

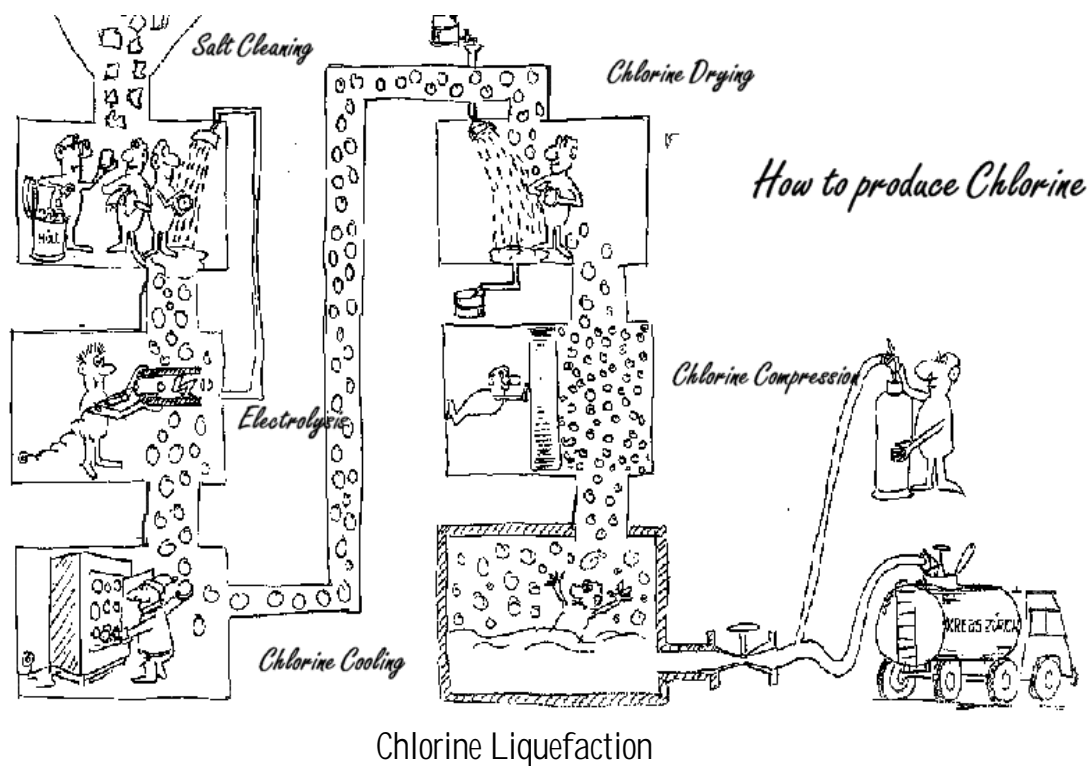
Recent Developments in Chlorine Processing

A summary of developments illustrated on
the chlorine processing units

Prepared for the presentation at TECHNOGERMA

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How to Produce Chlorine ?



How to produce chlorine ?

This illustration opens the door for improvements!!

General

Over the past years, the equipment fabrication industry developed rapidly in parallel with the chemical production industry. New, originally exotic materials of construction have become common and less costly. Their processing is now well consolidated and the limits of their application are established. Likewise, new equipment designs and their application range have been evaluated and are now commercially used.

Worldwide efforts to reduce the use of halogenated hydrocarbon refrigerants in the industry and increasing concern about the safety of chlorine processing facilities have also induced substantial changes in the concept of chlorine processing installations.

The chlorine processing, as illustrated below, integrates the following process units:

- 1) **Cooling and filtration of hot wet chlorine gas**
- 2) **Drying of „pre-dried“ chlorine gas**
- 3) **Scrubbing and cooling of dried chlorine gas, decomposition of NCl_3**
- 4) **Compression of dried chlorine gas**
- 5) **Liquefying of compressed chlorine gas**
- 6) **Storage, transfer and filling**
- 7) **Vaporisation of liquid chlorine**

For the production of dry gaseous or liquid chlorine most downstream process units are required to get an anhydrous, purified product.

This paper describes the technology currently implemented in modern chlorine processing installations with a view on economy as well as the effects of the developments.

Electrolysis

Major developments and improvements have been made in the construction of electrolysis cells and the electrolytic process. The availability of titanium and suitable membranes and other important materials allowed the development of membrane electrolysis cells. Advantages and disadvantages of this technology are

Advantages

- Lower energy consumption
- Lower capital investment
- Production of high purity caustic soda
- Insensitivity to cell load variations and shutdowns
- Low hydrogen content in chlorine

Disadvantages

- Requirement of high purity brine
- High oxygen content in chlorine
- Cost of membranes

The advantage of having very low hydrogen content in chlorine resulted in new developments and considerations of the chlorine liquefaction process.

A typical chlorine gas quality is

- | | | |
|-------------------|------------|--------|
| • Cl ₂ | 97 - 99.5 | vol. % |
| • O ₂ | 0.5 - 2.0 | vol. % |
| • H ₂ | 0.03 - 0.3 | vol. % |

New chloralkali plants are now equipped with either monopolar or bipolar membrane cells. The improvements, principles and construction of these membrane cells are, however, not subject of this paper.

1 Cooling

Basic Requirements

Chlorine cooling is generally designed for continuous cooling, filtration and, if required, boosting of wet chlorine gas generated in the electrolysis cells. The purpose is to lower the water content to the lowest possible value by means of cooling and chilling, to separate and remove brine mist (aerosol) which is carried over from the electrolysis cells and optionally to increase the gas pressure as may required for the downstream plant sections.

Conventional Concept

Most of the older chloralkali plants operating with mercury cells are equipped with packed towers to cool the gas directly by means of circulating water through the tower. One or two stages were installed to achieve the lowest possible gas temperature and to wash out the entrained brine mist. The circulating wash water was cooled by ordinary cooling water or, in a few cases by chilled water. Anyhow, due to the high temperature difference between the cooling medium and the circulation water, the gas temperature leaving the cooling tower and therefore the sulphuric acid consumption was quite high.

In certain cases the cooling water was contaminated with ammonia and the direct contact with the chlorine gas formed nitrogen trichloride (NCl_3) which is an explosive.

Modern Concept

The modern concept of chlorine cooling is designed for:

- Indirect cooling in shell and tube heat exchangers
- High efficiency filtration of the gas by use of glass fiber elements to separate the entrained brine mist

With these measures the dew point of the gas could be brought to the absolute minimum and the brine mist separation to the maximum.

The modern system is described below:

Chlorine Cooling

Cooling of the wet gas is normally done in two stages.

- First stage cooling from 90 to 40 °C by means of cooling water
- Second stage cooling from 40 to 15 °C by means of chilled water

Indirect cooling is achieved in shell and tube type heat exchangers (chlorine gas in the tubes, cooling medium in the shell) lowers the water content to approx. 4500 ppm. Gas temperature lower than 13 °C is not recommended due to the formation of

chlorine-hydrate (white crystals), which may plug of pipelines or filter elements. The final temperature of the cooled gas is also subject to the temperature increase in the blower and the remaining water content at this temperature to avoid the ignition of a Ti-Cl_2 fire. Below 13°C the water vapour pressure in the gas becomes too low to be safe. Under conditions of chlorine-hydrate formation ignition is still possible.

All parts that are coming into contact with the chlorine gas are made of titanium, these are the tube sheet as well as the tubes, which are seamless or welded. The shell is made of normal carbon steel suitable for cooling water. The heat exchangers are installed either vertically or horizontally with a slope of approx. 3° in direction of the flow.

The temperature split at 40°C results in 90% heat removal in the first stage and 10% in the second stage and similar heat transfer area for both coolers.

Condensate from both coolers is chlorine saturated and is recycled to depleted brine.

There is no need to provide standby heat exchangers. Also cleaning of the tubes is normally not necessary.

The advantages of this concept are:

- No possibility of NCl_3 formation
- Low space requirement
- Very low maintenance requirement
- Lowest possible gas temperature and water vapour content in the gas, which reduces acid consumption for chlorine drying.
- Low operating cost

Filtration

Cooled and water vapour saturated chlorine gas contains remaining brine mist which must be separated from the gas to avoid formation of sodium-sulfate during chlorine drying with sulfuric acid. The gas is fed horizontally through a chlorine resistant glass fibre bed. Particles are contacted and collected on individual fibres of the bed and then coalesce to form liquid films and droplets, which are pushed through the bed by the gas flow. The collected liquid then is drained off the downstream face of the bed by gravity. The particles are collected in three different ways: by internal agglomeration (mainly for larger particles > 3 micron) by direct collision for particle sizes between 1 and 3 micron and by Brownian diffusion for particles smaller than 1 micron.

The filter-elements are designed for an overall separation efficiency of 98% and a pressure drop of max. 150 mm WC. The brine mist quantity in the feed is normally less than 350 ppm NaCl. To achieve the high separation efficiency the gas flow rate should be kept at design conditions.

The filter elements are installed vertically and fixed in a filter plate. Gas is entering the filter vessel below the lowest point of the elements, flowing up and then horizontally through the elements. Inside the element the filtered gas leaves the vessel at the top.

The constant saturation of the gas with water vapour is important. Therefore the filter is installed upstream of the blower (if any) and close to the second stage chlorine gas cooler. To achieve saturation of overheated gas, water addition via a spray nozzle located at gas inlet nozzle of the filter is provided. Water addition is normally not necessary. If required it is added discontinuously. The water collected from the bottom of the filter vessel is drawn-off and added to the condensate from the chlorine coolers. The filter elements are normally self-cleaning and do not require maintenance. A replacement is required after 5-6 years of operation.

The advantages of this concept are:

- Very high separation efficiency for brine mist
- Very low maintenance and operating cost
- High reliability

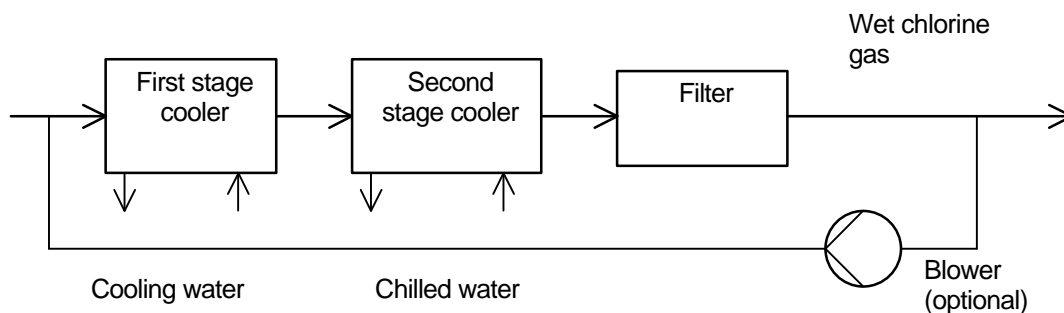
Boosting

If required, the cooled and filtered chlorine gas is boosted by means of centrifugal blowers to a pressure of up to 2000 mm WC. Boosting the entire or part of the gas stream is only required, if wet chlorine gas is branched off for the production of hydrochloric acid or iron-chloride. Alternatively the gas stream could be branched-off after the chlorine gas compression.

The blower is made of carbon steel with hard rubber lining and titanium impeller. Normally is the shaft sealed with a double acting mechanical seal, flushed and cooled with water. The mechanical seal is normally very sensitive to water failures, vibration etc. and special protections like water flow- and pressure control is required. The improvement consists in using a labyrinth sealing with gas flushing.

To avoid over heating of the boosted gas and therefore ignition of a $Ti-Cl_2$ fire at the blower impeller, recirculating part of the gas stream back to the inlet of the first chlorine gas cooler must control the capacity.

Modern Concept of Chlorine Cooling



2 Drying

Basic Requirements

Chlorine drying is designed for continuous drying, and if required, filtration of dried chlorine gas. The purpose is to adsorb the water vapour to the lowest possible content and to remove entrained acid mist (aerosol) from the dried chlorine gas.

Conventional Concept

Most of the drying units consist of three packed columns with circulation of sulphuric acid. Fresh concentrated acid is fed to the last column to adsorb traces of moisture which are remaining in the gas and flows then to the second column to absorb a partial amount of moisture and is finally overflowing to the first column to absorb most of the moisture. Each column is provided with centrifugal pumps, heat exchanger and instrumentation for the circulation of the acid. Due to the circulation of acid through the packing of the last column, the acid concentration at top of the column is already slightly diluted which does not allow the drying of the gas to moisture content lower than 30-50 ppm.

Beside the moderate achievable dryness, the concept is costly and needs a lot of space and maintenance and is presently not sufficient enough to fulfil the high quality requirements of anhydrous chlorine.

Modern Concept

The requirements of a modern concept are to get a better dryness to the gas (a few ppm of moisture only), to reduce the investment and operating cost and to get a high reliability. All aspects are integrated in the two stage drying system as described below.

KREBS SWISS is also developing a drying system, which operates without sulphuric acid.

Chlorine Drying in two Stages

The purpose of drying is to absorb the water vapour content of the chlorine gas coming from the chlorine cooling in order to prevent corrosion, formation of chlorine hydrate and hydrous iron chloride.

The process for drying of chlorine gas is based on the adsorption of the residual water vapour in concentrated sulfuric acid with a min. concentration of 98% H_2SO_4 . By the adsorption of the water vapour, the acid is diluted to about 75-80 % H_2SO_4 and the moisture content in the chlorine gas is reduced below 10 ppm w/w H_2O . Acid mist (approx. 600 ppm) entrained with the dried chlorine gas is usually separated in a gas filter, unless the gas is fed to liquid ring compressors where it is anyway again in contact with concentrated sulfuric acid. For such applications the top of the second

dryer is equipped with a wire mesh demister to separate up to 70 % of the entrained acid.

The drying system is improved by the use of only two columns connected in series: A packed column is followed by a column with special impingement baffle trays. The packed column is equipped with an acid circulation pump and a cooler. The moisture content in the gas is reduced to below 500 ppm. The gas leaving the packed column is finally dried in the tray column. The high adsorption efficiency results from the size, shape and numbers of the impingement trays (normally three plates are sufficient). Drying is achieved by very intensive contact of the gas with the acid. The principle is shown below. Because of the low water vapours concentration to be adsorbed in the second column, there is no need of acid circulation and cooling.

The tray column requires a constant gas flow and velocity through the impingement trays. Therefore the quantity gas which is be recirculated from the chlorine compressor discharge to control the suction pressure will be fed back to the tray column instead directly to the suction side of the compressor. This arrangement allows for all plant loads a constant gas flow through the tray columns as well as through the gas filter. The allowable turn down ratio of the impingement trays is not more than 20 %.

For plant capacities higher than 150-200 tpd the dried chlorine gas will be compressed in a turbo compressor. The suction pressure/capacity control is normally an integrated part of the compressor and does not allow the recirculation of gas back to the second drying tower. Therefore the second tower must be equipped with bubble cap trays, which are having a turndown ratio of more than 80%.

The acid consumption which is subject to the feed gas conditions is in the magnitude of 15-20 kg per ton of chlorine.

The drying system can be further improved by the reduction of the fresh acid (98%) consumption and the use of reconcentrated acid of 96% H₂SO₄. A part of the acid circulated in the first dryer is branched off and reconcentrated in a separate distillation unit. The achievable concentration is subject to the cooling water temperature available at site and will be not higher than 96% H₂SO₄. The reconcentrated acid is fed back to the middle part of the second column. The trays used for the column could be of impingement or bubble cap type, however, subject to the chlorine compressor type. Such a system is feasible if the plant capacity is very high and/or the use or disposal of diluted acid is difficult or expensive. The consumption of fresh 98 % acid is reduced to approx. 3-5 kg per ton of chlorine.

The heat load to be removed from the system is achieved in the acid circuit of the first column and is effected by:

- condensation heat of water vapour
- dilution heat of acid (approx. 82 kcal/kg)
- cooling of the gas (latent heat)
- cooling of fresh acid to process conditions. (30°C < t > 10°C)
- power requirement for the acid circulation,
- ambient conditions

The remaining water vapour content is measured with on-line instruments of high precision and reliability. The measuring is based on an electrochemical principle.

Filtration

Dried chlorine gas contains acid mist due to the high and intensive contact of the gas with the acid, which must be separated prior to the compression in piston- or centrifugal compressors. The gas is fed horizontally through an acid resistant glass fibre bed built-up in filter elements. Particles are contacted and collected on individual fibres of the bed and then coalesce to form liquid films and droplets, which are transported through the bed by the gas flow. The collected liquid is drained off from the downstream face of the bed by gravity. The particles are collected in three different ways: by agglomeration (mainly for larger particles > 3 micron) by direct collision for particle sizes between 1 and 3 micron and by Brownian diffusion for particle smaller than 1 micron.

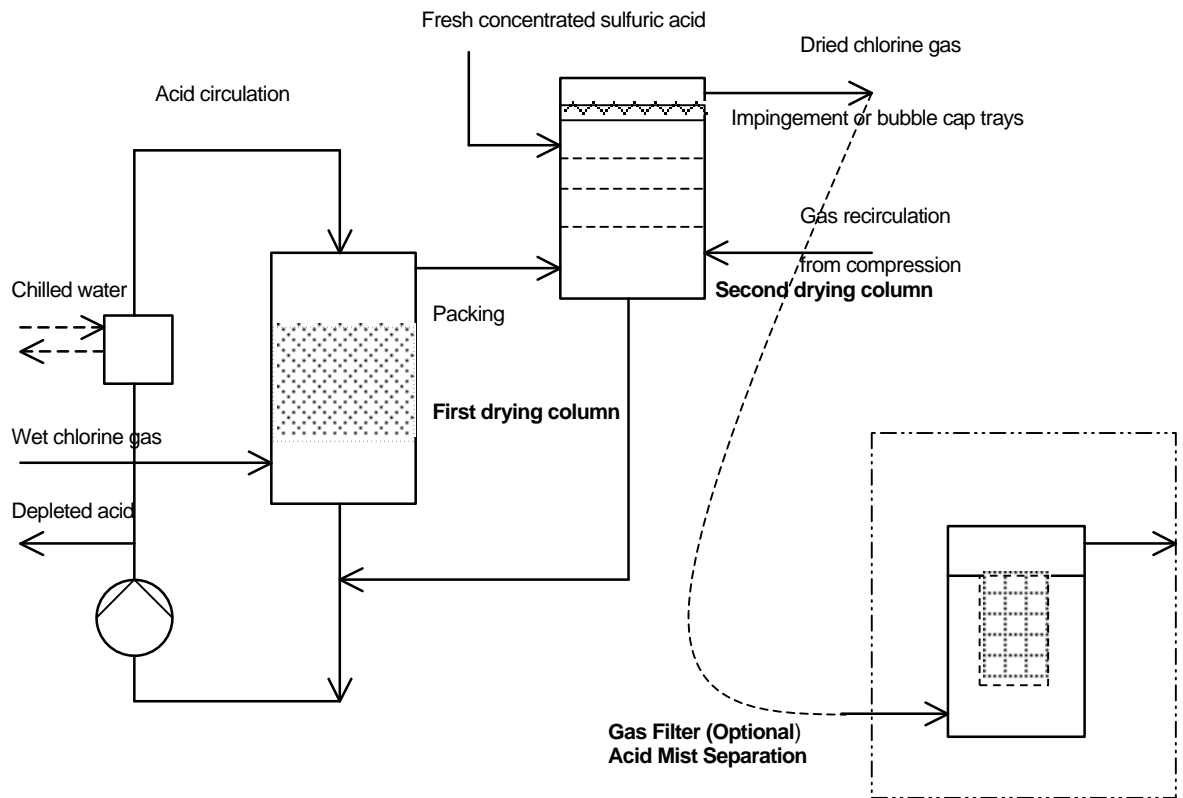
The filter-elements are designed for an overall separation efficiency of more than 98% and a pressure drop of max. 150 mm WC. The acid mist quantity in the feed is estimated to be less than 600 ppm H₂SO₄. To achieve the high separation efficiency the gas flow rate should be kept at design conditions.

The filter elements are installed vertically and fixed in a filter plate. The gas is entering the filter vessel below the lowest point of the elements, flowing up and then horizontal through the elements. Inside the element filtered gas flows to the top and leaves the vessel. The filter elements are self-cleaning and do not need maintenance. Normally the replacement is not before 5-6 years of operation.

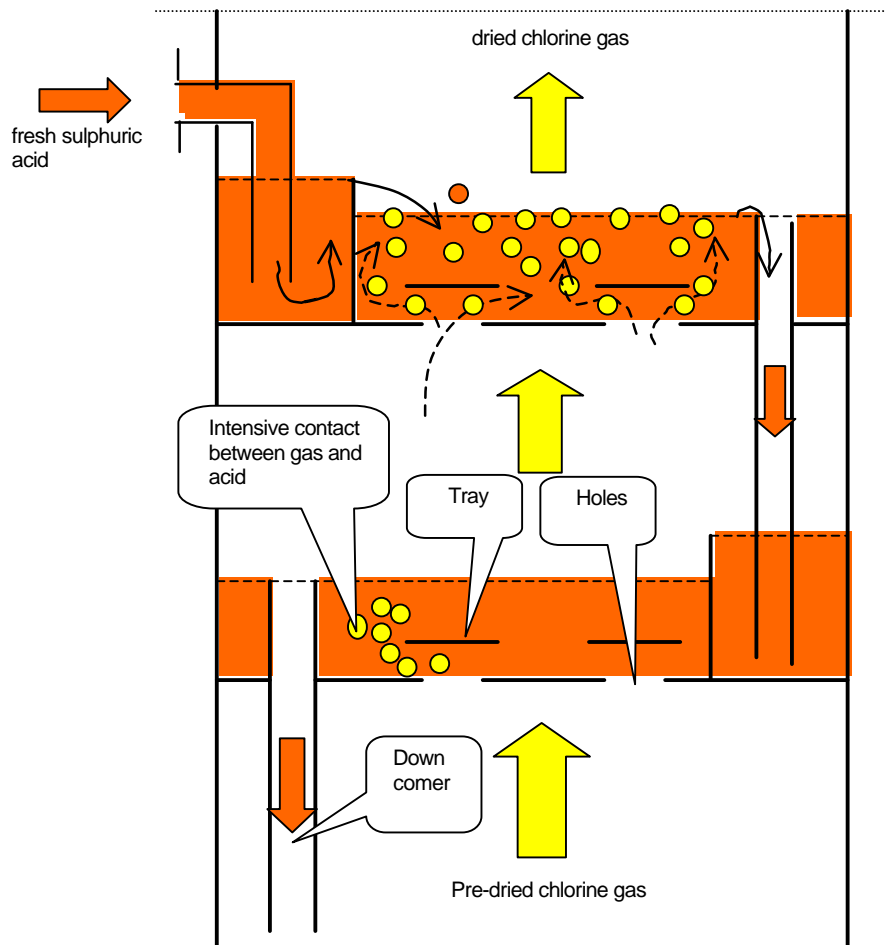
The advantages of the improved drying concept are

- Lower investment
- Lower space requirement
- Lower operating and maintenance requirements and cost
- High drying efficiency
- Better gas quality
- Lower acid consumption reducing to a minimum consumption of fresh and disposal of used acid.

Concept of Improved Chlorine Drying and Filtration



Principle of Impingement Tray Bottom



3 Scrubbing and Cooling

Basic Requirements

The purpose of chlorine scrubbing and cooling is to condense chlorinated organic and nitrogen trichloride and / or bromine (if present in the gas) continuously from the gas by liquid chlorine thereby cooling down the gas to a temperature of approx. – 30 to – 36 °C, as required for the compression in multi-stage piston compressors.

Conventional Concept

A simple injection of liquid chlorine into the suction line to the compressor does not fulfil the requirements of scrubbing and cooling of the gas.

Scrubbing and cooling of dried chlorine gas including the separation of NCl_3 and its decomposition is mainly applied when reciprocating compressors are used for boosting of chlorine gas to a higher pressure. A well designed and reliable process unit for scrubbing and cooling of dried chlorine gas was required for a reliable operation of reciprocating compressors. This requirement is not the only one when the gas is contaminated with NCl_3 and / or bromine. The adsorption of these impurities is best carried out in this section and there is no safer way to decompose NCl_3 .

Modern Concept

Our developments concern firstly the substitution of the solvent (CCl_4) used for the dissolving and decomposition of NCl_3 and secondly the adsorption of bromine from the chlorine gas.

The present concept and its improvements is described below. The improvements are presently under confirmation in trial operation.

Chlorine Scrubbing and Cooling

Dried chlorine gas leaving the chlorine drying steps (with filter to remove all acid mist) is passed through a scrubbing column for purification with liquid chlorine.

The column consists of an immersed gas distributor at the base and three impingement tray plates for cooling and scrubbing the gas. A demister at the top of the column removes entrained liquid chlorine droplets from the gas before leaving the column and entering the compressor.

Scrubbing and cooling is effected by the intensive contact of the chlorine gas with liquid chlorine and vaporisation of liquid chlorine at suction conditions of the compressor. The vaporisation of liquid chlorine at slightly negative pressure will lower the liquid chlorine temperature to –35 to –38 °C. At this low temperature the impurities are condensed and washed out by liquid chlorine leaving the column at the bottom. The level in the bottom part of the column controls the liquid chlorine rate to the column at the upper impingement plate. The impurities accumulate in the liquid

chlorine of the bottom and are drawn off to the decomposer when NCl_3 and bromine are present in the chlorine gas. In cases where only organic compounds are present, liquid chlorine will be drawn off either to the chlorine absorption or to other chlorine consumers, which can tolerate the presence of organic compounds.

NCl_3 is soluble in liquid chlorine and solvent (carbon tetrachloride) and is highly explosive when it is isolated from them. Ammonia compounds and chlorine react to NCl_3 during the generation of chlorine in the electrolysis cells or during chlorine processing (for example during the direct cooling of chlorine gas with water containing ammonia). The NCl_3 content in chlorine gas can be in the magnitude to 5 to 200 ppm, whilst the acceptable and safe level in liquid chlorine of the scrubber bottom is less than 10000 ppm. (20000 ppm limit as per Chlorine Institute)

The source and quantity of other impurities washed out by liquid chlorine depend on the raw materials used for the electrolysis, the materials of construction applied for electrodes, the equipment and pipelines as well as the utilities or chemicals used for the processing of the brine and chlorine.

Nitrogen Trichloride Decomposition

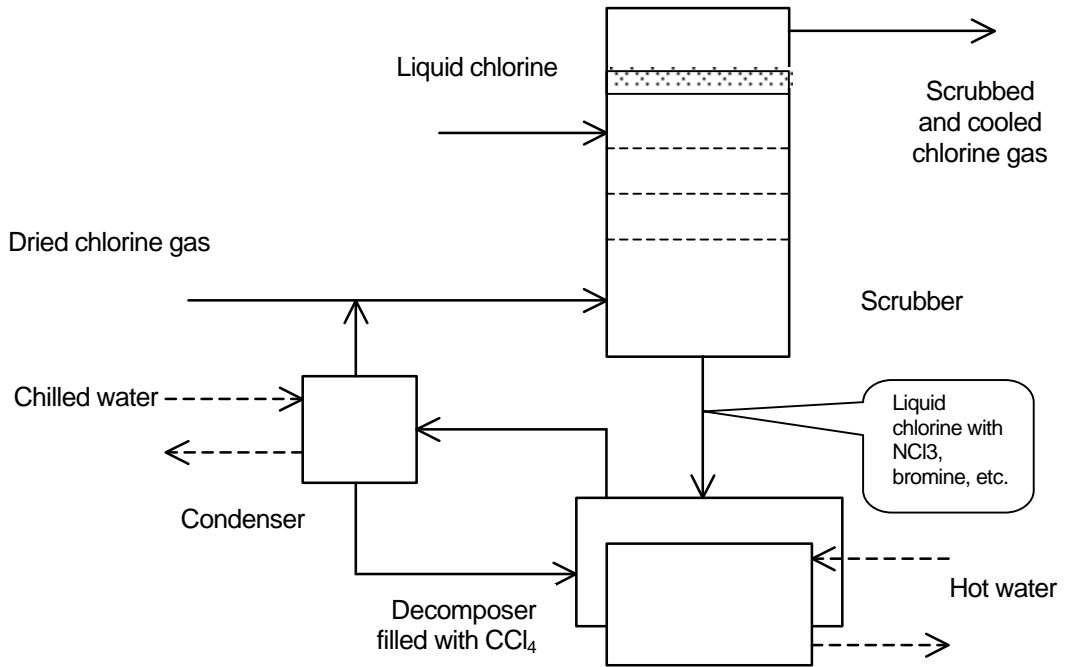
The thermal decomposition of NCl_3 is a safe and well-proven technology. This takes place in a decomposer where nitrogen-trichloride is dissolved with other impurities in carbon tetrachloride. This solvent is indirectly heated up to 50-60°C by means of hot water, which is circulated through a heating jacket of the decomposer. With the feed of cold liquid chlorine (-30 to -38°C) into the warm CCl_4 solution, the liquid chlorine vaporises and impurities dissolve in the solvent and thereby NCl_3 is decomposed in its elements. The decomposition heat is -54.7 kcal/mole.

The decomposition capacity depends on the solvent temperature and content of accumulated impurities. Generally, the decomposition rate of 12.5 gr. NCl_3 / h kg CCl_4 at 50 °C could be improved by increasing the solvent temperature, which should be in no case exceeding 65°C. The NCl_3 content in the solvent should never exceed 15000 ppm to avoid self-heating of thermal decomposition of NCl_3 .

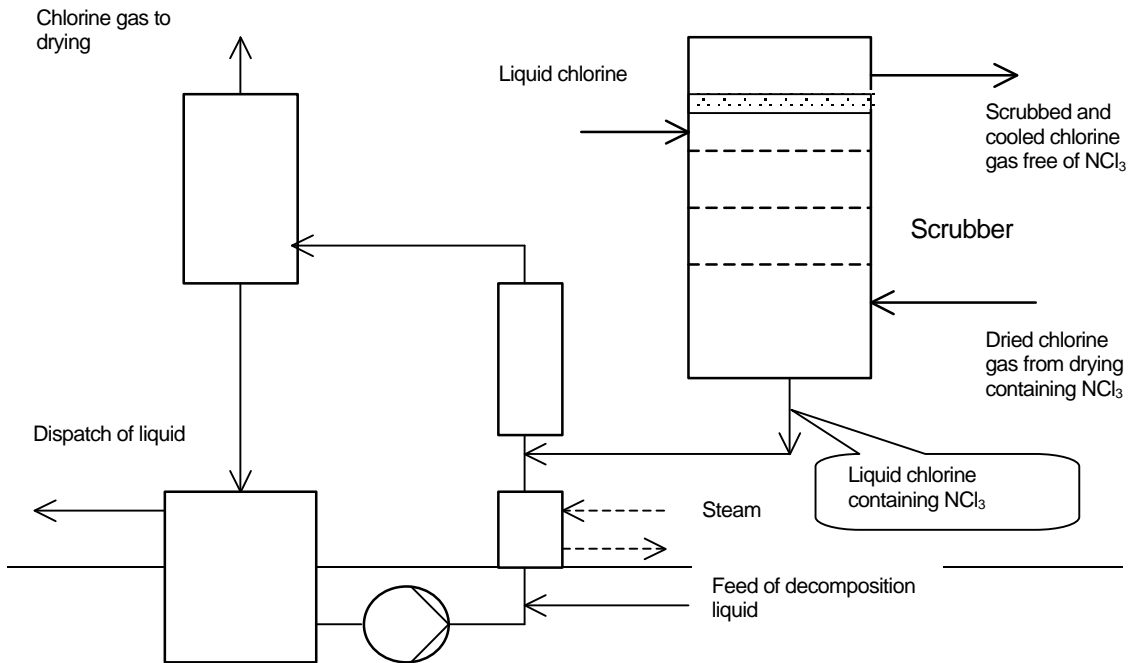
The vapours leaving the decomposer containing chlorine and solvent, which are to be cooled and condensed in cooler using chilled water. The condensate returns to the decomposer and the chlorine enters the scrubber, where entrained solvent is condensed.

The solvent filling of the decomposer must be replaced from time to time when the decomposition is no more sufficient (due to the effect of other dissolved impurities) and the NCl_3 is increasing to max. 15000 ppm. The service time of the filling is subject to the plant conditions and could be in the magnitude of 6-12 months.

Modern Concept of Chlorine Scrubbing and Cooling with NCl_3 Decomposition



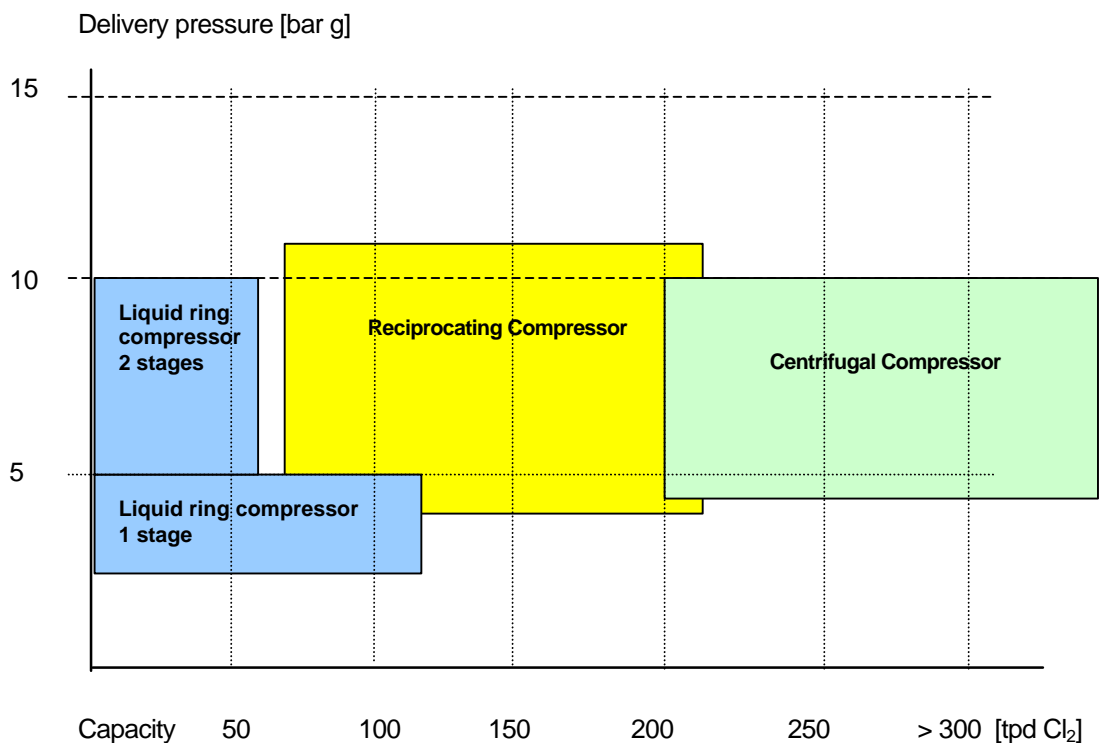
Improved Concept without use of CCl_4 for NCl_3 Decomposition



4 Compression

Basic Requirements

Chlorine compression is continuously boosting the pressure of dried chlorine gas as required for its liquefaction or its consumption/utilization in other processes. Basically three different compressors are available for the compression of dry chlorine gas. All types of compressor are suitable for compression of dry gas. The compression of wet chlorine gas is not practised. Typical operation ranges are shown for various types of compressors.



The above diagram shows the application range of single machines. The capacity range for centrifugal compressors is subject to the vendor selected.

When selecting a compressor for a certain capacity the specific properties of chlorine need to be considered: contact of chlorine with oil, grease or other materials which are not inert against chlorine have to be avoided.

These requirements are fulfilled with the liquid ring compressor, the vertical reciprocating compressor and the centrifugal compressor.

Modern Concept

Most modern chlorine compressors show an improved capacity range and delivery pressure (especially for two stage liquid ring compressors), selection of modern and

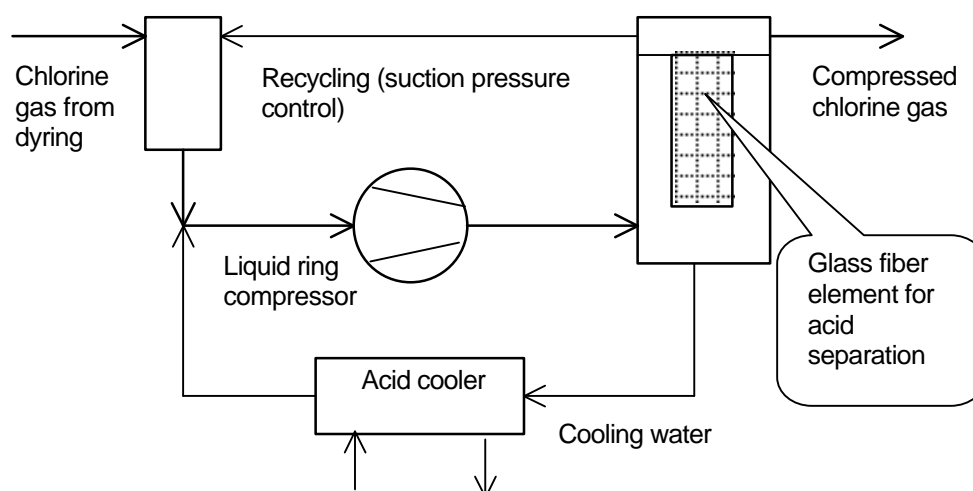
new materials of construction for important compressor components. However, certain developments and improvements were suggested by KREBS SWISS and concern the following aspects:

- Integration of glass fiber filter elements into the separator of the liquid ring compressor units. This brought an improvement of the acid separation and the remaining acid content in the compressed chlorine gas could be brought down to few ppm.
- Applying of chrome-oxide piston liners and piston rods for reciprocating compressors with the integration of the KREBS SWISS technology for the scrubbing and cooling of chlorine gas. Thereby the lifetime of the liners, rods and valves have been increased and maintenance frequencies (now only once per year) and costs have been reduced.

The principles of the different compressor types are given below:

Liquid Ring Compressor

The compression of gas is achieved by the rotation of an impeller in a casing, whereby concentrated sulfuric acid is used as sealing liquid for adiabatic compression. The gas leaving the compressor is passing a separator equipped with special baffles and special glass fiber packed filter elements for separation of acid from the gas. The acid content is brought to less than 10 ppm. Acid is circulated via a heat exchanger (plate- or shell and tube type) for removal of the heat of compression. Normally cooling water up to 30 °C is applied for acid cooling. The specific power consumption is relatively high, due to the demand required for the circulation of acid having a density of 1.85 kg /dm³. The acid used in the system is replaced from time to time by fresh concentrated acid of min. 98.5% strength. The compressor operates at a constant speed as a volumetric machine. Part of the compressed gas is recycled to the suction side (or back to the second stage dryer) to maintain a constant suction pressure. The capacity of the compressor is designed approx. 10-15% higher than the plant throughput capacity and the discharge pressure is designed at least 0.5 barg higher than the pressure required for liquefying or other use to compensate pressure drops in control valves and process variations.



Reciprocating Compressor

The compression of the dry chlorine gas, which is cooled and scrubbed with liquid chlorine, is achieved in non-lubricated, vertical multi-stage reciprocating compressors, specially designed for the application in chlorine service. Each compression stage is double acting, equipped with suction strainer, discharge cooler and damper. Dampers at suction and discharge are designed to keep pulsation amplitude within 1 to 2% pick to pick. According to the final pressure and the capacity the number of stages are selected. Gas cooling at each stage is required to keep the discharge temperature below 100°C. Cooling is achieved in fine tube type heat exchanger (cooling medium in the tube, chlorine gas around the tube) designed to avoid entering of water into the gas system. Chilled water is applicable for the first stage only, whilst for all other stages as well as for the cylinder heads cooling water is used to prevent partial liquefying of chlorine within the compressor.

The compressor is operating at constant speed (up to 380 rpm) as a volumetric machine. Part of the compressed gas is recycled to the suction side (back to the second stage dryer) to maintain a constant suction pressure. The capacity of the compressor is designed approx. 10-15% higher than the plant throughput capacity and the discharge pressure is designed at least 0.5 barg higher than the pressure required for liquefying or other use to compensate pressure drops in control valves and process variations.

Centrifugal Compressor

The rotation of the impellers and the increase of the gas velocity, which is converted into pressure, achieve the compression of the dried chlorine gas in a multi-stage horizontal centrifugal compressor. The speed of the impeller depends on the thermodynamic conditions of the process. The gas is cooled in intermediate stages (shell and tube type coolers) to keep the gas temperature below 100°C. Cooling water is applied for the gas cooling.

Centrifugal compressor is normally installed without stand-by unit, due to its high reliability and availability. Whether one or two compressors are selected for parallel operation is subject to plant capacity, concept and investment. For plant capacities higher than 600 tpd it is recommended to split up the compressor capacity in two or three units to maintain flexibility of operation.

The compressor is normally operating at constant speed. The suction pressure control is achieved by recycling part of the compressed gas back to the suction side. The capacity of the compressor is designed approx. 10-15% higher than the plant throughput capacity and the discharge pressure is designed at least 0.5 barg higher than the pressure required for liquefying or other use to compensate pressure drops in control valves and process variations.

5 Liquefaction

Basic Requirements

The chlorine liquefaction section is designed for the continuous liquefaction of dried and compressed chlorine gas. The purpose is to condense most of the chlorine contained in the gas at a certain temperature which is given by the pressure, the desired liquefaction ratio and the gas composition. Chlorine is liquefied in shell and tube type heat exchangers of single or multiple passes. Chlorine is fed to the tube side, the chilling medium to the shell side. Liquid chlorine leaving the heat exchanger is sent by gravity to the storage tank, which requires an elevated installation of the liquefier. The remaining non-condensed gases are fed to the chlorine absorption plant or to the hydrochloric acid synthesis plant.

The chlorine gas generated in the membrane electrolysis cells contains up to 2 vol. % inert gases like O₂, CO₂ and H₂. Therefore a total liquefaction of the chlorine is not possible. The liquefaction ratio depends on temperature and pressure. The higher the pressure and/or the lower the temperature the higher the liquefaction ratio. Normally a ratio of 98 to 98.5 % is considered. Due to the presence of H₂ in the chlorine gas, the H₂ content in the sniff gas must not exceed 5 vol. %. It is recommended to provide a continuous H₂ in chlorine analyser for recording and to actuate a high concentration alarm. (Note: Chlorine gas generated in membrane cells at normal conditions contains less than 0.1 vol. % hydrogen, however, this content could increase to 1-2 vol. % when a leakage in the membranes allows hydrogen entering into the chlorine system).

Modern Concept

Chlorine liquefaction at a high pressure by applying chilled water/brine results in the lowest total operating cost. The selection of the pressure is subject to the capacity and the selected type of chlorine compressor to manage this capacity. For smaller plant capacities up to 100 tpd Cl₂, normally single stage liquid ring compressors are selected. Therefore the liquefaction pressure is within 3-4 bar g. For this pressure chilling is achieved by vaporisation of a refrigerant. For higher plant capacities reciprocating or centrifugal compressors are used and the liquefaction pressure is then selected on the availability of the chilling medium. In most of the cases a central chilled water or chilled brine system is available to cover also other consumers. The pressure then is in the range of 7 to 13 bar g.

A modern concept considers the following :

- Medium or low pressure liquefaction
- Use of refrigerants which are fully halogenated
- Replacing refrigerants, which are not in confirmation with the Montreal Agreement, by substitutes
- No use of any refrigerant

Due to the physical properties of chlorine it is not possible to cover all aspects. The liquefaction of chlorine must be done under a certain pressure when using a refrigerant or even when no refrigerant is used at all, as shown in the table below:

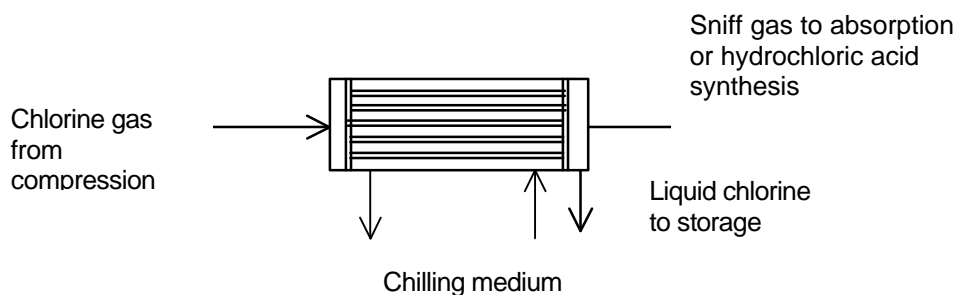
<i>Alternate</i>	<i>Chlorine Pressure</i>	<i>Type of Chlorine Compressor</i>	<i>Chilling Medium and Temperature</i>	<i>Plant Capacity tpd Cl₂</i>
1	13 bar g		Cooling water 30/35 °C	<ul style="list-style-type: none"> • between 100 and 200
2	7-10 bar g	<ul style="list-style-type: none"> • reciprocating • centrifugal • 2-stage liquid ring 	Chilled water 5/10 °C	<ul style="list-style-type: none"> • between 100 to 200 • over 200 • up to 50
3	3-4 bar g	<ul style="list-style-type: none"> • 1-stage liquid ring • centrifugal 	<ul style="list-style-type: none"> • chilled brine -10/-16°C • refrigerant (R404A, R407C) 	<ul style="list-style-type: none"> • up to 100 • over 200
4	0.2 bar g	<ul style="list-style-type: none"> • blower 	<ul style="list-style-type: none"> • refrigerant -40°C (R404A , R407C) 	<ul style="list-style-type: none"> • small capacities only
5	10-13 bar g	<ul style="list-style-type: none"> • centrifugal • reciprocating 	<ul style="list-style-type: none"> • cooling water and liquid chlorine 	<ul style="list-style-type: none"> • all capacities

The application of most of the well known refrigerants like R11, R12, R22, R134 A etc. is prohibited. For most of them are substitutes available, which however requires certain modifications of the existing installations. It was also reported that R22 and R134 A can react with chlorine and cause fire.

Two basic chilling concepts (one with an approved refrigerant and the other one without using any refrigerant) are described below:

Concept for use of Chilled Water or Brine, Alternate 1-3

The liquefaction system utilising chilled water or brine is relative simple and consists of a liquifier with the provision for the feeding chlorine gas and discharging liquid chlorine as well as sniff gas only. Double condenser tubes with leak detection devices are used, to avoid the contamination of water/brine with chlorine or the entrance of water into the chlorine system. The capacity control is achieved by keeping a constant chlorine pressure and adjusting the chilling medium flow rate by the temperature of the liquid chlorine leaving the unit. The chlorine pressure is increased or lowered to get the liquefaction efficiency under consideration of the sniff gas composition.



Concept with use of Refrigerant, Alternate 3-4

The liquefaction system utilising refrigerant consists of a liquefier, a refrigerant compressor, condenser, receiver and control devices. The entire system is designed according to UVV 20. The refrigerant compressor is normally a screw type, however, the selection depends on the oil type, refrigerant type and vaporisation temperature. The suction pressure at the compressor is normally always positive to avoid the intake of air in case of a leak. The refrigerant must be free of chlorine and hydrogen molecules and fully halogenated (FKW). By the end of 1999 the use of refrigerant R22 is no more permitted. Substitutes like R404A, R407C, R410 C or R507 are now used for new installations. The selection of the refrigerant to be applied in the proposed installation is subject to local regulations, availability, process conditions, investment cost etc.

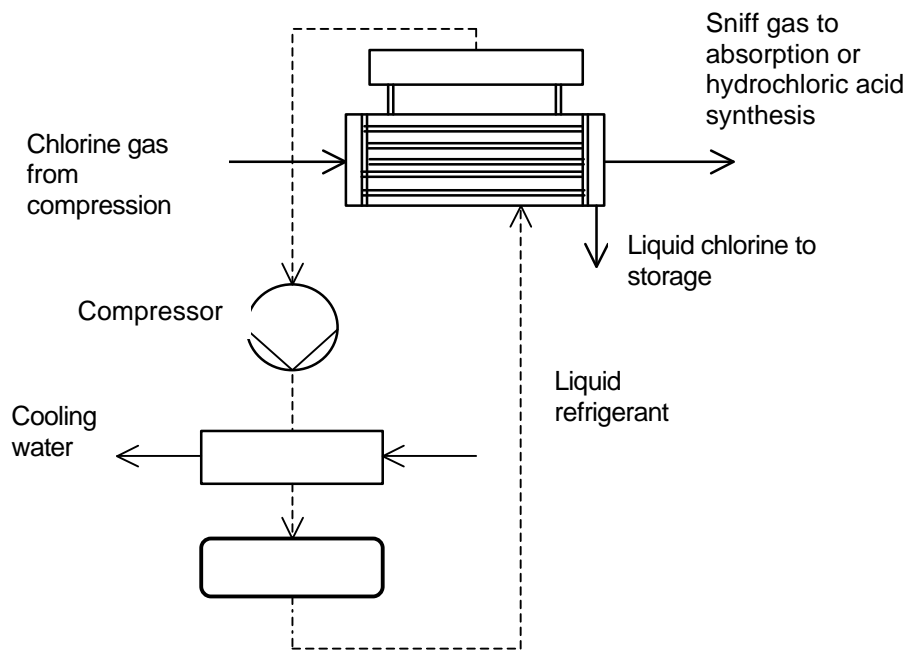
Other refrigerants like ammonia, propylene or propane are not recommended for the use in chlorine liquefaction systems. In the event of a leak in the liquifier, ammonia will react with chlorine to nitrogen trichloride which is explosive. To avoid this possibility a secondary circuit between the refrigerant and the liquifier is required with the consequence that the refrigerant temperature is much lower, which creates higher operating and investment requirements. The medium in this circuit is a special type of oil, which does not react with neither with chlorine nor with refrigerant. Propylene and propane refrigerants are flammable and therefore not acceptable.

The liquefaction capacity control is normally achieved by varying the chlorine pressure at a constant refrigerant temperature in the liquifier. The suction pressure at the compressor automatically controls the refrigerant capacity since this pressure is indirectly changing with the quantity of chlorine gas fed to the liquifier. A higher chlorine rate is vaporizing more refrigerant and leads to an increase in the suction

pressure of the compressor. A refrigerant level in the shell side controls the quantity of refrigerant required in the chlorine liquifier.

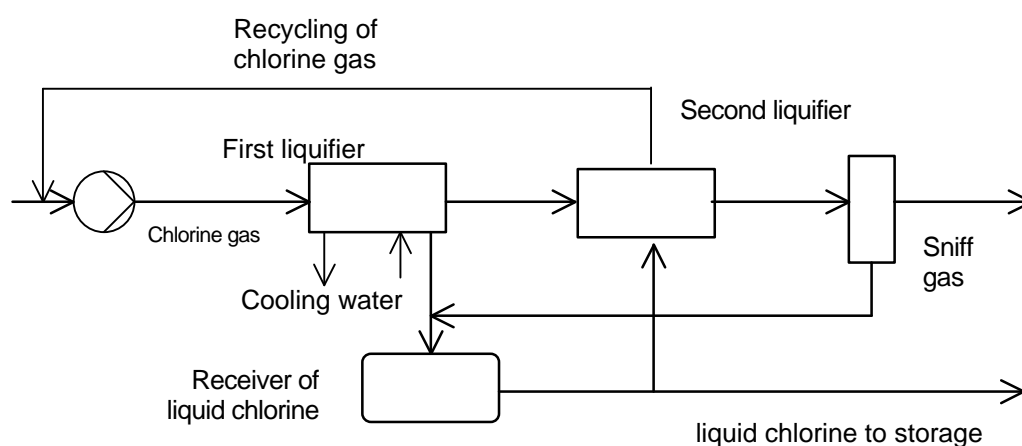
It is important that the refrigerant system is equipped with a reliable system to recover oil from the shell side of the chlorine liquifier.

The refrigerant receiver is normally designed to hold the entire refrigerant filling.



Modern Improved Concept without using Refrigerant, Alternate 5

Liquifying chlorine gas may also be achieved without the application of a refrigerant. The gas must be compressed to approx. 10-13 bar g, partially liquefied in the first stage by means of cooling water and finally in the second stage by the use of expanded liquid chlorine from the first stage. The vaporised chlorine gas is recycled back to the chlorine compressor. This concept is applicable for plant capacities greater than 100 tpd Cl_2 where reciprocating or centrifugal compressors are used to reach the high liquifaction pressure. The concept is illustrated below.



The advantages of this concept are:

- No use of refrigerant
- No refrigerant compressor required
- Low maintenance requirements
- Low investment requirement
- Safe and reliable

6 Storage, Transfer and Filling

Basic Requirements

The storage of liquid chlorine is required as a buffer between the continuous production and their consumption. With liquifying the gas their specific weight is increasing which makes it easier for storing, filling, and transportation.

Modern Concept

A modern concept for the storage, transfer and filling of liquid chlorine requires the following

- Store liquid chlorine under low pressure
- Provide one empty storage tank as spare
- Install storage tanks in closed buildings with provisions for collecting liquid chlorine and controlled vaporisation and suction to the chlorine absorption unit
- Transfer liquid chlorine by pumps only within the factory area and over short distance
- Transfer chlorine over long distance only in gaseous form.
- Apply articulated arms for filling into rail tankers
- Only use approved filling hoses for filling into tonners and cylinders
- Provide all safety measurements as recommended by Euro Chlor and the Chlorine Institute.

Modern concepts for storing, transfer and filling of liquid chlorine are described below.

Liquid Chlorine Storage

Chlorine is stored in vessels at low pressure and low temperature or in pressure vessels at ambient pressure or liquefaction system pressure. A vessel may be filled with liquid chlorine up to the maximum of 95 % of the vessel volume at the chlorine temperature of +50°C which is equal to the filling factor of 1.25 ton liquid chlorine / m³ volume. Most recommended is the storage at ambient conditions, even, where liquefaction is done under a higher pressure.

The requirements concerning design, material of construction, instrumentation, fabrication, controls and operation are defined in the AD Merkblätter and TRB regulations (-35/+55°C, 17 bar g). Basically four tanks are installed, one tank receiving

the product, one tank connected to filling and transfer to consumers, one tank ready for receiving and one empty spare tank. All tanks are of equal size and design. The tanks are installed in a closed building with a pit to accumulate liquid chlorine leakage and provisions for controlled vaporisation and venting the chlorine gas to the absorption unit. The allowable emission is defined in the TA Luft and/or other regulations applicable at the place of installation. As per EPA's Rule (Environmental Protection Agency, USA) is worst case release for chlorine as a 10-minute release of the entire contents, resulting from a vessel or pipe failure.

Liquid chlorine tanks are protected against fire or abnormal heat radiation for which the tank is not designed to avoid a possible reaction between the chlorine and the iron of the steel.

Liquid Chlorine Filling

Liquid chlorine is filled into transport vessels like

- Rail tankers of 20 to 60 ton capacity
- Road tankers (*) of 20 ton capacity
- ISO containers of 20 ton capacity
- Tonners of 1 ton capacity
- Cylinders of 50 to 100 kg capacity

(*) Transportation of liquid chlorine in road tankers is not permitted within European countries.

All vessels to be filled with liquid chlorine must be designed, fabricated and tested for this application. Filling is achieved in specially designed filling stations equipped with weighing- and control facilities. The filling capacity depends on the tank type and transfer method of liquid chlorine to the filling station and is summarised below:

<i>Type of Tank Capacity</i>	<i>Filling capacity</i>	<i>typical transfer method by</i>	<i>Filling device</i>
Rail / Road tanker 20 to 60 ton	min. 5 ton / hr	canned pump	articulated arms
ISO containers 20 ton	min. 5 ton / hr	canned pump	articulated arms
Tonners 1 ton	min. 1 ton / hr	air, nitrogen or chlorine gas padding	copper tubes
Cylinders 50 – 100 kg	min. 500 kg / hr	air, nitrogen or chlorine gas padding	copper tubes

The transfer of liquid chlorine from a storage tank to the filling station is achieved by either pumping with a canned pump or by padding with dry air, nitrogen or chlorine gas into the tank connected to the filling station. The transfer line is protected against rupturing, excess flow, low pressure, back flow etc. The required pressure is approx.

4-5 bar higher than the saturation of chlorine gas. When liquid chlorine is stored at ambient pressure, pumping is required to maintain the pressure in the tank. Any padding medium shall have a water vapour content of less than 0.2 gr/m^3 , which corresponds to a dew point of -35°C .

During filling, approx. 3 to 10% of the filling rate, is vaporised and fed as sniff gas to the absorption section. This loss depends on ambient and liquid chlorine conditions (temperature) as well as in the filling capacity and procedure.

The filling station for rail/rod- or ISO- tanker is designed with provisions for access to the tank cover and filling valves. The owner is responsible for the reconditioning of such tanks.

The filling station for tonners and cylinders consists of a storage area for returned tonners / cylinders where an input protocol is made, a venting and recondition area, a filling station with the weighing facility and a storage area for filled tonners/cylinders. Tonners are stored in one layer only, therefore a large building is required to cover the entire station.

The reconditioning of tonners and cylinders includes the following activities:

- Receiving report
- Venting of empty tonners/cylinders
- External inspection
- Internal inspection including pressure testing
- Painting
- Replacing of valves, tightness testing
- Stamping
- The frequency of above procedure is subject to the regulations applicable at clients location.

7 Vaporisation

Basic Requirements

Vaporisation of liquid chlorine is required in many applications because of process requirements and because of greater handling ease. It is common practice to withdraw vapour directly from cylinders or 1-ton containers, relying upon natural heat transfer to produce the necessary rate of liquid vaporisation. Usually vapour is not withdrawn from storage tanks, rail or road tankers. Consumers who require chlorine gas from such vessels must provide vaporisation equipment to generate continuous and reliable gas feed.

A chlorine vaporiser should be designed to deliver chlorine gas at a rate in excess of the peak load demand by the consumer. This includes considering flooding protection, liquid disengagement, superheating, accumulation of impurities like NCl_3 etc.

Modern Concept

Chlorine vaporisers are normally not installed at producers of liquid chlorine, except when chlorine is liquified and again vaporised in order to improve the chlorine gas quality.

A vaporiser in which injected liquid chlorine is vaporised on a hot surface allows the vaporisation of liquid chlorine which contains NCl_3 . This vaporiser has no liquid sump in which NCl_3 may accumulate. Normally vaporiser with a coil or with a vertical tube bundle in a bath of liquid chlorine is used. The vaporiser capacity is self controlling by increasing and decreasing the height of the liquid bath due to the chlorine gas pressure in-or decreasing above the bath which is subject to the consumption of vaporised chlorine gas at the consumer. Other developments concerning the heating method and design conditions as described below.

The heating method depends on the capacity of the vaporiser. For low capacity hot water vaporisers are used. An external heater injects steam into a water circuit pumped through the vaporiser water jacket, with an overflow for accumulated condensate. High capacity vaporisers are generally heated by low-pressure steam.

The maximum recommended operating temperature for steel vaporisers is 120°C . It is advisable to use the highest possible temperature, which is above 60°C . Overheating by $10 - 20^\circ\text{C}$ is normally necessary to avoid reliquefaction in the gas pipeline. Operation of a vaporiser below 0°C will introduce the danger of freezing water in the heating device. In normal operation this condition does not occur. The vaporisation temperature must be above $60-70^\circ\text{C}$ to decompose NCl_3 safely.

All chlorine vaporiser systems should include at the minimum:

- provisions for overheating the chlorine gas stream,
- automatic shut-off valve in the gas line to prevent discharge of chlorine gas if improper conditions exists,
- Overpressure protection,

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- Overfilling protection,
 - Protection against overheating and subcooling.

Summary

This paper illustrates that even for a well proven technology, which has been applied for many years, there is always room for developments, alterations and improvements. These measures result in improving the safety aspects, the product quality as well as the investments for the chlorine processing.

The target of KREBS SWISS is to improve continuously their technology, specially under the aspect of reducing the investments, reducing the operating and maintenance requirements and to improve the product quality of chlorine.

KREBS SWISS is your competent partner for supplying of

„Technology which fits“.