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Incinerators for chlorinated hydrocarbons and brine

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Incinerators for chlorinated hydrocarbons and brine

Wastes containing chlorinated hydrocarbons as well as organically loaded brine require special equipment for their disposal due to their chemical and physical properties.

This article discusses the incineration of gaseous and liquid chlorinated hydrocarbons and brine solutions with organic loads. Special consideration will be given to the following aspects: state of the art, legal (environmental) requirements, problems with corrosion and materials, safety aspects and energy conservation and heat recovery.

State of the art

Presuming that all components of the reaction are thoroughly mixed, the organic components of the chlorinated hydrocarbons or brine will be oxidized to a flue gas containing less than 20 mg C/ Nm³ at 10 % excess air and a combustion temperature of around 1000 °C at a residence time of 1.5 sec (1.2.3). The prerequisite for this are high turbulences in the combustion chamber and a fine, even atomization of liquid waste.

A cylindrically shaped combustion chamber offers – besides its advantage regarding the lining – the additional advantage of making it possible to maintain controlled turbulences during operation. The tangential intake of combustion air results in a strong rotation in the combustion chamber with the known recycling of gas in the center of the vortex back towards the air inlet. The disadvantage of this principle of mixing is the separation due to the centrifugal force which results from the rotation (4). Heavy particles accumulate at the wall of the combustion chamber resulting in incomplete combustion and a short life of the refractory lining. Recent studies at the Technical University of Munich solved this problem by introducing the combustion gas of the support burner and/or a secondary combustion air flow at a given angle. The additional semi-tangential introduction of gas forces the particles from the wall into the center of the combustion chamber (Fig. 1).

A fast vaporization of liquid waste is needed to obtain a thorough mixture and requires a fine and even atomization. Conventional steam or air atomizing nozzles are unsuitable for this purpose because of corrodibility of the waste and its content of solid particles. Clogging is avoided by using special nozzles which allow the unobstructed passage of liquid waste at low pressure through a wide central boring. Atomization takes place outside the nozzle by means of high frequency waves produced by steam or compressed air (Fig. 4). The unobstructed passage makes it possible to atomize – without any problem whatsoever – wastes which are liquid, viscous or contaminated by solid particles. The arrangement of the nozzle in the combustion chamber is as important as its design. The common practice of arranging the nozzle in an inclined position to the combustion chamber axle has the disadvantage that particles can impinge at the wall opposite the nozzle, thus resulting in insufficient combustion and erosion on the lining. The reason for the incomplete atomization lies in the overheating of the nozzle as a result of its arrangement in a high temperature environment. Positioning the nozzle in the

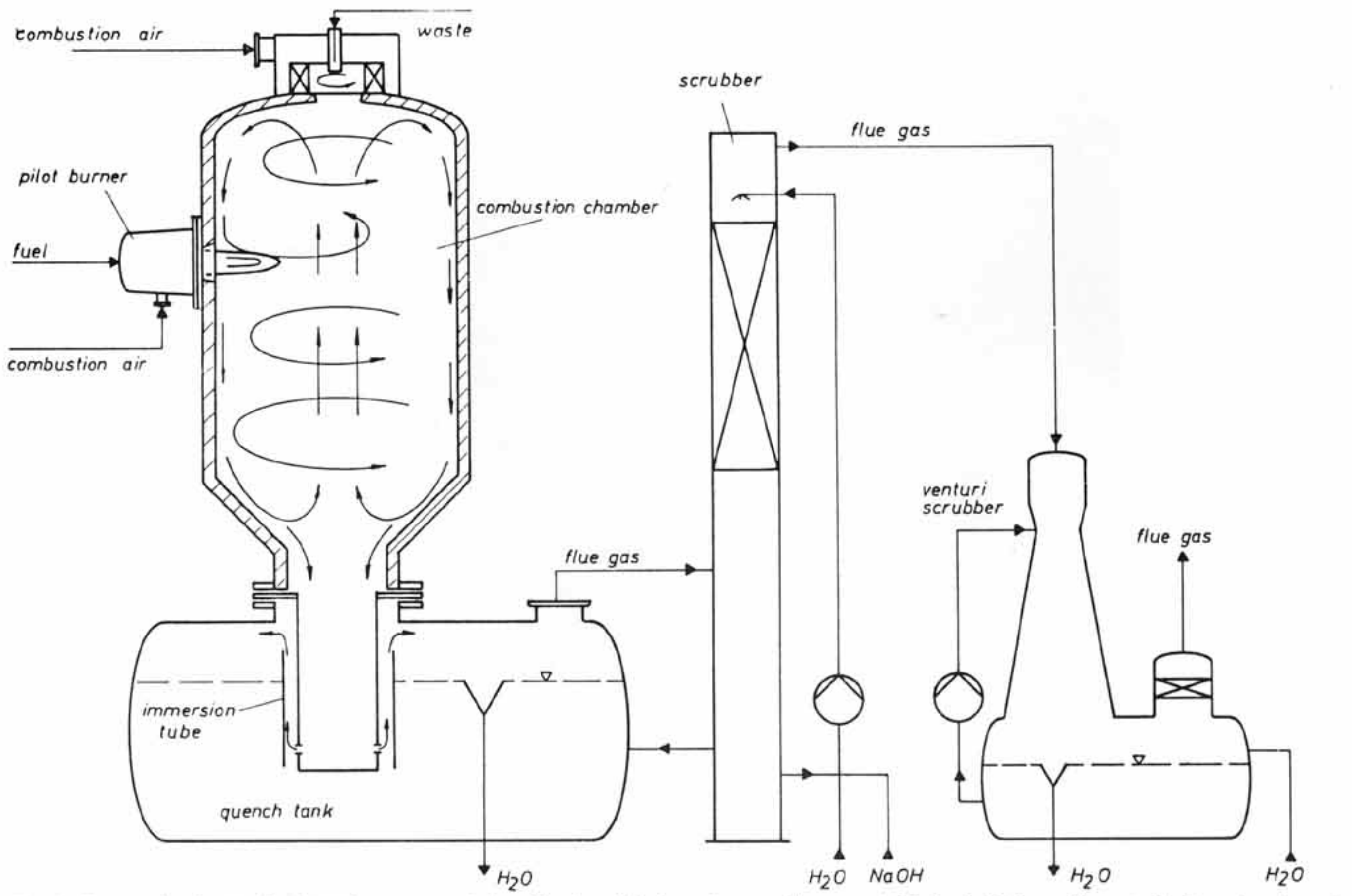


Fig. 1: Process for the combustion of wastes containing chlorinated hydrocarbons and/or organically loaded brine with neutralization of waste water and scrubbing of flue gas.

axle of the combustion chamber surrounded by combustion air avoids overheating and impingement of the refractory lining (Fig. 1).

After incineration and possible heat recovery, combustion products such as HCl, Cl_2 and salt aerosoles may be separated from the off gas. A sufficient high yield of HCl makes the production of aqueous hydrochloric acid by multiple stage absorption economically feasible (4.5.6.). A low yield of HCl can be dissolved in water and neutralized by adding NaOH, thus producing NaCl. If the temperature of this washing liquid is sufficiently low, Cl_2 is converted into NaOCl at the same time. Salt crystals are scrubbed out in insufficient quantities in packed columns because of their small size (in the range of 1 μ). Their removal requires the use of Venturi scrubbers or equivalent separators (1) with a degree of separation of 99 % at a sufficient pressure drop.

Legal environmental requirements

Present technology permits meeting the requirements for emission control (7.8). However, in order to meet regulations regarding combustion temperature, residence time and excess air, it is necessary to make compromises regarding the total effect of the process, as is demonstrated by the following example:

Presuming a complete incineration, the chlorine parts of waste are at the absence of SO_2 (1.2) converted into HCl and Cl_2 according to the Deacon reaction (Fig. 2). The desired production of HCl at the expense of Cl_2 ist favored by:

combustion temperature increase
increasing partial pressure of water vapor
decreasing partial pressure of oxygen.

Regulations requiring that an excess air of e.g. 30 % is maintained during combustion would result in an unnecessary increase of Cl_2 formation relative to a given temperature. In addition to that, an increase of 17,5 % energy demand based on an O_2 content of 2 % approximately will be required and the volume of the emitted gas will be increased accordingly.

Emission control is necessary and desirable. However, the question arises if additional regulations admitting individual process data can be considered as reasonable and acceptable if they prevent the application of present and future technology at the expense of ecology and economy.

Corrosion and materials

In order to reduce corrosion, it is necessary to choose suitable materials and to use them under controlled operating conditions. The attack of Cl_2 and HCl to metals at high temperatures makes a ceramic lining of the combustion chamber necessary. For wastes which are free of salt, ordinary refractory material can be used. However, salts – especially slag – react with most of the common refractory material forming a destructive lutective mixture with a low melting point. The use of specially developed presintered bricks with a high silicium content as ceramic lining is proved especially satisfactory as far as resistance against NaCl, Na_2SO_3 and Na_2SO_4 is concerned.

The selection of materials is not very critical for medium temperature ranges, i.e. for temperatures above the acid dew point and below the point where the attack of free chlorine and dry HCl is to be expected. Carbon steel is therefore suitable for the combustion chamber shell if a tolerable temperature is maintained everywhere through adequate design and insulation, even under varying environmental conditions.

On the other hand, the material used has to meet special requirements since the combustion gases leaving the combustion chamber or waste heat boiler have to be cooled down to the temperature of the liquid which is used for quenching and scrubbing. The use of metals is, for example, unsuitable if concentrated, aqueous HCl is employed as it is necessary for the recovery of hydrochloric acid. In this case, graphite is recommended because it is resistant against corrosion and temperature. Certain titanium alloys proved especially suitable when used for neutralized brines which are subject to corrosion by anions. They, moreover, have the advantage of being mechanically stronger than graphite. Other possibilities are zirconium and nickel alloys. The expectations placed on Hastelloy C on account of its favorable corrosion resistance data have not been fulfilled in practice (2.4). Provided that the temperature – even during operational failures – does not exceed 100 °C, FRP with especially selected inliners for vessels, columns and scrubbers is suitable and superior to rubber lined steel vessels.

Operational safety

The safety of personnel and equipment during operation and also during failures makes it necessary to take special precaution – in addition to legal requirements – for the design and equipment of the system. Combustion temperature and excess of oxygen in the combustion chamber should be continuously monitored and controlled automatically since they are important criteria for the performance and service life of the system. Supply and discharge should be continuously monitored, controlled and supervised by an automatic interlocking system of controllers. If possible, the process should be made intrinsically safe, for example by dispersing the combustion gases into the scrubbing liquid through an immersion tube below the surface of the liquid (Fig. 1). This step guarantees – because of the laws of physics – that in case of a break-down of the cooling water system the temperature of the combustion gases will not exceed 100 °C and thus heat damage to subsequent equipment is prevented (9). The fact that incineration and scrubbing take place below atmospheric pressure is an additional

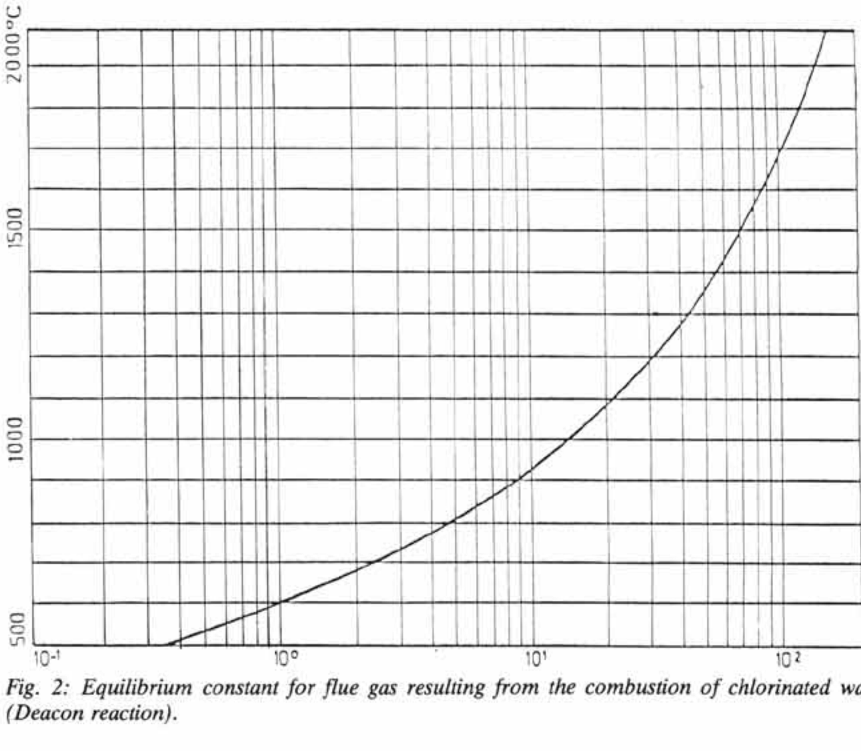


Fig. 2: Equilibrium constant for flue gas resulting from the combustion of chlorinated wastes (Deacon reaction).

advantage as far as safety is concerned. Prolonged usage almost inevitably results in leakages at loose connections, especially with the use of non-metallic material. Negative pressure within the plant between incineration and the stack prevents the leakage of combustion gases which is annoying and, if HCl and Cl_2 are produced, also dangerous.

Energy conservation and heat recovery

Because of corrosion, a preheating of chlorinated gaseous waste or of combustion air with hot combustion gases is hardly feasible. The same is true for liquid waste which can only be preconcentrated if its partial pressure does not entail an undue contamination of the vapors. For that reason, energy conservation efforts are mainly limited to defining optimum incineration conditions (temperature, O_2 content) and the insulation of the combustion chamber.

When incinerating chlorinated hydrocarbons as well as organically loaded brine, it is possible to recover the heat by producing steam in suitable waste heat boilers. Corrosion by HCl and Cl_2 is avoided by setting the upper and lower operating temperature of the steam boiler within the safe temperature limits. When burning waste containing salt, the salt film running off at the wall is drained at the bottom of the combustion chamber, whereas the hot flue gases leave sideways.

In order to avoid incrustation, the vaporized salts and aerosoles emitted with the flue gas can be turned into solid particles before they hit the surface of the boiler by lowering their temperature. Depending on the consistency of the waste, it is possible to recover up to 80 % of its calorific value, thus getting back at least part of the operational and investment costs.

Summary

The present state of the art permits the disposal of wastes containing chlorinated hydrocarbons as well as organically loaded brine through combustion in accordance with present emission control requirements. Corrosion problems are solved by selecting suitable material and its application under controlled conditions. Operational safety of the combustion installation requires a well-balanced and extensive monitoring and controlling system and makes it desirable to operate the installation below atmospheric pressure. Energy recovery is not only possible for the combustion of chlorinated waste but also for organically loaded brine. Depending on the type of waste, it is possible to compensate for at least part of the costs necessary for its disposal.

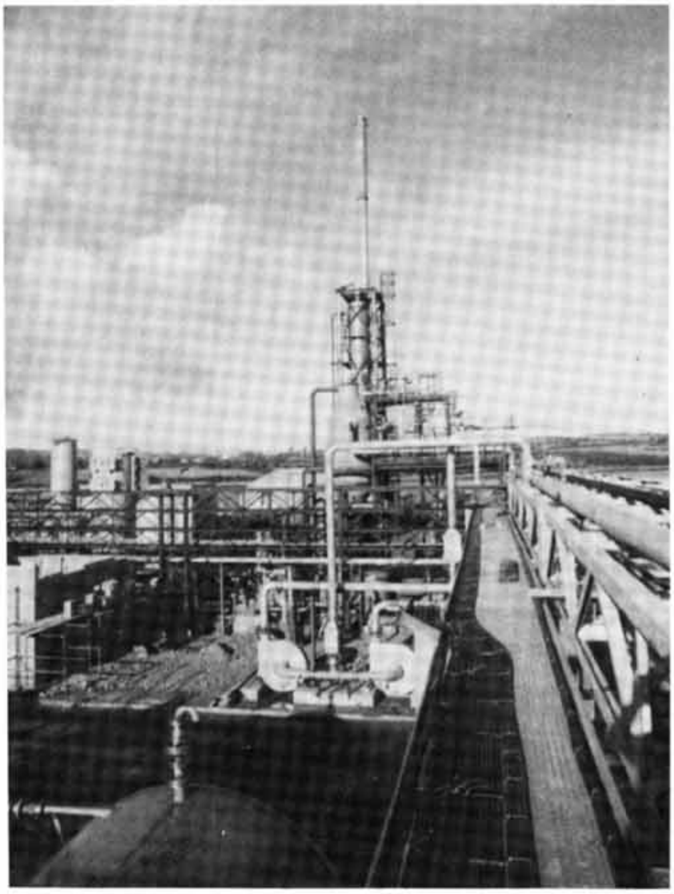
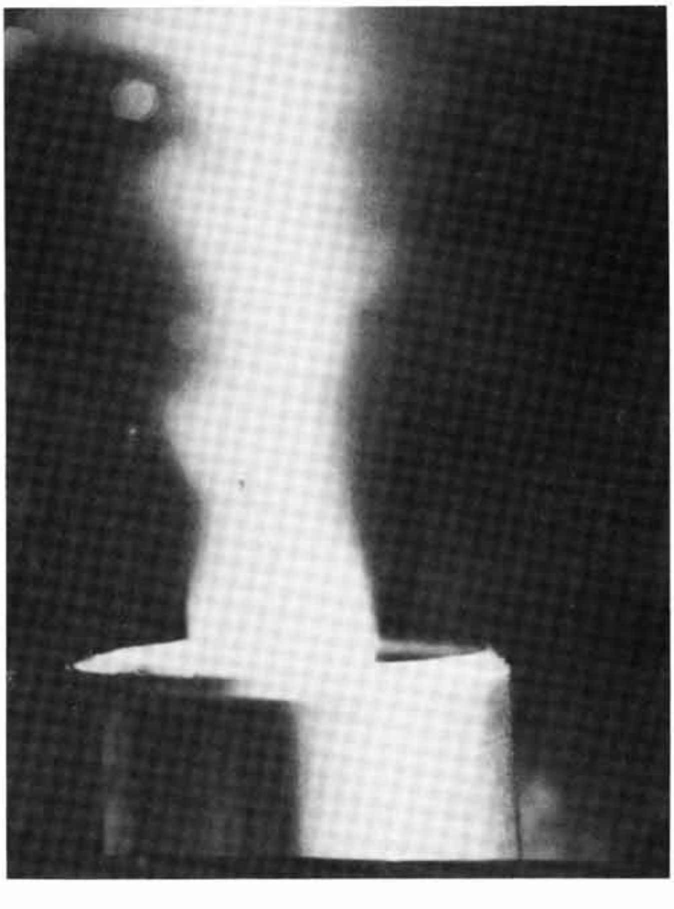


Fig. 3: Incinerator for the simultaneous combustion of chlorinated hydrocarbons and organically loaded brine.

Fig. 4: Atomization of liquid waste by means of high frequency oscillation.



References

(1) Germerdonk, Dr. R.: "Luftreinhaltung – Derzeitiger Stand und Möglichkeiten der industriellen Abluftreinigung" Umwelt Sonderausgabe – Markt und Köpfe, 19, p. 3–17, 1980.

(2) Fabian, Dr. H. W., Reher, Dipl.-Ing. P., and Schön, Dr. M.: "Verbrennungsanlage mit Rauchgaswäsche für die Beseitigung von Chemie-Abfällen" Chemie-Ingenieur-Technik 50 (1978), no. 11, p. 823–831.

(3) Hess, K., and Kotkamp, R.: "Phosgen-Vernichtung durch thermische Umsetzung" Chemie-Ingenieur-Technik 45 (1978), no. 13, p. 873–881.

(4) Tsuruta, H.: "Waste Liquid Incineration and Valuable Recovery in Chemical Industry" Chemical Economy & Engineering Review 4 (1972), no. 12, p. 45–51.

(5) Kurz, G.: "Verbrennung chlorierter Kohlenwasserstoffe" Chemische Rundschau (1974), no. 3, p. 9–11.

(6) Zimmer, J-C., and Guaitella, R.: "Incineration: Lowest Cost HCl Recovery" Hydrocarbon Processing (1976), no. 8, p. 117–118.

(7) Bundesimmissionsschutzgesetz (Textausgabe K. Hausmann), 2. Auflage, Nomos Verlagsgesellschaft, Baden-Baden 1975.

(8) Technische Anleitung zur Reinhaltung der Luft (TA Luft), 2. ergänzte Auflage (bearbeitet von D. Reil), Weka-Verlag, Kissing 1976.

(9) Kurz, G.: Verfahrenstechnik (Mainz) 2 (1968), no. 9, p. 374–378.