Chlorinated Hydrocarbon Waste Recovery and Pollution Abatement

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ABSTRACT

The rapid expansion in the production of chlorinated organics (e.g., carbon tetrachloride, vinyl chloride, perchloro and trichloroethylene) has resulted in large quantities of chlorinated organic waste being created at such plants. This poses a threatening problem for review by the process industries. Waste recovery methods have been proposed and then rejected because it is less expensive to dump the wastes (thereby polluting the streams and air) than to process them. Anti-pollution regulations have been enacted in many locations and are being proposed in others to prohibit this dumping. These recovery processes now start to make very good economic sense. Various methods for disposal and recovery of the chlorinated hydrocarbon wastes will be discussed in this paper.

FOREWORD

With the advent of synthetic materials replacing many items in all areas of domestic, commercial and industrial applications, many new plants and processes have sprung up over the last 20 years for the production of these materials. This is technological progress since these new materials are non-corroding, more easily maintained and produce a better appearance than materials which were formerly used. With each step forward, we often create new problems of pollution. One major source of pollution is the process plant itself. The waste materials being generated create new challenges to technology for their disposal. We will discuss in this presentation the problems created by waste chlorinated hydrocarbons. These wastes are generated in the following types of plants:

(1) Acetone,
(2) Vinyl Chloride Monomer,
(3) Caprolactum,
(4) Acetaldehyde,
(5) Chloroprene, and
(6) Carbon Tetrachloride.

In the production of these products chlorine reacts with organic chemicals such as acetylene, benzene, ethylene, methane or toluene to make intermediates that can be used in paints, plastics, synthetic rubber, herbicides, dry cleaning agents, soaps and the like. In producing intermediate chemicals, however, side-reactions take place during chlorination. Since the products of the side-reactions are undesirable impurities in the customer's final product, they must be removed [1-3].

In former days, such waste – in limited amounts – could be easily disposed of by incineration, used for land reclamation, or discarded in the deep sea. It is now industry's responsibility to the community to formulate a more effective method for disposal. Conventional incineration is costly and creates air pollution. Highly chlorinated residues do not support combustion in conventional incinerators. High performance burners or furnaces are required. Auxiliary fuel may be necessary dependent upon the heating value of the waste material [4].

If an ineffective incineration system is used, exhaust gases containing unburnt organics will enter the recovery system producing a black acid and the eventual black smoke out of the stack. This is caused by low temperatures which result from incomplete combustion. This will also permit free chlorine to form at these lower temperatures which will pass through the scrubbing system into the atmosphere.
NITTETU PROCESS

The Thermal/Nittetu system described in this paper is based on the Thermal Vortex burner for the incineration process and the Sub-X (submerged exhaust) system for quenching the exhaust gases by direct contact of the gas with liquid. The submerged exhaust system quenches hot gases without the need for heat exchanger surface [5].

The products of combustion of this system contain HCl gas at temperatures of 2730 F to 3000 F. These gases are contained in refractory lined vessels prior to entering the quench tank. In the quench tank these HCl gases are partially absorbed at the same time that they give up their heat to the liquid.

With this system it is possible to recover hydrochloric acid at a lower concentration than an azeotropic composition (approx. 18 percent) or at a higher concentration than this composition (approx. 35 percent) or even as anhydrous HCl gas (100 percent).

COMBUSTION PRINCIPLES

In the combustion of a waste chlorinated hydrocarbon, hydrochloric acid will be present in the exhaust gases as well as some free chlorine.

An example of such a problem is as follows:

Assume that trichloroethylene (CHCl=CCI2) is to be incinerated. If it is burned with air, it will produce the following reaction:

\[ \text{CHCl}=\text{CCI}_2 + 2\text{O}_2 \rightarrow 2\text{CO}_2 + \text{HCl} + \text{Cl}_2 \]

The HCl formed can be removed by scrubbing with water but relatively insoluble chlorine gas will pass through the water and into the atmosphere. By addition of natural gas or steam, the chlorine can be converted to HCl by the following:

\[ \text{CHCl}=\text{CCI}_2 + 3.5\text{O}_2 + \text{CH}_4 \rightarrow 3\text{CO}_2 + 3\text{HCl} + \text{H}_2\text{O} \]
\[ \text{CHCl}=\text{CCI}_2 + 1.5\text{O}_2 + \text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 3\text{HCl} \]

The effluent HCl can then be removed in a wet scrubber. Because of the low calorific value of trichloroethylene, auxiliary fuel (such as natural gas) is required for complete combustion; the excess CH4 present will effect conversion of the chlorine to HCl.

Fig. 1 shows the relation between the percentage of chlorine content and the heating value of the liquid waste. The liquid waste produced during the processing of vinyl chloride monomer by the oxy-chlorination process contains from 40 to 70 percent chlorine in most cases.

The Thermal Vortex burner will maintain stable combustion without auxiliary fuel with a waste having a heating value between 4500 and 5400 Btu/lb. (2500 to 3000 Kcal/kg) although it varies depending on waste composition. To burn waste containing more than 70 percent chlorine, it is necessary to use auxiliary fuel with the waste to bring total heating value to the level mentioned above.

The equilibrium conditions for chlorine, steam, hydrogen chloride and oxygen is based on the following:

\[ \text{H}_2\text{O} + \text{Cl}_2 \rightarrow 2\text{HCl} + 1/2 \text{O}_2 \]

\[ K_p = \frac{(\text{PHCl})^2}{(\text{PH}_2\text{O})(\text{PCI}_2)^{1/2}} \]

X: EXPERIENCED RESULTS

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**Fig. 1** Heat of combustion of chlorinated hydrocarbon.
The relationship between the equilibrium constant \( K_p \) and temperature is shown in Fig. 2. This illustrates the need for combustion taking place at a very high temperature with almost theoretical air/fuel ratios required. This is not always possible in conventional incineration systems which are of the low-heat release type. With the Thermal Vortex burner the high heat release characteristic permits operation at very near to stoichiometric with essentially complete combustion. This also insures complete decomposition of the organics. Fig. 3 is a cut-away of the Vortex burner. Heat release rates in the burner are in the range of 0.5 to 1.5 million Btu/h/ft\(^3\) [6-7].

The high temperatures create problems with the selection of refractory materials that can be used in this atmosphere. The upper limit of the combustion chamber temperature has been set at 3000 °F (1650 °C). The electric furnace mullite refractories have been used for the combustion chamber lining.

**EXHAUST GAS TREATMENT**

When waste liquids are burned in a furnace with the Thermal high heat release burner under conditions designed to reduce residual chlorine to a minimum, the
Fig. 3 Cross-section of thermal-vortex burner.

Fig. 4 Flow sheet for incineration of chlorinated hydrocarbon waste liquid (neutralization method).
temperature of the gas (containing HCl as the vapor) will range between 2572 F (1400 C) and 3632 F (2000 C). This upper limit sounds unreasonably high but we have had actual experience with a chlorinated waste material whose theoretical flame temperature at stoichiometric fuel-air ratio was at this level. The proof lay in the fact that a 3200 F refractory material actually melted during operation of the unit. Temperature controls have prevented this condition from occurring on future units. It would be hazardous to release this gas without neutralizing the hydrochloric acid vapor or recovering it.

The question then arises as to the economics of disposal or recovery of the liquid waste which is to be treated. This will depend upon the existing conditions at the particular plant before a policy can be established. For example, when treating waste liquid containing 60 percent chlorine, 800 lb/h of waste liquid is an economical borderline for a recovery system.

Neutralization

In most vinyl chloride monomer plants the acidic waste gases and liquids discharged at various points in the process are absorbed in water to produce a dilute hydrochloric acid. This dilute hydrochloric acid is then neutralized [3].

A flow sheet for this type of process is illustrated in Fig. 4. The combustion gases at high temperature are sparged into the liquid through a downcomer tube in the Sub-X quench tank. This figure depicts a basic submerged combustion system (Sub-X) which is essentially submerged exhaust. This is an ideal system for cooling the gases at these high temperatures.

![Flow sheet for neutralization process]

Fig. 5 Cross-section of submerged incinerator.
After the gases are cooled down to temperatures below 212 F (100 C) in the Sub-X tank they flow to the absorption tower where the hydrochloric acid vapor in the gas is scrubbed.

Fig. 5 shows the construction of the Sub-X tank. The downcomer tube is the flow passage between the incineration chamber and the liquid in the quench tank. In this tank a cylindrical weir is installed concentric with the downcomer tube. The gas is sparged into the liquid from the bottom of the downcomer tube. This permits many bubbles to form which will rise and mix with the evaporating water vapor in the annular space between the downcomer tube and the weir.

This creates an air lift effect which moves the liquid over the outer surface of the downcomer tube. The gas and water vapor will be disengaged at the upper end of the annular area. The separated liquid will flow over the top of the weir and circulate into the bottom of the weir through the openings provided.

In passing through the annular space between the weir and the downcomer tube the gas transfers heat to the liquid via the large amount of surface available in the gas bubbles. It has been estimated that 1 ft³ of gas when broken into bubbles of 0.001 in. diameter represent an area of 72,000 ft² of heat transfer surface. The gas is cooled to within 10 F of the liquid discharge temperature. Because of the direct contact between the high temperature gas and the liquid, heat transfer efficiency is almost 100 percent [8].

The boiling point of the liquid in the vessel in the tank is 18 F to 30 F lower than that at atmospheric pressure. This is due to the effect of the partial pressure of the non-condensing gases in the exhaust products from the incinerator, (CO₂ and N₂). In a typical Sub-X system where water is being evaporated this will take place at a temperature of approximately 190 F (88 C).

When incinerating chlorinated hydrocarbon waste liquids the gases produced contain HCl acid as well as a small amount of chlorine. These gases at very high temperatures do not condense in the incinerator proper. The incinerator design is therefore one of high temperature refractories design only. The Sub-X tank containing the downcomer tube presents other problems. The downcomer tube itself which contains these high temperature gases is cooled externally by the rising gas-liquid film. Condensation will occur on the inner face of the tube. Materials must then be selected for two considerations — high temperature and corrosion resistance. This corrosion problem has been solved by the use of graphite downcomer tubes. The high heat transfer co-efficients which are developed on the outside of the tube permit cooling of the downcomer tubes up to the level of the weir overflow point. However, above this point the cooling effect is only by radiation to the colder tank walls and to the surface of the liquid plus conduction through the graphite tube wall. This problem required a more critical analysis and review to enable this tube to operate at the same or very close to the temperatures which occur at its lower end.

Nittetu has developed a special water cooling system in this top zone which has worked out very well [5].

Normally the Sub-X tank walls would never operate above the liquid boiling point temperature. In order to design for ultimate safety and long operation without excessive maintenance, the Sub-X tank has been designed with acid-proof porcelain tiles on the inside backed up with a rubber lining. This has been done to prevent overheating of the tank walls in the event that mechanical failure of the downcomer tube would occur causing hot gases to leak into the tank.

**Absorption**

In the direct contact cooling which takes place in the submerged combustion tank the concentration of hydrogen chloride in the exhaust gases is usually less than 10 volume percent since it is combined with the evaporated water in the tank. This is of course much lower than that of the vapor over the azeotropic mixture in the temperature range of 120 F to 212 F (50 to 100 C). Therefore, it is difficult to recover HCl at concentrations greater than the azeotropic mixture in the absorption tower. The absorber is designed to produce dilute hydrochloric acid of 15 percent to 20 percent concentration which is purged from the absorption tower. In this manner the combustion gases and the hydrogen chloride vapor can be separated.

In order to recover HCl acid at concentrations of 15 percent to 20 percent the absorption process shown in Fig. 6 would be used. The inlet to the absorption tower is usually connected to the outlet from the Sub-X tank. The piping and bottom end of the tower are lined with Fiber Reinforced Plastics (FRP) or rubber. If the unit is to be used for recovery at higher than azeotropic mixtures, the lining is covered with an acid-proof porcelain brick in the piping as well as the bottom portion of the absorber. This is required because of the higher temperatures that would exist. The tower interior is filled with a high performance Tellerette packing made of polyethylene. The number of sections in the absorption tower is dependent upon the percent recovery up to 20 percent required. Liquid is circulated in the individual sections by individual pumps. Fresh water is supplied to the tower top and is allowed to run down through all the sections. Due to the use of the
1. SUBMERGED INCINERATOR
2. ABSORBER
3. HCl SOLUTION RECEIVER
P-1 WASTE LIQUID PUMP
P-2 DIL. HCl SOLUTION CIRCULATING PUMP
P-3 "
P-4 "
P-5 HCl SOLUTION PUMP
B-1 AIR BLOWER

Fig. 6 Flow sheet for HCl recovery process (15-20% HCl recovery process).

Tellerette packing the tower can be designed with a reduced diameter and height over that used with other types of packing. This also permits and maintains the pressure drop to approximately 0.2 in. of water column per foot.

The gas discharged from the tower top is composed primarily of nitrogen, carbon dioxide and water vapor. However, there are also traces of hydrogen chloride vapor and chlorine which pass through the tower and would require further scrubbing. This gas is then scrubbed by an alkaline solution in a tower placed directly above the absorption tower before the gases are discharged to atmosphere. This scrubbing tower is also packed with the Tellerette material. The stack gases contain less than 1 ppm of volume of HCl and 10 ppm by volume of chlorine. This is well within all existing pollution codes.

**Extractive Distillation Process**

In order to recover HCl acid at a higher concentration than the azeotropic composition from an acid that is less than the azeotropic (15 to 20 percent) it is necessary to extract this water from the solution by stripping with a solvent. This process is known as the extractive distillation process. Solvents that may be used for this purpose would be sulfuric acid, calcium chloride or magnesium chloride. The dilute solvent would then require concentration before reuse.

A combination of the Sub-X system for transferring heat from the incinerator exhaust gases by the direct contact of the gases with the solvent and the extractive distillation tower provides a tool for reaching HCl concentrations above 60 percent. The heat available is used to re-concentrate the solvent before use in the extractive distillation tower. This eliminates the need for a separate reheater as is normally used in this type of application. By this method acid concentrations from 20 percent to 100 percent may be obtained.

In the vinyl chloride monomer plants, acid at 35-36 percent concentration may be needed to supply an existing anhydrous HCl production plant. If this is not necessary then the recovery of anhydrous HCl can be made so that it would be used to supply the vinyl chloride monomer process directly.

The systems that would be used for either of these requirements are shown in Figs. 7 and 8. You will note the Sub-X and absorption process is the base system in either case. The 20 percent HCl produced in the absorber is mixed with the concentrated solvent solution and this is then fed to the top of the extractive distillation tower. If sulfuric acid or a water solution of a chloride such as calcium chloride is added to a weak HCl solution, the azeotropic composition is degraded.
Fig. 7 Flow sheet for HCl recovery process (35% HCl recovery process).

CONCENTRATED CaCl₂ SOLUTION FROM SUBMERGED INCINERATOR

1. CONC. CaCl₂ SOLUTION RECEIVER
2. HCl SOLUTION RECEIVER
3. STRIPPING TOWER
4. REBOILER
5. CONDENSER
6. CONDENSER
7. MST SEPARATOR
8. CONDENSER
9. MST SEPARATOR
10. MST SEPARATOR
11. CONDENSATE RECEIVER
P-1 CONC. CaCl₂ SOLUTION FEED PUMP
P-2 HCl SOLUTION FEED PUMP
P-3 DIL. CaCl₂ SOLUTION RETURN PUMP
P-4 CONDENSATE PUMP

Fig. 8 Flow sheet for dry HCl gas recovery process.
Hydrogen chloride vapor which is more concentrated than the azeotropic composition at atmospheric pressure can be obtained from the top of the distillation tower. This occurs by having the dilute hydrochloric acid from the absorption tower and the concentrated solvent solution from the submerged combustion tank mixed together at a solvent concentration above 30 percent for calcium chloride and 38 percent for sulfuric acid. The azeotropic mixture between the hydrogen chloride and the water would disappear.

Fig. 7 shows the process for recovering hydrochloric acid at a concentration of 35 percent. The dilute hydrochloric acid from the absorption tower and the concentrated solvent are fed to the tower top. A sufficient amount of heat is then supplied through the reboiler installed in the bottom of the tower to permit HCl acid vapor at approximately 60 percent concentration to be distilled from the top of the tower. The acid thus generated is sent to the water-cooled condenser where the acid is condensed and absorbed by adding water to reach the 35 percent concentration.

When this system is used, a mist separator is installed between the submerged combustion tank and the absorption tower. This prevents any carry-over of the concentrated calcium chloride salts from being carried into the absorption tower. A tank is also provided for the mixing of the 20 percent HCl from the absorption tower and the concentrated solvent from the Sub-X tank.

The extractive distillation tower is similar to the absorber in that it is a packed tower provided with either porcelain Raschig rings or Intalox saddles. The tower shell is constructed of a rubber-lined steel with acid-proof brick or impregnated graphite carbon.

**Anhydrous Hydrogen Chloride Gas**

As described above under the Extractive Distillation Process the vinyl chloride monomer plants require anhydrous hydrogen chloride gas as a raw material. In the event that the recovery process is to be designed to produce anhydrous hydrogen chloride gas the method described above for the 35 percent recovery is used as the base system. In order to produce a dry anhydrous HCl gas the overhead vapor leaving the extractive distillation process is cooled through water condensers and eventually through brine coolers to approximately -10 C (14 F). The recovered hydrogen chloride has a composition as follows:

- Concentration: 100%
- Chlorine: 100 ppm (WT)
- Water: 60 ppm (WT)
- Overall Recovery Efficiency: 95 percent
- Organics: 10 ppm (WT)

**CONCLUSIONS**

We have attempted to point out the features associated with the high-intensity incineration system and its ability to convert the chlorine to HCl gases at the low excess air high temperature conditions. We also have pointed out the features associated with Sub-X tank as a quench tank as well as a concentrator and its advantages, especially in the system producing 35 percent HCl and anhydrous.

These systems have been designed with the intent of eliminating a pollution problem and at the same time provide a system for recovery and reuse of the waste liquids. To date, over 22 plants have been designed and installed using the basic Sub-X system for chlorinated hydrocarbon waste disposal. Of these, approximately 17 have been built and installed by Nittetu Chemical Engineering, Ltd. in Japan for concentrations from 5 percent to anhydrous HCl. The remainder have been built and installed in the U.S.A. by Thermal Research & Engineering Corp. Many problems existed in the initial units. However, through operation experience plus continued research and development, these problems have been eliminated. At the present time these plants have been designed and installed with the optimum materials of construction, proper selection of auxiliaries with spares where required in critical service. This tends to minimize maintenance and reduce downtime which is so important in process plant operations today.

**REFERENCES**