Sulfur—all forms	11.4	9.8	6.7	5.1	0.9	1.5
—Frasch	5.0	0.9	-	4.4	-	-
—Native (mined)	-	1.7	-	0.5	0.3	-
—Pyrites	withheld	3.4	-	-	0.2	0.3
—By-products*	6.4	3.8	6.7	0.2	0.4	1.2
	(C,N)	(N)	(N)	(M)		(M,C)

*Primarily: N = natural gas, M = metallurgy, C = crude oil

Source: *“Industrial Inorganic Chemistry”* by *Buchner et al (1989)*

Sulfuric Acid

1. Pertinent Properties of Sulfuric Acid

- Pure 100% H_2SO_4:

Mol. wt. 98.08 M.P. 10.5°C B.P. 340°C (decomposition)

Solubility: Completely miscible with H_2O with large heat of solution. SO_3 soluble in H_2SO_4 to give varying percentage of oleum.

- Grades of acid

Grades of acid	%H_2SO_4	Sp. gr. at 18°C
50° Be (Fertilizer acid)	62.2	1.525
60° Be (Oil of vitriol)	93.2	1.833
95% acid	95.0	1.840
98% acid	98.0	1.843
Monohydrate acid (H_2SO_4)	100.0	1.834
20% oleum (fuming)	104.5—20% Free SO_3	1.924
40% oleum (fuming)	109.0—40% Free SO_3	1.963
65%	114.6—65% Free SO_3	1.987

2. Methods of Production

2.1. Classification of Processes

- Contact process
- Chamber process

Both processes are based on SO_2. Chamber process was developed first (1746) but produced acid of concentration less than 80%. Contact process yields 98% H_2SO_4 and higher which can be diluted, if necessary. Chamber process is virtually obsolete.

2.2. Contact H_2SO_4 Process

2.2.1. Reference flow sheets: Figures ID-1, IIA-4

2.2.2. Chemical reactions

(a) $S(s) + O_2(g) \rightarrow SO_2(g)$; $\Delta H = -70.9$ Kcal

(b) $SO_2(g) + \frac{1}{2}O_2(g) \overset{V_2O_5}{\rightleftharpoons} SO_3(g)$; $\Delta H = -23.0$ Kcal

2.2.3. Raw materials

- SO_2 is obtained from the following sources:

	W. Europe	USA
(a) Sulfur	47	82
(b) Pyrites	35	2
(c) CuS, ZnS, PbS, MoS_2	17	1.5
(d) Waste H_2SO_4	7	5.6
(e) H_2S sources		

(a) Sulfur source
Combustion yields very pure SO_2 which requires only filtration and drying.

(b) Pyrites source
Iron pyrites containing 40-45% S are roasted and must be purified by dust removal, cooling, scrubbing, filtering and drying by conc. acid scrubbing to remove dust, moisture, and catalyst poisons (As, Cl, F).

(c) Smelter sources
SO_2 obtained by roasting non-ferrous sulfide ores such as zinc, lead, and copper; given same treatment as pyrites gas. (See Chapter VI on Metallurgical Industries for further information.)

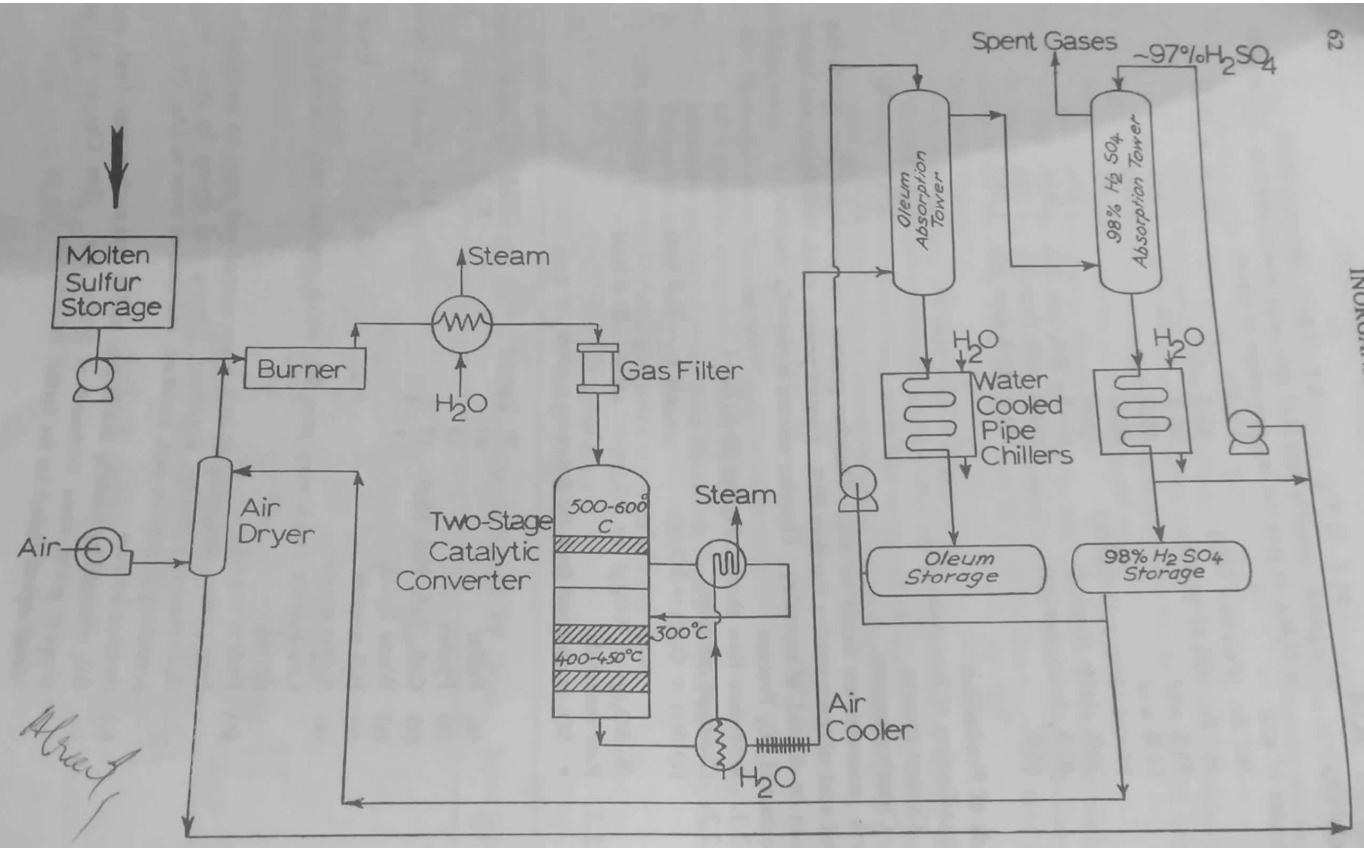

Fig. IIA-4. Simplified engineering flow sheet for manufacture of sulfuric acid and oleum by contact process.

(d) Waste H_2SO_4
$FeSO_4$ from iron and steel pickle liquors and H_2SO_4 from petroleum refinery operations are roasted to recover SO_2.

(e) H_2S sources
H_2S is recovered by scrubbing various fuel and refinery gases with ethanolamines followed by hot stripping. The sulfide gas is burned as in reaction 3.3.2(a) under Sulfur.

- Catalyst
  Most widely used catalyst is vanadium pentoxide dispersed on a porous carrier in pellet form. Platinum catalyst was previously used but suffers from easy poisoning, fragility, rapid heat deactivation, high initial investment.

* Characteristics of catalysts

(1) *Porous carrier* having large surface area, controlled pore size, and resistance to process gases at high temperature: in pellet form if used in fixed beds, powdered form for fluidized beds. Examples—alumina, silica gel, kieselguhr, zeolite.

(2) *Active catalytic agent*—V_2O_5 in this case. Preparations are secret for competitive reasons; usually consist of adding H_2O soluble compounds to gels or porous substrates and firing at temperatures below sintering point.

(3) *Promoter*—alkali, and/or metallic compounds added in trace amounts to enhance activity of catalytic agent.

* Advantages of V_2O_5 catalyst
— Relatively immune to poisons
— Low initial investment and only 5% replacement per year
— Requires only 10 kg of catalyst mass containing 7-8% V_2O_5 per daily ton of 100% acid

* Disadvantages of V_2O_5 catalyst
Must use dilute SO_2 input (7-10%); as catalyst is less active and requires high O_2/SO_2 to give economic conversion. Larger converters and higher initial investment are necessary.

2.2.4. Quantitative requirements

(a) Basis: 1 ton of 100% H_2SO_4

SO_2	0.67 ton
Air	1,450-2,200 Nm^3

(b) Plant capacities: 50-1,000 tons/day of 100% acid

2.2.5. Process description

Air-SO_2 gas containing 7-10% SO_2 and 11-14% O_2 is preheated by converter gas, if necessary, and sent to first stage reactors of steel construction. This is the high temperature (500-600°C) stage, contains 30% of total catalyst and converts about 80% of SO_2. The converter product is cooled by heat exchange at 300°C and fed to a second stage where total yield is increased to 97% by operating at 400-450°C for favorable equilibrium.

High yield product gases are cooled to 150°C by water and air heat exchangers and absorbed in oleum fed at a rate to allow not over a 1% rise in acid strength. Final scrubbing is done with a lower strength (97%) acid. Oleum concentrations up to 40% can be made by tower absorption. Higher strength oleum up to 65% is prepared by distilling 20% oleum.

2.2.6. Major engineering problems

(a) Design of multistage catalytic converter for a highly exothermic reaction: Some designs contain 3 or 4 stages rather than the conventional two-stage operation for large capacity plants. For equilibrium design information, see Table IIA-2 and Figure IIA-5.

(b) Optimization of space velocity in catalyst chamber: Pumping costs versus fixed charges of reactor.

(c) Corrosion problems: Optimization studies show that equilibrium yield can be increased by square root of system pressure p_T at a given temperature:

$$Y_{SO_3} = K_p Y_{SO_2} \cdot (Y_{O_2})^{1/2} \cdot (p_T)^{1/2}$$

but increasing compression costs & corrosion problems dictate low pressure (1 atm.) operation.

(d) Adaptation of process to various types of gas feeds.

(e) As the result of considering problems (a) and (b) above, thin catalyst beds result (30-50 cm height). Yield can drop due to longitudinal mixing if the convective gas velocity through the bed is too low.

(f) Removal of heat of absorption of SO_3 in acid. Pipe coolers with water dripping over external surface have been replaced by cast iron pipe with internal fins to promote better heat transfer. Pressure drop must be low so 8 cm stacked packing is often used.

Table IIA-2 Thermodynamic Data for SO_2 Oxidation

$$\text{Basis:}\quad K_p = \frac{P_{SO_3}}{P_{SO_2} \cdot (P_{O_2})^{1/2}} = \frac{Y_{SO_3}}{Y_{SO_2} \cdot (Y_{O_2})^{1/2} \cdot (p_T)^{1/2}}$$

Temperature		*Heat Evolved*	K_p
°K	*°C*	*Kcal/g mole.*	
600	327	23.42	4,170
700	427	23.27	257
800	527	23.08	32.0
900	627	22.87	6.47
1,000	727	22.63	2.03

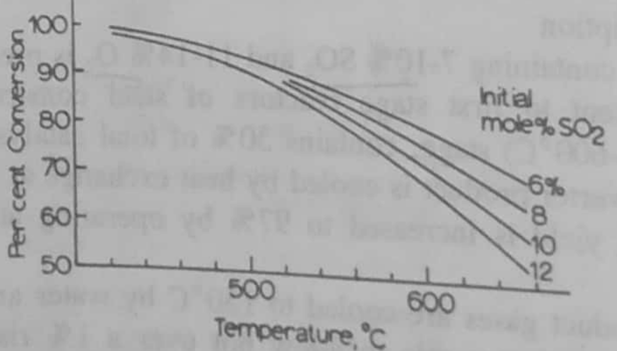

Fig. IIA-5. Equilibrium conversion versus temperature data for $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$ at 1 atm pressure.

HYDROCHLORIC ACID

INTRODUCTION

Hydrochloric acid (HCl), also known as muriatic acid, is a solution of hydrogen chloride in water. HCl exists in solid, liquid, and gaseous states and is water soluble in all proportions.

The first hydrochloric acid was prepared through heating common salt and sulfuric acid by Benedictine Monk and Basil Valentine in 15th century. Also, Libavius prepared free hydrochloric acid by heating salt in clay crucibles in 16th century.

In the 17th century, Johann Rudolf Glauber used NaCl and H_2SO_4 for the preparation of sodium sulfate in the Mannheim process, releasing hydrogen chloride gas as a by-product. Joseph Priestley prepared pure HCl in 1772, and chemical composition includes hydrogen and chlorine was proven by Humphry Davy in 1818.

Demand for alkaline substances increased during the Industrial Revolution in Europe, Nicolas Leblanc developed cheap large-scale production of sodium carbonate (soda ash). Using common salt, sulfuric acid, limestone and coal which release HCl as a by-product. Until the British Alkali Act 1863 and similar legislation in other countries, the excess HCl was vented to air. After the passage of the act, waste gas is absorbed in water, producing hydrochloric acid on an industrial scale.

In the twentieth century, the Leblanc process was effectively replaced by the Solvay process without hydrochloric acid by-product. Since hydrochloric acid was already fully settled as an important chemical in numerous applications, the commercial interest initiated other production methods, some of which are still used today. After the year 2000, hydrochloric acid is mostly made by absorbing by-product hydrogen chloride during a chemical manufacturing process such as chlorination of hydrocarbons.

Since 1988, hydrochloric acid has been listed as a Table II precursor under the 1988 United Nations convention against illicit traffic in narcotic drugs and psychotropic substances because of its use in the production of heroin, cocaine, and methamphetamine.

MANUFACTURE

HCl is manufactured by various methods as follows

1. Synthesis from hydrogen and chlorine
2. From salt and sulfuric acid
3. As by-product from chemical processes
4. From incineration of waste organics
5. Hydrochloric acid solutions

1. Synthesis from Hydrogen and Chlorine

There is large demand in the market for water white acid. Such acid is obtained by synthetic method, and most of the plants are based on this process.

Raw materials

Basis: 1000kg of Hydrochloric acid (98% yield)
Hydrogen = 28.21kg
Chlorine = 999.21kg

Sources of raw material

Both hydrogen and chlorine can be obtained during electrolysis of brine for manufacturing of NaOH as described in Module: 3, Lecture: 13.

Also, hydrogen can be synthesized from any one methods of following which are described in detail in Module: 2, Lecture: 4.

1. Lane process or iron steam process
2. Steam hydrocarbon process
3. Liquefaction of coal gas and coke oven gas
4. Bosch process or water gas-steam process

Reaction

$H_2 + Cl_2 \longrightarrow 2\ HCl \qquad \Delta H = -\ 43.9 kcals$

Manufacture

Block diagram of manufacturing process

Diagram with process equipment

Animation

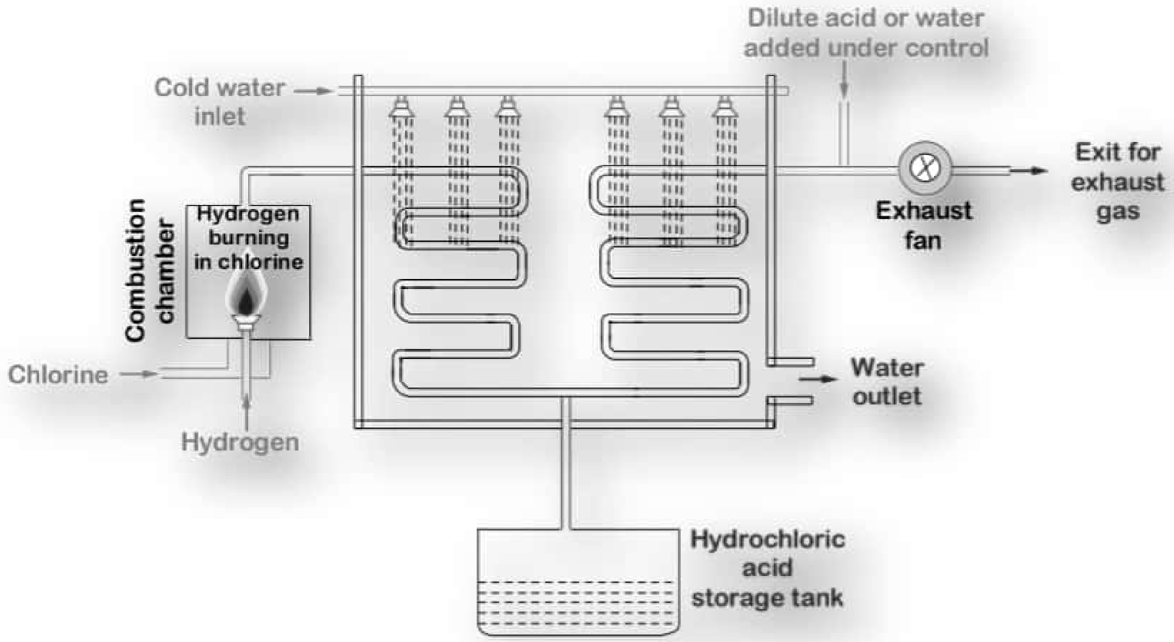

Figure: Manufacturing of Hydrochloric acid from hydrogen and chlorine combustion

The plant consists of combustion chamber of structural carbon or lined with silica bricks provided with cooling device which may consist even of cold-water circulation in the shell. To ensure all the chlorine reacts with hydrogen, excess of 10% hydrogen compare to chlorine is charged from the bottom of combustion chamber. Also, care should be taken that the combustion chamber and length of ducting which leads the gas to absorber should be sufficiently specious, otherwise hydrochloric acid will contain free chlorine. The burning of hydrogen is started by igniting the burner with an external air-hydrogen torch. Dry chlorine is passed into the combustion chamber, where hydrogen burns in an atmosphere of chlorine to produce HCl. The exothermic nature of the direct combination of both gases (H_2 and Cl_2) is such as to raise the temperature of the reagents, and the reaction products to a point where they are incandescent. The reaction is carried out at 2400^0C with greenish flame. The gases are always kept above dew point to avoid corrosion. The combustion chamber is then cooled externally by water and gas tight lid is fitted at the top of the reactor which suddenly opens to allow the gases to escape in case of emergency. Hydrochloric acid gas is cooled absorbed in water or dilute HCl solution by passing through cooler and absorber through the connecting pipe. The strength of acid produced is generally 32-33 %. The heat of absorption of HCl in water is removed by spray of cold water outside the absorber. The solution of HCl flows into a storage tank.

Anhydrous hydrogen chloride

Hot gases originating from combustion chamber are passing over anhydrous $CaCl_2$ or washing them with 98% sulfuric acid and then cooled and compressed to 60atm pressure. The cooled and compressed gas having 99.9% purity is filled in steel cylinders.

In another process, absorb the combustion gas into water and distilled it to 36% concentration of HCl. If one is to obtain 97% HCl at the top of the column. The 35% acid is cooled to -12^{0}C and aqueous liquid containing 50% HCl is left to condense, while residual gases, when they have been de nebulized as compressed to 60atm are of purity exceeding 99.5%.

Thermodynamics and kinetics

$$H_2 + Cl_2 \longrightarrow 2HCl \qquad \Delta H = -44\,kcal$$

Above exothermic reaction is much favoured by both by large evolution of energy and the product gas leaving the chamber, thereby circumventing the fact that equilibrium would otherwise be attained. The very fact that equilibrium is not established also precludes the large increase in temperature from having a negative effect on the yield of highly exothermic reaction.

On account of the existence of large energy barrier to the reaction, mixture of molecular H_2 and Cl_2 is stable at ambient temperatures and in absence of suitable wavelengths. Photons with frequencies which are able to furnishing the activation energy can be produced by creating an electrical spark in a mixture of molecular H_2 and Cl_2 or by first burning mixture of H_2 with air and then gradually replacing air with chlorine.

The initiation, propagation and termination of the chain reactions are as follows

Initiation

$Cl_2 + h\upsilon \longrightarrow 2Cl^{\cdot}$

Propagation

$Cl\bullet + H_2 \longrightarrow HCl + H^{+}$

$H\bullet + Cl_2 \longrightarrow HCl + Cl\bullet$

Termination

$Cl\bullet + Cl\bullet \longrightarrow Cl_2 + \text{heat}$

$H\bullet + H\bullet \longrightarrow H_2 + \text{heat}$

$H\bullet + Cl\bullet \longrightarrow HCl + \text{heat}$

A large amount of heat is developed both from chain propagation reactions and from chain termination processes, the continued renewal of the chain propagators by thermal route is ensured over the long term. In brief reaction between hydrogen and oxygen to produce hydrogen chloride is a chain reaction with a high quantum yield.

[redacted]

Engineering aspect

The combustion chamber and ducting to absorber should be sufficiently specious for avoiding wall effect. From physicochemical point of view if the walls of reactor in which chain reactions takes place by their varying nature, development, shape and orientation as to affect the chain carriers is called wall effect. In the present case wall tends to interrupt the process by promoting the chain breaking reaction (termination reactions). Physico chemically, chain terminators act as a third body in a system which already consists of the reactant bodies.

2. The Salt–Sulfuric acid process

The reaction between NaCl and sulfuric acid occurs in two endothermic stages.

Raw materials

Basis: 1000kg Hydrochloric acid
Sodium Chloride = 3206kg
Sulfuric acid = 2688kg

Sources of raw material

Sodium chloride can be obtained from sea water, salt lake and sub –soil water as described in Module: 3, Lecture: 8.

Sulfuric acid can be obtained by contact process as described in Module: 4, Lecture: 18

Reaction

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$$
$$NaCl + NaHSO_4 \longrightarrow Na_2SO_4 + HCl$$

Manufacture

Block diagram of manufacturing process

Diagram with process equipment

Animation

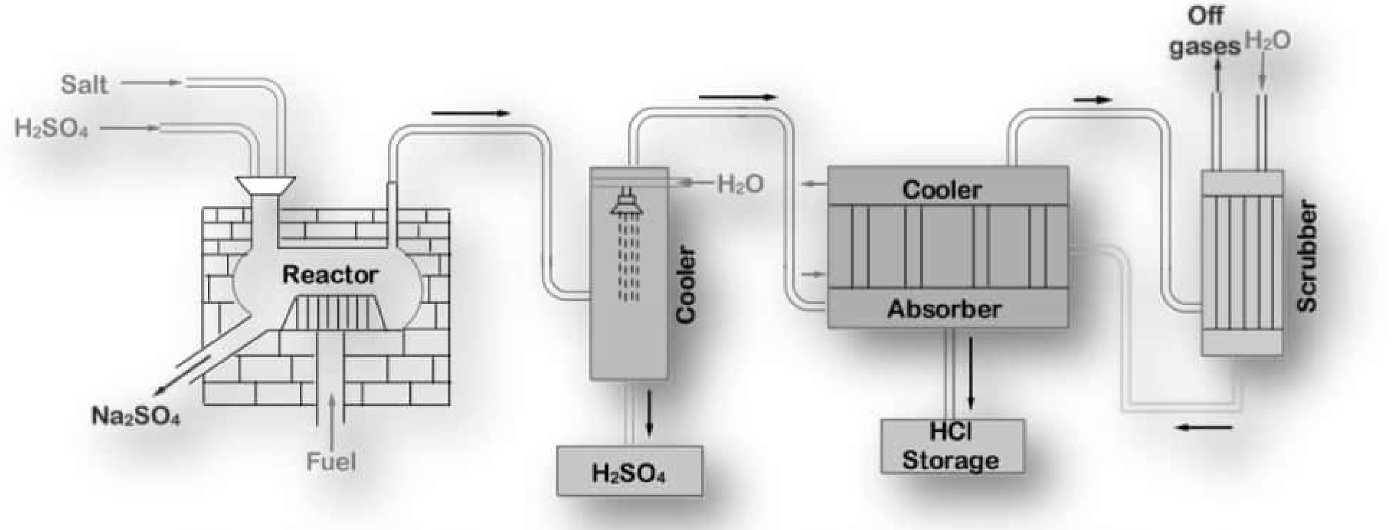

Figure: Manufacturing of Hydrochloric acid from salt and sulfuric acid

Salt (NaCl) and sulfuric acid are charged to the furnace. It is desirable to keep one of the components in the reaction mixture in a liquid form in both steps. The first step is carried out at the lower temperature compare to second step. Even so, for liquefaction of $NaHSO_4$, which is required to carry out in second step, material is heated up to 400^0C. Sodium sulfate in form of sludge is collected from the bottom of the furnace. The product and unconverted sulfuric acid is sent to further processing in which recovery of sulfuric acid and nitric acid in cooling tower and absorber respectively.

3. As by-product from chemical processes

Over 90% of the hydrogen chloride produced as a by-product from various chemical processes. The crude HCl generated in these processes is generally contaminated with impurities such as unreacted chlorine, organics, chlorinated organic and entrained catalyst particles. A wide variety of techniques are employed to treat these HCl streams to obtain either anhydrous HCl or hydrochloric acid. Some of the processes in which HCl is produced as by-product is the manufacture of chlorofluorohydrocarbons, manufacture of aliphatic and aromatic hydrocarbons, production of high surface area silica, and the manufacture of phosphoric acid and esters of phosphoric acid.

4. From incineration of waste organics

Environmental regulations regarding the disposal of chlorine-containing organic wastes have motivated the development of technologies for burning or paralyzing the waste organics and recovering the chlorine values as hydrogen chloride. Several catalytic and non-catalytic processes have been developed to treat these wastes to produce hydrogen chloride.

5. From hydrochloric acid solutions

Gaseous hydrogen chloride is obtained by partially stripping concentrated HCl acid using an absorber–desorber system. The stripper is operated at a pressure of 100–200kPa (1–2atm) for improved recovery of HCl. The overhead vapors consisting of 97% HCl and 3% H_2O is cooled to remove most of the water as concentrated HCl, and the residual water vapor is removed by drying the gas with sulfuric acid.

PROPERTIES

- Molecular formula : HCl
- Molecular weight : 36.5gm/mole
- Appearance : Colourless liquid
- Odour : Pungent
- Boiling point : -85^{0}C
- Melting point : -114^{0}C
- Density : 1.179gm/mL (35.2% HCl)
- Solubility : Extremely soluble in water
- Water solubility depends on temperature. At 760mmHg (1atm) pressure 1liter of water dissolves 525.2 liters of HCl at 0^{0}C (46.15%w of HCl) and at 18^{0}C, 451.2 liter of HCl are dissolved (42.34%w of HCl).
- Forms azeotropic mixture with water, containing 20.24% HCl which boils at 110^{0}C.
- Commercially available in 27.9%, 31.5% and 35.2%wt HCl solution in water.
- Anhydrous HCl is available in steel cylinders because completely dry HCl is not very reactive. But dry HCl often reacts only in the presence of catalysts.
- Solution of hydrogen chloride in a polar solvent is strong acid and, therefore, an aggressive reagent.

USES

Hydrogen chloride and the aqueous solution, muriatic acid, find application in many industries.

- Anhydrous HCl is consumed for its chlorine value, whereas aqueous hydrochloric acid is often utilized as a non-oxidizing acid.
- Used in metal cleaning operations, chemical manufacturing, petroleum well activation, and in the production of food and synthetic rubber.
- Used for the manufacture of chlorine and chlorides, e.g. Ammonium chloride used in dry cell.
- In the manufacture of glucose from corn starch.
- For extracting glue from bones and purifying boneblack.
- A saturated solution of zinc chloride in dilute HCl is used for cleaning metals before soldering or plating.