



Pamphlet 89

Chlorine Scrubbing Systems

Edition 3



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1. INTRODUCTION

1.1 <u>SCOPE</u>

Risk assessments of certain chlorine containing systems have indicated that installation of scrubbing systems should be one of the considerations for vapor release prevention as part of an overall environmental protection program. This pamphlet intends to provide general guidance and source information for chlorine producers and consumers for the effective containment and treatment of their gaseous chlorine effluents.

Included in this pamphlet are:

- Chemical properties of scrubbing and by-product liquids
- Practical design considerations and data
- Description of potential issues when choosing and operating a scrubber system
- General scrubber system reliability considerations
- Materials of construction

Other features required to be part of a scrubbing system but NOT a part of this pamphlet are:

- Determination if a scrubber is needed.
- Additional documentation that will be required to complete the design
- Design considerations for gas collection systems
- Review of the impact of the system on the total plant and neighboring area
- Review of all the applicable codes and regulations
- Conducting a process hazards review
- Developing manuals that support the operation and maintenance of the unit
- Training operations, start-up and maintenance personnel
- Performing a system reliability assessment including spare parts availability, maintenance, etc.
- Review of the current OSHA regulations for personnel exposure limits

1.2 CHLORINE INSTITUTE STEWARDSHIP PROGRAM

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

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

1.3 DEFINITIONS

Unless otherwise stated, the following meanings apply:

ABS acrylonitrile butadiene styrene

carbon steel a ferrous material for dry chlorine piping as described

in Institute Pamphlet 6

chlorine scrubber a device for removal of chlorine from a stream via

reaction, adsorption or absorption

CPVC chlorinated polyvinyl chloride

dry air dry, oil-free, compressed air, dried to a dew point

measured at operating pressure of -40°F (-40°C) or below; for ambient temperature below 10°F (-12°C),

lower dew point settings will be necessary

dry chlorine dry as defined in Pamphlet 100 (5.1.9)

ECTFE ethylene chlorotrifluoroethylene

EPR ethylene propylene rubber

FEP fluorinated ethylene propylene

FRP a reinforced plastic material made of glass fiber, with

a suitable resin (such as polyester, epoxy or

vinylester) to withstand the corrosive environment of

the application

kPa kilopascals

PE polyethylene

PFA perfluoroalkoxy

PPL polypropylene

psig pounds per square inch gage

PTFE polytetrafluoroethylene

PVC polyvinyl chloride

PVDF polyvinylidene fluoride

1.4 <u>DISCLAIMER</u>

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

1.5 APPROVAL

The Institute's Storage and Transport Committee approved Edition 3 of this pamphlet on April 4, 2006.

1.6 REVISIONS

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

1.7 REPRODUCTION

The contents of this pamphlet are not to be copied for publication, in whole or in part, without prior Institute permission.

2. CHEMICAL CONSIDERATIONS

2.1 TYPICAL SCRUBBING SOLUTIONS

Chemicals that have been used to scrub chlorine include:

- sodium hydroxide
- potassium hydroxide
- sodium carbonate
- calcium hydroxide
- sodium sulfite

- sodium thiosulfate
- ferrous chloride
- solid bed absorbents/adsorbents

Sodium hydroxide solutions are the most commonly used for typical scrubbing applications. However, the other chemicals listed above have been successfully used in many applications where they may be readily available, less expensive or satisfy the specific application (e.g. solid bed chemical adsorbents in emergency standby scrubber applications).

The information in this pamphlet is written primarily for sodium hydroxide solutions and their reactions with chlorine. All chlorine scrubbing applications are chemical processes requiring detailed knowledge of the reactions, including heat generated, end products, disposal of the finished products, and safe handling of all the chemicals involved in the reaction. Chemicals other than sodium hydroxide for chlorine scrubbing are outside the scope of this pamphlet and have not been addressed. However, selected properties of some of these chemicals can be found in Appendix B.

2.2 MAIN REACTION

The addition of chlorine to a solution of sodium hydroxide (NaOH) produces sodium hypochlorite (NaOCI) and salt (NaCI):

$$2NaOH + Cl2 \Rightarrow NaOCI + NaCI + H2O$$
 [E2-1]

On a weight basis, one pound (0.454 kg) of chlorine plus 1.128 lbs (0.512 kg) of sodium hydroxide will produce 1.05 lbs (0.477 kg) of sodium hypochlorite.

2.3 SIDE REACTIONS

Additional reactions occurring during the scrubbing of chlorine with sodium hydroxide may become a design consideration.

The sodium hypochlorite formed can decompose as follows:

$$3NaOCI \rightarrow NaCIO_3 + 2NaCI$$
 [E2-2]

$$2NaOCI \rightarrow 2NaCI + O_2$$
 [E2-3]

2.4 Overchlorination (Research work)

The importance of excess sodium hydroxide to avoid overchlorination cannot be overstated. When sodium hypochlorite is overchlorinated, the rate of chlorate formation is greatly accelerated. HOCl is formed in the event of overchlorination by the reaction:

$$NaOCI + CI_2 + H_2O \rightarrow 2HOCI + NaCI$$
 [E2-4]

Chlorate formation then occurs by the following reaction:

$$2HOCI + NaOCI \rightarrow NaCIO_3 + 2HCI$$
 [E2-5]

The rate of Reaction [E2-5] is several orders of magnitude greater than the rate of Reaction [E2-2]. The HCl formed in Reaction [E2-5] combines with the hypochlorite ion to form more HOCl so the excess chlorine has a catalytic effect on chlorate formation. The increased acidity causes Reaction [E2-5] to proceed. This is an exothermic reaction which can become violent in scrubbers under these conditions.

CAUTION: If excess chlorine is added to a scrubber, decomposition of sodium hypochlorite takes place. Reaction [E2-3] will become appreciable. This condition results in foaming, caused by the formation of steam and oxygen. Chlorine will no longer be absorbed or scrubbed. This situation must be avoided by guaranteeing that excess sodium hydroxide is present.

2.5 HEATS OF REACTION

A very important factor in operation and/or design of a chlorine scrubber is temperature. Significant quantities of heat are released by the sodium hydroxide-chlorine reaction. The most significant reactions involved in the chlorine scrubbing and the corresponding heats of reaction are as follows:

Scrubbing Reaction

$$2NaOH + Cl2 \Rightarrow NaOCI + NaCI + H2O$$
 [E2-1]

 $\Delta^{H}25 = -626$ Btu/lb (-348 cal/g) chlorine gas

Decomposition Reactions of Sodium Hypochlorite

$$NaOCI \rightarrow NaCI + \frac{1}{2}O_2$$
 [E2-6]

 $\Delta^{H}25 = -336 \text{ Btu/lb } (-187 \text{ cal/g}) \text{ hypochlorite decomposed}$

$$3NaOCI \rightarrow NaCIO_3 + 2NaCI$$
 [E2-2]

 $\Delta^{H}25 = -188 \text{ Btu/lb } (-104 \text{ cal/g}) \text{ hypochlorite decomposed}$

The above heats of reaction were calculated at 77°F (25°C) using these values of heats of formation.

Δ ^H 25 NaOH	=	-112.93 kcal/g · mole
Δ^{H} 25 NaCl	=	-97.234 kcal/g · mole
Δ^{H} 25 $H_{2}O$	=	-68.3174 kcal/g · mole
Δ^{H} 25 NaOCl	=	-83.39 kcal/g · mole
Δ ^H 25 NaClO ₃	=	-78.92 kcal/g · mole

NOTE: If liquid chlorine is injected directly into the sodium hydroxide, the heat of reaction is approximately 526 Btu/lb chlorine (292 cal/g) since the latent heat of vaporization of liquid chlorine is approximately 100 Btu/lb (55 cal/g) at room temperature. (See Graphs 3.1 – 3.6, which depict effluent temperature at various chlorine conditions and caustic strengths.)

2.6 OTHER CONSIDERATIONS

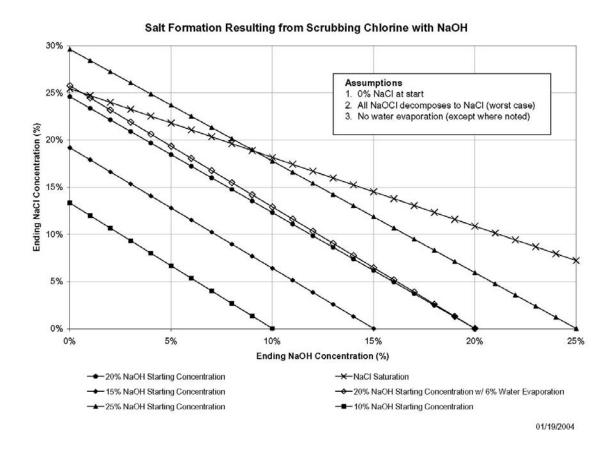
2.6.1 Solubility Considerations

Precautions should be taken to avoid or accommodate solids that could plug the system. Solids can form in scrubbing systems due to freezing, foreign materials and as a result of the following mechanisms:

Caustic Soda & Solid Salt Formation

Sodium Hydroxide (caustic) is normally used in the absorption of chlorine containing gases. When chlorine reacts with the caustic salt is formed. Salt has limited solubility in scrubber solutions. Therefore there is a risk of precipitating the salt when the caustic is depleted. This may be aggravated when commercial caustics that may contain salt (diaphragm, cell liquor, etc) are used as a scrubbing medium. This may be further aggravated by the fact that water evaporates when chlorine and caustic react.

Above concentrations of 20% initial caustic the possibility of solid salt precipitation exists as the caustic concentration is fully depleted. If higher concentrations are used the effluent caustic concentration must be maintained at higher levels to avoid solid salt formation. See Graph 2.1.



Graph 2.1

Caustic Soda & CO₂

Carbon dioxide is an impurity which is sometimes present in chlorine streams. It reacts with caustic to form sodium carbonate and sodium bicarbonate per the following reactions:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O (pH>12)$$

 $NaOH + CO_2 \rightarrow NaHCO_3 (pH<12)$

The solubility of sodium carbonate in scrubbing solution is low and the solubility of sodium bicarbonate is very low. Therefore, "salts" may drop out of solution when CO_2 is present in the chlorine or when caustic solution is allowed to contact the atmosphere. Provisions for handling these solids should therefore be taken into consideration in the design and operation of chlorine scrubbers, especially if the caustic is depleted to low concentrations so that the pH drops below 12.

2.6.2 Other Heat Effects

Other heat effects that should be considered are:

- heat of condensation
- heat of dilution

2.6.3 Decomposition

There are several factors that accelerate decomposition of scrubber by-product streams:

Thermal Decomposition

Thermal decomposition is based upon the fact that hypochlorite solution decomposition rate increases with higher temperature. Higher hypochlorite concentration and low residual caustic also accelerate the decomposition. A common method of decomposition is to heat a tank containing a hypochlorite solution with live steam. This heating combined with the heat of decomposition results in rapid decomposition of sodium hypochlorite to oxygen and salt.

Catalytic

The presence and/or addition of metal ions such as cobalt, nickel, copper, and iron in hypochlorite solutions catalytically accelerates decomposition. The presence of salts of these elements combined with the thermal process results in almost complete decomposition of sodium hypochlorite.

CAUTION: For environmental reasons, some metals, usually cobalt and nickel, may have special discharge permit requirements.

Time and Light

All hypochlorite solutions will decompose with time. The presence of sunlight accelerates the process. In some cases, shallow ponds with exposure to light have been used to decompose weak solutions of hypochlorite.

Chemical

Certain chemicals react with hypochlorite solutions. Some of these are sulfur dioxide (SO_2), sulfites (Na_2SO_3 , $NaHSO_3$), thiosulfate and hydrogen peroxide. In most cases, the use of these chemicals is too expensive to use as the method for strong hypochlorite decomposition. They are used most of the time in polishing and small batch reactions to remove traces of sodium hypochlorite. The use of certain chemicals result in high chemical oxygen demand and therefore discharge permits must be checked.

Waste acids are sometimes combined with spent scrubbing liquor to recover chlorine and return chlorine back to the process. The reaction of acids such as hydrochloric acid (HCl) and sulfuric acid (H_2SO_4) with sodium hypochlorite liberates chlorine gas.

3. PROCESS CONSIDERATIONS

Scrubber systems must be designed with environmental protection as the primary goal. All process aspects of both the scrubbing system and systems discharging to the scrubber must be fully defined so that the scrubbing system can meet environmental and other requirements.

3.1 CHARACTERISTICS OF THE CHLORINE STREAM

To properly design a scrubbing system, the chlorine stream must be carefully defined. The properties of the chlorine stream can dramatically influence the scrubbing system design. Graphs 3.1-3.6 depict effluent temperature at various chlorine conditions and caustic strengths.

Assurance of fluid state is critical. While most chlorine scrubbers are designed to handle gas, liquid chlorine can be effectively scrubbed with proper system design. The heat of vaporization of liquid chlorine reduces the temperature rise in the scrubber. If liquid chlorine is fed to a scrubber, it must be contacted with a large volume of scrubbing fluid to disperse the liquid chlorine. This will avoid localized overchlorination of the scrubbing fluid and pressure surging due to formation of large gas bubbles.

If the scrubbing system is not designed for liquid chlorine, then protective measures must be included to prevent liquid chlorine from entering the system.

From a mass transfer standpoint, pure chlorine is easier to scrub than chlorine that contains inert gases. The presence of inert gas increases the required contact area and increases the amount of evaporation from the scrubbing solution. While increased evaporation can help to remove heat from the system, it also increases the possibility of precipitating salts from the scrubbing solution.

The amount of moisture in the inlet chlorine stream should be known. If water vapor from the inlet chlorine is condensed in the scrubber, the condensation heat load could become significant compared to the total heat load. If sufficient cooling is not provided, water vapor will act as an inert and may reduce efficiency to the point where chlorine absorption is impaired.

The potential for the presence of trace components in the chlorine stream should also be considered. Hydrogen, nitrogen trichloride, hydrogen chloride, organic and other impurities are present in some chlorine streams. These impurities can concentrate in the scrubbing system to produce potentially dangerous situations. Impurities in the chlorine can also influence the selection of scrubbing system materials of construction.

The pressure at which the chlorine is available can influence the type of scrubbing equipment that can be used.

3.2 CAPACITY/RATE FOR SYSTEM DESIGN

There are two main factors to be considered in system sizing, design capacity and rate.

3.2.1 Capacity

The design capacity is the quantity of chlorine that can be scrubbed. It is limited by the amount of sodium hydroxide available to the scrubber during an event. This is usually controlled by the total volume of caustic available.

3.2.2 Rate

The rate is determined by the mass of chlorine per unit of time. This is usually limited by the sodium hydroxide delivery rate. If the chlorine stream is intermittent, the design rate for the scrubbing fluid is the stoichiometric equivalent to the peak chlorine flow plus the desired excess.

For example, a pressure relief device may vent to a scrubber for three hours. The peak chlorine flow at the relief point may be 10,000 lbs/hr. If 10% excess scrubbing fluid is desired, the design rate (if sodium hydroxide is the scrubbing fluid) should be 10,000 lbs/hr chlorine x 1.128 (caustic/chlorine molecular weight ratio) x 1.1 (10% excess) = 12,400 lbs/hr of 100% sodium hydroxide. The design capacity for the scrubber would be 3 hours x 12,400 lbs/hr or 37,200 lbs of 100% caustic.

3.3 SCRUBBING FLUID

The scrubbing fluid should be selected on the basis of availability, cost, by-product produced, reactivity with chlorine, solubility of the constituents in the starting and ending scrubbing liquors and susceptibility to freezing.

The practicality of disposing of spent scrubbing liquor must be considered. The ability to sell or recycle a waste stream may dictate scrubbing liquor selection.

The most widely used scrubbing fluid is sodium hydroxide. The following are some process considerations for the designer:

Initial Solution

Sodium hydroxide is most commonly sold as a 50% solution in water. This solution is too concentrated to use in most scrubbers. It contains too little water to absorb the heat of reaction and to maintain the reaction products in solution. It also has a high freezing point that can interfere with scrubber operation in cold weather.

Scrubber operation normally involves dilution of 50% sodium hydroxide or dissolving of flake or bead caustic. Heat of dilution of make-up solutions should be considered. For example, when a solution of 50% sodium hydroxide at 80°F is diluted to 20% with 80°F water, the resulting solution temperature is about 120°F.

Volume effects should be considered when diluting sodium hydroxide. One volume of caustic, when diluted with one volume of water, results in less than two volumes of solution.

Many scrubbers use 20% sodium hydroxide. It has a low freezing point, and the salt solution formed upon complete reaction with chlorine is not quite saturated. If the initial solutions are warm and if large amounts of water are expected to vaporize during operation, consideration should be given to lower initial concentration.

Final Concentration

In scrubbers that manufacture sodium hypochlorite for sale, the final concentration of sodium hydroxide is usually dictated by the product specification.

Some excess sodium hydroxide must be maintained at all times. Otherwise, chlorine will not be reacted. In extreme conditions, it can even be released. In controlled processes, very low residual sodium hydroxide concentrations can be achieved. In cases where chlorine flows are erratic or less sophisticated control systems are in place, relatively high residual caustic concentrations may be required to prevent chlorine emissions.

At concentrations greater than about 8%, sodium hydroxide strength has little effect on the system mass transfer coefficient. At lower concentrations, the mass transfer coefficient drops rapidly and will affect contactor sizing.

Solubility

Precautions should be taken to either avoid or accommodate formation of solids. Solids can form in scrubbing systems due to freezing, foreign material entry or chemical reaction.

As sodium hydroxide is reacted with chlorine, salt is formed. Salt is less soluble than sodium hydroxide and can precipitate if the initial sodium hydroxide concentration is too high or if too much water evaporates during the scrubbing process.

If air is allowed to flow through a sodium hydroxide containing scrubber, the caustic will scrub carbon dioxide from the air. The resulting sodium carbonate is less soluble than salt and will precipitate in solutions where salt alone is fully soluble.

See Section 2.6.1 for more detailed discussion

3.4 HEAT EFFECTS

Table 3-1 shows the reaction and water condensation heat load on a hypothetical chlorine scrubber that is reacting with chlorine at an instantaneous rate equivalent to 100 tons per day. On a hourly basis, this is equivalent to 8,333 lbs/hr. The "no decomposition" line assumes that all chlorine reacts to sodium hypochlorite. The "decomposition" line assumes that 25% of the sodium hypochlorite produced decomposes to oxygen and salt.

CAUTION: The assumed 25% decomposition is given for illustrative purposes only. The amount of decomposition will be influenced by the reaction temperature and the presence of impurities which can catalyze the decomposition reaction. The expected decomposition must be developed for each individual system. In the absence of external cooling and information on the specific catalysts present, a conservative estimate of the temperature rise is determined by assuming 100% decomposition.

Table 3-1. Typical Heat Load on a Chlorine Scrubber				
Dry Chlorine Feed	Dry Chlorine Feed			
No decomposition	5.2 x 10 ⁶ Btu/hr	(1.31 x 10 ⁶ kcal/hr)		
Decomposition	6.9 x 10 ⁶ Btu/hr	(1.74 x 10 ⁶ kcal/hr)		
Wet Chlorine Feed (saturated at 190° F)				
No decomposition	7.8 x 10 ⁶ Btu/hr	(1.97 x 10 ⁶ kcal/hr)		
Decomposition	8.5 x 10 ⁶ Btu/hr	(2.15 x 10 ⁶ kcal/hr)		

When scrubbing chlorine with stoichiometric quantities of 15% to 20% caustic, the heat generated can bring the solution to the boiling temperature. The water vapor generated by the boiling solution dilutes the chlorine and reduces the mass transfer efficiency of the scrubber. Thus, it is desirable to maintain the solution temperature well below the boiling temperature. The transfer of heat from the solution to an external cooling system can be the obvious choice. If external cooling is not available or impractical, temperature control can also be accomplished by reducing the initial sodium hydroxide concentration or scrubbing with greater excesses of sodium hydroxide. For water-saturated chlorine Graphs 3-1 and 3-2 show the effect on scrubber liquor temperature rise when initial sodium hydroxide strength varies from 5% to 20% and when one to four times the stoichiometric quantity of sodium hydroxide is used for neutralization. These graphs assume that the inlet chlorine is saturated with water vapor at atmospheric pressure and 190°F (95°C) with 5% excess sodium hydroxide. Dry chlorine scrubbers have lower heat loads which can be determined from the data in Table 3-1.

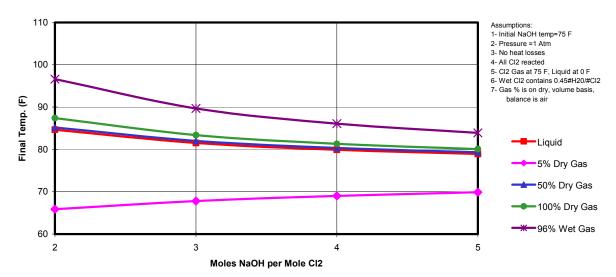
3.5 Considerations for Scrubbing Fluid Discharge

If liquid by-products are not sold or recycled, the following should be considered prior to discharge:

- limits on hypochlorite concentration (free chlorine)
- limits on heavy metals which may be present as a result of hypochlorite decomposition procedures
- limits on total dissolved solids
- limits on Ph
- limits on chlorinated organics

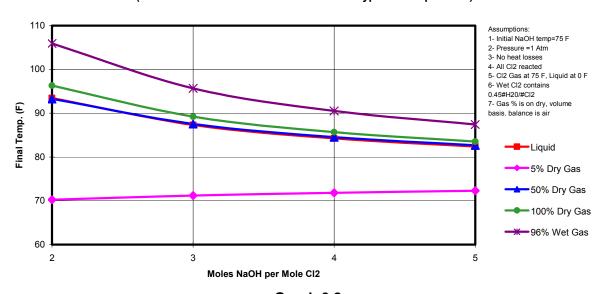
CAUTION: Acids should not be added to hypochlorite, because chlorine will be evolved.

Reaction Temperature vs. Excess NaOH (5% Initial Caustic Concentration & No Hypo Decomposition)

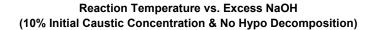


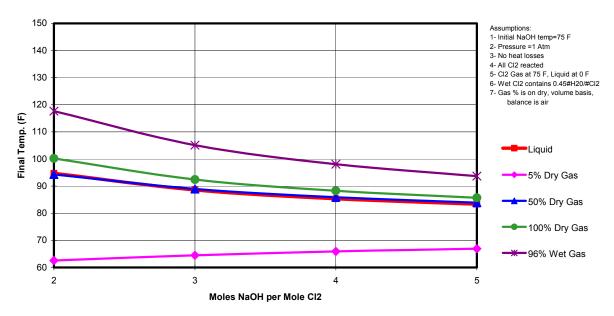
Graph 3.1

Reaction Temperature vs. Excess NaOH (5% Initial Caustic Concentration & Full Hypo Decomposition)



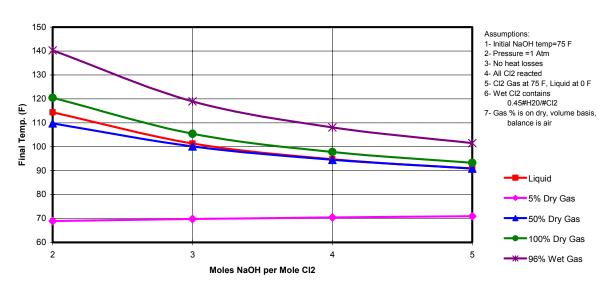
Graph 3.2



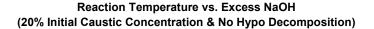


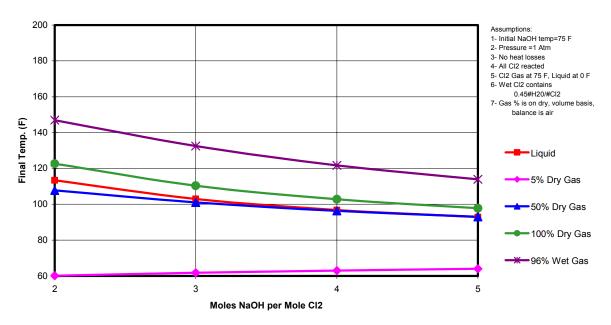
Graph 3.3

Reaction Temperature vs. Excess NaOH (10% Initial Caustic Concentration & Full Hypo Decomposition)



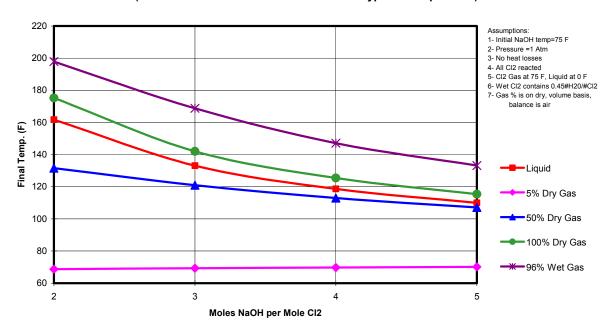
Graph 3.4





Graph 3.5

Reaction Temperature vs. Excess NaOH (20% Initial Caustic Concentration & Full Hypo Decomposition)



Graph 3.6

4. SYSTEM DESIGN

4.1 GENERAL

The primary function of a scrubbing system is to contact chlorine with a scrubbing fluid. Chlorine scrubbing systems have been installed to abate a wide range of process streams. Depending on the size and on the main objective of the scrubber, there are various options to select from when basic design choices are made. Examples of streams being scrubbed are continuous process vents, system emergency reliefs, discontinuous vents from loading or unloading operations and vents from containment areas or rooms storing chlorine containing equipment. The selection of a continuous system over a batch or emergency unit will impact the method used for transporting the fluids and the method for bringing them in contact. For emergency chlorine scrubbing systems the conservative system design assumes the chlorine is wet. A review of the location for the scrubbing system should consider the safety of adjacent areas. The use of redundant instrumentation, increased safety factors in the design, passive systems and/or stand-by electrical power supply should be considered. Sections 4.2 thru 4.8 give guidance to the designer relative to the selection of system components.

4.1.1 Design Documentation

Process Definition

The process becomes fully defined with the formalization of the system material and energy balance. The design of all chlorine scrubbing systems should include preparation of detailed material and energy balances.

The material and energy balance should show:

- Inlet chlorine stream
 - flow (normal, peak and average)
 - pressure, temperature and composition
- Scrubbing fluid make-up
 - average quantities
 - peak/batch quantities
 - concentration and temperature
- Contactor scrubbing fluid flows
 - inlet (or start of batch) design rate (flow, composition, temperature)
 - inlet (or start of batch) design capacity (volume, composition, temperature)
 - outlet (or end of batch) design rate (flow, composition, temperature)
 - outlet (or end of batch) design capacity (volume, composition, temperature)
- Scrubbed chlorine vent
 - flow (normal, peak, average)
 - pressure, temperature, composition

System Definition

A detailed piping and instrument design (P&ID) showing all components of the scrubbing system is developed as one of the first steps of system design.

The P&ID should show the following:

- All equipment
- All piping and valves
- · Instrumentation and safety devices

4.1.2 Materials of Construction

In the selection process for the materials to be used, the designer must consider the operating parameters in which the scrubbing system will be expected to perform not only under normal process conditions but also during upsets. Different concentrations and temperatures of hypochlorite and sodium hydroxide can affect the corrosiveness of these solutions. Therefore, the particular normal and upset operating conditions will impact the selection of the appropriate materials of construction. Each installation must be studied individually to obtain a safe, economic and efficient system. The use of improper materials can lead to premature failure of system components.

Titanium is an excellent material of construction for scrubbing system components as long as it is only exposed to wet chlorine. It can spontaneously ignite when exposed to dry chlorine.

Details of materials commonly used in scrubbing systems are shown in Appendix C.

4.2 CONTACTORS

4.2.1 Sparge Tanks

Sparge tanks use pressure to disperse chlorine through a distributor located beneath a sufficient level of scrubbing fluid. They do not depend on circulating systems to bring the scrubbing solution in contact with the chlorine. The system is simple, inexpensive and it has no moving parts.

Sparge tanks have several disadvantages, including the need to overcome the head of scrubbing fluid level and distributor pressure drop. Turndown capability is limited by distributor design and operation is usually limited to batch or semi-batch processing.

Provisions should be made to prevent the possibility of reverse flow of scrubbing solution into the chlorine source. This can be done with barometric legs, automated valving, gas purges or break tanks. Check valves are usually ineffective unless they are used in combination with other backflow prevention devices.

4.2.2 Spray Towers

This device is usually designed for counter flow operation with multiple layers of overlapping spray nozzles. Their simple design means that they can be built of highly resistant materials of construction at relatively low cost. Gas phase pressure drop is low, and the unrestricted gas passages allow spray towers to handle relatively large quantities of solids in the scrubbing solutions with proper nozzle selection.

Disadvantages of spray towers are limited number of contact stages using a single circulating source and difficulty in predicting performance except by experience or plant test. Spray towers also require a scrubbing fluid circulation system and can be susceptible to nozzle pluggage.

4.2.3 Tray and Packed Towers

Scrubbing towers constructed with either packing or trays are good mass transfer devices for the absorption of chlorine. Flows are usually counter-current with the gas entering the bottom of the tower and the scrubbing fluid into the top of the tower, which provides multi-stage contacting. Performance is readily predicted. Packed towers are typically more common than towers with trays due to lower cost and lower pressure drop. Packed towers require good liquid distribution to the top of the tower to assure the complete wetting of the packing, which is required for proper tower performance.

Disadvantages of towers with trays and packed towers are susceptibility to pluggage, moderate to high pressure drop and high costs.

4.2.4 Eductor Type Scrubbers

This device uses a high pressure liquid stream to create a vacuum. This vacuum pulls the chlorine vent stream into the eductor, where intimate contact with the scrubbing fluid takes place. This often eliminates the need for a gas mover. To withstand the corrosive service, plastic and titanium are commonly used to fabricate these devices.

Mass transfer is limited to a single stage per unit, and installations are often multi-staged in series to provide adequate chlorine removal.

4.2.5 Cyclonic Scrubbers

These systems are most useful when the chlorine to be scrubbed contains particulates that must be removed from the gas stream. They are frequently used in series with eductors or venturies and can be economical alternatives to other types of scrubbers.

4.3 CHLORINE MOVERS

The selection of the proper device for transferring chlorine to the scrubber chlorine is highly dependent on the specific system. The design is dependent on the process system pressure, pressure drop through the scrubbing system, vent flows and whether the chlorine is wet or dry.

4.3.1 Process Pressure

Chlorine can be transferred from process equipment to the scrubbing system using its own vapor pressure. Care must be taken to prevent damage to equipment due to low temperatures that occur when the pressure drops.

4.3.2 Eductors (Ejector or Venturi Scrubber)

An eductor is a simple mechanical device with no moving parts. An eductor uses scrubbing fluid to move and entrain the chlorine.

For chlorine service, an eductor must be constructed of materials suitable for wet chlorine service.

4.3.3 Compressors

Where water content of the chlorine is always above 2000 ppm, titanium liquid ring compressors have been used (using water as a seal fluid). Special design expertise is required.

4.3.4 Blowers

The term "blower" is a common industrial term to refer to a single stage centrifugal compressor. Typically, a blower will deliver high volumes at low discharge pressures. FRP or titanium blowers are used in wet chlorine service. Steel or Alloy 20 blowers can be used in dry chlorine service.

4.4 SCRUBBING SOLUTION MOVERS

Scrubbing solutions are generally transferred using a centrifugal pump, but gravity or feed from pressurized tanks can also be considered. Specifics of pump, vessel design and pump seal needs must be engineered for each application. The following are comments on pumping caustic and hypochlorites:

Centrifugal Pumps

For pumping various hypochlorite solutions, the materials of construction of the pump are dependent on the temperature and concentration of the solution. Some non-metallic corrosion resistant materials work well in limited situations. Titanium may be used at any temperature. It is important when using titanium that complete wetting is maintained.

For pumping sodium hydroxide solution (hypochlorite free) to scrubbing systems, all-iron construction is generally suitable; although, nickel and nickel-alloy pumps give longer service life. Above 140°F (60°C), a nickel or nickel-alloy pump should be used.

Differential Pressure

Caustic can be fed to scrubbers from head tanks or pressurized feed tanks. These systems may be particularly useful to assure feed during transient conditions (e.g. during the time required to put a back-up power source into service).

4.5 HEAT EXCHANGERS

It may be desirable to remove the heat of reaction and the heat of solution of the caustic soda for various reasons (e.g. reduced chlorate formation, equipment temperature design limits, etc.). The most commonly used material for heat transfer surfaces is titanium.

4.6 STORAGE AND DECOMPOSITION

Tanks for storage of scrubbing solutions and/or decomposition of spent scrubbing solutions may vary according to the reasons for end use (i.e. sale of the hypochlorite by-product or decomposition). If the solution is to be sold, the fluid is usually cooled during scrubbing and may be stored as a cool, hypochlorite solution in lined, steel tanks or polyethylene and vinyl ester fiber-glass-reinforced plastic tanks. Linings that may be economically used include chlorobutyl and ethylene propylene rubbers and polyvinyl chloride.

Decomposition tanks usually handle solutions at elevated temperatures; therefore, they are in extremely aggressive service. At the higher temperatures, titanium, brick-lined steel and in some cases rubber-lined steel are the materials of choice.

4.7 CONTROLS

The type and amount of instrumentation required is dictated by the type of scrubbing system chosen, the conditions of the installation and the degree of automation desired.

In general, the key to successful control is the availability of operating condition information. The designer should evaluate the need for instrumentation in the following areas:

- chlorine gas detectors (near the outlet of scrubber vent stacks, in scrubber process area, perimeter monitoring)
- pressures (pumping solutions, chlorine process and some relief headers)
- temperature (scrubbing liquids)
- scrubbing liquid end-point indicator (oxidation/reduction potential)
- level (storage and reaction tanks)
- flow (scrubbing liquids)

CAUTION: pH is not an accurate indicator of reaction progress. Although stand alone oxidation/reduction potential is a useful indicator of reaction progress and reaction endpoints, it should be backed up by a second on-line unit or periodic on-line analysis of the scrubbing fluid.

- Alarms should be considered to alert personnel to potential or actual abnormal performance.
- Stand-by electrical power supply should be considered.
- Start-up or shutdown can be automatic or manual, local or remote, as the needs and design of the situation dictate.
- Housing for instrumentation should conform to NEMA 4X standards as a minimum to ensure proper corrosion protection. Review all local regulations.

4.8 ANALYSIS

From time to time, the analysis of the scrubbing solution is recommended to ensure that the solution is at sufficient strength and can handle the amount of chlorine release for which the system is designed. Analysis of solution strengths are determined normally by titration. Care should be taken to differentiate carbonate alkalinity from caustic alkalinity.

Analysis frequency should be set consistent with remaining scrubbing system reliability.

4.9 RELIABILITY

Regardless of the type of scrubber design or configuration, the system reliability is a necessary component in order to successfully contain and treat gaseous effluents. As pointed out in Sec. 4.7 the exact type of instrumentation can vary depending on the type of scrubber but here are some questions to consider:

- How will the scrubber system detect when chlorine is coming to it?
- What will the response be to the detection of chlorine coming to it?
 - Automatic controls
 - Operator manual action
- What would the impact be if the scrubber system failed to detect chlorine coming
 to it or automatic controls fail to act? Is manual intervention sufficient to mitigate
 the event? If not then some of the following features should be considered:
 - The use of redundant instrumentation. This may include additional devices to detect chlorine coming to the scrubber as well as secondary control systems to supply scrubbing fluid

- Reliable scrubbing fluid supply/delivery. Passive systems and/or stand-by electrical power supply should be considered. Possibly even secondary sources of scrubbing fluid.
- Periodic analysis of the scrubbing solution as recommended in section 4.8 to assure the scrubbing fluid is of sufficient strength to handle the event.

Detection and response are the elements of the system that must be reliable. The following are actions that can be taken to improve the reliability of the scrubber system:

- Ensure that devices that detect chlorine coming to the scrubber such as flow meters pressure transmitters, analyzers, ORP's, etc. are:
- Calibrated and or checked on a set frequency.
- Not coming off of the same sample system or instrument line if they are intended to be redundant.
- Periodic function testing of the entire system to assure good operation
- While exact details of instrumentation may vary it is important that a couple key design areas be addressed to improve reliability:
 - Whatever scrubbing system is employed, sufficient caustic supply should be available to the scrubber. To this end a minimum of 15 minutes of supply (100% caustic basis) be available as feed to the scrubber.
 - One additional layer of protection should be in place. At least one separate online measurement (Stack Cl₂, area monitor, pressure, temp., flow etc.) linked with a corrective action such as (secondary scrubber, Cl₂ shutoff, additional alkalinity source, etc) should be part of every scrubber system in addition to the primary method of control.

5. REFERENCES

- 5.1 INSTITUTE PUBLICATIONS
- 5.1.1 *Chlorine Manual*, ed. 6; Pamphlet 1; The Chlorine Institute: Arlington, VA, **1997**.
- 5.1.2 *Piping Systems for Dry Chlorine*, ed. 15; Pamphlet 6; The Chlorine Institute: Arlington, VA, **2005**.
- 5.1.3 *Chlorine Pipelines*, ed. 5; Pamphlet 60; The Chlorine Institute: Arlington, VA, **2001**.
- 5.1.4 Emergency Shut-Off Systems Bulk Transfer of Chlorine, ed. 4; Pamphlet 57; The Chlorine Institute: Arlington, VA, **2003**.
- 5.1.5 Recommended Practices for Handling Chlorine Tank Cars, ed. 3; Pamphlet 66; The Chlorine Institute: Arlington, VA, **2001**.
- 5.1.6 Recommendations to Chlor-Alkali Manufacturing Facilities for the Prevention of Chlorine Releases, ed. 4; Pamphlet 86; The Chlorine Institute: Arlington, VA, **2001**.
- 5.1.7 Explosive Properties of Gaseous Mixtures Containing Hydrogen and Chlorine, ed. 2; Pamphlet 121; The Chlorine Institute: Arlington, VA, **1992**.
- 5.1.8 Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic): Storage Equipment and Piping Systems, ed. 2; Pamphlet 94; The Chlorine Institute: Arlington, VA, **2001**.
- 5.1.9 *Dry Chlorine: Definitions and Analytical Issues*, ed. 3: Pamphlet 100; The Chlorine Institute: Arlington, VA, **2002.**

APPENDIX A

CALCULATION PROCEDURE FOR A CHLORINE ABSORPTION UNIT

1. INTRODUCTION

The purpose of this appendix is to amplify the design principles of Section 4 as they apply to a typical absorption unit. It is written on the assumption that the absorbent selected is a solution (e.g., sodium hydroxide solution) rather than a slurry; certain other design principles have to be taken into account if it is anticipated that solids will be present in the absorbent.

2. SPECIFICATION OF DEMAND ON ABSORPTION UNIT

To begin the design of an absorption unit, it is necessary to specify the following quantities:

- Maximum gas flowrate and total quantity of chlorine
- Total time period for which the flow occurs
- Gas composition
- Gas temperature
- Maximum allowable chlorine concentration in absorber outlet
- Any limitation on pressure drop through absorber

It is usually assumed that the venting system has been designed to ensure that no liquid chlorine will reach the absorption system from the emission source.

3. DESCRIPTION OF UNIT

The absorption unit is assumed to consist of a random-packed tower, with the gas and the absorbent in counter-current flow. An inventory of absorbent, adequate for the total absorption duty, is held in a circulation tank below the tower, and the absorbent continuously circulated to the tower by a pump via a water-cooled heat exchanger. The gas flow enters at the base of the tower, and any inerts are vented to atmosphere from the top. Depending on the pressure of the source from which the gas is assumed to arise, it may or may not be necessary to install a fan after the absorber to vent any inerts to atmosphere.

4. SIZING OF EQUIPMENT

As for any design exercise, it is necessary to select equipment sizes and process conditions that simultaneously satisfying all the various design requirements. This implies that there may be more than one possible step-wise method of sequentially calculating the required sizes and conditions. It also implies that for any step-wise method chosen it may not be possible to go through the design sequence in a single pass; checking that the values selected or calculated at each stage meet all design requirements will be necessary, with possibly recycle to an earlier stage of the procedure if certain requirements are not met.

The step-wise method of sizing the absorption unit illustrated here is therefore not necessarily the only method that may be used.

Step 1 – Select Tower Packing

This is usually done on the basis of previous experience. It is necessary to ensure that the packing diameter selected is not too great a fraction of the tower internal diameter, and this requirement will have to be verified at a later stage of the calculation when the tower diameter has been calculated.

Step 2 – Select Wetting Rule

The value chosen will have to be greater than some minimum to ensure that the packing is fully wetted by the absorbent. It will also have to be sufficient to ensure that the total absorbent flow in the tower is adequate to absorb the flow of chlorine in the incoming gas without giving too great a temperature at the tower base, which will have to be calculated at a later stage.

In practice, the need to fulfill the second criterion of absorbent flow to chlorine inlet flow without an uneconomically large tower diameter is likely to be the more important in determining packing wetting rate. However typical wetting rates necessary to ensure full wetting of the packing may be found in literature¹.

Step 3 – Select Percentage of Flooding at Which the System will Operate

The value selected will again be on the basis of previous experience. It will need to be less than, for example 60%, to ensure that flooding does not occur in operation.

Step 4 – Calculate Tower Internal Diameter

The superficial gas velocity equivalent to flooding conditions may now be calculated from packed tower flooding correlations², using the selected wetting rate and gas and liquid physical properties. From this flooding velocity and the percentage of flooding selected at step three, it is possible to calculate the actual gas velocity and hence, given the total gas flow, the tower internal diameter.

The ratio of tower diameter to packing diameter can now be checked to ensure that it is not less than some minimum value below which excessive liquid channeling at the tower walls could occur; a minimum ratio of 8 is usually taken³. If, at this point in the calculation, the ratio is found to be too low, a new smaller value of packing diameter must be selected and the design reworked from stage I.

Step 5 – Check Absorbent Flow in the Tower

Check that the liquid absorbent flow is at least equal or larger than the stoechiometric value related to the quantity of chlorine to be absorbed.

<u>Step 6 – Temperature Rise of Absorbent in the Tower</u>

It is now possible to calculate the temperature rise in the tower due to the heat of the absorption reaction. This figure must be such that the temperature leaving the tower does

¹ Kister, H.Z., Distillation Design, McGraw-Hill, page 514

² Perry, R.H. & Green, D.W., Chemical Engineers', Handbook 6th, 1984, McGraw-Hill, page 18-22

³ Perry, R.H. & Green, D.W., Chemical Engineers', Handbook 6th, 1984, McGraw-Hill, page 18-28

not exceed the value at which damage to the tower, the packing or its ancillary equipment will occur. If this figure is exceeded, it will be necessary to increase the absorbent flow in the tower by selecting a new value of either the wetting rate of the packing or the percentage flooding and repeating the calculation from the appropriate point.

Step 7 – Select Absorbent Inventory

The inventory of absorbent to be available in the absorption unit must be adequate to absorb the total quantity of chlorine defined previously. It is also necessary to ensure that during the final stages of the absorption, there is sufficient absorption capacity remaining so that the concentrations at top and bottom of the absorption tower are adequate within the height of packing (see later) to give the necessary mass transfer from gas to liquid. At the present stage it is probably adequate to use a value of the absorbent inventory equal to the stoichiometric equivalent of the total chlorine to be absorbed plus an excess based on previous experience.

Step 8 – Calculate Absorbent Concentration at End of Absorption

It is now possible to calculate the absorbent concentration entering the absorption tower during the final stages of the absorption from the inventory estimated in the previous step of the calculation and the total quantity of chlorine in the tower and the chlorine flowrate. It is also possible to calculate the absorbent exit concentration at the same point in time.

It should also be checked at this stage for absorbents such as sodium hydroxide solution in the presence of carbon dioxide in the gas that the absorbent concentrations at the end of the absorption do not exceed the liquid solubility of eg. sodium carbonate. If such solubility is exceeded, it will be necessary to assume a weaker absorbent concentration in the initial inventory and rework the calculation accordingly.

Step 9 – Calculate Height of Packing

Using mass transfer correlation for random-packed absorbers⁴ the height of packing to achieve the required chlorine concentration in the vent from the absorber may now be calculated. Since the result of this calculation will depend at least in part on the inventory of absorbent, it is usually worth repeating the calculation for several different values of the inventory to see which combination of assumed inventory and calculated packing height gives the minimum capital cost for the unit. Some optimization may also be desirable between packing height and the liquid flow in the tower, since this latter quantity will in part determine the absorbent outlet concentration and hence the driving force for mass transfer at the tower bottom. As indicated in Step 6 above the liquid flow in the tower may be altered by selecting new values of the packing liquid wetting rate or the percentage flooding, and reworking the calculation from the appropriate point.

⁴ Perry, R.H. & Green, D.W., Chemical Engineers', Handbook 7th, 1997, McGraw-Hill, page 14-18 Semmelbauer, R., Chem. Eng. Sci., 1967, 22, page 1237-1255.
Onda, K., Journal of Chem. Eng. Jap., 1 (1), 56, 19
Onda, K., Mem. Fac. Eng. Nagoya University, 24 (2), 165, 1972

APPENDIX B

ALTERNATIVE SCRUBBING MEDIA

Many materials have properties which make them useful for chlorine scrubbing systems in special applications. The following is a listing of some known chemicals. Others may be in use.

B.1 Alkalis

The main differences are due to heats of reaction, solubilities of components and by-products formed.

B. 2 Oxidizing Agents

Oxidizing agents such as sodium sulfite, sodium thiosulfite and hydrogen peroxide typically are used for small and specialized applications.

B.3 Solvents

Solvents such as carbon tetrachloride, ferrous chloride, water, sulfur based compounds and organic solvents have also been used in certain situations. These fluids may warrant significant design and operational input to account for flammability, toxicity, environmental constraints and variations in physical and chemical properties.

B. 4 Solid Adsorbents

Solids of various types have significant adsorption/reaction potential for chlorine. Consideration should be given to disposal or regeneration of spent solids.

APPENDIX C

TYPICAL MATERIALS USED FOR SCRUBBING SYSTEMS

Component	Service	Typical Materials	Limitations
Piping	Dry chlorine gas	Carbon steel, other metals	See Pamphlet 6
		Plastics	See Pamphlet 6. Limited to manufacturer's recommendations for pressure and temperature.
	Wet chlorine gas	PTFE, PVDF, ABS, PVC, CPVC, PFA and others Alone or as liners	Limited to manufacturer's recommendations for pressure and temperature.
		FRP	Requires a thick inner corrosion barrier and a resin specifically recommended by the producer of that resin as suitable for chlorine.
		Titanium	Alloys are available to prevent crevice corrosion problems created by pH and temperature effects.
	Caustic soda solution	Carbon steel, stainless steel, nickel	See Pamphlet 94
		PP, PP-lined steel	Limited to manufacturer's recommendations for pressure and temperature.
	Hypochlorite solution	Titanium	Alloys are available to prevent crevice corrosion problems created by pH and temperature effects.
		Steel lined with PTFE, FEP, PFA and PPL	Limited to manufacturer's recommendations for pressure and temperature.
		CPVC	Limited to manufacturer's recommendations for pressure and temperature.
		PVC-lined FRP	Limited to manufacturer's recommendations for pressure and temperature.
		FRP	Requires a thick inner corrosion barrier with a synthic veil and a resin specifically recommended by the producer of that resin as suitable for hypochlorite solution.
Reaction vessel	Hypochlorite solution & Chlorine (wet or dry)	PVC-lined FRP	Limited to manufacturer's recommendations for pressure and temperature.
		Titanium	Same as for piping (wet gas only) - see Section 4.4

Component	Service	Typical Materials	Limitations
		Semag®-lined	For solution pH greater than 8
		Rubber-lined steel	For maximum temperature of 200°F (94°C)
		FRP	Same as for piping
Storage tanks	Caustic soda solution	Carbon steel	See Pamphlet 94. See Section 6.1.6
	Hypochlorite solution	Rubber-lined steel	Limited to manufacturer's recommendations for pressure and temperature.
		PVC-lined steel	Limited to manufacturer's recommendations for pressure and temperature.
		PVC-lined FRP	Limited to manufacturer's recommendations for pressure and temperature.
		Semag®-lined	For pH greater than 8
		FRP	Requires a thick inner corrosion barrier with synthic veil and a resin specifically recommended by the producer of that resin as suitable for sodium hypochlorite.
		Titanium	Same as for piping
Mechanical Equip	ment		
Heat	Hypochlorite solution	Titanium	Process side
Exchangers	Caustic solution	Nickel	Process side
		Stainless Steel	See Pamphlet 94
Pumps	Hypochlorite solution	Titanium, PTFE-lined	
	Caustic solution	Nickel, Alloy 20, Carbon steel	See Pamphlet 94
Blowers	Wet chlorine gas	Titanium, FRP	
	Dry chlorine gas	Carbon steel	
Valves	Hypochlorite solution and wet chlorine gas	Liners of PTFE, PFA, or ECTFE, CPVC, PVC	Limited to manufacturer's recommendations for pressure and temperature.
	Dry chlorine gas	Carbon steel, other metals	See Pamphlet 6
	Caustic solution	Carbon steel, Nickel alloys, Lined steel	See Pamphlet 94

APPENDIX D

CHECKLIST

This check list is designed to emphasize major topics for someone who has already read and understood the pamphlet. Taking recommendations from this list without understanding related topics can lead to inappropriate conclusions.

Place a check mark (✓) in the appropriate box below:

Yes	No	N/A		
			Do you understand that the scope of this pamphlet is limited	{1.1}
			2. Are the scrubbing reactions known?	{2.2 and 2.3}
			3. Are the heat effects for the reactions known?	{2.5}
			 Have the physical and chemical properties of the scrubbing fluid been considered: 	{2.6.2}
			5. Are overchlorination hazards understood?	{2}
			6. Is the scrubbing process full defined?	{3 and 4.1.1}
			7. Is the caustic content of scrubber solution checked on a periodic basis?	{3.3}
			8. Is the capacity based on a carefully thought out, worst case release scenario?	{3.2}
			9. Have the hazards of trace components been considered?	{3.1}
			10. Has a thermal analysis (including decomposition) been performed?	{3.4}
			11. Is it understood that Graphs 3.1 and 3.2 are for illustrative purposes, with specific conditions?	{3.4}
			12. Are the materials of construction consistent with design and Appendix C?	{4.1.2}
			13. Is contactor choice optimized for the applications?	{4.2}
			14. Has the proper chlorine mover been chosen for the system?	{4.3}
			15. Is titanium appropriately used in the system?	{4.4}

Yes	No	N/A	Is a means for maintaining desired temperature included in process design?	{4.5}
			17. If disposal is planned, have all environmental considerations been defined?	{4.6}

REMINDER:

Users of this checklist should document exceptions to the recommendations contained in this pamphlet.