



CHLORINE SAFETY SCRUBBING SYSTEMS

April 2011

Edition 1

Although chlorine is a hazardous material in terms of reactivity and toxicity it can be handled safely provided that appropriate precautions are observed. For many years, International Associations such as the Chlorine Institute, the Japan Soda Industry Association and Euro Chlor have developed guidelines to assist their members with the safe handling of chlorine.

Risk assessments of certain chlorine containing systems have indicated that installation of scrubbing systems should be one of the considerations for vapour release prevention on safety and environment program.

Installations handling chlorine generate gaseous effluents that need to be treated the appropriate way to avoid chlorine emissions to the environment. Companies do not always have the necessary information available for the implementation of treatment systems that are effective. The World Chlorine Council[®] provides this document to describe common worldwide practices for chlorine safety scrubbing systems and is intended to help facilities located in regions where no technical publications have been issued by a regional trade association. Where such guidance exists, that guidance should be used instead of these generic global recommendations. Along with this document, the WCC has posted the publications from regional WCC members applicable to their specific various regions around the world. See Section 7 of this document for more information.

For cultural, legal and historical reasons it is not possible to have a common detailed document applicable throughout the world. This document focuses on the most important items necessary to safely remove chlorine from gaseous effluents by scrubbing them.

It is highly recommended that all national and local legislation concerning this topic are carefully checked for compliance.

The document can be copied, translated, adapted and used under the sole responsibility of the user.

Suggestions for revision should be directed to the secretariat of WCC.

TABLE OF CONTENTS

1	GENERAL INFORMATION	6
1.1	Scope	6
1.2	Definitions	7
2	CHEMICAL CONSIDERATIONS	8
2.1	Absorption of Chlorine Gas Streams	8
2.1.1	Chlorine in Gas Streams	8
2.1.2	Typical Scrubbing Products	8
2.2	Sodium Hydroxide Utilisation	9
2.2.1	Main Reaction	9
2.2.2	Side Reactions	9
2.2.3	Over-Chlorination	9
2.2.4	Heat of Reaction	10
2.2.5	Water Condensation Heat Load	11
2.2.6	Solubility considerations	11
2.2.6.1	Caustic Soda and Solid Salt Formation	11
2.2.6.2	Caustic Soda & CO ₂	12
2.3	Decomposition of Scrubber By-Products Streams	13
3	PROCESS CONSIDERATIONS	13
3.1	Streams to be absorbed	13
3.2	Characteristics of the Chlorine containing Streams	14
3.3	Collection of Effluents Containing Chlorine	15
3.3.1	Capacity	15
3.3.2	Pressure	15
3.3.3	Sealing	16
3.3.4	Back Flow Prevention	16
3.3.5	Moisture Risk	16
3.3.6	Exceptional Flow Detection	17
3.3.7	Drainage	17
3.3.8	Flexible Connections	18

3.4	Absorption System	18
3.4.1	Capacity/Rate for System Design	18
3.4.2	Capacity	18
3.4.3	Rate	19
3.4.4	Scrubbing Fluid	19
3.4.5	Heat Effects	20
3.5	Considerations for Scrubbing Effluents	21
3.5.1	Gas Discharge	21
3.5.2	Liquid Effluent	21
4	SYSTEM SAFETY CONSIDERATIONS	22
5	SYSTEM DESIGN	23
5.1	General	23
5.1.1	Principles	24
5.1.2	Design Documentation	25
5.1.3	Materials of Construction	26
5.1.4	Safety Study	26
5.2	Contactors	27
5.2.1	Sparge Tanks	27
5.2.2	Foam based absorbers	27
5.2.3	Spray Towers	27
5.2.4	Tray and Packed Towers	28
5.2.5	Eductor Type Scrubbers	28
5.2.6	Cyclonic Scrubbers	28
5.3	Chlorine Movers	28
5.3.1	Process Pressure	28
5.3.2	Eductors (ejectors or Venturi systems)	28
5.3.3	Compressors	29
5.3.4	Blowers	29
5.4	Scrubbing Solution Movers	29
5.5	Heat Exchangers	29
5.6	Storage and Decomposition	30
5.7	Controls	30

5.8	Analysis	31
5.9	Reliability	31
6	LIST OF APPENDICES	32
7	REFERENCE DOCUMENTS	32
7.1	Euro Chlor	32
7.2	Chlorine Institute	33
7.3	Alkali Manufacturers' Association of India	33
7.4	RusChlor	33

1 GENERAL INFORMATION

This information is provided to assist companies involved with the safety scrubbing of **gaseous** effluents containing chlorine; it is not intended for regular bleach production. The principle consists in forcing the chlorine to react with a chemical substance extracting it from the gas flow, preventing discharge of chlorine to the atmosphere during all possible foreseeable situations, including power failure.

It is not intended as a substitute for the relevant national or international regulations. The user should review the National and Local regulations as these can be very different depending on the country.

1.1 Scope

This document intends to provide general guidance and source information for chlorine producers and consumers for the effective containment and treatment of their gaseous chlorine effluents. Emphasis is given to the chlorine absorption in caustic soda solution which is the most common process.

Included in this guideline are:

- Chemical properties of scrubbing and by-product liquids
- Description of potential issues when choosing and operating a scrubber system
- System and process safety ; non interruptible power supply
- Practical design considerations and data

There are many other scrubbing system issues that are NOT addressed in this document, including:

- Determination if a scrubber is needed
- Review of all the applicable codes and regulations, including the personnel exposure limits
- Design considerations for gas collection systems
- Additional documentation that will be required to complete the design
- Conducting a process hazards review
- Review of the impact of the system on the total plant and neighbouring area
- Detailed information on the construction of the scrubbing systems
- Detailed requirements for accessories such as pipework, flanges, joints, nuts, and bolts
- Performing a system reliability assessment including spare parts availability, maintenance, etc.

- Procedures for the initial commissioning of the installation
- The certification process for the equipment.
- Procedures for periodic inspection of the system.
- Developing manuals that support the operation and maintenance of the unit
- Training of the personnel for operations, start-up and maintenance

Important reminder: this document refers only to gaseous effluents and does not deal with special techniques where liquid chlorine is or can be sent to the scrubbing system.

1.2 Definitions

Unless otherwise stated, the following meanings apply (definitions for the material used are in appendix 1):

Caustic soda	Solution of sodium hydroxide (NaOH) in water (caustic potash exists also, based on potassium hydroxide (KOH))
chlorine scrubber	a device for removal of chlorine from a stream via reaction, adsorption or absorption
Chlorine Safety Scrubbing System	A safety installation process specially designed to avoid chlorine emissions to the atmosphere through the collection of chlorine effluents and its removal via reaction, adsorption or absorption
dry air	compressed air with low moisture content; air is typically considered “dry” for chlorine service when it has a dew point of -40°C (-40°F)
dry chlorine	Gaseous chlorine is typically considered “dry” if the moisture content exerts a vapour pressure of 2.0 millimetres of mercury or less; chlorine that does not meet the definition of “dry” will be considered “wet” and will have a moisture content that can cause a rapid corrosion of steel; the term "dry chlorine" is sometimes incorrectly used to describe a dry chlorinating compound (usually calcium hypochlorite or the chlorinated isocyanurates); this is a misuse of the term and is discouraged by the WCC. containing less than 20 mg water per kg gas
Eductor	Sometimes called also ejector or Venturi system, based on Venturi principle to create a depression by increasing a liquid’s velocity with the objective to entrain gas with the liquid
ppm	parts per million (usually expressed in weight)

2 CHEMICAL CONSIDERATIONS

The chlorine safety scrubbing system principle is that the chlorine from the gaseous effluents should be retained in a scrubbing solution. Later on, the resulting solution must receive the correct treatment and final environmentally healthy destination. There are a number of variables to be considered in this chemical process.

2.1 Absorption of Chlorine Gas Streams

2.1.1 Chlorine in Gas Streams

The gaseous chlorinated effluents can be of different sources and chlorine concentrations. They can contain impurities like CO₂ which affect the chemistry. It must also be noted that the water vapour content of the gaseous effluent will influence the thermal balance of the process (condensation).

2.1.2 Typical Scrubbing Products

Liquid chemicals that have been used to scrub chlorine include:

- sodium hydroxide
- potassium hydroxide
- sodium carbonate
- calcium hydroxide
- sodium sulphite
- sodium thiosulphite
- ferrous chloride
- hydrogen peroxide

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.

The information in this document 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 document and have not been addressed. However, selected properties of some of these chemicals can be found in appendix 2.

Note on active carbon absorbers

In specific cases, solid bed chemical adsorbents (activated carbon for example) can be used to remove chlorine from gaseous effluents; they are not detailed in this document for some information can be found in appendix 3.

2.2 Sodium Hydroxide Utilisation**2.2.1 Main Reaction**

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



On a weight basis, one kg (2.2 lbs) of chlorine plus 1.13 kg (2.48 lbs) of sodium hydroxide will produce 1.05 kg (2.31 lbs) of sodium hypochlorite.

2.2.2 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:

**2.2.3 Over-Chlorination**

The importance of excess sodium hydroxide to avoid over-chlorination cannot be overstated. As chlorine is continuously fed to a solution containing no caustic the solution becomes saturated with chlorine (between 0.24 and 2.4 g/l (0.002 and 0.02 pounds/gallon) depending on pH, temperature and ion concentrations). Once the solution is saturated with chlorine, chlorine will start venting from the scrubber. Generally it should be assumed that once the caustic is consumed in the solution, ALL chlorine entering the scrubber will vent from the scrubber.

Additionally, as chlorine continues to feed the chlorine saturated solution the solution pH will decrease via acid generation from the following reactions:



As the pH drops below 11, the following reaction takes place continuing to lower the pH via the formation of additional HCl:



The lack of alkali will then allow the chlorine to pass through the absorption unit without being absorbed.

As the pH drops below 5, the HOCl starts to decompose to HCl via the following reaction:



Once enough HCl is generated, chlorine will be released from the solution via the following reaction:



Once chlorine flow is stopped to the over-chlorinated solution, chlorine will continue to evolve from the solution via the above reaction until enough HCl is consumed to increase the pH above 5.

2.2.4 Heat of Reaction

A very important factor in operation and 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



$$\Delta H_{25} = -1\,463 \text{ kJ/kg} \text{ (-626 Btu/lb) chlorine gas}$$

- Decomposition Reactions of Sodium Hypochlorite



$$\Delta H_{25} = -782 \text{ kJ/kg} \text{ (-336 Btu/lb) hypochlorite decomposed}$$



$$\Delta H_{25} = -435 \text{ kJ/kg} \text{ (-188 Btu/lb) hypochlorite decomposed}$$

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

$$\Delta H_{25} \text{ NaOH} = -473\text{kJ/g}\cdot\text{mole}$$

$$\Delta H_{25} \text{ NaCl} = -407\text{kJ/g}\cdot\text{mole}$$

$$\Delta H_{25} \text{ H}_2\text{O} = -286\text{kJ/g}\cdot\text{mole}$$

$$\Delta H_{25} \text{ NaOCl} = -349\text{kJ/g}\cdot\text{mole}$$

$$\Delta H_{25} \text{ NaClO}_3 = -330\text{kJ/g}\cdot\text{mole}$$

2.2.5 Water Condensation Heat Load

The condensation of the water vapour contained in the gaseous effluent sent to the absorption unit and the progressive dilution of the caustic release significant quantities of heat (see point 3.4.5).

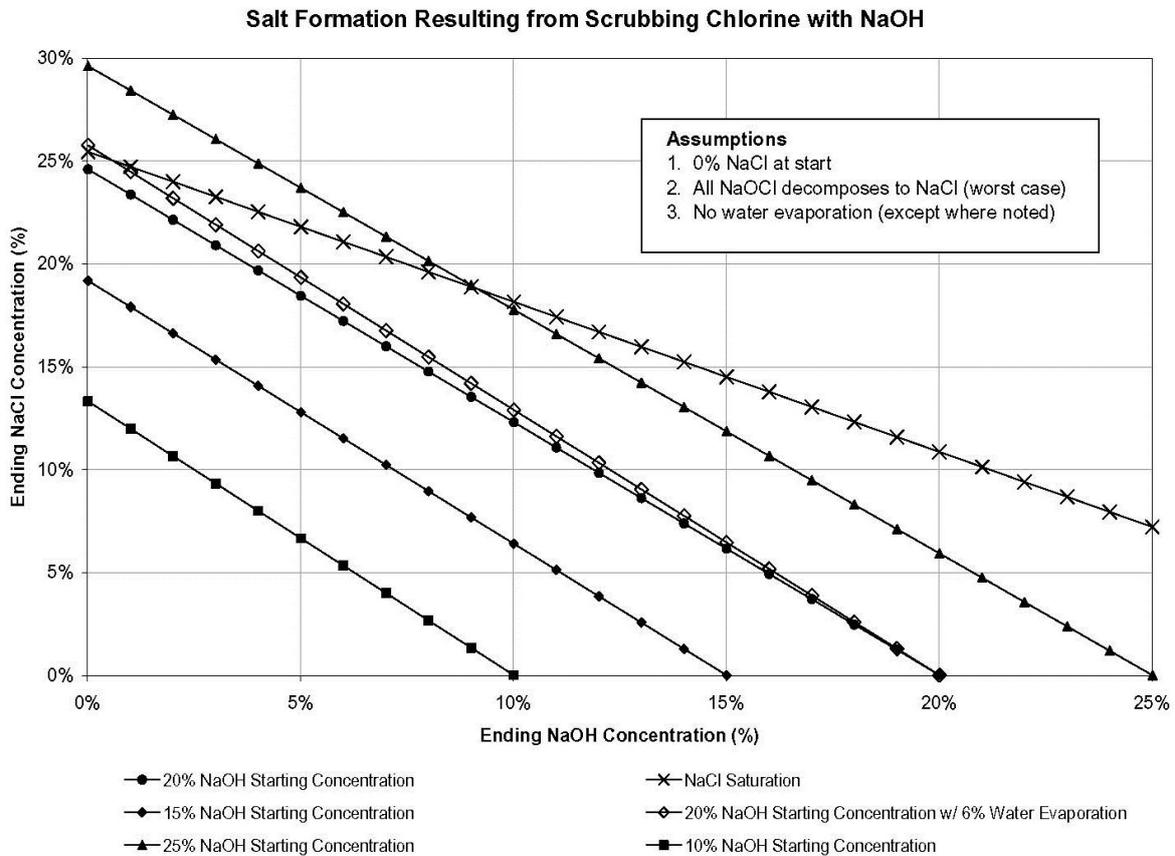
2.2.6 Solubility considerations

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:

2.2.6.1 *Caustic Soda and Solid Salt Formation*

Sodium hydroxide (caustic soda) 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.

If the initial concentration of the caustic is higher than 20% (w/w), the possibility of solid salt precipitation exists when the caustic concentration is fully depleted, and so the reaction should be stopped before consuming all the caustic (see Graph 1 below).



Graph 1: salt formation in chlorine – caustic soda scrubbing

2.2.6.2 Caustic Soda & CO₂

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



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 CO₂ 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.

2.3 Decomposition of Scrubber By-Products Streams

All hypochlorite solutions will decompose with time. 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. These reactions (see 2.2.2.) are auto-accelerating. Higher hypochlorite concentration and low residual caustic also accelerate the decomposition.

- 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.

- Ultraviolet Light

The presence of sunlight (UV) accelerates the decomposition.

- Chemical

Certain chemicals react with hypochlorite solutions. Some of these are sulphur dioxide (SO_2), sulphites (Na_2SO_3 , NaHSO_3), thiosulphite and hydrogen peroxide. The reaction of acids such as hydrochloric acid (HCl) and sulphuric acid (H_2SO_4) with sodium hypochlorite liberates chlorine gas.

3 PROCESS CONSIDERATIONS

Safety scrubber systems must be designed with community/environmental protection and people safety as main goals. All process aspects of both the scrubbing system and systems feeding the scrubber must be fully defined so that the scrubbing system can meet all requirements.

3.1 Streams to be absorbed

The process shall be designed to collect all sources of gas containing chlorine (continuous and intermittent flows). These may arise from a variety of origins and can be made up by:

- Venting of vessels or equipment containing chlorine contaminated liquids (brine, chlorine pipe condensates ...).
- Venting of chlorine on-line analysers.
- Tail gas from chlorine liquefaction unit.
- Vent gas arising from start-up and shutdown of electrolytic plant.

- Emergency depressurisation of chlorine systems.
- Release from relief pressure valves or hydraulic seals.
- Vent gases from chlorine containing systems, such as containers, flexible connections, pipework before maintenance or during loading and off-loading into storage etc.
- In some cases, ventilation air from a building used for handling chlorine.

Particular attention must be paid to the possible combinations of the above mentioned streams, especially for continuous and discontinuous ones.

3.2 Characteristics of the Chlorine containing Streams

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.

In the identification the different modes of operation must be considered: start-up, shutdown, normal operations, maintenance, abnormal operations and emergencies, composition, flow, continuous or intermittent generation, temperature and pressure.

Assurance of fluid state is critical. This guideline deals only with gaseous effluents and protective measures must be included to prevent liquid chlorine from entering the system: if there is a risk of occasional entrainment of liquid chlorine into the system, liquid/gas separators should be installed on the line. These separators should be fitted with a level or low temperature alarm, which will indicate the presence of liquid chlorine in the separator.

From a mass transfer standpoint, pure chlorine is easier to scrub than mixtures of chlorine and inert gases. The presence of inert gas increases the required contact area and increases the amount of water 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 vapour 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 vapour will act as an inert and may reduce efficiency to the point where chlorine absorption is impaired.

The potential for the presence of impurities in the chlorine stream should also be considered. Hydrogen, nitrogen trichloride, hydrogen chloride, organic and other impurities can be present in some chlorine streams. These impurities can concentrate in the scrubbing system to produce potentially dangerous situations (explosive mixtures for example). If necessary, sufficient inert gas must be introduced to remain outside the flammability limits after chlorine absorption.

Impurities in the chlorine can also influence the material selection for the scrubbing system construction.

Presence of trace elements leading to hypochlorite decomposition (like Ni, Fe, Cu, etc) should also be considered.

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

3.3 Collection of Effluents Containing Chlorine

The design of the effluent collection system is very important. Besides the sizing of the system for adequate collection of all effluents, it can include devices which ensure the safe operation of the absorption system and avoid negative effects on its efficiency. This includes the items described here below.

Important remark: it is recommended to avoid mixing these chlorine containing waste gasses with other gaseous effluents if there is a risk the last ones could contain undesirable products that could react with chlorine, reduce the absorption efficiency or damage the absorption equipment (hydrogen, organics ...).

3.3.1 Capacity

The collection network should be of adequate size so that chlorine vented in a section could not lead to an escape from another part.

The design capacity should take the maximum probable gas flow into account, including emergency circumstances (for example when the whole production of the cell room has to be vented for a limited period of time).

The possible flow/pressure surges coming from opening of pressure relief valves or bursting of rupture disks should also be considered and tempered, if necessary by the use of expansion tanks or buffer capacities.

3.3.2 Pressure

The design of the whole system should take into account the maximum and minimum pressures that may occur in the network; it should be gas tight where overpressure is possible.

The usual practice is to create a vacuum to draw the vent gases through the absorption unit. Three different designs may be used:

- a fan in an intermediary position between collecting piping system and absorption unit,
- a fan at the outlet of the absorption unit,
- liquid ejectors.

Hydraulic seals can be installed to protect the collection system and other equipment against excessive under pressure or vacuum (see Figure 2 here below as an example).

Precautions should be taken to ensure continuous water supply and to prevent freezing in cold weather.

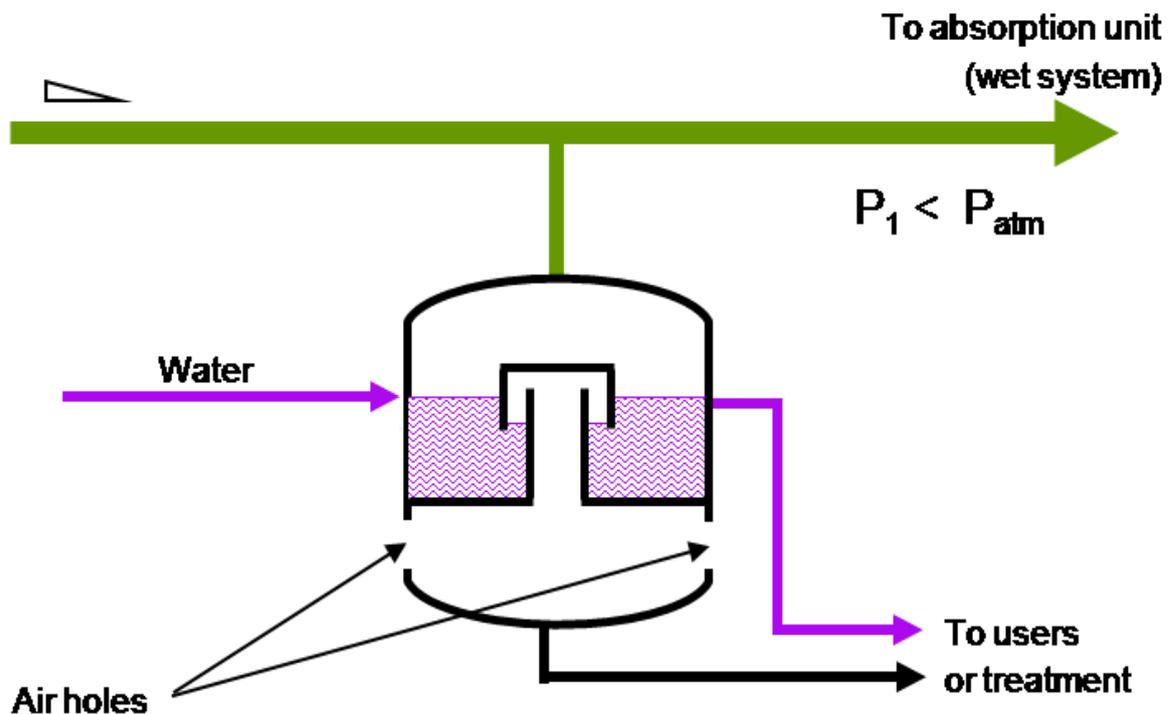


Figure 2: Hydraulic Seal to Prevent Under-pressure

3.3.3 Sealing

Sealing of the gas headers (for example on condensate drains) helps to restrict possible ingress of air from which CO₂ content could result in additional consumption of reagents.

3.3.4 Back Flow Prevention

Measures must be taken to prevent reagent liquid from being sucked back into the chlorine gas system. Typical measures include hydraulic guards, knock out drums etc.

3.3.5 Moisture Risk

The parts of the system intended for dry gas duties should be designed to cope with or protected against all return of moisture from the absorber system. This can be achieved either by a permanent controlled flow of dry purge gas (nitrogen or air) to avoid backflow from diffusion at low gas speed, or by separating dry and wet system by a thin rubberised or PTFE membrane working like a rupture disk (see Figure 3 here below). The dry part of the system can be put under slight pressure with dry inert gas to avoid diffusion through the membrane and allow for detection of its rupture. Any parts of the system where moisture could be present must be constructed from materials which are resistant to wet and dry chlorine.

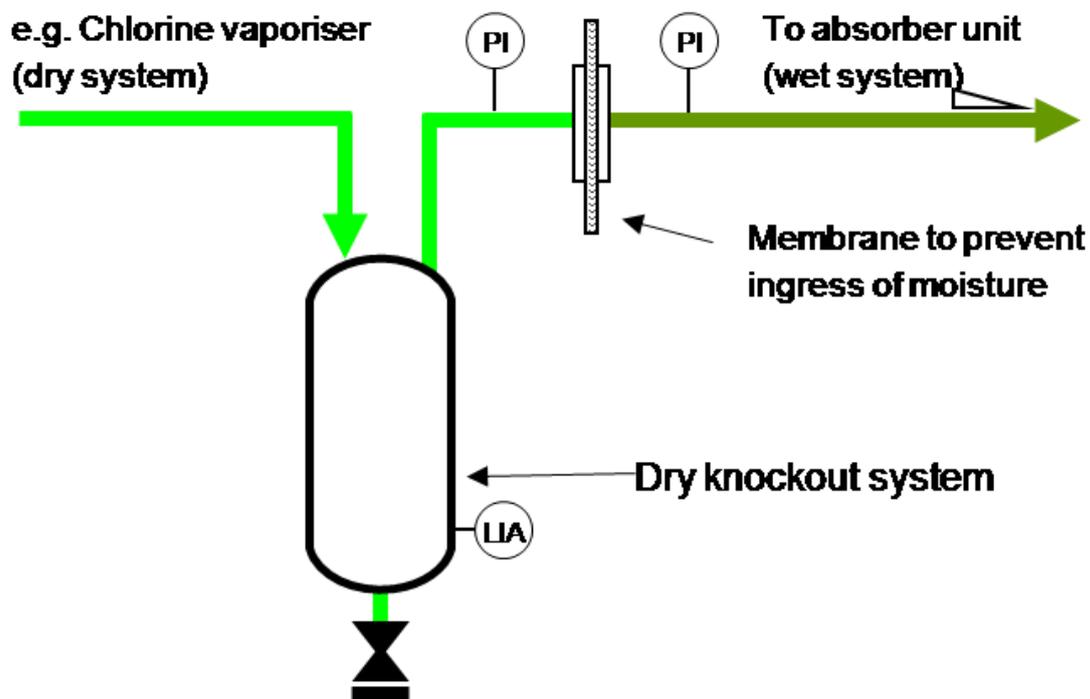


Figure 3: Sealing of Dry/wet Sections by a Membrane

3.3.6 Exceptional Flow Detection

Connection to the vent gas network from exceptional points of emission (for example relief valves) can be designed with a mean to indicate flow. This can be achieved, for example, by the use of a rupture disc upstream of the relief valve, combined with the installation of a pressure gauge with alarm between the rupture disc and the relief valve.

For liquid flow, it can also be achieved by the installation of a level alarm on a hydraulic guard.

3.3.7 Drainage

The presence of any liquids in the low points of the network or the pressure side of a vent fan should be avoided, and the necessary drainage systems installed (see Figure 4 as an example).

Branches should preferably be at the top of the headers.

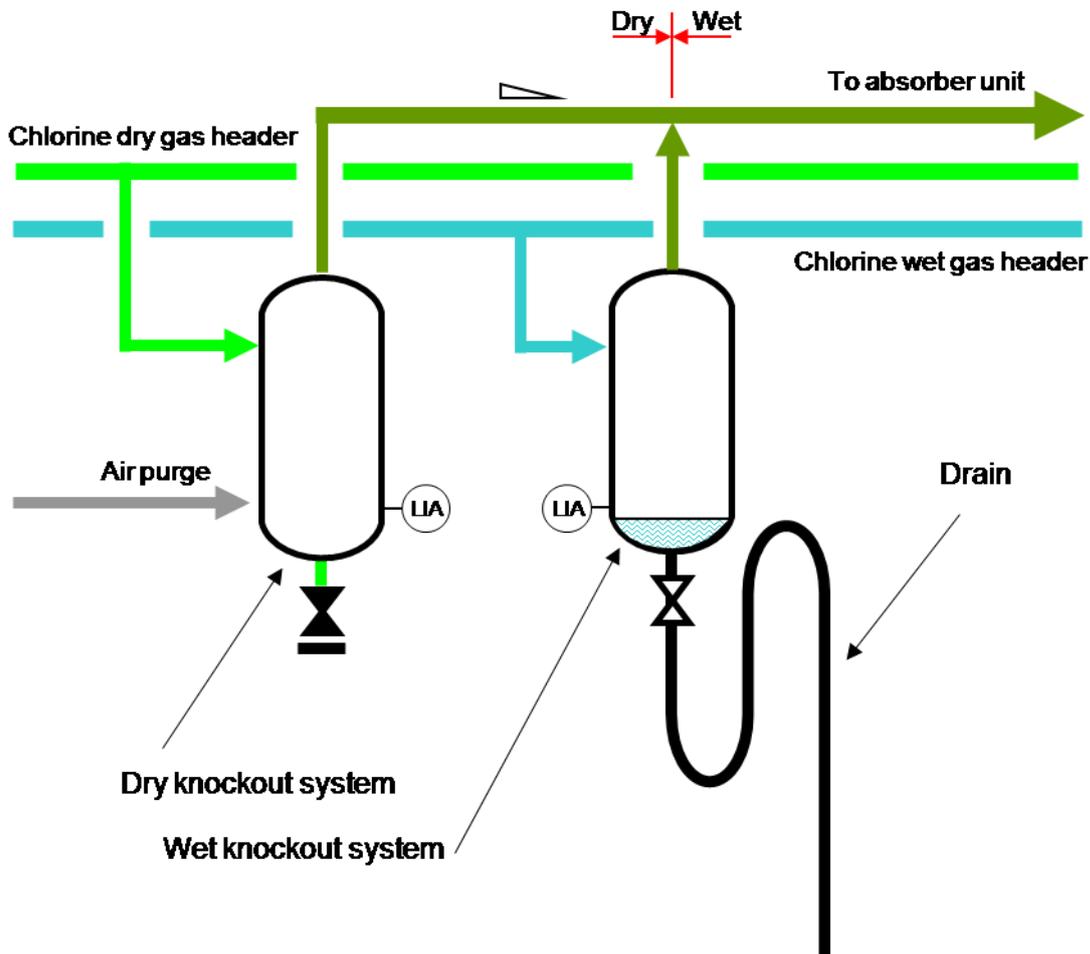


Figure 4: Drain Facilities

3.3.8 Flexible Connections

In any place where chlorine handling could lead to a possible small leak (for example in the loading/off-loading area) flexible hoses can be installed to be rapidly connected to the aspiration of the gaseous effluents network leading to the chlorine safety scrubbing unit.

3.4 Absorption System

3.4.1 Capacity/Rate for System Design

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

3.4.2 Capacity

The design capacity is the quantity of chlorine that can be scrubbed by the total amount of caustic present in the system.

3.4.3 Rate

The rate is the mass of chlorine absorbed per unit of time.

This is usually limited by the sodium hydroxide delivery rate function of flow rate and concentration).

Note: 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 5 000 kg/h (about 10,000 lbs/hr). If 10% excess scrubbing fluid is desired, the design rate (if sodium hydroxide is the scrubbing fluid) should be 5 000 kg/h chlorine x 1.128 (caustic/chlorine molecular weight ratio) x 1.1 (10% excess) = 6 200 kg/h of 100% sodium hydroxide. The design capacity for the scrubber would be 3 hours x 6 200 kg/h or about 19 000 kg (41 000 lbs) of 100% caustic.

3.4.4 Scrubbing Fluid

The scrubbing fluid should be selected on the basis of availability, by-product produced, reactivity with chlorine, solubility of the constituents in the starting and ending scrubbing liquors and susceptibility to freezing; the quantity and quality of the gases to treat should also be taken into consideration.

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

Most of the scrubbers use 18 to 22% 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.

In the presence of CO₂, the concentration of the fresh caustic soda should be reduced or the caustic excess in the final effluent kept higher in order to prevent formation of sodium bicarbonate and carbonate which can precipitate in the 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 (salt) 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 27°C

(80°F) is diluted to 20% with 27°C water, the resulting solution temperature is about 50°C (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.

- Final Concentration

Some excess sodium hydroxide must be maintained at all times. Otherwise, chlorine will not be reacted and will be released. 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. Lower residual sodium hydroxide concentrations can be accepted in well controlled processes.

At concentrations greater than about 5 to 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.

3.4.5 Heat Effects

When scrubbing chlorine with stoichiometric quantities of 15% to 20% caustic, the heat generated could bring the solution to the boiling temperature. The water vapour generated by the boiling solution will then dilute the chlorine and reduces the mass transfer efficiency of the scrubber. 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 is the first obvious choice. If external cooling is not available or impractical, limitation of the temperature increase can also be accomplished by reducing the initial sodium hydroxide concentration or scrubbing with greater excesses of absorbing solution. Dry chlorine scrubbers have lower heat loads than wet chlorine scrubbers (see table below).

This table shows the reaction and water condensation heat load on a hypothetical chlorine scrubber that is reacting with chlorine at an instantaneous rate equivalent to 4 tonnes per hour (9 186 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 (up to 40°C there is practically no decomposition, above this temperature the decomposition starts taking place) and the presence of impurities (like copper, cobalt, chromium, iron and manganese) which can catalyse 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 Heat load on a chlorine scrubber (rounded values) (assuming a feed of 4 t/h)		
Dry chlorine feed		
No decomposition	5 900 MJ/h	5.6 x 10 ⁶ Btu/hr
Decomposition	6 700 MJ/h	6.4 x 10 ⁶ Btu/hr
Wet hot chlorine feed saturated at 90°C (194° F) – 60% volume water (*)		
No decomposition	9 700 MJ/h	9.2 x 10 ⁶ Btu/hr
Decomposition	10 500 MJ/h	10.0 x 10 ⁶ Btu/hr

(*) at atmospheric pressure, saturated above diluted brine (180 g NaCl/kg)

3.5 Considerations for Scrubbing Effluents

3.5.1 Gas Discharge

The final vent gas from the absorber should be discharged into the atmosphere at a high point of the installation. The points of discharge should be well away from any air intake into other operating units or workplaces and it is recommended to monitor the residual chlorine content (detector or analyser).

3.5.2 Liquid Effluent

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

- limits on free chlorine (hypochlorite) concentration in plant or site effluent and/or receiving water, usually requiring destruction of the active 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.

The free chlorine in the liquid effluent can be destroyed by different means (see also point 2.3).

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.

There exists at least one patented technique using reactors with nickel catalyst to destroy the active chlorine in liquid effluents.

In some cases, shallow ponds with exposure to light have been used to decompose weak solutions of hypochlorite.

Chemical destruction is also applied, but sometimes as polishing and small batch reactions to remove remaining traces of sodium hypochlorite. The use of certain chemicals can result in high chemical oxygen demand and discharge permits must be checked accordingly.

CAUTION: in principle acids should normally never be added to hypochlorite, but in some case this technique is used as hypochlorite destruction process; this will then need a detailed engineering and particular attention because chlorine will be evolved and will need to be recovered. If the liquid effluents are discharged to drain, it should be noted that the contact between an effluent containing hypochlorite and acidic or organic material could lead to the formation of chlorine or the risk of explosion. As a consequence one should take all possible measures to avoid the contacting of incompatible effluent streams, such as designing separate sewers.

4 SYSTEM SAFETY CONSIDERATIONS

The chlorine safety scrubber system should always be available and measures should be established to guarantee it can operate when requested.

The definition of safety measures for chlorine safety scrubbing systems should be obtained by risk analysis studies; however it is possible to consider the following aspects.

For systems designed to operate under continuous negative pressure, this condition must be ensured, for example with a fan in operation and a stand-by fan installed (with automatic start-up in case of failure of the one in service); additionally a complete fan (or at least critical parts) should be kept in stock.

The guarantee of a continuous circulation can be accomplished, for example, with a pump in operation and a stand-by pump installed; additionally a spare pump (or at least critical parts) should be kept in stock; there should also be an appropriate quantity of caustic soda solution ready for use in the system.

According to the results of a risk assessment, taking into account the capacity of the installation, a redundant scrubber in series with the one in service may be required to guarantee the safety; this is the case when continuous chlorine containing gas flow is sent to an absorption unit working in batch.

If the system relies on electric power supply, an independent power source shall be installed (for example a diesel generator or DC batteries with an inverter) as back-up; this back-up power supply should feed the gas collection aspiration system, the caustic circulation pumps the key-instruments on the process and local lighting; an automatic switch from the mains to the emergency power source should be foreseen and periodical tests should be performed on the emergency power source and the switching system with written record of such tests. In some cases, depending of the results of the risk assessment, a double back-up system combining two different solutions may be advisable.

The fail safe position of the valves should be correctly designed (open or close) in case of lack of instrument air or instrument power (based on a risk study).

The chlorine absorption system should be kept in operation and controllable even if the plant Emergency Shut Down System (ESD) of the Distributed Control System (DCS) fails.

Some specific spare parts should be available in stock (gauge of analysers for example), according to the probable supply delays.

Due the key safety role of this installation, regular inspection and maintenance by competent personnel is of vital importance, based on written procedures.

5 SYSTEM DESIGN

5.1 General

The absorption unit should be designed so that, under most stringent conditions, chlorine concentrations should not exceed acceptable levels at the outlet of the system.

The primary function of a chlorine safety scrubbing system is to contact chlorine with a scrubbing fluid removing it from the gas phase.

Depending on the characteristics of the stream to be absorbed, there are various options to select from when basic design choices are made.

The selection of a continuous system over a batch unit will impact the method used for transporting the fluids and the method for bringing them in contact.

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, and passive systems should be considered.

Sections 5.2 thru 5.9 give guidance to the designer relative to the selection of system components and other operational considerations.

5.1.1 Principles

The design of the absorption unit should be based on a risk assessment study to avoid discharge of chlorine to the atmosphere during all possible situations including the case of power failure. The basic elements to consider are:

- Maximum instantaneous gas flow
- Composition of the gas stream
- Maximum quantity of chlorine to be absorbed in emergency condition

The chlorine content of the gas discharge from the unit should be monitored. The design should ensure that during routine operation this figure is less than 3 mg/m³.

Note: concentrated chlorine vents from vessels and gas pressure balance lines from storage systems etc. will normally be recycled back to the process or sent to the user plant, whenever possible.

The absorption installation can be based on one of the following techniques:

- Packed column system with recirculation of liquors;
- Liquid ejector or Venturi scrubber.
- Spraying tower with recirculation of liquors;
- Sparge pipe immersed into a tank filled with reagent;

In general, the differences between the systems can be characterised as follows:

- Packed columns should be operated in the range of temperature/concentration/composition where solid deposition will not occur (for indication of the principle, see appendix 4). Such a device has the advantage of larger caustic retention volume useful to absorb peaks of high chlorine contents and also to present a high efficiency. Packed columns use relatively low liquid rates compared to ejectors.
- An ejector system has a simple construction as only one pump is needed for caustic transport and gas suction; it remains effective at low and high chlorine concentration in the vent gases and is less sensitive for salt deposition, but could be more sensitive to erosion; it has a high power consumption and the design is mainly based on experience. This configuration may need to be backed-up by a packed column to guarantee low concentrations of chlorine in the off-gases; ejectors are normally more suited to absorb high chlorine concentration and high flowrates.
- Spraying tower is not recommended in general, because of limited efficiency and difficulty to guarantee low chlorine concentration in the off-gases, except with a conservative and well documented design and with periodic inspection.
- Sparge tank system is delicate in design because of the risk of breakthrough of chlorine and back suction of caustic. It is not often used and only as part of an emergency system (not for normal treatment of vent

gases) because of inability to guarantee low concentrations of chlorine in the off-gases.

Remarks:

- Safety absorption units will be designed to handle chlorine gas, usually close to atmospheric pressures, and not liquid. Where some liquid chlorine can be present in the vent (e.g. relief devices), a knock out drum (see also point 3.3.4) fitted with suitable means of detecting liquid (temperature, level) should be installed in the line to trap any liquid chlorine before it can reach the absorption unit. This chlorine can then be allowed to vaporise to the absorption unit at an acceptable rate.
- It is possible to use a combination of these different systems in series, such as ejector and packed column as mentioned earlier, to improve the overall performances and guarantee limited chlorine concentration in the off-gases (see example in appendix 5).
- Care will be taken to avoid risk of explosion when the concentration of hydrogen increases due to absorption of the chlorine; additional injection of air can help to reduce the hydrogen concentration below the flammability limit.
- Except for ejectors, suction fans are used where chlorine is not delivered to the system by its own pressure.
- To protect it against possible small leaks of absorption fluid, the flooring of the absorption areas shall be covered with a material resistant to caustic and bleach; the surface will have a slope to collect these possible leaks in an appropriate sewage system for neutralisation.

5.1.2 Design Documentation

- Process Definition

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, minimum and average)
 - pressure, temperature and composition ranges
- Scrubbing fluid make-up
 - average quantities
 - peak/batch quantities
 - concentration and temperature
- Scrubbing fluid flows
 - inlet design rate (flow, composition, temperature)

- outlet design rate (flow, composition, temperature)
- Scrubbing fluid volume
 - start design capacity (volume, composition, temperature)
 - end design capacity (volume, composition, temperature)
- Scrubbed chlorine vent
 - flow (normal, peak, average)
 - pressure, temperature, composition
- System Definition

A detailed piping and instrument diagram (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

A general arrangement plan should be prepared.

5.1.3 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 1.

5.1.4 Safety Study

A HAZOP or equivalent study should be performed to define the most critical case to which the system can be submitted, including power failures, and help in a correct design.

5.2 Contactors

5.2.1 Sparge Tanks

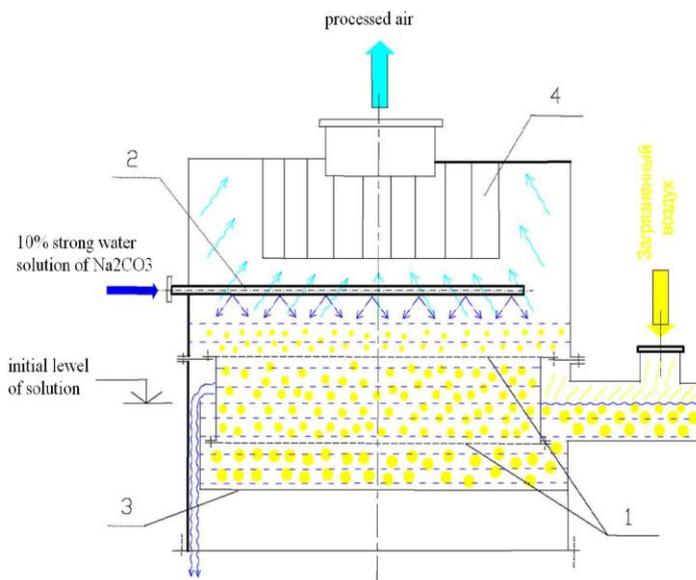
Sparge tanks use pressure to disperse chlorine through a distributor located beneath a sufficient level of scrubbing fluid. They do not depend on circulating systems to bring the scrubbing solution in contact with the chlorine. The system is simple, inexpensive and it has no moving parts.

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 valves, gas purges or break tanks. Check valves are usually ineffective unless they are used in combination with other backflow prevention devices.

5.2.2 Foam based absorbers

A particular case of equipment is represented by the “foam” scrubber used for example in Russia, where the absorbing solution is sent to a system of packed meshes allowing the liquid (usually a sodium carbonate solution) to form foam (high surface contact) together with the chlorine containing gas (see example of drawing here under).



This absorber is installed above the storage tank of carbonate solution which is recirculated to the absorption section.

- 1: the packed meshes
- 2: solution spraying
- 3: bottom return of solution to tank
- 4: liquid trap

Note: the spraying of the absorbing solution can be replaced by a sparge system.

5.2.3 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 solids in the scrubbing solutions provided proper nozzle selection and adequate design and choice of piping, pumps, valves

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 plugging.

5.2.4 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 plugging, moderate to high pressure drop and high costs.

5.2.5 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 specific gas mover.

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

5.2.6 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 Venturi systems.

5.3 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.

5.3.1 Process Pressure

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

5.3.2 Eductors (ejectors or Venturi systems)

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 erosive conditions.

5.3.3 Compressors

Where water content of the chlorine is always above 4000 ppm, titanium liquid ring compressors can be used with water as a seal fluid; particular precaution will be taken to make sure the compressor will not run dry (with titanium-chlorine fire as consequence).

Special design expertise is required.

5.3.4 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.

5.4 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 hypochlorite:

- 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 plastic, nickel and nickel-alloy pumps can also be used. Above 60°C (140°F) 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).

5.5 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.

5.6 Storage and Decomposition

The absorption fluid is usually cooled during scrubbing and may be stored as a cool, hypochlorite solution in lined, steel tanks or plastic tanks with fibre-glass reinforcement. Depending on the temperature, different types of linings may be used, including chlorobutyl and ethylene propylene rubbers and polyvinyl chloride.

Decomposition tanks usually handle solutions at elevated temperatures; therefore, they are in extremely aggressive service. At temperatures above 60°C (140°F), titanium, brick-lined steel and in some cases rubber-lined steel are the materials of choice.

5.7 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.

As a minimum, it is recommended to have the following instrumentation:

- Chlorine gas detectors at the outlet of the scrubber vent stacks;
- Temperature monitoring of the scrubbing liquids;
- Low flow alarm on the scrubbing fluid.

Additionally, the designer should evaluate the need for instrumentation in the following areas:

- Chlorine gas detectors in scrubber process area as perimeter monitoring;
- Pressures (pumping solutions, chlorine process and some relief headers);
- Scrubbing liquid end-point indicator (oxidation/reduction potential);
- Level (storage and reaction tanks);
- Flow measurement (scrubbing liquid).

CAUTION:

- pH is not an indicator of reaction progress.
- Oxidation/reduction potential is a useful indicator of reaction progress and reaction endpoints but it should be backed up by a second on-line unit or periodic on-line analysis of the scrubbing fluid.
- Stand-by electrical power supply should be considered.
- To guarantee the efficiency of the installation, it is important to maintain good conditions and ensure periodic calibration of the critical instruments.

5.8 Analysis

Periodic analysis (usually by titration) of the scrubbing solution is recommended to ensure that the solution is at sufficient strength (alkalinity) and can handle the amount of chlorine release for which the system is designed. Care should be taken to differentiate carbonate alkalinity from caustic alkalinity.

Analysis frequency should be determined to ensure the correct functioning of the absorption process at any time.

5.9 Reliability

A safety study has to be performed to ensure sufficient reliability of the system.

Typically, the following questions have to be considered:

- Does the scrubber system need to detect when chlorine is coming to it? How can this be performed?
- Will it respond automatically or via an operator manual action?
- What would the impact be if the scrubber system fails 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.

The following actions 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, oxidation-reduction potential meters, 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 independent
- Test periodically the entire system to assure good operation

While exact details of preventing over-chlorination may vary it is important that several design areas be addressed to improve reliability:

- Whatever scrubbing system is employed, sufficient caustic should always be available to neutralize chlorine. A minimum amount of caustic should always be available based on the time required to safely stop chlorine flow to the scrubber in an upset situation.

- For all chlorine scrubbing systems and bleach manufacturing systems at least one online measurement (vent gas analysis for chlorine, caustic supply pressure for spray tower or eductor, caustic temperature, caustic concentration, etc.) must continuously monitor the effectiveness/ability of the system to neutralize/consume chlorine. If problems are detected chlorine flow should be stopped or additional caustic should be sent to the system.
- For all sparge tank style chlorine scrubbing systems or bleach manufacturing systems chlorine releases to the atmosphere must be prevented. Regardless of the system (sparge tank style chlorine scrubbing systems or bleach manufacturing systems) proper layers of protection should be in place (based on a risk analysis) to prevent over-chlorination and a chlorine release to the atmosphere. Special consideration should be given to containing and routing the vents from devices that regularly operate at low caustic levels to a scrubbing system that meets the requirements of this document.

This list is not exhaustive and need to be completed according to the specific design of the unit, but a check list is proposed anyway in appendix 6 to assist users verifying the compliance with this document,

6 LIST OF APPENDICES

Appendix 1: Typical Materials used for Scrubbing Systems

Appendix 2: Alternative Scrubbing Media

Appendix 3: Active carbon absorbers

Appendix 4: Calculation Procedure for a Chlorine Absorption Unit

Appendix 5: Example of Combined Chlorine Absorption System

Appendix 6: Check-List

7 REFERENCE DOCUMENTS

7.1 Euro Chlor

GEST 76/52, Equipment for the Treatment of Gaseous Effluent Containing Chlorine

GEST 79/82 - Materials of Construction for Use in Contact with Chlorine

7.2 Chlorine Institute

Pamphlet 6, Piping Systems for Dry Chlorine

Pamphlet 89, Chlorine Scrubbing systems

Pamphlet 94, Sodium Hydroxide Solution and Potassium Hydroxide Solution (Caustic) Storage Equipment and Piping Systems

7.3 Alkali Manufacturers' Association of India

Technical Data Book on Chlor-Alkali Industry, chap. 5

7.4 RusChlor

Safety Rules for the Safe Production, Storing, Transportation, and Use of Chlorine, approved by the Federal Committee for Mining and Industrial Supervision (Rostekhnadzor) with number PB 09-594-03 (available only in Russian)

APPENDIX 1: TYPICAL MATERIALS FOR CHLORINE SCRUBBING SYSTEMS

Component	Service	Typical Materials	Limitations
Piping	Dry chlorine gas	Carbon steel, other metals	Chlorine has a low atmospheric boiling point, and its vapour pressure rises rapidly with increasing temperature. It is important to select materials that have adequate strength and maintain ductility at low temperature.
		Plastics	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	Caustic soda is a hazardous material and piping systems should be designed carefully. Material selection must be based on expected service temperatures, pressures, and concentrations.
		PP, PP-lined steel	Limited to manufacturer's recommendations for pressure and temperature.

Component	Service	Typical Materials	Limitations
	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 synthetic 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)
		Semag®-lined	For solution pH greater than 8
		Rubber-lined steel	For maximum temperature of 94°C (200°F); the type of rubber should be selected after field tests
		FRP	Same as for piping
Storage tanks	Caustic soda solution	Carbon steel	Material selection must be based on expected service temperatures, pressures, and concentrations

Component	Service	Typical Materials	Limitations
	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 (polyethylene or vinyl ester)	Requires a thick inner corrosion barrier with synthetic veil and a resin specifically recommended by the producer of that resin as suitable for sodium hypochlorite.
		Titanium	Same as for piping
Mechanical Equipment			
Heat Exchangers	Hypochlorite solution	Titanium	Process side
	Caustic solution	Nickel	Process side
		Stainless Steel	Stainless steel plate such as 304 and 316 has been used successfully; however, increased corrosion rates at higher temperatures generally limit the practical upper temperature to 60°C (140°F)
Pumps	Hypochlorite solution	Titanium, PTFE-lined	

Component	Service	Typical Materials	Limitations
	Caustic solution	Nickel, Alloy 20, Carbon steel	Ductile iron pumps or stainless steel have been used for caustic solutions below 50°C (122°F). Alloy 20, nickel or other nickel-alloy pumps provide a longer service life at temperatures above 50° (122°F)
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	Valves for chlorine service require special attention by all associated with the application. Chlorine service valves are highly engineered products and cannot be considered a routine commodity valve application
	Caustic solution	Carbon steel, Nickel alloys, Lined steel	Valves for caustic service requires special attention by all associated with the application

Definition of materials

ABS	acrylonitrile butadiene styrene
carbon steel	a ferrous material compatible with dry chlorine piping, typically used for piping
CPVC	chlorinated polyvinyl chloride
ECTFE	ethylene chlorotrifluoroethylene
EPR	ethylene propylene rubber

FEP	fluorinated ethylene propylene
FRP	a reinforced plastic material made of glass fibre, with a suitable resin (such as polyester, epoxy or vinyl ester) to withstand the corrosive environment of the application
PE	polyethylene
PFA	perfluoroalkoxy
PPL	polypropylene
PTFE	polytetrafluoroethylene
PVC	polyvinyl chloride
PVDF	polyvinylidene fluoride

APPENDIX 2: 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.

ALKALIS

Alternatively to caustic soda, diaphragm cell liquor can be used (but higher risk of salt precipitation).

Lime milk and sodium carbonate are also a possible scrubbing media, but the equipment must be designed to avoid blockage by lime and calcium carbonate precipitate.

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

OXIDISING AGENTS

Oxidising agents such as sodium sulphite, sodium thiosulphate and hydrogen peroxide (in alkali solution) typically are used for small and specialized applications.

SOLVENTS

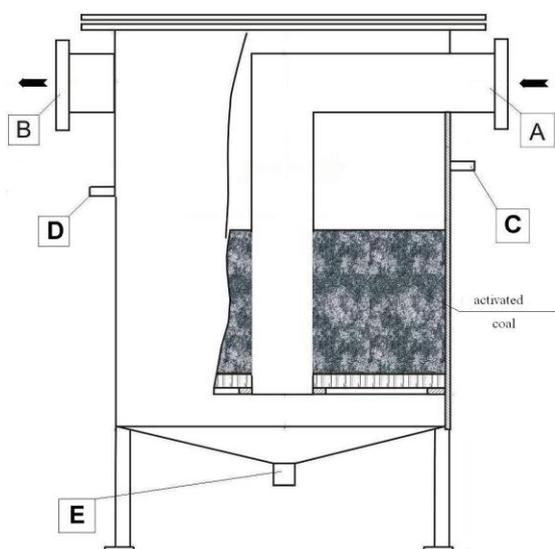
Solvents such as ferrous chloride, water, sulphur-based compounds and organic solvents have also been used in certain situations. These fluids may warrant significant design and operational input to account for flammability, toxicity, environmental constraints and variations in physical and chemical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

Note: solid ab/adsorbents like activated carbon are only used in specific cases, usually with low chlorine concentration, as the reaction is exothermic and could lead to strong temperature increase with potential risk of chlorine-iron fire. Consideration should also be given to the disposal or regeneration of spent solid.

APPENDIX 3: ACTIVE CARBON ABSORBERS

In specific cases, solid bed chemical adsorbents (activated carbon for example) can be used to remove chlorine from gaseous effluents. As absorption of chlorine is exothermic they are designed to treat quite low quantities (usually 50 kg Cl₂ maximum) to avoid the risk of strong temperature increase with the potential risk of chlorine-iron fire.

They usually apply for low chlorine concentration (e.g. on external air supply to control room) or, in some cases, by chlorine customers working with bottles and very small containers. A typical drawing of such a unit is represented here below.



- A. Inlet opening for the gas
- B. Outlet opening for the gas
- C. Overflow outlet for the soda solution
- D. Inlet opening for the soda solution
- E. Drainage of the soda solution

NB: the soda solution is used to remove the chlorine at the end of the absorption batch

Usually 2 beds are placed in parallel, with one in operation and the other one in regeneration or stand by.

The advantages of this technique are:

- Prompt launching
- Not pumps (no caustic fluid in permanence)
- No operability problem outdoors at negative temperatures
- Small size (easy to install or transport)

The disadvantages are:

- Very low absorption capacity
- Progressive destruction of absorbent by caustic soda flushing

See also the presentation made by RusChlor at the WCC stewardship workshop of Brazil (Guarujá) in November 2010 (available on CVn)

APPENDIX 4: CALCULATION PROCEDURE FOR A CHLORINE ABSORPTION UNIT**INTRODUCTION**

The purpose of this appendix is to amplify the design principles of Section 5 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 slurry; certain other design principles have to be taken into account if it is anticipated that solids will be present in the absorbent.

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.

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 inert gasses 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 inert gases to atmosphere.

SIZING OF EQUIPMENT

As for any design exercise, it is necessary to select equipment sizes and process conditions that simultaneously satisfy 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 compared to 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 determined.

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 have also 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 a too high temperature in the tower base, which will have to be calculated at a later stage.

In practice, the need to fulfil the second criterion of absorbent flow related to the chlorine inlet flow without an uneconomically large tower diameter is likely to be more important in determining packing wetting rate. However, typical wetting rate necessary to ensure full wetting of the packing may be found in the literature (for example Kister H.Z., Distillation Design, McGraw-Hill, page 514).

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 typically 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 correlations, using the selected wetting rate and gas / liquid physical properties (Perry R.H. & Green D.W., Chemical Engineers' Handbook, 6th 1984, McGraw-Hill, pages 18-22). From this flooding velocity and the percentage of flooding selected at step 3, 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 channelling at the tower walls could occur; a minimum ratio of 8 is usually taken (Perry R.H. & Green D.W., Chemical Engineers' Handbook, 6th 1984, McGraw-Hill, pages 18-28). If, at this point of 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 the appropriate point.

Step 5 – Check absorbent flow in the tower

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

Step 6 – Temperature rise of absorbent in the tower

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 not exceed the values at which damage to the tower, the packing and the 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 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 step 9) 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, 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.

For absorbents such as sodium hydroxide solution in presence of carbon dioxide in the gas, it should also be checked at this stage that the absorbent do not exceed the solubility limit (sodium carbonate concentration for example) at the end of the absorption. If such limit 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 absorbers the height of packing to achieve the required chlorine concentration in the vent from the absorber may now be calculated (see Perry R.H. & Green D.W., Chemical Engineers' Handbook, 7th 1997, McGraw-Hill, pages 14-18; Semmelbauer R., Chem. Eng. Sci, 1967, pages 1237-1255; Onda K. and all., Journal of Chem. Eng. Jap., 1(1), 52-62, 1968; Onda K., Mem. Fac. Eng. Nagoya University, 24(2), 165, 1972).

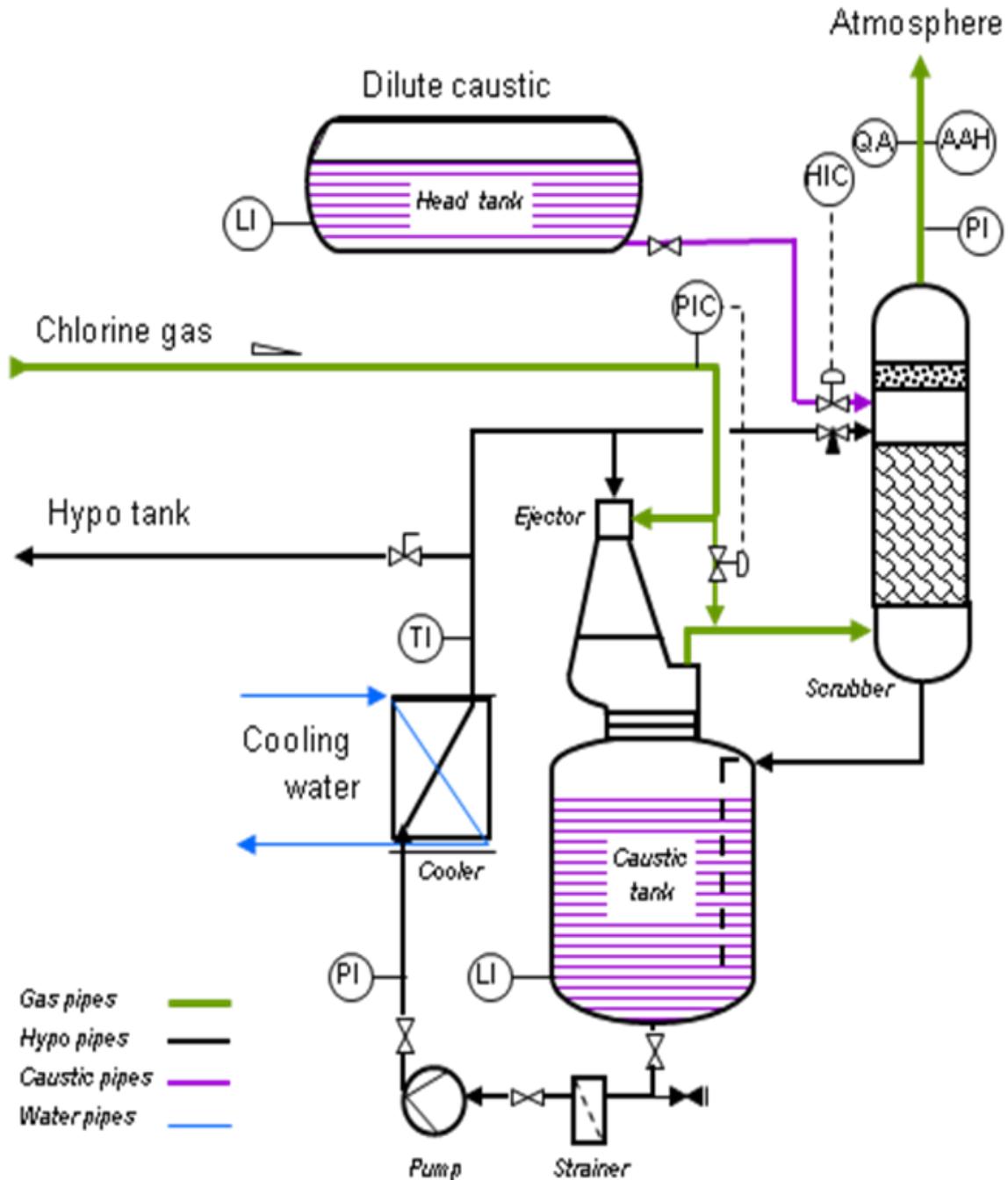
Since the result of this calculation will depend at least in part on the inventory of absorbent, it is usually worth repeating the calculation for several different values of the inventory to see which combination of assumed inventory and calculated packing height gives the minimum capital cost for the unit.

Some optimisation may also be desirable between packing height and liquid flow in the tower, since the 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.

APPENDIX 5: Example of Chlorine Combined Absorption System

This drawing shows an ejector combined with a downstream absorption scrubber.



APPENDIX 6: CHECK-LIST

Sample checklists have been prepared to assist the user of this document in verifying compliance with key aspects of the topic area. These sample checklists were prepared by a regional association member (The Chlorine Institute) of WCC. Not all of the items listed may be applicable to the user's region. The user is encouraged to review the checklists provided and modify them as deemed appropriate for use at the user's site. The check lists should not be considered all-inclusive of the recommendations in this publication. The checklists have been designed to emphasize major topics for someone who has already read and understood the publication. Taking recommendations from such checklists without understanding related topics can lead to inappropriate conclusions.

An example of check-list for chlorine safety absorption system is added on the next page.

Sample Checklist for gaseous chlorinated effluents.

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

Yes	No	N/A	
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Do you understand that the scope of this guideline is limited
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Are the scrubbing reactions known?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Are the heat effects for the reactions known?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Have the physical and chemical properties of the scrubbing fluid been considered:
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Are over-chlorination hazards understood?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is the scrubbing process full defined?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is the caustic content of scrubber solution checked on a periodic basis?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is the capacity based on a carefully thought out, worst case release scenario?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Have the hazards of trace components been considered?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Has a thermal analysis (including decomposition) been performed?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Are the materials of construction consistent with design and Appendix 1?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is contactor choice optimized for the applications?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Has the proper chlorine mover been chosen for the system?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is titanium appropriately used in the system?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	Is a means for maintaining desired temperature included in process design?
<input type="checkbox"/>	<input type="checkbox"/>	<input type="checkbox"/>	If disposal is planned, have all environmental considerations been defined?

N/A = not applicable