



SODIUM HYPOCHLORITE MANUAL

January 2016



This manual provides users of sodium hypochlorite with information needed to receive, handle, store and use this product safely.

**Olin Chlor Alkali Products
Sodium Hypochlorite Manual
Table of Contents**

About Olin Chlor Alkali Products	1
Introduction	2
Safety – Setting the Stage.....	3
Product Stewardship and Responsible Care® at Olin.....	3
Manufacturing	5
Locations	5
Process	6
Product Grades.....	6
Units.....	7
Table 1	7
Density.....	8
Personal Safety & Spill Remediation.....	9
Personal Protective Equipment.....	9
First Aid Procedures.....	10
General	10
Eye Contact	10
Skin Contact.....	10
Ingestion.....	10
Inhalation	10
Safety Shower and Eyewashes	10
Spill Control Plans	11
Spill Recovery	11
Neutralization	11
Disposal	12
Shipping.....	12
Hazardous Materials System	12
Shipping Containers.....	13
Tank Trailers	13
Railcars	14

Unloading Procedures and HAZMAT Training	14
Unloading Stations	15
Tank Trailers	15
Railcars	15
Pad Gas System	16
Figure 1.....	17
Table 2.....	17
Table 3.....	19
Pumps	19
Valves	20
Piping.....	20
Design Considerations.....	20
Installation.....	20
Support.....	21
Glues.....	21
Labeling.....	21
Materials of Construction.....	21
Inspection and Replacement.....	22
Tanks	23
Design Considerations.....	23
Sizing	23
Venting	24
Overflows	24
Receiving Pipeline	24
Outlet Nozzles	24
Flexible Connections and Piping Support.....	24
Level Measurement.....	25
Labeling	25
Tie Downs.....	25
Materials of Construction.....	25
Titanium	25
Rubber-lined Steel.....	26
FRP and Dual Laminates.....	26
Poly Tanks.....	26

Fabricator Evaluation	27
Operation	27
Cleaning.....	27
Inspection.....	27
Containment Systems.....	28
Transfer Hoses.....	29
Incompatible Chemicals	30
Stability	31
Graph 1.....	32
Graph 2.....	33
Dilution	34
Chemistry.....	34
Manufacturing.....	34
Oxidation Power	35
Decomposition.....	36
Titration/Chemical Analysis	36
Crystallization Points.....	37
Table 4.....	37
Product Assay	37
Residual Alkalinity	38
Sodium Hypochlorite Assay Detail	38
Sample Preparation	39
Sample Analysis	39
Calculations.....	39
Residual Alkalinity Analytical Detail	40
Sample Preparation	40
Calculations.....	40
Reagents	40
Acknowledgments	41
Quick References.....	41
Emergency Contacts.....	42
Disclaimer	43

About Olin Chlor Alkali Products

Olin Chlor Alkali Products is a business division of Olin Corporation, with division offices located in Cleveland, TN. Since our founding, chlorine chemistry has been the foundation of our business. With production and distribution facilities located strategically across eastern Canada and the United States, Olin is a true North American chemical manufacturer.

Safety and quality are integral to everything we do at Olin. Our **GOAL IS ZERO** focus on accidents, injuries, or chemical incidents is an important component of our stewardship program. ISO 9001 and RC 14001 certification of our processes help foster continuous improvement in the areas of product quality, environmental protection, safety, and product stewardship.

Our customer service and national sales teams are ready to provide personal, professional assistance when placing orders. Technical information about the safe handling, storage, use, and stewardship of our chemical product lines can be readily obtained from our experienced technical services staff. Additional information can be obtained by telephone, on the web, or via U.S. mail as noted below.

Olin Chlor Alkali Products

490 Stuart Road NE

Cleveland, TN 37312

(423) 336-4850

www.olinchloralkali.com

Introduction

Sodium hypochlorite has been an important bleaching agent since it became commercialized by Claude Louis Berthollet, a French chemist, in 1789. Early sodium hypochlorite solutions were known as "Eau de Javel" or "Javel Water" paying homage to the District of Javelle in Paris where Berthollet manufactured and commercialized sodium and potassium hypochlorites. Today, sodium hypochlorite is also often referred to as "hypochlorite", "hypo," "bleach," or "NaOCl."

Production of sodium hypochlorite began at Olin after the completion of the Mathieson Alkali Works' chlor alkali facility in Niagara Falls, NY, which produced the raw materials needed for sodium hypochlorite: chlorine and sodium hydroxide. Sodium hypochlorite was first manufactured in smaller quantities with the purpose of neutralizing chlorine sources obtained from chemical piping, process streams, processing equipment, or shipping containers before performing maintenance activities. Today, sodium hypochlorite represents one of Olin's most strategic businesses. This product is used extensively in a variety of industrial, municipal, and household applications.

Manufacture of hypochlorite solutions via the batch process of bubbling chlorine into diluted solutions of hydroxides (typically sodium hydroxide) was the industry standard for most of the 20th century. The ability to transform chlorine from a pressurized liquid material into a more-easily stored and handled chemical solution was a key factor in solution sodium hypochlorite gaining popularity, and this practice continues today. The industry began transitioning to automated manufacture of sodium hypochlorite solutions in the late 1960s, and this provided important industry advancements in safety, quality and production efficiencies.

Historically, sodium hypochlorite was transported by tank trailer or smaller packages to nearby markets. Beginning in 2007, Olin initiated North America-wide railcar service for this product, allowing for long-distance transportation. No longer is sodium hypochlorite distribution considered a local activity. This innovative transportation mode, along with the acquisitions of Pioneer Americas and K. A. Steel Chemicals, has transformed Olin into the largest producer of sodium hypochlorite (bleach) in North America.

Safety – Setting the Stage

Understanding the unique attributes of sodium hypochlorite solutions and equipment is key to long-term safety.

Although sodium hypochlorite is an alkaline chemical, its physical properties require handling systems that are often not typical of many corrosives. Materials normally associated with a robust storage and handling system such as stainless or carbon steel are reactive with sodium hypochlorite, and as a result, the use of non-metallic materials is common with this product. The use of non-metallic components, while often endorsed from a cost perspective, requires an understanding of the physical and chemical interactions between the product and these materials, as well as how the components interact with a variety of external stressors. Despite their excellent chemical compatibility, non-metallic components are not easily evaluated for the effects of these stresses, and as such a different approach for assessing their service condition is needed.

By taking a holistic approach and considering all attributes, better decisions can be made about materials of construction selection, on-going maintenance/inspection, and long-term component-replacement planning. Such an approach should also incorporate the documenting of component installation dates and the recording of inspection findings and maintenance activities. These "historical" reference points will be of tremendous assistance when choosing from the wide variety of differing materials of construction (non-metallic and metallic) available and will help achieve the ultimate goal of avoiding failed components and associated chemical incidents. Proper planning and budgeting can lead to continuous improvement with regard to materials of construction for systems handling hazardous chemicals.

Product Stewardship and Responsible Care® at Olin



RESPONSIBLE CARE®
OUR COMMITMENT TO SUSTAINABILITY

Olin has a long history of embracing and promoting chemical safety. As a founding member of The Chlorine Institute—a technical trade association of companies involved in the safe production, distribution and use of chlorine, sodium and potassium hydroxides and sodium hypochlorite, and the distribution and use of hydrogen chloride--in 1924, Olin has supported the development of the Institute as an industry trade association charged with fostering **continuous improvement in**

safety, protection of human health and the environment, and security associated with the production, transportation, handling, and use of sodium hypochlorite and related chemicals, including chlorine, sodium and potassium hydroxide, and hydrochloric acid. As a Chlorine Institute member, Olin is committed to adopting the Institute's safety and stewardship initiatives to achieve measurable improvement over time. A number of Chlorine Institute bulletins and pamphlets discussing the safe handling of sodium hypochlorite are referenced in this handbook.

Olin is also an active member of the American Chemistry Council (ACC)-- America's oldest trade association of its kind, representing companies engaged in the business of chemistry and committed to continuously improving the safety, health, environmental, and security performance of the chemical

industry-- and the Chemistry Industry Association of Canada (CIAC)—a trade association representing Canada's leading chemistry companies adhering to the principles of Responsible Care[®] and sustainable stewardship. We incorporated the ACC's Responsible Care[®] program and the CIAC's standards into our business model at their introduction into the marketplace. Key aspects of the ACC's and CIAC's Responsible Care[®] initiatives include:

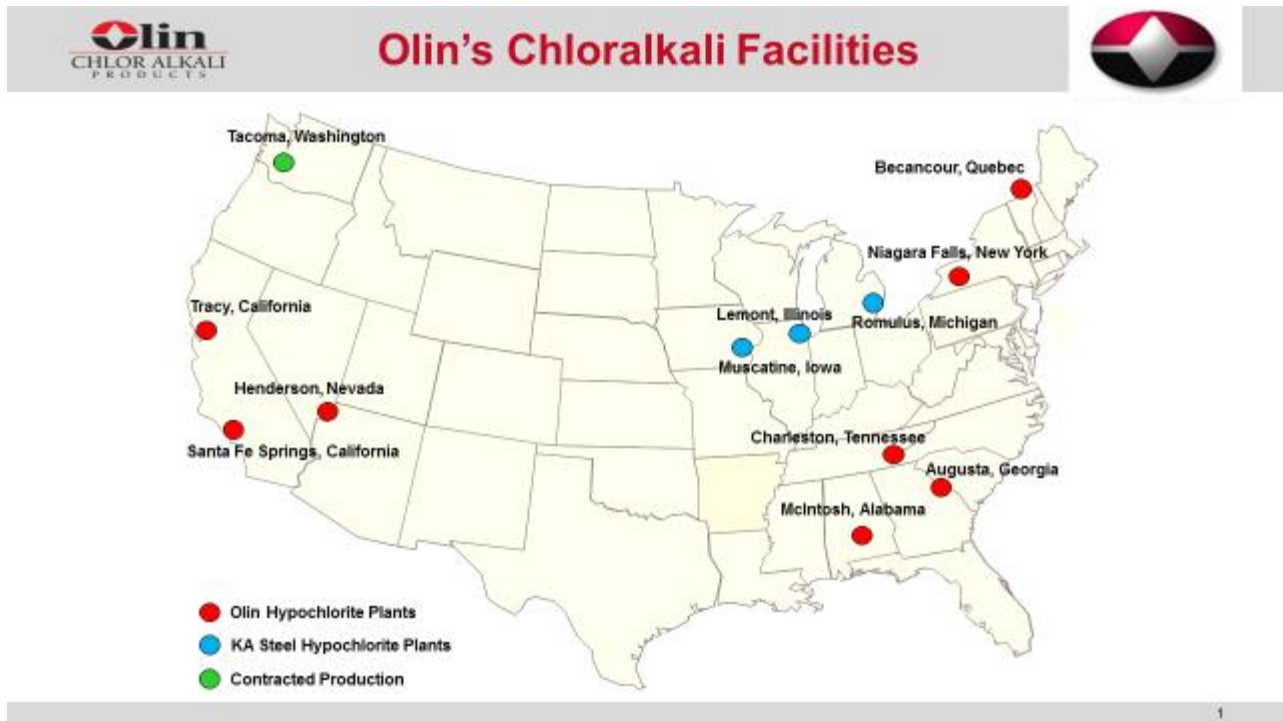
- Commitment made by the chemical industry to the **safe, responsible, and sustainable** management of chemicals through their entire life cycle, and for their intended end use.
- World-class performance initiative for the chemical industry.
- Companies who are industry leaders, bound together by a commitment to address challenges and **continuously improve the performance** of the chemical industry.
- Verifiable management systems to achieve Responsible Care[®] goals via third-party auditors.

Olin has a number of programs intended to foster continuous improvement with use of our chemicals. This handbook is intended to assist customers in understanding the chemistry, delivery, receipt, storage, and safe handling of sodium hypochlorite solutions.

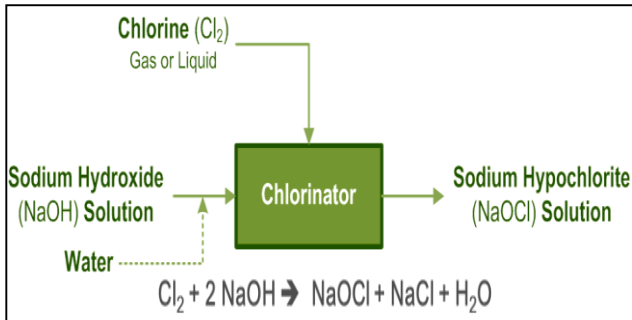
Manufacturing

Locations

Olin has multiple sites throughout North America that manufacture sodium hypochlorite solutions, commonly referred to as “bleach.” The capabilities of these sites are similar with slight differences in the grades of product available to meet specific market needs. Olin is uniquely positioned to service your sodium hypochlorite needs as a true North American manufacturer with production facilities, terminals and joint ventures located throughout the United States and eastern Canada. Production sites representing Olin and our chemical distribution business, K. A. Steel Chemicals, are shown on the map included in this section. With the capability of railcar shipments, we can ship anywhere in this geography. For more information about your specific needs, contact an Olin representative.



Process



Several of these manufacturing sites produce chlorine and sodium hydroxide solutions that provide the raw materials for sodium hypochlorite production at all manufacturing sites. Conventional sodium hypochlorite is easily produced in batch and continuous processes by the introduction of chlorine into a diluted sodium hydroxide solution. The ratio of chlorine addition to the amount of sodium hydroxide is controlled to allow for the

excess caustic necessary to stabilize the final product. Automated blending equipment allows for meeting various customer quality and strength requirements depending on the final application. Once chlorination is completed, product is filtered to remove suspended impurities and then chilled where needed before being sent to storage or shipping container loading. By incorporating filtration and cooling steps as integral components of the manufacturing process, customers receiving Olin-produced sodium hypochlorite are provided an inherent advantage, as these two practices play important roles in minimizing product decomposition. Similar attention to detail is carried through our quality assurance process. Each Olin facility laboratory follows ISO-9001-certified procedures, assuring our customers accurate, reproducible analytical data.

Product Grades

Sodium hypochlorite solution grades are typically defined by differences in product assay and/or alkalinity content. From an industry perspective, solution strengths of 12.5 and 15.5 weight percent as NaOCl represent the two most common grades of product. Olin offers a variety of different product grades depending upon industries served and local market demands with 12.5 and 15.5 weight percent as NaOCl solutions being the most prevalent. Several of the Olin production facilities incorporate additional blending systems that provide the ability to customize the assay and alkalinity component concentrations to meet particular application requirements.

Olin's sodium hypochlorite solutions are well-suited for use in a variety of industrial and municipal applications. We offer product certification upon request for various industry and regulatory standards including the American Water Works Association (AWWA B300), National Sanitation Foundation (NSF standard 60 requirements), as well as U.S. EPA pesticidal registration. Contact your Olin sales representative to discuss specifications, certifications, and product grades available in your particular market.

Units

Strength or concentration of sodium hypochlorite may be expressed in a number of different ways in supplier certificates of quality, invoices, product labels, dosage rates, or bid requirements. As a result, it is always critical to specify the units of concentration when referencing product strength. **Table 1** illustrates the importance of specifying assay units. A **12.5 weight percent NaOCl solution** (a common industry strength standard) is considerably different from a **12.5 trade percent solution**. Additionally, a 12.5 weight percent solution is not the same as a 12.5 solution having units of volume percent. **ALWAYS specify units of concentration!**

Table 1

Wt% NaOCl	Wt% AvCl ₂	g/L AvCl ₂	Trade %	Equivalent Cl ₂	Density (Theoretical)	
(g NaOCl/100g soln.)	(g AvCl ₂ /100g soln.)	(g/L soln.)	(g AvCl ₂ /100 mL soln.)	(lb Cl ₂ /gal soln.)	g/ml	lb/gal
Note 1		Note 1	Note 1			
9.00	8.6	97	9.7	0.81	1.134	9.46
10.04	9.6	110	11.0	0.92	1.150	9.59
10.84	10.3	120	12.0	1.00	1.163	9.69
11.00	10.5	122	12.2	1.02	1.165	9.72
11.23	10.7	125	12.5	1.04	1.169	9.75
12.38	11.8	140	14.0	1.17	1.187	9.90
12.50	11.9	142	14.2	1.18	1.189	9.91
12.76	12.2	145	14.5	1.21	1.193	9.95
13.00	12.4	148	14.8	1.24	1.197	9.98
13.13	12.5	150	15.0	1.25	1.199	10.00
13.87	13.2	160	16.0	1.33	1.211	10.10
14.00	13.3	162	16.2	1.35	1.213	10.12
15.50	14.8	183	18.3	1.52	1.238	10.32
16.00	15.2	190	19.0	1.58	1.246	10.39
16.70	15.9	200	20.0	1.67	1.258	10.49

AvCl₂ – Available Chlorine

Soln. – Solution

g/L – can also be expressed as gpl

Note 1 – the conversion between wt% NaOCl, g/L AvCl₂ and Trade% will change depending on the density used in the calculation.

One of the complicating factors in converting units involves the role of the density in the calculation. Some units of measure, such as weight percent (wt%), compare the *weight* of NaOCl (gram) to the solution *weight* (100 grams) while other units, such as grams per liter (g/L), compare the *weight* of the NaOCl (grams) to the solution *volume* (liter).

When converting between these units, the density of the solution must be used in the calculation. Because there is no direct relationship between density and concentration for sodium hypochlorite

solutions, the conversion between weight % and trade % can *never* be precise unless density of the particular solution in question is measured.

Within a given context, e.g. 1) a company department, 2) a manufacturer's production and customer service group, or 3) the ordering communication between a customer and a specific supplier, etc., the communication of concentration may be well understood; but for clarity when dealing with others outside that context, units should always be clearly defined and mentioned in the communication.

Density

Density is a prevalent analytical tool used in petroleum and some chemical industries to quickly identify contaminations and correlate product quality without the use of expensive laboratory instrumentation or performance of time-intensive "wet chemistry" tests. Appropriate applications for use of density determination in sodium hypochlorite should be well-understood and judiciously chosen. When determining weight-based calculations, performing an actual density analysis is critical to predicting the most precise assay value for a just-collected sample as discussed in the preceding paragraphs. However, the unique nuances associated with chemical composition and production, as well as the decomposition attribute of sodium hypochlorite, can lead to erroneous conclusions when density is incorrectly used to predict hypochlorite solution assay.

Sodium hypochlorite density is affected by a variety of factors. The sodium hydroxide used in hypochlorite manufacture includes a number of dissolved components, such as sodium chloride and sodium carbonate that can vary significantly depending upon the grade and production source used. Changes in sodium hydroxide sourcing or in the amount remaining in the hypochlorite solution for stability will measurably change the density of the hypochlorite solution. Chlorination efficiencies also can affect hypochlorite density, as the amount of salt and chlorate relative to the amount of hypochlorite will change with chlorination efficiencies. Well-controlled manufacturing processes typically demonstrate consistent product densities if all other variables are held constant. However, a change in any variable—sodium hydroxide quality/source, manufacturing technology (automated versus batch process), or even different production *systems* from the same manufacturer using the identical raw materials and technology will result in a different density "fingerprint."

Sodium hypochlorite strength is time dependent, with all solutions starting to lose assay immediately after production. Unlike hypochlorite strength, density will remain unchanged over time. For immediately produced product, density will generally correlate with assay. However, the correlation will continue to change as the solution ages and will yield increasingly erroneous conclusions the older the hypochlorite solution is. Other factors such as metallic content of the hypochlorite, temperature exposure, and solution age become increasingly critical with time because product assay is significantly affected by these contributors. These attributes provide the rationale explaining why an aged hypochlorite solution will have a significantly different assay than a freshly produced one, but density of the solutions will remain unchanged. As a result, **hypochlorite solution density (or specific gravity), should not be specified in chemical purchase specifications or acceptance criteria because it is not a reliable predictor of sodium hypochlorite strength. When precision is required for determining strength, assay titration is preferred.**

For applications where density must be determined, there are several different test methodologies available, including density meters, hydrometers, or use of a pipette-and-weigh combination. When

determining density via meter or hydrometer, the results will need to be temperature-adjusted to yield the most accurate results. Facilities that have an analytical balance accurate to four decimal places often favor the pipette-and-weigh method. In this method, a 10mL sample is pipetted into a sample bottle and weighed. The corresponding weight is then divided by the sample volume (10mL) to obtain the solution density.

Personal Safety & Spill Remediation

Personal Protective Equipment

As a hazardous material, safe sodium hypochlorite handling requires knowledgeable, well-trained personnel, proper personal protective equipment, well-designed and maintained equipment, and adequate handling procedures. All personnel should be instructed in the properties of sodium hypochlorite and applicable operating procedures to handle this material safely. Personnel should be prepared to deal with both normal and abnormal situations. The following safety and health information is intended to provide general guidelines only. Consult a current Safety Data Sheet (SDS) to obtain the most up-to-date information. All personnel should have access to and understand the SDS.

Sodium hypochlorite is an oxidant and corrosive material that can cause serious health hazards if improperly handled. It is corrosive to the skin, eyes, mucous membranes, and respiratory tract, and it may cause severe chemical burns to the eyes and skin. Bodily attack will vary with solution strength and duration of exposure. Clothing can be damaged upon contact with this material. Flame resistant clothing (FRC) may have a higher rate of attack from sodium hypochlorite than non-FRC cotton materials, especially at higher solution strengths. Consult your PPE manufacturer for additional guidance.

Personal protective equipment (PPE) requirements will vary by task and surrounding work environment. A formal PPE hazard assessment should be performed to evaluate the appropriate PPE gear necessary for a given task. Typically, such a risk analysis will result in different levels of PPE based upon work duty. Basic PPE required for routine work assignments such as process monitoring should include safety glasses and the availability of chemical goggles and a face shield. It is especially important that face and eye protection match the potential hazards. In many instances, wearing goggles *and* a face shield is desired since the natural tendency is to turn the head when there is sudden movement toward the face, such as from a spray or splash event. A face shield alone or in combination with safety glasses will not ensure complete eye and face protection in such an event.

When work duties include line-breaking activities such as transfer hose connection/disconnection or maintenance work, use of full PPE, including chemically resistant jacket and pants, chemically resistant boots and gloves, goggles and a face shield are required. Where there is the potential for sodium hypochlorite mist or vapors which exceed the recommended OSHA Short Term Exposure Limit (STEL), an OSHA/NIOSH-approved acid gas respirator should be worn. Consult the most current Safety Data Sheet for additional details.

First Aid Procedures

General

Prompt response to bodily exposures is critical to minimize potential injurious consequences. Ensure that medical personnel are aware of the chemical(s) involved if exposure or injury occurs. Always review the most current Safety Data Sheet (SDS) and provide it to medical personnel administering care to injured persons.

Eye Contact

Immediately flush eyes with copious amounts of water for at least 15 minutes. Hold eye lids open to facilitate irrigation. If contact lenses are present, begin eye irrigation immediately and remove contact lenses as soon as *practical*. Do not delay irrigation while waiting for contact lens removal. Do not add other agents to the eyes without medical direction. Seek medical attention immediately.

Skin Contact

Immediately flush with copious amounts of water for at least 15 to 20 minutes. If there is sodium hypochlorite on the head and face, do not remove goggles until this area has been thoroughly flushed with water. Remove clothing and jewelry that have come into contact with sodium hypochlorite and continue water flushing. Seek medical attention immediately. Wash all contaminated clothing before re-use.

Ingestion

Do not induce vomiting, and never give anything by mouth to unconscious persons. Rinse mouth with water. Seek medical attention immediately.

Inhalation

Move to fresh air and seek immediate medical attention.

Safety Shower and Eyewashes

A safety shower and eyewash station provides an important line of defense against chemical injury should bodily contact with sodium hypochlorite occur. Safety shower and eyewash units should fully comply with the most current version of the American National Standards Institute (ANSI) Z358.1 standard, which addresses items such as equipment performance requirements, accessibility, and testing.

In general, safety shower and eyewash units should be located in areas that have the potential for chemical exposure, such as unloading, pumping, or sampling locations. The safety device should be easily accessible and highly visible to expedite a user's ability to locate and reach the device quickly. In some applications, multiple safety shower and eyewash stations may be required to provide unimpeded access to the safety device under "normal", "abnormal", and emergency conditions. Typical guidance includes locating a safety shower and eyewash unit within 10 seconds of unobstructed access to a potential source of exposure. Unobstructed access requires the safety appliance to be located on the same level as the hazard and be void of impediments such as containment walls, steps, doors, etc., which can interfere with the ability to reach the safety appliance quickly.

Locating and operating the safety shower and eyewash unit at the onset of area work is encouraged as it provides the greatest assurance of device operability. In addition to scheduled device activations

to verify water flows, safety shower and eyewash inspections should focus on changes that have recently occurred affecting access and visibility, such as the “temporary” storage of work equipment or materials near the device. Workers should always be reminded that access to safety equipment must never be compromised for convenience or improved efficiency.

Spill Control Plans

All facilities should have Spill Control Plans (SCPs) in place to address potential leak or spill events. Should such an incident occur, the site SCP should be immediately activated to minimize injurious effects to facility personnel, the environment, and the community. The SCP should address items such as evacuation, First-Responder notification, personal protective equipment, mitigation, spill clean-up, residue disposal, neutralization, and regulatory notifications to name several components.

A review of the SCP with the local Fire Department and pertinent regulatory agencies should occur on a frequent basis to maximize effectiveness of the Plan and any external response to a potential incident. Performance of periodic drills which includes site personnel and these external agencies is desirable.

Spill Recovery

Spill clean-up methods will vary depending upon factors such as quantity involved, potential for off-site impact, expertise of the first responders, and whether the spilled material is contained. Special care must be exercised when attempting to contain, neutralize, and dispose of sodium hypochlorite spills. Spill mitigation may manifest itself in the form of recovery/reuse, dilution, absorption, neutralization, or a combination of these actions.

If the end-application is not sensitive to impurities obtained from the spill event, reuse is often a preferred method because remediation costs are minimized and the initial value of the product is recovered. In events where small quantities of spillage occur, spill dilution with water may be favored. However, for large spill quantities, dilution is generally not favored because of the tremendous increase in total volume resulting from massive water addition.

The strong oxidizing power dictates that any absorbent material must be chemically inert to sodium hypochlorite. Avoid use of items such as sawdust and rags, which can react with sodium hypochlorite under certain conditions, and materials such as “floor dry,” which typically contain organic components. Spill collection equipment, such as shovels or recovery drums, should be verified clean and void of incompatible residues.

Never introduce sodium hypochlorite to local sanitary treatment plants or bodies of water without proper approvals. Sodium hypochlorite can irreparably disrupt the biological processes of sewage treatment operations and will result in harm to aquatic life. Chlorine gas also might be released at the treatment plant if acidic waters are encountered by the hypochlorite. Processing and containment area drains should be periodically reviewed to ensure protective features such as engineering and procedural controls are in place to prevent automatic release.

Neutralization

Neutralization is often favored for larger quantity spills, those which are heavily contaminated and cannot be re-used, or in situations where the resulting neutralized solution will be sent to a waste water treatment plant. Neutralization methods for spill events described in this publication are not intended to treat bodily exposures. Although the result of neutralization is a less-hazardous material,

the process itself involves other chemicals, rapid reactions, and in some instances the potential to generate other gases and hazards. When neutralizing hypochlorite solutions, safety must be an integral component throughout the process. Because of the potential for aggressive reactions, only well-trained personnel should attempt neutralization. Completing a hazard analysis before work commences will help identify the critical engineering and procedural controls necessary for safe neutralization.

There are a number of chemical options for neutralizing sodium hypochlorite, including sodium sulfite, sodium bisulfite, sodium thiosulfate, hydrogen peroxide, and sulfur dioxide. Regardless of method chosen, the sequence of neutralization steps is critical. **To prevent generation of chlorine gas, always neutralize the hypochlorite solution before lowering solution pH.**

Disposal

Sodium hypochlorite must be properly handled, including during spill clean-up events. Proper clean-up and disposal requires that liquids, residues, and neutralized materials are handled, stored, transported, and disposed of in accordance with local, province, state, and federal regulations. Consult the most current Safety Data Sheet for additional guidance.

Shipping

Hazardous Materials System



The safe transport of hazardous materials such as sodium hypochlorite involves four different organizations:

- Regulatory Agencies (Department of Transportation, Transport Canada, Federal Railroad Administration, etc.)
- The Manufacturer (Olin)
- The Carriers (Railroads & Trucking Companies)
- The Receiving Customer

Each of those listed above plays an important role in the safe shipment of hazardous materials.

SHIPPING MODE	ENFORCEMENT AGENCY
Rail	Federal Railroad Administration (FRA); Transport Canada
Roadway	Department of Transportation (DOT); Transport Canada

The **Regulatory Agencies** are the governing bodies in the transportation arena that oversee the safe movement of all hazardous materials whether by land, air, or water. They define and enforce the rules covering the safe handling and transport of hazardous materials. Each regulatory agency has an enforcement arm to assure compliance with record-keeping and equipment regulations. Penalties including fines and potential jail terms for corporations and individuals can be imposed for violations of regulatory requirements.

While the U.S. Department of Transportation (and Transport Canada for Canadian shipments) regulates the movement of hazardous materials by rail, road, and pipeline, enforcement of these regulations is carried out by different agencies depending on the mode of shipment.

Olin's responsibility in the hazardous material transportation system includes the safe operation of its loading facilities as well as maintaining and delivering the transportation equipment in good working order for shipment whether owned, leased, or contracted by Olin. A variety of inspection and maintenance procedures are carried out before the shipping container is released for shipment after loading. Olin's goal is to ensure the safety of our personnel and, to the extent possible, all those who come in contact with a shipment of sodium hypochlorite, while effectively using our fleet and complying with all applicable laws.

The **carriers'** (Railroads & Trucking Companies) responsibility in the hazardous transportation system is to safely move the sodium hypochlorite shipping containers from the shipper to the customer. The carriers must comply with a variety of regulations governing the movement of hazardous materials from agencies including the Department of Transportation, Transport Canada, the Association of American Railroads, and individual state governmental agencies. It is important to note that in the case of railcars (empty after use), the customers or end-users become the shipper of record when they offer the sodium hypochlorite container for shipment back to Olin. Carriers (Rail and Truck) rely on the shipper (Olin and/or the customer) to provide them with clean, safe, and secure sodium hypochlorite shipping equipment.

The sodium hypochlorite **customer's** responsibilities in the hazardous materials shipping process are similar to Olin's. Customers must follow the appropriate regulations in the handling and unloading of sodium hypochlorite containers, and in the case of railcars, prepare them for shipment back to Olin. A customer's goal is to safely handle and unload sodium hypochlorite containers, comply with all regulatory requirements, and where applicable, prepare the container for safe shipment back to Olin.

Shipping Containers

Sodium hypochlorite solutions are shipped in a wide variety of container sizes, bulk and non-bulk, to meet customers' needs. Olin currently ships product only in tank trailer and railcar bulk containers. Olin personnel are available to help you determine which type of delivery method best suits your company's needs.

Tank Trailers

Olin contracts with trucking companies to deliver sodium hypochlorite solutions by tank trailer (cargo tank). In some areas of the United States, Olin operates its own trucking fleet for delivery of the product. Tank trailers used in sodium hypochlorite service must meet standards issued by the regulatory agencies (U.S. DOT, Transport Canada) and include equipment that conforms to the **MC-307, DOT-407, MC-312, and DOT-412 designations**. While tank trailer capacities can vary significantly, they usually contain about 5,000 gallons of product based on over-the-road weight limitations. The two major trailer constructions are rubber-lined steel and fiberglass reinforced plastic (FRP) tanks with a compatible resin corrosion barrier. Product unloading configurations include bottom discharge or a top-unloaded dip-leg arrangement.

Olin sodium hypochlorite trailers typically have a double valve arrangement on the unloading line and are configured for bottom-unloading. The internal valve is pneumatically or hydraulically operated and can be closed remotely in case of an emergency. The unloading connections on each tank trailer are typically located at the rear. A data plate specifying tank fabrication, inspection, and other regulatory

information is located on the driver's side of the trailer frame near the front. Transport regulations require these trailers to be inspected periodically (includes internal and external visual inspections as well as leak, thickness and pressure testing) and that inspection dates be stenciled on the front head of the trailer. Tank trailers can be unloaded by the driver or by properly trained employees (DOT/Transport Canada function-specific) at the customer's or end user's facility. Clearly defined procedures should be followed to ensure communication and coordination between the driver and the appropriate customer/plant representatives. Delivery tractors are equipped with an air compressor for pneumatic product transfer. Pumps are not provided with delivery equipment for unloading.

Railcars

In 2007 Olin added railcars to its shipping mode. This proprietary fleet of specially designed railcars maintains sodium hypochlorite quality throughout the shipment cycle. This Olin innovation, along with process capabilities, has allowed the creation of a bulk distribution paradigm to reach distant marketplaces effectively. The typical shipping volume by railcar is approximately 17,500 gallons.

Numerous, important regulatory, environmental, safety, and health informational items are available on each railcar. Tags and stenciling display required regulatory, car maintenance, and operating information as well as safety, spill mitigation, and first-aid information along with emergency response contacts.

Olin's entire rail fleet is designed for top unloading only. The specific unloading method and additional requirements are described in separate white papers available for reference and future discussions.

Unloading Procedures and HAZMAT Training

Establishment of robust unloading procedures should occur before product is received and then be reviewed on a periodic basis or revised when operational practices dictate. Unloading procedures will be unique to each facility, receiving area and delivery mode. However, well-written unloading procedures include a number of common attributes and components. Although the primary focus of the unloading procedure is to ensure the correct product is safely delivered into the storage facility, it also should be written to address unexpected events such as spills or other incidents. All procedures should be documented with periodic training provided to ensure personnel understand the procedure requirements. Verbal procedures for unloading should be avoided as they foster inconsistency between staff members and an ever-changing standard.

Use of pre and post-unloading checklists offers the advantage of physically carrying the key elements of the unloading procedure to the work area for review/completion. Errors that potentially can occur from relying upon recollection of the formal unloading procedure's detail can be avoided. Checklists help ensure all key unloading items are reviewed / inspected and foster consistency between different staff members. Typical components include a review of paperwork (bill-of-lading and certificate of quality) to verify they match the shipping container placard and receiving pipeline label; the delivery address and purchase order numbers are verified; adequate tank inventory exists to safely receive the entire shipping container contents; safety shower and eyewash units have been located and PPE has been inspected; and a mechanical inspection of the shipping container and transfer hoses has been completed.

Because it is a hazardous material (Hazmat), all personnel handling sodium hypochlorite must be properly trained or "qualified" on the topics of General Awareness, Function Specific, Safety, and

Security as required by 49CFR172.704 (U.S. DOT) and Transport Canada Transport of Dangerous Goods Act S.C. 1992, c.34 (Canada). Regulations require Hazmat personnel to undergo this training at least once every three years.

Unloading Stations

Unloading stations for receipt of tank trailer and railcar shipments should be designed with safety and operational efficiency in mind. In general terms, either delivery mode requires appropriately located safety shower and eyewash stations, adequate lighting for possible night-time work, filtered pad gas, adequate secondary containment, chemically compatible transfer hoses and connectors, and a source of rinse water to facilitate product residue removal. The ideal site design will minimize the length of hose required for shipping container unloading as well as the pipe run for delivery of product to the tank.

Tank Trailers

Tank-trailer serviced unloading stations should be laid out to provide easy access to the receiving pipeline connection. Where possible, drive-through unloading stations wherein backing of the trailer into the unloading station can be avoided is preferred. In-plant street access should be designed to accommodate tractor/trailer combinations and incorporate wide intersections. Reinforced concrete unloading pads sloped to a containment device such as a dedicated sump, French drain, or the like provide a hard surface for trailer parking and an effective means to collect and contain product drippage that might occur during the unloading process. Where multiple chemicals are received in the same area as sodium hypochlorite, engineering and/or procedural provisions should be incorporated to avoid mixing of incompatibles.

Receiving pipelines for tank trailers are typically installed approximately three feet above grade, (hip level). A two-inch male, quick connect fitting is standard for customer receiving locations and should include a block valve to prevent possible chemical drain-back when the delivery hose is disconnected. Placement of a drain valve in the receiving pipeline can facilitate safe sample collection during the unloading process. Quick-connect fittings should be of fluoropolymer-lined stainless steel or high density polyethylene (plastic) construction. To minimize the "mechanical hammer" and torque stresses exerted on the receiving connector and pipeline during the unloading process, installation of the receiving connector at a 22.5- or 45-degree downward angle is suggested. Angled receiving connectors are especially beneficial when 'plastic' components are used.

Railcars

Railcar unloading stations should incorporate level track to maximize product transfers. An elevated platform with a folding gangway and fall protection cage should be available to enhance worker safety and expedite efficiency. Pad gas piping and filtration devices, and the receiving pipeline are typically located within arm's reach of the unloading platform which limits hose length and associated clutter, while maximizing convenience for component access.

Railcars require a three-inch, four-bolt flanged connector to attach to the product outlet valve. Because of the elevated potential for "mechanical hammer" and other unloading stresses, the transfer hose requires a robust support system in place to limit stresses on the railcar connection. Because of these unloading stresses, a fluoropolymer-lined, flanged metal connector is preferred for railcar unloading. Federal regulation (DOT- 49CFR 177.834 (i) and Transport Canada (CSA B622) require

shipping containers to be continuously monitored during the entire unloading process by a qualified person located within 25-feet of the transfer. Where staffing is limited, use of unloading station surveillance cameras could be considered for monitoring the unloading process.

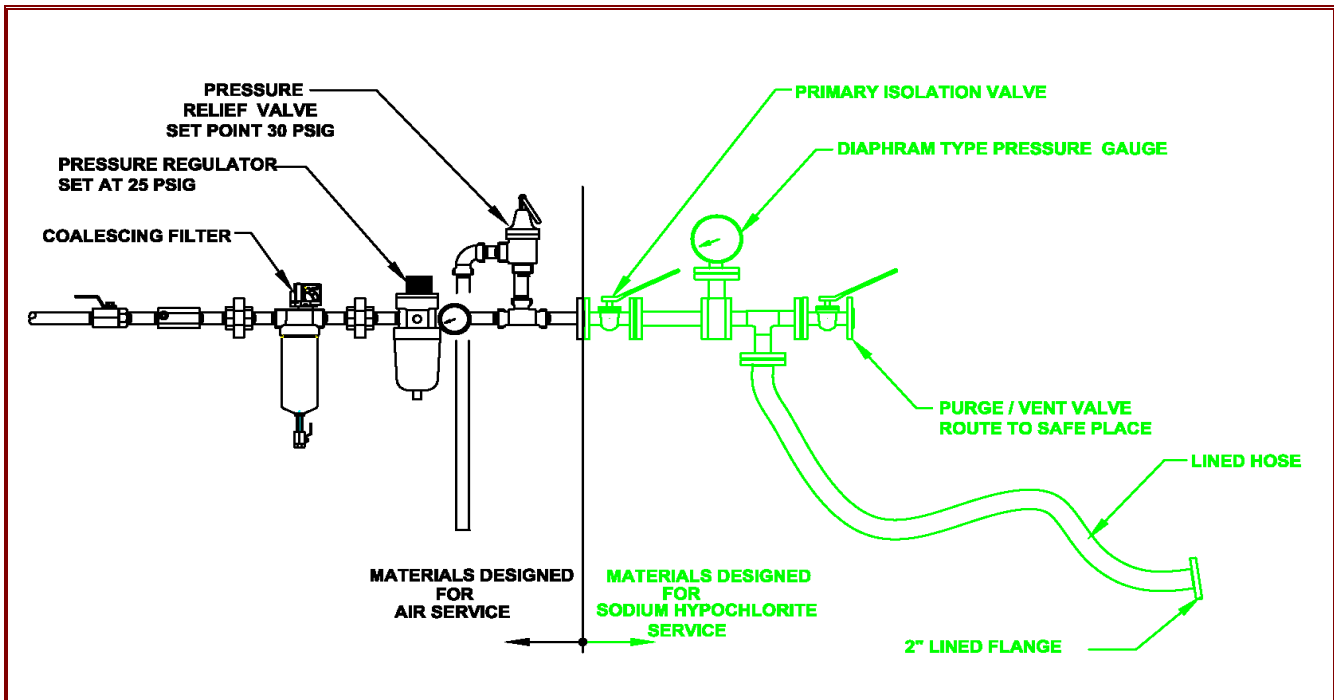
Pad Gas System

The air padding system used for unloading can be a significant source of metallic, organic, and particulate contaminants, which can foul the shipping container and can increase product degradation rates, despite having a filtration system in place at the compression source. By installing a point-of-use filter and by using proper materials of construction from that point to the shipping container's connector, these contaminants can be avoided. An additional series of engineering controls placed at the pad air distribution point to the shipping container will provide further layers of protection against introduction of pad air contaminants and over-pressurization of the shipping container. This will require the following components to be appropriately sized and installed. Good operating practices and an effective preventive maintenance program for the air compression and distribution system must be in place to ensure its continued successful protection against contamination:

1. Coalescing filter designed to remove oil, moisture and particulates, and delivering pad air quality meeting ISO Class 1 of the ISO STANDARD 8573 – 1
2. Safety components: Pressure regulator, pressure gauge and pressure relief valve
3. Primary isolation valve
4. Piping made of compatible material of construction downstream of the primary isolation valve
5. Pad air connector hose made of compatible material of construction

Figure 1 illustrates the key features required for railcar pad air supplies. A customer-supplied pad air system for tank trailer unloading is identical except for the use of a 1-inch air hose and pinned crow's foot connector (Chicago coupling).

Figure 1



Because of the sensitivity of sodium hypochlorite to pad air contaminants, all system components including the air compressor, air cooling and water drainers, pre- and after-filters, air drying and point-of-use pad air filters/condensate drainers should be evaluated to determine appropriate equipment upgrades. System operation also should be evaluated because oil/water/particulate loads can vary under start/stop conditions. **The minimum requirement for sodium hypochlorite shipping container pad air is ISO STANDARD 8573 – 1 (ISO Class 1) noted in red inside Table 1.** Note that the air does not have to be “dry” to a specific dew point, only “water droplet free.”

Table 2
International ISO Standards ISO 8573-1

Particulate		Water		Oil
Class	Max. Size	Max. Conc.	Max. Press. Dew Point	Max. Conc.,
	µm	ppm / mg/m ³	°F / °C	ppm / mg/m ³
1	0.1	0.08 / 0.1	-94 / -70	0.008 / 0.01
2	1	0.80 / 1	-40 / -40	0.08 / 0.1
3	5	4.20 / 5	- 4 / -20	0.83 / 1
4	15	6.70 / 8	37 / +3	4.2 / 5
5	40	8.30 / 10	45 / +7	21 / 25
6	-	- / -	50 / +10	- / -

High-pressure pad air can over-pressure the shipping container, resulting in activation of the safety relief device and chemical leakage. The pad air should be regulated to a maximum of 25 psig for both railcar and tank trailer unloading activities and be protected with a pressure relief device downstream of the regulator.

The primary isolation valve (see **Figure 1**) marks the piping specification breakpoint between components designed for standard pad air service and components designed for sodium hypochlorite vapor, and should be constructed of lined steel as discussed below. All components downstream of this valve must be designed to accommodate possible exposure to sodium hypochlorite vapors.

Downstream of the point-of-use filter, lined metallic piping or titanium must be used. Iron, galvanized steel, copper or other common pad air piping materials will corrode and re-introduce contaminants downstream of the filter. These materials should be avoided in their unlined versions downstream of the point-of-use filter location. For a lined piping system, the liner offers the chemical resistance needed while the metallic piping provides the structural strength. Liners such as polyethylene, Teflon[®] polymer (PFA, FEP, PTFE), PVDF (fluorinated polyvinylidene or Kynar[®] polymer) and PVC/CPVC (polyvinylchloride/chlorinated polyvinylchloride), etc., are compatible with sodium hypochlorite. A careful evaluation of material of construction compatibility with sodium hypochlorite should be completed during the liner selection process because product vapors can potentially back feed into the pad air piping system under certain conditions.

The preferred hose fitting for the railcar padding connection is a four-bolt, 150-pound, two-inch flange permanently affixed to the hose. A flanged adapter equipped with a quick-connect fitting for attachment to the pad air hose is a variation that may be a desired alternative. Fluoropolymer-lined stainless steel fittings are preferred as they offer enhanced mechanical strength, are chemically compatible and can safely manage stored energy and stresses. Tank trailers are typically connected to the pad air supply hose via a one-inch “crow’s foot” connector (or Chicago coupling) appropriately pinned to ensure a secure connection.

A timely and effective preventive maintenance program (see **Table 3 Inspection Guidelines**) is critical for ensuring delivery of clean, water-droplet-free and oil-free pad air to the shipping container over the long term. Several general guidelines are applicable regardless of equipment or operating conditions. Maintenance guidelines issued from the compressor manufacturer should be consulted and typically represent the minimum frequency at which maintenance should be performed. In addition to performing scheduled component maintenance, a “white-rag” test should be performed at least once monthly to provide redundant verification of proper system operation. When performed correctly, a clean “white rag” should be used to collect the compressed gas stream at regular, full-flow rates for a duration of –one to two minutes. Any discoloration will provide indications of a malfunctioning filtration system.

In addition to providing clean, filtered pad gas (air), all air sources should be regulated to prevent potential overpressurization of the shipping container. A 25psig pressure regulator setting (maximum) is suggested for both tank trailer and railcar unloading stations. Installation of a safety relief valve, installed downstream of the pressure regulator, can provide an added layer of protection against overpressurization should the regulator fail.

Table 3 Inspection Guidelines	
White rag test at point of use	At least monthly
Trap & filter inspection/service	Inspection at each use Service per manufacturer guidelines
Pressure drop indicators	Daily inspection during use
Filter replacement	Per manufacturer guidelines, white rag test or pressure drop
Hose & connector	Daily visual inspection for evidence of fatigue
Regulator or check valves	Annual preventive maintenance
Pressure relief device	Annual preventive maintenance

Pumps

Pumps are typically selected based upon service. Centrifugal, diaphragm, canned, and magnetically driven pumps are more common for high-volume transfers or for recirculation-type activities whereas positive-displacement and peristaltic designs are more common in metering applications. Regardless of application, all internally wetted components must be sodium hypochlorite-compatible materials, and the use of all metals except titanium must be avoided. Non-metallic materials such as Teflon[®], Tefzel[®], Halar[®], or Kynar[®] polymers, and polyvinylchloride are common internal components for pumps.

Design features are influenced by the type of pump selected. Positive displacement pumps should incorporate a pressure relief device to protect against ‘dead-heading’ situations whereas mechanically sealed centrifugal pumps should employ a seal/shaft shroud to help prevent potential seal leakage from being slung onto nearby personnel or equipment. A low-amp cut-off switch should be considered for magnetically driven pumps to protect against “burn-out” resulting from operating under damaging low or no-flow conditions.

Although piston, gear, and peristaltic positive displacement pumps are most frequently used in metering situations, all pump styles have been used successfully in these situations. The overriding factor in determining which type of pump to use may lie in past plant experience. The pump type most familiar to maintenance personnel and for which spare parts are readily available may be the best choice. A centrifugal pump coupled with a measuring device (rotameter, mag meter, or mass flow meter, etc.) may prove easier to calibrate and more compatible with automated control systems than metering pumps. Without an independent flow-measurement device, metering pumps require routine calibration to ensure accurate output.

“Vapor lock” caused by entrained gas can be a problem with centrifugal, diaphragm, and peristaltic pumps, especially in low-flow metering applications. Typically, entrained gas is a result of trace-metal-induced product decomposition (oxygen gas formation), so efforts to eliminate the source of such contamination would be the preferred solution. However, this problem can be minimized by sloping

pump intake piping so that entrained gas bubbles move away from the pump suction or by employing other means of separating entrained gases before liquid reaches pump suction.

Valves

Selection of valve type will depend upon the intended application. Materials of construction range from fluoropolymer-lined steel valves to plastic. Where cavity valves, such as ball or plug designs are used, a vented valve design should be employed to prevent pressure buildup and potential valve or piping damage resulting from metallic-induced decomposition of sodium hypochlorite and associated buildup of decomposition gases. Vented valve body designs will also be critical in pipe runs wherein sodium hypochlorite liquid or residues may remain trapped between closed valves. Storage tank outlets should be equipped with positive shut-off capability and avoid the use of “butterfly” designs. Flanged or glued valves are preferred over threaded valves as they eliminate the threaded area, which is a potential leakage point.

Piping

When making initial decisions about piping, it is critical to select the appropriate material of construction because sodium hypochlorite is incompatible with all metals except titanium. Use of nonmetallic materials throughout is often embraced when only economic and compatibility perspectives are considered. However, the role of external stresses in pipe life, effective means to mitigate their detrimental effects, and the mechanical abilities of the organization should be evaluated before choosing pipeline materials. Exposures to direct sunlight and wide temperature extremes, to identify just two common examples, are external stresses that can weaken non-metallic piping and lead to premature component failure. Consideration for lined-steel or titanium at critical points in the piping system where mechanical stresses are a routine part of the operation may be warranted, such as the quick-connect hose fittings for unloading and the initial portion of the fixed unloading line. Employing a more robust pipeline inspection, maintaining detailed records of installation dates and significant inspection findings, and assigning a scheduled replacement cycle should be every user’s goal when non-metallic components are favored.

Design Considerations

Installation

Where possible, pipe runs should be installed to eliminate the presence of low points because product left standing in pipelines can experience product decomposition (oxygen generation and chlorate formation) when not in use. Where low points cannot be avoided, installation of drain valves discharging to a suitable containment system should be considered. Piping feeding metering pumps creates a special situation wherein oxygen gas formation can result in pump vapor lock. Installation of suction piping sloped up away from the pump can minimize gas collection and associated cavitation concerns. Placement of underground piping inside of an impermeable trench with adequate removable covers will afford convenience in performing mechanical inspections and maintenance, while providing secondary containment. Threaded pipe should be avoided as the pipe wall section containing the threads is thinner and more prone to failure or leakage.

Support

Adequate pipeline support is important regardless of material of construction. However, support becomes increasingly critical for non-metallic systems as they generally have lower structural strength and require additional support consideration. Proper spacing of the support system (e.g. hangers, trays, or clamps) will be influenced by the pipe size, operating temperature range, and the weight load of the filled pipe. Special care is required with hangers, support devices, and clamps to ensure a smooth contact surface, free of rough edges. They should not compress or distort the pipe but should allow axial movement resulting from changes in thermal expansion and contraction. Because of these factors, use of a continuous support system should be strongly considered for nonmetallic pipe runs. If non-continuous support systems are chosen, consult your pipe vendor for recommended support spacing.

Glues

Sodium hypochlorite will attack the fumed silica additive used as a thickening agent in some glues or cements intended to join PVC/CPVC (polyvinyl chloride and chlorinated polyvinyl chloride) components. Because of the likelihood of joint separation or leakage, only glues/cements which are fumed silica-free should be used. Containers for these glues typically indicate their compatibility with oxidizers and alkalis. Proper preparation of the surface and application techniques for the primer and cement are important, but often overlooked, aspects of pipe installation. Proper preparation of the glued joint is critical to long-term performance. Diligently follow the glue manufacturer's guidance for all assembly steps.

Labeling

Labeling of pipelines provides critical information regarding the intended contents and associated product hazards. General pipeline labeling indicating the product and flow direction can be especially helpful when performing line-tracing activities. The labeling of *receiving* pipelines is particularly important because it can provide an additional layer of protection against accidental delivery of the wrong chemical by providing a visual reference of intended contents for delivery and unloading staff. For maximum impact, receiving pipelines should be clearly identified near the delivery hose attachment point and include the words, "Sodium Hypochlorite" and "UN 1791." This label terminology incorporates the information found in bills-of-lading and other delivery paperwork, and therefore allows the delivery driver and site unloading staff to compare delivery documents against the receiving pipeline label and shipping container placard. Consult The Chlorine Institute's bulletin, "Avoiding Accidental Mixing of Sodium Hypochlorite," at www.chlorineinstitute.org for additional details.

Materials of Construction

There are a number of acceptable materials of construction for sodium hypochlorite piping systems. Each material of construction presents unique attributes, and in some instances requires special care in installation and inspection to help ensure successful long-term use. Structural strength, chemical resistance, and operational conditions are important factors to consider when selecting piping materials of construction.

Because of their superior structural strength, metals are widely used in piping service for many alkali chemicals. However, unlike many alkalis, sodium hypochlorite is highly reactive with most metals and

metal alloys and is compatible only with titanium or tantalum metal. Lined-steel piping using thermoplastics such as polypropylene, polyvinylidene fluoride (PVDF or Kynar® polymer) or polytetrafluoroethylene (PTFE or Teflon® polymer) as the liner is often used as an alternative pipe material for portions of the systems where mechanical stresses or impacts are expected. The initial portion of the receiving pipeline, especially near the hose connector where external stresses are expected to be more significant, is often chosen for lined metal.

PVC and CPVC are chemically compatible, nonmetallic materials often used in lower-mechanical stress applications. Certain specialty grades of polyethylene also have been successfully used in sodium hypochlorite service. Pipe specifications should be at least schedule 80 or higher for most applications. Mechanical impact from hazards such as liquid/gas mechanical hammer, temperature expansion/contraction cycles, pressure surges from pump start-up and operation, sunlight/ultraviolet light degradation, and potential foot or vehicular contact should be carefully considered when selecting PVC/CPVC for sodium hypochlorite service. PVC/CPVC materials are sensitive to these types of external stresses and if not properly installed, supported, and inspected, can often fail unexpectedly during use.

For end-use applications such as dosing meters, small diameter PVC/CPVC piping is often used. As with larger diameter piping, proper support is required. A protective enclosure such as a conduit or equivalent device should be used where foot or vehicular traffic is likely.

Most polyvinyl chloride monomers have recommended temperature ranges which should not be exceeded. In many instances, ambient conditions exceed these recommendations and elevate the risk of fracture. A related factor is ultraviolet damage as a result of long-term sunlight exposure. Repeated sunlight exposure will weaken monomer bonds, making the pipe more prone to fracture. Consult with your pipe vendor for added guidance.

Fiberglass reinforced plastic (FRP) has been used successfully in hypochlorite service, but it requires extreme diligence in carefully managing all aspects of fabrication and installation. Successful service is typically dependent upon fabricator experience (those specializing in manufacturing pipe expressly intended for sodium hypochlorite), selecting the correct resin composition and the curing process (avoiding cobalt naphthenate chemical cures), and using certified installers that employ stringent quality assurance methods, to name several critical aspects.

Inspection and Replacement

Pipe systems should undergo scheduled inspections on a regular basis. Although the entire pipeline system should be inspected, special focus should be given to joints, sags, support systems and connectors. Pipe joints/flanges should be inspected for evidence of product drippage indicating a softening of the joint glue. Evidence of pipe sags, which can develop over time if inadequate support system spacing was chosen, should be reviewed. Pipe supports, hangers and clamps should be closely inspected for loose pipe (pipe movement) or evidence of wear at the contact point. The connecting surfaces of plastic, quick-connect hose fittings are prone to wear/crack and should also be an inspection component. Inclusion of detailed training for your inspector will be critical to maximizing inspection results.

Unlike metallic counterparts that can be subjected to a periodic, mechanical integrity inspection such as X-ray or ultrasound analysis, there is not an effective and objective evaluation to predict end of useful life for nonmetallic piping. Despite a frequent, robust inspection of the exterior of the pipeline, stresses from external factors such as excessive temperature swings, the "mechanical hammer"

phenomenon of compressed-air transfers, or pump start-up cycles can go unnoticed until failure occurs. Establishment of a scheduled pipeline replacement cycle, in which all pipe components are replaced before failure occurs, can be an effective means to ensure mechanical integrity. By using a checklist and providing training to personnel performing the inspection, the effectiveness of the inspection process can be maximized. Scheduled replacements also can avoid unexpected downtime and leak events and can be helpful in budgeting efforts. Your pipe supplier should be consulted for replacement cycle guidance.

Detailed records of previous inspections that include photos and notes about the location of minor flaws or repairs will be extremely helpful regarding adjustments to both inspection frequencies and future component replacement cycles. When coupled with records of installation dates and maintenance performed, this historical knowledge will help provide the basis for determining pipe replacement and inspection dates. Consultation with your pipe supplier and your knowledge of the past performance of the chosen material along with your understanding of the unique features of your system (type of piping support, normal temperature swings, unloading method, etc.) can lead to an intelligent, effective replacement schedule. Careful record-keeping of installation dates (age) of various piping sections/components is essential for scheduling replacement. Proper budgeting for replacement costs can help prevent economic considerations from overriding safety as the major factor in the timing of piping replacement.

Tanks

The tank selection process has a number of important components to consider. While many are obvious, others are not intuitive because of the unique attributes of sodium hypochlorite. Tanks should be located to minimize piping runs, accommodate shipping container movement for inbound deliveries, and be installed in secure areas to avoid tampering/vandalism concerns. Local, state, and federal environmental regulations should be reviewed before tank installation. Local building codes and fire regulations also may influence tank farm construction and location.

A part of the process of the purchase and installation of a new storage tank should be planning for future inspection and replacement. Accurate records about the particulars of the tank design (drawings and notes) and materials of construction should be provided to those responsible for ongoing maintenance and inspection of each tank. The tank vendor should be asked to supply recommendations for initial inspection scheduling and tank life expectancy. Proper replacement timing should always be intended to replace the vessel well before the end of its expected useful life.

Design Considerations

Sizing

As part of the storage system strategy, the vessel should be large enough to easily accommodate a full inbound bulk shipping container and compensate for likely transit times and tank heels. A general rule of thumb is to size the tank at least 1.5 times as large as the full bulk shipping container to maximize freight savings and have ample room to avoid tank overflows during filling. However, consumption rates also should be considered because of the decomposition nature of the product. For low volume requirements or where the tank is subjected to high ambient temperature and sunlight

exposure, a smaller tank volume might be appropriate. Vertical tank designs, rather than horizontal, are preferred.

Venting

Adequate venting is critical for ensuring a rapid release of air surge when tanks are filled via pneumatic transfer. The tank will be subjected to a nearly immediate, large volume of compressed air at the end of the shipping container unloading process using pad air as the motive force. Compressed air surges approaching 1200 SCFM, (Standard Cubic Feet per Minute) are typical from tank trailers, for example. Without an adequately sized vent, the tank will temporarily act as a pressure vessel, which can lead to tank wall flexing to accommodate the pressure load. Repeated flex cycles can weaken tank walls and could lead to catastrophic tank failure.

As a general guide, tank vent diameters should be at least twice (2X) the size of the inlet piping diameter. Factors such as the length of the vent piping and number of turns can impede the release of compressed air and will require further upsizing of the vent. Consult your tank vendor for specific guidance.

Overflows

If the tank becomes over-filled, overflow nozzles allow chemical that normally would spray out of the tank vent or man-way opening in a wide and undirected pattern to be safely channeled via directional piping into the containment system. Overflow nozzles and directional piping are generally sized at least 1.5 times (1.5X) larger than the inlet pipe to ensure adequate capacity. Overflow nozzles should be installed below the roof line and on the sidewall of the tank. This overflow piping should discharge near ground level in an area and direction away from the typical area occupied by personnel.

Receiving Pipeline

Two-inch piping is typical for tank trailer-serviced locations, while three-inch diameter pipelines are often used for railcar unloading to facilitate rapid product transfer. Pipe diameter guidance will vary depending upon site layout.

Outlet Nozzles

Selection of tanks with a low-point drain should be considered. Low-point drains offer the benefits of complete product heel removal for applications that are sensitive to product decomposition byproducts, such as chlorate. Low-point drains also facilitate periodic internal tank inspection and cleaning activities.

Flexible Connections and Piping Support

Non-metallic tanks are also easily stressed from axial and lateral forces originating from factors such as the act of tank filling and the expansion/contraction of attached discharge piping as ambient temperatures change. Unsupported discharge piping connected to a heavy valve can exert significant torque on the tank's outlet fitting area that can culminate in sidewall cracks/damage. Rigid connections tend to concentrate these stresses in the nozzle area of the tank. Installation of proper piping support and/or use of flexible connectors may help eliminate many of these potential tank

stressors. Tank nozzles on nonmetallic tanks should *never* be used for support of valves and piping. Consult your tank vendor for specific guidance.

Level Measurement

A level measurement system is important for maintaining process operation and for avoiding a possible overflow condition during inbound delivery. Gauging systems range from simple visual readings to complex remote readouts. Under certain scenarios, the inventory may be read directly from the “shadow” of a translucent, clear-tinted “poly” tank equipped with markers molded into the side wall. External “sight glasses” can provide effective level indications. However, similar to reading inventories from the “shadow” of a translucent tank, use of external “sight glasses” may also lead to erroneous readings under certain lighting conditions. External “sight glasses,” such as polyethylene or polypropylene tubing, also present an opportunity for catastrophic loss of tank contents upon “sight glass” failure or damage. Differential pressure or electronic level indicators are frequently used for tank level measurement. Level indicators that are not immersed in the product typically perform best, but all electronic level transmitters should be assigned a scheduled, periodic recalibration cycle to ensure accurate readings over the long term. Equipping the indicator to activate an alarm or automatic shutoff at preset inventory levels can provide an important additional layer of protection against accidental tank overflow conditions. The reliability of the high level alarm or automatic shutoff can be enhanced by using an activation device independent of the regular level transmitter (redundancy).

Posting the maximum allowable storage tank volume in a location clearly visible to unloading personnel will facilitate calculation of available volume for incoming chemical. This, coupled with a local level readout, will allow the unloading staff (and delivery driver for tank trailer shipments) to monitor tank levels more effectively during unloading.

Labeling

Tanks should be clearly labeled to identify chemical contents. Labels or stencils noting the entire, formal product name, e.g. “sodium hypochlorite,” are preferred and especially beneficial to contractors and others not intimately familiar with the tank farm. Avoid use of “Chlorine” or “Liquid Chlorine” for identification as these terms are inaccurate and confusing. A misunderstanding may lead to unnecessary or inappropriate precautions being taken by emergency response personnel in an actual chemical incident. Such distractions and confusion can prevent prompt action to address the emergency condition to which they have responded. Labels should comply with OSHA’s Globally Harmonized System of Classification and Labeling of Chemicals (GHS) or with Canada’s WHMIS (Workplace Hazardous Materials Information System) for Canadian sites. Certain local regulations, codes, or agencies may also dictate label content.

Tie Downs

Tanks should be adequately secured using tie downs installed from the factory to prevent tank movement from high winds or seismic activity.

Materials of Construction

Titanium

There are a limited number of materials that are chemically compatible with sodium hypochlorite.

These materials can be categorized into metallic and nonmetallic systems. Titanium and tantalum are the only chemically compatible metals and offer the longest lifetime. Their high cost generally limits use except in those situations where the benefits justify the cost for critical systems components such as reactors for product manufacture and internal components of pumps, meters, valves, etc.

Rubber-lined Steel

Rubber-lined steel tanks are often selected for high capacity vessels or ones that are subjected to multiple fill/discharge cycles. The lining should be of a 100 percent chlorobutyl rubber composition that has been successfully used for hypochlorite service. Rubber-lined storage tanks require a simple, but specialized mechanical integrity test (IP-4-13 “Procedure for Spark Testing Elastomeric Sheet Lining”) to evaluate lining integrity on a periodic basis. Exposure of lining to the product can result in the exposed rubber surface dislodging or flaking over time. This dislodging or flaking phenomenon is often more pronounced for tank/liner combinations that have been exposed to different chemical service. For sensitive applications, a particulate filter on the tank discharge nozzle may be required.

FRP and Dual Laminates

Fiberglass Reinforced Plastic (FRP) is frequently used in storage applications and offers good mechanical strength and a failure mechanism that is typically preceded by small leaks that warn of its weakened condition. However, fabricator experience, resin, curing mechanism, and stored product strength are important variables influencing vessel performance. FRP vessels are sensitive to ultraviolet (UV) degradation and should incorporate the use of a UV inhibitor for tanks located outdoors.

Hand-laid application of the reinforcement mat or chopped strand filament winding is preferred over continuous filament wound construction. Should the corrosion barrier fail, continuous wound filament reinforcement is at a higher risk of chemical attack via product wicking which increases the risk of catastrophic failure. Avoid the use of cobalt naphthenate as a curing agent because cobalt may catalyze hypochlorite decomposition.

FRP tanks also can be lined with a fluoropolymer such as PTFE, PVDF, etc. or PVC to produce a dual laminate vessel. Dual laminate construction offers the mechanical strength of FRP combined with a robust, chemically compatible internal liner.

Poly Tanks

High-density polyethylene (HDPE), cross-linked (XHDPE) and linear (HDLPE), have been successfully used in sodium hypochlorite service and are typically known as ‘poly’ or ‘plastic’ tanks. However, fabricator experience, resin, product strength, “mechanical hammer,” temperature, sunlight exposure, and pipe connection methods are important variables influencing vessel performance. If cross-linked HDPE is used, it is important to confirm that the resin chosen is suitable for sodium hypochlorite. Additionally, tanks should comply with ASTM D-1998, “Standard Specification for Upright Polyethylene Storage Tanks.”

“Poly” tanks have excellent chemical resistance, but their mechanical strength is generally less robust than alternative materials that are typically used when tank volumes exceed 10,000 gallons. Lateral expansion and contraction of the tank wall is a significant concern with “poly” tanks as the walls will tend to flex depending upon the product level inside the tank. The “mechanical hammer” associated

with compressed air chemical deliveries, automated valve cycling, and pump operation that introduce structural stress on “poly” tanks are other significant factors affecting tank service lifetimes. Additionally the use of bulkhead type fittings may significantly shorten the life of the tank because of the tendency to experience stress cracking around the cutout for this type of fitting. As with FRP, “poly” vessels are sensitive to ultraviolet (UV) degradation and should incorporate the use of a UV inhibitor for outdoor installations. Consult the Chlorine Institute’s Pamphlet 96 for more tank material of construction details.

Long-term contact with hypochlorite causes embrittlement of the polymer so that a sudden mechanical shock can cause a sudden, catastrophic failure of the tank. As with other nonmetallic piping and tank materials, an inspection and replacement plan should be developed for “poly” tanks so they are replaced before failure occurs.

Fabricator Evaluation

The fabrication and lining processes are critical to long-term success when storing sodium hypochlorite. Industry experience has shown merely utilizing chemically compatible material alone is not a guarantee for lengthy tank service lifetimes. **The aggressiveness of sodium hypochlorite dictates that special evaluations of the fabricator and the material of construction should be performed, regardless of the type of construction chosen.** Fabricators should be selected based upon 1) their experience in fabricating tanks intended for this product, 2) the performance record of their tanks in sodium hypochlorite service, and 3) the fabrication process used.

Operation

Cleaning

Tank cleaning frequencies will be affected by factors such as the purity of the incoming product, consumption volumes, and internal tank inspection cycles. Tank rinsing may be desired for removal of sedimentation that can occur over time, as well as removal of residual metallic contaminants that may adhere to tank walls after the product has been consumed. Tank cleaning and flushing needs should be considered at the design stage so consideration can be given to the addition of a full tank drain nozzle. A ground-level man-way also could allow for more complete removal of sediment and other materials with use of a high-velocity water stream without the need for vessel entry.

Inspection

A periodic, scheduled inspection should be performed regardless of material of construction chosen. Personnel performing inspections should be given specific guidance regarding areas to inspect and the types of failure/damage to identify. Detailed criteria and photos can be useful inspection aids. Use of a checklist has been found to be particularly helpful to ensure inspection consistency between different personnel. For non-metallic tanks, the exterior of the tank should be inspected for evidence of drips or seepage, side-wall or roof bulges, and surface cracks or crazing, to name several key attributes and areas for inspection.

To enhance the efficacy of tank inspections, detailed records of previous inspections that include photos and notes about the location of minor flaws or routine wear will be extremely helpful. This information can be used in determining the progress of wear and tear on the vessel and/or liner or corrosion barrier. Over time these comparisons can improve the accuracy—and the economy—of

future inspection and replacement scheduling. Without an understanding of the performance characteristics of a particular material of construction and tank design under your specific storage conditions, it is impossible to make wise decisions about the timing of future tank inspections and replacement. Your tank vendor's initial recommendations for the frequency of these activities may be effectively modified by using information from well-documented inspections.

Containment Systems

A well-designed handling system should incorporate an effective secondary containment system to contain potential drips or spills in product storage and unloading areas. Secondary containment regulations often vary by location, so it will be important to review local codes/city ordinances, as well as province, state, and federal requirements when considering storage of sodium hypochlorite, whether the tank is indoors or outdoors. As a general guide, containment systems should be capable of holding at least 110 percent of the largest tank capacity found in the contained area. Incompatible chemicals--especially those that release hazardous gases when mixed—should be separated by walls within the overall containment area and in the drain-system piping.

There are a number of options for secondary containment systems including concrete, double-walled tanks and open-top containment tanks. Concrete is typically the preferred choice for bulk storage containment systems. A well-designed system will employ reinforced floors and walls. The concrete should be sealed with an industrial coating to extend containment lifetime and to limit the potential of chemical migration through cracks or open expansion joints. The effectiveness of industrial coatings will be largely influenced by the overall condition of the concrete, amount of surface preparation before application, and the type of coating applied. Two-part epoxy coatings intended for strong alkalis are preferred. The use of cinder blocks for containment walls should be avoided because of their porous nature and relatively weak strength. For newly poured concrete systems, the concrete should be allowed to fully cure and to potentially settle before surface coatings are applied.

Good maintenance and housekeeping practices that eliminate small piping or pump leaks soon after they develop and that keep the area clean and dry will extend the life of the enclosure. Maintenance becomes critical as minor imperfections that allow chemical to contact the concrete structure may not be adequately rinsed away from rainfall or housekeeping events.

Double-walled tanks are often considered for vessels if there is limited room for the tank and containment system. Use of a liquid-detection monitor in the open space between the tanks can provide notification of internal vessel failure. The double-walled feature does, however, impede the ability to perform important visual inspections of the tank wall.

For small capacity process or “day” tanks, an oversized, open-top containment tank can be used as the secondary containment system. This style of containment system is available from most nonmetallic tank fabricators and is often favored for indoor locations with limited free space or where the presence of a concrete containment dike may make future tank replacement difficult.

Shipping container unloading stations also should incorporate secondary containment to collect leaks, spills, or wash-down water. Reinforced concrete is generally the preferred material of choice for tank trailer unloading station containment systems because most unloading areas must be able to accommodate vehicular traffic weight loads. For railcar unloading, the presence of railroad ties and the occasional need for track maintenance make removable containment pans preferable to concrete

sumps or pits. Polyethylene or fiberglass reinforced plastic (FRP) containment pans are offered from many containment system vendors for liquids collection between track rails. They offer the benefit of being removed for future track maintenance purposes. Routing of the containment system drains should avoid exposure to incompatible chemicals.

In addition to providing containment in storage and unloading areas, pipe-within-a-pipe design for long runs of in-plant piping can provide containment from storage to end use. This can be an especially important safety enhancement when piping is routed over work or traffic areas where personnel may be exposed to chemical contact should a leak occur. Leaks in piping often generate drips or sprays that may present unexpected 'hidden' exposure hazards. Flange guards may be used to prevent exposure to product sprays that are typical at flanged connections when gaskets fail.

Transfer Hoses

Bulk shipments of sodium hypochlorite will require a flexible hose to connect the shipping container to the storage tank's receiving pipeline. Although most tank trailer-serviced customers rely upon the carrier to provide the transfer hose, use of customer-provided hoses remains an option. Railcar deliveries require customers to supply the transfer hose.

Hoses should be constructed of sodium hypochlorite-compatible materials and be rated to withstand the working pressures expected during the transfer process. Hose construction must avoid any wetted metallic surfaces, such as pipe nipples or quick-connect fittings, because of the corrosive nature of sodium hypochlorite and the sensitivity of this product to experience metallic-induced decomposition. From a mechanical integrity standpoint, metallic connector components that have a fluoropolymer or HDPE lining on the wetted surface are the preferred construction. Polyethylene, including the Ultra-High Molecular Weight Polyethylene (UHMWPE or UHMW) subset and polypropylene are common tube materials of construction. The choice of material should be discussed with your hose vendor regarding expected service conditions including, but not limited to, strength of sodium hypochlorite and likely temperature ranges to be experienced throughout a calendar year. The potential for external surface abrasion can also influence the type of protective sheath, if any, chosen for the hose.

Hoses should undergo a visual inspection prior to each use to identify and prevent potential failures. Use of an inspection checklist by a knowledgeable inspector trained in defect identification helps maximize inspection effectiveness. The Association for Rubber Products Manufacturers' bulletin, IP-11-7, (www.arpminc.com) can provide added details regarding maintenance, testing and inspection of chemical hoses.

Proper storage of chemical hose can influence useful lifetime. Storage wherein the hose can be laid out straight, has continuous support, is purged of chemical residue, and is located out of direct sunlight exposure is preferred. An enclosed hose carrier such as an oversized pipe can address these issues and if positioned properly can minimize the ergonomic concerns associated with ground storage of hoses. Proper storage can be especially important in areas where hoses can potentially be subjected to vehicular traffic.

As with all expendable unloading system components, a replacement schedule is essential to ensure hoses are retired before normal wear and tear leads to failure. For hoses with non-metallic fittings, these are likely the weakest points and should be replaced on a more frequent basis. The hose body

itself is likely to be the determining factor for the replacement schedule for hoses with fluoropolymer-lined fittings.

Incompatible Chemicals

The excellent oxidizing property of sodium hypochlorite requires that special care be taken to avoid incompatible chemical contact, also known as accidental mixing. Accidental mixing may result in personnel injury or environmental damage as a result of introducing sodium hypochlorite residues to a wide variety of incompatible chemicals. Although reactions vary depending upon the chemical composition, sodium hypochlorite will generate chlorine gas upon exposure to acids, acid residues, or other chemicals that may lower the pH of the hypochlorite solution. Production of oxygen gas and significant amounts of heat may accompany other reactions with sodium hypochlorite.

The opportunities for incompatible chemical contact at a storage facility are many and variable but typically can be grouped into three categories: 1) the shipping container unloading process, 2) secondary containment for unloading and storage, and 3) small-container handling. Unloading stations often consolidate bulk chemical receipt into a single area that shares a common containment/drainage system.

1. A common unloading area is often favored for new facilities because construction costs are reduced and the footprint of the unloading area can be minimized. However, such an unloading station enhances the risk of unloading the wrong chemical into a given storage tank due to the close proximity of other product unloading connections. This highlights the importance of installing *and maintaining* proper labeling of all unloading connections. Common unloading stations generally share a single containment system sump and drain piping. Any spill or incidental drippage will mix in the containment, sump, or drain piping.

Because unloading sodium hypochlorite into a tank containing an acidic product (or unloading an acidic product into the sodium hypochlorite tank) may lead to a significant release of chlorine gas, engineering controls should be employed in addition to administrative controls to prevent such scenarios. Use of locked connections and unloading checklists are but two examples of these controls. With outdoor storage tanks, such releases not only will potentially affect employees in the area but may affect neighboring properties and personnel at great distance from the release.

2. Well-designed containment systems employ elements to keep sodium hypochlorite separate from incompatible chemicals both in the containment dike and in the discharge piping system. Separate containment systems sharing a common drain are often designed to include locked drain valves for each containment area. The locked valve concept can provide an administrative control against incompatible contact and allows the facility to evaluate options for handling the collected liquid before it contacts potential incompatible chemicals or residues. Such a design typically requires a Process Hazard Analysis (PHA) evaluation to assess risks and means of handling incompatible chemicals in common drain systems. Since introduction of incompatible chemicals can potentially result in generation of chlorine gas, the PHA should consider both in-plant and off-site impacts.

Storage areas for non-bulk containers, such as tote bins or drums, also should be reviewed for potential of incompatible chemical contact. Such an evaluation not only covers the use/feed

area, but also the staging area where larger numbers of containers are typically stored temporarily before being unloaded.

3. Small-containers can present a source of incompatible chemicals. Buckets or pans used for incidental drip collection at an unloading station or small containers and sample thieves and related devices used in product sampling can appear empty and clean but may have incompatible chemical residues. All small containers used in sodium hypochlorite service should be expressly designated for this use and clearly labeled “Sodium Hypochlorite Only.”

The Chlorine Institute (www.chlorineinstitute.org) bulletin, “Sodium Hypochlorite Incompatibility Chart,” provides a list of chemical families that are incompatible with sodium hypochlorite.

Stability

All sodium hypochlorite solutions continually decompose on standing after they are produced. There are many factors affecting the stability of hypochlorite solutions, and as such there is not a standard shelf life for this product.

Decomposition of hypochlorite solutions cannot be avoided, but the rate of decomposition can be altered. The major factors affecting stability are: temperature, hypochlorite/ionic strength, and contact with catalyzing metallic impurities. Other factors such as pH, exposure to sunlight, organic impurities, and other contaminants can contribute to losses as well.

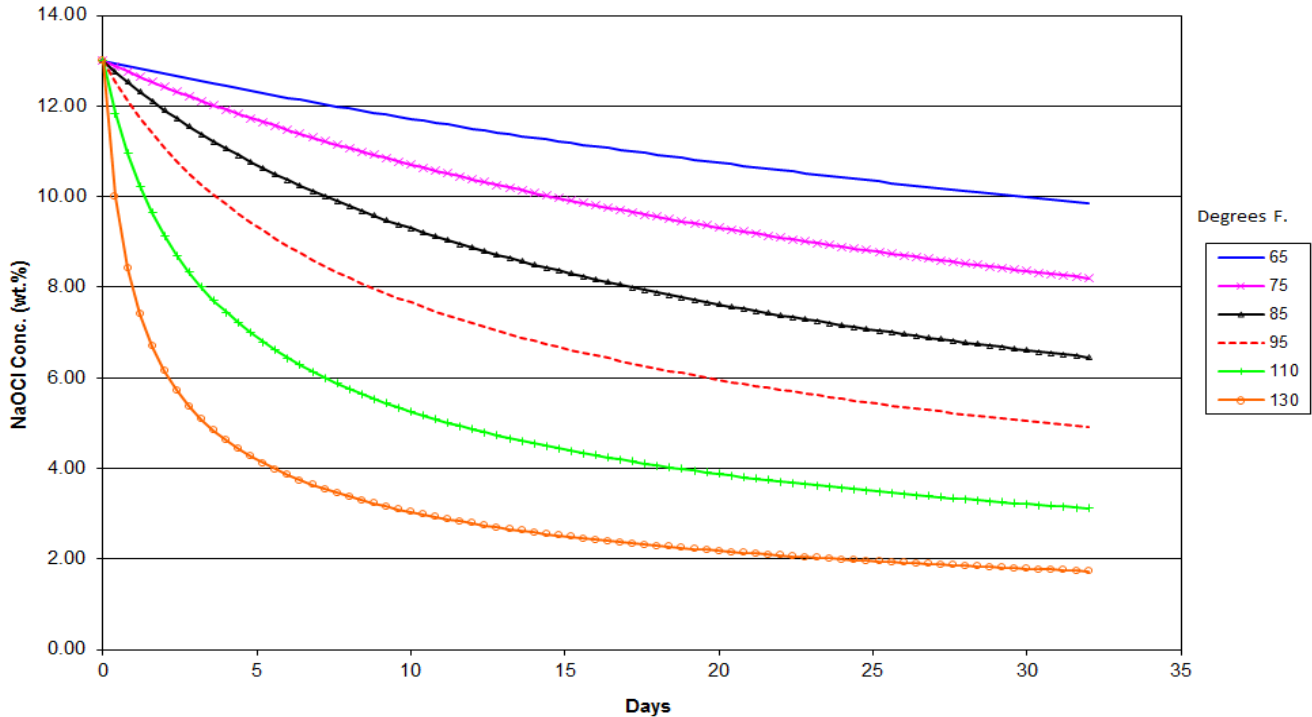
In most situations, the temperature and concentration at which the sodium hypochlorite solutions are stored have the most impact on their stability because decomposition is slowed as concentration and temperature decrease, assuming all other conditions are similar and unchanged. As a general rule, lower concentration solutions are more stable than higher strength solutions, assuming that other conditions such as temperatures, pH and metal ion concentrations are similar. Studies of sodium hypochlorite solutions have shown that the decomposition rate increases by a factor of approximately two to four times for every 10°C (18°F), (see **Graph 1** below for 13 wt% Sodium Hypochlorite). In order to determine your best option for minimizing product decomposition, each application should be reviewed based on hypochlorite strength, storage temperature, and storage time.

Closely related to temperature exposure is ultraviolet light-induced decomposition. Shielding of storage systems, qualification samples, and the like from sunlight exposure can eliminate this variable.

Graph 1

Estimated Decomposition Profile for 13 wt% Sodium Hypochlorite* Versus Temperature, °F

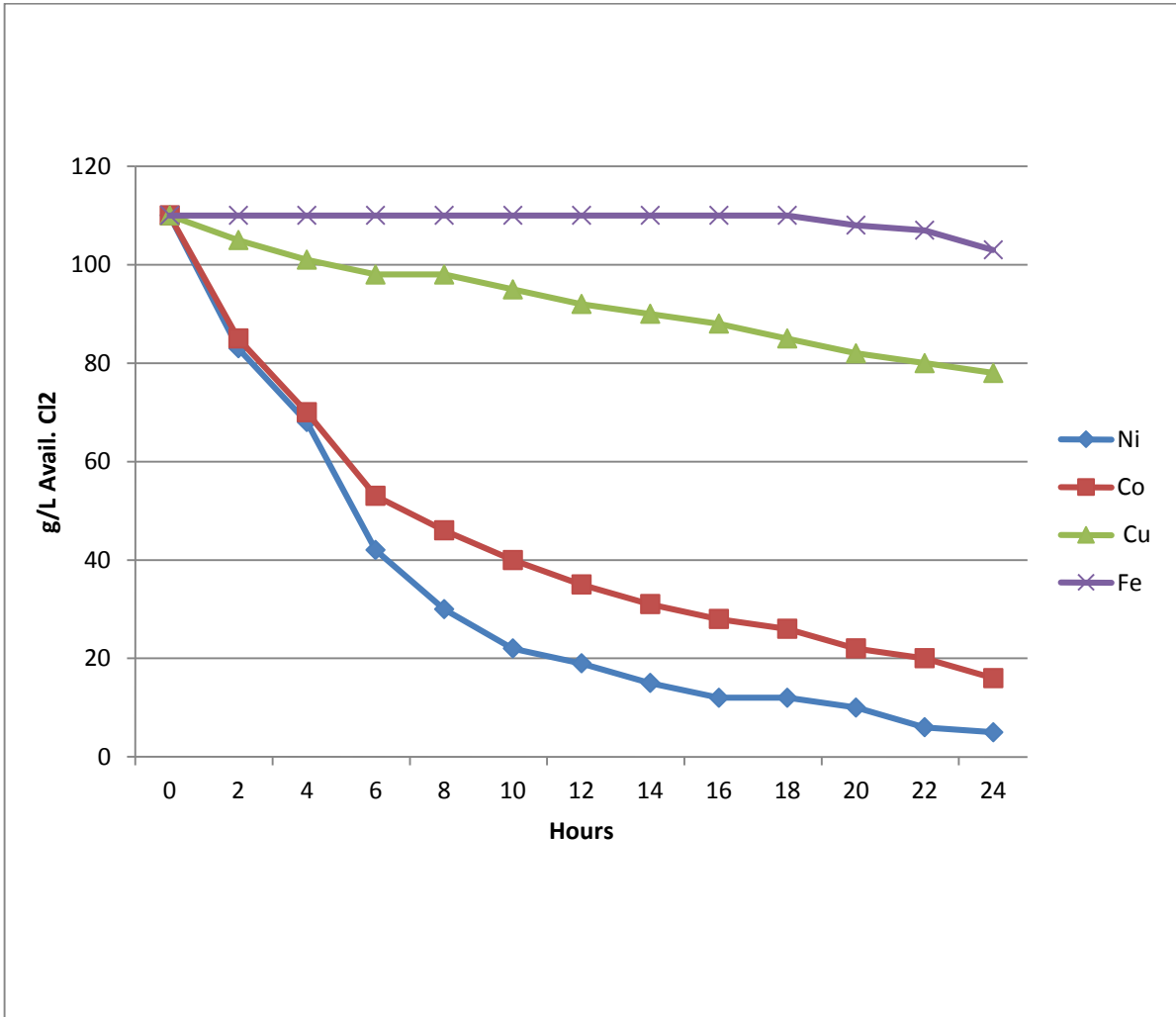
* Standard solution using rayon grade caustic soda; no additional filtration



Exposure to certain metals also can affect stability of sodium hypochlorite, with nickel, cobalt, copper, and iron having the greatest impact, respectively. **Graph 2, Metal-induced Assay Loss**, depicts the significance of trace metallic exposure to hypochlorite stability. While cobalt is particularly reactive with sodium hypochlorite solutions, it is rarely found in day-to-day operations and shipments, and therefore is typically not a significant contributor in most applications. On the other hand, nickel is often encountered since stainless metals are used in many chemical handling applications. Simply transferring sodium hypochlorite through an unlined stainless steel hose connector can initiate the decomposition reaction because of the presence of the nickel component in stainless steels.

The major sources of metallic contamination are the quality of caustic soda and dilution water used in the manufacturing process, and the exposure to metals during delivery and handling. Many manufacturing processes incorporate various types of filtration to control and/or remove metallic contamination. However, for certain applications such as product bottling, additional filtration steps may be required to further reduce metallic contents. Customer-controlled exposure opportunities encompass all areas of product handling beginning at the unloading process and continuing through to product formulation and use. Because of the potential significant impact to product quality, a rigorous management of all handling processes will be required to ensure all wetted surfaces are metals-free (except for titanium and tantalum), as discussed in preceding handbook sections.

Graph 2
Metal-induced Assay Loss (g/L)
Versus Time (hours)



Solution pH also can affect sodium hypochlorite stability. For most sites receiving inbound sodium hypochlorite, pH is not a significant stability factor as the importance of alkalinity (the ultimate source of pH) is well-understood by most commercial producers. Because of this, adequate alkalinity (and the resulting pH level) is added at the point of manufacture. However, alkalinity levels can become an important consideration for customers who significantly change the solution composition, such as in major product dilution, formulation, or during spill neutralization activities. The adage, “if a little is good, then a lot will be better,” does not correlate with sodium hypochlorite stability and alkalinity/pH levels. In fact, stability can be adversely affected by either too little or too much alkalinity. Alkalinity levels of at least 0.1 – 0.2 weight % as NaOH are needed for stability. As alkalinity increases, solution instability also increases.

Dilution

Dilution of sodium hypochlorite is often chosen by customers to slow the rate of product decomposition while in storage or to meet assay-specific applications. Although many sources of water can be used for sodium hypochlorite dilution, the most important aspects to consider when choosing a dilution water source are generally hardness and metals content. Hard water (high calcium and magnesium content) can cause precipitates and scaling to occur in sodium hypochlorite solutions. Exposure of sodium hypochlorite to dissolved metals in dilution water can accelerate product decomposition similar to physical contact with metallic components and /or may alter the color of the hypochlorite solution. In general, as water quality improves, product scaling and precipitation are reduced and decomposition rates decrease.

The dilution water should be analyzed to develop an impurity profile. Depending upon impurities, a treatment system may be required to upgrade water quality to help minimize quality problems with the diluted product. A reputable water treatment specialist can determine the best treatment method and capacity to generate purified water for your particular application. For most applications, water impurities should not exceed the general quality requirements noted in the adjacent chart. For sodium hypochlorite bottling operations, additional water treatment and product filtration may be required.

Another consideration for significant strength dilutions is the excess alkalinity in the diluted product. For minor dilutions, the excess actual sodium hydroxide content in the product should be sufficient to maintain the minimum level of about 0.1 wt% to ensure product stability. With more significant dilutions, a small addition of caustic soda (sodium hydroxide) may be required to achieve the minimum level necessary for a stable product. The quality of the caustic soda added can also negatively impact sodium hypochlorite quality, especially in the areas of trace metals and salts.

Unlike dilution of hypochlorite with water which is non-exothermic, addition of significant quantities of caustic soda will result in a temperature gain of the solution. Solution cooling capabilities may be required for large volume alkali additions to minimize temperature-induced product decomposition.

Component	Concentration
Nickel	< 10 ppb
Copper	< 10 ppb
Cobalt	< 10 ppb
Iron	< 10 ppb
Silica	< 0.2 ppm
Conductivity	< 10 μ S/cm
Total Dissolved Solids	< 5 ppm
Total Hardness	< 5 ppm

Chemistry

Manufacturing

Sodium hypochlorite solutions are most often produced today using an automated continuous process. In the early development of commercial production, the batch process was based on the same approach used to scrub various fugitive chlorine streams as piping and equipment were purged for maintenance and other procedures. All of these processes involve the bubbling of gaseous chlorine or direct injection of liquid chlorine into a dilute caustic solution. To avoid over-chlorination and to maintain the excess alkalinity required to produce a stable hypochlorite solution, chlorine addition must be discontinued prior to complete depletion of the caustic present in the solution.

Conventional sodium hypochlorite follows the manufacturing chemical reaction below which combines caustic soda and chlorine to produce one mole of sodium chloride (NaCl) for each mole of sodium hypochlorite (NaOCl). (A mole is a measure of the number of molecules of a compound). This one-to-one ratio of production products often garners the name of 'equimolar sodium hypochlorite' as a result.



Oxidation Power

The major uses for sodium hypochlorite solutions are directly related to its oxidation power. Before the development of sodium hypochlorite solutions, chlorine was used directly for many of these applications. With the storage advantages of an aqueous solution, sodium hypochlorite solutions have replaced chlorine in many of these typical uses.

This leads to the obvious question: How much chlorine (Cl₂) is available in a sodium hypochlorite (NaOCl) solution? Equations 2 and 3 below show that one mole of NaOCl can oxidize two moles of potassium iodide to form one mole of Cl₂. (In other words a mole of sodium hypochlorite will oxidize the same amount of iodide as will a mole of chlorine). The molecular weight of NaOCl is 74.5 (23 + 16 + 35.5); the molecular weight of chlorine (Cl₂) is 71 (2 × 35.5). The term, available chlorine, was coined to describe this relationship in the sodium hypochlorite context. The ratio of molecular weights (74.5/71), or 1.05, quantifies this relationship.



To relate gallons of sodium hypochlorite solution to pounds of chlorine, the hypochlorite's strength as expressed in units of available Cl₂ must be converted to the equivalent pounds of chlorine to answer the question above using the equation:

$$\text{Avail. Cl}_2 \text{ g/L (A)} \times 3.785 \text{ liters/gal} \times 2.205 \text{ lbs/1000 grams} = \text{lbs Avail. Cl}_2 \text{ /gal solution} \quad \text{Eq. 4}$$

For example, 120 g/L available Cl₂ × 3.785 × 2.205/1000 = 1 pound available Cl₂/gallon of solution. Expressed differently, one gallon of sodium hypochlorite solution having 120g/L available chlorine provides the equivalent oxidizing power of one pound of chlorine, (120 g/L available Cl₂ = 1 lb chlorine per gallon of solution). The unique one-to-one ratio provides a convenient basis point when other hypochlorite solution strengths (in grams per liter of available Cl₂) are considered.

When evaluating other hypochlorite solutions for chlorine equivalency using available chlorine, always divide the grams per liter available chlorine by 120 g/L. For example, (150 g/L available Cl₂ /120 g/L avail. Cl₂) = 1.25. In this example, one gallon of 150 g/L available Cl₂ solution yields the equivalent of 1.25 pounds of chlorine gas. This ratio will then indicate how much more (or less) equivalent chlorine

is present in a given hypochlorite solution compared to a fixed amount of chlorine gas. Refer to Table 1 for additional details.

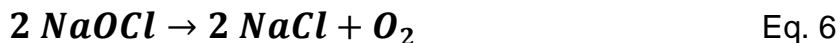
Similar calculations can be performed using wt% NaOCl provided the solution density is known.

Decomposition

The conditions and impurities in the sodium hypochlorite solution determine the reaction(s) defining the solution composition resulting from decomposition of the NaOCl molecules. The thermal decomposition route primarily results in production of chloride and chlorate ions.

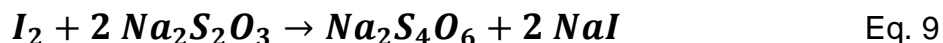


The presence of trace metals catalyzes the sodium hypochlorite decomposition according to the following equation, which produces oxygen and salt. Small bubbles of the gas emanating from particles, often barely visible to the naked eye or even microscopic, within the solution and rising to the surface are often telltale evidence of this problematic reaction. Small amounts of nickel, cobalt, and copper are particularly reactive even at parts per billion (ppb) levels. Oxygen generation and the corresponding loss in assay (NaOCl) will continue until all hypochlorite has been decomposed or until the trace metal(s) has been removed from the solution. Operational and safety concerns associated with this reaction are discussed in greater detail in the preceding Stability section.



Titration/Chemical Analysis

The chemistry involved in the typical analysis used to determine the assay of NaOCl in a sodium hypochlorite solution is shown below. The color of the iodine molecule (I_2) provides a visual cue to the endpoint of the manual titration procedure used for this analytical process.



The yellow-to-clear titration end-point using iodine is difficult to determine accurately. Addition of starch indicator with the potassium iodide will significantly improve the accuracy of this titration by providing a more distinct blue-to-clear colorimetric end-point.

Crystallization Points

Since sodium hypochlorite solutions can contain varying amounts of several dissolved salts, the ability to predict accurately the crystallization point of the solution can be difficult. The amount of crystallization and the exact temperature at which these attributes begin to appear are composition-specific and may vary noticeably. For example, identical solution "grades" of product supplied from different manufacturers or production facilities will probably exhibit differing crystallization properties when subjected to the same temperature conditions. Solutions with higher concentrations of hypochlorite and/or the other dissolved salts will generally begin to crystallize at higher ambient temperatures than solutions containing lower concentrations of hypochlorite and/or the other salts.

Frozen hypochlorite solutions can be thawed and used; however care must be exercised to avoid excessive heat application which will initiate temperature decomposition of the solution. In some instances, the crystallization process may result in precipitation of suspended materials which will not easily dissolve upon thawing. Crystallization effects typically first appear on the solution surface or in small diameter piping/tubing subjected to no or low-flow conditions.

Table 4
Crystallization Points
(Chlorine Institute Data)

Weight % NaOCl	Crystallization Point (Deg. F.)	Crystallization Point (Deg. C.)
15.5	-21.5	-29.6
12	-3	-19.4
6	18.5	-7.5

Product Assay

A simple titration test is used to determine sodium hypochlorite strength and, if performed correctly, will yield highly accurate data. The titration is based upon the principle of ion substitution in a pH-buffered environment, where the substitution element (iodine) is more easily titrated than the hypochlorite ion. Advances in technology have resulted in the adoption of autotitrators for analyses because they offer excellent reproducibility and are well-suited for facilities performing high volumes of testing. However, the procedure can also be performed manually using a burette for titration. As with all titrations, use of good lab protocols and attention to detail will be important in obtaining accurate, reproducible results.

Sample handling in the areas of time, temperature, ultraviolet light, and metals exposure can have a significant impact on analytical results when determining sodium hypochlorite assay. To minimize decomposition from these influences, samples should be collected using sampling devices, bottles, and bottle cap inserts that are nonmetallic on the wetted surface, and that are dedicated to sodium hypochlorite use. Avoid exposure to sunlight and immediately analyze the samples upon collection. When assay testing may be delayed, samples should be refrigerated / chilled to retard temperature-induced product decomposition and corresponding loss of assay. Storage temperatures in the 35- 40

degree F. range are common. It will be important to record the temperature of the chilled solution if specific gravity-based calculations are made.

When collecting samples from sample ports, an adequate purging process should be implemented to ensure a representative sample is obtained. Sample bottles should avoid being filled liquid-full to accommodate potential volume expansion if cold product is sampled and allowed to warm before testing. Adequate “head space” also will minimize the potential for sample bottle damage resulting from metallic-induced product decomposition and the associated pressure build-up of oxygen gas.

The procedure in the following reference section is based upon the Chlorine Institute’s test method, “Potentiometric Titration of Sodium Hypochlorite Solutions.” This procedure offers the flexibility of using a weighed sample or a volumetric sample.

Residual Alkalinity

All sodium hypochlorite solutions require residual alkalinity, particularly sodium hydroxide, to ensure product stability and to avoid generation of chlorine gas. Sodium hydroxide and sodium carbonate are the typical alkalinity sources. Sodium carbonate is not as effective in stabilizing hypochlorite solutions, and is typically not intentionally added to achieve higher alkalinity contents. Alkalinity determination becomes particularly important in dilution activities or in chlorine-scrubbing applications where dilute sodium hypochlorite is being produced. Once the available chlorine has been neutralized with hydrogen peroxide, a simple acid–base titration is performed to determine alkalinity. If the determination of amount of sodium hydroxide and sodium carbonate is needed, the titration is essentially the same but has two endpoints. Use of pH testing to determine alkalinity levels is not recommended because of the inability of pH test methods (probes or litmus papers) to yield accurate, reproducible test results. The Chlorine Institute’s test method, “Determination of Sodium Hydroxide and Sodium Carbonate,” follows in the reference section. Like the assay analysis, this test can be performed by manual or auto titration.

Sodium Hypochlorite Assay Detail

Proper Personal Protective Equipment (PPE) should be worn when handling sodium hypochlorite and chemical reagents. Consult the supplier’s most current Safety Data Sheet (SDS) for each reagent as well as the Chlorine Institute Pamphlet 65 for PPE guidance for sodium hypochlorite. The ultimate goal of any laboratory is to generate accurate and precise data. Good laboratory practices, including robust personnel training, documented procedures using validated test methods, and the use of statistical controls on equipment and reagents should be employed to achieve the goals of data accuracy and precision.

The sodium hypochlorite assay/available chlorine analysis requires the hypochlorite be treated with excess potassium iodide and acidified with excess glacial acetic acid. Iodine is liberated from the acidification process and is titrated with sodium thiosulfate to a straw yellow end-point. **Addition of starch indicator can improve the accuracy of titration results due to the difficulty in determining the colorimetric end-point of iodine-based titrations.** Analytical steps must be followed carefully and in the correct sequential order to ensure accurate results. The analytical procedures were obtained from The Chlorine Institute’s Pamphlet 96, ‘Sodium Hypochlorite Manual’,

with minor adjustments made to the procedural order of several steps. Consult the most current Pamphlet 96 edition for any procedural changes.

Sample Preparation

(Sample Preparation - Direct Weight Method)

1. Tare-weigh (zero) a 250-mL Erlenmeyer flask on a calibrated analytical balance capable of weighing to at least +/- 0.001g.
2. Secure lid on sample container and thoroughly mix.
3. Transfer 0.6 g of sample to the tared Erlenmeyer flask and record weight to the nearest +/- 0.001g.
4. Add approximately 10mL of deionized (DI) water for dissolving KI crystals.

(Sample Preparation – Volume Addition Method)

1. Tare-weigh (zero) a 250-mL volumetric flask (without the stopper) on a calibrated analytical balance capable of weighing to at least +/- 0.001 g.
2. Secure lid on sample container and thoroughly mix.
3. Transfer 25-mL of sample from the container into the tared 250-mL volumetric flask.
4. Dilute to the final 250-mL volumes using DI water; insert the stopper into the flask; mix well.
5. Transfer 10 mL of the diluted sample into a 250-mL Erlenmeyer flask.

Sample Analysis

1. Place a magnetic stir bar in the Erlenmeyer flask.
2. Add 2–3 grams of Potassium Iodide (KI) crystals; gently swirl to dissolve all crystals.
3. Add 10 mL of glacial acetic acid; gently swirl to mix.
4. Rinse sides of flask down with DI water.
5. Titrate with 0.1N Sodium Thiosulfate until solution is a pale yellow color.
6. Add starch indicator and continue titration until the solution turns from blue to colorless.
7. Record the volume of Sodium Thiosulfate used.

Calculations

Weight percent sodium hypochlorite (wt% NaOCl) and weight percent available chlorine (wt% AvCl₂) can be determined from the assay titration. The calculations will differ depending upon whether a direct weight or a volume aliquot of the sample was used in the analysis.

Using Direct Sample Weight

$$\text{Wt\% NaOCl} = (\text{mL Thiosulfate} \times \text{N Thiosulfate} \times 3.722) / \text{Sample weight (g)}$$

$$\text{Wt \% AvCl}_2 = (\text{mL Thiosulfate} \times \text{N Thiosulfate} \times 3.5453) / \text{Sample weight (g)}$$

Using Aliquot Sample Volume

$$\text{mL Aliquot} = 25/250 \times 10 = 1 \text{ ml}$$

$$\text{Wt \% NaOCl} = (\text{mL Thiosulfate} \times \text{N Thiosulfate} \times 3.722) / (\text{mL Aliquot} \times \text{Density})$$

$$\text{Wt\% AvCl}_2 = (\text{mL Thiosulfate} \times \text{N Thiosulfate} \times 3.5453) / (\text{mL Aliquot} \times \text{Density})$$

Reagents

- Sodium Thiosulfate (Na₂S₂O₃) solution standard, 0.1 normality Potassium Iodide (KI), granular, certified ACS reagent grade
- Glacial Acetic Acid, 98.8%, certified ACS grade
- Starch indicator
- Deionized (DI) water

Residual Alkalinity Analytical Detail

Proper PPE should be worn when performing analytical work with sodium hypochlorite and chemical reagents. Consult the most current Safety Data Sheet (SDS) for laboratory reagents as well as the Chlorine Institute's Pamphlet 65 before performing analytical work.

In determining the complete alkalinity analysis of sodium hypochlorite solutions, the hypochlorite ion is first neutralized by the addition of hydrogen peroxide. Analysis involves a double-end point titration wherein the first titration end-point represents the amount of hydroxide present. The second end-point denotes the alkalinity contribution of the carbonate ion. It will be important to use fresh hydrogen peroxide to ensure complete neutralization. Hypochlorite solution strengths in excess of ~ 15 weight % as NaOCl will require additional hydrogen peroxide additions. **Use of pH testing to determine the amount of alkalinity should be avoided because of the inability to produce accurate results.** This test method was obtained from the Chlorine Institute's Pamphlet 96, "Sodium Hypochlorite Manual" and re-formatted. Consult the most current copy of The Chlorine Institute's Pamphlet 96 to ensure the most up-to-date method is used.

Sample Preparation

- Prefill an 300-mL Erlenmeyer flask with ~ 50mL of deionized water
- Weigh filled flask and tare
- Pipette a 5-mL aliquot of the hypochlorite solution into the Erlenmeyer flask
- Record flask weight to the nearest 0.1 gram
- Add 20-mL of neutral, 3% hydrogen peroxide, stirring gently
- Add 3 drops of phenolphthalein indicator
- While gently stirring, titrate solution with 0.1N hydrochloric acid solution until all pink color is dispersed
- Record mL of hydrochloric acid used to achieve clear solution (A)
- Add 3 drops of methyl orange indicator and continue titration while stirring until the yellow color changes to red
- Record mL of hydrochloric acid used to achieve red color (B)

Calculations

$$\text{Wt\% NaOH} = [(A-B) \times N \times 4] / \text{sample weight (W)}$$

$$\text{Wt\% NaCO}_3 = [B \times N \times 10.6] / \text{sample weight (W)}$$

$$\text{Wt\% Total alkalinity as NaOH} = [(A + B) \times N \times 4] / \text{sample weight (W)}$$

A = mL of hydrochloric acid used at the phenolphthalein endpoint

B = mL of hydrochloric acid used at the methyl orange endpoint

N = Normality of hydrochloric acid solution

W = Weight of sample

Reagents

- 0.1N hydrochloric acid
- Deionized (DI) water
- Reagent grade, pH neutral hydrogen peroxide solution (3%)
- Phenolphthalein indicator
- Methyl orange indicator

Acknowledgments

Responsible Care® and Our Commitment To Sustainability, the hands logo, (and design) are registered trademarks of the American Chemistry Council.

Teflon® is a registered trademark of The Chemours Company.

Tefzel® is a registered trademark of The Chemours Company.

Halar® is a registered trademark of Solvay Solexis Corporation.

Kynar® is a registered trademark of Arkema, Inc.

All product names, logos, and brands are property of their respective owners. All company, product and service names used in this website are for identification purposes only. Use of these names, logos, and brands does not imply endorsement. All other trademarks cited herein are the property of their respective owners.

Quick References

The Chlorine Institute

1300 Wilson Blvd.

Suite 525 Arlington, VA 22209

(703)-894-4140

www.chlorineinstitute.org

- Pamphlet 96, "Sodium Hypochlorite Manual"
- "Avoiding Accidental Mixing of Sodium Hypochlorite" bulletin
- "Sodium Hypochlorite Incompatibility Chart"

The Association for Rubber Products Manufacturers

7321 Shadeland Station Way

Suite 285

Indianapolis, IN 46256

(317)-863-4072

www.arpminc.com

- IP-11-7 "Manual for Maintenance, Testing & Inspection of Chemical Hose"
- IP-4-13 "Procedure for Spark Testing Elastomeric Sheet Lining"

ASTM International

100 Barr Harbor Drive

West Conshohocken, PA 19428

(877)-909-2786

www.astm.org

- Standard Specification for Upright Polyethylene Storage Tanks

Emergency Contacts

In the event of an accident or chemical incident, refer to your site's emergency preparedness plan and the most current Safety Data Sheet (SDS). Should a chemical leak or spill occur, immediately contact the applicable regulatory agency and implement your Site Control Plan (SCP).

In Canada:	Call CANUTEC (collect)	(613) 996-6666
In the U.S.:	Call CHEMTREC (toll-free)	(800) 567-7455

As a hazardous chemical, sodium hypochlorite spills equating to 100 pounds of active ingredient as NaOCl (~ 80 gallons of 12.5 wt% as NaOCl solution) or more require the immediate notification of the National Response Center at 800-242-8802 within 15 minutes of the spill occurrence in the U.S. Consult local and regional regulatory agencies for other notification requirements unique to your particular geography.

Disclaimer

The information in this Manual is offered only as a guide to the handling of this specific material and is not a substitute for your proper knowledge of applicable laws and regulations. The recipient must make its own determination as to the utility of the information contained in this report for recipient's purposes. Olin undertakes no duty to provide or update the information in this Manual.

The information in this Manual is not intended to be all-inclusive as to the manner and conditions of use, handling and storage. Other factors may involve other or additional safety or performance considerations. Olin may respond to questions regarding safe handling of Olin's products, but safe handling and use remains the responsibility of the product's consumers and/or customers. NO WARRANTY OF MERCHANTABILITY OR FITNESS FOR PURPOSE, OR ANY OTHER KIND, EXPRESS OR IMPLIED, IS MADE REGARDING PERFORMANCE OR STABILITY AND IS OTHERWISE HEREBY DISCLAIMED. Olin will not be liable for any damages, losses, injuries or consequential damages that may result from the use of or reliance on any information contained herein. Olin assumes no liability whatsoever for the use of or reliance upon this information. No suggestions for use are intended as, and nothing herein shall be construed as a recommendation to infringe any existing patents or violate any federal, state or local laws, rules, regulations or ordinances.

Sodium Hypochlorite Manual, January 2016, Edition 1, Rev 0
© 2016 Olin Corporation