite from the daytank. Compare strengths to see the amount of deterioration.