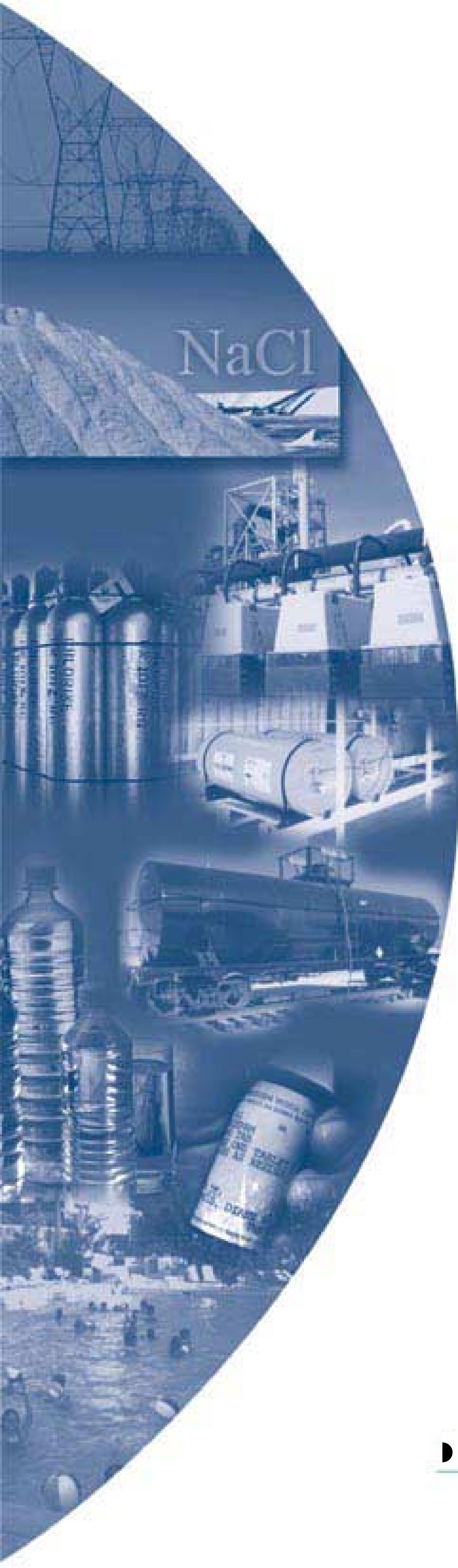

THE CHLORINE INSTITUTE, INC.

Pamphlet 96

Sodium Hypochlorite Manual

Edition 3

A LEGACY OF SAFETY STEWARDSHIP since 1924

April 2006

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1 INTRODUCTION

1.1 Scope

This publication is intended to provide useful information about sodium hypochlorite, its properties, manufacture, safe handling, packaging, transportation, and uses, and the regulations affecting these areas. This pamphlet is not intended to serve as a detailed guide for the manufacture of sodium hypochlorite, but will provide health, safety and environmental information for this operation. The same equipment used to handle and store sodium hypochlorite may not be suitable in the manufacturing process for the conditions encountered during its production. Additional information on this chemical can be found on the CI website at www.chlorineinstitute.org .

1.2 Chlorine Institute Stewardship Program

The Chlorine Institute, Inc. exists to support the chlor-alkali industry and serve the public by fostering continuous improvements to safety and the protection of human health and the environment connected with the production, distribution and use of chlorine, sodium and potassium hydroxides, and sodium hypochlorite; and the distribution and use of hydrogen chloride. This support extends to giving continued attention to the security of chlorine handling operations.

Chlorine Institute members are committed to adopting CI's safety and stewardship initiatives, including pamphlets, checklists, and incident sharing, that will assist members in achieving measurable improvement. For more information on the Institute's stewardship program, visit CI's website at www.chlorineinstitute.org.

1.3 Disclaimer

The information contained in this pamphlet is drawn from sources believed to be reliable. The Institute and its members, jointly and severally, make no guarantee and assume no liability in connection with any of this information. Moreover, it should not be assumed that every acceptable procedure is included or that special circumstances may not warrant modified or additional procedures. The user should be aware that changing technology or regulations might require a change in the recommendations herein. Appropriate steps should be taken to insure that the information is current when used. These suggestions should not be confused with federal, state, provincial, municipal or insurance requirements, or with national fire, building or safety codes.

1.4 Approval

The third edition of this document received its final review and approval by the Institute's Sodium Hypochlorite Committee on April 3, 2006.

1.5 Revisions

Suggestions for revisions should be directed to the Secretary of the Institute.

1.6 Reproduction

2 CHEMISTRY AND PHYSICAL PROPERTIES OF SODIUM HYPOCHLORITE

2.1 Formation Reaction

A sodium hypochlorite solution is formed when sodium hydroxide (caustic soda) solutions are reacted with chlorine.

Equation 1

$$Cl_2 + 2NaOH \Rightarrow NaOCl + NaCl + H_2O + \text{heat}$$

chlorine + sodium hydroxide (caustic soda) ⇒ sodium hypochlorite + sodium chloride + water

The reaction of chlorine and sodium hydroxide is highly exothermic. This must be accounted for in the design and operation of a bleach manufacturing system to prevent overheating of the bleach solutions.

A slight excess of sodium hydroxide is needed for stability (Section 5). If chlorine continues to be added during the manufacturing process after all of the sodium hydroxide has reacted according to Equation 1, then the solution becomes over chlorinated. Over chlorination is a potential problem experienced only during the manufacturing process and does not transfer to the customer as a product stability concern. See CI Pamphlet 89 for additional information on over chlorination conditions and hazards.

The temperature of sodium hypochlorite is a critical parameter and affects solution stability, both during the manufacturing stage and during storage (Section 3.8).

2.2 Purity

The purity of sodium hypochlorite is important to its stability. The raw materials must be very low in heavy metals, for example, nickel, copper, cobalt. Care should be taken in the design of storage tanks and piping to avoid contamination by these metals.

Magnesium and calcium form insoluble salts in sodium hypochlorite solutions and produce white precipitates. These can cause turbidity, but have no effect on stability. Settling and/or filtration can remove these precipitates.

Iron is often present in sodium hypochlorite solutions in concentrations as high as 0.5 to 2.0 PPM. This results in a slightly pinkish discoloration of the bleach. However, a study funded by the AWWA Research Foundation found that samples of sodium hypochlorite containing 41 PPM of iron did not appear to decompose at a higher rate over 60 days than solutions containing minimal levels of iron. Since iron has a limited solubility in sodium hypochlorite, even a solution saturated with iron would not likely enhance decomposition.

Chloride, sulfate, and carbonate anion levels normally found in raw water have negligible effects on product stability.

2.3 Strength of Solutions

There are several common ways that the concentration of sodium hypochlorite may be expressed. These are listed below along with explanations.

2.3.1 Available Chlorine

The term available chlorine came into usage as a means of comparing oxidizers in different applications. Since chlorine was among the first widely used oxidizers it became the standard against which other oxidizers are measured. As shown in Equations 1, 2a) and 2(b), sodium hypochlorite is capable of oxidizing the same amount of iodide ion, as the chlorine (Cl2) that it takes to manufacture the sodium hypochlorite.

Equation 2(a)

$$NaOCl + 2KI + 2HAc \Rightarrow I_2 + NaCl + 2KAc + H_2O$$

This may be compared with the reaction of chlorine with potassium iodide:

Equation 2(b)

$$Cl_2 + 2KI \Rightarrow I_2 + 2KCl$$

One molecule of hypochlorite ion has the equivalent oxidizing power of two atoms (1 molecule) of chlorine. Therefore sodium hypochlorite behaves as if all of the chlorine consumed in making it is "available" for oxidizing purposes, even though half of that chlorine is in the chloride form (Equation 1).

The term "available chlorine" refers to the amount of chlorine equivalent, in the sense of oxidizing power as described above, to hypochlorite. It is a measure of strength and bleaching power and, in one or another of its related units of measurement, denotes the concentration of the bleach solution.

2.3.1.1 Grams per Liter (gpl) Available Chlorine

The weight of available chlorine, in grams contained in one liter of sodium hypochlorite solution.

2.3.1.2 Trade Percent Available Chlorine

Commonly used to denote the strength of commercial sodium hypochlorite solutions, is similar to grams per liter, except that the unit of volume is 100 milliliters instead of one liter. Its value is therefore one tenth of the grams per liter. This is also sometimes referred to as “available chlorine volume percent”.

Equation 3

$$\text{trade percent available chlorine} = \frac{\text{gpl available chlorine}}{10}$$

2.3.1.3 Weight percent available chlorine

Dividing trade percent by the specific gravity of the sodium hypochlorite solution gives weight percent, or percent available chlorine by weight.

Equation 4(a)

$$\text{weight percent available chlorine} = \frac{\text{gpl available chlorine}}{10 \times (\text{specific gravity of solution})}$$

Equation 4(a)

$$\text{weight percent available chlorine} = \frac{\text{trade percent available chlorine}}{(\text{specific gravity of solution})}$$

2.3.2 Sodium Hypochlorite

To facilitate a variety of calculations and operation in different chemical process, it is often important to know the concentration of the actual chemical species, NaOCl, in sodium hypochlorite solutions. In addition, *weight percent sodium hypochlorite* must be displayed on FIFRA registered pesticide products.

Weight percent of sodium hypochlorite is defined as the weight of sodium hypochlorite per 100 parts by weight of bleach solution. It may be calculated by converting weight percent of available chlorine into its equivalent as sodium hypochlorite; that is, multiplying by the ratio of their respective molecular weights as shown below:

$$\frac{\text{molecular wt. NaOCl}}{\text{molecular wt. } Cl_2} = \frac{74.44}{70.91} = 1.05$$

Equation 5(a)

$$\text{wt.\% NaOCl} = (\text{wt. \% available } Cl_2) \times \frac{\text{molecular wt. NaOCl}}{\text{molecular wt. Cl2}}$$

OR

$$\text{wt.\% NaOCl} = \text{wt. \% available chlorine} \times 1.05$$

Equation 5(b)

$$\text{wt. \% NaOCl} = \frac{\text{gpl available chlorine}}{10 \times (\text{specific gravity})} \times 1.05 = \text{wt. \% available chlorine} \times 1.05$$

OR

Equation 5(c)

$$\text{wt. \% NaOCl} = \frac{\text{trade \% available chlorine} \times 1.05}{(\text{specific gravity})}$$

Generally sodium hypochlorite solutions are produced at strengths up to 20 percent by weight sodium hypochlorite. As strength increases, stability generally decreases. Frequently manufacturers provide a range of strengths depending on customer requirements. Typically bleach solutions with strength of less than 7.0 weight percent sodium hypochlorite are used in household bleach applications.

2.4 AQUEOUS CHEMISTRY

Sodium hypochlorite exists as sodium and hypochlorite ions in water.

Equation 6

$$NaOCl \Rightarrow Na^{+} + OCl^{-}$$

sodium hypochlorite ⇒ sodium ion + hypochlorite ion

The sodium ion does not undergo further change but the hypochlorite ion can either remain as is, react with one of numerous materials or if the pH is low enough form hypochlorous acid.

Equation 7

$$OCl- + H+ \Rightarrow HOCl$$

hypochlorite ion + hydrogen ion ⇒ hypochlorous acid

This reaction becomes significant at a pH of 9 or less and a ratio of hypochlorite ion to hypochlorous acid exists until the pH is about 6 where virtually no hypochlorite ion exists. This pH decreases as the concentration of available chlorine decreases. If a strong mineral acid is added in quantities that can cause a rapid pH drop, elemental chlorine can be released as noted in Equation 8.

Equation 8

$$H^{+} + NaCl + HOCl \Rightarrow Na^{+} + H_2O + Cl_2$$

If the concentration of elemental chlorine exceeds its solubility at any temperature, some chlorine gas may be liberated from the solution (Institute's *Chlorine Manual*, Figure 9.3). As the pH is reduced gradually via excessive chlorination, chlorate ions form at significant rates.

2.5 REACTIONS OF SODIUM HYPOCHLORITE

Sodium hypochlorite in aqueous solutions will react and produce the same results as elemental chlorine in aqueous solutions as long as the concentration of available chlorine, the temperature and the pH are the same.

Unlike elemental chlorine, sodium hypochlorite adds alkalinity to a solution. Elemental chlorine removes alkalinity. This can be very important in the destruction of cyanides or sulfides where acidic conditions could release toxic hydrogen cyanide gas or hydrogen sulfide gas.

2.6 Dangerous Reactions of Sodium Hypochlorite

2.6.1 Reaction with Acids

Sodium hypochlorite solutions must not be mixed with acids. Excess acidity will enable the hypochlorite ion to form chlorine gas and evolve from the solution. A serious chlorine release can result (Section 2.4, Equation 8).

2.6.2 Reaction with Ammonia Compounds

Sodium hypochlorite solutions must never be mixed with any ammonia solutions or solids or solutions containing ammonia salts such as those found in many common household cleaners. Both toxic and hazardous gases can be formed.

2.6.3 Reaction with Organic Compounds

Solutions of sodium hypochlorite may react violently with many organic compounds including greases, oils, fuels, etc. Care must be taken to avoid contact between sodium hypochlorite and these types of compounds unless you are certain they are compatible or adequate engineering controls and personal protective equipment (PPE) are employed.

2.6.4 Other Chlorinating Compounds

Care must be taken when storing or using sodium hypochlorite solutions in conjunction with other chlorinating compounds. In swimming pool applications, never attempt to pre-blend sodium hypochlorite solutions with concentrated forms of any chemicals including other chlorinating compounds. Concentrated forms of these compounds may react violently with water or sodium hypochlorite solutions.

2.7 Vapor Pressure of 12.5% Sodium Hypochlorite Solutions

Table 2-1 illustrates temperature/vapor pressure data from one study.

Some speculation exists on the exact chlorine species that are present in the vapor. However, oxygen may be one of the components due to catalytic decomposition of the sodium hypochlorite (Equation 11, Section 3.2.2). The vapor pressures of sodium hypochlorite solutions that are not decomposing due to metal catalysis are less than the vapor pressure of water at the same temperature. This is a normal phenomenon caused when salts are dissolved in water. Hypochlorous acid and chlorine monoxide are believed to be the predominate chlorine species in the vapor phase above sodium hypochlorite solutions under normal conditions.

Table 2-1. Vapor Pressure Measurements for 12.5% Weight Percent Sodium Hypochlorite Solution			
Temperature (°F)	**Temperature (°C)**	**Vapor Pressure (mm Hg)**	**Vapor Pressure (psia)**
48.2	9	3.7	0.071
60.8	16	8.0	0.15
68	20	12.1	0.23
89.6	32	31.1	0.60
118.4	48	100	1.93

2.8 SPECIFIC GRAVITY OF SODIUM HYPOCHLORITE SOLUTIONS

The specific gravity of sodium hypochlorite solutions is dependant on the following variables:

Temperature
GPL Available Chlorine in solution
GPL Sodium Chloride in solution – The amount of sodium chloride will vary due to type of caustic used, sodium chlorate levels, and type of manufacturing process.
GPL Sodium Chlorate in solution

Therefore, the specific gravities (SG) of sodium hypochlorite solutions are determined by direct measurement (Sections 11.3). This measured property will vary depending on the chemical composition of the product and may have no relationship to the product quality.

Table 2.2 shows the typical specific gravity of sodium hypochlorite solutions under the following conditions:

68°F/20°C
Sodium Chloride levels only from the reaction of chlorine and caustic and no salt from chlorate formation.
No Sodium Chlorate in solution (100% efficient reaction without chlorate reaction).

Specific gravity is not an indication of sodium hypochlorite quality or strength and should not be specified in product quality requirements.

Table 2-2. Specific Gravity of Sodium Hypochlorite Solutions With Various Levels of Excess NaOH @ 20°C						
gpl Available Chlorine	gpl Excess Sodium Hydroxide (NaOH)					
	0	2	4	6	8	10
6.0	1.082	1.085	1.087	1.090	1.093	1.096
8.0	1.107	1.110	1.112	1.115	1.118	1.121
10.0	1.132	1.135	1.137	1.140	1.143	1.146
12.0	1.157	1.160	1.162	1.165	1.168	1.171
14.0	1.180	1.183	1.185	1.188	1.191	1.194
15.0	1.192	1.195	1.197	1.200	1.203	1.205
16.0	1.204	1.207	1.209	1.212	1.215	1.218
18.0	1.227	1.230	1.232	1.235	1.238	1.241
20.0	1.249	1.252	1.254	1.257	1.260	1.263

The specific gravities for the solutions shown in Table 2-2 were calculated using Equation 9 below. In this calculation, a correction factor, developed from experimental data, is added to the measured specific gravity of sodium hypochlorite solutions that contain no excess sodium hydroxide. Good agreement has been found between the measured SG for hypochlorite solutions containing excess caustic soda and the calculated SG using this equation.

Equation 9

SG NaOCl Sol. w/Excess NaOH = SG NaOCl Sol. w/o Excess NaOH + (0.00135 x gpl excess NaOH)

2.9 APPROXIMATE FREEZING POINT OF SODIUM HYPOCHLORITE SOLUTIONS

Sodium hypochlorite solutions will freeze at different temperatures depending upon strength.

Table 2-3. Approximate Freezing Points of Sodium Hypochlorite Solutions*		
Weight Percent NaOCl	**Freezing Point (°F)**	**Freezing Point (°C)**
2	28.0	-2.2
4	24.0	-4.4
6	18.5	-7.5
8	14.0	-10.0
10	7.0	-13.9
12	-3.0	-19.4
14	-14.0	-25.6
15.6	-21.5	-29.7
16	-16.5	-26.9

* Data obtained from a graph produced by the Dow Chemical Company.

Freezing is accompanied by expansion that can damage equipment. However, the solutions can be thawed without adverse impact on quality. Under some conditions (especially for solutions above 10% sodium hypochlorite), freezing of hypochlorite solutions may result in precipitation of sodium chloride and/or sodium hypochlorite. If solids should precipitate, care should be taken to prevent interruption of operations or damage to handling equipment.

2.10 Sodium Chlorate Crystals

Bleach solutions, especially higher concentrations, that are allowed to dry completely can contain sodium chlorate crystals. For example, as bleach around pump seals dries and decomposes, the resulting white powder can contain high levels of sodium chlorate in addition to sodium chloride solids. This is due to the elevated temperatures at pump seal faces (on outside seals this is more common.)

If the dry powder is impacted, such as being struck by a hammer, during the disassembly of the seal or pump head, the chlorate can explode or ignite and seriously injure anyone near by.

If this powder is present, wash the equipment and the area with large volumes of water into a drain. Run extra water to thoroughly flush the drain. Any clothing or shoes that are contaminated with a solution of this sodium chlorate must be washed immediately before they dry. Any spark or heat source can ignite cloth or shoes if significant residual sodium chlorate is present when the item dries. Shoes may need to be soaked in water for extended periods.

3 STABILITY OF HYPOCHLORITE SOLUTIONS

3.1 General

There are many factors affecting the stability of hypochlorite solutions. As a general rule, lower concentration solutions are more stable than higher strength solutions. This assumes that other conditions such as storage temperatures, pH and metal ion concentrations are similar.

Decomposition of hypochlorite solutions cannot be avoided, but the rate of decomposition can be altered. The major factors affecting stability are as follows:

- concentration of the hypochlorite solution
- temperature of the solution
- contact with catalyzing metallic impurities
- pH of the solution
- exposure to light sources
- ionic strength of the solution

- contact with organic impurities

3.2 BLEACH DECOMPOSITION REACTIONS

Bleach loses its strength by two decomposition pathways. Under normal conditions, the dominant pathway leads to the formation of chlorate and chloride ion, and a slower second bleach decomposition pathway leads to oxygen and chloride formation.

3.2.1 Chlorate Ion (ClO_3^-) Formation

Equation 10

$$3OCl^- \Rightarrow ClO_3^- + 2Cl^-$$

hypochlorite ion chlorate ion chloride ion

The decomposition of OCl^- involves chlorite ion (ClO_2^-) as an intermediate in the following generally accepted mechanism:

Equation 10(a)

$$OCl^- + OCl^- \Rightarrow ClO_2^- + Cl^-$$

Equation 10(b)

$$OCl^- + ClO_2^- \Rightarrow ClO_3^- + Cl^-$$

3.2.2 Oxygen (O_2) Formation

The formation of oxygen from decomposing OCl^- is a very slow side reaction. However, in the presence of transition metal ions the rate of bleach decomposition by the oxygen pathway is increased.

Equation 11

$$OCl^- + OCl^- \Rightarrow O_2 + 2Cl^-$$

3.3 CONCENTRATION EFFECT

Bleach decomposition is 2^{nd} order with respect to NaOCl concentration (Section 3.9). The second order rate law predicts that diluting the NaOCl by a factor of 2 should decrease the rate of NaOCl decomposition by a factor of 4. However, actual decomposition data for sodium hypochlorite solutions shows that a factor of 2 decrease in NaOCl concentration results in an approximate factor of 5 decrease in the rate of decomposition. This is because of the effect on the decomposition rate by the decrease in the total ionic concentration of the solution. Since the dilution of a bleach solution not only decreases the NaOCl concentration but also decreases the concentration of all the ions in the solution (chloride ions, the chlorate ions, hydroxide ions, etc.), the total ionic strength is also decreased and further reduces the decomposition rate.

3.4 EFFECT OF TRANSITION METAL IONS

It is well known that the presence of certain transition metal ions (such as Ni^{2+}, Cu^{2+} and Co^{2+}) in bleach results in oxygen formation. The magnitude of the transition metal ion contamination during bleach manufacturing depends both upon the purity of the NaOH (caustic) solution and the dilution water used in manufacture of the bleach solution. Filtration can be used to remove transition metal ions from bleach. Metal contamination can also be introduced during handling and storage of bleach solutions. Materials of construction, lubricants, etc. for piping, storage and transportation systems, including pumps and instrumentation, must be selected carefully to avoid contamination.

Studies have shown decomposition of NaOCl can be significantly lowered by reducing the level of nickel and copper in addition to removal of suspended solids. Reduction of these contaminates can be done by filtration. There is a direct correlation between the reduction of suspended solids and reduction of heavy metals.

Therefore, final filtration of the NaOCl prior to storage is helpful in improving its quality. Filtration in the range of 0.2 to 0.5 micron absolute is the best range of particle removal. Testing the NaOCl with a standardized suspended solids test provides a repeatable quality control method to indicate bleach quality.

3.5 UV-LIGHT EFFECT

In the presence of UV-light, sodium hypochlorite will decompose with the major products being O_2 and chlorate ion. Storage tanks and vessels which do not transmit UV-light (metals walls, coated plastics or FRP) and opaque non-bulk containers will prevent or minimize this form of bleach solution decomposition.

3.6 EFFECT OF ANIONS

Certain soluble negative ions have an adverse effect on the stability of sodium hypochlorite if they are added to these solutions and are listed here in the order of maximum to minimum effect: chlorate, chloride, nitrate, and carbonate.

In most situations the impact of these ions is small, see Section 3.3. Ammonia and ammonium compounds increase the rate of the decomposition through other reactions (see Section 2.6.2).

3.7 PH EFFECT

The pH of the sodium hypochlorite solution is an important factor affecting stability. Solutions stored at a pH of 11.9 to 13 are the most stable in typical applications. This corresponds to a range of approximately 0.025% to 0.35% by weight of excess sodium hydroxide in a sodium hypochlorite solution with a concentration of 12 trade percent available chlorine. Therefore, excess sodium hydroxide usually is maintained to prevent decomposition. In some applications, a pH range from 11 to 11.9 may be acceptable depending on manufacturing process and the storage time until it is used. Below a pH of 10.8, the rate of decomposition begins to increase significantly reaching a maximum decomposition rate in the 5-9 pH range because of the very rapid acid catalyzed decomposition.

It is important to note that decomposition also begins to increase at pH above 13. This is due to an increase in the ionic strength of the solution caused by the increasing level of excess caustic soda (NaOH).

When diluting higher strength sodium hypochlorite solutions care should be taken to ensure that minimum levels of excess sodium hydroxide are maintained. Consult with your supplier and review Appendix C of this pamphlet on dilution of sodium hypochlorite solutions, for additional information.

3.8 TEMPERATURE EFFECT

The temperature at which sodium hypochlorite solutions are manufactured, shipped and stored greatly influences their stability because bleach decomposition accelerates as temperature increases. For example, a generally used "rule-of-thumb" would predict a doubling of the decomposition rate for every 10°C (18°F) rise in temperature. However, studies of sodium hypochlorite solutions have shown that the decomposition rate increases by a factor in the range of 3 to 4 times for every 10°C for solutions in the range of 5% to 16% by weight of sodium hypochlorite, which is not unusual. Table 3-1 shows the change in the decomposition rate for a 15 weight percent sodium hypochlorite solution over a temperature range of 25°C to 45°C.

Table 3-1. Rate Constants for Sodium Hypochlorite Decomposition*

	Wt% NaOCl				
Temperature	15.89%	13.46%	10.82%	7.93%	4.74%
131°F (55°C)	250	189	138	98.2	65.5
113°F (45°C)	80.7	58.7	43.9	30.2	19.3
95°F (35°C)	23.1	17.0	12.2	8.43	5.45
77°F (25°C)	6.33	4.68	3.22	2.19	1.58
59°F (15°C)	1.65	1.15	0.8	0.53	0.30

* Data supplied by Powell Fabrication & Manufacturing, St. Louis, MI

Application use: sodium hypochlorite stored at 15°C will decompose 14 times slower than sodium hypochlorite when stored at 35°C.

Storage of sodium hypochlorite at low temperatures such as 15°C will greatly reduce decomposition of sodium hypochlorite for any practical application in strength ranging from 10 – 16% by weight sodium hypochlorite. With decrease temperatures to 5 degrees C and no heavy metal contamination, the decomposition of the sodium hypochlorite will be virtually eliminated.

3.9 ESTIMATING THE DECOMPOSITION RATE

The following equations were developed for an EPA FIFRA registration for sodium hypochlorite from experimental data and may be used for *estimating* the decomposition of sodium hypochlorite solutions that meet the following criteria. This estimate is not an exact measure of the decomposition rate. For a better result based on this chemistry, visit the website of Powell Fabrication and Manufacturing Company in St. Louis, Michigan. Also, the AWWA (American Water Works Association) published a document titled "Minimizing Chlorate Ion Formation in Drinking Water When Hypochlorite is the Chlorinating Agent." Copyright 1995 ISBN 0-89867-781-5.

- C_o: 10% to 15.5%
- T: 55°F to 85°F
- O: 28 days to 140 days

Equation 12 allows one to calculate the current concentration based on initial concentration time elapsed and storage temperature.

Equation 12

$$\ln C = \ln C_o - K C_o^{3} \Theta$$

The calculation for determining the decomposition rate constant for a given temperature in Equation 12 is:

Equation 13

$$\ln K = 18.56 \ln T - 129.65$$

Definitions of the terms used in Equations 12 and 13 are listed below:

- C = final concentration (percent available chlorine)
- C_o = initial concentration (percent available chlorine)
- K = decomposition rate constant
- Θ = aging time (in days)
- T = temperature [degrees Rankine (°F + 460)]
- ln = natural logarithm

The above equations assume good practice in preparation of the solutions with respect to variables such as excess caustic, concentration of heavy metals, exposure to sunlight, and adequate filtration.

To estimate the decomposition rate of sodium hypochlorite solutions at conditions other than those listed at the beginning of this section, contact the American Water Works Association (AWWA) in Denver, Colorado and request their publication "Minimizing Chlorate Formation in Drinking Water when Hypochlorite Ion is the Chlorinating Agent (Section C.3.1). This publication provides detailed descriptions and calculation methods to accurately estimate the decomposition rate of sodium hypochlorite solutions over a wide range of concentrations and temperatures.

4 OVERVIEW OF PRODUCTION METHODS FOR SODIUM HYPOCHLORITE

4.1 OVERVIEW

The objective of this section of the pamphlet is to highlight special design and operating considerations to help ensure safe and environmentally sound operation of bleach manufacturing facilities. These considerations should be a part of any new plant designs as well as part of any process safety management program, including hazard/risk analysis, for an on-going operation. These listing are not all inclusive and each facility should thoroughly review its own individual system to insure proper design and operation.

Sodium hypochlorite is produced by adding chlorine to a solution of sodium hydroxide. There are hazards associated with both these raw materials as well as the final product. These should be understood and accounted for to ensure safe, reliable and environmentally sound operation. In addition to the information presented here, there are a number of other Chlorine Institute Pamphlets that should be followed when working with systems containing either chlorine or sodium hydroxide, see the C.I. Chlor-Alkali Technical and Safety Resources Catalog.

Sodium hypochlorite is primarily manufactured by two basic methods, batch or continuous. There are many variations on both types of processes. In the batch system, chlorine is injected into a fixed volume of sodium hydroxide solution that has been diluted to a predetermined concentration under controlled temperature conditions. Once the correct amount of chlorine has been introduced, the process is stopped resulting in a tank containing sodium hypochlorite solution.

In the continuous or steady state process, chlorine is injected into a reaction chamber or pipe where it is mixed with dilute sodium hydroxide solution that is being continuously pumped into the system. The resulting chemical reaction yields a solution of sodium hypochlorite. Cooling is needed downstream of the reaction chamber to remove the heat generated during the reaction.

Steady state sodium hypochlorite production units typically consist of two basic units, the caustic dilution system and the chlorine addition system.

A third technology can be used to produce low concentrations of sodium hypochlorite solutions. This manufacturing method utilizes a sodium chloride feed to an electrochemical cell where the salt is converted to sodium hypochlorite using electricity. Typically these units produce bleach solutions in the range of 0.5% to 1.0% weight% sodium hypochlorite.

The detailed design of these manufacturing systems is beyond the scope of this pamphlet. Consult engineering and systems suppliers for additional information.

4.2 TRAINING

Each company should provide appropriate and specific training for personnel responsible for operating and maintaining a bleach manufacturing facility. It is important to develop and maintain qualification criteria for operating and maintenance personnel. Those criteria will include but are not limited to product, process, and regulatory knowledge as well as specific work skills. See Chlorine Institute video, Handling Sodium Hypochlorite Safely.

4.2.1 Individual Safety Training

Individuals involved in the production of sodium hypochlorite should be trained in the:

- proper use and care of personal safety equipment such as respirators, protective clothing, hard hats, safety glasses, chemical goggles, boots, and gloves.
- proper use of emergency equipment such as safety showers, eye wash stations, and self-contained breathing apparatus.
- proper use and care of emergency response equipment for those involved and authorized to execute emergency response plans.
- the hazards and safe handling practices associated with all the materials involved with bleach production process, including chlorine, sodium hydroxide and sodium hypochlorite.

4.2.2 Operating Procedures

Operating procedures should cover the following situations:

- routine startup
- routine shutdown
- routine operations
- emergency operations and shutdown
- inspection, testing and maintenance

4.3 DESIGN AND OPERATING GUIDELINES

4.3.1 Production Systems

One of the most important design and operating considerations that should be considered in a bleach production process is the prevention of the release of chlorine gas or liquid. Means to accomplish this in the chlorine handling system include redundant instrumentation, installed spare equipment, scrubbing systems, specific operating procedures and preventive maintenance programs. See Chlorine Institute publications pertaining to the design and operation of chlorine systems.

Chlorine can also be released from the reaction equipment if the material is over chlorinated (Section 2.1). Means to prevent or respond to an overchlorination condition include:

- The use of redundant instrumentation such as ORP to monitor the chlorination reaction with adequate back up instrumentation and manual analysis of the bleach solution to measure excess caustic soda.

- A means to prevent hypochlorite or caustic solutions from flowing back into the chlorine lines such as flow interlocks, vacuum breaks, duplicate valves and barometric loops. It should be noted that barometric loops are effective back flow prevention devices for vacuum systems but can be defeated by positive pressure pump systems. Designed, installed and maintained correctly, these devices will effectively prevent back flow of solution into the chlorine system.

- Continuous atmospheric chlorine monitors connected to alarms and/or shutdown systems.

Other design and operating guidelines include:

- Materials of construction selection and inspection programs consistent with the process under both design and upset conditions (e.g. if titanium, which is excellent in wet chlorine, is allowed to contact dry chlorine, spontaneous combustion will result). See Section 6.

- Use of temperature monitoring/control systems to prevent overheating of the sodium hypochlorite solution.

- Limit access to process, storage and handling areas to authorized personnel. Regulations may require containment and or restrictive barriers to minimize or eliminate exposure risks.

4.3.2 Critical Utilities

The plant should be designed so that loss of primary power and/or any other key utility (e.g. instrument air, electric, cooling water, etc.) would not result in a chlorine release.

4.3.3 Instrumentation

Adequate instrumentation should be provided for monitoring, analyzing, recording, and controlling all critical operating parameters in the sodium hypochlorite production process. This may include:

- chlorine detector(s) and alarms

- flow indication and a low-flow alarm for any circulating absorption/neutralizing chemical

- indication of abnormal chlorine feed to the chlorination system and safeguards to prevent accidental chlorine automatic valve opening

- caustic concentration in chlorination reactor system

- abnormal chlorine concentration in process vent streams

- process and storage tank levels

- status of chlorine unloading and handling systems

- caustic and bleach temperature controls
- indication of flow and/or mixing problems in the chlorination reactor system
- oxidation/reduction potential (ORP)

Instruments should be designed to fail in the fail-safe mode. For example, control valves should fail in the open position, the closed position, or the current operating position dependent on which mode provides for the least risk of a chemical release or adverse reaction. In addition, a plant-wide alarm system can be used to notify personnel of hazards.

When continuous sodium hypochlorite generator systems are used, these units will generally have redundant ORP sensors, transmitters and alarms to prevent over-chlorination of the sodium hydroxide. Other recommended instrumentation for these systems includes:

- an automatic block valve upstream of the chlorine control valve to stop the flow of chlorine and sodium hydroxide pressure alarms
- product to storage flow alarms
- high reaction temperature alarms

4.3.4 Process Chemicals

4.3.4.1 Dilution Water

The quality of the dilution water directly influences sodium hypochlorite purity as well as its stability.

4.3.4.2 Sodium Hydroxide

The quality of the sodium hydroxide may affect the quality of the sodium hypochlorite depending on the production process used.

The major contaminant in sodium hydroxide that can adversely affect sodium hypochlorite is nickel. Nickel is a contaminate and is most common in caustic made from the diaphragm cell process. It can exist in caustic made from the membrane cell caustic, but at typically lower levels. These two caustics can be contaminated with nickel during the evaporation process. Caustic made from the mercury cell process has the least nickel typically found in any of the three types since it is produced at 50% concentrations and does not require evaporation.

Nickel and other metals such as copper and cobalt can reduce the stability of the sodium hypochlorite solutions, etc.

The transition metals can reduce the stability of sodium hypochlorite solutions and cause oxygen generation or “gassing” problems (Section 3.4). If the oxygen generation becomes excessive it can cause equipment damage or rupture. If excessive amounts of sodium carbonate are present in the caustic solution, it may interfere with the chlorination endpoint measurement/analysis and lead to an over chlorination.

Generally sodium hydroxide is purchased as a 50% solution by weight. This is then diluted to produce the final sodium hypochlorite strength desired. Automated dilution control systems are available.

The dilution of sodium hydroxide is very exothermic. It is important to take this into account in system designs, operating procedures and selection of PPE. As a general rule, sodium hydroxide should always be added to the water and never add water to the sodium hydroxide solution.

4.3.4.3 Chlorine

Chlorine is generally shipped as a liquefied gas under pressure. This material must be transferred to the sodium hypochlorite production system in piping and equipment specifically designed and maintained for this service.

This requires knowledge of the properties of chlorine as well as the handling and operating practices that are recommended by the Chlorine Institute.

a) Chlorine Railcar/Truck Unloading Systems

Those bleach producers who unload bulk chlorine from truck or railcar stations, should be following the guidelines given in Chlorine Institute Pamphlet 49, Recommended Practices for Handling Bulk Highway Transports and Pamphlet 66, Recommended Practices For Handling Chlorine Tank Cars. (Note: if ton containers are used as the chlorine source, contact The Chlorine Institute for applicable reference information.) Personnel involved in the unloading operation should be properly trained in vessel connection and disconnection procedures, as well as emergency procedures. Unloading system design and operating considerations include:

- an evacuation or absorption system (i.e. a vent scrubber system) or other means of purging the transfer piping after shutoff and during disconnection.
- an emergency response plan including the location of self-contained breathing apparatus, protective clothing, an Emergency C Kit.
- atmospheric chlorine monitors and alarms and leak detection means such as a plastic squeeze bottle of aqua ammonia (ammonium hydroxide solution).
- if a pad gas (nitrogen or dry air) system is used it must be moisture and contaminant free and have a means to prevent back flow of chlorine into the pad system.
- adequate lighting and appropriate weather protection especially in emergency situations.
- an emergency shut-off system designed to remotely isolate the chlorine railcar/truck and transfer piping (See C.I. Pamphlet 57).

b) Chlorine Piping Systems

Chlorine piping systems should be designed in accordance with Chlorine Institute guidelines found in Pamphlet 6, Piping Systems For Dry Chlorine. These systems must be protected from the intrusion of moisture as it can cause severe corrosion and premature failure. All disconnected pipes and fittings should be covered or plugged to prevent exposure to excess moisture.

c) Chlorine Feed Systems

Chlorine can be fed to the sodium hypochlorite reaction chamber or vessel as a liquid or a gas. A vaporizer system may be required to convert the chlorine from a liquid to a gas, see Chlorine Institute Pamphlet 9, Chlorine Vaporizing Equipment. There are specific conditions and criteria that should be met to ensure safe, reliable and environmentally sound operation of these systems, contact your equipment supplier or the Chlorine Institute for additional information.

In general, the control scheme in a sodium hypochlorite production unit is based on adjusting the chlorine flow to react with a fixed volume or flow of sodium hydroxide. . There are several ways to adjust the amount and rate of chlorine added to the system, including:

- Oxidation/reduction potential (ORP) control systems where an ORP measurement in the reaction tank or chamber discharge monitors the alkalinity in the sodium hypochlorite solution and can be used to adjust the chlorine flow. It is important to have the correctly constructed ORP electrodes and meter properly set for the desired parameters. Direct contact platinum and silver electrodes work very well and can be used for both sodium hypochlorite production and for chlorine scrubbers as well.

- Analytical control methods where samples of the product during production are taken and analyzed for the excess sodium hydroxide using the analytical procedures described in Section 11.6. With this control system, care must be taken not to over chlorinate the product as the batch nears the endpoint of the reaction.

It is important to note that the rate of chlorine addition to a fixed volume or flow of sodium hydroxide will determine the cooling requirements of the reactor system. If the solution temperature gets too high, the sodium hypochlorite solution stability will be adversely affected.

4.3.5 Emergency Scrubber Systems

Since chlorine is a primary raw material for the manufacture of sodium hypochlorite and potentially released from the over chlorination or acidification of bleach, a means to prevent discharge of chlorine to the atmosphere such as a scrubbing system should be considered. Chlorine Institute Pamphlet 89, Chlorine Scrubbing Systems, describes alternate scrubber systems.

5 ADDITIONAL SAFETY CONSIDERATIONS

Key safety information is provided throughout this document in what the Institute believes is the most appropriate location for specific information. This section includes additional information not covered elsewhere.

5.1 General

All persons who manufacture, distribute, store or use sodium hypochlorite solution should have in their possession and be thoroughly familiar with the Material Safety Data Sheet (MSDS). The product's MSDS contains information regarding its chemical characteristics, physical hazards, health hazards, first aid, transportation information, fire fighting information and environmental information. Contact a manufacturer of sodium hypochlorite solutions or the Chlorine Institute for assistance in obtaining this information.

Sodium hypochlorite will also react with acids, ammonium hydroxide (ammonia water) or cleaners containing ammonia compounds to produce hazardous gases. Sodium hypochlorite solutions may also react violently with some organic compounds. Care must be taken to prevent mixing of these non-compatible compounds. See Chlorine Institute website for further information on mixing of sodium hypochlorite with other materials.

Sodium hypochlorite decomposes when exposed to heat. If sodium hypochlorite solutions are contaminated, a vigorous reaction along with a pressure build-up is possible if the product decomposes in the container (Section 2.6 and 3.4). Vented closures can be used when storing industrial strength sodium hypochlorite solutions to avoid excessive pressure build up. Most household bleach containers do not have vented caps. Care must be taken when opening these containers to make certain excess pressure is not present. Although spraying of the product is unlikely, eyes and skin must be protected if the container is under pressure.

Sodium hypochlorite can cause damage to skin and eyes. Proper safety equipment must be worn when handling sodium hypochlorite solutions. This could include the use of respiratory equipment when necessary (if fumes are present), goggles, impervious gloves, boots and aprons. For household bleach refer to label directions for proper handling instructions.

5.2 Precautions for Handling Sodium Hypochlorite Solutions

Precaution for handling sodium hypochlorite solutions include:

- Keep container closed when not in use.
- Insure adequate ventilation or use an approved appropriate respiratory protection mask.
- Avoid breathing fumes.
- Avoid contact with eyes, skin and clothing.
- Wash thoroughly after handling.

- Wear appropriate personal protective equipment which may include goggles and face-shield, impervious gloves, boots and apron or suit when handling this product.
- Do not allow contact with organic materials (e.g. rags, wood fibers, paper debris, etc.) or reducing chemicals except under controlled conditions. Do not discard indiscriminately. A spontaneous combustion (fire) could result.
- Do not mix with acids, ammonia or reducing agents. To do so may release hazardous gases or cause a violent reaction.

6 HANDLING, STORAGE AND EQUIPMENT

6.1 GENERAL GUIDELINES

6.1.1 Handling

Anyone working with sodium hypochlorite should be aware of the precautions necessary for its safe handling, storage, and use. Avoid all direct contact with sodium hypochlorite solution. It is irritating to the eyes, skin, and mucous membranes.

6.1.2 Storage and Equipment

Relatively few materials of construction can withstand the highly reactive nature of sodium hypochlorite. Improper selection of materials may result in damage to equipment and contamination of the product. As a general rule, do not allow metals (except for titanium and tantalum) to come in contact with sodium hypochlorite.

6.1.3 Site Selection and Preparation

While federal regulations only broadly address site selection and preparation issues, some state and local agencies have specific construction requirements for hazardous materials storage and handling facilities. These requirements are typically part of fire regulations and/or building codes. In the absence of specific requirements, the location for storage and handling system should be selected so as to limit access to unauthorized personnel and to allow containment in the event of accidental spillage.

6.2 STORAGE CONTAINERS

6.2.1 Drums

Sodium hypochlorite solution is often shipped in 55 gallon and smaller drums. While considered shipping containers, they can also serve as storage containers. Please refer to Section 7 on drumming and Appendix B for information on regulations related to the shipping of sodium hypochlorite.

6.2.2 Bulk Storage Tanks

Tanks and tank lining materials can vary considerably in their suitability and performance. Before selecting an appropriate storage vessel, be sure to perform a thorough and complete evaluation of potential alternatives. Consultation with suppliers of tanks and lining materials, and obtaining recommendations from those using their products in similar applications is recommended.

Sodium hypochlorite solutions will decompose with age. They can also leave sediment in the bottom of storage vessels. (Section 2.2 and 3.8) To avoid transferring this sediment into the process, locate the primary discharge nozzle 1 to 3 feet above the bottom of the tank. An additional discharge point, located as close to the bottom as possible, will allow for complete drainage and periodic cleaning. Cone bottom tanks can facilitate removal of sediment. Filtration systems are available to remove virtually all sediments.

6.2.2.1 Inlet Piping

Fill lines should be sized to allow flow rates of approximately 150 to 250 gallons per minute at a truck discharge pressure of approximately 30 psig. Where possible, avoid low points or install drain valves to prevent product contamination from previous deliveries. Connect the inlet piping to the storage tank near or on top of the vessel. Vertical discharge into the tank will minimize lateral stress on the tank and its piping systems.

6.2.2.2 Venting/Overflow System

A venting system must be in place to eliminate excessive pressure or vacuum when filling or discharging from the tank. At a minimum, the system should have a vent on top of the tank sized at twice the inlet diameter. When filling the tank from bulk trucks with air pressure, air hammer may occur. Secure all vent and product piping to minimize vibration. The tank should be designed to prevent overfilling. Install piping to direct the overflowing liquid away from personnel into a containment area.

6.2.2.3 Gauging Devices

Some tank materials are sufficiently translucent to permit visual gauging from level markers painted or molded on the side of the tank. Where lighting conditions or tank construction do not permit this, an external gauging system is necessary. Differential pressure or radar systems are usually specified. Manometers and sight glass gauges are also suitable, but require additional liquid-filled potential failure points. These devices must also be protected from accidental contact that might crack or break them. An independent, back-up level sensor should be in service to prevent tank overflow in the event of level gauge failure. Installation of a high level liquidation alarm is recommended. Some state or local regulations may require two step alarms.

6.2.2.4 Materials of Construction

a) Rubber-Lined Steel

Tanks of this type are generally custom fabricated for a specific process. They may be any size or shape depending on the needs of the user, but are typically atmospheric vertical or horizontal cylindrical vessels from 1,000 to 30,000 gallons capacity. Some have a capacity up to or exceeding 250,000 gallons.

b) Fiberglass

The success or failure of this type of tank when used in sodium hypochlorite service depends upon a large number of variables including resin type and additives, fabrication technique, storage temperature, environmental exposure and the characteristics of the solution. While many tanks of this type are currently in use, it is advisable to deal only with fabricators having experience with sodium hypochlorite and who are willing to warranty the vessel for the intended applications. It is also important to ensure that the tank has adequate UV (ultra violet) stabilizer or a gel coat outer layer designed for the area of intended use and if possible, locate tank in a shaded area.

c) High Density Polyethylene Tanks

Linear and cross-linked high density polyethylene tanks or tanks with these materials as liners have been used in sodium hypochlorite service. The success or failure of these types of tanks depends upon a number of factors including resin type and additives, fabrication technique, product temperature, environmental exposure, the characteristics of the solution (particularly trace metal contaminants) and the installation and piping connection methods. It is advisable to deal only with polyethylene tank manufacturers having experience with sodium hypochlorite and who are willing to warranty the vessel for the intended applications. Tanks used in more dynamic situations (i.e. loading and unloading several times per day) failed by developing stress cracks at the junction of the bottom and straight shell of the tanks.

d) Titanium Tanks

These tanks are generally very expensive compared to other alternatives, but due to their potential long service life (30-50 years), they may be cost effective in some applications.

6.3 TRANSFER SYSTEMS

6.3.1 Materials of Construction Selection

The materials listed below are examples of materials of construction that are compatible with sodium hypochlorite solutions and may be used alone or as linings for non-compatible materials of construction. Some may not be suitable for use in processes that manufacture sodium hypochlorite.

- PVDF (fluorinated polyvinylidene)
- PTFE (polytetrafluoroethylene)
- titanium
- ethylene propylene rubber
- 100% chlorobutyl rubber
- polypropylene

- PVC (polyvinyl chloride)
- CPVC (chlorinated polyvinyl chloride)
- tantalum
- Viton™ A with a minimum durometer of 70
- FRP (fiberglass-reinforced plastic with compatible resin and cure system)
- poly dicyclopentadiene

6.3.2 Piping

The two factors used to select the piping materials for sodium hypochlorite solutions are structural strength and chemical resistance. Where piping systems may be subject to physical stress or impact, lined steel pipe should be selected. Lining types include polypropylene, PVDF, PTFE, or similar thermoplastics. In lighter stress situations, poly dicyclopentadiene and reinforced PVC are suitable. Where piping will not be subject to impact, Schedule 80 PVC or CPVC is often used. At a minimum, conventional support spacing standards should be observed when using this type of piping system. If there is any risk of impact (foot/vehicle traffic, liquid/gas hammer, temperature expansion or contraction, maintenance or operations activities) continuous support systems or the equivalent should be considered for PVC/CPVC piping systems in sodium hypochlorite service.

When PVC and CPVC piping is assembled using glue, it is extremely important to use glue specifically made for use with PVC or CPVC in chemical systems. Other glues may not work properly. It is also critical that the recommended procedures for using the glue for assembling the system be followed exactly.

When metal piping must be used, titanium is recommended. Virtually all common metals such as mild steel, stainless steel and Hastalloys will corrode rapidly on contact with sodium hypochlorite solutions. Additionally, the resulting corrosion products will contribute to product degradation. Alloy 20 has been reported to corrode in contact with sodium hypochlorite solutions causing product decomposition.

6.3.3 Valves

Structural strength of the valve must be considered with respect to its specific application. Valve selection will depend upon the type of piping system being used. Precautions must be taken with cavity valves, particularly those made of all plastic materials, such as ball or plug valves to prevent product leakage and/or pipe/valve damage should there be any pressure build up in the closed cavity due to the transition metal catalyzed decomposition of the hypochlorite solution (Sections 3.4).

6.3.4 Pumps

Due to the numerous individual components comprising a complete pump, special care should be used when specifying this device. The centrifugal pump is the most common style found in sodium hypochlorite solution transfer systems. Casings and impellers may be of materials previously mentioned as chemically resistant to sodium hypochlorite. Impeller shafts should be made of titanium or protected by another compatible material. Pumps constructed of titanium are available and while more costly than "plastic" pumps will typically provide longer service. It is also important to utilize protective pump designs (i.e. magnetic drive), devices, covers, or shields to ensure that any leaks from the shaft seal or possibly pipe connections do not pose a risk to people or the environment.

6.3.5 Storage Tank System Design

6.3.5.1 Storage Tank Inlet Systems

Sodium hypochlorite solutions are typically delivered in bulk tank trucks of up to around 5,000 gallon capacities. Air pressure applied to the transport vehicle for off loading product must be free of oils, greases, and other compounds. A regulator must be installed to limit the air pressure to a level specified by the carrier. Typically air systems should be able to deliver air at 40 scfm and reach pressures of 15 to 25 psig. Unloading pressures must be compatible with the design working pressure of the tank trailer as well as the rest of the system. The carrier will also supply a hose to connect from the truck to the customer's receiving system. As the size and style of hose connections vary, the customer should contact his sodium hypochlorite supplier to determine the type of mating connection to install on the receiving system.

While the type of pipe used in the receiving system should be selected on the criteria defined in 6.4.2 (Piping), the section to which the truck hose connects requires special consideration. Due to the physical stress of the weight of the hose and frequent connection and disconnection, this component should be designed with these factors taken into account and be adequately supported to prevent fracturing and resulting spillage or personnel injury. This connection fitting should be no more than 3 feet above grade and should be clearly labeled as to the product to be received to avoid unloading hypochlorite into a tank that contains another or even an incompatible material. It should also be provided with a valve to prevent back flow of product when the hose is disconnected.

Inlet system lines should be sized to allow flow rates of approximately 150 to 250 gallons per minutes assuming a truck discharge pressure of 30 psig. Where possible, low points should be avoided or drain cocks installed. This will prevent product left in the lines from previous deliveries from contaminating subsequent deliveries. Discharges from any drain connection must be routed to an appropriate containment or treatment system. Connection of the inlet piping to the receiving tank should be made to a nozzle located near or on the top of the vessel. Vertical discharge into the tank will minimize lateral stress on the tank and it’s piping systems. The installation of a high level liquid alarm is recommended.

6.4 SODIUM HYPOCHLORITE FEED SYSTEMS

Feed systems are typically used for the application of sodium hypochlorite in waste and water treatment plants, swimming pools, paper production, cooling towers, and other industrial applications. Product quality is critical when utilizing a feed system. A few basic systems are used for the application of sodium hypochlorite and the type chosen depends on the process chemistry, instrumentation choices, operating cost, and available capital for equipment expenditures.

An important criteria for all sodium hypochlorite feed systems is to incorporate safety interlocks to prevent the addition of sodium hypochlorite to the process unless all process flow requirements are satisfied. This is extremely important for systems feeding acids for pH adjustment in addition to the sodium hypochlorite. If sodium hypochlorite and an acid are mixed, the pH of the solution is reduced and chlorine gas may be released. A process safety review of the feed system is recommended during design to eliminate the possibility of this occurrence.

6.4.1 Application Systems

Sodium Hypochlorite is a highly corrosive chemical that requires special pumps, control valves, transmitters, and piping methods to achieve satisfactory results. Therefore, the design of any feed system should be simplified when possible and choice of materials of construction is extremely important.

6.4.1.1 Gravity Systems

It is possible to gravity feed the sodium hypochlorite from the storage tank(s) to the process. This may be done manually in a batch mode or automatically with the appropriate manual and automatic valves and other process instrumentation. Therefore, under the right conditions, all pumps can be eliminated since the unloading of the sodium hypochlorite to the storage tank is to be done by the vendor.

6.4.1.2 Pumps

Pumps are normally chosen to feed sodium hypochlorite. Typical pumps are positive displacement or centrifugal pumps using titanium and many types of non-metallic components such as PVC, TFE, Kynar®, Tefzel® and Halar® brand fluoropolymers. When using positive displacement pumps, pressure relief systems are required and a centrifugal pump may require bypass loops for temperature and flow considerations. Centrifugal pumps using seals should consider silicon carbide seal faces with product flush on single seals and seal pots on double seals. No metal should be considered for internal seal components in contact with the sodium hypochlorite except titanium. Optional centrifugal pumps with magnetic drives and no seals have been successful in many sodium hypochlorite applications.

6.4.1.3 Vacuum Systems

Sodium hypochlorite is successfully applied using the motive force of the process stream to operate an eductor (venturi) to produce a vacuum at the throat of the device. This reduction of pressure at the throat of the eductor will allow the sodium hypochlorite to flow to the inlet of the device due to the differential pressure between the storage tank and the eductor. Care must be given to the materials of construction of the pump, eductor, and piping to eliminate corrosion.

6.4.2 Instrumentation Choices

A few basic choices of instrumentation are useful to the industry for the application of sodium hypochlorite.

6.4.2.1 Application Control – Titration

In addition to manual titration, automatic titration systems can repetitively titrate a finished product and produce a proportioned signal relative to the available chlorine in the solution. This signal is used for control of pumps and valves.

6.4.2.2 Application Control – Oxidation-Reduction Potential (ORP)

ORP measurements in the industrial sense generally apply to aqueous (water) solutions of acids, bases or salts or their combinations. Unlike pH and other ion selective electrodes that are highly specific in nature, ORP electrodes are inert elements that measure the ratio of the activities of the oxidized to the reduced forms of various ions in solution. When ORP is applied to available chlorine measurements a platinum-silver electrode pair should be used.

6.4.2.3 Application Control – Ratio Control

Continuous systems can apply sodium hypochlorite using a simple ratio system. The process stream is measured with mass or volume flow rate instrumentation and the sodium hypochlorite is measured and proportioned to the process stream. With the choice of proper instrumentation, this method will result in accurate control of the process.

7 NON-BULK PACKAGING AND SHIPPING OF HYPOCHLORITE SOLUTIONS

Please note that much of the information contained in Sections 7 and 8 has been duplicated particularly the training and safety sections. This was done intentionally to make each section stand alone and ensure that everyone using this manual has the applicable information.

7.1 PRODUCT REGISTRATION

Federal and most state agencies require the registration of products used as pesticides/antimicrobials or used in contact with food and or food equipment. Refer to Appendix B.

7.2 HAZARDOUS MATERIALS REGISTRATION

Companies which engage in the transportation of hypochlorite solutions should inquire into the requirements of registering their operations with the DOT as some shipments may require registration with the department. Refer to Appendix B for additional information.

7.3 TRAINING

7.3.1 Orientation

Employers who handle hazardous materials such as sodium hypochlorite solutions should develop a company policy and introductory training program to orient all new or transferred employees to their new work environment. Orientation programs should aim to educate these employees to the possible hazards of the workplace, to assist the new employee in their understanding of the job requirements, responsibilities, safety measures and procedures that must be followed at the work site. An abbreviated form of orientation is also necessary for temporary and part time employees depending on their job function. Examples of pertinent topics include: employee handbooks, company policies, facility tours, evacuation procedures and emergency plans, introduction to hazard communications, job descriptions, responsibilities of the employee and management, among others. Periodic refresher training is needed for existing employees.

7.3.2 DOT Training

The Department of Transportation requires training for employees who are employed by a company involved with any aspect of transporting hazardous materials. For personnel who's responsibilities include the drumming of this product, employers must provide the appropriate specific function training. This DOT training must be provided within the first 90 days of employment for all employees who are involved with hazardous materials and then repeated every third year. Refer to Appendix B.

7.3.3 OSHA Training

Employers also have a legal obligation to train employees under many of the required OSHA training programs. Refer to Appendix B.

7.3.4 Additional Training

Even though most required training programs regarding hazardous materials are generated from the two agencies mentioned above other training may be necessary to complete the employees knowledge of today’s regulations. One example is the EPA's FIFRA regulation that governs sodium hypochlorite solutions when sold or used as an antimicrobial.

7.4 CONTAINERS

7.4.1 Compatibility

Containers used in sodium hypochlorite service must be compatible with the product. Therefore, non-bulk containers are generally made of polyethylene or other compatible plastics because steel readily reacts with these solutions. Non bulk packages of various sizes not exceeding 119 gallons.

Non-bulk packages are emptied in a variety of ways, the most common of which is gravity flow. For those systems that use a pressure or pump system to empty the hypochlorite solution, it is important to make sure that the container design is suitable for the unloading system.

7.4.2 Container Venting Requirements

Drums used in this service may be vented as long as the gases and/or liquids released do not pose a danger, see the US DOT regulations for detailed information on venting requirements. Refer to Appendix B.

7.4.3 UN Packaging Standards

US DOT regulations require containers used in hypochlorite service to be manufactured and tested to UN standards. Under these standards, containers must meet performance requirements identified in the regulations.

Two different packing groups (2 or 3) are allowed in the regulations for use with hypochlorite solutions. To determine the applicable packing group designation, including the excess alkalinity in product, it will be necessary to conduct dermal irritation/corrosion and metallic corrosion testing as defined in the US DOT regulations.

7.4.4 Container Reuse

Both DOT and EPA (for F.I.F.R.A. registered sodium hypochlorite) regulate the reuse of containers. DOT requires all drums used as single packagings to be marked permanently with the thickness of the packaging in order for the drum to be reused. In addition to this marking requirement, the drum must be leakproof tested prior to each use by an authorized test facility. However, a drum may be reused for a period of five years without the required leakproof test if it is refilled with a materials which is compatible with the previous chemical, is refilled and offered for transportation by the original filler and is transported in a transport vehicle under the exclusive use of the refiller. Other DOT and EPA rules may apply to the reuse of these containers. Refer to Appendix B for additional information.

7.4.5 Container Markings

UN standards identified in the DOT regulations reveal the appropriate markings that must be present on all regulated containers. These markings are a series of codes that must appear in the proper order. Refer to Appendix B for more information.

7.5 SHIPPING PAPERS

7.5.1 General Entries

Shipping papers are required by DOT and Transport Canada regulations when hazardous materials are being shipped. Entries for shipping papers are governed by the regulations. See Appendix B and consult 49 CFR for detailed information.

7.5.2 Hazardous Materials Description

US DOT regulations define specific information and formats that are required to be on the shipping papers for sodium hypochlorite solutions. Refer to Appendix B.

7.6 EMERGENCY RESPONSE INFORMATION

Information deemed necessary for mitigation of emergencies involving hazardous materials are required to be carried by the shipper during transportation. Refer to Appendix B and 49 CFR for specific regulatory requirements.

7.7 LABELS AND MARKINGS

7.7.1 DOT Labels

Containers of hypochlorite solutions are required to be properly marked and labeled as designated by DOT regulations. The correct label is the corrosive label. Depending on the packing group, one gallon and smaller volume containers require different labels. Refer to Appendix B for additional information.

7.7.2 Other Label Requirements

Other federal agencies such as OSHA, EPA, as well as state government agencies may also have labeling requirements which may apply depending upon the strength and intended use of product. Agencies are the USDA (food use) and state agriculture departments (pesticide registration programs) may have additional requirements for products that fall under their jurisdiction. Refer to Appendix B.

7.7.3 Package Markings

DOT regulations require the marking of packages that contain hazardous materials in bulk and non-bulk packages. Refer to Appendix B.

7.8 PLACARDS

Placarding requirements for non-bulk loads of hypochlorite solutions vary depending on the amount of material and the size (bulk or non-bulk) of the package being transported. Refer to Appendix B.

7.9 PERSONAL PROTECTIVE EQUIPMENT

OSHA, the agency which governs the requirements for protecting employees in the workplace, states that, administrative and/or physical engineering techniques must be exhausted first in order to try to eliminate a hazard from the workplace before requiring employees to wear protective equipment. When it is determined that personal protective equipment is necessary, companies with employees working in a hypochlorite drumming or other non-bulk packaging area, have the duty of providing appropriate PPE to ensure a safe workplace. Equipment requirements for these employees would consist of protection from the obvious hazards along with extra protection due to the hazards associated with hypochlorite solutions. Refer to CI Pamphlet 65 on PPE. To ensure the protection of employees, OSHA requires employers to develop a PPE program where workplace hazards are identified, evaluated, and controlled in the best manner. In addition, training is required in the use of personal protective equipment to ensure that employees know both the limitations of the equipment and also how to properly wear, clean, and care for the gear.

General protection for employees in the workplace include gear for the protection of body parts such as the eyes (safety glasses), hands (gloves), and the feet (steel-toed PVC or rubber boots) and may include, head (hard hats). Companies should develop Standard Operating Procedures that identify these requirements for each process.

Proper personal protective equipment (PPE) must be worn when handling sodium hypochlorite. The minimum safety equipment for handling sodium hypochlorite is properly fitting chemical splash goggles, rubber gloves, and rubber boots, but may include a face shield, hard hat, chemical resistant suit, and an approved respirator. A hazard assessment must be performed on each operation to determine what PPE will be needed for that operation. Refer to CI Pamphlet 65.

7.10 SAFETY EQUIPMENT

OSHA requires certain protective equipment to be within the workplace for corrosive materials. These items include safety eye wash stations, and safety showers both of which are used to remove corrosive liquids from the skin and eyes. First aid stations should also be available to employees. OSHA provides guidance for what should be contained in the First Aid Kit in 29 CFR.

Another item for companies with non-bulk packaging systems to consider would be the air quality of the storage and filling process areas as hypochlorite solutions can pose problems from small amounts of vapor from the hypochlorite solution. Ventilation whether mechanical or natural can be an answer to prevent exposure levels from becoming an issue. Companies should have the workplace evaluated and tested to ensure compliance (Refer to Appendix D, 3.2).

7.11 MEDICAL EVALUATION

Employers are required to ensure that all employees are capable of safely wearing any protective equipment required by the PPE program. Employers meet these obligations by having workers medical evaluated before placing them in work areas that require certain personal protective equipment. Medical evaluations are dependent upon the workers job duties. Examples of evaluations that may be necessary include items such as pulmonary function tests, and respirator fit tests, both of which are used to ensure the workers ability to safely use a respirator.

7.12 PRODUCTION/FILLING EQUIPMENT

7.12.1 Materials of Construction

The chemical compatibility of materials used in a hypochlorite packaging system is one of the most important issues when choosing equipment for this production process. The manufacturers of hoses, pipes, pumps, tanks and other equipment used in the process should be contacted in order to determine the compatibility of a material before use. Typical materials used in drumming systems are plastics such as polyethylene, polypropylene, PVC, CPVC, among others. (See also Section 6 Handling/Storage Equipment)

7.12.2 Weighing Equipment

Regulations require the calibration of weighing equipment used in the filling of drums and other containers to ensure the container has been filled to the correct amount. These scales also require greater protection than normal from the hazards associated with hypochlorite solutions (corrosive liquids and corrosive vapors).

7.12.3 Process Equipment/Systems

Piping systems, pumps and tanks used in the drumming and for the storage of hypochlorite solutions are discussed in Section 6 of this pamphlet.

In drumming operations, fill nozzles are frequently used in conjunction with pumps to control the flow of product during the filling process and are normally equipped with recycling valves which allow the operator to shut off the flow of material without stopping the pump. Automated filling systems are also equipped in this manner.

7.12.4 Storage Precautions

Important factors should be considered when storing hypochlorite solutions as several conditions can cause the premature deterioration of the product. Factors include direct sunlight, temperature during manufacturing and storage, and specific compounds of the solution to name a few (Section 3). Other storage precautions for bulk and or drum storage areas would include items such as containment structures, and emergency vapor releases.

7.13 SHIPPING DRUMS AND OTHER NON-BULK CONTAINERS

Only workers who have received proper instruction in the handling of hazardous materials shall perform any shipping operations. They should be fully aware of the product's properties, its potential hazards, and proper loading, shipping and unloading procedures, including all necessary safety precautions. The following should be considered when shipping non-bulk containers-

- Workers should exercise extreme care and wear proper safety equipment because of the potential release scenarios (Section 7.9).

- Suitable spill control equipment should be available to isolate and contain any potential leaks. Personnel should be trained to handle spills of any size.

- Spot the transport vehicle on a level preferably paved surface in the designated loading/unloading area. Secure the vehicles, set brakes, and block the wheels to prevent movement during loading/unloading.

- Inspect all loading/unloading equipment for signs of defects. Do not load/unload if there is a question about the condition of any equipment. If a folk lift is used to load/unload, the operator must follow all safety and regulatory guidelines for its operation and be trained in its use.

- Containers shall be loaded onto transport vehicles and secured to prevent movement while in transit. Leaking or damaged containers shall not be shipped. All containers should be loaded to meet DOT requirements Refer to Appendix B.

- US DOT also regulates other hazardous materials that may be transported on the same vehicle. Check the segregation tables in 49 CFR for allowable compatible materials and for any separation requirements during transport.

- Drivers of transport vehicles (US) must have a Commercial Drivers License (CDL) with Hazmat endorsements and meet all training requirements set forth by DOT.

7.14 STANDARD OPERATION PROCEDURES

Companies involved with the production and handling of hazardous materials should have a program where all standard operating procedures for their processes should be written in simple and understandable language and step by step format, reviewed for safety and environmental issues and validated for accuracy. This program should be developed to cover topics such as details of tasks performed, procedures used to ensure compatible materials of construction, replacement materials, new materials, etc., used in the process, equipment knowledge, types and frequency of instrument readings and samples to be taken. Other pertinent information includes safety precautions, critical parameters, safe operating limits, human factors (i.e. communication issues, operator/equipment interfaces) and adequate measuring devices. A preventive maintenance program should also be incorporated into these procedures to avoid a failure in a process system. The goals of the program should be to educate the new employee, update the existing employees, and maintain the integrity of the production system thereby, eliminating most problems before they occur.

7.15 WASTES

Hypochlorite solutions released during a spill may be considered as a hazardous waste depending on the pH and/or state regulations. Employees whose responsibility it is to clean up such spills should be trained to do so. Applicable training (OSHA or NFPA) for these employees would depend upon the extent of their duties during such a release. Refer to Section 10 and Appendix B.

7.16 REPORTING REQUIREMENTS

Several agencies (federal, state, and local) such as the DOT EPA, SERC, LEPC, and or the local fire department may require reporting when a release of a hazardous material occurs. Reporting may be required when the release is above and/or below the Reportable Quantity (RQ). Refer to Appendix B for further information.

8 BULK PACKAGING AND SHIPPING OF SODIUM HYPOCHLORITE SOLUTIONS

Please note that much of the information contained in Sections 7 and 8 has been duplicated particularly the training and safety sections. This was done intentionally to make each section stand alone and ensure that everyone using this manual has the applicable information.

8.1 PRODUCT REGISTRATION

Federal and most state agencies require the registration of products used as pesticides/antimicrobials or used in contact with food and or food equipment. Refer to Appendix B.

8.2 TRAINING

8.2.1 Orientation

Employers who handle hazardous materials such as sodium hypochlorite solutions should develop a company policy and introductory training program to orient all new or transferred employees to their new work environment. Orientation programs should aim to educate these employees to the possible hazards of the workplace, to assist the new employee in his understanding of the job requirements, responsibilities, safety measures and procedures that must be followed at the work site. An abbreviated form of orientation is also necessary for temporary and part time employees depending on their job function. Examples of pertinent topics include: employee handbooks, company policies, facility tours, evacuation procedures and emergency plans, introduction to hazard communications, job descriptions, responsibilities of the employee and management, among others. Periodic refresher training is needed for existing employees.

8.2.2 DOT Training

The Department of Transportation requires training for employees who are employed by a company involved with any aspect of transporting hazardous materials. For personnel who's responsibilities include loading/unloading bulk containers of this product, employers must provide the appropriate specific function training. This DOT training must be provided within the first 90 days of employment for all employees who are involved with hazardous materials and then repeated every third year. See Appendix B.

8.2.3 OSHA Training

Employers also have a legal obligation to train employees under many of the required OSHA training programs. See Appendix B.

8.2.4 Additional Training

Even though most required training programs regarding hazardous materials are generated from the two agencies mentioned above other training may be necessary to complete the employees' knowledge of today's regulations. One example is the EPA's FIFRA regulation that governs sodium hypochlorite solutions when sold or used as a antimicrobial.

8.3 BULK TANK TRAILERS (TANKERS)

Bulk sodium hypochlorite solutions are typically delivered in tank trailers of various capacities. Legal weight restrictions limit the capacity of these trailers in most states to a maximum of around 5000 gallons or less. (Note: Some states & Canadian provinces allow greater weights)

8.3.1 Materials of Construction/Liners

Tankers used in the transportation of this product are normally constructed of FRP or lined carbon steel, as hypochlorite solutions are not compatible with the carbon or stainless steel composites. Examples of lining materials used include rubber such as chlorobutyl, and selected fluoropolymers (Section 6.3.1). Many factors should be considered when selecting a material for these tanks; such as volume to be transported, strength of solution, climate and the expected life of the material.

8.3.2 Pressure Vessels

Most tanks in this service are pressure vessels equipped with rupture protection and an eduction tube, therefore, product is usually unloaded by pressuring the tanks, typically with air, though other gases can be used. This process forces the product through the eduction tube, the external piping, the unloading hose, the ridge storage tank piping, and finally into the storage tank itself. Many precautions, which should be identified in each location Standard Operating Procedures, must be observed before, during, and after the unloading process to ensure the safe operation of this equipment.

Pressure and Vacuum Relief – Each cargo tank must be equipped to relieve pressure conditions. In addition, DOT 407 and 412 cargo tanks must be equipped with vacuum relief devices.

The pressure and vacuum relief system must be designed to operate and have sufficient capacity to prevent cargo tank rupture or collapse due to pressure changes resulting from loading, unloading, heating or cooling of the lading. All 407 and 412 cargo tanks must be equipped with self closing devices on the process valves.

8.3.3 Tank Requirements

Tankers used in hazardous material service must built to DOT or equivalent Transport Canada specifications, tested, and marked according to the appropriate regulations. The specifications for the cargo tanks that may be used to transport sodium hypochlorite are found in 49 CFR 173.242. The current design specifications for sodium hypochlorie Tankers shall be properly equipped with the appropriate accessory equipment (i.e. manway, rupture disks, vents, etc.) and inspected annually. Tankers can only repaired by a certified facility. DOT regulations cover the use of these bulk tank trailers during loading, unloading and driving. See Appendix B for additional information.

8.3.4 Equipment In Mixed Service

It is generally not recommended to ship other liquids in a bulk tank trailer that has been used in sodium hypochlorite service. If this is done, it is the shippers responsibility to ensure that the products are compatible and/or that the trailer is completely cleaned between services to prevent any contamination of products or adverse chemical reactions. It is important to confirm the effectiveness of any trailer washing system used.

8.4 SHIPPING PAPERS

8.4.1 General Entries

Shipping papers are required by DOT and Transport Canada regulations when hazardous materials are being shipped. Entries for shipping papers are governed by the regulations. See Appendix B and consult 49 CFR for detailed information.

8.4.2 Hazardous Materials Description

US DOT regulations define specific information and formats that are required to be on the shipping papers for hypochlorite solutions, refer to Appendix B.

8.5 HAZARDOUS MATERIALS REGISTRATION

Companies which engage in the transportation of bulk hypochlorite solutions should inquire into the requirements of registering their operations with the DOT as some bulk tank trailers will have a capacity great enough to require registration with the department. Refer to Appendix B for additional information.

8.6 HAZARDOUS SUBSTANCES

Solutions of sodium hypochlorite are considered hazardous by DOT and Transport Canada. The Reportable Quantity for the US is 100 pounds of sodium hypochlorite. See Appendix B.2.2.3.

8.7 EMERGENCY RESPONSE INFORMATION

Information deemed necessary for mitigation of emergencies involving hazardous materials are required to be carried by the shipper during transportation. See Appendix B and 49 CFR for specific regulatory requirements.

8.8 LABELS AND MARKINGS

The US DOT and Transport Canada have specific requirements covering the use of labels and markings for some bulk shipment scenarios. See Sections 7.6.1 and 7.6.2 and Appendix B for additional information as well as 49 CFR for specific regulatory requirements.

8.9 PLACARDING

Placarding requirements for bulk loads of hypochlorite solutions vary slightly depending on the style and size of the tank, and how the tank is transported. For normal tank trailers placarding consist of the Corrosive, Class 8 placard in association with the appropriate identification number which must be affixed to both sides and both ends of the transport vehicle. Review Appendix B.

8.10 PERSONAL PROTECTIVE EQUIPMENT

OSHA, the agency which governs the requirements for protecting employees in the workplace, states that administrative and or physical engineering techniques must be exhausted first in order to try to eliminate a hazard from the workplace before requiring employees to wear protective equipment. When it is determined that personal protective equipment is necessary, companies with employees working with hypochlorite solutions in bulk packaging and shipping have the duty of ensuring a safe workplace. Equipment requirements for these employees would consist of protection from the obvious hazards along with extra protection due to the hazards associated with hypochlorite solutions (irritant and potential air pollutants). To ensure the protection of employees, OSHA requires employers to develop a PPE program where workplace hazards are identified, evaluated, and controlled in the best manner. In addition, training is required in the use of personal protective equipment to ensure that employees know both the limitations of the equipment and also how to properly wear, clean, and care for the gear.

General protection for employees in the workplace include gear for the protection of body parts such as the eyes (safety glasses), hands (gloves), and the feet (steel-toed PVC or rubber boots) and may include, head (hard hats). Companies should develop Standard Operating Procedures that identify these requirements for each process.

Proper personal protective equipment (PPE) must be worn when handling sodium hypochlorite. The minimum safety equipment for handling sodium hypochlorite is properly fitting chemical splash goggles, rubber gloves, and rubber boots, but may include a face shield, hard hat, chemical resistant suit, and an approved respirator. A hazard assessment must be performed on each operation to determine what PPE will be needed for that operation.

8.11 SAFETY EQUIPMENT

OSHA requires certain protective equipment to be within the workplace for corrosive materials. These items include safety eye wash stations, and safety showers both of which are used to remove corrosive liquids from the skin and eyes. First aid stations should also be available to employees.

Another item for companies with packaging systems to consider would be the air quality of the storage and filling process areas as hypochlorite solutions can pose problems from small amounts of vapor from the hypochlorite solution. Ventilation whether mechanical or natural can be an answer to prevent exposure levels from becoming an issue. Companies should have the workplace evaluated and tested to ensure compliance.

8.12 MEDICAL EVALUATIONS

Employers are required to ensure that all employees are capable of safely wearing any protective equipment required by the PPE program. Employers meet these obligations by having workers medical evaluated before placing them in work areas that require certain personal protective equipment. Medical evaluations are dependent upon the workers job duties. Examples of evaluations that may be necessary include items such as pulmonary function tests, and respirator fit tests, both of which are used to ensure the workers ability to safely use a respirator.

8.13 RECEIVING AND SPOTTING SODIUM HYPOCHLORITE SOLUTION CARGO TANKS

When a cargo tank motor vehicle arrives at a facility the proper identification of the carrier and the product to be transferred should be verified before the cargo tank is directed to the transfer site. If a tank is empty and clean there should be a cleaning certificate. If the tank is empty but not cleaned, then a document certifying the last product loading should be available.

8.14 SODIUM HYPOCHLORITE SOLUTION CARGO TANK LOADING

8.14.1 General

When loading a sodium hypochlorite cargo tank, the safety aspects of the operations should be uppermost in the minds of loading personnel. The loader must verify that proper spotting and receiving have been completed before beginning transfer operations. Proper personal protective equipment (which may include hard hat, chemical splash goggles, full face shields, chemical protective suit, gloves and boots) should be worn during the transfer operations. See Pamphlet 65 (Section 7). Safety showers and eye wash facilities should be located in the immediate work area within sight of the loading operation.

Note: The reader's attention is drawn to 49 CFR 177.834(i) covering the attendance requirements during the loading operation.

DOT (49 CFR 177.834 (i)) and TC (CSA Standard B622) (12.5.4) regulations require a cargo tank to be attended by a qualified person at all times during loading. The person attending the loading must be alert and be within 25 feet of the cargo tank. A qualified person is one that has been made aware of the hazards of sodium hypochlorite and the procedures to be followed in an emergency, is authorized to move the cargo tank and has the means to do so.

An inspection check list should be used for all aspects of the loading operation. It should include all recommendations contained in this pamphlet plus any company procedures or special requirements specific to each facility. The checklist documents that the proper loading and securement procedures have been completed and, if necessary, proper corrective actions have been taken.

8.14.2 Pre-Load Inspection Checklist

The purpose of the pre-load inspection is to identify problems before loading. The pre-load portion of the checklist should at a minimum include:

- Determination that the proper cargo tank has been supplied.
- Check of the cargo tank for DOT/TC specification plate to determine the compatibility of the material of construction or lining for use in sodium hypochlorite service. A cargo tank that does not have a DOT/TC specification plate should not be loaded.
- Confirmation that the test dates on the specification plate are current and that the material to be loaded will not exceed the weight and density limit.
- A check that there is written certification or documentation stating whether the trailer has been cleaned or identifying the last contained product.
- A check to ensure only compatible materials are loaded into compartmented tank trucks.
- An inspection of the running gear, safety appliances, marking, and placarding.
- Verification that all tank fittings are closed tightly to prevent any leakage.
- Verification that the unloading valves are closed tightly to prevent an accidental discharge.
- Visual inspection of the top and bottom fittings, manway cover including gaskets and bolts, and the tank interior for lining condition, cleanliness and heel.

- Mechanical problems that would prevent proper sealing should be corrected prior to commencing the transfer operation.

- Verification that the cargo tank has been depressurized prior to opening the manway to the interior of the tank Prior to inspecting the interior of the tank, the tank needs to be depressurized to allow for the manway to be safely opened.

Because of the risk of contamination or reactivity of cargo tank contents, if a liquid heel is discovered during the pre-load inspection, appropriate plant procedures must be followed.

8.14.3 Product Transfer

After the pre-load inspection is complete and the cargo tank is found acceptable, product transfer can begin. Before making connections, four corrosive placards (UN 1791, Class 8 Corrosive) should be applied to the cargo tank.

It is recommended the following be included in procedures for loading a cargo tank:

a. Determine the amount of product to be loaded.

b. Ensure all outlet valves are closed.

c. Ensure the loading line is secured to prevent movement. Product surge through the piping could cause the loading line to "jump" and cause a product release.

d. When loading is done on a scale, flexible-filling lines must be used to insure accurate weighing.

e. When ready to transfer, open product valve, engage transfer pump and begin product flow.

f. During the transfer process, periodically inspect the tank outlet valve to ensure there is no leakage. If leakage is detected, immediately stop the transfer, and determine cause of leak. Ensure defect has been corrected prior to continuing with transfer.

g. Fill the tank to the proper level following established plant procedures ensuring the cargo tank's weight capacity is not exceeded. This is defined as the load limit, and consists of both the design capacity of the tank, and the gross vehicle weights (GVW) of the power unit. Exceeding this limit may result in an unsafe condition. In addition, state or provincial axle and gross load limits must not be exceeded.

h. Secure all the valves, valve plugs, valve caps and the manway cover using a properly sized wrench. All fittings must be tool tight.

8.14.4 Post-Load Inspection Checklist

The post-load inspection checklist should, at a minimum, include the following:

- Verification of the proper securement of all components and fittings.
- Verification that the cargo tank motor vehicle is not overweight.
- Application of seals, product information tags or other information required by regulation and the facility.
- Washing off of any product residue from the cargo tank following established plant procedures.
- Confirmation the cargo tank is properly marked and placarded.
- Confirmation the manway covers are securely fastened, and all other openings, securely closed and tightened before transit.
- Completion of the cargo tank inspection checklist report and a release of the tank for shipment.
- A visual inspection of the cargo tank for leakage or mechanical problems.
- A check that proper shipping papers have been prepared are given to the driver.
- A check that the driver has the appropriate guidebook (or appropriate page) in the cab if the hazard communication notation on the shipping paper is the emergency response guide number.
- If used, ensure the proper MSDS accompanies the shipping papers.

8.15 SODIUM HYPOCHLORITE CARGO TANK UNLOADING

8.15.1 General

When unloading a sodium hypochlorite cargo tank, the safety aspects of the operations should be uppermost in the minds of unloading personnel. The unloader must verify proper spotting and receiving have been completed before beginning transfer operations. Proper personal protective equipment (which may include hard hat, chemical splash goggles, full face shields, chemical protective suit, gloves and boots) should be worn during the transfer operations. See Pamphlet 65 (Section 7). Safety showers and eye wash facilities should be located in the immediate work area within sight of the unloading operation.

An inspection checklist should be used for all aspects of the unloading operation. It should include all recommendations contained in this pamphlet plus any company procedures or special requirements specific to each facility. The checklist documents that proper unloading and securement procedure have been completed and, if necessary, proper corrective actions have been taken.

Note: The reader's attention is drawn to 49 CFR 177.834(i) covering the attendance requirements during the unloading operation.

8.15.2 Pre-Unload Inspection Checklist

The purpose of the pre-unload inspection is to identify problems before unloading begins. The pre-unload inspection checklist should at a minimum include:

- Verification that shipping papers and other required documentation have been delivered to a responsible authority at the user destination. A signed delivery receipt should be obtained before the motor carrier leaves the area.
- Verification that the tank is loaded with sodium hypochlorite solution by careful inspection of the bill of lading, the vehicle number, commodity marking and placards and/or sampling. Extreme care should be taken to ensure cargo tank contents are properly identified.
- Inspection of the running gear, safety appliances, marking (including stenciling), placarding and other pertinent items to identify all defects in the cargo tank motor vehicle before unloading the sodium hypochlorite solution.
- A check of the tank fittings to verify there is no leakage.
- Verification that the sodium hypochlorite solution will be unloaded into the correct receiving tank. (Visit the CI website at www.chlorineinstitute.org for more information on assuring this is done.)
- Verification that the receiving tank has sufficient capacity to receive the sodium hypochlorite solution to be transferred.
- A check of all unloading connections.
- A check that unloading equipment such as transfer hoses, fittings, pumps, lines, valves air system are compatible with the sodium hypochlorite solution.
- Inspection of transfer hoses.
- Verification that grounding cables have been connected to the trailer if required by plant procedures.
- Establishment by the unloader of the location of the nearest safety showers and eyewash.

8.15.3 Product Transfer

After the pre-unload inspection is satisfactorily completed, product transfer can begin. Pumps, pressure padding, or in some cases by gravity can be used to unload sodium hypochlorite solution cargo tanks. Unloading can take place through either a bottom fitting or a top fitting. If an unfamiliar unloading arrangement is encountered, the carrier should be contacted immediately.

Monitoring the Unloading

DOT (49 CFR 177.834(i)) and TC (CSA Standard B622) regulations require a cargo tank to be attended by a qualified person at all times during unloading. The person attending the unloading must be alert and be within 25 feet of the cargo tank. A qualified person is one that has been made aware of the hazards of sodium hypochlorite solutions and the procedures to be followed in an emergency, is authorized to move the cargo tank and has the means to do so.

Bottom Unloading by Pump

Product transfer through the bottom outlet can be accomplished by pumping. It is recommended the following be included in procedures for the bottom unloading by pump.

- Keep the manway cover open or maintain a continuous positive pressure to avoid pulling a vacuum on the tank.
- Ensure the plant's unloading connection is securely attached to the cargo tank's bottom outlet before any product valves are opened.
- Ensure all unloading systems are leak free throughout the product transfer process
- Disconnect unloading lines after blowing it out or gravity clearing. It is important to completely clear product from pumps and lines after use.

Top or Bottom Unloading by Air Pad

When top or bottom unloading by air padding, a positive pressure is applied through the valve on the cargo tank to force the product out of the tank. Extra precautions should be observed with this method of product transfer to minimize the effect of a leak from a pressurized cargo tank. Clean, oil-free air must be used.

It is recommended the following be included in procedures for unloading using an air pad:

- The dust cap should be removed from the trailer outlet valve and the unloading hose connected after inspection of the hose and fittings. Unloading connections must be securely attached before any product valves are opened.
- All unloading systems must be leak free throughout the product transfer process.
- The manway cover must be secured before applying pressure.

- The unloading pressure must not exceed the safe working pressure of the cargo tank. Air pressure can be adjusted to regulate the flow of sodium hypochlorite through the unloading line. Approximately 15 to 20 psig should be sufficient depending on location of storage tank.

- A drop in air pressure or the sound of rushing air generally indicates the tank is empty. The air supply should be turned off and the air line and the cargo tank depressurized.

- Unloading lines should be emptied by blowing them out or gravity draining them before they are disconnected. It is vital to completely clear product from pumps and lines after use.

- All valves should be closed and all caps replaced.

8.15.4 Post-Unload Inspection Checklist

The post-unload inspection checklist should, at a minimum, include the following:

- Verification of the proper securement of all components and fittings.

- Application of seals, product information tags or other information required by regulation and the facility.

- Confirmation of the cargo tank is properly marked and placarded.

- Wash off of any product residue from the cargo tank exterior following established plant procedures.

Complete the inspection check list and release the cargo tank for shipment.

Good operating practice should include notations on the delivery receipts such as storage tank gallons delivered with content readings before and after, identification of containers filled, containers filled and net weight of each, analysis sheet (if required), quantity in pounds or gallons delivered to the storage tank, before and after readings, and weight tickets (if available).

8.16 MAINTENANCE REQUIREMENTS

As with all hazardous material transport containers, sodium hypochlorite solution cargo tanks must be maintained in a safe operating condition. It is essential that all scheduled tests and inspections be carried out with great diligence and care.

8.16.1 Daily Inspection and Maintenance

Prior to operation the assigned driver must be satisfied that critical devices and accessories of the vehicle are in good working order. Title 49 CFR 392.7 outlines these critical devices and accessories. The driver is required to review the previous driver’s Driver Vehicle Inspection Report (DVIR) for any problems, safety deficiencies and corrections. A DVIR is required to be completed at the end of the driver’s tour of duty.

Inspections must be conducted on the vehicle at the completion of the day's work and any necessary deficiencies corrected before the unit resumes service on the public highways. Records must be kept and be available for reference during future scheduled maintenance events to assure that a uniform and cohesive flow of information is available to future inspectors. DOT requirements for inspection, repair and maintenance can be found in 49 CFR Part 396.

8.16.2 Periodic Maintenance

Careful and thorough vehicle maintenance should be performed on a fixed schedule as dictated by operating conditions and environment. For example, colder climates may cause maintenance problems such as corrosion due to road salting and spring and tire failure due to potholes caused by frozen roadways.

Internal valve leak testing is a required procedure at many loading facilities, and roadside inspections may include checking for leakage through the closed internal valves. The valve seats should be replaced as needed to maintain full sealing capability. If reliable sealing becomes a problem, a higher grade of seat material should be used. There are suitable elastomeric seats available that have high chemical resistance and good physical resilience. It is the shipper and carrier's responsibility to ensure compatibility of the gasket and seat material with the product.

8.16.3 Hose and Fitting Maintenance

Hose assemblies used to transfer sodium hypochlorite solutions should be constructed of appropriate materials, assembled by the manufacturer or distributor and hydrostatically tested prior to first use. Hose assemblies should be carefully examined prior to each subsequent use to assure none of the following conditions exist: leakage, frayed or worn braid, ballooned or bunched braid, hose elongation or corrosion. It is recommended that an acceptable procedure for maintenance, testing and inspection of hoses be set by each facility/carrier based on experience and equipment use.

8.16.4 Tests and Inspections

Title 49 CFR Part 180 contains the requirements for maintenance, use, inspection, repair, retest and requalification of cargo tanks. Report and record retention requirements can be found in 49 CFR 180.417. Testing requirements in Canada are very similar to those in the U.S. Reference is made to CSA B620 (12.5.1).

Any required weld repairs, as described in 49 CFR 180.413, may only be accomplished by a repair shop awarded a National Board "R" Stamp.

8.17 STANDARD OPERATING PROCEDURES

Companies involved with the production and handling of hazardous materials should have a program where all standard operating procedures for their processes should be written in simple and understandable language and step by step format, reviewed for safety and environmental issues and validated for accuracy. This program should be developed to cover topics such as details of tasks performed, procedures used to ensure compatible materials of construction, replacement materials, new materials, etc., used in the process, equipment knowledge, types and frequency of instrument readings and samples to be taken.

Other pertinent information includes safety precautions, critical parameters, safe operating limits, human factors (i.e. communication issues, operator/equipment interfaces) and adequate measuring devices. A preventive maintenance program should also be incorporated into these procedures to avoid a failure in a process system. The goals of the program should be to educate the new employee, update the existing employees, and maintain the integrity of the production system thereby, eliminating most problems before they occur.

8.18 WASTE

Hypochlorite solutions released during a spill may be considered as a hazardous waste depending on the pH and/or state regulations. Employees whose responsibility it is to clean up such spills should be trained to do so. Applicable training (OSHA or NFPA) for these employees would depend upon the extent of their duties during such a release. See Section 9 and Appendix B.

8.19 REPORTING REQUIREMENTS

Several agencies (federal, state, and local) such as the DOT EPA, SERC, LEPC, and or the local fire department may require reporting when a release of a hazardous material occurs. Reporting may be required when the release is above and/or below the Reportable Quantity (RQ). Refer to Appendix B for further information.

9 SECURITY

9.1 GENERAL

All shippers of hazardous materials should develop and implement security measures for the handling of the chemicals both onsite and during transportation. It is also important that the sites receiving these materials have appropriate security plans in place for their sites. The shipper should confirm this before a delivery is made.

9.1.1 Security Plans

U.S. DOT requires a security plan for shippers of hazardous materials in 49 CFR 172(1). They have also developed a guidance document for their plan which can be obtained from the agency as a guide. This provides information for all classes of HazMats.

9.1.2 Background Checks

The U.S. Transportation Safety Agency, part of the Department of Homeland Security, requires that all drivers have background checks as well as a CDL (Commercial Drivers License). Drivers cannot transport hazardous materials until this background check is complete and the driver meets the standards dictated by TSA.

9.1.3 Security Training for Employees

DOT also requires specific security training in 49 CFR 172(H). This requires specific documented training for employees at sites using HazMats.

9.1.4 AWWA

The American Water Works Association has a security plan for potable water plants. This was developed with a grant by EPA which is responsible for security at drinking water plants. Water treatment facilities should be able to confirm that they have implemented this plan. The AWWA in Denver, Colorado can be contacted to obtain a copy of the plan.

9.1.5 Sodium Hypochlorite Production Facilities

Security plans must be prepared for sodium hypochlorite production sites. Security plans already exist for rail cars of hazardous materials available for these sites from the Chlorine Institute and the American Chemistry Council, both in Arlington, Virginia. The Chlorine Institute also has a plan for shipping and receiving sites handling packaged chlorine. Some of the information in this plan may be applicable for the shipment of sodium hypochlorite as well as chlorine and should be considered.

10 EMERGENCY RESPONSE AND DISPOSAL

10.1 NOTIFICATION OF A SPILL

Notification of spills may be necessary if the RQ was released or if local regulations require reporting. Please refer to Appendix B.

10.2 SPILLS

In the event of a spill of any magnitude prompt action is required to minimize hazards to employees the community and to the environment. Preplanning is essential for a Spill Control Plan. This plan should include operations such as evacuation, mitigation, diking, recovery, neutralization, dechlorination, absorbtion, dilution, and notification. This plan should be coordinated and reviewed with local fire departments and the local environmental regulating agencies. This plan should include fixed site spills and transportation spills.

Whenever there is an imminent or actual spill of sodium hypochlorite your company Spill Control Plan must be immediately activated. Each spill of sodium hypochlorite should be handled by taking into account the nature and circumstances of that spill. Items that may be included in a spill plan include:

- Evacuation of all unnecessary personal from the area. The first responsibility of personal in the area should be to their own safety. They should take no action that would endanger themselves or others. Their next concern should be to keep other personal and the possible effected community safe. These actions would include any necessary evacuation of the effect area, and to denial entry to the spill area.

- Mitigation of the spill should start as soon as responders have equipped themselves and determined the source of the spill and what actions should be taken to stop the release.

- Responders should contain the spilled material in the smallest possible area. Diking should be used to contain the spill if not in a containment area. Do not allow the bleach to enter sewers, streams, or unpaved land. Avoid contamination of contained material with acidic materials since this would result in a release of chlorine gas.

- Absorption can be used to clean up a sodium hypochlorite spill. If absorbents are used to soak up a spill, avoid sawdust and other combustible materials. Certify in advance that the absorbent can be safely used with sodium hypochlorite solutions. Note: The spill is now a solid waste and may be more difficult to disposal of in a solid form.

- Dilution of spilled sodium hypochlorite is an option if the spilled product can be diluted to the point where it is no longer a danger to personal or the environment. For larger spills this may require very large amounts of water.

10.3 RECOVERY OF SPILLED MATERIAL

Recovery of contained spilled material should be given first priority, keeping in mind that the material is most likely contaminated in some way. Recovered material could be reused, or neutralized, pH adjusted and recovered in an approved process.

10.4 DISPOSAL AND NEUTRALIZATION OF SODIUM HYPOCHLORITE SOLUTIONS

Disposal of significant volumes of aqueous solutions of sodium hypochlorite may require both reduction of the active chlorine followed by pH adjustment before discharging the liquid to any sanitary discharge system or receiving body of water. The issue should be discussed with the local authority and/or plant management first. The reason for the neutralization is the sodium hypochlorite can seriously disrupt sewage or other treatment plant operations resulting in failure of the biological processes at the sewage plant (extreme cases) or disruption of chemical treatment processes. In addition, waste streams containing sodium hypochlorite may come into contact with acidic conditions and chlorine gas may be released.

Sodium hypochlorite can be treated either in a batch operation or a continuous system. After neutralization of the spill the remaining material still may need to be pH adjusted, possibly in place, diluted and/or flushed with water, or removed as a liquid and solid material for proper disposal. This should be coordinated with the local environmental regulating agency.

WARNING: Lowering the pH of a liquid bleach solution without first reducing the hypochlorite ion to chloride ion could result in the release of chlorine gas.

All of the neutralization reactions progress relatively quickly. Destruction of all available chlorine can be confirmed by adding 3% hydrogen peroxide to a waste sample. If the sample fizzes, then free chlorine remains in the waste. By-product salts may also accumulate in the form of sulfates and chlorides that can cause corrosion problems. Also, there may be a notable shift in the pH valve results and control of the reactions is relatively complicated since the endpoint of the neutralization cannot be measured with simple instrumentation methods.

CAUTION: These reactions may produce heat, this must be taken into account!

IMPORTANT: Neutralizing materials of any kind should never be used on skin or eyes unless directed to do so by qualified medical personnel.

10.4.1 Neutralization Chemicals

Neutralization reactions can be controlled using available chlorine titrations or oxidation/reduction potential (ORP) measurements. It is important to have adequate equipment and/or process systems and operating procedures to handle neutralization reactions and to always read and follow information contained in the MSDS for each of the neutralization chemicals including proper personal protective equipment.

10.4.1.1 Hydrogen Peroxide

One of the chemicals suitable for the reduction of hypochlorite ion available chlorine in sodium hypochlorite is hydrogen peroxide (H_2O_2), less than 35% concentration. The chemical reaction is as follows:

Equation 14

$$NaOCl + H_2O_2 \Rightarrow NaCl + H_2O + O_2$$

The sodium hypochlorite reacts spontaneously with the hydrogen peroxide and the resulting salt solution is adjusted for pH before discharge. The oxygen is vented to atmosphere at a safe point of discharge. An advantage of using hydrogen peroxide is the only end products are salt and water.

This reaction can easily be done on a batch basis in one tank with neutralization of the bleach first and pH adjustment second. On a continuous system, the solution is neutralized in a reactor vessel in the first step and then the pH is adjusted downstream in a second reactor. The hydrogen peroxide is added in the first tank and acid is added to the second with the appropriate ORP and pH control systems.

10.4.1.2 Sulfur Dioxide

WARNING: Sulfur dioxide (SO_2) is a corrosive gas and a safety program must be developed. The use of sulfur dioxide to neutralize sodium hypochlorite may result in release of gaseous chlorine if the pH is allowed to drop too low; a release of gaseous SO_2 may also result. Therefore, it is important to control the pH until all hypochlorite ions is destroyed and to be sure sulfur dioxide can no longer be released.

Sulfur dioxide can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:

Equation 15

$$NaOCl + 2NaOH + SO_2 \Rightarrow Na_2SO_4 + NaCl + H_2O$$

10.4.1.3 Sodium Sulfite

Sodium sulfite can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:

Equation 16

$$NaOCl + Na_2SO_3 \Rightarrow NaCl + Na_2SO_4$$

Small spills of standing sodium hypochlorite have been neutralized using sodium sulfite applied to the spill. This method has been used to neutralize spills on roadways, bar ditches, and in parking lots. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

10.4.1.4 Sodium Bisulfite

Sodium bisulfite can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:

Equation 17

$$NaOCl + NaHSO_3 \Rightarrow NaCl + NaHSO_4$$

Sodium bisulfite has been used to neutralize the available chlorine in bleach solutions. This reaction can be more vigorous than the other neutralizing chemicals listed. Appropriate personal protective equipment (PPE) and engineering controls should be used. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

10.4.1.5 Sodium Thiosulfate

Sodium thiosulfate can be used for the reduction of available chlorine in sodium hypochlorite. The chemical reaction is as follows:

Equation 18

$$4NaOCl + Na_2SO_3 + 2NaOH \Rightarrow 4NaCl + 2Na_2SO_4 + H_2O$$

Sodium thiosulfate has been used to neutralize the available chlorine in bleach solutions. This reaction requires that caustic soda be added in addition to the thiosulfate. This reaction can generate less heat than some of the other neutralizing agents but can also produce significant quantities of solids. Appropriate personal protective equipment (PPE) and engineering controls should be used. This method should be covered with the local environmental regulating agency in the review of the Spill Control Plan.

11 ANALYTICAL PROCEDURES

11.1 GENERAL

Specific gravity, excess sodium hydroxide, sodium carbonate, suspended solids, pH, available chlorine, and excess alkalinity are tests that can be done by similar titrations . These may be necessary for control purposes.

Some of the reagents are hazardous materials and the analyst should be familiar with all potential hazards and take appropriate precautions as shown on the MSDS and the label. To insure accurate analysis it is important to use high quality reagents that have been correctly standardized.

11.2 SAMPLING

Due to the relatively unstable nature of sodium hypochlorite solutions, special attention should be given to the collection and preservation of the sample. Exposure to heat and ultraviolet light promotes decomposition and should be avoided. Samples should be tested immediately or refrigerated and stored without exposure to ultraviolet light until the analysis is performed. Delays before testing should be avoided.

To achieve accurate available chlorine comparisons of sodium hypochlorite that has been delivered between the producer and the consumer, samples from the delivered product should be stored in iced containers near 32°F. The iced samples can then be titrated if required by both the manufacturer and the consumer at the same time upon receipt of the samples by both parties. Since the delivered product is stored at 32°F until titrated by both parties, no addition decomposition of the delivered product will occur. If the titration procedures for both parties are the same, data from each of the samples should be within acceptable limits.

11.3 SPECIFIC GRAVITY

Specific gravity is needed if the results of analyses are to be expressed as percent by weight sodium hypochlorite (NaOCl) or percent by weight available chlorine.

However, all measurements of specific gravity introduce some error in the analytical procedure by the nature of the measurement and it can require additional raw material use to manufacture the product. therefore, to reduce the error in measuring the strength of solution, it is recommended to use gpl of available chlorine as the indication of solution strength.

Additional benefits will result in better repeatability of available chlorine since this unit of measure will not be affected by changes in excess caustic, salt levels or sodium chlorate. For example, in table 2.8 120 gpl available chlorine at 2 gpl excess caustic is a 1.157 specific gravity and at 10 gpl excess caustic is 1.171 specify gravity. Therefore, at 120 gpl, the solution with 2gpl is 10.86 percent by weight sodium hypochlorite.

The end result of using weight percent as the indication of strength in this example is the product at 10 gpl excess caustic has to be 1% stronger in gpl available chlorine and it also used approximately 6% more caustic to produce the product to produce the same weight percent sodium hypochlorite.

11.3.1 Procedure to Determine Specific Gravity Using a Hydrometer

Cool the solution to 68°F in a glass cylinder of suitable size and insert a 12 inch hydrometer calibrated to read directly in specific gravity at that temperature. Record the specific gravity of the sodium hypochlorite to the third decimal place, i.e. 1.218.

11.3.2 Procedure to Determine Specific Gravity by Weighing

Pipette a 10-ml sample of the bleach solution into a weighing bottle and weigh to 4 decimal place accuracy using a digital scale. Typical results may be 12.180. Dividing this weight by 10 will provide the specific gravity, i.e. 1.218. To get good accuracy it is recommended to weight 3 samples and average the results.

11.4 DETERMINATION OF PH

11.4.1 Determination of pH by Direct Measurement

It is not recommended to use direct measurement of pH as an accurate indication of levels of excess sodium hydroxide or the amount of alkalinity. Direct measurement of pH is extremely difficult to do accurately and repeatability.

11.4.1.1 Equipment

One method of determining the pH of a sodium hypochlorite solution is with a high quality, pH meter. Most of the commercially available types of meters are satisfactory. Because of the possible high pH associated with some sodium hypochlorite solutions, normal range electrodes will not be accurate, therefore, "high-alkalinity" electrodes should be used.

11.4.1.2 Procedure

The pH meter should be standardized before measuring the pH of the sample solution. For this purpose, commercially available standard buffer solutions covering the various pH ranges may be used. After standardizing the pH electrode, carefully rinse the electrode with distilled water and insert the electrode in the sodium hypochlorite solution to be measured. After the pH reading as stabilized, record the measurement to 2 decimal places, i.e. 12.35 pH.

11.4.2 Determination of Liquid Bleach pH by Calculation

The pH of liquid bleach can be calculated from the concentration (weight percent) of the sodium hydroxide in the sodium hypochlorite solution. This concentration can be found by titration (See Section 11.6). To insure the accuracy of this approach, it is important to account for any sodium carbonate in the liquid bleach solution, therefore, using the results of a total alkalinity titration is not recommended.

Determine the specific gravity (S.G.) of the liquid bleach solution (Section 11.3)

Calculate the Trade % NaOH
Trade% NaOH = Wt.% NaOH x S.G.

Calculate the grams per liter (gpl) NaOH
gpl NaOH = Trade% NaOH x 10

Calculate the moles per liter (M) of NaOH. A mole is a unit of measure used in chemistry to describe an amount of a particular substance in terms of basic structural units of matter such as molecules, atoms or ions. Using this type of unit makes it much easier to understand and work with chemical equations.
M NaOH = gpl NaOH / 40

Calculate the pH of the liquid bleach solution
pH = 14 + log(M NaOH)

Table 11.1 contains the calculated pH for sodium hypochlorite solutions for different concentrations of sodium hydroxide.

Table 11.1. Liquid Bleach pH Calculated from Sodium Hydroxide Concentration (Wt% NaOH)

Trade% NaOH	g/L NaOH	Moles NaOH	pH		Trade% NaOH	g/L NaOH	Moles NaOH	pH
0.001	0.01	0.00025	10.40		0.245	2.45	0.06125	12.79
0.002	0.02	0.00050	10.70		0.250	2.50	0.06250	12.80
0.003	0.03	0.00075	10.88		0.255	2.55	0.06375	12.80
0.004	0.04	0.00100	11.00		0.260	2.60	0.06500	12.81
0.005	0.05	0.00125	11.10		0.265	2.65	0.06625	12.82
0.010	0.10	0.00250	11.40		0.270	2.70	0.06750	12.83
0.015	0.15	0.00375	11.57		0.275	2.75	0.06875	12.84
0.020	0.20	0.00500	11.70		0.280	2.80	0.07000	12.85
0.025	0.25	0.00625	11.80		0.285	2.85	0.07125	12.85
0.030	0.30	0.00750	11.88		0.290	2.90	0.07250	12.86
0.035	0.35	0.00875	11.94		0.295	2.95	0.07375	12.87
0.040	0.40	0.01000	12.00		0.300	3.00	0.07500	12.88
0.045	0.45	0.01125	12.05		0.305	3.05	0.07625	12.88
0.050	0.50	0.01250	12.10		0.310	3.10	0.07750	12.89
0.055	0.55	0.01375	12.14		0.315	3.15	0.07875	12.90
0.060	0.60	0.01500	12.18		0.320	3.20	0.08000	12.90
0.065	0.65	0.01625	12.21		0.325	3.25	0.08125	12.91
0.070	0.70	0.01750	12.24		0.330	3.30	0.08250	12.92
0.075	0.75	0.01875	12.27		0.335	3.35	0.08375	12.92
0.080	0.80	0.02000	12.30		0.340	3.40	0.08500	12.93
0.085	0.85	0.02125	12.33		0.345	3.45	0.08625	12.94
0.090	0.90	0.02250	12.35		0.350	3.50	0.08750	12.94
0.095	0.95	0.02375	12.38		0.355	3.55	0.08875	12.95
0.100	1.00	0.02500	12.40		0.360	3.60	0.09000	12.95
0.105	1.05	0.02625	12.42		0.365	3.65	0.09125	12.96
0.110	1.10	0.02750	12.44		0.370	3.70	0.09250	12.97
0.115	1.15	0.02875	12.46		0.375	3.75	0.09375	12.97
0.120	1.20	0.03000	12.48		0.380	3.80	0.09500	12.98
0.125	1.25	0.03125	12.49		0.385	3.85	0.09625	12.98
0.130	1.30	0.03250	12.51		0.390	3.90	0.09750	12.99
0.135	1.35	0.03375	12.53		0.395	3.95	0.09875	12.99
0.140	1.40	0.03500	12.54		0.400	4.00	0.10000	13.00
0.145	1.45	0.03625	12.56		0.405	4.05	0.10125	13.01
0.150	1.50	0.03750	12.57		0.410	4.10	0.10250	13.01
0.155	1.55	0.03875	12.59		0.415	4.15	0.10375	13.02
0.160	1.60	0.04000	12.60		0.420	4.20	0.10500	13.02
0.165	1.65	0.04125	12.62		0.425	4.25	0.10625	13.03
0.170	1.70	0.04250	12.63		0.430	4.30	0.10750	13.03
0.175	1.75	0.04375	12.64		0.435	4.35	0.10875	13.04
0.180	1.80	0.04500	12.65		0.440	4.40	0.11000	13.04
0.185	1.85	0.04625	12.67		0.445	4.45	0.11125	13.05
0.190	1.90	0.04750	12.68		0.450	4.50	0.11250	13.05
0.195	1.95	0.04875	12.69		0.455	4.55	0.11375	13.06
0.200	2.00	0.05000	12.70		0.460	4.60	0.11500	13.06
0.205	2.05	0.05125	12.71		0.465	4.65	0.11625	13.07
0.210	2.10	0.05250	12.72		0.470	4.70	0.11750	13.07
0.215	2.15	0.05375	12.73		0.475	4.75	0.11875	13.07
0.220	2.20	0.05500	12.74		0.480	4.80	0.12000	13.08
0.225	2.25	0.05625	12.75		0.485	4.85	0.12125	13.08
0.230	2.30	0.05750	12.76		0.490	4.90	0.12250	13.09
0.235	2.35	0.05875	12.77		0.495	4.95	0.12375	13.09
0.240	2.40	0.06000	12.78		0.500	5.00	0.12500	13.10

11.5 DETERMINATION OF SODIUM HYPOCHLORITE CONCENTRATION

11.5.1 Reagents

The Sodium Thiosulfate Method is typically used to determine the available chlorine. The following reagents are needed:

- glacial acetic acid (99.8% CH_3COOH)
- starch solution indicator
- sodium thiosulfate 0.1 N ($Na_2S_2O_3$)
- Potassium iodide (KI) crystals (pH neutral)

11.5.2 Preparation of Sample

Pipette a 25-ml sample of the bleach solution into a weighing bottle and weigh to 1.0 mg. Transfer the sample to a 250-ml volumetric flask, washing the entire sample out of the weighing bottle into the volumetric flask. Dilute to the mark and mix thoroughly. Aliquots of this sample are used for the following determinations.

11.5.3 Procedure

Pipette a 10-ml aliquot of the sample solution into a 300-ml Erlenmeyer flask containing about 50 ml of distilled water. Add 2 or 3 grams (½ teaspoon) of potassium iodide (KI) crystals and 10 ml of 1:1 acetic acid, in the order named. Titrate with 0.1 N sodium thiosulfate solution until the mixture is straw yellow in color. Add 5 ml of starch indicator and continue the titration until the blue color disappears. Calculate the sodium hypochlorite concentration.

$$\%\ NaOCl = \frac{\text{ml } Na_2S_2O_3 \times N^* \times 3.723}{0.04 \times \text{weight of original sample}}$$

* N = normality of $Na_2S_2O_3$ solution

11.6 DETERMINATION OF SODIUM HYDROXIDE AND SODIUM CARBONATE

11.6.1 Reagents

- 0.1 N hydrochloric acid
- Only reagent grade (pH neutral) hydrogen peroxide solution (3.0%) No other grade of hydrogen peroxide is acceptable. Note: it is important that the peroxide solution used is fresh or the titration results may not be accurate.
- phenolphthalein indicator
- methyl orange indicator

11.6.2 Procedure

Pipette a 50-ml aliquot of the sample solution into a 300-ml Erlenmeyer flask containing about 50 ml of distilled water. Add 20 ml of neutral 3% hydrogen peroxide solution (cool to 0°C to 5°C). Add 3 drops of phenolphthalein indicator and titrate with 0.1 N hydrochloric acid solution until the pink color disappears. Record the milliliters of 0.1 N hydrochloric acid used. Add 3 drops of methyl orange indicator and continue the titration until the yellow color changes to red. To convert to other concentration units (gpl, etc.) see Section 11.4.2.

$$\% \text{ NaOH (by weight)} = \frac{D - 2(D-C) \times N \times 4}{0.2 \times \text{weight of original sample}}$$

$$\% \text{ NaCO3 (by weight)} = \frac{2(D-C) \times N \times 5.3}{0.2 \times \text{weight of original sample}}$$

- C = ml reading at the phenolphthalein end point
- D = ml reading at the methyl orange end point
- N = normality of the hydrochloric acid solution

APPENDIX A DEFINITIONS

A.1 Definitions

The following definitions and abbreviations are used in this pamphlet:

ANSI	American National Standards Institute, Inc.
ASTM	Formally known as American Society for Testing and Materials.
available chlorine	The amount of oxidizing power of a compound compared to chlorine (Cl_2), chlorine equivalent.
bulk package	A package or container, other than a vessel or barge, including a transport vehicle or freight containers, in which hazardous materials are loaded and which has a maximum capacity greater than 119 gallons, 882 pounds or a water capacity greater than 1000 pounds as a receptacle for gas.
CCMA	Canadian Chemical Manufacturers Association
CEPA	Canadian Environmental Protection Act
CERCLA	Comprehensive Environmental Resource and Conservation Liability Act (U.S.)
CFR	Code of Federal Regulations (U.S.)
chlorine gas	The element chlorine in the gaseous state
chlorine	The chemical element existing as either a liquid or a gas
chlorine solution (chlorine water)	A solution of chlorine in water **(The term "chlorine solution" is sometimes used to describe hypochlorite solutions. This is a misuse of the term and should be discouraged.)**
CMA	Chemical Manufacturers Association
DOT	Department of Transportation (U.S.)
dry chlorine	Chlorine, liquid or gas, whose water content does not exceed the saturation point of water in chlorine. The saturation concentration depends on the temperature and pressure of the chlorine. For example, liquid chlorine containing 30 ppm water will be dry at 50°F but is considered wet at –4°F. (The term "dry chlorine" is sometimes used improperly to describe a dry compound (usually calcium hypochlorite or one of the chlorinated isocyanurates) often employed for

	swimming pool sanitation. This is a misuse of the term and should be discouraged.)
EPA	Environmental Protection Agency (U.S.)
EPCRA	Emergency Planning and Community Right-To-Know Act (U.S.)
FIFRA	Federal Insecticide, Fungicide, Rodenticide Act (U.S.)
gpl	grams per liter
grams per liter available chlorine	The weight of available chlorine, in grams, contained in one liter of sodium hypochlorite solution (Section 2.3.1)
hazmat employee	An employee who during the course of their employment directly affects hazardous material transportation safety. This includes, but is not limited to, the operator of the motor vehicle which transports hazardous materials, the employee loading, unloading, handling or preparing the shipment of the hazardous material, and the employee's direct supervisor and personnel responsible for the transporting the hazardous materials safely.
HMTA	Hazardous Materials Transportation Act (U.S.)
household bleach	A solution of sodium hypochlorite, generally containing 5.25% (by weight) sodium hypochlorite or less
industrial strength hypochlorite solution	A solution of sodium hypochlorite generally containing sodium more than 7.0% (by weight) sodium hypochlorite (These solutions are erroneously referred to as "hypo" solutions; this terminology should be discouraged.)
Institute	The Chlorine Institute, Inc.
liquid chlorine	The element, chlorine, in the liquid state. (The terms "chlorine" and "liquid chlorine" are sometimes used to describe a hypochlorite solution employed for swimming pool sanitation. This misuse of the terms should be discouraged as it could cause significant confusion especially in emergency response situations.)
liquid bleach	A solution of hypochlorite, usually sodium hypochlorite (this term rather than "liquid chlorine" should be used to describe a liquid hypochlorite product).
moist chlorine	Synonymous with wet chlorine
MSDS	Material Safety Data Sheet

mole	A mole is a unit of measure used in chemistry to describe an amount of a particular substance in terms of basic structural units of matter such as molecules, atoms or ions. Using this type of unit makes it much easier to understand and work with chemical equations.
NACD	National Association of Chemical Distributors
NIOSH	National Institute for Occupational Safety and Health (U.S.)
non-bulk package	A package which has a maximum capacity of 119 gallons or less, 882 pounds or less, or 1000 pounds or less water capacity as a receptacle for gas.
OHSA	Occupational Health and Safety Act (CANADA)
OSHA	Occupational Safety and Health Administration (U.S.)
pesticide	FIFRA defines the term "pesticide" as: (1) any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest, and (2) any substance or mixture of substances intended for use as a plant regulator, defoliant, or desiccant, except that the term "pesticide" shall not include any article that is a "new animal drug" within the meaning of section 201(w) of the Federal Food, Drug, and Cosmetic Act (21 U.S.C. 321(w)), that has been determined by the Secretary of Health and Human Services not to be a new animal drug by a regulation establishing conditions of use for the article, or that is an animal feed within the meaning of section 201(x) of such Act (21 U.S.C. 321(x)) bearing or containing a new animal drug
pH	The negative logarithm of the hydrogen ion activity used to describe the acidity or alkalinity of a chemical compound or mixture.
PPE	Personal Protective Equipment
PSM	Process Safety Management (U.S.)
RCRA	Resource Conservation and Recovery Act (U.S.)
RMP	Risk Management Plan (U.S.)
RMPR	Risk Management Program Rule (U.S.)
RQ	Reportable Quantity
SARA	Superfund Amendments and Reauthorization Act (U.S.)
SERC	State Emergency Response Commission (U.S.)

TDGA	The Transportation of Dangerous Goods Acts and Regulations (CANADA)
trade percent available chlorine	Commonly used to denote the strength of commercial sodium hypochlorite solutions in terms of available chlorine; is similar to grams per liter available chlorine, except that the unit of volume is 100 milliliters instead of one liter; its value is therefore one tenth of the grams per liter (Section 2.3.1)
trade percent sodium hypochlorite	Used to denote the strength of commercial sodium hypochlorite solutions in terms of sodium hypochlorite, is similar to grams per liter sodium hypochlorite, except that the unit of volume is 100 milliliters instead of one liter; its value is therefore one tenth of the grams per liter. Not commonly used.
weight percent available chlorine	The weight of available chlorine per 100 parts by weight of sodium hypochlorite solution. This can be calculated by dividing the trade percent by the specific gravity (Section 2.3.1.2 - Equation 3a)
weight percent sodium hypochlorite	The weight of sodium hypochlorite per 100 parts by weight of solution; it may be calculated by converting weight percent of available chlorine into its equivalent as sodium hypochlorite; that is, multiplying by the ratio of their respective molecular weights (Section 2.3.2 - Equation 5a)
wet chlorine	Liquid or gaseous chlorine with a water content exceeding the amount that can be completely dissolved in the chlorine. See Pamphlet 100, Dry Chlorine: Definitions and Analytical Issues. Chlorine is not wet just because it is in the liquid state.
UN1791	This is the internationally recognized identification number for sodium hypochlorite solutions. The US DOT and Transport Canada regulate how and when it should be used. Refer to Appendix B.
WHMIS	Workplace Hazardous Materials Information System (CANADA)

APPENDIX B REGULATIONS

B.1 General

The following briefly explains regulations that affect the sodium hypochlorite industry. It is strongly advised that all manufacturers, distributors, users, transporters, etc. of sodium hypochlorite carefully review the noted regulation in the prescribed U.S. Code of Federal Regulation (CFR) and/or Canadian regulations, and/or other state and local agency or technical association standards.

B.2 United States Regulations

B.2.1 Department of Transportation (DOT) Regulations

In the United States, the Department of Transportation (DOT) under Hazardous Materials Transportation Act (HMTA) regulates air, rail, vessel and highway shipments all hazardous materials.

While the US DOT is responsible for enforcing the hazardous material regulations, the Research and Special Programs division is responsible for issuing hazardous material rules. Title 49 CFR is where the regulations dealing with transportation, and hazardous materials, are found. The following sections give a brief overview of many of the sections of 49 CFR applicable to packaging and transporting sodium hypochlorite solutions.

B.2.1.1 49 CFR Section 107, Subpart G Registration

Registration and fee requirements for transporting or shipping hazardous materials in foreign, interstate or intrastate commerce. It also specifies record keeping requirements for the application and Certificate of Registration.

B.2.1.2 49 CFR Section 171.8 Definitions

Explains terminology used by the DOT in 49 CFR.

B.2.1.3 49 CFR Section 171.15 and 171.16 Reporting Hazardous Material Incidents

Sets forth the requirements for immediate verbal notifications of hazardous material releases. Requires all hazardous material releases, regardless of the quantity, during transport, loading or unloading be documented on DOT form F 5800.1 and submitted within 30 days from the incident to the DOT.

B.2.1.4 49 CFR Section 172, Subpart B HMT

Hazardous Material Table (HMT). It identifies all hazardous materials and lists their hazard class, packaging and labeling requirements, identification number, proper shipping name, packing group, etc.

B.2.1.5 49 CFR Section 172, Subpart C Shipping Papers

The shipper is required to prepare shipping papers to accompany each shipment of a hazardous material during transportation. The DOT specifies the description for the hazardous material shipment and mandates a shipper certification that the hazardous materials have been properly prepared for transportation and are in compliance with the regulations. This section also describes the required minimum information and formatting and what to do when the shipping paper covers both hazardous and non-hazardous materials.

B.2.1.6 49 CFR Section 172, Subpart D Markings

It is the responsibility of the shipper to properly mark each package of hazardous materials for transportation. Markings must be durable, in English, and printed on packages or labels, tags, or signs affixed to packages. Marking requirements are addressed in the context of non-bulk (drums, boxes, jerricans, etc.) and bulk packages (portable tanks and cargo tanks).

B.2.1.7 49 CFR Section 172, Subpart E Labels

It is the responsibility of the shipper to properly label hazardous material packages prior to shipment. Labels warn those handling the package or shipment of its contents.

Required labels for each hazardous material are listed in Column 6 of the HMT. The required label for Hypochlorite Solutions at the time of this publication is 8, Corrosive. There is not a subsidiary risk label.

B.2.1.8 49 CFR Section 172, Subpart F- Placards

Placarding is required for vehicles transporting hazardous materials. The shipper is responsible for providing placards applicable to the shipment being offered for transportation. The regulations describe the situations where placard is required as well as the locations, sizes, shapes and other physical parameters that must be met. There are a number of different scenarios described in this section, bulk, non-bulk, mixed loads, etc., therefore it is strongly recommended that anyone shipping sodium hypochlorite solutions familiarize themselves with these regulations.

B.2.1.9 49 CFR Section 172 Subpart G, Emergency Response Information
Emergency response information must be available away from the hazardous material being transported, be printed in English and must contain the information specified in this section. This information must be communicated in one of two ways:

(a) Printed on the shipping papers

(b) In a separate document such as a Material Safety Data Sheet, North American Emergency Response Guidebook or the a copy of the appropriate Guide Page from the North American Emergency Response Guidebook

B.2.1.10 49 CFR Section 172 Subpart H, Hazardous Material Training

All hazardous materials employers are required by the DOT to provide training and testing to all of their hazardous material employees (please see definition of a Hazmat employee in Appendix A). Hazardous material training must include:

(a) General awareness, familiarity with the rules and regulations

(b) Function-specific, rules applicable to the employee's job tasks and procedures for performing the job tasks properly

(c) Safety, measures to protect the employee from hazardous material exposure, accident prevention and emergency response information as required by 49 CFR 172 Subpart G Training is required immediately upon employment or change of job function, unless an employee performs his or her job function under the direct supervision of a trained and knowledgeable hazmat employee or supervisor. Hazmat training is required to be completed within 90 days after employment or change of job function. Refresher training is required every three (3) years.

This section also describes the record keeping requirements necessary to meet these regulations.

B.2.1.11 49 CFR Section 173 Subpart B, Preparation of Hazardous Materials for Transportation

DOT general requirements for transporting hazardous materials in non-bulk packages, bulk packages, over packs, portable tanks, intermediate bulk containers, and cargo tanks. Specifies the conditions that packages may be reused, reconditioned or remanufactured, and when a package is permitted to be vented to reduce internal pressure.

B.2.1.12 49 CFR Section 176, Carriage by Vessel

Additional requirements for transporting a hazardous material by water, including additional requirements for the separation and segregation of hazardous materials.

B.2.1.13 49 CFR Section 177, Carriage by Highway

DOT requirements for transporting a hazardous material by highway, including requirements for the separation and segregation of hazardous materials during loading, storage and transport.

At the time of publication of this pamphlet, the segregation table for hazardous materials forbid Hypochlorite Solutions to be loaded, stored or transported with hazard class 1.1, 1.2, 1.3, 1.5, 2.3 Hazard Zone A, 4.2 and 6.1 materials.

B.2.1.14 49 CFR Section 178, Specifications for Hazardous Material Packagings

DOT regulations regarding all non-bulk and bulk packaging specifications, testing requirements, and identification requirements.

Table B-1. Explanation of the Hazardous Material Packaging Codes for Non-Bulk Single and Composite Packages, and Intermediate Bulk Containers*	
United Nations Symbol	Identifies that the package conforms to a United Nations standard.
Packaging Code	Designates the type of packaging and the material of construction. Common packaging codes for Hypochlorite Solutions are 4G (Fiberboard Box), 1H1 (plastic drum, non-removable head), 1H2 (plastic drum, removable head), 31H1 (rigid plastic IBC), and 31HA1 (rigid plastic inner receptacle and an outer steel body IBC).
Performance Level	Identifies the performance standard to which the package was tested. X is for packages meeting packing group I, II and III tests, Y is for packages meeting packing group II and III tests, and Z is for packages meeting packing group III tests.
Specific Gravity	Maximum specific gravity of product permitted.
Hydrostatic Test Pressure	Internal hydrostatic test pressure in kilopascals.
Year of Manufacture	Last two digits of the year the package was manufactured. Plastic drums and jerricans must be marked with the month and year.
Country of Authorization	Country designating code where the package is manufactured and marked.
Name or Symbol of Manufacturer or Testing Agency	Name and address or authorized symbol of the manufacturer or certification agency.
Minimum Thickness	For metal or plastic drums, jerricans or other outer packaging of a composite packaging intended for reuse or reconditioning, the minimum thickness in millimeters (mm).
R	Reconditioned packages.
L	For a reconditioned package that has successfully passed a leak proof test.
Month and Year	For IBCs, the month and year of manufacture.
Stack Test Load	For IBCs, the stacked load test in kilogram. A number “0” shows that the IBC is not designed for stacking.
Gross Mass	For IBCs, maximum gross mass in kilograms.

* Note: at the time of publication of the pamphlet, these codes were authorized by the DOT in 49 CFR Section 178 Subpart L and N.

B.2.1.15 49 CFR Section 180, Continuing Qualification and Maintenance of Packagings

DOT testing (types and frequency) and marking requirements for the continued use of cargo tankers, intermediate bulk containers (IBC's), portable tanks and tank cars.

B.2.2 Environmental Protection Agency (EPA) Regulations

Environmental conditions and issues, including the manufacture, distribution and use of pesticides, are administered by the Environmental Protection Agency (EPA) in the United States. This section describes many of the regulations and programs that can cover the manufacture, distribution and use of sodium hypochlorite solutions.

B.2.2.1 Pesticides - FIFRA – 40 CFR Chapter I, Subchapter E, Pesticide Programs

In the United States, sodium hypochlorite solutions when labeled and used for disinfection and/or sanitization are pesticides subject to the provisions of the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA). The term "antimicrobial" may also be used in relation to EPA/FIFRA requirements for sodium hypochlorite solutions. All manufactures and distributors who produce, package, repackage and sell sodium hypochlorite must register with the EPA. Registration includes:

- Obtaining an EPA Pesticide Establishment Number
- Registering or Sub-registering the Sodium Hypochlorite product

In addition to the registrations, EPA has mandated specific container pesticide label and/or label wording for sodium hypochlorite as well as transportation and storage requirements, (see 40 CFR section 156). Pesticides can be transferred into smaller containers for end use. A registered pesticide cannot be transferred to a different package size and relabeled for sale as a pesticide unless the distributor has sub-registered under the pesticide manufacturer.

All manufacturers and distributors with a pesticide establishment numbers are required to report to EPA annually, March 1 of each year, the amount of Sodium Hypochlorite they produced, sold, and exported in the past year, and the amount they plan to produce for next year.

B.2.2.2 Other Pesticide Laws

All states, and some local governments, have laws requiring the registration of sodium hypochlorite that is packaged, repackaged and labeled for sale in their respective states. These registrations normally expire on an annual basis.

Contact the state agency that regulates the production and sale of pesticides in the state for further instructions.

B.2.2.3 Hazardous Substances - Designation, Reportable Quantities and Release Notification – 40 CFR Section 302

Most government agencies have reporting requirements for hazardous substance releases. Sodium hypochlorite facilities must be aware of the Reportable Quantities (RQ) for sodium hypochlorite and all relevant reporting requirements.

In the United States under the Comprehensive Environmental Resource and Conservation Liability Act (CERCLA), any release of 100 lbs. (45.4 kilograms) or more of sodium hypochlorite to the environment within a 24-hour period, not specifically allowed by an operating permit, must be reported immediately (within 15 minutes) to the National Response Center (NRC) at 1-800-424-8802 or 202-426-2675.

A written follow-up report is required by the U.S. EPA for all RQ releases. The report is usually submitted to the State Emergency Response Committee and the Local Emergency Planning Council in a time frame specified by the state. Sodium hypochlorite facilities should contact their state emergency services or environmental agency to obtain these requirements.

B.2.2.4 Hazardous Substances - Community Right-to-Know Reporting Requirements – 40 CFR Section 370, Subpart B

All facilities which are required to prepare or have available a MSDS for a hazardous chemical under OSHA may be subject to MSDS and/or Inventory reporting.

B.2.2.5 Hazardous Substances – Risk Management Program (RMP) – 40 CFR Section 68

The Clean Air Act Amendments of 1990 requires EPA to address concerns that chemical accidents could pose a risk to the public and environment. EPA published its Risk Management Program standard to address this concern and prevent accidental chemical releases or minimize their impact. The RMP regulation only applies to certain chemicals identified by the EPA in the “list rule” (see 40 CFR Section 68.130). If a facility contains a listed chemical above the threshold quantify, the facility is subject to RMP regulation.

In 1999, the Senate Bill 880 mandated that all facilities required to comply with EPA’s RMP standard communicate their Risk Management Program to the affected communities.

A letter must be sent, in a time frame specified by the law, to the Director of the Federal Bureau of Investigation indicating that such a public meeting has been held.

At the time this publication was printed, Sodium Hypochlorite is not a RMP listed chemical, but Chlorine, used in the manufacturing of Sodium Hypochlorite, is. The Chlorine Institute has published Pamphlet 162, Generic Risk Management Plan for Chlorine Packaging Plants and Sodium Hypochlorite Production Facilities, which is designed to help sodium hypochlorite manufacturing sites and chlorine packagers comply with the RMP standard.

In 1999, EPA published a fact sheet that explains how EPA intends to interpret the general duty clause under Section 112(r) of the Clean Air Act Amendments of 1990. The fact sheet outlines the responsibilities imposed by the clause on any facility, which may include a sodium hypochlorite facility, that produces, handles, processes or stores extremely hazardous substances, as defined by EPA, regardless of quantity. The general duty clause, as it is called, is similar to the OSHA general duty clause, and defines specific requirements of the owner or operator of a facility.

B.2.3 Occupational Safety and Health Act (OSHA) Regulations

In the United States, under the Occupational Safety and Health Act of 1970, OSHA, and various approved OSHA state plans, regulate worker health and safety issues as well as enforce health and safety standards in the workplace. This section gives an overview of this information, it is strongly recommended that everyone involved in the manufacture, transport and use of sodium hypochlorite review these regulations to determine how they apply to their specific operations.

B.2.3.1 Process Safety Management (PSM) – 29 CFR Section 1910 Subpart H

Requires facilities that use, manufacture, store or handle certain chemicals (which are listed in the regulation) to identify and analyze potential hazards associated with their handling of the chemicals as well as implement a specified accident prevention program. Sodium Hypochlorite is not listed in this regulation, but Chlorine is a listed PSM chemical and companies which manufacture Sodium Hypochlorite using chlorine may be subject to this regulation.

B.2.3.2 Hazardous Communication – 29 CFR Section 1910 Subpart Z

Requires that all chemicals in the workplace be evaluated for possible physical and health hazards, and mandates that all information related to the chemical's hazards be made available to the employee through a written Hazardous Communication Plan.

Hazardous Communication Plans must include at a minimum chemical hazard identification, labeling requirements, Material Safety Data Sheets (MSDS), and training.

B.2.3.3 Personal Protective Equipment (PPE) – 29 CFR Section 1910 Subpart I
Requires that the employer assess workplace hazards to determine if and what type of personal protective equipment (PPE) is needed for the employees. The PPE hazard assessment is to be documented and maintained onsite at all times. If PPE is required, employees must be trained on:

- When PPE is required
- Why the PPE is needed
- How to properly put on, take off, adjust, and wear the prescribed PPE
- PPE limitations
- Proper care, maintenance, useful life, and disposal of PPE.

All training must be documented, and all employees must be certified that they have received and understand PPE training.

B.2.3.4 Hearing Protection – 29 CFR Section 1910 Subpart G

OSHA standard mandates protection against the effects of noise exposure. A hearing conservation program must be developed and implemented as prescribed by this subpart when the sound levels in the workplace exceed the OSHA permissible noise exposure as indicated in Table G-16 of the regulation.

B.2.3.5 Respiratory Protection – 29 CFR Section 1910 Subpart I

If respiratory protection is needed to protect the health of the employee or when the employer requires respirators to be worn in the workplace, OSHA requires that a written respiratory protection program to be established and implemented by the employer. In 1998, OSHA issued a Compliance Directive to assist compliance with this regulation. This regulation describes the minimum elements that must be included in the respiratory protection program.

B.2.3.6 Fire Extinguishers – 29 CFR Section 1910 Subpart L

When fire extinguishers are provided in the workplace, documented employee training is required regarding the general principles of fire extinguisher use and hazards involved with incipient stage fire fighting. Additional requirements include, but are not limited to, monthly visually fire extinguisher equipment inspections, and annual servicing by an approved agency.

B.2.3.7 Powered Industrial Trucks – 29 CFR Section 1910 Subpart N

Contains specifications and requirements for powered industrial truck safety and training.

In 1998, OSHA revised its powered industrial truck operator training requirements and specifically outlined elements that must be included in the operator training program. Powered industrial truck training is required prior to operating a powered industrial truck, and refresher training is required every three (3) years, unless operator actions and/or changes in the workplace or power industrial truck warrant earlier refresher training. All truck operators must be tested to ensure operators understood the training provided and can operate the power industrial truck safely. All training and testing must be documented as prescribed in the regulation.

B.2.3.8 Control of Hazardous Energy – 29 CFR Section 1910 Subpart J

OSHA requires the control of hazardous energy when servicing or maintaining equipment where unexpected energization or start-up of equipment could cause injury or death to an employee. At a minimum, the standard mandates employers to develop a written energy control program that clearly identifies authorized and affected employees, explains all procedures for controlling energy sources (lockout/tagout), training and audits.

B.2.3.9 Confined Spaces – 29 CFR Section 1910 Subpart J

A confined space is a space that is large enough for an employee to enter, has restricted means of entry or exit, and is not designed for continuous human occupancy. Examples of confined spaces include, but are not limited to cargo tanks, storage tanks, vats, tunnels, sewers and vaults. This OSHA standard mandates identification of confined spaces in the workplace, determining if they are a permit required or non-permit required confined space, and requirements for working in confined spaces safely.

B.2.3.10 First Aid – 29 CFR Section 1910 Subpart K

Requires employers to have first aid supplies readily available for employees. This includes, in the absence of a clinic or hospital in near proximity to the workplace, a person or persons adequately trained to render first aid.

In addition, if any part of the body of a person may be exposed to a corrosive material, suitable eye wash and shower stations for quick drenching or flushing are to be provided in the workplace. The American National Standard Institute (ANSI) has developed a standard which details the requirements for emergency eye wash and shower stations. It is recommended that these stations be inspected daily to ensure that they are working properly.

B.2.3.11 Bloodborne Pathogens – 29 CFR Section 1910 Subpart Z

Any employer having an employee(s) with the likelihood of an occupational exposure to blood or other infectious materials as a result of his or her job, is required by OSHA under this subpart to establish a written Exposure Control Plan designed to eliminate or minimize employee exposure. In 1999, OSHA issued a Compliance Directive to assist compliance with this regulation. This regulation describes the minimum elements that must be included in an exposure control plan. It also requires that the exposure control plan is to be made accessible to all employees and reviewed and updated annually, or whenever changes in the workplace affecting the plan occur.

B.2.3.12 Evacuation and Contingency Planning – 29 CFR Section 1910.38

OSHA requirement for employers to establish an emergency action plan and/or a fire prevention plan to ensure employee safety from fire and other emergencies. Depending upon the number of employees in the workplace, the plan may be communicated to the employees orally or may be required to be written.

Training is required for all employees when the plan is developed, at the time of employment, or when the employee’s responsibilities under the plan or the plan changes. A “mock drill” activating either or both plans is recommended annually.

B.2.3.13 Emergency Response – 29 CFR Section 1910.120 (q)

OSHA requirement for an emergency response plan to be developed and implemented when employees are expected to handle anticipated emergencies involving hazardous material releases no matter where they occur. Employees are required to have adequate training and medical evaluations as prescribed in the regulation.

B.2.4 United States Department of Agriculture (USDA) Regulations

The U.S. Department of Agriculture requires any substance or compound used in the preparation of product and non-food compounds to be evaluated and authorized for use by their department. This applies to any plant environment involved in slaughtering or food processing under USDA meat and poultry, shell grading and egg, fruit and vegetable and laundry washing and/or sanitization.

B.3 CANADIAN REGULATIONS

B.3.1 Transportation of Dangerous Goods Regulations

Canadian Transportation of Dangerous Goods Regulations are applied to handling, offering for transport, and transportation of dangerous goods. This system is designed for product identification and emergency procedures. Labeling requirements are: (1) hazard symbol; (2) class and division number; (3) shipping name as published in the TDGA regulations. Labeling under TDGA regulations is in addition to all other label requirements.

B.3.2 Hazardous Product Regulations

The Canadian Hazardous Product Act regulates products sold as consumer products. Labeling requirements include: (1) hazard symbol; (2) the signal word "DANGER", "WARNING", or "CAUTION"; (3) a statement of the nature of the primary hazard and secondary hazard (if appropriate); (4) precautions to be followed; (5) first aid treatment; (6) source of the hazard; (7) first aid treatment antidotes; (8) directions for the proper and safe use and storage.

B.3.3 Pest Control Product Regulations

Any product used for the control of any injurious, noxious, or troublesome insect, fungus, bacterial organism, virus, weed or rodent must meet the PCP regulations. Section 4(1) of these regulations prohibits the sale of any product used for the control of pests unless it is packaged and labeled as prescribed. Sections 26-40 of the regulations specify label content and format. Label requirements are as follows: (1) product name and common name of active ingredient; (2) product class (restricted, commercial, domestic); (3) concentrations of the active ingredient; (4) a product registration number (issued by Agriculture Canada); (5) identify significant hazards with instructions on methods of alleviating the hazards; (6) first aid instructions; (7) toxicological information; (8) degree of hazard symbol; (9) symbols identifying hazards; (10) signal words to indicate degree of hazard and nature of hazard.

B.3.4 Workplace Hazardous Materials Information System

The Workplace Hazardous Materials Information System (WHMIS) is a nationwide system to provide information on hazardous materials used in the workplace. Labels on hazardous materials and their containers are designed to alert employers and workers to the dangers of products and basic safety precautions. Requirements on a product supplier label are: (1) a hazard symbol; (2) product identifier; (3) risk phases; (4) precautionary measures; (5) first aid measures; (6) a reference to the Material Safety Data Sheet; (7) supplier identifier. WHMIS labels are not required for products carrying a PCP label or a consumer label.

B.4 STATE/PROVINCE & LOCAL REGULATIONSB.4STATE/PROVINCE & LOCAL REGULATIONS

Different States/Provinces or locations may have other regulatory agencies that must be consulted with/adhered to and may require permits to operate within their guidelines/jurisdictions. Anyone manufacturing, transporting, packaging, distributing or using sodium hypochlorite solutions is responsible to ensure compliance with all applicable laws and regulations. Examples of other regulatory agencies are:

- Air Quality Boards
- Air Pollution Control Agencies
- Departments of Health
- Departments of Agriculture
- Water Quality Agencies
- State/Provincial Environmental Agencies
- Public Utilities Commission
- Fire and Building Codes
- Zoning Codes

APPENDIX C DILUTION OF SODIUM HYPOCHLORITE SOLUTIONS (NaOCl) (11/16/04)

Note: It is also necessary to obtain CI Pamphlet 96, *The Sodium Hypochlorite Manual*, and CI Pamphlet 65, *Personal Protective Equipment for Chlor-Alkali 8Chemicals.* You must review them before attempting to establish your procedures for diluting sodium hypochlorite. (Order from CI's website @ www.chlorineinstitute.org.com)

Reasons for Diluting Sodium Hypochlorite Solutions

Reasons to dilute sodium hypochlorite solutions include:

- To meet specific process or product requirements.
- Enhanced accuracy in hypochlorite feed/metering systems. (CI Pamphlet 96, Section 6.4)
- Enhanced product stability. Sodium hypochlorite (NaOCl) continually decomposes on standing after it is produced. If the solution is diluted to 50% of its initial concentration, the rate of decomposition will be about 25% of the pre-dilution rate if all other conditions are kept basically the same. Since preserving the strength of the product is important, dilution is a simple way to help decrease decomposition. (CI Pamphlet 96, Section 3.3)

Dilution Water Quality Considerations

It is important that dilution water be of suitable quality to prevent precipitants from forming and to protect against the addition of ionic species that can promote product decomposition. (See CI Pamphlet 96, Section 3) Soft water (well or tap) should be used which can be generated using an ion exchange softening unit that uses salt (sodium chloride) as the regenerate. These units are commercially available in a wide range of sizes.

Adjusting the pH/Excess Caustic of the Diluted Bleach Solution

When diluting solutions of sodium hypochlorite it is important to also consider adjusting the pH (level of excess alkalinity or caustic soda) of the diluted solution to ensure the final solution remains stable. Section 3.7 of CI Pamphlet 96, describes the effect of pH on the stability of a bleach solution.

Check the diluted bleach solution with a pH meter (using high alkalinity pH electrodes) or titrate as indicated in CI Pamphlet 96, Section 10 to be certain the solution contains adequate excess alkalinity. Do not use litmus papers to check this pH; experience has shown they do not work. If the pH is below 11.9 consider adding additional sodium hydroxide to the solution. The amount of caustic soda to be added can be estimated using a small volume of the diluted sodium hypochlorite solution. Collect about 500 ml of bleach solution in a beaker and add a dilute solution of caustic soda drop wise from a calibrated burette while monitoring the pH. The amount of caustic soda needed to adjust the pH of the bulk bleach solution can now be calculated.

While the effect of the dilution on the level of excess alkalinity in the bleach is typically not significant, the need to add additional alkali to the diluted solution will depend on the pH (excess caustic level) of the initial bleach solution and how far the solution is diluted. As a rule of thumb, the closer the pH of the initial solution is to 11.9 pH or the more it is diluted, the more likely it will be necessary to increase the pH of the diluted solution.

Precautions When Adding Caustic Soda to Sodium Hypochlorite Solutions

Care must be taken when adding sodium hydroxide (caustic soda) to bleach solutions as this involves an exothermic reaction that will cause the bleach solution to heat up. How hot the bleach solution gets will depend on the strength of the caustic solution used and how much is added. In extreme cases this could result in an unsafe situation due to splattering/splashing of the solution. For this reason it is generally better to use a dilute solution of caustic soda and add it slowly to a well agitated sodium hypochlorite solution. It may be necessary to cool the solution during the pH adjustment.

The quality of the caustic soda used must also be considered. Some of the contaminants (trace metals, sodium chloride, etc.) typically found in sodium hydroxide can affect the stability/shelf life, color and/or the overall quality of the sodium hypochlorite solution. It is generally better to use a high purity caustic to adjust the pH of a bleach solution. See section 4.3.4.2 of CI Pamphlet 96, for additional information.

Temperature Considerations When Diluting Sodium Hypochlorite Solutions

The dilution (addition of water) of sodium hypochlorite is not exothermic (release of heat), therefore, cooling equipment is not necessary. NOTE: Dilution with water is different than the addition of sodium hydroxide to meet a product specification or for pH adjustment. When sodium hydroxide is added to sodium hypochlorite, cooling or extensive mixing may be necessary due to the exothermic reaction that occurs (see Precautions When Adding Caustic Soda section above).

Equipment Recommendations for Diluting Sodium Hypochlorite Solutions

The dilution of sodium hypochlorite is a relative simple matter. Small batch operations can be designed by utilizing a storage tank and adding the known amount of sodium hypochlorite and then adding the calculated amount of soft water. Automatic dilution systems are available to dilute higher concentration solutions down to a lower concentration with great accuracy and speed. All equipment that may come into contact with the sodium hypochlorite must be made of compatible materials. Section 6 of CI Pamphlet 96 should be referenced when choosing equipment for the dilution process.

Calculations for Diluting Sodium Hypochlorite Solutions

This can be done with the following information:

A	=	weight percent of initial (strong) sodium hypochlorite.
B	=	weight percent of desired final (diluted) sodium hypochlorite.
X	=	gallons of initial (strong) sodium hypochlorite
H	=	specific gravity of initial (strong) sodium hypochlorite
V	=	volume of water in gallons needed to be added for dilution per gallon of initial sodium hypochlorite solution.

$$V = X \times H \times \frac{(A - B)}{B}$$

Gallons (V) of water needed per gallon of initial NaOCl solution for dilution = gallons (X) of initial (strong) bleach x sp. gr. (H) of initial (strong) bleach x [(A - B) divided by B].

For example: To dilute one gallon of 10% to 5% sodium hypochlorite by weight.

Gallons of water = (1 gal.) x 1.154 x (10-5) / 5 = 1.154 gallons added per initial one gallon of NaOCl. (For ten gallons of initial strength NaOCl, 10 x 1.154 = 11.54 gal. of water to be added to the ten gallons of initial strength solution).

Care must be taken to obtain an accurate reading of the concentration (weight percent) and specific gravity of the strong solution. If these two factors are wrong the concentration of the diluted solution will be off.

Analytical Procedures

Appropriate analytical procedures can be found in Section 10 of the CI Pamphlet 96.

Personal Protective Equipment (PPE)

The level of PPE needed for diluting sodium hypochlorite solutions is highly dependent on the task or tasks involved in your operation. If lines or connections are disconnected or there is a chance for NaOCl to leave a closed system, then recommended PPE levels are higher. Splash goggles and a face shield along with protective gloves are virtually always recommended. Chemical suits, hats or hoods, boots and respiratory protection are recommended for certain operations. CI Pamphlet 65 on PPE for sodium hypochlorite solutions covers this subject in Section 7.

Chlorine Institute Publications

CI offers many publications and videos on its six mission statement chemicals. These can be reviewed and ordered from our website at www.chlorineinstitute.com. Some documents like Pamphlet 96, The Sodium Hypochlorite Manual, can be downloaded from the website for a small fee. You should also consider ordering the video on the safe handling of sodium hypochlorite and Pamphlet 65 on PPE. This information can be very helpful in developing your procedures for handling and diluting sodium hypochlorite.

APPENDIX D REFERENCES

D.1 SPECIFICATIONS FOR SODIUM HYPOCHLORITE

These specifications may apply for potable water use.

D.1.1 American Water Works Association: Denver, CO: Specification AWWA-B300-92, Hypochlorites

D.1.2 Drinking Water Treatment Chemicals - Health Effects: ANSI/NSF Standard # 60.

D.2 CHLORINE INSTITUTE MATERIALS (PAMPHLETS, VIDEOS, ETC.)

D.2.1 *Chlorine Manual*, ed. 6; Pamphlet 1; The Chlorine Institute: Arlington, VA, **1997**.

D.2.2 *Piping Systems for Dry Chlorine*, ed. 15; Pamphlet 6; The Chlorine Institute: Arlington, VA, **2005**.

D.2.3 *Chlorine Vaporizing Systems*, ed. 6; Pamphlet 9; The Chlorine Institute: Arlington, VA, **2002**.

D.2.3 *Recommended Practices for Handling Chlorine Bulk Highway Transports*, ed. 8; Pamphlet 49; The Chlorine Institute: Arlington, VA, **2001**.

D.2.4 *Emergency Shut-Off Systems for Bulk Transfer of Chlorine*, ed. 4; Pamphlet 57; The Chlorine Institute: Arlington, VA, **2003**.

D.2.5 *Emergency Response Plans for Chlor-Alkali, Sodium Hypochlorite, and Hydrogen Chloride Facilities*, ed. 6; Pamphlet 64; The Chlorine Institute: Arlington, VA, **2006**.

D.2.6 *Recommended Practices for Handling Chlorine Tank Cars*, ed. 3; Pamphlet 66; The Chlorine Institute: Arlington, VA, **2001**.

D.2.7 *Recommendations to Chlor-Alkali Manufacturing Facilities for the Prevention of Chlorine Releases*, ed. 4; Pamphlet 86; The Chlorine Institute: Arlington, VA, **2001**.

D.2.8 *Chlorine Scrubbing Systems*, ed. 3; Pamphlet 89; The Chlorine Institute: Arlington, VA, **2006**.

D.2.9 *Dry Chlorine: Definitions and Analytical Issues*, ed. 3; Pamphlet 100, The Chlorine Institute: Arlington, VA, **2002.**

D.2.10 *Training Guide for Distributors and End-Users of Packaged Chlorine*, ed.2; Pamphlet 151; The Chlorine Institute: Arlington, VA, **2000**.

D.2.11 *Generic Risk Management Plan for Chlorine Packaging Plants and Sodium Hypochlorite Production Facilities*, ed. 2, Revision 1; Pamphlet 162; The Chlorine Institute: Arlington, VA, **2004**.

D.2.12 *Handling Sodium Hypochlorite Safely*; HYPO-VIDEO; The Chlorine Institute: Washington, DC, **1998**

D.3 <u>OTHER REFERENCES</u>

D.3.1 *Minimizing Chlorate Ion Formation in Drinking Water when Hypochlorite is the Chlorinating Agent*, American Water Works Association (AWWA) Research Foundation, G. Gordon and L. Adam, Miami University, Oxford, OH & B Bubnis, Novatek, Oxford, OH

D.3.2 Eyewash and Shower Stations: ANSI Standard.