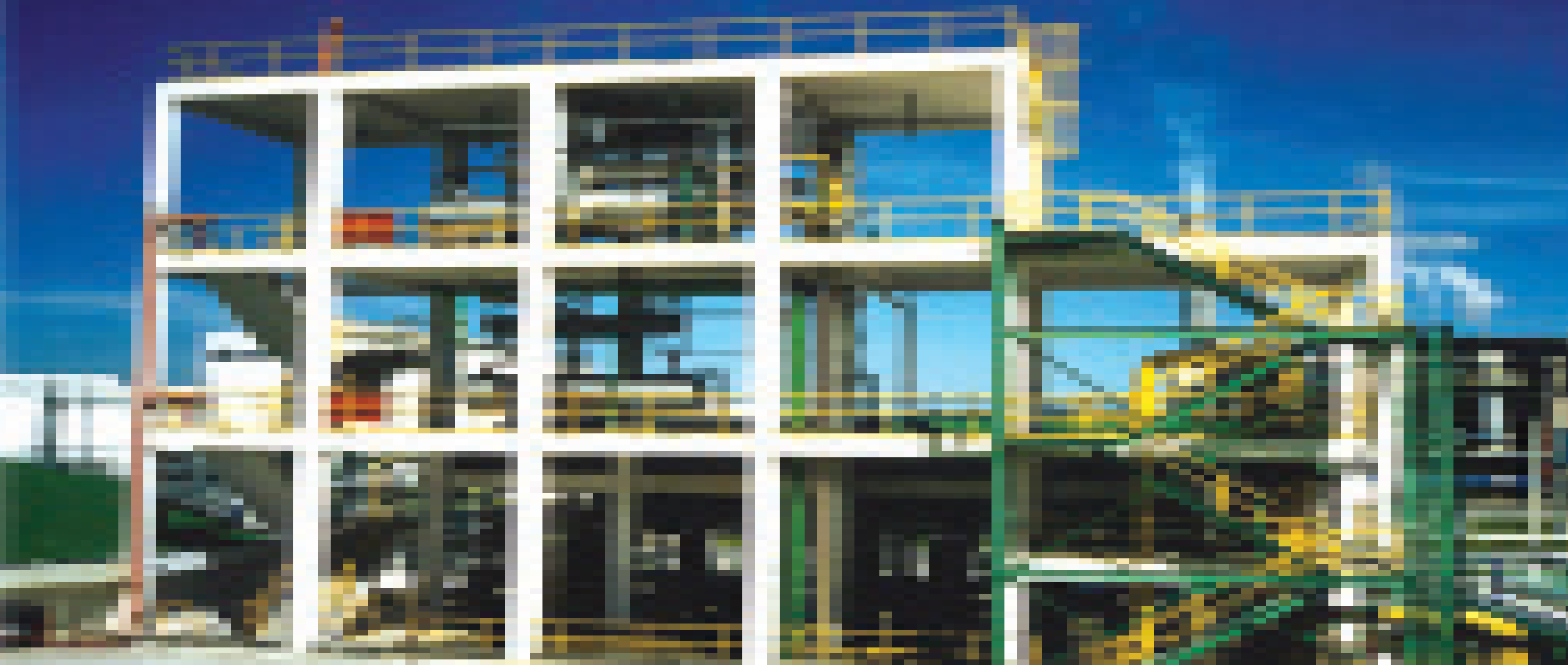


Refrigeration for Chlorine Liquefaction

By *Krishna V. Jog* *and*
Technical Advisor, ACR Division,
Kirloskar Pneumatic Co. Ltd., Pune

Abhijit V. Gokhale
Senior Engineer, ACR Division
Kirloskar Pneumatic Co. Ltd., Pune

Chlorine is widely used in the manufacture of thousands of everyday products. It is used for producing safe drinking water the world over. Even the smallest water supplies are usually chlorinated to make it safe for drinking. It is extensively used in the production of paper products. It is used in dyestuffs, textiles for decolourizing of artificial fibres, petroleum products and chemicals, medicines, antiseptics, insecticides, foodstuff, solvents and cleaners, paints, plastics, refrigerants such as HCFC's, chloromethane, ethylene glycol, chloroform, carbon tetrachloride and many other consumer products.

Most of the chlorine produced is used in the manufacture of chlorinated compounds for sanitation, pulp bleaching, disinfectants and textile processing. It is also used in the extraction of bromine. It is used as an oxidizing agent and in substitution since it brings many desired properties in an organic compound when substituted for hydrogen as in one form of synthetic rubber.

How is Chlorine Manufactured?

Chlorine is mainly manufactured by electrolysis of chlorides in which chlorine is evolved as a gas at the anode while hydrogen and hydroxide ions are formed at the cathode.

The production of caustic soda (NaOH) and chlorine (Cl_2) is one of the most important industries. The basic reaction in the chlorine - caustic process can be shown as $NaCl + H_2O \rightarrow NaOH + ½\ H_2 + ½\ Cl_2$.

A brief description of the membrane cell process in which chlorine gas is evolved is given below:

Electrolysis System (Membrane Cells)

Brine is fed to the anolyte compartment of the cell and water is fed through diluted caustic soda to the catholyte compartment as shown in *Figure 1*.When DC current is applied to the cell the ion selective membrane passes mainly positive sodium ions from the brine to the catholyte compartment. The chloride ions from the brine are oxidized to chlorine gas at the anode

About the Author

Krishna V. Jog is an M. Tech from IIT Bombay with 43 years experience of which 8 years are in teaching and research and 35 years in the ACR industry. He retired as MD of Kirloskar McQuay. He is a presidential member of ISHRAE, Pune chapter as well as an ASHRAE member.

Abhijit Gokhale is a mechanical engineer from Pune University.

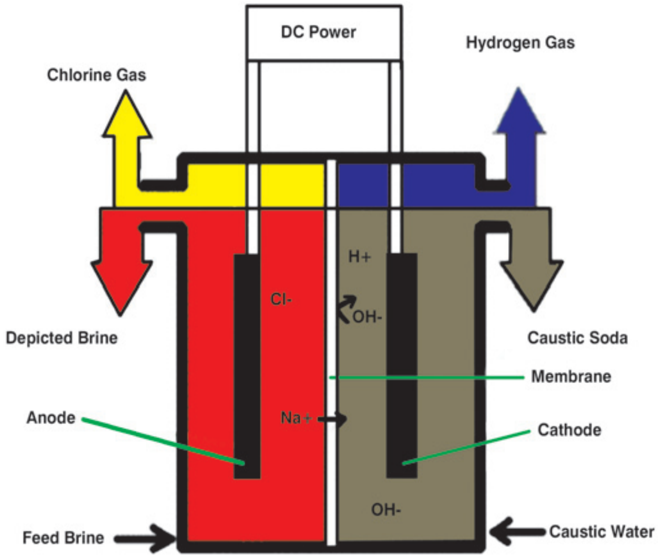


Figure 1: Electrolysis System for Chlorine Manufacture

while hydrogen and hydroxide ions are formed at the cathode. The membrane is highly efficient in separating the chlorine and the chloride from the hydrogen and caustic soda produced. A significant property of the membrane is the current efficiency (the higher the current efficiency, the lower the hydroxide leakage through the membrane). Hydroxide passing through the membrane into the anolyte compartment leads to the formation of oxygen and hypochlorite. The most efficient membrane offers a current efficiency of approximately 96 percent when producing 31-35 percent caustic soda.

The chlorine and hydrogen produced in the electrochemical membrane process leave the cells at a pressure slightly higher than atmospheric pressure. After cooling in heat exchangers, the gases undergo additional processing in the form of chlorine liquefaction, hydrochloric acid production or hypochlorite production.

Chlorine Liquefaction

The chlorine liquefaction system consists of four sections namely :

- Chlorine drying is carried out in a multi-stage operation, which places the wet chlorine in contact with varying strengths of sulphuric acid. The sulphuric acid is pumped into the packed drying columns in a counter-current fashion to the chlorine gas flow in order to

History

Chlorine (Chloros means greenish yellow in German) was first discovered in 1774 by Scheele, who thought it contained Oxygen It was named Chlorine by Humphry Davy in 1810 who believed it was not a mixture but an element. Chlorine has an atomic no.17, atomic weight is 35.453 gm and molecular weight is 70.906 gm. It has a melting point of –100.98°C (–149.8°F) & an NBP of –34.05°C (–29.3°F). It has a critical temperature of 144°C (291°F) and a pressure of 78.63 kg/cm^2 abs (1118.36 psia). It is in the Halogen Group and is in group no.17 of the periodic table.

Chlorine is a greenish yellow gas, which combines directly with almost all elements. Chlorine is a respiratory irritant. The gas irritates the mucous membranes and liquid chlorine burns the skin. As little as 3.5 ppm can be detected as odour and 1000 ppm is likely to be fatal after a few deep breaths. It is not found in a free state in nature but is found commonly as sodium chloride NaCl in seawater.

Chlorine gas was first used in World War I on April 22,1915 by the German army. It was the first time that a chemical weapon had been used against human beings. Total Allowable Exposure Limit (TAEL) is 0.5 ppm, which is based on 8 hour time - weighted average of 40 hour week exposure.

After the first German Chlorine gas attacks, allied troops were supplied with masks of cotton pads that had been soaked in urine. It was found that ammonia in the pad of urine neutralized the chlorine. These pads were held over the face until the soldiers could escape from the poisonous fumes.

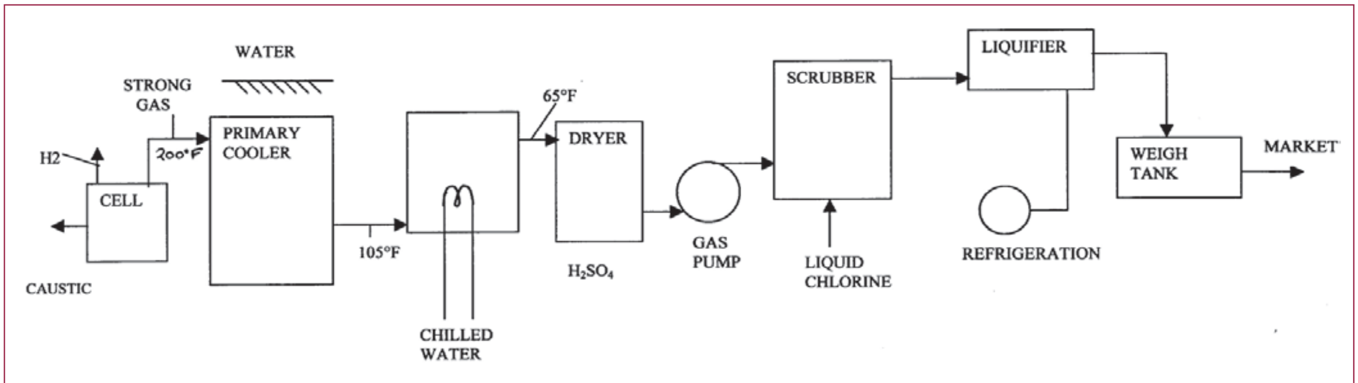


Figure 2: Various Steps in the Complete Cycle from Cells to Market

continued on page 96

continued from page 94

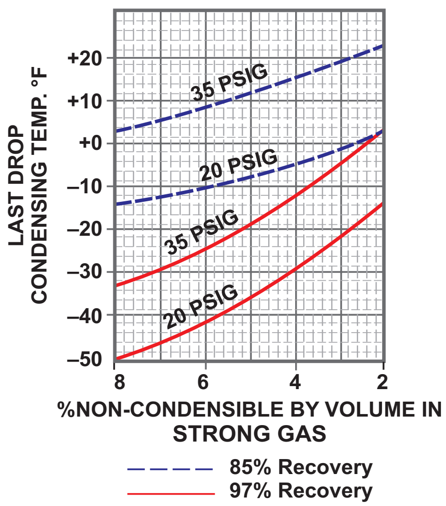


Figure 3: Determining Last Drop Condensing Temperature

minimize consumption of acid. From the drying system, the chlorine gas is piped to the chlorine gas compressor.

- Chlorine compression - the chlorine gas pressure is increased to a suitable level for the downstream liquefaction unit. The dry compressed gas is passed through a high efficiency demister for removal of all entrained acid before entering the chlorine condenser.
- Chlorine liquefaction takes place in a chlorine liquefier that is a horizontal or vertical shell and tube heat exchanger where the chlorine gas is cooled and condenses to a liquid inside the exchanger tubes. This cooling is performed by means of a closed-loop compressor based refrigeration system, which will be described later.
- Liquid chlorine storage - the liquid chlorine then flows by gravity from the condenser to the liquid chlorine receiving tanks. The condensation efficiency is dependent on the amount of inert gases in the system, but typically around 97 percent is achieved.

Mercury Cells

The other method used is by using mercury type cells. In the mercury cell, the mercury itself acts as the cathode. Sodium forms an amalgam with the mercury during electrolysis and is continuously removed. It reacts with water to form a high purity caustic and the mercury is returned to the cell by a mercury pump.

The cells are maintained just above atmospheric pressure by 6 mm to 12 mm WG (¼ to ½ inch) of positive pressure to keep air from entering the cells and forming an explosive mixture with the hydrogen.

Chlorine Gas

Electrolysis of brine in a diaphragm or membrane cell or in a mercury cell gives chlorine gas at the anode. This gas leaving at the anode is hot –79°C to 93 °C (175 to 200°F) and saturated with water. Since it is wet, it is also very corrosive. It is fed through to glass or fiberglass reinforced polyester materials to heat exchangers for cooling. A simple sketch of various steps involved in the complete cycle from cells to despatching to market in cylinders or tonners is shown in *Figure 2*.

Chlorine from cells at about 79 °C to 93 °C (175 to 200°F) is cooled by cooling tower water to about 40°C (105°F) in the primary cooler. It is further cooled with chilled water at about 10 to 15 °C (50 to 59°F) to a leaving temperature of about 18 to 20°C (65 to 68 °F). A chlorine hydrate is formed at 12.2°C (54°F). Therefore, Cl_2 gas cooling is restricted to about 15°C to 20°C (60°F to 70°F) and not lower. Considerable water from the chlorine gas is condensed in these coolers and drained.

The chlorine is then further dried by passing it through drying towers where concentrated sulphuric acid H_2SO_4 is used. The process of drying of chlorine gas is based on the adsorption of the residual water vapour in concentrated sulphuric acid with a minimum concentration of 98 percent H_2SO_4. By the adsorption of the water vapour, the acid is diluted to about 75 to 80 percent H_2SO_4 and the moisture content in the chlorine gas is reduced to less than 10 ppm. Acid mist entrained with the dried chlorine gas is separated in a gas filter.

The drying system is improved further by the use of two columns in series. The first one is a packed column and the other one is provided with impingement baffle trays.

The dried chlorine gas coming out from the dryer is compressed by a suitable type of compressor depending upon the capacity (TPD-tons per day) of chlorine liquid being condensed.

For smaller capacities upto about 50 TPD, liquid ring compressors of single stage or two stage are used depending upon the discharge pressures of upto 5 atg or 10 atg respectively.

For medium capacities from about 50 to 150~200 TPD of liquid chlorine, reciprocating compressors are used and for very high capacities above 200 TPD, normally centrifugal or turbo compressors are preferred since they can handle high flows being high rpm machines.

The percentage of chlorine recovered can be increased by raising the gas pressure and lowering its temperature. The "strong gas" discharged from the compressor usually is at 1.8 to 2.5 kg/cm^2 g (25 to 35 psig) pressure and from 25 to 40°C (77 to 104°F).

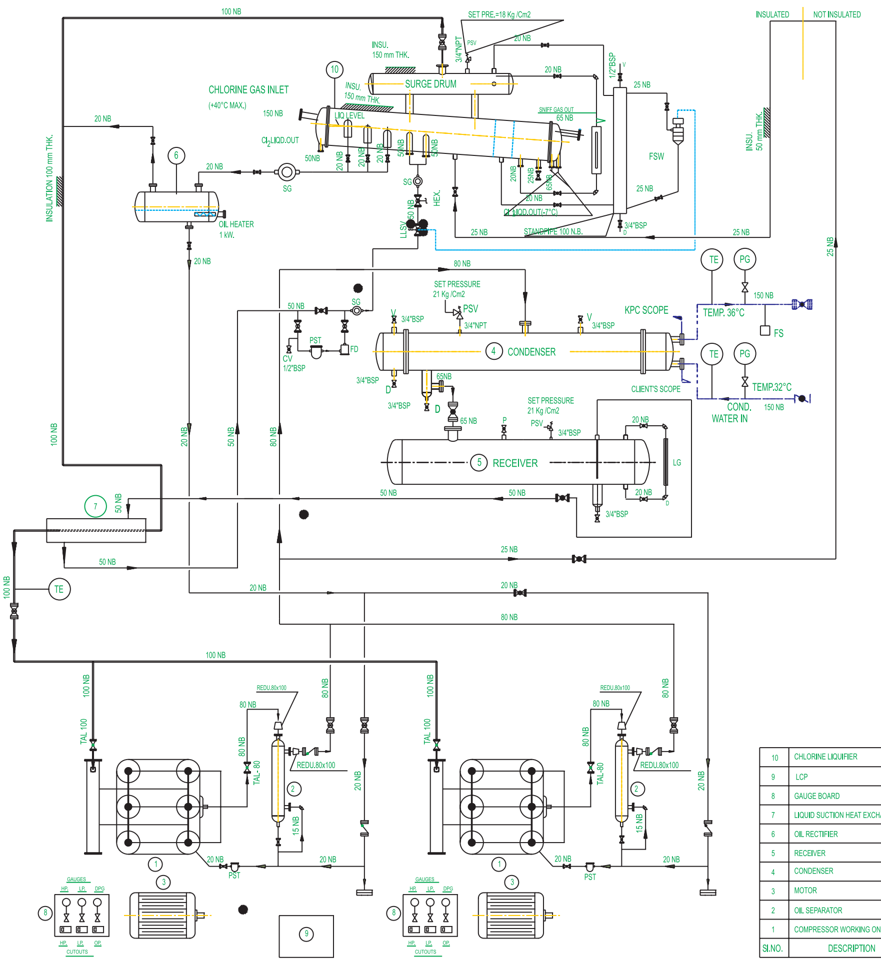
After the gas is compressed, it goes to a scrubber where entrained acid and other organic material is removed. The scrubbing process is very important, as the "clean gas" entering the liquefier will decide the maintenance aspects and cleaning frequencies of the liquefier on the chlorine side.

Liquefaction

The strong gas coming out after the compression and scrubbing is not 100 percent chlorine, but contains inerts

continued on page 98

continued from page 96



SI.NO.	DESCRIPTION	QTY.
10	CHLORINE LIQUIFIER	1
9	LCP	1
8	GAUGE BOARD	
7	LIQUID SUCTION HEAT EXCHANGER TUBE IN TUBE TYPE	1
6	OIL RECTIFIER	1
5	RECEIVER	1
4	CONDENSER	1
3	MOTOR	1W+1S
2	OIL SEPARATOR	
1	COMPRESSOR WORKING ON R22	1W+1S

Figure 4 : P & I Diagram for Chlorine Liquefaction Plant

and hydrogen in varying quantities. The refrigerating or evaporating temperature will depend upon the "strong gas" composition, pressure and temperature, percentage recovery required and the hydrogen content in the "tail gas" or "sniff gas". If the percentage of non-condensables increases, the evaporating temperature in the liquefier must be decreased for a given percentage recovery.

A typical chlorine gas or "strong gas" composition falls in the following:

Cl_2 97 to 99.5 percent
O_2 0.5 to 2.0 percent
H_2 0.03 to 0.3 percent

Sometimes, percentage of CO_2 and or percentage of inerts (clubbed together) are also given.

The last drop condensation temperature depends upon the percentage recovery expected and of course the pressure of the strong gas and the percentage of non-condensables in the composition. This is shown in *Figure 3*.

The strong gas enters the shell and tube liquefier, either horizontal or vertical, mostly flooded but sometimes DX, gets cooled (or desuperheated) and then gets liquefied and subcooled. The strong gas is a mixture of two or three components and only chlorine will condense at the evaporating / condensing temperature at its partial pressure. The other components such as H_2, CO_2 or inerts will only get sensibly cooled from the initial mixture temperature to the final Cl_2 condensation temperature without undergoing any change of phase, at their corresponding partial pressures. p-h, t-s, t-h or any other Mollier diagram or tables for each of the components are to be used for finding out the enthalpies at their respective partial pressures.

Chlorine will condense at its saturation temperature at the partial pressure of chlorine. Majority of the chlorine will condense at the higher portion of the condensation temperature range. The last drop condensing temperature is very low and the majority of the gas condenses at the average temperature and gets sub-cooled. The last drop condensing temperature determines the purity of the "tail gas" or "sniff gas" and hence the percentage recovery. The liquefied chlorine goes to storage (weight) tanks or goes to cylinders and tonners to be despatched to various end users.

Refrigeration Cycle and Equipment for Liquefaction

Here, in the complete cycle, chilled water is used for cooling the chlorine gas. The chilled water at about 10°C (50 °F) is used from standard or built-up packaged chillers operating with either halocarbons or ammonia. Depending upon the TR capacity of the requirements, reciprocating, screw or centrifugal packaged chillers can be used. Since chlorine is an industrial product and its manufacture is therefore located in an industrial area and not in a residential area, ammonia will be the preferred refrigerant but considering the explosive nature, if mixed with chlorine, in case of leakages, so far refrigerants such as R-22 or its HFC equivalents are used.

Liquefaction Cycle

The refrigeration system for actual chlorine liquefaction consists of field-installed components such

continued on page 100

continued from page 98

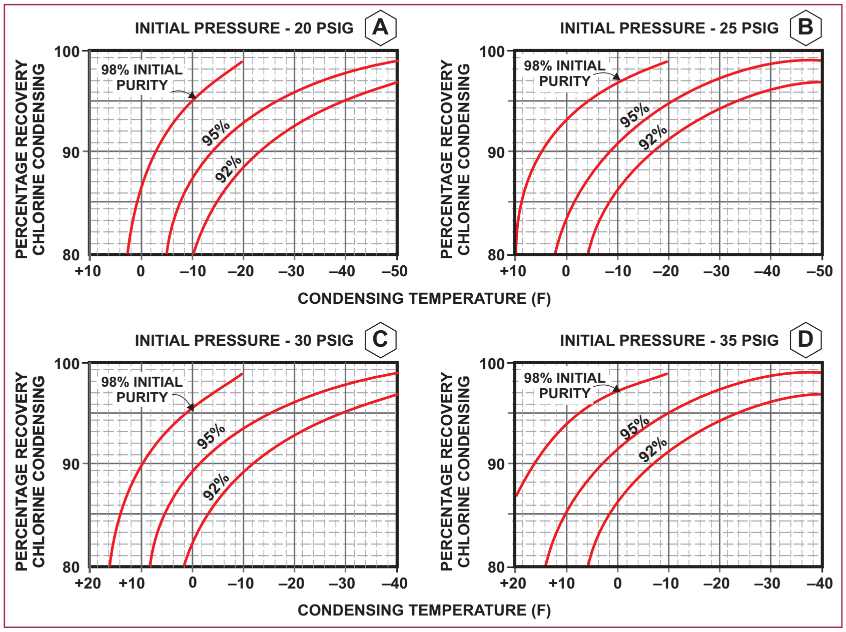


Figure 5 : Graphs to Determine Cl_2 Condensation Temperature

as compressor, condenser, receiver, shell and tube horizontal or vertical liquefier, controls, accessories and piping. A typical P& I diagram for such a system is shown in *Figure 4*.

To select the above components the refrigeration tonnage capacity and evaporating and condensing temperatures have to be established.

Based on the strong gas pressure and initial purity and percentage recovery required the condensation temperature of liquid Cl_2 can be found by referring to the four graphs as shown in *Figure 5*.

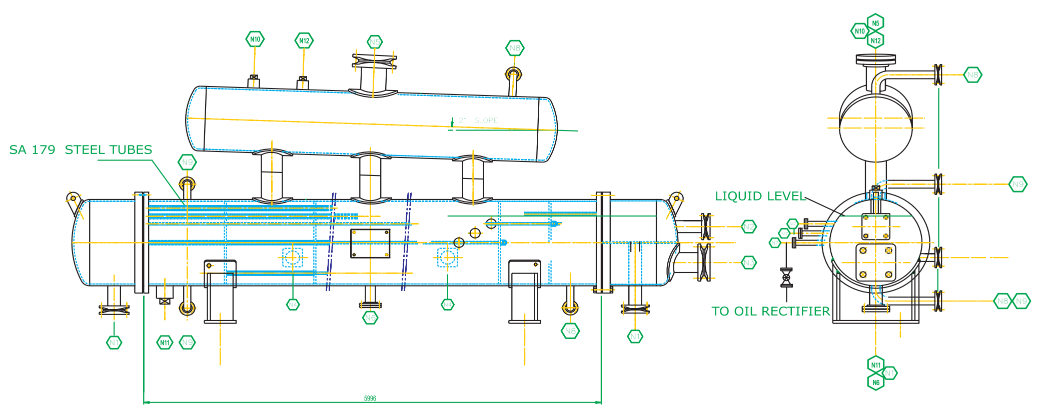
After the condensing temperature for chlorine is determined, the evaporating temperature is selected by keeping a terminal temperature difference of about 6°C to 9°C (15°F to 20°F) between the chlorine condensing temperature and evaporating temperature.

Based on the mixture of the components of the strong gas, the cooling load can be determined for each of the components at their respective partial pressures. The only condensation load will be that of chlorine, plus of course the sensible cooling in desuperheating and sub-cooling plus the individual components cooling (only sensible) from the mixture temperature to the liquefaction condensation temperature at their respective partial pressures. Then by adding a suitable factor of safety, of say about 10 percent, the total load is calculated. As a rule of thumb, about 1 to 1.2 TR per TPD of liquid chlorine is taken as the refrigeration load. If the exact analysis of gas is known and if the flow is accurate and if all other data is accurately known then 1 TR per TPD may suffice. Otherwise, it is safer to take about 1.1 to 1.2 TR / TPD.

In case of large capacities and large variations in the mixture components, it is advisable to do the calculations for cooling load from first principles otherwise, in most cases the rule of thumb works just fine.

Selection of Components

Once the capacity TR and evaporating temperature are determined, the components of the system are to be selected.



NOZZLE SCHEDULE

NOZZLE	QTY	SERVICE
N1	2	CL2 LIQUID OUTLET
N2	1	SNIFF GAS OUTLET
N3	1	CL2 GAS INLET
N4	2	R22 LIQUID INLET
N5	1	R22 GAS OUTLET
N5	1	R22 GAS OUTLET
N6	1	R22 HOT GAS INLET
N7	3	OIL DRAIN
N8	2	STAND PIPE
N9	2	LEVEL GAUGE
N10	1	SAFETY VALVE

NOZZLE	QTY	SERVICE
N11	1	DRAIN
N12	1	VENT

NOTE
LIQUEFIER IS INSTALLED IN SUCH A WAY THAT THE SURGE DRUM WILL BE HORIZONTAL AND LIQUEFIER TILTED BY 2 DEG

Figure 6 : Horizontal Shell and Tube R-22 Flooded Chlorine Liquefier

continued on page 102

continued from page 100

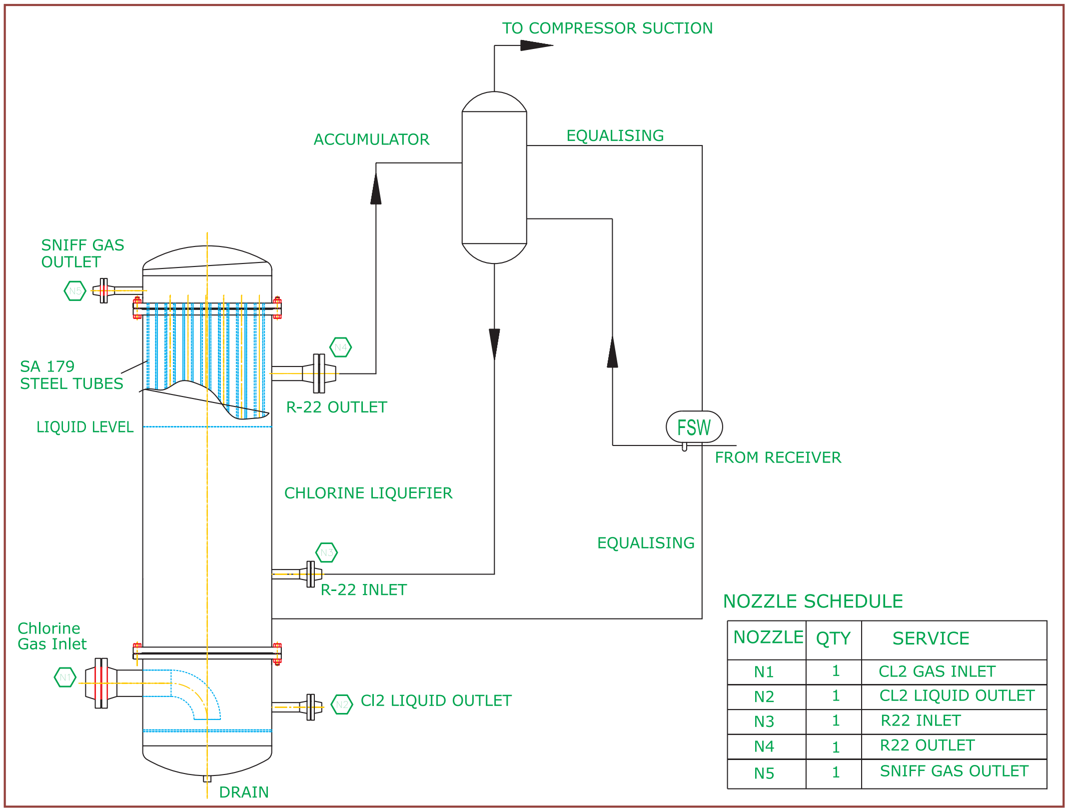


Figure 7 : Vertical S&T R-22 Flooded Chlorine Liquefier

and more elaborate articles are published and can be referred to.

Condensers

Normally, shell and tube, horizontal vessels are selected with copper tubes having 26 FPI integrally finned tubes. The water flow is based on 4°C Dt (7~7.5°F) across the condenser inlet and outlet. The number of passes are selected for a water velocity of around 1.8 to 2.1 m/sec (6 to 7 fps) through the tubes. Sometimes PHE type of condensers can be selected based on other considerations of space etc. The condensers should be checked for pull down conditions. At the start of the system, the compressor operates at a higher evaporating temperature giving higher capacity and consuming higher power. Condensers should be sized by taking into consideration the load at start up and the load at final conditions.

Compressor

Usually for small and medium capacity liquefaction plants, reciprocating compressors are used. They are quite economical in both the first cost and the running cost. For capacities of 200 TPD or more, generally screw compressors can be considered but never select one 100 percent compressor unless one 100 percent standby is also planned. It is better to select two numbers of 50 percent capacity with one additional standby compressor. This combination gives the optimum selection. For industrial, continuous duty application, twin screw compressors are preferred over mono-screw, which are normally restricted for air conditioning duties.

For selection of reciprocating compressors, separate

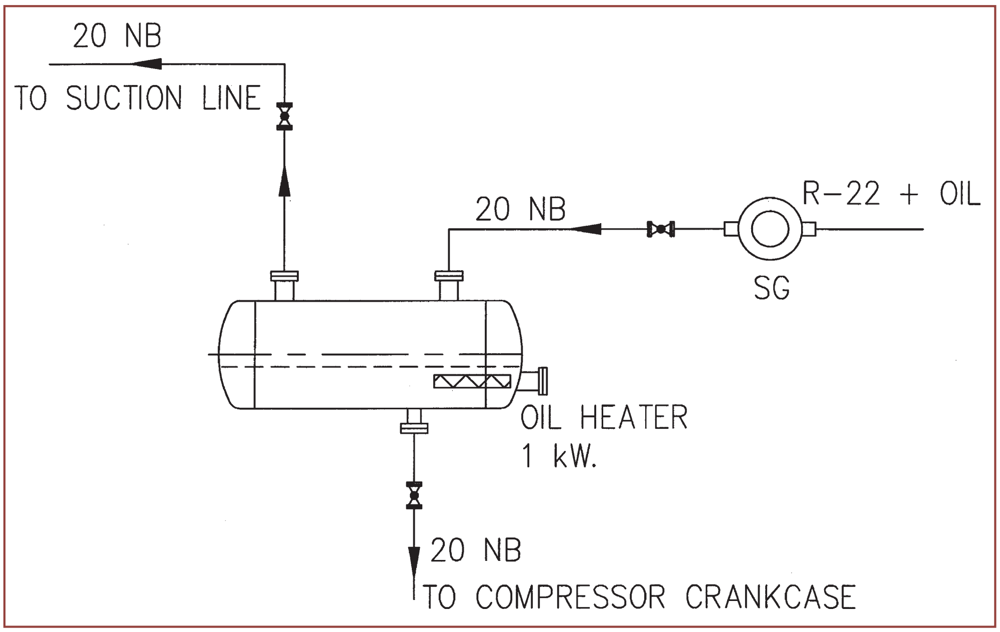


Figure 8 : Oil Rectification System

continued on page 104

continued from page 102

Receiver

The receiver is selected after the liquefier selection is done. The receiver must be capable of holding the full charge in the system and should not be more than 80 percent full when it holds the full charge.

Liquefier

The liquefier is of the shell and tube type. Generally, R-22 is still used in India in almost all such applications. R-22 is an HCFC and will be banned after 2040 in India. The other probable substitutes for R-22 are R404A, R410A, R407C, R507A etc. The most promising of these seems to be R404A since it has a very low temperature glide of 0.5°C (1°F) and acts almost like an azeotrope, although strictly speaking it is a zeotrope. R407C has a large glide and R-410A has high pressures. In some cases, R-134a may also be used but the compressor size will go up by about 40 percent as compared to R-22 and hence becomes costly.

Shell & Tube Liquefiers

The shell and tube liquefiers used in these applications are mostly horizontal flooded type. For capacities of about 20,30 to 40 TPD, 3/4" OD, 14 gauge, steel tubes conforming to SA 179 are used. For medium capacities of upto 100 TPD, 1" OD, 12 gauge, SA 179 and for large capacities above 100TR, 1-1/4" OD, 10 gauge SA 179 steel tubes are almost standard.

The flooded horizontal vessels are installed at an inclination of about 2° to 3° so that chlorine condensed in the tubes can be drained easily. The flooded vessels are provided with a surge drum directly mounted on the top of the liquefier, so that no liquid slop-over to the compressor takes place. The shell and tube liquefiers are manufactured to meet the TEMA B or C class and sometimes the TEMA-R class as well.

Chlorine gas inlet, liquid outlet, sniff gas outlet refrigerant liquid inlet, hot gas outlet etc. and a general outline of a typical horizontal shell and tube liquefier with surge drum is as shown in *Figure 6*.

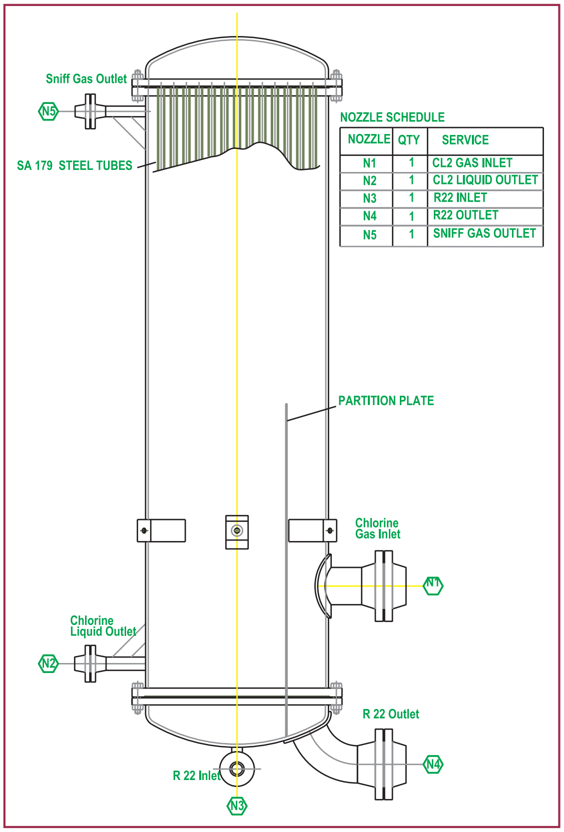


Figure 9 : Vertical DX R-22 Chlorine Liquefier

Shell & Tube Vertical Liquefier

When space is a problem, sometimes vertical liquefiers are used. They are also flooded vessels and the liquid refrigerant levels in the shells are about 65 to 70 percent of shell diameter in case of horizontal vessels and a height of about 65 percent to 70 percent in case of vertical design. A typical vertical flooded liquefier is shown in *Figure 7*.

The oil separation in R-22 flooded vessels is a tricky job and proper oil rectification systems are to be incorporated otherwise the efficiency of the chiller drops down over a period of time as the oil concentration goes on increasing in the chiller. The oil rectification system is shown in *Figure 8*.

The horizontal flooded liquefier is more efficient than a vertical flooded vessel. These are generally designed on the basis of a 'U' value of about 35 Btu/ hr sq.ft°F for horizontal and 25 Btu / hr sq.ft °F for vertical chillers. The 'U' value for vertical DX liquefier will be in the region of 20 Btu / hr sq.ft°F.

DX-Liquefier

The oil rectification in flooded R-22 chillers has to be correctly designed and operated. The liquid level must be properly maintained, otherwise no oil-rich mixture will be drawn and oil will get accumulated in the system with loss in the compressor sump. To eliminate the problem of proper oil recovery, sometimes a DX vertical liquefier is used. The 'U' value for these is lower than those that are flooded. A typical vertical DX R22 liquefier is shown in *Figure 9*.

Chlorine liquefiers whether DX or flooded and whether horizontal or vertical are always installed at a higher elevation so that draining of liquid chlorine is easy and also installation of oil recovery system is possible.

Conclusions

Chlorine is one of the most useful industrial products and its usage is increasing day-by-day. Future units will use new HFC substitutes such as R-134a or R-404A.

Reference

Carrier Industrial Process Refrigeration, Carrier International, USA.