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review of theory and practice

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SUMMARY

The book describes the state-of-the-art technology for environmentally acceptable incineration of chlorinated chemical waste.
The information presented has been collected by means of an extensive literature study and by several in-depth interviews with experts in the field. Regarding the latter, also five major incineration firms in Europe were visited: HIM (W.Germany), Kommunekemi (Denmark), AKZO Zout Chemie (The Netherlands), AVR Chemie (The Netherlands) and OCS (The Netherlands).
Equipment, waste acceptance procedures and operating conditions of these firms are critically reviewed.

Chlorinated waste forms one of the major chemical waste problems. Due to stricter legislation, increasing amounts of this chemical waste become subject to government control and have to be destructed in an environmentally acceptable way (in as far as recycling is not possible). Presently insufficient incineration capacity is available in Europe for incinerating chlorinated organic waste such as PCBs.
The incineration of chlorinated chemical waste has received special public attention within the field of waste disposal techniques due to its possible relation to the "dioxin-issue." The basis of this issue is the public concern about the possible formation of dioxins, and other toxic products, during incineration of chlorinated waste and the possible effects on the public health and the environment. Public concern has led to a great deal of scientific research relating to hazardous waste disposal by means of incineration and its environmental impact.
These research projects have increased the understanding of the chemical reactions and the reaction mechanisms taking place during incineration. Most of the equipment now being used for incinerating organochlorine waste was not, however, designed taking this knowledge into account. Aside from being able to withstand the high temperatures involved and the occurrence of strongly acidic flue gases, no special attention is paid to the particularities of the chemical reactions involved during thermal destruction, including even possible new formation (the forming of PICs), of chlorinated organics.
The technical sophistication of incineration process control varies greatly in practice, and in some cases is very limited. Good process control, including an emergency shut-down system, is essential for proper incinerator operation; i.e., without good control, process disturbances can lead to serious emissions of environmentally dangerous substances, even in those incinerators fitted with effluent cleaning equipment.
On the basis of thermodynamic calculations it can be concluded that the complete destruction of dioxin-like compounds by means of incineration is possible. Whether dioxin-like compounds are in practice completely destroyed, or indeed even formed during combustion, is therefore a matter of chemical kinetics, being determined by conditions existing within the incinerator (temperature, residence time, turbulence). The current level of understanding the kinetics involved is still insufficient to produce models which quantitatively describe the destruction, or formation, of dioxin-like compounds.

It is also shown that the use of a number of key parameters now being used by environmental authorities for incineration specification and design, such as destruction efficiency, combustion efficiency and incinerability rankings, often lacks a sufficiently scientific base and can result in contradictory results. To overcome such situations it is important to come to an international consensus on the questions concerning incinerability rankings and performance tests.

PREFACE

Incineration of chlorinated organic waste has become an important research field over the last decade. In order to maintain a full view over the developments in this field, a literature study and several in-depth interviews were carried out to come to a state-of-the-art description. The literature was first collected by means of computersearch. The databases which were used include the Chemical Abstracts, Energy, Chemical Hazards in Industry and Dechema. In addition several bibliographies, like Pollution Abstracts and Verfahrenstechnik, were consulted at the library of the Delft University of Technology. With the literature as background, several experts in the field of chemical waste incineration were interviewed. To give an idea of the Western European chemical waste incineration practice five major incineration firms (AKZO, AVR, HIM, Kommunekemi and OCS) were visited.

In order to make full use of this study, the limitations should be noticed. This study is limited to the use of incineration and its impact on the environment, no relations with other waste treatment methods are made. However, it should be noted that reuse of waste streams obviously can have more merits under certain conditions than incineration. Furthermore no attention is paid to the impact on environment due to transport of chemical waste, which, when taken into account, may result in the use of mobile waste incinerators on the site of waste production instead of transporting chemical waste to an off-site incinerator. Within these boundries this study may give a good idea of the current level of knowledge towards theory and practice of chlorinated organic waste incineration.

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1 INTRODUCTION

In the past decade much interest has been paid to the problem of incinerating chemical wastes. The main reason for this interest is the increasing concern for environmental pollution caused by emissions of chlorinated organics from such incineration units.
During the last decade many reports have been published concerning the emissions of incineration facilities. Some of these reports stimulated a scientific discussion about the formation of polychlorinated dibenzodioxins and dibenzofurans (publicy referred to as "dioxins") in incinerator units and subsequent emissions. From that point on, the interest in chemical waste incineration ceased to be an academic issue, becoming more and more a public and political issue.
Stimulated by this general interest and supported by government funding, the scientific community increased its research efforts in this field. The goal of this research was to create a scientific basis from which policy questions could be answered.
During the last five years this research has led to a large number of publications covering this subject.In this report this literature is summarized and critically reviewed, and the state of the art of incinerating chlorinated hydrocarbons is described. This special group of chemical waste, chlorinated organics, is chosen because of the specific difficulties which are experienced during incineration, such as the formation of chlorine and dioxins.

The report consists of two parts. The first part is based on literature concerning the description of the combustion of organochlorine waste, generally, although incorrect, referred to as chlorinated hydrocarbons (CHCs). This description includes the theoretical side of the combustion process as well as a more practical side. Also included is a discussion concerning equipment, which is a dominating theme in terms of number of publications.

The second part of this report is based on interviews with experts in various fields concerning CHC-combustion and includes descriptions of visits to several leading companies involved in CHC-combustion.
In both parts of this report attention is paid to the influence of various factors on the operation, reliability and process stability of CHC-incinerators.

2 GENERAL BACKGROUND

Incineration of chemical waste for disposing unwanted production residues has been in practice for the last thirty years. Originally incineration was used primarily to achieve volume reduction; later it became more and more the only possibility of destructing certain waste streams in a legal way (1). The results of illegal solutions of hazardous waste disposing are well known in every country with a substantial chemical industry. It is because of these illegal dumpings that attention has been drawn to the field of chemical waste management.

The history of the TCDD problem goes back some 10 years. In 1977 Olie et al. (2) discovered the presence of polychlorinated dibenzodioxins (PCDDs) and dibenzofurans (PCDFs) in fly ash from municipal incinerators in the Netherlands. Shortly thereafter Buser et al. (3, 4) reported that these compounds were also present on particulates emitted from a municipal incinerator and an industrial heating facility in Switzerland. It was already known by that time that PCDDs are extremely toxic for some animal species, and that 2,3,7,8-TCDD is probably the most toxic substance made by man (5).
These two discoveries caused considerable discussion on the issue of PCDD formation by thermal treatment of chlorine containing wastes and fuels. The basis of this discussion concerned the possibility of a continuous (probably low level) pollution of the environment, and the possible and probable effects of such pollution.
Throughout the history of the TCDD problem a key question has been that concerning the origin of these compounds. Basicly two points of view are represented. First the "trace chemistries of fire"-hypothesis, which is supported by Dow Chemical. In 1978 a group of scientists from Dow Chemical reported several unexpected sources of PCDDs, among them fireplaces, cigarettes and gasoline and diesel-fueled automobiles. This report resulted in the "trace chemistries of fire"-hypothesis (6,7,8,9). This theory states that numerous chemical reactions occur during combustion, which produce numerous chemical products, some of which are present at very low concentrations and are emitted in smoke or adsorbed on the ash particulates. An important part of this theory is the conclusion that chlorinated dibenzo-p-dioxins are ubiquitous, and have been present since the advent of fire. A second theory is the "precursor hypothesis", which is posed by Buser and Rappe. This theory states that TCDD can only be formed when synthetic chlorinated compounds (precursors) are present (10,11,12,13).

The Dow-hypothesis has been heavily criticized. One of the main arguments is that coal-fired power plants are ruled out as an important source of 2,3,7,8-TCDD (13). In a recent study Czuczwa and Hites (14) state that the input of dioxins and furans to the sedimentary environment is probably mainly due to the combustion of chlorinated organic products present in various chemical wastes. Direct dumping and coal or natural combustion (e.g. forest fires) can be sources, but it is clear that the high levels of PCDDs and PCDFs found in presently accumulating sediments are not due to the "advent of fire." However, neither the Dow-hypothesis nor the precursor hypothesis is conclusively supported or refuted by the available data (15).

As a result of the dioxin formation discussion the US EPA started a study, the TIER 4 DIOXIN TEST PROGRAM, to assess combustion source emissions of PCDDs. In a preliminary report (15) concerning the literature search of this program, some factors affecting the dioxin emissions were presented.
These factors are:

- presence of dioxins in the feed
- presence of dioxin precursors in the feed
- chlorine in the feed
- combustion conditions (temperature, oxygen level, turbulence)
- feed processing.

On the base of a list of major combustion source categories and the above-mentioned factors, a ranked list of combustion source categories with the potential to emit dioxin was developed. A source test program is now being carried out to evaluate the ranked list.

Concerning toxicity and occupational exposure of PCDDs and PCFDs much has been published, but most of this specialized research goes beyond the scope of this paper. Some reviews in this field were made by Reggiani (5) and Rappe et al. (16). Other interesting sources are Josephson (17) and Rawls (18) describing the present discussions of 2,3,7,8-TCDD toxicity. Table 1 compares the minimum lethality of 2,3,7,8-TCDD with other poisons. The most acute effect of dioxin exposure to man is chloracne, a severe skin disease (5). Concerning the carcinogenicity of 2,3,7,8-TCDD to man no consensus has yet been reached. With regard to the acceptable daily intake (ADI) of 2,3,7,8-TCDD the EPA Scientific Advisory Panel suggested a level of 0.6 ng/person/day, for the Netherlands an ADI-level of 0.24 ng/person/day is suggested by the National Institute of Public Health and Environmental Hygiene (RIVM).

Although most of the scientific efforts have concerned the dioxin issue, the emission of waste incinerators consists of many more substances at much higher concentration levels. Junk and Ford (19) published a review of the different organic compounds reported to be present in waste incineration emissions. They end up with a list of 211 organic compounds, of which 27% are halogenated organic compounds, 26% polycyclic organic compounds and 21% aliphatic organic compounds. But according to Junk and Ford, these ratio's

reflect analytical interest and capability rather than any true distribution of compounds in the emission of waste incineration. In another article Bartelds (20) reviews the chlorinated organic compounds produced during waste incineration.
In both these publications the data refer not only to the field of chemical waste incineration, but mainly to the field of municipal waste incineration. Basicly the difference between those two fields is limited to the incineration temperature and the incinerator design. The resemblance lays in the fact that both fields concern incineration of a relatively undefined waste stream, which can vary very much. In both publications no attention is paid to the emission of heavy metals from waste incinerators, which may be an important source of environmental pollution.

The relevance of chemical waste incineration can be illustrated by the amounts of waste incinerated. Table 2 gives some estimations of waste incinerated in 1980 in several western countries (21). More accurate data are only available for West-Germany and the Netherlands. In 1983 461,350 tons of chemical waste of German origin was incinerated in West-Germany, where a total incineration capacity of 620,000 ton existed (22). In the period from July 1982 to June 1983 19,450 tons of chemical waste of Dutch origin with a chlorine content higher than 4% was incinerated on land and at sea. In total 114,370 tons of chemical waste of Dutch origin was incinerated in various countries (23). Considering the large amount of waste being incinerated and the extreme toxicity of products which can be formed during the combustion (e.g. dioxins), it will be obvious that chemical waste incineration can be the cause of a potentially very large risk.

One specific stream of chlorinated chemical waste, which also has attracted much public attention, is the stream containing polychlorinated biphenyls (PCBs). This public interest is partly due to the toxicity of PCBs themselves and to the ability of PCBs to form PCDFs, up to a yield of 10%, under extremely unfavourable conditions (13,45). Because of these two aspects, and because of the wide use of PCBs up until now, incineration of PCBs is being widely studied. Most countries are banning PCBs for industrial use, and so end up with a big waste problem. For example, in the USA at the moment 340,000 tons of PCBs are in service, and have to be disposed of in the next decade (24). In Western Europe at the moment 250,000 tons of PCBs have to be treated, while the land-based capacity for destroying concentrated PCB waste is only 13,500 tons a year.

This capacity problem, which is not only specific for PCBs, is one of the most important issues in the field of chemical waste incineration. To prevent improper disposal of chemical waste, this capacity problem has to be solved in the near future

TABLE 1

Minimal lethality of several natural and man-produced toxins
Source: Ref.18

substance	animal	minimum lethal dose (moles per kg body weight)
Botulinum toxin A	Mouse	$3.3 * 10^{-17}$
Tetanus toxin	Mouse	$1.0 * 10^{-15}$
Diphteria toxin	Mouse	$4.2 * 10^{-12}$
2,3,7,8-TCDD	Guinea pig	$3.1 * 10^{-9}$
Bufotoxin	Cat	$5.2 * 10^{-7}$
Curare	Mouse	$7.2 * 10^{-7}$
Strychnine	Mouse	$1.5 * 10^{-6}$
Muscarin	Cat	$5.2 * 10^{-6}$
Diisopropylfluorophosphate	Mouse	$1.6 * 10^{-5}$
Sodium cyanide	Mouse	$2.0 * 10^{-4}$

TABLE 2

Survey of the Occurence of Hazardous Wastes in Individual Countries

COUNTRY	TOTAL VOLUME OF WASTE (t/a)1)	AMOUNT INCINERATED (t/a)	(%)
France	2,000,000	400,0002)	20
Germany	3,500,000	540,0003)	16
Great Britain	3,000,000	150-200,0004)	5-6.6
Netherlands5)	420,000	210,000	50
Norway	200,000	50,0006)	25
United States	35,000,000	1,960,000	5.67)

REMARKS

1) including waste oils etc.
2) not including on-site incineration
3) not including appr. 320,000 t/a which are coincinerated in household waste incineration plants
4) not including in-house (on-site) incineration of about 600,000 t/a in 73 in-house plants of which substantially more than 50% is accounted for by the oil refineries and the largest chemical manufacturers
5) including waste oil and substitute fuel
including incineration at sea
excluding biological sludges
excluding on-site treatment
6) including 50% of waste oil used as fuel substitute
7) another 9.7% are uncontrolled incineration (all figures being estimated)

Source: Nels Ref.21

3 SOCIAL BACKGROUND AND LEGISLATIVE ASPECTS OF CHEMICAL WASTE INCINERATION

In this chapter the social background and legislation concerning chemical waste incineration will be discussed. Firstly general legislative trends and the public response to these are discussed. Secondly, two examples of legislation are given. The first concerns the Netherlands, reflecting the Dutch origin of this report and also functioning as an example of an European approach. Secondly, the United States is discussed, because of its influence on incineration research and design standards. Because of the complexity of environmental legislation only basic ideas and trends are discussed.

3.1 General

Environmental legislation concerning chemical waste treatment can be divided into two parts. Firstly, the part which defines which waste streams are considered to be chemical waste streams, and therefore have to be treated separately from industrial and domestic waste. Secondly the part which prescribes treatment of these chemical waste streams. The legislation defining chemical waste is relatively new, and it can be seen as a reaction of society to the mismanagement of chemical waste by many chemical industries over a period of many decades. The treatment legislation usuallly concerns normal regulations and procedures which have to be carried out when operating a chemical plant. These regulations prescribe among others emission levels of contaminants to air, water and soil and safety procedures which have to be implemented in operating activities.

In most countries the present environmental legislation can be seen as the result of a series of conflicts between the chemical industry and the environmental interest groups, which served to change existing laws.
Once legislation has been implemented, it starts to act as a regulating factor between the industry and the public. This regulatory function is personified by the officials of the various environmental protection agencies. "Personification" is used because the legislation is not absolute, but has to be interpreted to be applicable to an actual situation, and this interpretation has subjective elements. The legislator has to be fully aware of the fact that the regulations are going to be used as design directions, and therefore

have to be as practical as possible. On the other hand it is obvious that the regulations themselves must not lead to unacceptable risk. These two opposing demands can - and do - lead to tension

The question of practicality is often solved by using the principle of the best technical means or best practical means. The use of these concepts (particularly the first), however, can lead to long licensing periods and also to inequalities in design and operating standards between different facilities (25). The development of technology is also influenced by legislation, so it therefore can be useful to set high standards for the industry which have to be met in a certain period, provided there is an interim solution which is environmentally acceptable.

In the last decades a certain public mistrust of technology has manifested itself, fed by a number of major accidents, like Seveso, Bhopal, and most recently Tsjernobyl, and an apparent reserve of officials to inform the public sufficiently on the health risks of some industrial activities. In the case of chlorinated hydrocarbon incineration such a situation has also occured, mainly because of the dioxin-issue. Because of poor information and, in our opinion, the reserves of a too-industry-minded official world, the "not-in--my-backyard syndrome" ("NIMBY") arose. Nowadays, this public mistrust of technology is perhaps not as sharp as a decade ago (because of the economic crisis), but still an almost automatic "NIMBY"--reaction often arises when discussing the siting of a hazardous waste incineration facility. This essentially social-political problem, which has not yet been adequately resolved, contrasts sharply with the improvement of some aspects of incineration technology. On the other hand, however, these improvements are presented to the public as the "ultimate" solutions. Areas of scientific uncertainty or even complete gaps in knowledge are not even mentioned, let alone discussed.

In our opinion the only way to solve this problem is to provide adequate information to the public and also to explain those aspects of the issue which are not fully understood i.e., hiatuses in scientific knowledge. Officials must respond to the arguments of the public, even though these may not be rational in the eyes of the "experts." This view is elegantly expressed by Tschirley (25a). For all these reasons the environmental protection agencies are an important party in the conflicts and compromises of interests which define environmental policy. Officials and experts have to be aware of these aspects, and respond to them in a way compatible with a democratic society.

3.2 The Dutch situation

In the Netherlands there is no specific law concerning the incineration of chemical waste. Only a law defining chemical waste and preventing its irresponsible disposal exists ("Wet Chemische Afvalstoffen" = "Chemical Waste Act", 1979). According to the Chemical Waste Act no chemical waste may be treated off-site, unless the waste is treated by a chemical waste treater with a Chemical Waste Act license. To obtain such a license, the suitability of the treatment and the operational continuity of the facility are examined by the authorities.

Regulations concerning the treatment facility itself are much more complex. First there are the emission restrictions to air, water and soil, all three based upon in a different act. Then there are regulations to ensure proper operation and a safe working environment for plant operators. Most of these regulations are coordinated by the General Regulations Environmental Hygiene Act ("Wet Algemene Bepalingen Milieuhygiene"), to prevent different permit procedures from interfering with one another. All the regulations are worked out in a facility permit, which is different for each situation. Thus there are no general regulations stipulating a certain destruction efficiency or a destruction temperature for certain waste streams. All these specifications are provided for in the facility permit, as a filling in of best practical or best technical means, which is an environmental legislative principle in the Netherlands. It is a fact that this way of carrying out environmental legislation can only be done because the Netherlands is a small country with a relatively small number of off-site chemical waste treatment facilities.

Besides these national regulations, there are some international treaties concerning chemical waste treatment recognized by the Dutch government, e.g. the Oslo convention and the London Dumping Convention. This convention is enforced in the Sea Water Pollution Act ("Wet verontreiniging zeewater"), which forbids the dumping of a group of compounds, among them mercury and cadmium, in the ocean. The dumping of halogenated hydrocarbons is also prohibited, but an exception is made for disposal at sea by means of incineration on board of a ship, which is allowed to license holders.
At the moment the policy concerning sea-incineration is one of an interim solution. At the moment a governmental study concerning sea--incineration is being conducted to come to a definite policy for the use of sea-incineration in the 1990's.

3.3 The American situation

In the United States a number of different acts exists. These acts deal with chemical waste incineration, not as a major point in itself, but as one way of disposing of chemical wastes. The most important acts are the Resource Conservation and Recovery Act (RCRA), the Toxic Substance Control Act (TSCA) and the Marine Protection, Research and Sanctuaries Act (MPRSA).
The oldest act, the RCRA, is based on the " cradle to grave " principle, tracing the hazardous waste from the point of its manufacture to its ultimate disposal (26). With regard to incineration, the RCRA demands a trial burn, which has to provide information upon which approval or denial of a permit will depend. During such a test burn the following occurs: for each waste stream which is going to be burned a relevant compound has to monitored for destruction effiency calculations. These test compounds, the "Principle Organic Hazardous Constituents" (POHC), are chosen on the base of their incinerability index, which is defined in the RCRA-regulations. When a POHC with a high incinerability index is destroyed during the trial burn with a sufficient destruction efficiency, all waste categories with a lower incinerability index are assumed to burn with the same, or higher, destruction effiency.

The trial burn has to prove that the destruction and removal efficiency (DRE) is at least 99.99% for each POHC tested. Operating conditions which have been demonstrated to be adequate to achieve the performance standards will be specified as operating requirements in the permit.
This procedure in itself is very useful. Unfortunately the EPA chose the heat of combustion per weight of the POHC as the basis of the incinerability index; this criterium is not accepted to provide for a safe method (27). Put in a more general scientific perspective, the American incinerability index is based exclusively on thermodynamic consideration; kinetic effects, often the bottleneck, are completely ignored.
The TSCA gives regulations for the use and disposal of PCBs. The most important incinerator operational requirements for liquid PCB--wastes are a combustion efficiency (CE) of at least 99.9% and a residence time of 2 seconds at 1200°C (± 100°C) and 3% excess oxygen in the stack gas or a residence time of 1,5 seconds at 1600°C (± 100°C) and 2% excess oxygen in the stack gas. For non-liquid PCB--wastes the same requirements are set except for an additional requirement which concerns a limitation on the stack emissions rate. The mass air emissions from the stack may not contain more than 1 mg per kg of PCB introduced into the incinerator, which means a DRE of 99.9999%. This DRE has to be proven in a trial burn. In practice it is found that the DRE for liquid PCB-incinerators is also 99.9999% when operating according to the requirements for solid PCBs.

The MPRSA is presently the American version of the London Dumping Convention, which sets regulations for ocean-incineration (27). The two main requirements are a DE and CE of at least 99.9% and a minimal wall temperature of 1250°C. The US EPA has been conducting research on the assessment of incineration as a treatment method for liquid organic hazardous wastes, in order to define a policy concerning sea-incineration (28). As a result of this research effort new standards for sea-incineration will be promulgated under the MPRSA.

In spite of, or maybe because of, all these regulations, in the United States an ironic situation has arisen. The use of properly executed incineration, which of all disposal methods for hazardous waste probably presents the least serious long term threat to human health and environment, has not risen to the level which was expected. This situation is partly due to the complex and time-consuming licensing process (25), and also due to the existence of an inadequate interim policy, which until recently left the possibility of land filling of hazardous waste open (26).

4 THEORY OF THERMAL DESTRUCTION OF CHC BY COMBUSTION

In this chapter the theoretical background of thermal destruction of chlorinated hydrocarbons by means of combustion is described. First the importance of this theoretical background is explained. This is followed by some basic remarks concerning thermodynamics and kinetics. Secondly, different aspects of thermodynamic and kinetic modeling are described.

4.1 General aspects

In the past, the physical conditions of thermal destruction were the main research subject. Under pressure of environmental regulations and energy constraints, however, the chemical theory of thermal destruction has become the more important subject. Models predicting concentrations of various toxic substances in the post-combustion zone are needed to review the probable efficiency of equipment to be built. One difficulty in developing this chemical theory is the complexity of the reactions involved. Because of the diversity of the burning mixture one cannot speak about a single set of reactions of one chemical substance. A complex set of reactions needs to be considered; unfortunately the exact nature of this set of reactions cannot as yet be determined. But before going into any details, the elementary difference between thermodynamic and kinetic models will be explained.

According to the second law of thermodynamics, every closed, isolated system will approach an "equilibrium" state in which its properties are independent of time. If the enthalpies, entropies and the equations of state of the chemical species involved are known, the chemical composition of this final equilibrium state can be accurately predicted. However, thermodynamics is unable to say anything about the time required to attain equilibrium, or about the behavior or the composition of the system during the period of change. These latter problems are covered by chemical kinetics

Chemical kinetics is directly concerned with the description of the composition of chemical systems with time.

The equilibrium constant (K_1) for a typical reaction,

$$aA + bB \underset{-1}{\overset{1}{\rightleftharpoons}} pP + qQ \qquad (1)$$

is given by

$$K_1 = \frac{[P]^p \; [Q]^q}{[A]^a \; [B]^b} \qquad (2)$$

where P, Q are products and A, B are reactants: whilst a, b, p and q represent stoichiometric coefficients, K_1 is related to the forward and reverse specific rate constants k_1 an k_{-1}, respectively, by the following expression:

$$K_1 = \frac{k_1}{k_{-1}} \qquad (3)$$

Eq. (3) indicates that, of the three quantities k_1, k_{-1} and K_1, only two are independent. A detailed knowledge of any two of them completely specifies the third, via the relation (3). In general, equilibrium data are much more readily available than kinetic data.

For a chemical reaction e.g. Reaction 1, occuring at low pressure, the measured equilibrium constant K_t is related to the standard free-energy change ΔG^o_t of the reaction by the relation

$$\Delta G^o_t = -RT \ln K_t = -2.303 \; RT \log K_t \qquad (4)$$

where R is the molar gas constant and T is the absolute temperature (in K); while 2.303 reflects the change from natural base to base ten logarithms.

By definition,

$$\Delta G^o_t = \Delta H^o_t - T \; \Delta S^o_t \qquad (5)$$

where ΔH^o_t is the standard enthalpy change and ΔS^o_t is the standard entropy change of the reaction at temperature T.

One of the most precise methods for obtaining ΔG^o_t is by the direct measurement of K_t and then by the use of Eq.4. If we can measure the equilibrium concentration of reactants and products, K_t can be obtained directly, and the error in ΔG^o_t is simply related to the error in the measurement of K_t. If K_t is measured to ± 10%, the resulting error in ΔG^o_t is ± 0.1 (RT), or, at 500 K, ± 0.10 kcal/mole. The alternative method for obtaining ΔG^o_t from known values of ΔH^o_t and ΔS^o_t is generally subject to uncertainties at least tenfold larger, because ΔH^o_t is not often known or measurable to better than ± 0.5 kcal/mole; likewise ΔS^o_t is not usually known to better than ± 1 cal/mole K (29).

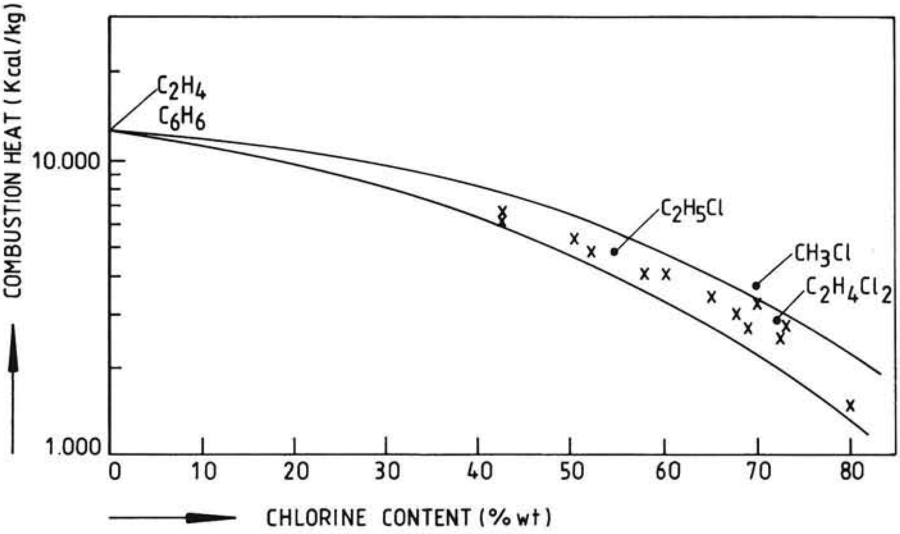


Figure 1. Heat of combustion of chlorinated hydrocarbons.
Source: Ref. 74.

4.2 Modeling aspects

One way of describing thermal destruction of chlorinated hydrocarbons is to assume a compound with a molecular formula $C_xH_yCl_z$, which is destroyed by means of elementary reactions into CO_2, HCl and H_2O. Senkan (30) operates in this way, which gives the possibility to produce an oxygen equivalence ratio, this being the ratio of actual to stoichiometric fuel/oxygen ratios. When working with CHC in which $y < z$, the formation of molecular chlorine can occur, depending on the oxygen equivalence ratio and the amount of auxiliary fuel (reaction 6). For instance 1,2-dichloroethane, one of the main components of EDC-tar, has enough hydrogen in its molecule to prevent formation of molecular chlorine (i.e. HCl is formed during the combustion process). Chlorinated aromatic hydrocarbons, like pentachlorophenol (PCP), however, often lack (sufficient) hydrogen to form HCl during combustion. Furthermore the heat of combustion of chlorinated hydrocarbons decrease with increasing chlorine content (see Fig.1); this factor is also undesirable, since lower temperatures can lead to lower destruction efficiencies. For these cases of highly chlorinated hydrocarbons extra measures have to be taken to prevent the formation of molecular chlorine; mixing with high caloric (i.e., hydrogen-rich) waste is the most commonly used method for this purpose.

CHC combustion : $C_xH_yCl_z + xO_2 \rightleftharpoons xCO_2 + yHCl + \frac{z-y}{2} Cl_2$ (6) $\Delta H_r^o << 0$

Deacon equation: $H_2O + Cl_2 \rightleftharpoons 2HCl + \frac{1}{2} O_2$ (7) $\Delta H_r^o = 14$ kcal/mole

auxiliary fuel : $C_aH_b + (a + \frac{1}{4} b)\ O_2 \rightleftharpoons aCO_2 + \frac{1}{2} bH_2O$ (8) $\Delta H_r^o << 0$

The formation of Cl_2, undesirable because of its high corrosiveness, can also be suppressed by using auxiliary fuel as an hydrogen-donor, and as an external energy source for raising the reaction temperature, which is also unfavourable for the formation of Cl_2. Reactions (6),(7) and (8) present contradictory demands, assuming that a minimal Cl_2-content and minimal fuel consumption are desired. To prevent the formation of carbon-based pollutants during combustion, extra oxygen is used (reaction 6). But this will induce more Cl_2-formation according to reaction (7),see Fig.2. To reduce the free Cl_2-concentration more auxiliary fuel (reaction 8) is needed. Extra fuel, however, lowers the oxygen content, which might cause formation of carbon-based pollutants or result in very stable pollutants not being fully oxidized.On the condition that sufficient excess oxygen is present (ca. 10% in the effluent gas) and that the oven can withstand an increased operational temperature, injection of extra fuel will in general always result in an increased destruction efficiency and a lower Cl_2 concentration, due to the reasons already mentioned.

Another, more fundamental approach is made by Tsang and Shaub (31). By making estimations of the thermodynamic functions of compounds which are known to be difficult to incinerate and harmful to the environment, they create a base on which it can be concluded whether hazardous emissions are present due to a thermodynamic or kinetic control of the reactions involved. These estimations, made by Shaub, are based on models predicting the heat of formation in the gas phase (32, 33) and the heat capacity and entropy as a function of temperature (34). Table 3 and 4 give examples of these estimations for 2,3,7,8-tetrachlorodibenzo-p-dioxin and 3,4-dichlorophenol (34). These tables are only adequate for determining whether or not thermodynamic equilibrium controls the destruction of chlorinated organic compounds at elevated temperatures. Table 3 shows that the equilibrium constant of the gas phase formation of 2,3,7,8-TCDD at elevated temperatures strongly disfavours the gas phase formation of 2,3,7,8-TCDD.

TABLE 3

JANAF type for 2,3,7,8-tetrachlorodibenzo-p-dioxin
Source Ref. 34

2,3,7,8-tetrachlorodibenzo-p-dioxin $C_{12}H_4O_2Cl_4$ (Ideal Gas State)

T (K)	C_p^o (cal mole^{-1} K^{-1})	S_t^o (cal mole^{-1} K^{-1})	$-(G_t^o-H_o^o)/T$ (cal mole^{-1} K^{-1})	$H_t^o-H_o^o$ (kcal mole^{-1})	H_f^o (kcal mole^{-1})	G_f^o (kcal mole^{-1})	log K_p
298	56.79	114.26	83.22	9.27	-82.49	-46.65	34.212
300	56.96	114.61	83.41	9.37	-82.50	-46.41	33.809
400	70.03	132.84	93.23	15.77	-82.90	-34.34	18.762
500	80.46	149.67	102.60	23.32	-83.03	-22.21	9.708
600	88.58	165.05	111.46	31.82	-83.01	-10.07	3.668
700	94.92	179.21	119.94	41.00	-82.86	2.06	-0.643
800	99.90	192.23	128.07	50.75	-82.59	14.17	-3.871
900	103.87	204.24	135.78	60.94	-82.29	26.24	-6.372
1000	107.08	215.37	143.11	71.49	-81.85	38.28	-8.366
1100	109.70	225.69	150.07	82.33	-81.35	50.25	-9.984
1200	111.87	235.32	156.71	93.41	-80.80	62.19	-11.326
1300	113.67	244.33	163.05	104.69	-80.27	74.09	-12.455
1400	115.19	252.80	169.10	116.13	-79.75	85.94	-13.416
1500	116.48	260.78	174.89	127.72	-79.24	97.74	-14.240

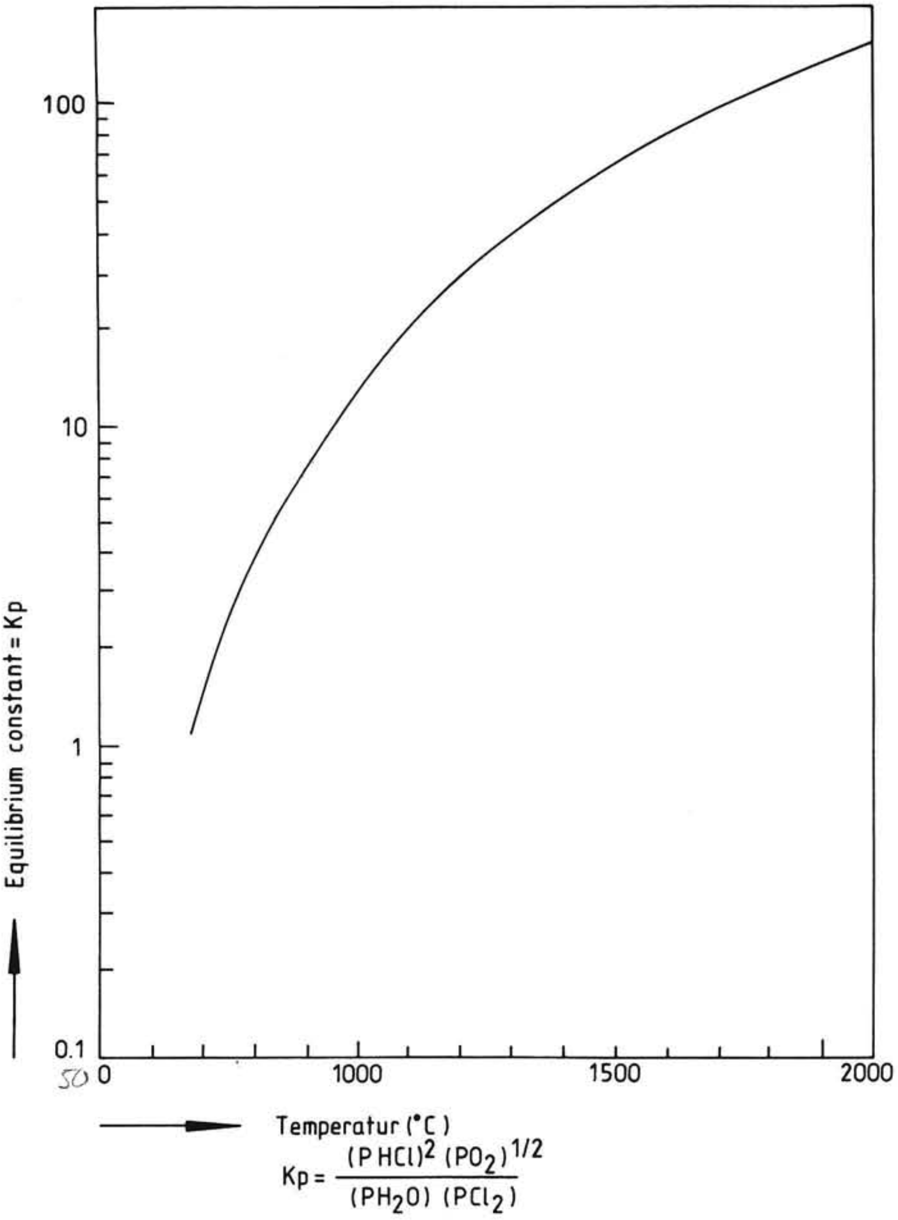


Figure 2. Temperature dependancy of the equilibrium constant of the Deacon equation.
Source: Ref. 74.

TABLE 4

JANAF type for 3,4-dichlorophenol
Source Ref.34

3,4-Dichlorophenol $C_6H_4OCl_2$ (Ideal Gas State)

T	C_p°	S_t°	$-(G_t^\circ-H_o^\circ)/T$	$H_t^\circ-H_o^\circ$	H_f°	G_f°	log K_p
(K)	(cal $mole^{-1}$ K^{-1})	(cal $mole^{-1}$ K^{-1})	(cal $mole^{-1}$ K^{-1})	(kcal $mole^{-1}$)	(kcal $mole^{-1}$)	(kcal $mole^{-1}$)	
298	32.03	88.25	69.89	5.46	−46.46	−28.33	20.776
300	32.18	88.44	70.00	5.52	−46.47	−28.21	20.550
400	40.16	98.78	75.80	9.12	−46.97	−22.07	12.058
500	45.23	108.21	81.21	13.36	−47.27	−15.84	6.923
600	49.76	116.95	86.36	18.12	−47.45	−9.54	3.475
700	53.16	124.87	91.26	23.26	−47.52	−3.23	1.008
800	55.95	132.15	95.87	28.72	−47.50	3.08	−0.841
900	58.21	138.77	100.13	34.43	−47.45	9.39	−2.280
1000	60.08	144.90	104.17	40.34	−47.31	15.68	−3.427
1100	61.66	150.79	108.20	46.43	−47.12	21.97	−4.365
1200	62.98	156.30	112.04	52.66	−46.89	28.24	−5.143
1300	64.11	161.42	115.61	59.01	−46.66	34.49	−5.798
1400	65.08	166.25	119.13	65.47	−46.42	40.73	−6.358
1500	65.92	170.81	122.39	72.02	−46.17	46.94	−6.839

TABLE 5

The equilibrium constant, K_p, as a function of the temperature for the combustion with oxygen of some (poly)chlorodibenzo-p-dioxins.

temp. K	1-CDD log K_p	2-CDD log K_p	2,3,7,8-TCDD log K_p	OCDD log K_p
500	582.1	586.4	526.0	482.9
700	420.8	423.9	384.2	351.9
900	331.0	333.4	305.3	282.0
1.100	273.8	275.7	254.9	236.1
1.300	234.1	235.8	220.0	204.2
1.500	204.9	206.4	194.3	180.8

Table 5 gives the equilibrium constant, K_p, for the complete combustion of some dioxins with oxygen at different temperatures. These equilibrium constants give an idea of the dioxin concentration when chemical equilibrium has been reached. The conclusions which can be reached on the basis of these thermodynamic considerations are of crucial importance to the subject of this study, and it is essential that they be discussed clearly.
Firstly, relative to the elements from which they are formed (C, H,Cl and O), dioxins are highly stable compounds at low tempera-

tures. At high temperatures dioxins will decompose. When present, however, in an atmosphere composed of the elements from which they are formed, and in the ratio corresponding to the molecular structure (e.g. 12C + 4H + 2O + 4Cl; that is, a highly reducing atmosphere), decomposed dioxins can re-convert back into their original form, that is, dioxins. In other words, dioxins need not be destroyed by heat in a reducing atmosphere.

Incineration, however, normally occurs not in a reducing but in a strongly oxidizing atmosphere, that is, in contact with excess air. Under such oxidizing conditions (excess air present), thermodynamics tells us, firstly, that at chemical equilibrium dioxins will be completely converted to carbon dioxide, water vapour and hydrogen chloride. A second important thermodynamic conclusion is that once dioxin is completely destroyed by oxidation (converted to CO_2, H_2O and HCl), these decomposition products will not re-convert to dioxin upon cooling. In other words, once dioxin is completely oxidized, it is destroyed for ever.

It should be noted that the presence or absence of possible catalytic effects has no effect whatsoever on these conclusions, since catalysis influences only the rate at which equilibrium is reached, but not the equilibrium position.

It must be emphasized, however, that thermodynamics can only tell us what is possible under ideal conditions (i.e., chemical equilibrium). The key question of whether dioxins in reality be completely destroyed cannot be answered by thermodynamics, but by chemical kinetics, that is, which reactions occur and how rapidly these reactions occur.

It is for this reason that it is necessary to study kinetic aspects (mechanisms and rates) of the destruction problem.

The formation of hazardous organic compounds during the incineration of CHC has been a subject of many research programs. Most of these studies describe the formation and degradation of PCDDs and PCDFs from a mechanistic point of view (12, 35 to 48).

A very complete review of these reactions is given by Choudhry and Hutzinger (29), who conclude their work with a set of hypotheses concerning the thermal generation of chlorinated -benzenes, -dibenzofurans and -dibenzo-p-dioxins in incinerators. According to their theory it is possible that PCFDs and PCDDs:

-1 are trace components of refuse and do not undergo effective thermal destruction

-2 are produced during the pyrolysis and combustion of chlorinated precursors like PCBs, chlorophenols, chlorinated phenoxyacids, polychlorinated diphenylethers (PCDPEs) and chlorinated phenoxy-2-phenols

-3 are formed as a consequence of a complex array of pyrolytic processes of chemically unrelated organic compounds (see Fig.3).

It should be noted that this theory is based on data concerning the incineration of both municipal and chemical waste.

Tsang and Shaub (31) give a quantitative approach to the two main reaction mechanisms involved in CHC combustion: the unimolecular and

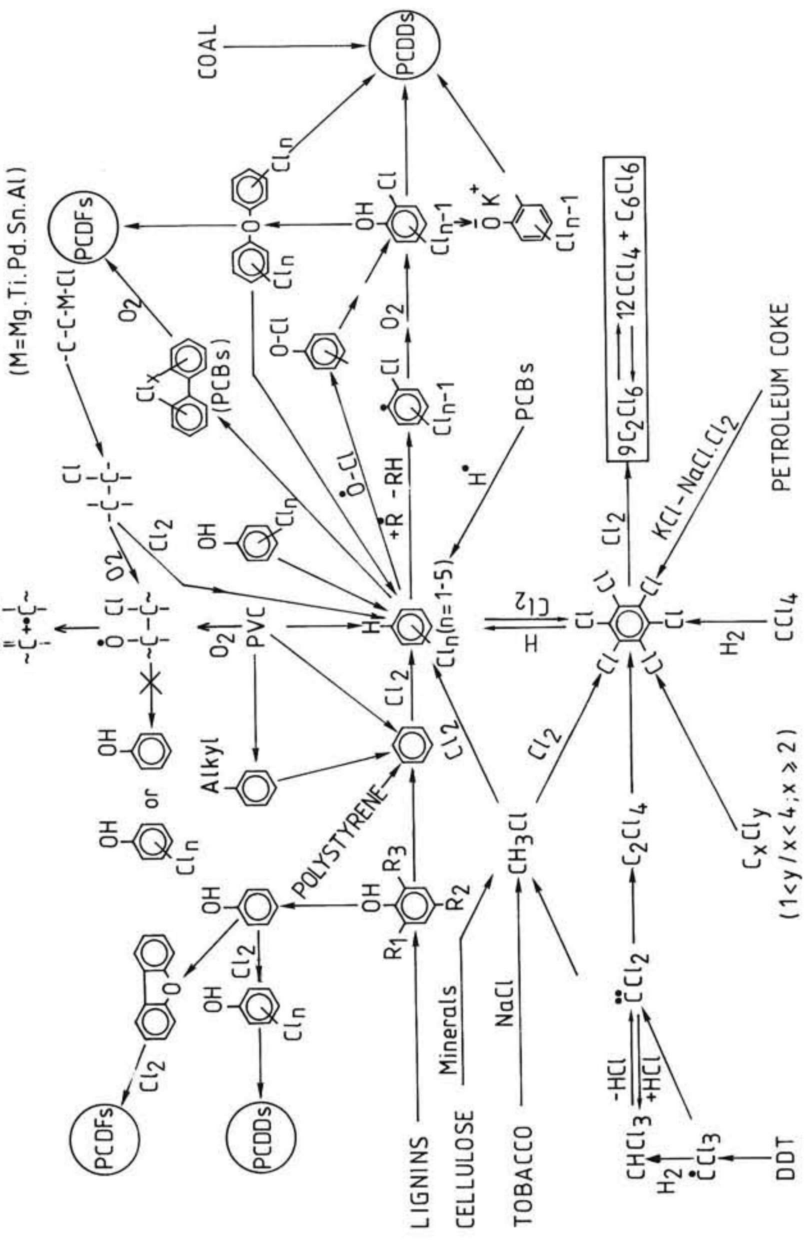


Figure 3. Complex array of syntheses of polychlorinated dibenzofurans (PCDFs) and polychlorinated dibenzo-p-dioxins (PCDDs) from chemically unrelated organic matter i.e. de novo syntheses of PCDFs and PCDDs.
Source: Ref. 29.

the bimolecular reactions. As a unimolecular reaction the elimination of hydrogen chloride from a chloroalkane to form the appropriate alkene is the main decomposition route. For the bimolecular reaction the attack by hydrogen - and hydroxyradicals is the most important.
In general the unimolecular decomposition will be important for compounds with their weakest bond in the 80 to 85 kcal.range, which covers many of the larger organics. The radical attack is only of importance for the simple aromatics and the other unsaturated molecules without organic substituents.
This total concept can give an idea of the rate constant and reaction energy involved.

Senkan (30) also pays attention to the kinetic side of CHC combustion, but in a more phenomenological way than Tsang and Shaub. According to Senkan the difference between HC-combustion and CHC--combustion lies within the relative weakness of the C-Cl bond compared to the C-H bond. Because of this weak C-Cl bond the ignition temperature of CHC/HC mixtures is decreased. On the other hand, at higher temperatures the decomposition of CHC inhibits hydrocarbon combustion. This inhibitory effect is due to free radical scavenging by Cl-radicals, which decreases the H- and OH-radical concentration; these latter two radicals are necessary for combustion. These two contrasting aspects can be recognized in the two-stage ignition character of CHCs. An important feature of two-stage ignition is that although there is an appreciable temperature increase as the first stage proceeds, the reaction rate does not increase but decreases. This fact clearly indicates that the self-quenching must be of chemical origin.

In later publications by Bose and Senkan (41,42) this phenomenon is described more thoroughly on the base of research carried out on the combustion of trichloroethylene. During the first stage the CHC undergoes a rapid oxidation reaction, with the formation of CO, HCl, and Cl_2 as the principal intermediates (reaction 9), followed by the slower, by HCl and Cl_2 inhibited, oxidation of CO as the second step (reaction 10).

$$\mathrm{CHC}, O_2 \xrightarrow{\text{fast}} \mathrm{CO}, Cl_2, \mathrm{HCl} \quad (H_2O, CO_2) \qquad (9)$$

$$\mathrm{CO}, O_2 \xrightarrow[\substack{Cl_2 \text{ and HCl} \\ \text{inhibited}}]{\text{slow}} CO_2 \qquad (10)$$

The temperature in the first stage and the intermediate zone is relatively low, because of the heatsink effect of the Cl_2-dissociation to Cl-radicals. Bose and Senkan also report the formation of products of incomplete combustion (PICs) during the first stage. These intermediates are formed and then decomposed to low concentration levels in a relatively narrow region of the flame. However, many of them persisted at trace concentration levels throughout the flame, indicating the potential for emission problems in practical incineration systems. Besides these kinetic aspects of CHC combus tion, Senkan also describes the more physical aspects of CHC combustion.

The formation of soot during the combustion of CHC and the burning velocity of CHC-flames have been the subject of fundamental research. Senkan (30,49) describes the soot formation of CHC-methane--air flames. Basicly soot is formed if the rates of carbon formation are higher than the rates of carbon gasification. Miller et al. (46) report on the same subject, concluding that in the methyl chloride flames the presence of chlorine promotes the formation of acetylene, which may explain the propensity of soot formation from chlorinated hydrocarbons. Soot is a product of incomplete combustion and is therefore often accompanies, and is therefore a sign of, the production of toxic polycylic aromatic hydrocarbons.

The formation of soot in chlorinated hydrocarbon flames occurs more readily than in corresponding flames with nonchlorinated compounds. This is due to:

1 - the relatively weak C-Cl bond strenghts, when compared to C-C and C-H bonds;
2 - the lower enthalpies of combustion of chlorinated hydrocarbons, which may then result in relatively lower flame temperatures;
3 - the H, OH and O-radical scavenging characteristics of chlorine and its derivatives.

Senkan (30) describes the temperature dependency of the burning velocity, which in the case of CHC combustion leads to a relatively low burning velocity because of a lower flame temperature for CHC than for HC. According to Valeiras et al. (50) the suppression of the burning velocity is increased by an increasing chlorine content of the burning mixture. This inhibition is not only due to the decrease of the flame temperature, but also, as generally is accepted, due to the free radical scavenging characteristics of chlorine and chlorinated compounds. As a consequence, complete combustion of CHC would require longer reaction times and/or higher operating temperatures to achieve the same degree of destruction as HCs.

As already stated in the previous paragraphs, in the last five years much effort has been put into fundamental chemical research on the combustion of CHC. This research has lead to different models describing the chemical processes during CHC-combustion. One model, developed by Shaub and Tsang (51), deals with the homogeneous gas phase formation of PCDDs from chlorophenols in an incinerator environment. On the basis of a reaction mechanism, which is not isomer-specific, kinetic rate constants are estimated. With this model calculations are made, which lead to the conclusion that the probability of gas phase formation of PCDDs is likely to be very low at high temperatures (>1200 K) if mixing between fuel and air is efficient. Furthermore, the production of PCDDs from chlorophenols is found to depend upon the square of the chlorophenol concentration. Shaub and Tsang also point out the limitations of the model, which works with a kinetic mechanism, which, in principle, does not take any change of physical circumstances into account, such as apparatus form, turbulence, etc. The influence of mixing inhomogenities and temperature fluctuations are discussed, as well as the non-gas phase formation of PCDDs during the combustion process. From a theoretical point of view this model indicates clearly the direction which should be taken to prevent the formation of hazardous emissions. This direction is: working at high temperatures ($>$ 1200 K), in an oxygen rich environment with a high turbulence, with a minimal solid concentration in the incineration air.

Senkan (52) presents another model, which in contradiction to the model of Shaub and Tsang (51), predicts the formation of PIC or combustion intermediates. By using a set of 130 reversible reactions, involving about 40 species, the combustion of trichloroethylene is simulated. As a result the mole fractions of the main PICs can be calculated under different circumstances (variation of oxygen level and temperature). According to Senkan this calculation can also be performed with other waste streams, assuming the existence of a mechanisms database. For as long as the reaction rate constants are estimated, this model should be viewed as an "engineering" model. However, by undertaking numerical sensitivity studies the important reactions in the mechanisms can be identified. Following their identification, these sensitive reactions may be isolated and studied individually for the accurate determination of their rate constants. It will be clear that the accuracy and relevance of this model is defined by the completeness of the database and the accuracy of the reaction rate constants.

In summary it can be stated that much progress has been made in understanding the reactions involved in thermal destruction of CHC. This progress, however, has not been sufficiently great that the present models can accurately predict the destruction efficiency of a specific waste stream in an incinerator at given conditions. To increase the applicability of the present knowledge more research must be carried out, mainly in the field of multi-component waste stream incineration. A first step in this direction was made by Graham et al. (48).

5 EQUIPMENT

In this chapter equipment used to incinerate CHC is discussed. First general plant design will be explained, followed by specific design criteria for the various pieces of equipment. Subsequently all the different parts of an incinerator facility will be reviewed in more detail, and examples of different possibilities will be given. Finally some new technologies are discussed.

5.1 General plant design

All incinerators which currently operate have been designed for a specific waste stream. Therefore a wide range of plant designs exists. All these various designs, however, have elements in common. In general an incinerator can thus be described as a combination of: feeding zone, combustion zone, heat recovery zone and effluent cleaning zone. Because of siting aspects the heat recovery zone and effluent cleaning zone may be absent (e.g. sea-incineration). All the other zones are always present, in various forms, whose specifications are dictated by requirements set by the waste input composition and the restrictions placed on the emission output.
For each of the above mentioned zones some concrete examples, in which a number of specific parts or types are described, will be given, as described in the following paragraphs. These include the:

ZONES		PARTS/TYPES
1. FEEDING ZONE	:	- liquid atomizer - solid waste crane - barrel feeder
2. COMBUSTION ZONE	:	- refractory lined stationary oven - rotary kiln oven - fluidized bed oven - afterburner
3. HEAT RECOVERY ZONE	:	- waste heat boiler
4. EFFLUENT CLEANING ZONE	:	- wet scrubber - dry scrubber - electrostatic precipitator - HCl recovery

Furthermore, some emerging technologies are described to give an idea of the developments in the field of equipment design. The four technologies which are reviewed, a molten salt reactor, a high temperature electric reactor, cement kiln co-incineration and a plasma reactor, are typical examples of new thermal techniques which might be suitable for organo-chlorine waste incineration

Data on incineration statistics are rather scarce, but Oppelt (53) gives some information about the incineration practice in the United States. In 1981 more than 5.5 million metric tons (mt) of hazardous waste was thermally destroyed; 1.7 mt was disposed of in 240 incineration facilities, and 3.8 mt was disposed of in 1300 industrial boilers and furnaces. The EPA estimates that as much as 25 mt of the waste generated in 1981 could have been destroyed thermally. In the United States in 1981 liquid injection was the most commonly used incineration technique, followed by fixed-hearth incineration which is often used for on-site disposal of solid wastes. The third most common incinerator type is the rotary kiln incinerator. This is the most versatile incinerator type and often used at commercial off-site incineration facilities. The situation for Europe is somewhat different from North America. In Europe most commercial off-site incineration facilities operate a rotary-kiln incinerator equipped with extra liquid burners. Fixed-hearth incinerators are not used in Europe as off-site incinerators and are therefore not discussed in this paper.

5.2 Design criteria

Designing equipment for chlorinated hydrocarbon combustion is largely based on the "normal" design rules for ovens, combined with certain trial and error practices. There are, however, some specific principles for chemical waste combustors, as formulated by Cope et al.(2). These design principles are:

a - The furnace volume must be capable of receiving the physical bulk of the material and of providing sufficient residence time for the burnout of suspended particulate matter.
b - The correct combustion air requirements must be met and usually must be kept in the order of 50% - 150% above stoichiometric requirements.
c - There must be minimal use of underfire air so as to keep solids, particulates and ash on the grate and prevent them from becoming entrained in the gas stream.
d - A maximal use of overfire must be made to ensure ample oxygen and high turbulence in the combustion chamber.
e - The design temperature must be attained and maintained. Minimal combustion temperature must not fall below 800°C to ensure that carbon particles are completely oxidised and not emitted as soot.
f - The high-temperature zone must have a gas path of sufficient length and volumetric capacity to enable complete combustion of volatile constituents.

Depending on the type of waste, some principles are more relevant than others. Together, however, they define the main variables which effect proper waste combustion. These three main variables are the so-called "three T's": temperature, turbulence and residence time, which together define the degree of destruction of a certain waste compound.
Unfortunately, no general model exists which can predict with high accuracy the destruction efficiency (DE) as a function of a chosen temperature, residence time and turbulence (54). For some specific situations or on the basis of certain assumptions some specialized models work satisfactorily. For example, Wolbach (55) describes a model which can predict the destruction efficiency of a boiler. It assumes pseudo-first order kinetics for the oxidative reactions in the combustion zone. On the basis of a temperature-time boiler curve and an estimated rate constant the destruction efficiency is predicted. But this model takes neither account of the waste input composition dependency of the temperature-time curve, nor of the waste/air ratio. It should be mentioned that in the normal practice of designing an incinerator, only the temperature-time curves of previously built incinerators burning a given waste stream are known. Another important point is the rate constant, which has to be estimated. Because of the complex composition of the waste stream, no theoretical models exists to accurately calculate the reaction rate constant. Therefore, the rate constant has to be estimated on the basis of lab tests. When these test results are applicable to plant conditions, the destruction efficiency can be calculated by assuming a minimal temperature; a temperature-time curve is not needed. When the test results are not applicable to plant conditions, they also cannot be used with the model suggested by Wolbach. Nevertheless, Wolbach's approach can be useful when designing an incinerator which only has to handle one specific, chemically well described, waste stream.

In general a certain DE is usually required by the enforcement regulations. These regulations set a standard for operating conditions, which has to be translated to actual design specifications. For the three main variables, only residence time and temperature are described in the regulations. Turbulence is not specified, probably because this variable is difficult to quantify. For DE standards a direct translation to actual design specification is impossible, because of the varying waste stream composition and the lack of a reliable DE-predicting model. Most regulations also set a maximal emission level, or minimal removal efficiency, for HCl, HF and particulate matter. In contrast to DE standards, standards for air pollution control equipment can often be directly translated to standard design specifications for typical equipment of this type. From here on the designing process starts with a waste characterization, which includes specifications for average and extreme operating circumstances. This is followed by preliminary test burns and preliminary engineering assessment. During the design process special attention has to be paid to equipment reliability and operating safety and hygiene. Lastly the design is finalized, a proces which is still more an art than a science due to the lack of fundamental knowledge about the correlation between waste properties, burner design and operating conditions (56,57).

Basic ideas, like operating with underpressure to prevent gas leak and using recycle connections on liquid waste input, are common knowledge after several years of operating practice (58). Bonner et al. (59) compiled literature on the incineration of chemical wastes, which can be very useful when evaluating an incinerator design on operating specifications and reliability.
As already mentioned, however, even though much data on heat balances, temperature profiles, etc. are present, the design of incinerators is still largely a "black box" process with regard to the chemical processes taking place (57). To improve this situation several research programs are being conducted to provide information which is essential to improving the design process. Union Carbide is investigating the spray combustion of liquid chemical wastes. Spray nozzle selection, fuel mist and combustion air mixing pattern and burner selection are being studied to provide information about destruction efficiency improvement (57). Other studies performed by EPA involve the reliability and controlability of incinerators, the variables affecting incinerator failure, time/temperature requirements for solid wastes detoxification and the so-called emerging technologies (60).

5.3.1 Feeding zone

Depending on the type of waste, different feeding equipment is required. We start with solid wastes.
Solid waste is present in two categories: unpacked solid waste, usually stored in a bunker, and drummed solid waste. Unpacked solid waste can be fed continuously or in batches. For reasons of operating stability, the continuous feed method is preferred. Continuous feeding is carried out by a moving belt or a screwfeeder. The batch feed method, carried out either by open charging or by air lock feed, is performed by a charging hopper.In spite of the improved oven operating stability associated with continuous feed, batch feeding is usually preferred above continuous feeding because of the higher operating reliability. Drummed solid waste is fed semi-continuously by a moving belt. The general practice of dropping small containers into a rotary kiln without emptying them has certain disadvantages. Explosions (deflagrations) can occasionally occur with resultant strong soot generation and excessive thermal and mechanical loading of the kiln refractories, which can lead to damage.

With liquid wastes the viscosity and, for liquids which contain particles (e.g. slurries), the maximal particle size is important for choosing the right type of atomizer. An atomizer is necessary to increase the exposed liquid surface area in the combustion chamber.
Some atomizer types are:

- rotary cup atomizer
- single fluid pressure atomizer
- two-fluid, low pressure atomizer
- two-fluid, high pressure air atomizer
- two-fluid, high pressure steam atomizer

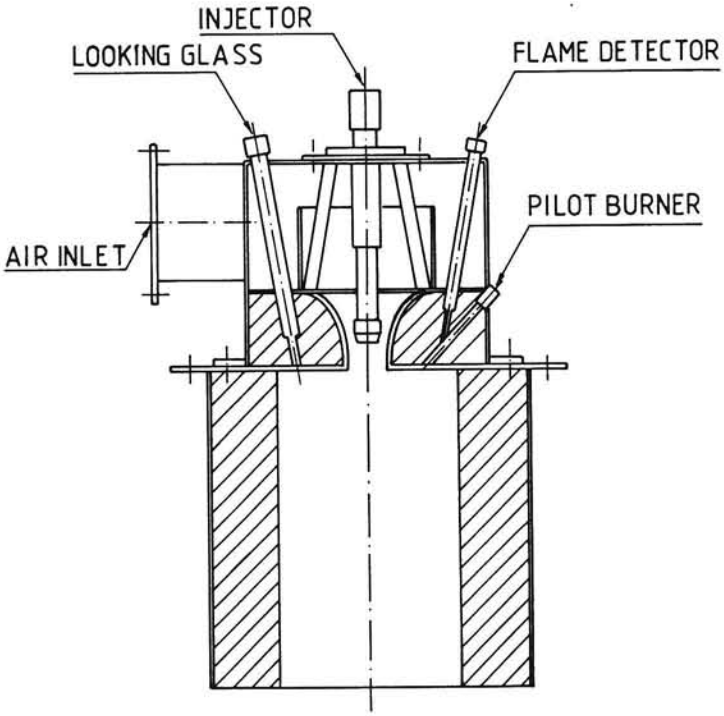


Figure 4. Scheme of a Vortex burner
Source: Ref. 74

All atomizers have a specific operating range (59). Some atomizers are part of a burner, like the Vortex burner (see Fig. 4) and the rotating cup burner. Others are used only as atomizers, combustion being brought about by ignition with pilot burners. Depending on the liquid waste throughput, it may be necessary to use more than one atomizer to ensure a sufficient droplet surface area.

Santoleri (58) reports on atomizer design and atomizer location. In the United States most incinerators use pressure spray nozzles using air or steam to assist atomization. In Europe, on the other hand, the rotary cup atomizer is often applied. According to a recent EPA report (28), although some experimental information is available on burner operating characteristics, sufficient data do not exist to correlate liquid injection chemical waste burner performance with the destruction and removal performance achieved by the incinerator system.

A very important aspect of liquid waste feeding is the mixing and blending of the various batches of liquid chemical wastes prior to the waste injection. This blending is necessary to obtain a homogenous liquid input, which facilitates operating stability; such stability is absolutely necessary in order to meet emission levels. Greater operating stability also extends the lifetime of the equipment. To achieve blending, special blending tanks are usually used, with or without mixing equipment; these tanks usually contain the waste which has to be incinerated within one day.

Various types of mixing equipment exists. The simplest mixing device consists merely of two tubes which are joined together to form one tube. This solution is used when dealing with a small number of waste streams, of which each has an almost constant composition. This mixing method can also be used for adding oil to a low caloric waste stream, to ensure a sufficiently high oven temperature. When working with viscous liquids it is advisable to use recirculation circuits in the feeding line to prevent blocking. These recirculation circuits also increase the ability to achieve flexible dosage, which is necessary when operating a rotary kiln.

5.3.2 Combustion zone

Presently three types of ovens are being used for [illegible] ydro-
carbon combustion. Two of them, [illegible] lined
oven and the rotary kiln oven, are [illegible] ype,a
fluidized bed oven, is used less. [illegible] spe-
cific waste streams, are describe [illegible] are
used to increase the destruction [illegible] lia-
bility, are also described.

5.3.2.1 Refractory lined stationar [illegible]

This oven is the oldest type used f [illegible]
The chamber is designed to promote [illegible] com-
bustion air, and to allow sufficient residence time for the reactants to achieve complete combustion. In practice usually simple

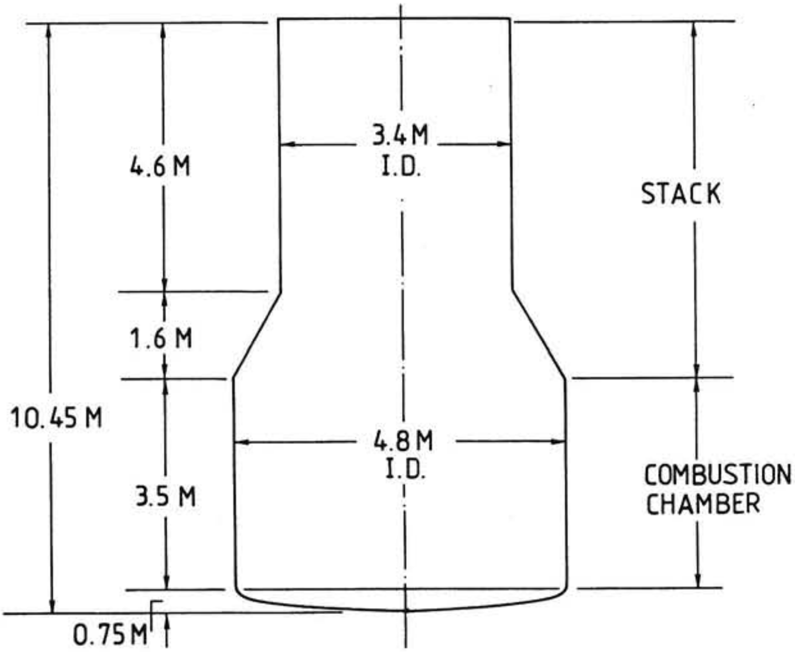


Figure 5. Typical example of a sea-going refractory lined stationary oven.
Source: Ref. 28.

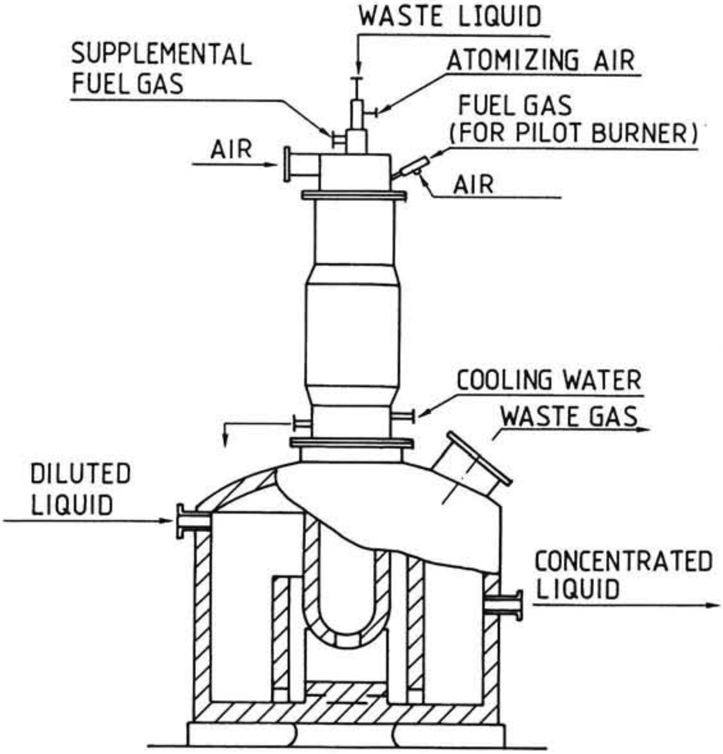


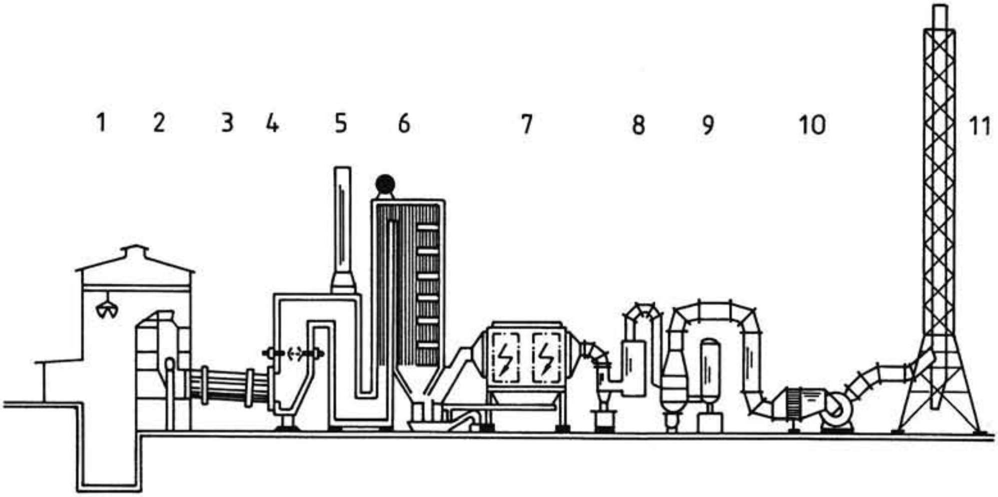
Figure 6. Scheme of a submerged incinerator.
Source: Ref. 74.

cylinders, either horizontally or vertically aligned, are used.
Two examples are given in Fig. 5 and 6, one typical for a sea-going incinerator and one as a part of a complete facility.
Several burners can be placed in the oven, together with temperature and gas monitoring equipment. In order to prevent unnecessary erosion burners have to be located in the chamber in such a manner that the flames do not impinge on the refractory walls. The refractory material has to be inert to acid gases at high temperatures. (see page 33 and Table 6)

5.3.2.2 Rotary kiln oven

The rotary kiln was originallly developed for applications such as drying and calcining, and only since the early seventies has it been used for solid chemical waste combustion. The kiln, which is a large cylinder rotating on steel wheels turning on trunnions, is sloped slightly from the feed to the discharge end so that the solid material being processed will move along the length of the cylinder. The cylinder is lined with some type of refractory, usually a heavy--duty, hard surfaced firebrick (61). The waste material is charged at the high end of the kiln and is usually ignited by a burner located at the low end of the kiln. More recent models, however, use another configuration. In these models the burning equipment is located at the feed-end of the kiln for injecting the waste which is combustible in itself and therefore does not need a great deal of auxiliary heat. These burners are also used for the initial refractory heat up, in which case oil is used as fuel. The kiln dimensions vary with each facility. A typical kiln is about 14 m long and 3 m in diameter, with an average rotating speed of 9 revolutions per hour. The residence period for the solid waste in the kiln is appr. 1.5 hour (62).

Unlike liquid injection incinerators, which have no moving parts, rotary kiln designs incorporate high temperature seals between the stationary end-plates and the rotating section. The air tightness of these seals is inherently difficult to maintain, a problem which creates the potential for release of unburned wastes. Rotary kilns burning hazardous wastes therefore almost always operate at below atmospheric pressure to circumvent this problem. Difficulties, however, can still arise when batches of waste are fed semi-continuously. When drums containing relatively volatile wastes are fed into the kiln, for example, extremely rapid gas expansion occurs. The expansion results in a pressure surge at the feed-end of the kiln, which forces unburned waste out through the end plates seals. This phenomenon is known as "puffing" and can pose a major problem if extremely toxic or otherwise hazardous materials are being burned (59). Sittig (63) describes some of the various types of air seals. The simplest type is a floating T-section ring mounted on a wearing pad around the feed-end of the kiln shell. The web of the T-ring is confined within circular retainer plates. Air infiltration through this type of seal is usually less than 10%.



1 Solid waste bunkers
2 Kiln charging system
3 Rotary kiln
4 Liquid waste burners
5 Afterburner chamber with emergency stack
6 Heat recovery boiler
7 Electrostatic filters
8 Flue-gas scrubber
9 Scrubbing water oxidation
10 Suction blower with heat exchanger
11 Stack

Figure 7. Typical example of a rotary kiln incinerator.
Source: Ref. 62. Reproduced by permission of Gulf Publishing Company.

Another difference with a liquid burner is the presence of ash. This ash is made up primarily of slag and other nonburnables such as drums and other metallic material. The ash discharges from the end of the kiln into a conveyor trough that contains water. After quenching, the material is conveyed into a dumping trailer, and then to a landfill. Figure 7 gives an example of a rotary kiln incineration facility.

In general rotary kiln incinerators are usually also equipped with an afterburner chamber to destroy the unburned volatile organics. This is done because the kiln oven is designed for burning solid wastes, and therefore the residence time of the solid waste is the primary concern, not the residence time of the gas phase. Presently, however, most of the newly designed rotary kiln incinerators have a sufficiently long gas phase residence time to achieve the designated degree of destruction.

Both a stationary oven and a rotary kiln oven are lined with refractories. Table 6 gives data on some commercially available materials. Besides the refractory composition, the physical form of the material can be different for specific usages. Suspended refractory brick is normally used in stationary liquid injection-units and afterburners. In kilns, however, castable refractories are normally used to better withstand the physical abrasion and vibration caused by rotation and contact with moving solid wastes. Castable refractories are made of the same clays as those used in aluminosilicate fire brick, but bonding agents are added to impart strength until the temperature in the incinerator during the initial start-up has become sufficiently high to "cure" the material and to develop ceramic bonds (59).

5.3.2.3 Fluidized bed oven

The fluidized bed incinerator consists of a refractory-lined vertical vessel containing solid granular material. Gases are blown through this material at a rate sufficiently high to cause the bed to expand and to act as a fluid. The gases are injected through nozzles that permit flow up into the bed and restrict downflow of the bed material. Waste feed enters the reactor either above or from the side of the bed. Preheating of the bed to start-up temperature is accomplished by a burner located above and impinging down on the bed (59). See figure 8.

The main advantage of the use of a fluidized bed furnace is the presence of a homogeneously mixed combustion zone. Because of this and the relatively long residence time (for liquids ± 12 seconds compared to ± 2 seconds in a liquid burner), the temperature of the furnace can be considerably lower than a liquid incinerator and still achieve a given destruction efficiency. Lower incineration temperatures result in longer incinerator lifetimes and lower emissions of acidic nitrogen oxides.

Another advantage of the fluidized bed oven is the possible reduction of sulfuric oxide emission because of the scrubber characteristics of some types of bed material, e.g. $CaCO_3$, which reacts with SO_2 (64). A specific point of interest with fluidized bed incinerators is the salt content of the waste being burned.

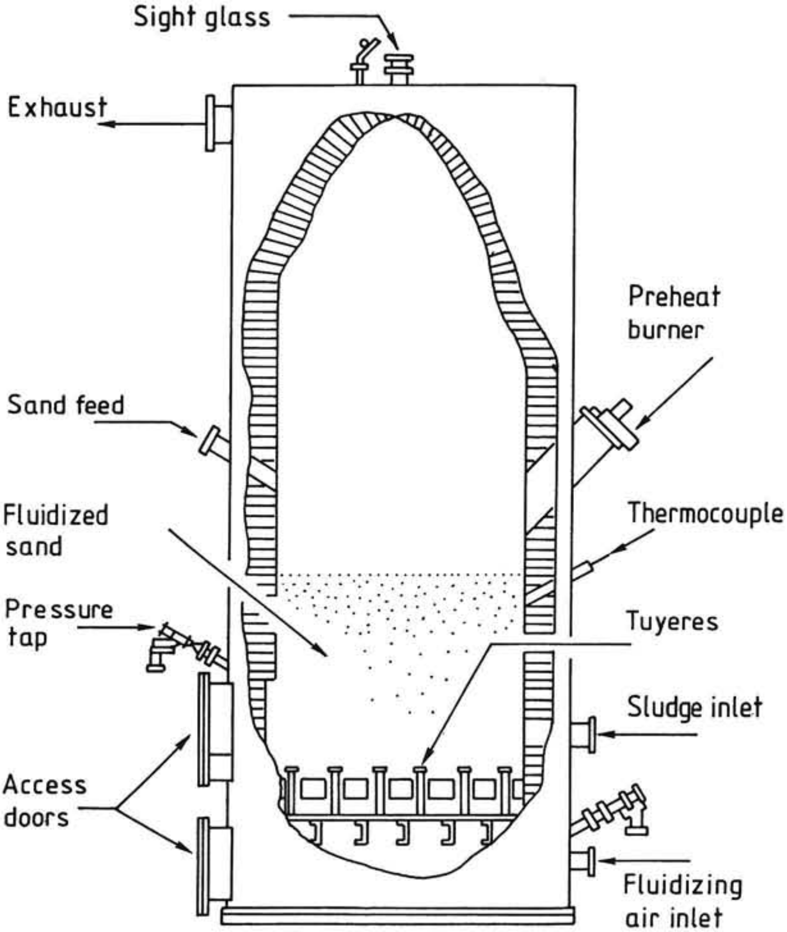


Figure 8. Cross section of a fluidized bed furnace.
Source: Ref. 63. Reproduced by permission of Noyes Data Corporation.

Table 6

General characteristics of silica and aluminosilicate refractory brick

Type	Typical composition	Fusion temperature °C[a]	Resistant to	Degraded by
Silica	95% SiO_2	1705	HCl, NH_3, acid slags	Basic slags, Al, Na, Mg, F_2, Cl_2, H_2 (T>1,670°C)
High-duty fireclay	54% SiO_2 40% Al_2O_3	1720	Most acids, slag conditions	High-lime slags, other bases at high temperature
Super-duty fireclay	52% SiO_2 42% Al_2O_3	1745	HCl, NH3, SO_2, most acids	Basic slags, Na, Mg, F_2, Cl_2, H_2, (T>1,670°C)
Acid-resistant (type H)	59% SiO_2	1670	Excellent for most acids; bases in moderate concentration	HF, H_3PO_4
High-Alumina	50-85% Al_2O_3	1760-1870	HCl, NH_3, SO_2	Basic slags, Na, Mg, F_2, Cl_2, H_2, (T>1,670°C)
Extra-High-Alumina	90-99% Al_2O_3	1650-2010	HCl, HF, NH_3, SO_2, S_2, HNO_3 H_2SO_4, Cl_2	Na, F_2 (T>1,225°C)
Mullite	71% Al_2O_3	1810	HCl, SO_2, NH_3	Na, F_2, Cl_2, H_2 (T>1,670°C)

[a] A safety factor of at a least hundred degrees (°C) between refractory fusion temperature and incinerator operating temperature is advisable.

Source: Ref. 59

These salts, and also the acid gases formed during combustion, can react with the bed material and, under certain circumstances, form eutectic mixtures which melt at a relatively low temperature. If these eutectics are allowed to accumulate, the fluidized bed may collapse (65).

A typical reactor has an inside diameter of 3 to 8 m and a height of 5 to 10 m. Silica beds are commonly used and have a depth of 1 m at rest and extend up to 2 m in height when fluidizing air is passed through the bed. Waste and auxiliary fuel are injected radially into the bed and react at temperatures from ca. 450°C to 800°C. Further reactions occur in the volume above the bed at temperatures up to about 1000°C (59). The maximum bed temperature is 900-950°C because of the occurance of sintering and glassification. It is therefore essential to use an afterburner when destroying chlorinated hydrocarbon wastes in a fluidized bed incinerator (66).

The technique of fluidized bed incineration is a relatively new method for disposal of waste materials. It was first used commercially in the United States in 1962 and has found limited use in the petroleum and paper industry. Up until now this technique has not been widely used for CHC combustion, although several research projects currently are evaluating the applicability of fluidized bed combustion for CHC incineration. Sittig (63), for example, describes some present applications of fluidized bed furnaces for waste destruction. Most of the information concerns sludge and waste incineration, like the work of Becker and Wall (67) and Kerkhof and Van Ham (66), all involved in designing fluidized bed furnaces. Recent publications by Freeman (68,69) describe fluidized bed combustion, combined with the use of a afterburner, as a viable solution for chlorinated hydrocarbon incineration.

5.3.2.4 Afterburner

Afterburners are simple combustors employed to destroy gaseous hydrocarbons not destroyed in the incinerators. The types most employed are the direct flame and thermal afterburner. Thermal and direct flame afterburners are usually an integral part of rotary kilns used for chemical waste incineration (59,63). Direct flame and thermal afterburners are similar, but they destroy organic vapors by different methods. A high percentage of the vapors pass directly through the flame in a direct flame unit. In a thermal unit the vapours remain in a high temperature oxidizing atmosphere long enough for oxidation reactions to take place. A thermal afterburner can be described as a lengthened combustion chamber, with an extra air addition to ensure the presence of an oxygen-rich environment.
In order to increase the temperature some afterburners are equipped with liquid waste burners. These direct flame afterburners can be described as a liquid waste incinerator with extra gas input from a rotary kiln.
Afterburners are equipped with secondary air inlets and wall profiles to ensure good mixing between the rotary kiln off-gas and the secondary air. This mixing can be a problem because of the viscosity differences between the two gas streams, which are caused by the

large temperature difference between the off-gas and ambient secondary air. Little is known about this effect, although the presence of cold air pockets can cause the formation of pollutants (51).

5.3.3 Heat recovery

Heat recovery has been used since the beginning of the seventies, at that time mostly in the form of direct recuperation (70). Later on waste heat boilers were installed in chemical waste incinerators. Several types are used, the majority being water-tube boilers.

In the beginning there were fears concerning corrosion problems which were expected to occur when the tube bundles were exposed to high-temperatures gases containing hydrogen chloride, chlorine, oxygen and water vapour. Under certain conditions these gases will certainly destroy carbon-steel boiler tubes by corrosion. Studies conducted on these problems, however, show that a carbon-steel surface may indeed be used provided that metal temperatures do not exceed 300°C or drop below the dew-point of the combustion products (71). Because many operating facilities use waste heat boilers with an exit temperature of ± 350°C, other materials than carbon steel are used, for instance high nickel alloys, like Hastelloy.
Another problem with operating a waste heat boiler in a rotary kiln incinerator is the presence of salts and oxides in the flue gas, present in the form of vapour, liquid droplets and particles, which can solidify on the waste heat boiler tubing upon cooling. This encrustation reduces thermal efficiency and can also cause plugging of the waste heat boiler tubing bundle.
These problems can be avoided by cooling the incinerator exhaust gas below the salts' melting points (± 760°C) before they enter the waste heat boiler, either by quenching with water, ambient air, or recycle gas from the waste heat boiler exhaust (65). Under these conditions the ash passes through the tube bundle in the form of fine particles.
Because of the importance of high operating reliability and a long operating life, gas conditions in a waste heat boiler have to be as follows (71):

- a uniform gas temperature entering the tubes;
- a high gas velocity through the pipe bundel to prevent ash build up and to promote good heat transfer;
- stack-gas temperatures sufficiently high to prevent dew-point corrosion (condensation which includes water).

Some recently built incinerators are equipped with a waste heat boiler which meets all of these three criteria. Such a boiler is divided into two parts, first a section for radiative heating, second a section using direct, i.e. convective and conductive, heating.

5.3.4 Effluent cleaning zone

In this paragraph various types of effluent cleaning equipment will be discussed. The equipment can be roughly divided into two categories:

-1 for removal of airborne particles only;
-2 for removal of both gas phase pollutants and particulate matter.

The effluent gas contains ash particles (particulate matter) and, as gas phase pollutants, HCl, Cl_2, NO_x, HF, HBr, SO_2, P_2O_5, metals and PICs; for the rest the effluent gas contains nitrogen, carbon dioxide, water vapor and oxygen. The removal of airborne particles is mainly important when operating a rotary kiln or a fluid--bed incinerator. For this use the electrostatic precipitator will be described. The ash-particles which are produced by a liquid waste incinerator are in general removed by the equipment which is mainly designed for removing gas phase pollutants, but which is also able to remove the small amounts of ash produced. As examples for category 2, two wet scrubbers (i.e. a venturi scrubber and a packed bed scrubber) and a dry scrubber will be described.
For the removal of HCl and Cl_2 a recovery installation is sometimes used. This option is also briefly discussed.

5.3.4.1 Electrostatic precipitators

Electrostatic precipitation is a process by which particles suspended in a gas are electrically charged and subsequently separated from the gas. In this process suspended particulate matter is charged in a strong electric field as a result of bombardment by gaseous ions, and migrates towards the grounded collecting plates due to electrostatic forces. Particle charge is lost at the collecting electrode, where subsequent removal is effected be periodically rapping or rinsing. Figure 9 gives an example of an electrostatic precipitator.
Electrostatic precipitators are effective for the collection of fine particles (less than one micron in diameter), but are unable to capture gases. The particle removal efficiency can be up to 99%. The collection efficiency of the precipitator is influenced by the resistivity of the particles. When this resistivity is less than about 10^7 $ohm.cm^{-1}$, the electrical forces holding the material to the collection plates may be too low. Excessive re-entrainment can occur yielding lower performance.
Increasing moisture content lowers the resistivity. A change in the moisture content will normally only occur with a change in the feed material moisture.
Changes in the gas flowrate can also affect removal efficiency. This factor becomes more critical as the particles get smaller. If the gas flowrate increases beyond design capacity, a degradation of the removal efficiency will occur, due to re-entrainment.
It is important to inspect the automatic removal of the collected material daily, because of the high failure chance of the hopper.
The major operation problem with precipitators is the build-up of dust in the precipitator due to hopper malfunction (59).
Another possible problem with precipitators is corrosion caused by HCl. When halogenated wastes are incinerated careful waste blending must occur so that HCl-concentrations remain below ± 1000 ppm HCl.

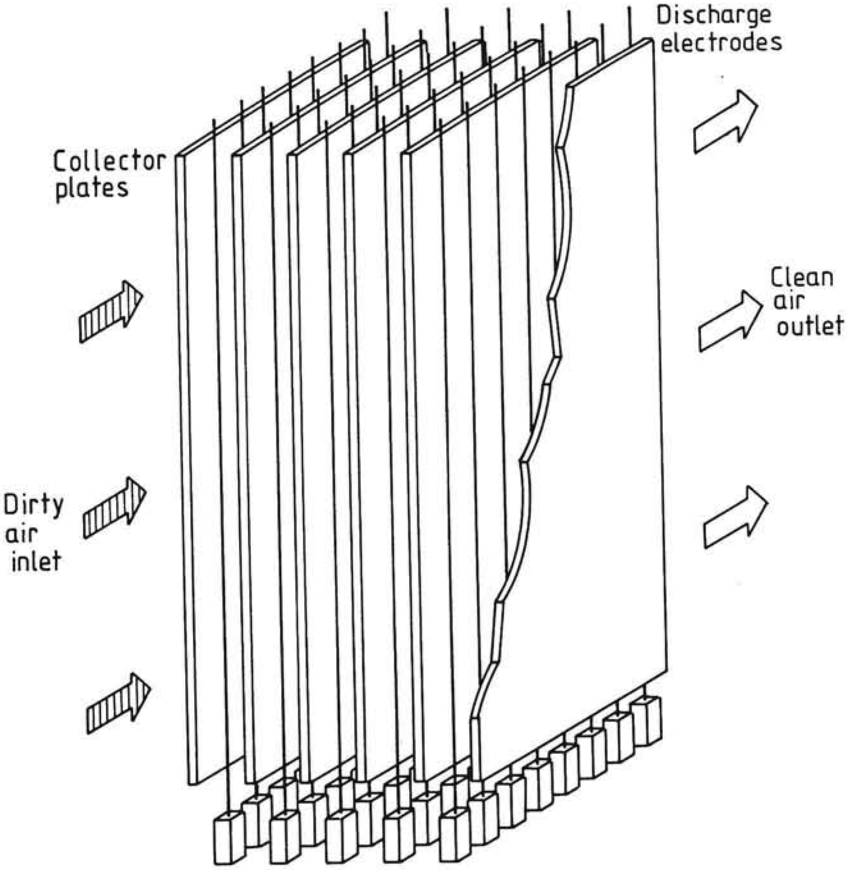


Figure 9. Scheme of an electrostatic precipitator.
Source: G.D. Clayton and F.E. Clayton; Patty's Industrial Hygiene and Toxicology, 3rd ed. 1978. Reproduced by permission of John Wiley & Sons.

5.3.4.2 Wet scrubbers

Wet scrubbers are mainly designed to remove gaseous emissions, although some types are also capable of removing airborne particles. Wet scrubbers cannot remove organic compounds from the effluent gas. After describing two specific wet scrubbers, a venturi scrubber and a packed bed scrubber, the main parameters influencing their operational effectiveness are discussed.

a venturi scrubber

A venturi scrubber utilizes the kinetic energy of a moving gas stream to atomize the scrubbing liquid into droplets. In the venturi scrubber liquid is injected into the high velocity gas stream either at the inlet to the converging section or at the venturi throat. In the process, the liquid is atomized by the formation and subsequent shattering of attenuated twisted filaments and thin, cup-like films. These initial filaments and films have extremely large surface areas available for mass transfer.

Venturi scrubbers are usually designed for particulate collection, but they can be used for simultaneous gas absorption as well. High energy venturi scrubbers are capable of 99% removal of particulates in the 1 to 2-micron range and above, 90-99% removal of particulates in the 0.5 to 1-micron range, and 50% removal of particulates in the 0.3 to 0.5-micron size range.

For gas scrubbing venturi scrubbers reach removal efficiencies for HBr, P_2O_5 and SO_2 of 50-75% when using water as the scrubbing medium; for HCl or HF the removal efficiency is usually higher, but a 99% efficiency, often required by civil authorities, cannot usually be reached. However, when using a lime slurry, typically 10-32 wt% $Ca(OH)_2$ in water, the removal efficiency for HCl, HF and P_2O_5 is much higher.

An important characteristic for a venturi scrubber is the pressure drop, which is relatively high compared to other scrubber types. For the venturi scrubbers used at hazardous waste incineration facilities, a pressure drop in the range of 7.5 to 12.5 kPa is normal. The pressure drop can be used to calculate the "cut diameter", i.e. the diameter of the particles wich are removed with 50% efficiency. See figure 10. Typical liquid-to-air ratios for venturi scrubbers are 0.7 to 2.7 l/m^3 (59). For a schematic drawing of a venturi scrubber see figure 11.

b packed bed scrubber

The packed bed scrubber is a vessel filled with packing material. The scrubbing liquid is fed into the top of the vessel, with gas flowing in either a co-current, counter-current, or cross-current mode. As the liquid flows through the bed, it wets the packing material, which provides interfacial surface area for mass transfer with the gas phase. Packing materials, which vary greatly in shape and type, are usually made of ceramic or some inert other material that will withstand corrosion from acids; obviously the main purpose of the packing is to provide a very large specific surface area (m^2/m^3) for effecting rapid mass transfer.

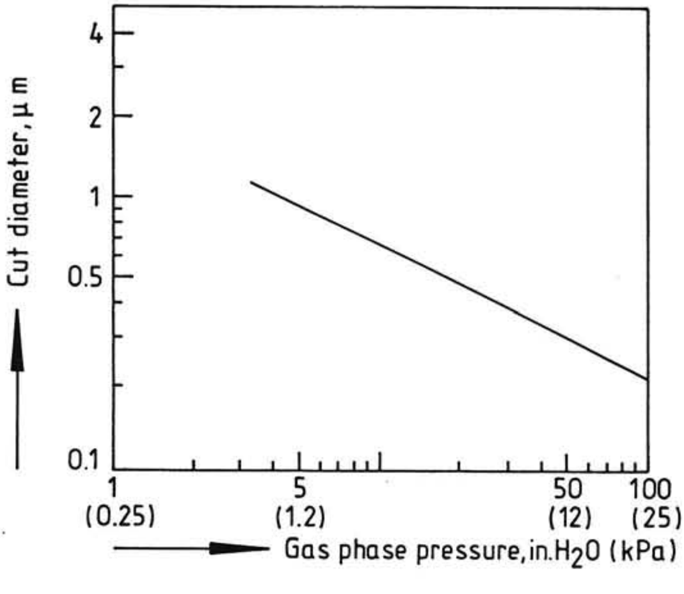


Figure 10. Pressure drop versus cut diameter for gas-atomized scrubber systems.
Source: Ref. 59. Reproduced by permission of Noyes Data Corporation.

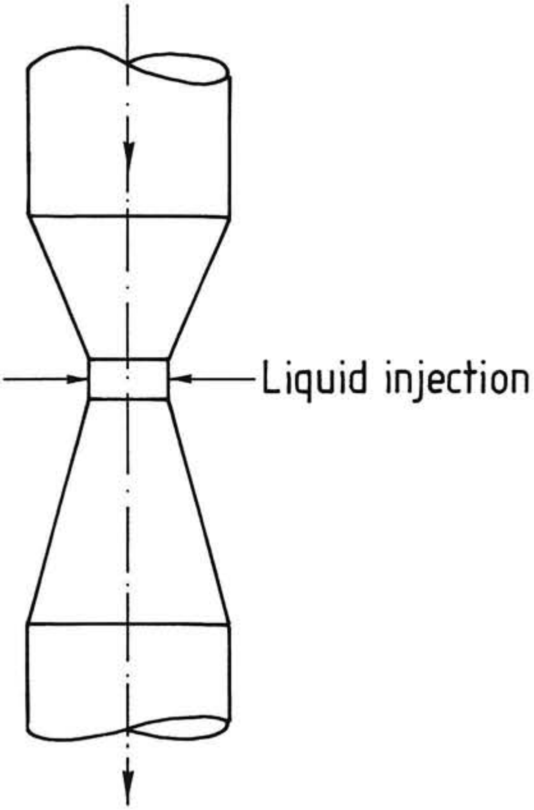


Figure 11. Schematic diagram of a venturi scrubber.
Source: L. Svarovsky; Solid-gas separation, 1981. Reproduced by permission of Elsevier Science Publishers.

Packed bed scrubbers are suitable for the removal of gaseous and aerosol pollutants, even up to very high efficiencies (99% for HCl). However, exhaust gases with high particulate loadings have to be treated before entering the packed bed scrubber; otherwise clogging in the scrubber will occur.
Sometimes, instead of water, a caustic solution (typically 18-20 wt% caustic soda (sodium hydroxide) in water) is used as the scrubbing liquid, which allows for a higher removal efficiency for HCl and HF emissions.
A packed bed scrubber also creates a gas pressure drop, because of the hindrance the gas encounters. This pressure drop ranges from 0.5 to 1.8 kPa, a higher pressure drop indirectly giving a higher removal efficiency for gaseous and particulate contaminants. Normal liquid-to-air ratios in packed beds vary from 0.8 to 10 l/m^3, with most units operating between 3 and 7 l/m^3. See figure 12.

Much is already known about wet scrubbing devices. Each scrubber is designed for a given gas stream, with a given particulate concentration, an operating temperature, gaseous pollutants concentration, required removal efficiency, etc. The operating temperature (appr. 60 to 150°C) is reached by effluent cooling using a quench tower or a waste heat boiler. Deviation from this temperature can cause several adverse effects. Excessive temperatures can cause rapid loss of scrubbing liquid by evaporation, a sharp decrease in absorption efficiency, undue corrosion, and structural damage to the unit. One or more of these occurences can increase emissions from the unit. Insufficient temperatures can cause poor plume rise, resulting in increased ambient pollutant concentrations. Temperature monitoring is therefore strongly advised.

The liquid and gas flows through the scrubber have to be within the design range to provide a sufficient removal efficiency. Therefore not only the gas flow, but also the liquid flow and the moisture content of the gas leaving the scrubber have to be measured to be able to set a liquid-gas ratio which gives a high removal efficiency.

Another important parameter is the pH of the scrubbing liquid.
Deviation from the design pH-range may result in corrosion and resulting deterioration of the scrubber structure in contact with the liquid. Furthermore, constancy of the pH-design condition is important for maintaining high scrubber absorption efficiency when removing acidic gaseous contaminants.
The pressure drop in the scrubber can be used to sensitively monitor changes in the gas flow rate, liquid flow rate and the possible occurrence of clogging problems in the system. Pressure drop provides a continuous, additional check on the normal operation of the scrubber.
Because of vaporization losses in the contacting area, make-up liquid has to be provided to the scrubber, and changes in the liquid pH have to be adjusted. Collected material also can create abrasion, contamination and corrosions problems in the scrubbing liquid and/or transport system. In addition, when hazardous materials are collected, a need for further treatment may be created prior to disposal.
General reference: 59.

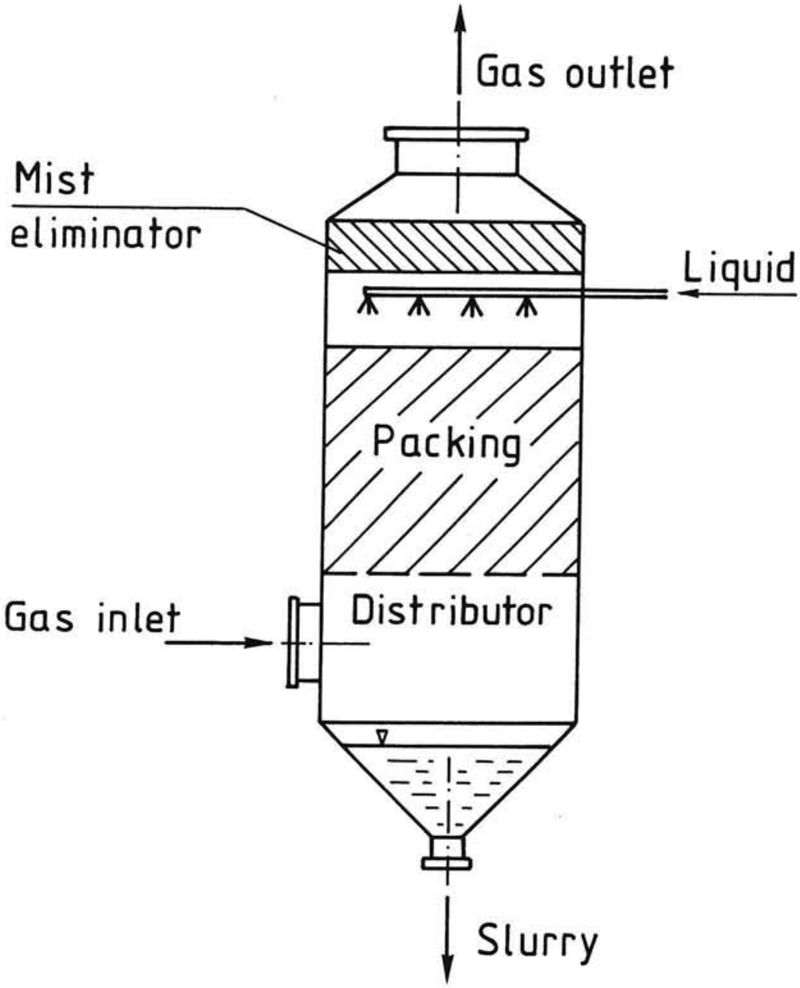


Figure 12. Schematic diagram of a packed bed scrubber.
Source: L. Svarovsky; Solid-gas separation, 1981. Reproduced by permission of Elsevier Science Publishers.

5.3.4.3 Dry scrubbers

Dry scrubbers use a liquid, alkaline absorbent, which is atomized by means of a spray dryer or a nozzle. During this atomization the water in the liquid evaporates, leaving a stream of small solid absorber particles. These absorber particles, in contrast with the water used in wet scrubbers,do not only physically absorb the flue gas components, but also react chemically with the acidic gases. Table 7 gives examples of these reactions in simplified form.

Table 7 Examples of reactions taking place in a dry scrubber

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad (11)$$
$$Ca(OH)_2 + SO_2 \longrightarrow CaSO_3 + H_2O \qquad (12)$$
$$NaOH + HF \longrightarrow NaF + H_2O \qquad (13)$$
$$Ca(OH)_2 + SO_3 \longrightarrow CaSO_4 + H_2O \qquad (14)$$

These physical and chemical processes result in a solid product with a moisture content in the range of 2-5%. The fly-ash, which is usually somewhat sticky, is conditioned at the process conditions into a free-flowing powder mixed with the reaction products.
Because only the surface layer of the absorber particles reacts with the flue gas, the inner core of the particles remain unused. Therefore a recycle circuit is used, by feeding a part of the dry powder back to the absorber feed tank. This recirculation enhances the overall system performance by reducing the absorbent consumption and creating a larger absorber surface.

The major parameters influencing the removal efficiency of dry scrubbers are the type of absorbing agent, the particle size, the operating temperature and the chemical equivalence ratio.
Generally NaOH, being more strongly alkaline (higher pH), is a better absorbing agent than $Ca(OH)_2$. However, the method of dosage can effect this order (72).
A small particle size, which strongly increases the reactive surface area, is preferred in order to reach a high removal efficiency; for example the efficiency increase effected by lowering the average particle size from 200 micron to 50 micron is 10 to 20% (absolute), depending on the temperature drop in the scrubber (72). Proper particle size requires very careful nozzle design.

The working temperature in the scrubber has to be as low as possible to achieve a high efficiency. This is so since too high temperatures result in too rapid evaporation of the liquid phase, where most of the reaction occurs, leading to insufficient reaction. Temperature can be influenced by the water concentration of the absorbent liquid, decreasing the temperature in the scrubber chamber by appr. 100°C to 130-150°C (73). The last, obvious, parameter is the equivalence ratio, which is appr. 2 for HCl. The equivalence ratio can be lowered by employing recirculation of the dry particles (73).
In contrast with the expected, there is no influence of the residence time in the scrubber on the removal efficiency. Average removal efficiencies reached by a dry scrubber are 93-99% for HCl, 95-99% for HF and 70-95% for SO_2, using $Ca(OH)_2$ as the chemical absorbing agent (73). See figure 13.

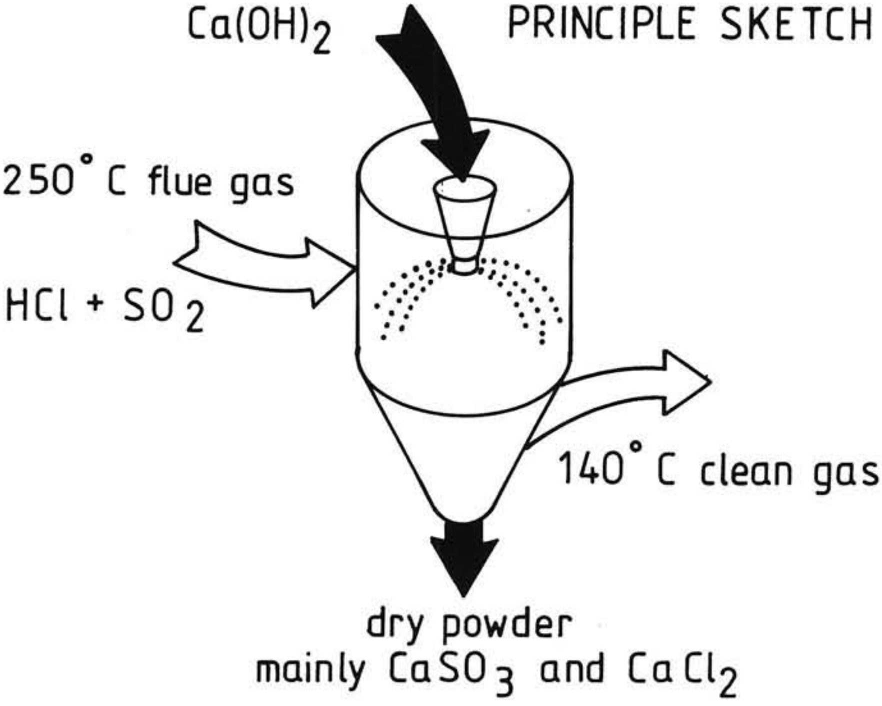


Figure 13. Schematic diagram of a dry scrubber.
Source: Ref. 73

5.3.4.4 HCl recovery

In an attempt to make the combustion of CHC more economical, the recovery of HCl has become a much studied subject. Most reports deal with the complete design of a liquid waste incineration plant with HCl-recovery (71,74 until 79). Because of the scope of this paper, the HCl-recovery system will only be discussed briefly.
Most recovery units start with a quench, which is sometimes an integral part of the incinerator, the so-called submerged incinerator (see figure 6). This quench is used to lower the temperature of the flue gases and to freeze the position of the equilibrium between HCl and Cl_2. From the quenching section the quench liquid continues through an extractive distillation tower to lower the water content. The flue gas continues through a set of absorbers to remove the remaining HCl and Cl_2, at the end through a neutralizing tower operated with an alkaline solution. See figure 14.

Because of the HCl-recovery, extra operating limits are set for the incinerator. The two main demands are the chlorine content of the waste, which has to be ± 60% to work economically, and the oxygen excess in the flue-gas. The oxygen in the flue-gas influences the HCl-Cl_2 equilibrium, that is, a higher oxygen concentration lowers the HCl-concentration, which is not favorable for the recovery process. These facts follow from the equilibrium equation of the Deacon reaction (see also section 4.2.):

$$2H_2O + 2Cl_2 \rightleftharpoons 4HCl + O_2$$

Figure 2 gives the temperature dependency of the Deacon reaction. Because of this reaction the incinerator is often operated at a 2 to 3% oxygen flue-gas level, which is rather low compared with the 10% oxygen flue-gas level in other incinerators.
Another difference with non-HCl-recovery installations is the overpressure of appr. 40 kPa in the incinerator, which is necessary to maintain a sufficiently high gas flow through the recovery equipment. This excess pressure introduces an extra safety risk, due to the possibility of leakage of HCl and Cl_2, both of which are toxic, in particular the latter.

5.3.5 EMERGING TECHNOLOGIES

In this chapter some emerging technologies for chlorinated hydrocarbon combustion will be discussed. Several reports have been published on this subject, all describing a set of options.
In one of its studies EPA describes a total of 25 processes which are being developed for hazardous waste combustion (28). All the reports consider four thermal techniques to be the most promising. These techniques are:

- high temperature electric reactors;
- co-incineration in cement kilns;
- plasma reactors;
- molten salt reactors.

In the following sections these techniques will be discussed.

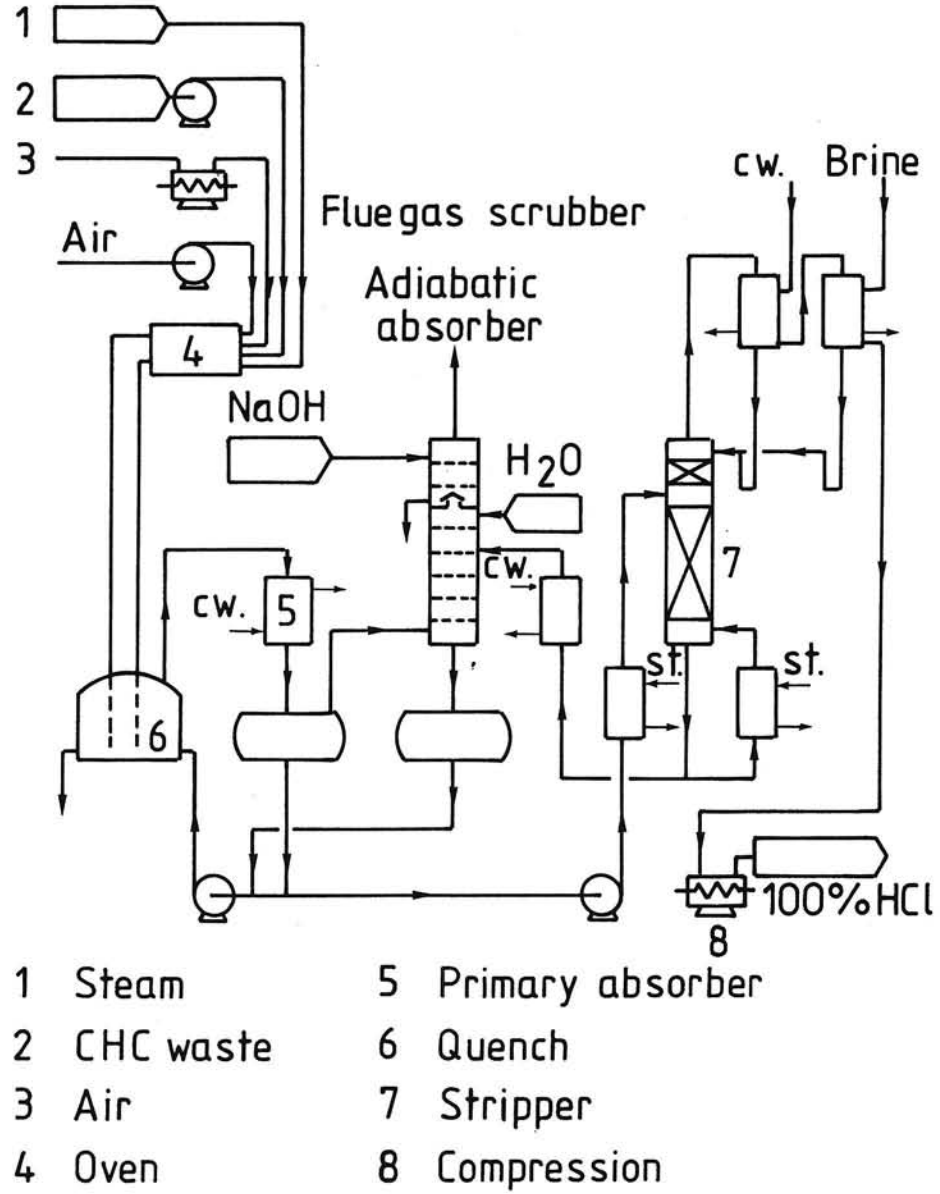


Figure 14. Schematic diagram of a HCl recovery unit.
Source: Ref. 79. Reproduced by permission of Ingenieurspers.

5.3.5.1 High temperature electric reactor

This process utilizes a vertical reactor heated by electrodes implanted in the wall whose heat pyrolizes organic waste. The reactor consists of a tubular core of porous refractory material capable of absorbing radiant energy from the electrodes and emitting this heat energy to activate reactants fed into the tubular space. The entire assembly is completely jacketed and insulated in a fluid-tight pressure vessel. Electrodes located in the annular space between jacket and tubular core provide the energy required to heat the core to radiant temperatures (68). To prevent the oxidation of the electrodes and to reduce the contact of reactants with the heat radiating surface, nitrogen injection is used to obtain a so-called fluid wall. See figures 15a and 15b.
The reactor operates at temperatures between 2200 and 2760°C, at an unspecified residence time, followed by a post-reactor treatment zone of 1370°C and a 5 seconds residence time. The post-reactor treatment takes place in an insulated vessel, without any extra energy input (60). Because of the high temperature in the reactor, a glass-like residue is produced which appears to be non-leachable (64,68,69).
Due to the rapid energy transfer effected by radiation and the resulting high reactor temperature the destruction and removal efficiency reached by this type of reactor is appr. 99.9999% (60,69).
A disadvantage of this method is the necessity of absorbing liquid and gaseous wastes into solid carriers before they can enter the reactor. There are also limits for the particle size of the introduced waste (68). In the United States a facility of this kind is used to destroy PCB contaminated solids (69).

5.3.5.2 Co-incineration in cement kilns

Already since 1974 several experiments have been carried out on the use of liquid chemical waste as an auxiliary fuel in cement kilns. Therefore this technique can hardly be called an emerging technology, but in most reviews it is still suggested as a "new" solution to the chemical waste problem (64,68,80,81).
A cement kiln, which is 50 to 170 m long and 3 to 6 m in diameter, is used for calcining and burning limestone to form clinker. The kiln is usually positioned at a slight incline, and rotates at about one revolution per minute. Raw feed enters the kiln at the high end and travels slowly towards the lower end where the fuel burner is installed. When using chemical waste as auxiliary fuel an extra burner is installed next to the main burner at the lower end of the kiln. See figure 16.
In the kiln temperatures up to 1600°C are reached. Figure 17 shows a typical temperature profile of a cement kiln. Because of the high temperature and the long residence time of several seconds, high destruction efficiencies are reached (80,81,82). Another advantage of co-incineration is the absorption of HCl into the clinker, to form sodium, potassium and calcium chloride.

This chloride formation, however, has a negative effect on the quality of the cement above a chlorine percentage of 1% in the waste

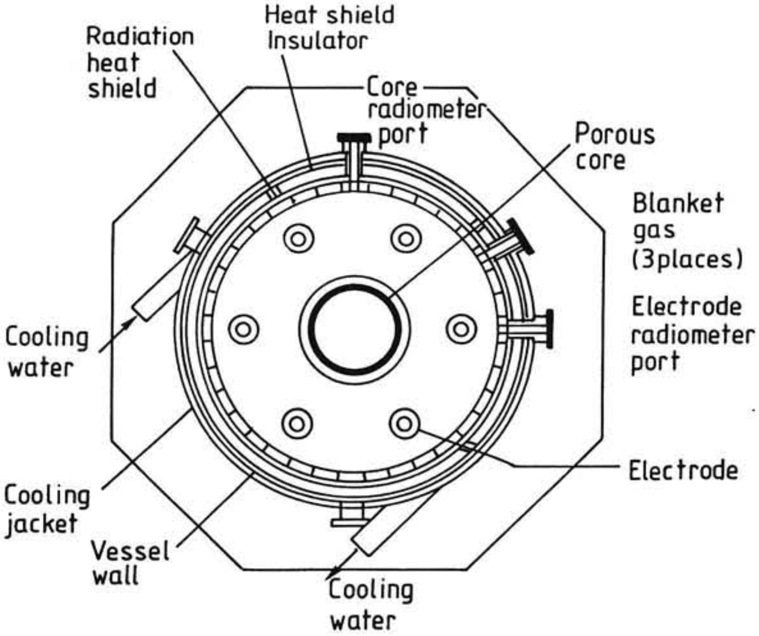
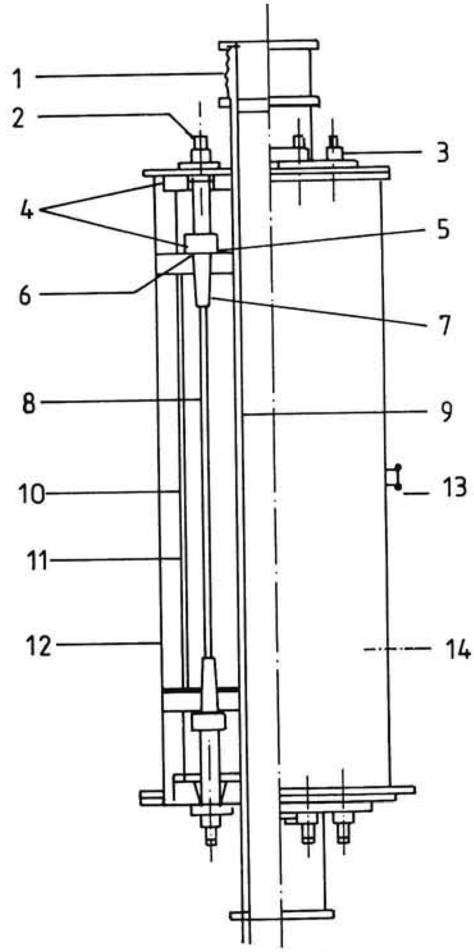


Figure 15a. Horizontal cross section of a typical high temperature electric reactor.
Source: Ref. 64.



1 Expansion bellows
2 Power feedthrough cooling manifold
3 Power clamp
4 Power feedthrough assembly
5 Radiation deflector
6 End Plate
7 Electrode connector
8 Electrode
9 Porous core
10 Radiation heat shield
11 Heat shield insulator
12 Cooling jacket
13 Radiometer port
14 Blanket gas inlet

Figure 15b. Vertical cross section of a typical high temperature electric reactor.
Source: "Hazardous waste destruction processes," by H.M. Freeman; Environmental Progress, Volume 2, No. 4, p.206 (November 1983)
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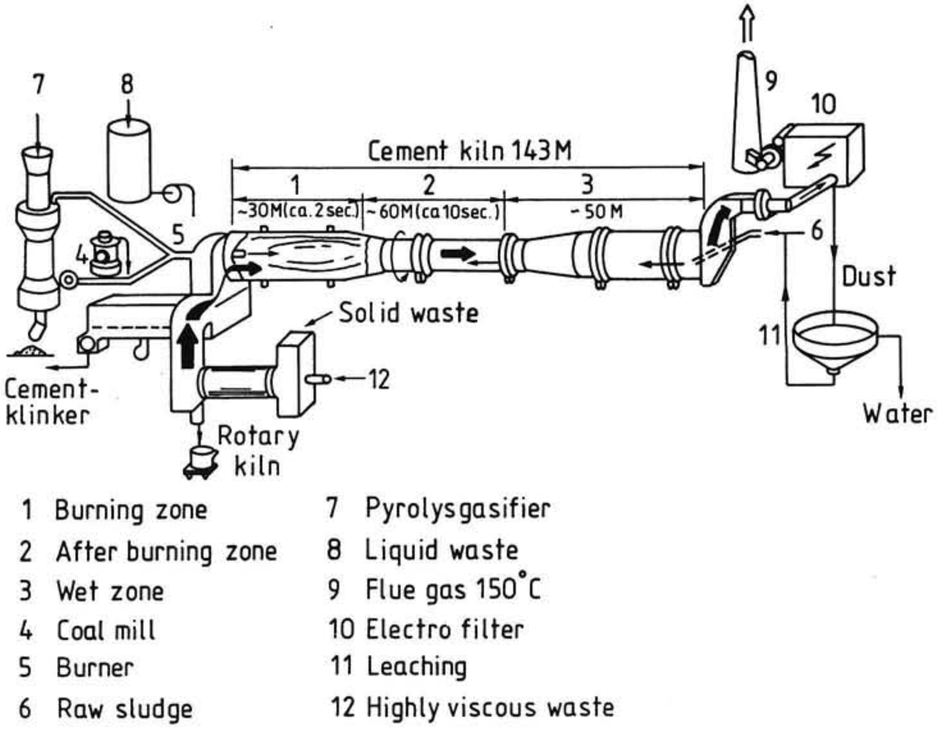

Figure 16. Schematic diagram of a cement kiln used for co-incineration.
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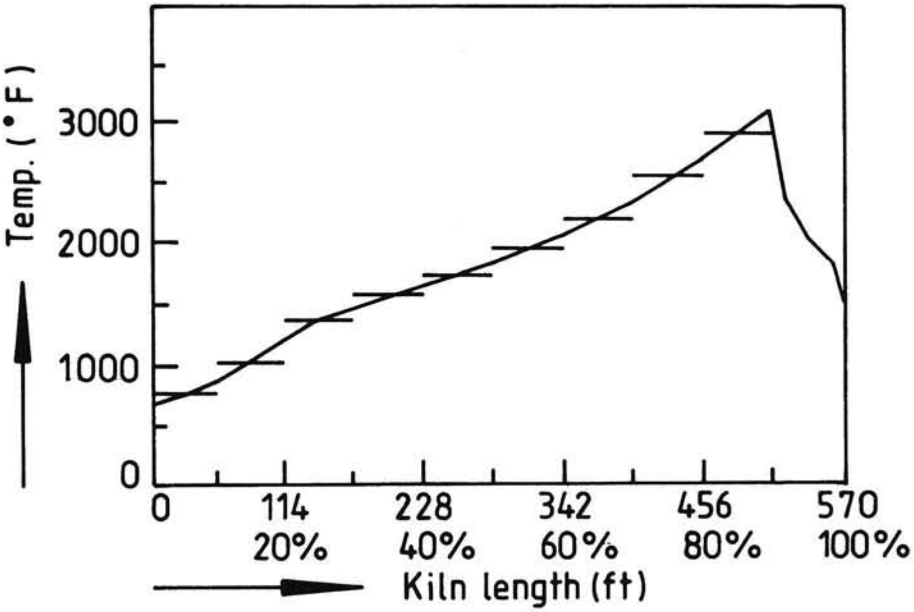

Figure 17. Typical temperature profile of a cement kiln.
Source: "Cement kilns as hazardous waste incinerators," by Leo Weitzman; Environmental Progress, Volume 2, No. 1, p. 13 (February 1983). Reproduced by permission of the American Institute of Chemical Engineers.

feed, depending on the alkalinity of the clinker feed (84). The amount of particles emitted also increases with an increasing chlorine content of the waste, caused by a decreasing average particle size which cannot be removed efficiently by a electrostatic precipitator. This can be avoided by the use of a fabric air filter.
Mix and Murphy (83) report on dioxin emissions during process disturbances, which can occur because of sudden changes in the clinker feed. At normal conditions no PCDDs and PCDFs are formed (84).
According to EPA estimations in 1981 3.5 million tons of liquid waste was disposed of in this way in the U.S. (28).

5.3.5.3 Plasmareactor

A plasma is a fluid medium consisting of charged and neutral particles with an overall charge near zero. A plasma arc is generated by electricity and can reach kinetic temperatures of up to 27,000°C. When applied to waste disposal the plasma arc can be considered as an energy conversion and energy transfer device. The electrical energy is transformed into a plasma in the form of heat (i.e. kinetic) energy. As the activated components of the plasma decay, their energy is transferred to the waste materials exposed to the plasma. The wastes are activated and ultimately destroyed as they interact with the decaying plasma (28,60).
A typical plasma incinerator system designed for PCB destruction is described by Hollis (85). This incinerator consists of a preheater, a combustion chamber (the plasma reactor), a residence chamber and a quench chamber. See figure 18. The preheater is operated at 1000°C to preheat the oxygen, which is introduced into the combustion chamber with the PCBs. The combustion chamber is a water-cooled cylinder with a refractory lining which is operated at 600 to 900 kPa overpressure to increase the combustion efficiency. The gas temperatures reached in the combustion chamber are between 2600 and 2760°C. The combustion chamber is followed by the residence chamber which minimizes the heat loss to maintain a high reaction temperature. The combined chambers provide a residence time of appr. 0.3 seconds. The exhaust gases are quenched and treated with a lime solution to remove HCl (85).
According to Ellehauge (64) destruction efficiencies up to 99.9999999% have been reached with a prototype, but no detailed analysis information is given to substantiate these claims.
The main drawbacks of this system are the high operating pressure in the combustion chamber, which may cause gas leakage, and the very high temperature, which can cause corrosion problems resulting in loss of durability of the discharge unit (64).

5.3.5.4 Molten salt reactor

Molten salt destruction is a method of oxidizing organic material and simultaneously scrubbing any objectionable byproducts of that oxidation, thus preventing their emission in the effluent gas stream. This oxidation process, which is combustion, is accomplished by injecting the material to be burned with air under the surface of a pool of molten salt. The melt is maintained at temperatures on the

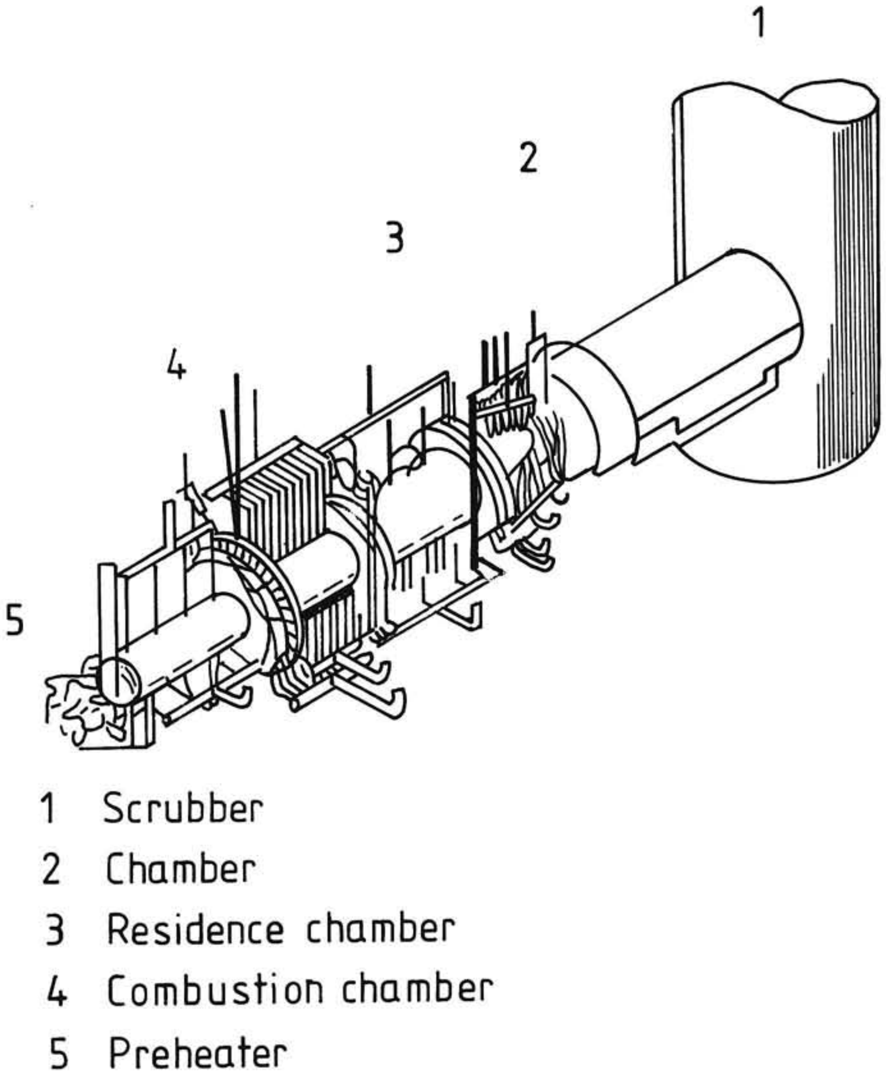

Figure 18. Schematic diagram of a plasma reactor.
Source: "Plasma temperature incineration," by J.R. Hollis; Environmental Progress, Volume 2, No. 1, p. 8 (Februari 1983). Reproduced by permission of the American Institute of Chemical Engineers.

order of 900°C. The combustion byproducts, containing elements such as phosphorous, sulfur, arsenic and halogens, are retained in the melt as inorganic salts. To prevent build up of these inorganic salts and ashes, which affect the fluidity of the melt, some of the melt has to be discharged and new melt added (68). See figure 19.

Several types of salts, or salt mixtures, can be used. For a temperature ranging from 800-1000°C, however, sodium carbonate containing 10% sodium sulfate is usually used (28,63,86). Because of the corrosiveness of the molten salt, specific engineering alloys are used for combustion chamber construction (68,86). Test results show destruction efficiencies between 99.99% and 99.999999% (28,64).

There are, however, two drawbacks to this method. Firstly, the ash content of the waste should be relatively low. Secondly, this method cannot be used for acidic wastes because of the risk of explosion (64,86).

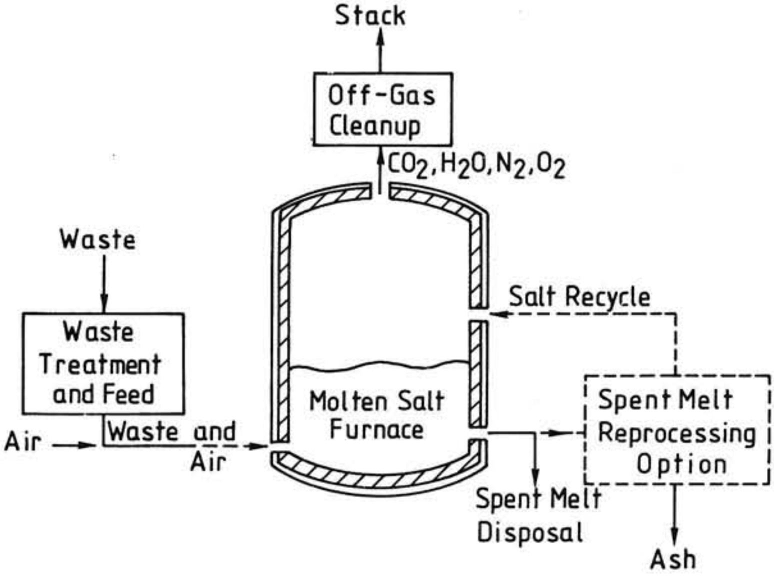

Figure 19. Schematic diagram of molten salt reactor.
Source: Ref. 63. Reproduced by permission of Noyes Data Corporation.

6 PROCESS CONTROL

Process control can be divided into two different parts. A first part concerns the monitoring of the process variables, giving information about the state of the combustion process. A second part concerns the procedures which have to be followed to maintain proper combustion conditions. The monitoring of the process variables is carried out by measuring, directly or indirectly, the main process parameters (temperature, turbulence, waste-air ratio (or excess oxygen) and residence time), and the emissions resulting from the combustion process (CO, CO_2, total hydrocarbons). Both these options (monitoring process variables and emissions) are described. The control procedures, which are sometimes prescribed in environmental regulations, are for the most part based on common sense. Mistakes, however, can still be made. Examples of control and emergency shut-down procedures are given in the following sections.

6.1 Main process parameter monitoring

When designing an incinerator the "three T's" (time, temperature and turbulence) are the main parameters. However, when operating an incinerator, the waste-air ratio is also considered to be a main process parameter, which is vital in maintaining proper combustion conditions.

Of all the four main process parameters, only the temperature can be monitored directly. The waste-air ratio is monitored by measuring the oxygen content in the flue gas, which is for solid waste the only method of monitoring which can be carried out (aside from temperature measurement). The two last main process parameters are monitored by measuring the gas-flow through the equipment. With the form and dimensions of the incinerator known, it is then possible to calculate the residence time and to characterize the average turbulence (e.g. in the form of a Reynolds number) in the incinerator.

Besides these general process parameters, there are specific parameters for every part of the facility. In general air pollution control devices a need specific monitoring operation. These monitoring operations are not described in this paper because of the type specificity of such systems. Readers who are interested in these aspects are advised to consult Bonner et al. (59).

6.1.1 temperature monitoring

Incinerator temperature is monitored on a continuous basis to assure that the minimal acceptable temperature for waste destruction is maintained. Generally, wall temperatures and gas stream temperatures are determined by using shielded thermocouples as sensors. Optical pyrometers are not recommended for these measurements due to spectral bias factors present in the combustion area, which can cause unacceptable measurement errors. Usually platinum-rhodium versus platinum thermocouples are used, with a protection tube to prevent mechanical damage and corrosion. The maximum temperature which can be measured continuously is about 1600°C. The thermocouple is metered by a long (30 sec.) time constant amplifier when measuring average temperatures.

The location at which temperature measurements are made is very important. Ideally, temperatures are measured in the bulk gas flow at a point after which the gas has traversed the combustion chamber that provides the specified residence time for the unit (59).

Some facilities, however, use temperature monitoring on the outside of the rotary kiln; this procedure has a double function: firstly to indirectly measure the combustion temperature and, secondly to indirectly measure the thickness of the refractory lining. Most facilities are equipped with a temperature monitor at the end of the rotary kiln and with a temperature monitor in the afterburner chamber down stream to the secundary combustion air inlet.

6.1.2 oxygen monitoring

The waste-air ratio is monitored by measuring the result of the waste-air ratio, that is, the oxygen concentration in the flue gas. For liquid waste it is possible to monitor the waste-air ratio directly, but for solid waste this option is not possible.

When monitoring the oxygen level, generally a place with high turbulence is chosen for the monitoring location. The measurement can be done by an in-stack system or by an extractive system. An extractive system has the disadvantages of a sampling interface, which may modify the flue-gas composition. The so-called in-situ or in-stack systems do not modify the flue-gas composition and are designed to measure gas concentrations in the presence of particulate matter (59). For oxygen monitoring three different methods are available, i.e. the polarographic analyser, the electrocatalitic oxygen analyser and the paramagnetic oxygen analyser. The polarographic analyser and the electrocatalytic analyser are based on the changes in the current in the electric cell due to changes in the oxygen concentration in the cell. The paramagnetic analyser uses the paramagnetic behavior of oxygen to measure the oxygen concentration in the cell. Bonner et al. (59) give information on the various methods of detecting oxygen concentrations and give examples of commercially available systems.

6.1.3 gas-flow monitoring

Gas flow rates can be measured in several ways: by insertion of an air pressure measuring element in the flue gas duct (pitot-tube) or by measuring the drop in pressure across a restriction to the gas flow (baffle plate, venturi section) downstream of the incinerator. Exhaust gas flow, however, is for several reasons the most difficult flow measurement application on the incinerator. These reasons are:

1. -Because the gas is dusty, moist and corrosive, pressure taps tend to plug.
2. -If two pressure sensing points are at widely different temperatures, the resulting difference in gas density will create a measurement error.
3. -If taken across a restriction to gas flow, the fouling tendencies of the dirty gas will cause the restriction area to decrease with time, thereby changing the differential pressure measurement for a given rate of flow.

For the reasons stated above, the usefulness of this measurement as an indication of quantitative flow rate is limited, and care should be taken in its interpretation (59).

6.2 Emission monitoring

The main aim for emission monitoring is to check the efficiency of the combustion process. According to most operating regulations, CO and CO_2-measurements are necessary to continuously monitor the combustion efficiency (CE). The definition of the CE is given in formula 15. Much has been published on the relation between the CO-concentration and the destruction efficiency (DE) of the incinerator (87,88,89). The definition of the DE is given in formula 16. These aspects will be discussed in the chapter on Process Evaluation. The monitoring of unburnt hydrocarbons (which, however, is not often used) can be very useful for efficiency evaluation.

$$\text{Combustion efficiency} = \frac{CO_2 - CO}{CO_2} * 100\% \qquad (15)$$

$$\text{Destruction efficiency} = \frac{\text{input A} - \text{output A}}{\text{input A}} * 100\% \qquad (16)$$

6.2.1 CO and CO_2-monitors

While other methods exist for monitoring CO and CO_2, the method most applicable to stack monitors appears to be based on infrared spectrophotometry. In these "non-dispersive" infrared (NDIR) monitors, the absorption of infrared radiation is measured at wave lengths specific to the subject gas. Drift is within 2-5% of full scale in a typical eight hour period, and calibration is performed by drawing gas from a cylinder with a known composition of CO and CO_2 that is close to the concentration being measured (59,90). A disadvantage of NDIR monitors in general is the possibility of interference by other compounds with significant IR absorption in the IR-detector range (59,88). La Fond et al. (88) found a CO analyser to respond to CO_2 levels typical of those present in stack gases. The CO yielded a reading of 10 ppm for 4% CO_2 and 30 ppm for 13% CO_2. The instrument did not respond to hydrocarbons up to 500 ppm. By using a special calibration gas the effect of the CO_2-interference can be overcome (98).

6.2.2 Total hydrocarbon monitoring

In contrast with other effluent monitors a total hydrocarbon (THC) monitor can give information directly relating to the destruction efficiency of the incinerator. The monitor is equipped with a flame ionization detector (FID) which is commonly used with gas chromatographs. The detector basically responds in proportion to the number of carbon-hydrogen and carbon-carbon bonds in a molecule.
It has essentially no response to highly oxidized products such as CO_2, H_2O and CO. Test results show an inverse proportional relationship between the THC-concentration and destruction efficiency (88). A THC monitor can only be used to monitor volatile hydrocarbons. The major difficulty in the application of the THC-monitor is the dependence of the THC-emissions on the waste feed composition. Since the FID responds far more strongly to hydrocarbons than to halocarbons, the apparent level of THC in the exhaust gas will decrease with increased halocarbon content of the emissions (89).

6.3 Control procedures

Monitoring the different parameters and concentrations is obviously not enough; action has to be taken to prevent the formation and/or the continuation of a malfunction condition in the equipment. Some of these control procedures are required by specific environmental regulations; others are in general for responsible operation of the combustion process.
For example U.S. regulations for liquid PCB-incinerators require that waste flow to the burners be cut off automatically whenever:

- the combustion temperatures drops below the minimal allowable temperature for thermal destruction, or
- excess oxygen falls below the required percentage, or
- monitoring and recording devices for CO, CO_2 or O_2 malfunction, or
- measuring and recording devices for PCB feed rate malfunction

Although not required by the regulations, the process control system should be designed also to cut off waste flow in the event of:

- loss of combustion air and/or auxiliary fuel flow, or
- burner flame-out, or
- malfunction in the pollution control system

The necessity of these last requirements is obvious, since in the event of these malfunctions occurring environmentally responsibele operation will be impossible, and permit values will be exceeded. Therefore, they have to be implemented in the control procedures (90). A procedure to evaluate the control procedures is given by Bonner et al.(59).

Another important process control question is whether or not to use a fully automated process control system. Some safety operations have to be automatic because of regulations, but most of the control actions can be done by on the job trained operators. Gregory (54) gives a short description of a fully automated system. At the moment most of the facilities are controlled semi-automatically, leaving much of the responsability to the operator. Human process control is used to present unnecessary system shut-down because of monitor malfunction. However a balance between unnecessary automatic system shut-down and unwanted release of emissions has to be found.

7 PROCESS EVALUATION

In this chapter the methods and techniques which are used to evaluate the performance of incinerators are discussed. First, analysis techniques to reliably and accurately determine concentrations are reviewed. Secondly some issues concerning the use and applicability of the results obtained by the analyses are pointed out.

7.1 Analytical aspects

The importance of analytical chemistry lies in the fact that most environmental authorities demand a test burn or regular certification burn. In most of these cases the results have to be presented in terms of a destruction efficiency for certain compounds. The analytical procedure which is used must be able to determine at least the regulatory minimal DE, which can be 99.9999%. Carrying out this determination, however, can lead to almost impossible demands. For example, when a DE of 99.9999% or more has to be measured with an input of 50 ppm, an output level of 5 ppt has to be detected, which means a detection limit of one fifth of this value: 1 ppt. Presently dioxins can be routinely detected in outdoor air samples down to 1 pg/m^3 (117) (1 ppt w/w is at standard conditions for dry air equal to 1.2 ng/m^3). In practice for chemical waste incinerators stack gas concentration down to 1 ng/m^3 can be determined (91).

To overcome these problems much effort has been made in developing extremely reliable and sensitive analytical techniques. In the following sections sampling equipment, analytical methods (i.e. sample cleanup, identification and quantification of compound) and quality control procedures will be discussed.

7.1.1 Sampling equipment

During testburns most of the attention is drawn to the sampling of stackgas components. Several methods are available, all having a specific working field. The most common methods in the U.S. for sampling organic compounds in stackgas are the source assessment sampling system (SASS), the modified method 5 train (MM5) and the relatively new volatile organic sampling train (VOST) (92,93). In Western Europe other sampling trains are used, but no standardization is applied nor are there any publications which compare these sampling trains with the standardized American equipment.

The SASS (see Fig. 20) has been successfully used for environmental sampling of numerous sources, and it is considered to be a useful method for collection of semi-volatiles, PCBs and other lower volatility organics. The SASS consists of cyclones for particle sizing,a glass or quartz fiber filter for the collection of fine particles, a sorbent module for collecting semi-volatile organic compounds, and impingers for collecting volatile metals. The system operates at 110-140 l/min and is usually operated long enough to collect 30 m^3 of flue gas. The materials of construction employed in the SASS train (all stainless steel) make it very heavy and cumbersome and very susceptible to corrosive attack from the acid content of sample gases, especially HCl and Cl_2.

The MM5 train (see Fig. 21) is conceptually similar to the SASS, but it operates at a lower flowrate, usually 14-28 l/min.
The MM5 train does not include particle-sizing cyclones, and it is usually constructed of glass rather than stainless steel. Its sorbent module is inserted between the filter and the first impinger. The sorbent module must be positioned vertically so that the gas and any condensed liquids flow downward through it. A limitation of the standard rate MM5 train is that, by design, it only employs a single trap. This single trap does not provide a check for organics breakthrough, especially when large sample volumes are collected. The non-standard, high volume MM5 train (standard flow rate 140 l/min) employs a back-up trap. The use of this trap, however, causes a very high pressure loss.

The VOST method of collecting volatile organics (see Fig. 22) is a relative newcomer, having only recently (Feb. 1984) completed EPA's peer review process and having become available in final draft form in March 1984. The VOST has proven to be a reliable and accurate method for collection of a broad range of volatile and semi-volatile organic compounds. The system consists of a sorbent tube, which is positioned at the beginning of the train to remove organics from the gas stream as soon as possible. A second sorbent tube, consisting of two stages, is attached to the condensate collector to act as a backup in case of breakthrough. The sampling train is designed to use six pairs of sorbent tubes sequentially, each operating for 20 min. at 1 l/min. The limitations of VOST are:

- the limited flowrate and the limited sample volume per tube pair, therefore requiring frequent change-over of tube pairs for tests that exceed 20 min.
- the frequent change-over of the tube pairs makes the samples more susceptible to ambient contamination and to loss from breakage due to the relatively large amount of handling required.

In addition to the considerations discussed above, each of the three methods has a common concern: the selection of the best sorbent material for specific source or condition. Although the SASS train specifies the use of XAD-2 sorbent and the VOST train uses Tenax-GC with a Tenax-GC/charcoal backup, other sorbents have been used in the MM5 train with success. Florisil, Spherocarb and other polymer-based sorbents also have been used successfully. Each sorbent has its limitations with regard to, firstly, the class of

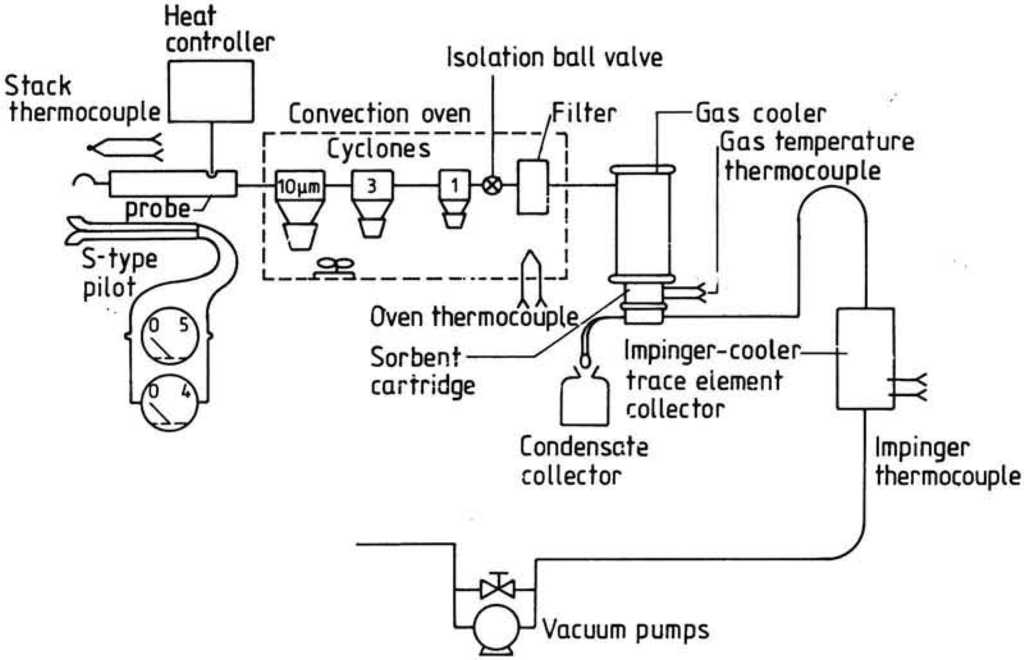

Figure 20. Source assessment sampling system.
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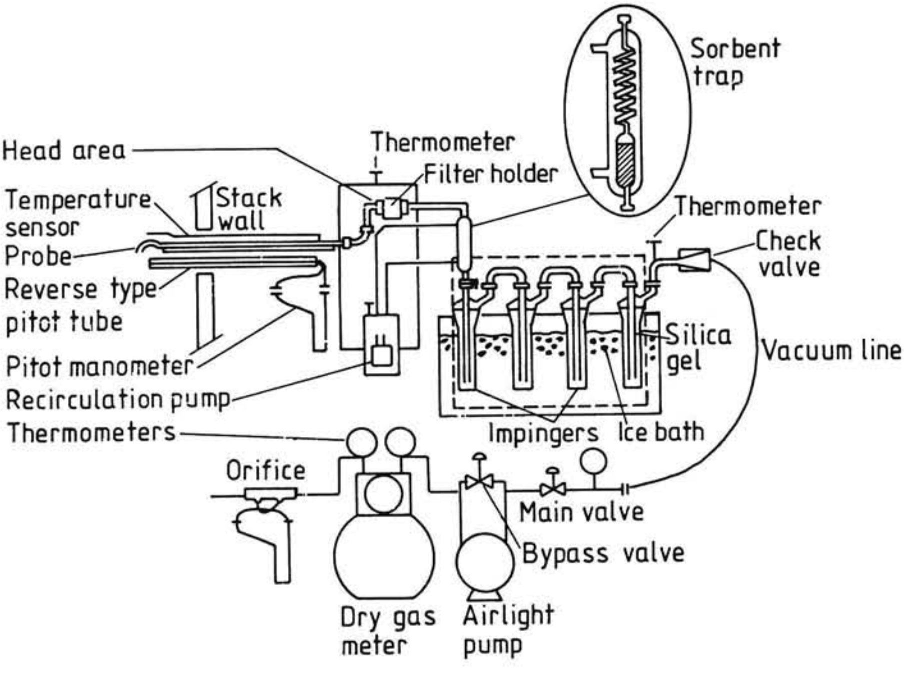

Figure 21. Modified method five train.
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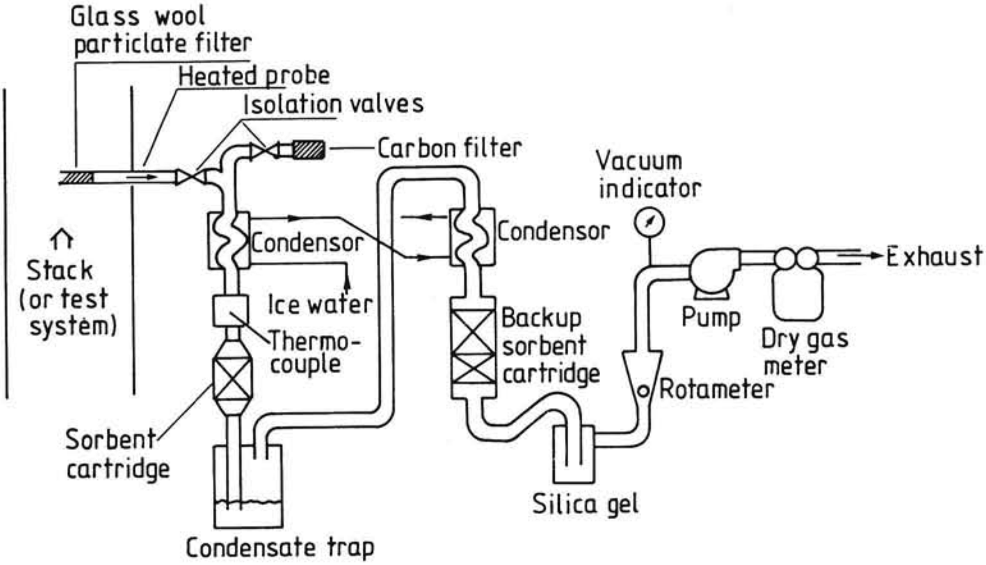

Figure 22. Volatile organic sampling train.
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organics it is best suited to collect efficiently, secondly, how efficiently the collected analytes can be removed (93), and thirdly, the level of micro-contamination of the blancs (117).

Other methods for sampling, like instantaneous and integrated grab, are hardly used for stack gas sampling during testburns. However, solids and liquid samples are often collected by simple grab sampling (94). With these input sampling techniques it is very difficult to come to a representative sample.

Some additional remarks concerning the placing of the sampling probe in the incinerator stack must be given.The normal procedure is to traverse the stack with the sampling probe, which is operated under isokinetic conditions when aerosols are being measured (i.e. the velocity of the sample into the probe nozzle is matched closely to the velocity of the gas stream being sampled), to obtain a representative sample. However, when operating for instance a SASS, train the stack is not traversed, but sampled at a single point in the stack under pseudo-isokinetic conditions (92). Pseudo-isokinetic sampling is the term used to describe the following approach to stack sampling:

- a full velocity traverse of the duct is carried out to measure the gas velocity distribution and to select a representative sampling point at which a probe nozzle is placed.
- the probe is fitted with a nozzle so that sampling is initially nearly isokinetic, as based on a given sample suction rate.
- as sampling progresses, the flow is monitored but the sampling rate is not altered to match small changes in the stack velocity.
- major changes in stack velocity or pressure drop in the sampling train are cause for shutdown and corrective action.

Under most circumstances, this mode of operation results in samples that are indistinguishable from those taken under true isokinetic conditions. However, isokinetic or pseudo-isokinetic sampling is only possible when the gases in the stack are stratified. Therefore when the Reynolds number of the gas stream is high enough, indicating high turbulence in the gas stream, a constant flow, single point sampling probe is enough to give a representative sample (95). When a gas stream with a temperature of about 1000 °C has to sampled for various PICs, isokinetic sampling is not necessary to obtain a representative sample. At such high temperatures all the PICs will be in the gas phase, so no particles have to be sampled, which is the specific use of isokinetic sampling (95).

7.1.2 Analytical methods

After having collected a representative sample of the stream which has to be analysed, the cleanup procedure starts. Most of the cleanup procedures which are discussed in the literature concern PCDD and PCDF-containing samples. For example, Tiernan (96) gives nine different cleanup procedures for PCDD and PCDF, all designed for a specific chemical matrix. Rappe (13) recognizes two different cleanup trends for PCDDs and PCDFs. Firstly, all PCDD and PCDF isomers can be analyzed in one single fraction by the containment enrichment method, or secondly, specific isomers are analyzed in different fractions, usually after reversed-phase and normal-phase high pressure liquid chromatography (HPLC). Wong et al. (97) describe a complete analytical method, cleanup and determination, for 2,3,7,8-TCDD in water, which is part of the US Clean Water Act, serving as an international reference for 2,3,7,8-TCDD analysis in water.

For other compounds analytical standards are also present, as described in Ref. 98 and Ref. 99. However, these standards are not as detailed as those for PCDD, because these standards have been created for a broad group of chemical compounds and not just for one group of related compounds.

The most critical step in a cleanup procedure is the isolation during which the analyte has to be separated from the matrix. When an improper isolation method is used, more than 90% of the analyte can be lost (20). By spiking the sample with surrogate compounds, i.e. compounds labeled with ^{13}C or ^{37}Cl, it is possible to quantify this loss. However, this method is rather expensive.

After the cleanup procedure, the identification and quantification of the sample components has to take place. For this last step various options are also open, dependent on the compound which is being determined. Table 8 gives the analytical techniques which are used to identify and to quantify the concentrations of toxic and hazardous organic materials. Of these techniques, GS-MS is preferred because its operation is independent of the chemical or electrical characteristics of the compounds being determined. Although the normal detection level that can be achieved by a GC-MS instrument is not as low as that of other GC detection methods, it can be improved significantly by operating in the selective ion monitoring (SIM) mode. In this mode one examines the ratio of the major ion or ions of a suspected compound relative to that of a known standard in order to confirm the presence of the suspected compound. The SIM mode of a GC-MS instrument allows detection levels to the lower picogram level (93).

James et al. (100) and Adams et al. (101) report on the use of analytical methods for the determination of POHC in combustion products. These two publications give specific information on response factors for GC-FID and GC-MS determinations of 56 POHCs, together with information on the masses of characteristic ions for MS identification and optimal HPLC-UV operating conditions for detection of several POHCs. Rappe (13) and Tiernan (96) report on the use of analytical techniques for PCDD and PCDF identification and quantification. Several examples for isomer-specific analyses are given. Other sources giving information on the analysis of PCDD and other POHCs are the various test reports on incinerators burning hazardous wastes. (91,94,98,99,102,103,104,105,106,107,108)

Table 8 Analytical methods for toxic and hazardous organic materials

Analytical method	Compound applicability	IDL[a] (ng/m^3) volatile[b]	IDL[a] (ng/m^3) non-volatile[c]	Method notes
Gas chromatography (GC)				
Flame ionization detection (FID)	Volatile organic compounds (VOC),polynuclear aromatic hydrocarbons (PAH)	0.1	10-100	
Photo-ionization detection (PID)	Aromatic VOC	0.01	1-10	Excellent field screening method but at higher detection level.
Hall electrolytic conductivity detection (HECD)	Halogenated VOC	1	100-1000	Halogen specific, capable of achieving low-detection levels, even when mixtures of numerous chlorinated compounds are present. A difficult analysis method.
Micro coulometric detection (MCD)	Halogenated VOC	1	100-1000	See HECD
Electron capture detection (ECD)	Some chlorinated hydro carbons,polychlorinated biphenyls (PCB), organochlorine pesticides,cycloketons, phtalate esters,nitro-aromatics	0.0001	0.01-0.1	Also specific for a number of compounds. Important for pesticide and PCB analysis.
Gas chromatography-mass spectrometry (GC/MS)				
Single ion monitoring (SIM)	VOC, semi-VOC, PCB, halogens, PCDD, PCDF, etc.	0.005	0.5-5	Ideal for identifying individual compounds in a mixture of numerous compounds. Can be used semi-quantitatively or under certain conditions quantitatively.
Total ion scanning (TIS)	VOC, semi-VOC, PCB, halogens, PCDD, PCDF, etc.	5	500-5000	
High performance liquid chromatography (HPLC)[d]	PAH	1	100-1000	Highly specific for certain polynuclear aromatic hydrocarbons.

note: With halogens Cl,I and Br are meant, but not F because detection limits for F are much higher.

[a] IDL-instrument detection limit; values given are based on the lowest value for a specific compound.

[b] Volatile means those organic compounds which can be removed from the sorbent material by thermal desorption.

[c] Non-volatile means those organic compounds which can only be removed from the sorbent material by means of extraction.

[d] With fluorescence detector.

7.1.3 Quality control aspects

Because of the possible far reaching consequences of analysis results, the importance of quality control procedures and quality assurance is evident. Polcyn and Hesketh (93) stress the importance of quality control procedures throughout both the sampling and the analytical phases of a test. These procedures do not only increase the reproducibility of the results, but also give an indication of the accuracy of the analysis. To give an idea of this reproducibility, Bartelds (20) gives an example where the GC reproducibility was ± 5%, but the values of the concentrations found varied ± 200%. To prevent such fluctuations, laboratories operating in this field must carry out quality assurance programs. Some examples of quality assurance are given by Wong et al. (97), McMillin et al. (109) and Jayanty et al. (110); the first two concern the determination of 2,3,7,8-TCDD in water and the last concerns POHC measurements during hazardous waste trial burn tests.

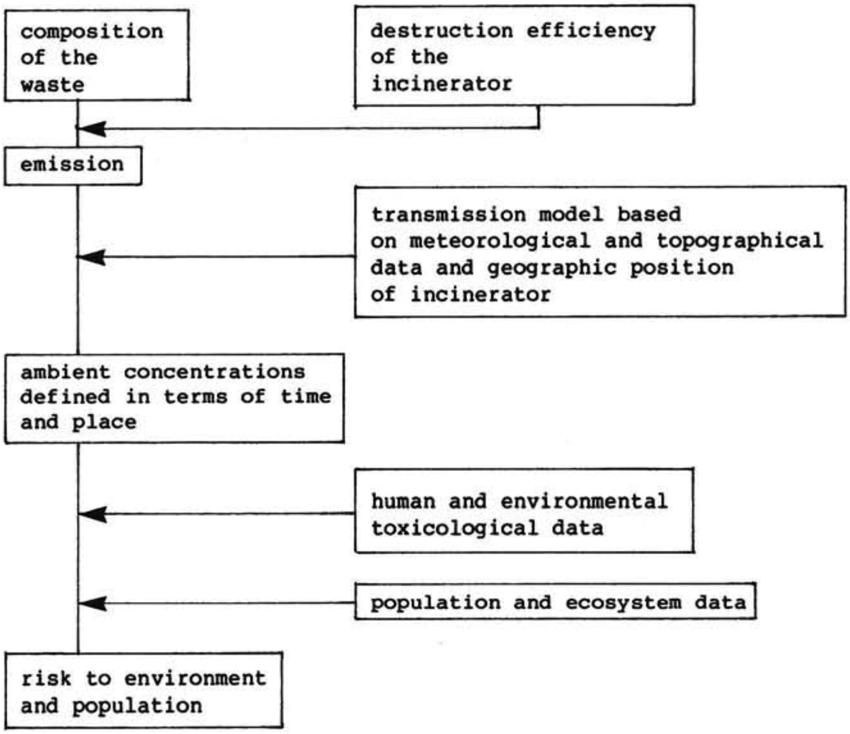
The point, which becomes clear after describing the analytical aspects of process evaluation, is that even though the possibilities of chemistry have been improved in the sense of greatly lowered detection limits, it still requires good "scientific judgement" to properly interpret the often large fluctuations in the analytical results obtained. This very important and to a certain extent subjective factor should be kept in mind, not only by the analytical experts themselves, but even more so by the persons who have to make policy decisions based on these analytical results.

7.2 Evaluation aspects

In the following sections some issues concerning the evaluation of incineration processes are described. First the use of environmental models is described, followed by a section concerning the use of combustion efficiency and destruction efficiency and their relation to one another. Finally the POHC and PIC issues are discussed.

7.2.1 Environmental modeling

After obtaining the analytical data from an incineration test, the results are normally compared with the environmental regulations concerning chemical waste incineration. Another option is to put the results into perspective with other environmental data. In order to do this models are being developed. In the future these models can be used to calculate ambient concentration of stack gas components and to estimate the risk due to CHC incineration to the population, for example in terms in incremental cancer risk. Put in a block diagram the general approach is as follows:



Most of the elements used in this general model are models themselves. In the literature concerning incineration often only elements of this general model are described.

Sekulic et al. (111) presents a study of the air-quality effects of a hazardous waste incineration system. An atmospheric-dispersion analysis was performed to estimate the ground-level air concentrations of contaminants that would be emitted from the incinerator stack. This resulted in a correlation of the maximum average ambient concentration to the stack-emission rate. This correlation can be used to calculate maximal average concentrations in the surrounding area of a model incinerator, so that these concentrations can be compared with the environmental guidelines for ambient air concentrations.

Holton and Travis (112) present a model for predicting fugitive emissions of hazardous waste incineration facilities. All these fugitive emissions of volatile organic compounds are caused by faulty equipment, such as leaking pumps, fittings, sampling connections, flanges and other non-stack equipment. Knowledge of these fugitive emissions is important for estimating the health risks for on site personnel. Certainly as important can be the risk for the public living nearby.

Kelly (113) describes methodologies for assessing the health risks of hazardous waste incinerator stack emissions to surrounding populations. Kelly concludes that assessment of health risks of hazardous waste incineration facilities to the surrounding population is generally quite complex due to a variety of factors. These include the wide variety of data required to estimate population health risks, a lack of input data available (in particular toxicological data, such as exposition-effect models) and the uncertainties inherent in the use of estimated data.

EPA (28) performed a detailed risk analysis for land-based and ocean-based incineration as part of the study "Assessment of incineration as a treatment method for liquid organic hazardous waste." The report gives an idea of the possibilities and limitations of such a study. Some of the limitations are the lack of sufficient toxicological data on products of incomplete combustion emission, the absence of data on the occurrence of periodic incinerator malfunction and the applicability of this study for only two kinds of waste streams. Based on this risk analysis and other analysis, the EPA concludes that incineration is a valuable and an environmentally sound treatment option for destroying liquid hazardous wastes. Unfortunately, the EPA decided not to include solid and semi-solid hazardous waste in the assessment study, which causes a loss of possible relevance for this study. Nevertheless, the EPA report gives some idea of the state-of-the-art concerning risk assessment of incinerator facilities.

7.2.2 CE versus DE

The use of a destruction efficiency to express the incineration performance is an accepted and widely used evaluation technique. The use of the combustion efficiency to measure the on line efficiency of an incinerator is also a commonly used practice. The assumption that is sometimes implicitely made that a correlation between CE and DE exists, which would be very helpful in day-to-day performance control, is based more on wishful thinking than on scientific evidence. Reed and Moore (87) state that the CO concentration in the effluent gas of several hazardous waste incinerators does not correlate with the degree of destruction of hydrocarbons. Dellinger and Hall (89) explain the possible kinetic background of the absence of a correlation.

Because of the possible formation of stable intermediates during the thermal destruction of hazardous waste, the CO level is not necessarily directly related to the destruction efficiency of the waste. In such situations an increase in the destruction efficiency may correspond to either an increase in the CO level, a decrease or no change. This phenomenon becomes clearer with thermally stable compounds, such as acetonitrile. For example in one test in which a DE of 98% corresponded with 60 ppm CO and a DE of 10% corresponded with a CO level of 20 ppm, at a constant CO_2 level for both cases.

However, these considerations involving acetonitrile do not indicate that CE monitoring is without use. La Fond et al. (88) state that CE can be used as an early warning signal for possible emissions of

PICs. Furthermore, flame conditions which minimize CO emissions usually result in optimum waste DE. These two relations are important for online process control.
In conclusion it can be stated that CE has no correlation to DE, which means that on the base of the CE no quantitative conclusions can be drawn with regard to the organic emissions of an incinerator. Nevertheless CE is an important parameter for operational process control.

7.2.3 The POHC issue

On issueing the RCRA, the EPA introduced the use of "principal organic hazardous constituents" (POHCs), which have to be monitored during a trial burn to demonstrate incinerator performance. A list of POHCs is given in reference 27. According to the regulations the waste compounds with the highest POHC values have to be monitored. The POHC value is defined as follows:

$$\text{POHC value} = C \times \frac{100}{Hc}$$

where C: weight percent of hazardous constituent in the waste
Hc: heat of combustion, kcal/gram of constituent

When the destruction efficiency of the chosen POHCs is demonstrated to be 99.99% or higher an incineration permit can be obtained. This permit allows incineration of waste similar to the trialburn waste, but also incineration of waste with lower POHC values, assuming a same or higher DE for these waste streams (27).
The use of heat of combustion as a ranking of compound incinerability has received considerable criticism and alternative scales, which have also been criticized, have been proposed (89). The main basis for this criticism is that it is insufficient to base incinerability exclusively on thermodynamic data (e.g. heat of combustion). It is necessary to also consider kinetic data (e.g. activation energies) and incinerator conditions (e.g. combustion temperature). According to Ackerman et al. (27) "incinerability" should fundamentally depend on:

1 the activation energies of the combustion reactions,
2 the combustion temperature (which depends on the heating value and elemental composition of the waste), and
3 the molecular structures and bond energies of components in the waste.

Because of the difficulties in obtaining data on the thermal stability of various compounds at incineration conditions, a thermal decomposition unit (TDU) is widely used to generate lab scale data on thermal stability (43,47,59,114). The obtained data, mostly presented as the temperature at which 99.99% DE occurs at a residence time of 2 seconds (T99.99), can then be used as standard. Cudahy and Troxler (114) performed linear regression analysis on several suggested incinerability ranking procedures with T99.99 as the base. They come up with a correlation coefficient of 0.94 for the auto--ignition temperature procedure (AIT) and of 0.39 for the heat of combustion ranking procedure. Kramlich et al. (115) studied the relation between different incinerability ranking procedures and different flame failure conditions. They came to the conclusion that no single ranking procedure was appropriate for all the flame mode conditions that were studied. Rankings were dependent on the particular reactor used and on the particular conditions used for each test.

This implies that single-parameter ranking procedures cannot a priori be assumed to rank incinerability within a given time. Among the ranking procedures tested were T99.99, AIT and the heat of combustion procedure.

Dellinger and Hall (89) make another approach to the problem of monitoring the effectiveness of incineration units. Instead of using the POHC system, they suggest the use of a surrogate compound for continuous monitoring that would serve as a DE indicator for the incinerator system. Based on earlier work (48) they suggest the use of Freon 113 as surrogate compound, even though it is thermally moderately stable. Additional research in this field is strongly recommended.

The present situation is that EPA is continuing to assess the reliability of the POHC system, but it believes that the heat of combustion unit is still the best method currently available (28). This policy, however, leaves the questions concerning the use of the current POHC system as a decision instrument unanswered.

7.2.4 The PIC issue

Another issue, strongly related to the use of DE and the POHC system, is the formation of products of incomplete combustion (PICs) (89,116). PICs are defined as organic compounds not in the original waste feed that show up at 100 μg/g of feed or more during and after an incineration run. First it was assumed that an incineration facility which operated with a sufficiently high DE, was sufficiently monitored, and therefore no possible threat to the environment existed. Recent findings, however, are challenging this assumption. For instance, a field study by Castaldini et al. (108) showed PIC levels higher than the POHC levels leaving the stack. This phenomenon is partly due to the definition of the destruction efficiency, which assumes destruction after only one atom has been broken off the molecular species originally in question. The remaining product can, of course, still be thermally stable and require more residence time for destruction into HCl, CO_2 and H_2O. This very obvious aspect is, however, not implemented in the DE definition, which decreases the relevance of this parameter. Nevertheless permit decisions are still made on the basis of this parameter.

Altogether this issue makes it clear that the only way to guarantee proper operation of an incinerator is to use a minimal DE and a maximal organic emission level as regulating instruments. The use of these parameters go a long way to prevent unnecessary exposure of the environment to possible toxic emissions. Meanwhile, identification of the principal PICs should be an important research goal.

The authors' conclusion is that the most rational basis of deciding whether a given incineration facility is acceptable, is that using the concept of risk. In the ideal case one should be able to monitor continuously emissions of undesired components, and the toxicity of these components should be known. From emission data ambient concentrations should be able to be estimated by means of transmission models or better, should be measured.

Thus concentration-time-place-values can be estimated, so that the toxic exposition can be calculated. From toxicology data the risk associated with this exposure can be estimated. If this risk is too high, higher DE's will be necessary. It will be obvious that the required DE is related to ecotoxicological impact, as it should be.

8 INDUSTRIAL PRACTICE

In this chapter practice at some European incineration facilities will be described. These descriptions are based on literature studies and interviews with officials of the given companies.
Each of the following parts will describe a specific facility with its own operating characteristics. These operating conditions differ because of the use of different waste streams, different equipment and different environmental regulations.
In each part the following subjects will be discussed:

- waste acceptance
- incineration equipment
- operating conditions
- test results

Each of these subjects are compared with the state-of-the-art described in earlier chapters. Table 9 gives some characteristics of the five incinerators which are described.

Table I.P.1 Some charateristics of the five incinerators which are described.

Subjects	AVR Chemie	AKZO Zout Chemie
1.type of incinerator	rotary kiln	liquid burner
2.type of waste	solid & liquid	liquid
3.capacity	75,000 ton/year	30,000 ton/year
4.number of incinerators	2,one under constr.	2 ovens
5.sitting situation	land based	land-based
6.function of firm	national	international
7.operating temp. (°C)	1200 to 1300	1600-1650
8.afterburner temp. (°C)	1000	not present
9.residence time (s)	gas:10,solids: 45 min.	0.2 to 0.3
10.average Cl-content waste	new:5wt%,old < 4 wt%	55 to 70 wt%
11.effluent cleaning	new:E-filter&wet scrubber	HCl-recovery
12.incineration price 1986	130 to 520 Hfl/ton	not available
13.minimal CE (%)	not prescribed	not prescibed
14.PCB-burns	will be allowed after test	not applicable
15.max.HCl emission (mg/m3)	old: 500, new: 100	5
16.max.dust emission(mg/m3)	50	not prescribed
17.average CO level (ppm)	not available	50
18.average O_2level (vol%)	not available	3
19.average HCl level(mg/m3)	not available	5
20.type of temp.monitoring	thermocouples	thermocouple
21.stack monitored for	HCl,HF,SO_2,O_2, CO and THC	O_2
22.particularities	no CE monitoring	no CE monitoring, operates at overpressure

HIM	Kommunekemi	OCS
1.rotary kiln	rotary kiln	liquid burners
2.solid & liquid	solid & liquid	liquid
3.60.000 ton/year	90,000 ton/year	160,000 ton/year
4.2 incinerators	2 incinerators	2 vessels, 5 ovens
5.land-based	land-based	sea-based
6.regional	national	international
7.1200	1100 to 1150	1300 to 1500
8.1000	900 to 950	not present
9.gas: 6, solid: 60 min	gas: 2	1.1 to 1.5
10.average 5 wt%	average 2 wt%	up to 70 wt%
11.dry and wet scrubber	E-filter and dry scrubber	not present
12.485 to 3800 Dm/ton	-700 to 5000 Kr/ton	200 to 700 Hfl/ton
13.not prescribed	99.785	99.9
14.is allowed at 1400 °C	is allowed at normal cond.	is not allowed
15.50	old:150, new: 100	not prescribed
16.30, average 15	old: 1000, new: 250, aver.:30	not prescribed
17.28	10 to 50	8
18.10.5	old: 13, new: 11	10
19.10, as Cl^-	old: 525, new: 122	not applicable
20.optical & thermocouple	thermocouple	thermocouples
21.O_2,CO,HCl,SO_2 and dust	CO,CO_2,O_2 and dust	CO,CO_2 and O_2
22.no CE monitoring, optical pyrometer is not accurate enough	extreme high CO alarm level	waste characterization is most detailed

8.1 AKZO

The incinerator at the AKZO Zout Chemie-plant in Rotterdam is an installation, built in 1974, designed to burn chlorinated hydrocarbons with recovery of the HCl formed. The unit, which is an on-site facility, is operated to dispose of vinyl chloride monomer (VCM) production residues and herbicide production residues (HCB) generated by AKZO. These wastes occupy one third of the plant capacity, which is approximately 30,000 ton waste per year. Other loads, mainly VCM and trichloropropane-residues, are purchased from third parties.

Because this installation is part of a privately owned company, no public financial data on the incinerator are available. However, it is common knowledge that the installation has been out of operation for some time because of economic reasons.

8.1.1 Waste acceptance

Only liquid waste with a solid content lower than 10 g/kg can be incinerated. The total amount of waste which can be incinerated is appr. 30,000 ton per year with an average chlorine content of 55 to 70 wt%. When incinerating waste with a lower chlorine content, and therefore a higher caloric value, the capacity will be lower.

Because the HCl formed during the incineration is recovered, the composition of waste liquids has to be of a high chlorine content and purity and constant quality. When external waste is accepted it is tested with regard to the concentration of chlorine, fluorine, bromine, sulfur, phosphor, heavy metals, iron salts, alkaline compounds and water content. The presence of solids, solids particle size, caloric value and tendency to polymerize are also measured. When a process stream necessitates it, toxicity is also tested.

Average acceptance criteria are:

Br	$\leq$ 500 mg/kg
S	$\leq$ 20 mg/kg
F	$\leq$ 1 mg/kg
P	$\leq$ 500 mg/kg
Fe	$\leq$ 100 mg/kg
Solids	$\leq$ 10 g/kg

The liquids are mixed in a 200 m^3 tank to prevent rapid composition fluctuations of the burner input. In the near future three tanks will be installed to be able to burn different mixtures of waste.

8.1.2 Incineration equipment

The installation is equipped with two ovens, each with one atomization lance. By using a windbox for tangential air input a short, broad flame is obtained. The lance nozzle and air input are designed to give optimal atomization and to prevent flame contact with the refractory lining. The refractory lining is composed of heavy duty fire clay and insulation stones, giving the steel wall a temperature above the dew-point of $HCl-H_2O$ mixtures.

When operated properly, the life of the lining is expected to be 30,000 to 40,000 hours. (appr. 4-5 years of continuous operation)

Because the incinerator is used for HCl-recovery, steam is injected into the flame to decrease the Cl_2-formation. For the same reason the oxygen-waste ratio is kept low, which results in a oxygen content between 2 and 3% in the flue gas.
After leaving the oven the flue gases pass through a quench, which lowers the temperature of the gases to appr. 100 °C. At the moment AKZO Engineering is performing a study on the economic performance of various heat recovery schemes.
The quenchtank is filled with hydrochloric acid from the recovery unit, which removes the Fe, SO_4, PO_4 and heavy metals from the flue gas. The flue gas continues through a cooled absorber and an adiabatic absorber to remove the remaining HCl. The remaining effluent gases, mainly O_2, N_2, CO_2 and H_2O, but also traces of Cl_2, Br_2 and HCl, are purged to the atmosphere after being washed in an alkaline washtower. See Fig. AKZO
The hydrochloric acid which is formed in the primairy, cooled absorber, is distilled at elevated pressure and temperature, after which the gas mixture is cooled to -15 °C to remove the water vapor almost completely. The thus formed anhydrous HCl is recycled to the VC-plant.
The equipment is monitored for temperature and oxygen level. The temperature is measured at the end of the oven by a thermocouple. The oxygen concentration was previously measured after the quench vessel, but this practice gave unreliable information because of salt deposits forming on the probe. Recently a new oxygen monitor was installed at the end of the oven. Next to the burner, three UV-sensors are installed to monitor the status of the flame. The installation is not equipped with CO and CO_2 monitors.

Besides the flue gas, which is purged to the atmosphere, another emission source is the quench vessel, where Fe, SO_4, PO_4 and heavy metals are collected. From this vessel 50 to 100 liter per hour are removed. The liquid effluent is then neutralized with the effluent of the alkaline wash tower and the resulting mixture flows as effluent into surface water.

8.1.3 Operation conditions

The ovens are operated at 1600 - 1650 °C with a residence time of 0.2 to 0.3 seconds and an overpressure of appr. 30 kPa. The air conditions give 3% oxygen and 50 ppm CO in the flue gas. The effluent gas which is purged into the atmosphere contains: HCl $\leq$ 5 mg/m^3; Cl_2 $\leq$ 2 mg/m^3 and organic-bound-chlorine $\leq$ 1 mg/m^3. The maximal permit values for flue gas concentrations are 8.5 mg/m^3 for HCl and 2.4 mg/m^3 for Cl_2.

Control conditions are as follows. When the oxygen level in the flue gas drops below 2% an alarm is sounded, but no automatic trip follows, due to the unreliability of the oxygen monitor. An automatic trip system will probably be installed if the new oxygen monitor works sufficiently well. The temperature must exceed 1450 °C, otherwise an oven trip occurs, resulting in a waste flow shut down and the ignition of a natural gas pilot burner. This also occurs when

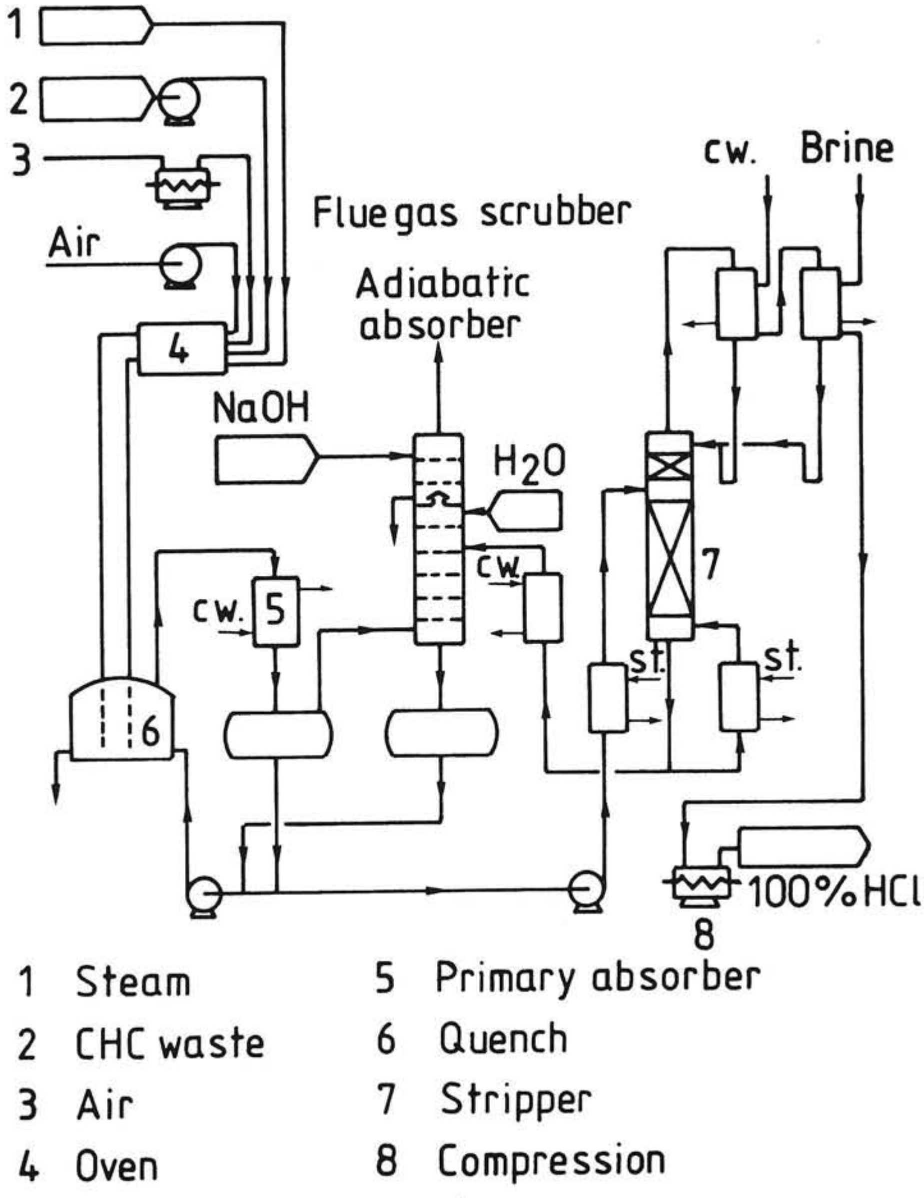


Figure AKZO. Schematic diagram of the HCl recovery unit.
Source: Ref. 79. Reproduced by permission of Ingenieurspers.

two of the three flame sensors give a flame out signal. Because the CO-level is not monitored, no combustion efficiency alarm level is available. The overpressure in the system must be below 40 kPa, otherwise distortion of the quench tank will occur, resulting in loss of acid-resistant ceiling tiles.

8.1.4 Test Results

The data available on the emission levels of the incinerator are all based on non-public reports.
Emissions to air, as analyzed by DCMR, show a total PCB-concentration lower than 10 $\mu g/m^3$, which is the detection limit of the analysis equipment used. No tests for PCDD or PCDF emission to air are carried out. Emissions to water are lower than 1 gram per year for total PCBs and lower than 0,1 gram per year for TCDD-equivalents. Up until now no analysis of the heavy-metal content of the waste water has been performed.

8.1.5 References

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- personal communication with F.J.Spijk, AKZO Zout Chemie
- A.H.M.Beekwilder, I^2 Procestechnologie 1985 n°4, p.23-25 "Vernietiging van gechloreerde afvallen (2)", ("Destruction of chlorine containing wastes"), in Dutch.

8.2 AVR Chemie

AVR is a limited partnership consisting of eight privately owned major chemical companies, the city of Rotterdam and the state of the Netherlands. AVR operates a rotary kiln incinerator and several grate ovens for municipal waste. At present it is building a new rotary kiln incinerator for chemical waste. Of the appr. 100,000 ton chemical waste which was treated in 1985, 35,000 ton was burned in the rotary kiln oven and at least 35,000 ton was burned in the grate ovens. With annually 10,000 waste streams to handle AVR has a sort of balancing function for the Dutch chemical waste market. The 1985 price for incinerating 1 ton of chemical waste, ranged from Hfl. 130.-- to Hfl. 520.-- and more, depending on the chlorine content, caloric value, etc.

8.2.1 Waste acceptance

AVR Chemie can incinerate liquid, sludge and solid chemical waste. The new rotary kiln incinerator will have a capacity of 40,000 ton per year with an average chlorine content of 5 wt %. The old rotary kiln incinerator has a capacity of 35,000 ton per year. At the moment the old incinerator can handle waste with an average chlorine content of 4%, but this will become less because of more severe emission levels required by new permit regulations. The grate ovens have a capacity between 35,000 and 70,000 ton per year, depending on the composition of the waste. The chlorine content of the waste may not result in a larger HCl and Cl_2 emission than the emission produced by the burning of the domestic and industrial waste, which is normally burned in the grate ovens as basic load.

As with all Dutch chemical waste incineration firms, the first thing to be done when a new stream of chemical waste is offered is to establish the specifications of the chemical waste offered in terms of the Chemical Waste Act; these are recorded on a form consistent with this Act. Then, depending on the type of waste, the following analysis can be performed:

- chlorine content (total and inorganic chlorine)
- fluorine content
- caloric value
- flash point
- mixing test
- ash content
- metal content, qualitative and quantative

When the waste stream is accepted, a treatment price is set and a delivery day is chosen. The waste, which can be delivered in tanks, wagons or drums, is then stored and pretreated. Drums filled with liquids are emptied under vacuum, and the liquids are mixed in storage tanks, which are emptied into smaller daytanks. Solid waste is stored in drums. With the installation of the new incinerator, a solid waste bunker will also become available.

8.2.2 Incinerator equipment

The old rotary kiln incinerator is equipped with a liquid burner at the high end of the kiln. The liquids are atomized in the nozzle by means of steam. The solid waste is introduced in drums, which are transported automatically into the kiln by a moving belt and an elevator. To prevent unnecessary wear on the refractory lining, sand and earth are added to the oven to form a protective layer on the bottom of the kiln. At the end of the kiln the solids are collected in a clinker channel. The gases continue through the afterburner chamber which is equipped with a liquid burner. The purpose of the afterburner, which can operate using oil and liquid waste, is to maintain a sufficiently high temperature. The airborn particles are then removed in the electrostatic precipitator, after which the flue gas is purged directly into the atmosphere. The whole incineration process is operated at a slight underpressure.
No HCl-removal equipment is present, and will not be installed in the near future either.
The old incinerator is equipped with two optical pyrometers (see section 6.1.1.), one for the kiln outlet temperature and one for the gas temperature in the afterburner chamber. The CO-concentration and the O_2-concentration are monitored continuously in the stack, as is also the flue gas optical density. The CO_2 concentration in the flue gas is not monitored, therefore no combustion efficiency calculations are performed.

The new rotary kiln incinerator is generally based on the same concept as the old incinerator. However some, necessarily major, improvements have been worked out in the new design. Some of these improvements are:

- solid waste can be introduced with a hopper
- liquid waste will be atomized by air instead of steam
- the secondary air is introduced by high pressure lances to improve the mixing with the combustion gases
- a heat recovery unit, which concists of a radiative and a convective section, is employed to produce steam of appr. 350 °C at 340 kPa
- a wet scrubber unit is introduced to remove the acidic gases, mainly HCl and HF.

The new incinerator will be monitored continuously for HCl, HF, SO_2, O_2, CO and total hydrocarbon. No CO_2 monitor is installed.
The temperature will be monitored at least at two points: at the end of the kiln and in the afterburner chamber. Furthermore the CO-concentration will be monitored in the stack and at the begin of boiler to prevent explosion in the electrostatic precipitator.

The grate ovens, which are standard municipal waste ovens, are not relevant to this paper, and are therefore not further described.

8.2.3 Operating conditions

In the Waste Act permit ("Afvalstoffenwetvergunning") all the emission levels to air and some process conditions are described.
For the old incinerator roughly the following conditions are applied:

- the temperature in the kiln and the afterburner chamber has to be at least 800 °C.
- the residence time in the afterburner chamber has to be at least 2.5 seconds.
- the average concentration in, respectively, the emission level of, the flue gas may not exceed: 50 mg/m^3 or 4.5 kg/hr for dust, 500 mg/m^3 or 45 kg/hr for HCl, 2 mg/m^3 or 0.18 kg/hr for HF, and 400 mg/m^3 or 36 kg/hr for SO$_2$, all as 24 hours averages.
- for the following components the 50 percentile of the cumulative distribution of the hour average values over a year may not exceed the stated concentrations:

Pb	1.5	mg/m^3
Zn	50	mg/m^3
Cu	2	mg/m^3
Cd	0.05	mg/m^3
Cr	5	mg/m^3
Ni	1	mg/m^3
Sn	20	mg/m^3
Co	1	mg/m^3
Ag	0.1	mg/m^3
As	0.5	mg/m^3
Hg	0.05	mg/m^3

- it is forbidden to burn chlorine- and/or fluorine-containing polycyclic components (CFPC).
  These CFPCs are defined as:

  a solids contaminated with or filled with CFPC (no concentration value given)
  b liquids containing more than 50 mass ppm of CFPC

For the new incinerator roughly the following conditions are applied:

- the temperature in the kiln must be at least 800 °C.
- the temperature in the afterburner chamber must be > 900 °C.
- the residence time in the afterburner chamber must be at least 2.5 seconds.
- the average concentrations in the stack gas may not exceed 50 mg/m^3 or 4.5 kg/hr for dust, 100 mg/m^3 or 9 kg/hr for HCl, 2 mg/m^3 or 0.18 kg/hr for HF and 400 mg/m^3 or 36 kg/hr for SO$_2$, all as 24 hours averages.
- when CFPC containing waste is incinerated a destruction efficiency of 99.999% must be obtained. To reach this DE, the temperature has to be $\geq$ 1200 °C, the residence time at this temperature has to be $\geq$ 2 seconds, giving an oxygen content in the flue gas of at least 3%.

Before CFPCs can be incinerated on a regular base, the destruction efficiency for CFPC has to be demonstrated by means of a test burn.

- the metal emissions in the flue gas are bound to the same levels as for the old incinerator.

In the permit no carbon monoxide level or total hydrocarbon level is specified, nor is a general combustion efficiency or destruction efficiency level demanded. For an incineration facility with a very diverse waste stream, this is a very unusual situation. Another strange situation is created by the formulation concerning the CFPCs. The ultimate consequence of this permit article leaves no other solution than to analyse all solid and liquid waste for the presence of CFPCs. For the old incinerator this unscientific definition concerning solid waste (i.e. no concentration limit) can lead to the prohibition of incinerating solid waste in the incinerator. This prohibition, however, can hardly be the intention of the permit writers.

Normally the old incinerator is operated at 1200-1300 °C in the kiln, and 1000 °C in the afterburner chamber, with a total residence time for gases of 10 seconds and for solids between 45 to 60 minutes. The new incinerator is designed to operate at 1.200 to 1.300 °C, with a residence time of appr. 1 hour for solids. The flue gases will be cooled to appr. 250 °C in the waste heat boiler.
The wet scrubber is designed to have a removal effiency of 97 to 99% for HCl. For compounds like PCBs a destruction efficiency of 99.999% is guaranteed by the designers. According to the Waste Act permit it is allowable to incinerate pentachlorophenol containing soil at 900 °C; however, AVR incinerates this kind of waste at 1200 °C.

8.2.4 Test results

No test results are available.

8.2.5 References

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8.3 KOMMUNEKEMI

KOMMUNEKEMI is a corporation, the share holders being the National Association of Municipalities, the City of Copenhagen and the Borough of Frederiksberg. As starting capital a non-interest loan of 160 million Kroner was obtained from the municipalities. With this money two rotary kiln incinerators were built, one in 1975 and one in 1982, resulting in a capacity of 90,000 ton per year. While Kommunekemi does not have an official monopoly on chemical waste treatment, most of the Danish chemical waste is processed at the Nyborg-facility. The average incineration price is 1,100 Kroner per ton with a range of minus 700 Kr/ton (for non-polluting, high energy wastes, which are purchased) to 5,000 Kr/ton (for very highly polluting wastes) in 1986. At the moment Kommunekemi is planning to build another rotary kiln incineration to enlarge the incineration capacity, which is being fully used at the moment.

8.3.1 Waste acceptance

The installations are capable of burning liquid, sludge and solid waste, to a total of 90,000 ton per year. Of this 90,000 ton appr. 30,000 ton consists of waste water contaminated with organics.
Because no specific PCB-legislation exists in Denmark, the liquid PCB is mixed with other organic solvents to an average chlorine content of 2%.

When a new waste stream is offered to Kommukemi for incineration, first an information form has to be filled in with a description of the production process producing the waste. Based on this information, an analysis scheme and a provisional treatment plan is made up. Usually when the waste is delivered a sample is taken for analysis. Standard analysis concerns the concentration of Cl, Br, F, S and heavy metals and the caloric value and water content.

The liquid waste is stored in 100 m^3 and 250 m^3 tanks, which can be sampled at different heights to achieve information on the average waste content. From the primary storage tanks the waste can be transferred to 3 mixer tanks equipped with stirrers. The mixer tanks are used for preparing the feedstock for the incinerators. Solids are stored in special storage halls. The drums containing liquid and sludge are pretreated. Liquids are sucked out by vacuum pumps, and sludge is divided over several drums in order to minimize the problems arising from a discontinuous feeding of the kilns. The feeding hall is equipped with a lower explosion limit monitor to prevent explosions.

8.3.2 Incineration equipment

Kommunekemi operates two rotary kiln incinerators, one built in 1975 and the other in 1982. The old incinerator, incinerator I, consists of a rotary kiln, an afterburner chamber, a waste heat boiler, a simple dry scrubber and an electrostatic precipitator.
In the rotary kiln two burner nozzles for liquid waste are located

at the feed end of the kiln, together with an oil pilotburner which is always in operation. A third burner is designed for pasty waste injection. Solid waste is introduced through a sluice by a waste handling crane, or if packed in drums, by a drum conveyor.

The solid waste is used as a base load, the liquid waste being introduced intermittedly. The input of liquid waste is performed automatically, and is controlled, to prevent overfeeding, by the afterburner temperature and the actual liquid waste input occuring at that time.

The primary combustion air is preheated to ensure better combustion. The kiln is lined with two types of lining, the first six meters consisting of 40% Al_2O_3 alumina brick. The second part consists of six meters of 85% Al_2O_3 bricks with chrome oxide. Two types of lining are used because of the increasing wear of the lining towards the end of the kiln, due to high temperatures and a molten slag layer bath. No sand is used as a protective layer in the kiln.

At the end of the kiln the liquid slag is collected and quenched. In the afterburner chamber secondary air is introduced, as is also waste water containing appr. 1% oily components. In the waste heat boiler the gases are cooled to appr. 270 °C, the steam being formed is used in the Nyborg district heating system. At the end of the boiler a simple lime injection is used to decrease the acid gas emission, after which the airborn particles are removed by an electrostatic precipitator.

Because of the relatively primitive effluent air cleaning unit, only low concentrations (up to 1%) of sulphur and halogens are allowed in the waste of incinerator I.

The new facility, incinerator III, has the same scheme as incinerator I, except for the air cleaning equipment.

A dry scrubber is used to remove acid gases and heavy metals. This scrubber is a spraydryer which is operated with a lime slurry. Part of the dry powder is recycled into the lime feedtank to lower the lime consumption and to increase the removal efficiency. Behind the dry scrubber two electrostatic precipitators are operated parallel, to improve the operation flexibility. Two precipitators are used because of the difficulties encountered with incinerator I, where the ash conveyer often refused to work, which resulted in a build-up of ash in the electrostatic precipitator. This problem is now prevented by a control check by one of the operators once every 48 hours.

The temperature is monitored in the afterburner chamber with a thermocouple. Earlier the temperature at the end of the kiln was also monitored, but this gave no reliable extra information for process control. The levels of CO, CO_2 and O_2 are monitored in the afterburner chamber upstream towards the waste water inlet and in the stack. The results of these measurements are not compared because of the different sampling temperatures. In the stack the particulates in the flue gas are measured. No continuous monitoring of HCl, HF or SO_2 is performed; only once a week a sample is analyzed.

To monitor the wearing of the refractory lining, the outside kiln temperature is measured at several places.

The slags and ashes, which are generated during the incineration, are disposed of at a controlled landfill.

8.3.3 Operating conditions

According to environmental regulations the following conditions have to be met:

- a minimum afterburner temperature of 900 °C
- maximum of 7% CO_2 in the stack
- for incinerator I the stack concentrations may not exceed for
  $CO \leq$ 1% (v/v)
  $THC \leq$ 300 mg/m^3
  $HCL \leq$ 600 mg/m^3
  $HF \leq$ 5 mg/m^3
  $SO_2 \leq$ 1300 mg/m^3
  $Cl_2 \leq$ 250 mg/m^3
  $NO_x \leq$ 300 ppm (360 mg/m^3)
  dust $\leq$ 150 mg/m^3

- for incinerator III the stack concentrations may not exceed for
  $CO \leq$ 250 ppm
  $THC \leq$ 300 mg/m^3
  $HCL \leq$ 300 mg/m^3
  $HF \leq$ 5 mg/m^3
  $SO_2 \leq$ 750 mg/m^3
  $Cl_2 \leq$ 25 mg/m^3
  $NO_x \leq$ 300 ppm (360 mg/m^3)
  dust $\leq$ 100 mg/m^3

- the combustion efficiency has to be at least 99.785.
- the destruction efficiency of diphenyl, $(C_6H_5)_2$, in solid waste has to be at least 99,990% with a minimal input of 10 kg diphenyl per hour.
- when pesticides are incinerated, the kiln temperature has to be at least 1200 °C and CO in the stack may not exceed 150 ppm.
- in the flue gas metal concentrations may not exceed the following levels:

  $Cd \leq$ 100 $\mu g/m^3$
  $Hg \leq$ 50 $\mu g/m^3$
  $Pb \leq$ 5 mg/m^3

Normally the incinerators are operated with an afterburner temperature between 900 to 950 °C, which means a kiln temperature of 1100 to 1150 °C. The residence time at this temperature is appr. 2 seconds. The equipment is operated at a slight underpressure. Average afterburner conditions give 10 to 50 ppm CO and 6 to 7% CO_2 in the stack gas.

Various alarms are installed in the installation to ensure good operating conditions. When burning pesticides, the waste input is stopped within seconds when the temperature drops below 1200 °C or the CO-content exceeds 150 ppm.

Other alarm conditions are set when underpressure disappears, when primary air input fails or when 15% lower explosion limit in the feeding hall is reached. Only when the CO-level exceeds 4%, an automatic system shut-down is tripped. The relevance of this CO-alarm is doubtful, because the alarm level is appr. 80 times the normal operation level. Aside from this one automatic shut-down procedure, no other automatic shut-down is present.

8.3.4 Test results

The Danish EPA has prescribed that every half year an emission report has to be made by an independent laboratory. Some concentrations obtained in such an analyses are given in Table KK.1.
Rappe et al. report on the PCDD and PCDF concentrations in the flue gas and particulate matter formed before and during a PCB test burn. They come to the conclusion that no obvious differences in the levels are observed between the samples taken before and during the PCB test burn. See Table KK.2. The isomer distributions in these samples are very similar to those found in samples from municipal incinerators. In the authors' opinion, however, Table KK.2 should be interpretted with some reservation. It would seem anomalous that the emission level for PCDDs and PCDFs sharply fall, under identical incineration conditions, when PCBs are being destroyed. At best one should expect similar results, indicating that the destruction efficiency does not decrease when PCBs are incinerated.

8.3.5 References

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- C. Rappe, S. Marklund, L-O. Kjeller, P-A. Bergqvist, M. Nygren and M. Hausson; "Formation of polychlorinated dioxins and dibenzofurans in municipal and hazardous wastes incinerators", in 103rd seminar of FGU Berlin: Dioxine, eine gefahr führ jedermann, 1984.

Table KK.1 Some results of the independent analysis of the stack gas

COMPONENT	INCINERATOR I	INCINERATOR II
HCl	404 mg/m^3	87 mg/m^3
HF	8,9 mg/m^3	0,37 mg/m^3
CL_2	0 mg/m^3	0,6 mg/m^3
SO_2	444 mg/m^3	153 mg/m^3
dust	43,8 mg/m^3	8,0 mg/m^3
NO_2	80 ppm	122 ppm
CO	288 ppm	106 ppm
CO_2	6,4 %	7,3 %
O_2	12,9 %	10,8 %

Table KK.2 Levels of PCDDs and PCDFs (ng/m^3) in flue gas and particulate before and during a PCB test burn. Source: Rappe et al.

COMPONENT	BEFORE TEST	DURING TEST
2,3,7,8-TCDD	0.02	0.03
Σ TCDD	5.7	5
2,3,7,8-TCDF	36	8
Σ TCDF	108	40
Σ PeCDD	25	5
Σ PeCDF	26	5
Σ HxCDD	10	1
Σ HxCDF	22	4
Σ HpCDD	15	1
Σ HpCDF	23	3
OCDD	2	0.2
OCDF	6	0.6

8.4 HIM

The Hessische Industriemüll (HIM) is a limited partnership of the federal state of Hessen and 15 major Hessian chemical companies. According to Hessian regulations all the chemical waste generated in Hessen has to be delivered to the HIM; in return the HIM must accept all chemical waste produced in Hessen.

Of the 60,000 ton waste per year the HIM incinerates, appr. 90% is of Hessian origin, the rest coming from other German states. The installation, which began operation in 1982, consists of two identical kiln incinerators with heat recovery and effluent cleaning equipment. The investment made for this installation was about 140 million DM.

Incineration prices vary from DM 485.-- to DM 3,800.-- per ton for 1986, the latter being for PCB-containing chemical waste.

At the moment the HIM is planning a third rotary kiln incinerator to enlarge the waste capacity, which is at the moment fully occupied.

8.4.1 Waste acceptance

The HIM can treat liquid, sludge and solid chemical waste delivered in bulk or barrels, with an average chlorine content of 5%. The capacity of the installation is 20,000 to 25,000 ton per year for solid and semi-solid chemical waste, about 30,000 ton per year for liquid waste and 5,000 to 10,000 ton per year for organicly contaminated water. The total capacity is about 60,000 ton per year.

When a new waste stream is to be handled the composition of the waste is analysed. The concentration of Cl, Br, F, I, S, P and Si are determined, as is also the caloric value, the pH, the water content, oil content, solid content and average heavy metal content. If the origin of the waste stream makes it necessary, PCB-analyses are performed by an external laboratory.

At the actual delivery the waste is checked for pH, Cl-content, S-content, solid content and oil content. A X-ray-fluorescense--spectrometer and an Atomic Absorption Spectrometer (AAS) are used for metal analyses; recently a GC was installed to perform PCB-analyses in the future.

The liquid waste is stored in the tankfarm, which consists of 27 reception and storage tanks, 9 of them equipped with stirrers. The solid and semi-solid waste is stored in a 1,500 m^3 bunker. Waste which is delivered in drums, is stored in the barrel storage area, where pretreatment of drums can be performed.

Special, reactive liquids are not mixed in the tankfarm, but stored in a portable container, which is emptied directly into the oven by means of nitrogen pressure without premixing.

8.4.2 Incineration equipment

The installation consists of two identical incinerator trains, with one solid waste bunker.

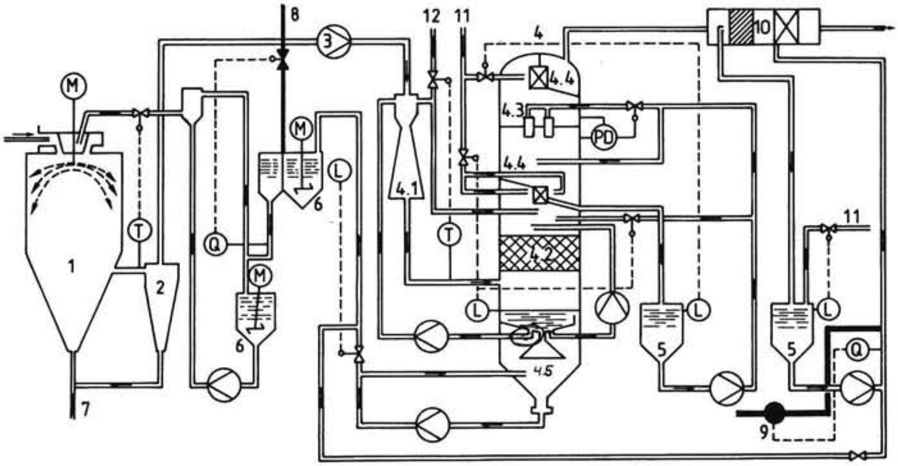
Each incinerator train consists of the following plant units:

- waste reception and feeding installation

- rotary kiln
- afterburner chamber
- waste heat boiler
- flue gas cleaning equipment

The waste reception and feeding installation consists of a crane installation, a feeding hopper, a drum elevator, a semi-solid container and a special pump for highly viscous liquids.
The liquid waste is introduced through specially designed atomization lances, one for ordinairy liquid waste, one for waste with a high caloric value (heating fuel and PCB-containing oil (PCBs < 200 ppm)) and one for dilute sludges. The rotary kiln, which is 11 m. long and 4 m. in diameter, can be operated with solid or liquid slag discharge.
The afterburner chamber is equipped with three injection lances, one for liquid waste, one for water waste and one for domestic light oil to serve as pilot burner to ensure a minimal afterburner temperature. In the afterburner chamber two air inlets are present, the first to increase the destruction efficiency and the second to lower the flue gas temperature. This last air inlet, the tertiary air inlet, is present to prevent excessive encrustation of the boiler surface by molten ash particles.
The steam boiler system is a natural circulation, waste heat recovery design. The steam produced has a temperature of 280 °C and a pressure of 255 kPa. These conditions are chosen to prevent possible fouling and high temperature corrosion.
The flue gas cleaning equipment consists of two processes, first a dry scrubbing section, which is followed by a wet scrubbing section. See Fig. HIM 1. The dry scrubbing is performed with a dilute sludge, made with lime and the scrubbing liquid of the wet section. In the dry scrubber a part of the acid gases and ash particles are removed. A cyclone is used to remove airborn particles. The wet cleaning section consists of four stages.
First is a venturi scrubber, followed by a packed bed scrubber, which both operate with water. Part of this water is recycled to the venturi and the packed bed scrubber. After the packed bed a section with ring-jet elements is installed for the removal of aerosols. The pH in the first three wet stages varies between 0 and 3. As a fourth wet stage, a water scrubber was recently installed to lower the SO_2-content of the flue gas. In this stage NaOH is added to maintain a constant pH of 8.5.
The whole system is operated without any liquid effluent. Water is added to compensate the vaporization losses. All unwanted material leaves the system with the solid which is collected in the dry scrubber and cyclone.

The incinerator is equipped with one optical pyrometer which monitors the slag temperature at the kiln end. This method of temperature monitoring is not very accurate (see section 6.1.1.). Downstream to the secondairy air inlet the temperature of the gas is monitored by a thermocouple. The flue gas is monitored for O_2, CO, HCl, SO_2 and dust content. No CO_2 monitoring is performed, and therefore the combustion efficiency is not calculated.



1 Spray dryer
2 Cyclone
3 Suction blower
4 Cleaning unit with
4.1 Venturi scrubber
4.2 Absorption stage
4.3 Ring-Jet aerosol remover
4.4 Droplet separating unit
4.5 Sludge separating device
5 Circulation tank

6 Mixing tank
7 Discharge of hazardous solids to secured landfill
8 $Ca(OH)_2$ for neutralization sludge
9 NaOH for neutalization SO_2 removal stage
10 SO_2 removal stage
11 Process water
12 Emergency water

Figure HIM1. Schematic diagram of the effluent cleaning equipment at the HIM facility.
Source: G.Erbach; "Experiences with special waste reception, intermediate storage and incineration at the hazardous waste incineration plant at Biebesheim", in *Proc. Int. Conference on new frontiers for hazardous waste management*, EPA/600/9-85/025, 1985.

The waste which is generated by the incineration process, appr. 7,000 ton per year of slag and 5,500 ton per year of salts, is disposed of in a controlled landfill and an underground deposit. The salts, because of their water solubility, are packed in special containers before they are moved to the underground deposit.

8.4.3 Operating Conditions

The minimum conditions which are required by environmental regulations are:

- a minimal temperature in the afterburner chamber of 900 °C.
- a minimal oxygen content in the stack of 11%.
- flue gas conditions: CO $\leq$ 100 mg/m^3; HCl $\leq$ 50 mg/m^3; F $\leq$2 mg/m^3; SO_2 $\leq$ 100 mg/m^3; total hydrocarbons $\leq$ 20 mg/m^3 and dust $\leq$ 30 mg/m^3;
- sum of As, Pb, Cr, Co and Ni emission 1 mg/m^3;
- sum of benz(a)pyrene, dibenz(alpha, beta)anthracen and beryllium compounds, as Be 0.1 mg/m^3.

At normal operation conditions the temperature at the end of the rotary kiln is 1,200 °C, which results in an afterburner temperature of appr. 1,000 °C. Figure HIM 2 gives the temperature, residence time and velocity of the flue gases at various places in the incinerator. The residence time for solids is appr. 1 hour.
When PCBs or PCTs are burned, the kiln temperature is 1,400 °C, resulting in an afterburner temperature of 1,200 °C. When pure PCBs are incinerated, they are introduced directly by portable containers, and not mixed with other liquid waste in the storage tanks.
Because of the discontinuity of the solids input, the temperature fluctuates by appr. 50 °C. When the temperature of the afterburner chamber is lower than the required level, the light oil burner is ignited and all waste feed is stopped until the temperature is again sufficiently high.

In the period from 1982 until mid 1986 three incidents with the solid waste bunker occurred. Two incidents arose due to undefined chemical waste of domestic origin in the solid waste bunker, which caused a fire in the solid waste bunker. These fires were put out by foam from the fire extinguisher system.
The most recent accident happened begin May 1986, when the semisolid waste bunker caught fire, possibly due to ignition by static electricity. Because of the high flames, part of the bunker ceiling caught fire, and some plexiglas window panes at the back side of the bunker caught fire and collapsed. In their fall the window panes damaged a set of controlling cables, resulting in the shut down of all waste feed to the kilns and the shut down of the fire extinguisher system. The rotation of the kilns, however, was not disturbed, nor was the underpressure or the primary air blower. After 10 minutes the primary air blower of one of the kilns broke down, with still appr. 1 ton solid waste in the kiln.
The damage which occurred to the equipment is estimated at 1.5 million DM. The authorities have ordered an investigation concerning the emissions produced during the accident and the consequences of these emissions for the immediate environment.

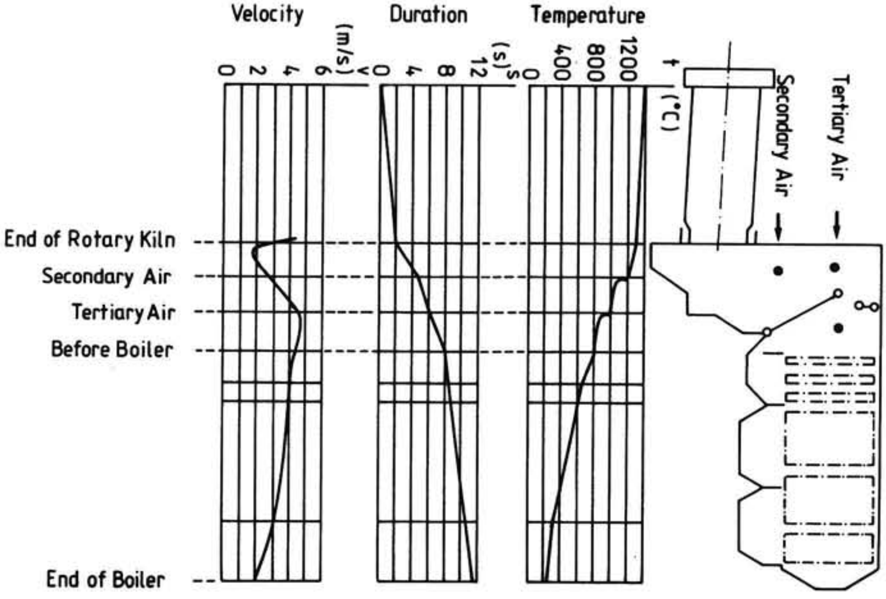


Figure HIM2. Temperature, residence time and gas velocity of the combustion gases in the thermal sections of the HIM facility.
Source: G. Erbach; "Experiences with special waste reception, intermediate storage and incineration at the hazardous waste incineration plant at Biebesheim", in Proc. Int. Conference on new frontiers for hazardous waste management, EPA/600/9-85/025, 1985.

8.4.4 Test results

Several tests have been performed by the NUKEM to analyze the performance of the incinerator, and in particular the effluent cleaning equipment. Average stack concentrations during these tests are shown in Table HIM 1. These test reports show that the flue gas concentration of some compounds is much higher after the spraydryer than before entering the spraydryer. This is possibly due to the use of the wash tower effluent as washing liquid in the spraydryer. This increased concentration effect concerns mainly chlorine, copper, lead and zinc, whose concentration increase some 50 to 100% after leaving the spraydryer.
In the last NUKEM report results of PCDD and PCDF emissions during and after a PCB burn were published. No obvious difference between the levels during and after the PCB burn were found. See Table HIM 2.

8.4.5 References

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- NUKEM report FuE-85008
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Table HIM 1. Average stackgas concentration during the NUKEM tests (mg/m^3)

Compound	NUKEM report FuE-83077 (mg/m^3)	NUKEM report FuE-84071 (mg/m^3)	NUKEM report FuE-85008 (mg/m^3)
As	< 0.03	< 0.03	-
Be	< 0.02	< 0.02	< 0.02
Pb	3.0	0.68	1.2
Cd	0.05	0.06	0,07
Cr	0.06	0.14	0.07
Co	< 0.03	< 0.03	< 0.03
Cu	0.5	0.13	0.3
Ni	0.06	< 0.06	< 0.05
Hg	0.1	0.05	0.3
Zn	7.1	0.7	1.8
Cl	15	10	12.3
F	0.25	0.6	0.6
SO_2	60	100	377
CO	10	77	< 10
THC	5	5	< 1

Table HIM2. Average PCDD- and PCDF-concentrations in the flue gas during and after the PCB-burn

Component	during PCB-burn ng/m^3	after PCB-burn ng/m^3
2,3,7,8-TCDD	0.02	0.02
ΣTCDD	0.37	0.48
2,3,7,8-TCDD	0.22	0.15
ΣTCDF	2.9	1.6
1,2,3,7,8-PeCDD	0.06	0.06
ΣPeCDD	0.6	0.6
1,2,3,7,8-PeCDF	0.42	0.20
ΣPeCDF	4.9	3.2
1,2,3,6,7,8-HxCDD	0.11	0.13
ΣHxCDD	1.3	0.9
1,2,3,6,7,8-HxCDF	1.1	0.9
ΣHxCDF	10.7	11.3
ΣHpCDD	1.4	1.1
ΣHpCDF	8.9	6.3
OCDD	2.9	2.1
OCDF	3.5	2.9

8.5 O.C.S.

Ocean Combustion Service (OCS), a privately owned company founded in 1972, is a subsidiary company of Waste Management International Inc., a major chemical waste handling company. OCS operates with two incineration vessels, the Vulcanus I and Vulcanus II, on the European and North-American chemical waste market. The incineration vessels are able to burn liquid waste only. The total capacity of chemical waste which can be incinerated on both ships together amounts to 160,000 metric tons of waste annually.
The incineration price depends on the caloric value, water content, salt content and the amount of waste offered. The metal content of the waste, as permitted by the authorities, does not change the incineration price. The average incineration price lies between Dfl.200,-- to 300,-- per ton of waste in 1986, with a maximum price of Dfl.700,-- per ton for high fluorine containing waste.

At the moment OCS is planning to station the Vulcanus II in North America, upon receiving all the required EPA-permits, and to use the Vulcanus I only for the European market. The position of at-sea incineration in Europe, however, is presently a subject of discussion. According to the London Dumping Convention (LDC), at-sea incineration is an interim method of waste disposal. Whether at-sea incineration remains an interim solution must be decided before 1990, possibly on the LDC meeting in 1987.

8.5.1 Waste acceptance

OCS, being a privately owned firm, is not directly controlled by the environmental policy of national government authorities, as are AVR, HIM and Kommunekemi. These companies operate largely nationally, i.e. they have a special function, indeed a duty, for their region, namely to process the region's chemical waste. Since OCS is a completely private company, it can more easily choose which wastes it will destroy and which wastes it will not accept. The impression is that OCS employs more and stricter criteria which the waste has to meet before being accepted. Some of these criteria arise because of the prohibition to incinerate waste containing more than 5 ppm PCBs and more than 1 ppm for certain heavy metals. Table OCS 1 gives the general acceptance criteria.

When a waste stream is offered, a pre-acceptance procedure is first followed for a sample of this waste. Ash content, metal content, PCB content, chlorine value, reactivity with water and miscibility are determined as a minimal standard test set. When the origin of the waste stream gives reason for it, supplementary tests can be performed, e.g. for content of dioxins, S, N, peroxides etc. These test results are compared with the information given by the waste producers. When the waste is accepted for incineration, a set of tests for the total waste stream is defined, which have to be carried out before accepting the actual delivery of waste. This is done to make sure that the pre-acceptance sample is representative for the whole stream.

When the waste is delivered at the Antwerp harbour, it is stored in tanks. These storage tanks are used to compose a mixture of liquid wastes with a good incineration behaviour. Only waste in bulk is delivered in Antwerp; waste packed in drums is collected in Rotterdam. There the drums are emptied after analysis, and combined when possible. After some time the waste is brought to Antwerp in bulk. The emptied drums are washed with xylene or toluene and then reused or crushed and sold to Hoogovens (a Dutch steel producer) as scrap iron.

Most of the analyses which are needed for the pre-acceptance and acceptance tests are carried out in the Antwerp laboratory of OCS. For analysis of fluorine, metals and dioxins, determination performed by external laboratories are used. Of the PCB-content analyses, 90% are performed by OCS itself, while 10% of these analyses are carried out by external laboratories. To maintain the high level of accuracy of the analytical instruments, a quality control program with cross checks of samples is performed in co-operation with the external laboratories (TNO, Techcentre CWM).

At the moment OCS is working on a method to demonstrate the chemical similarity of two samples without identifying all the components. This method is based on the GC-ECD (Electron Capture Detector) fingerprint of the most relevant solvents. In the future this method will be used to check the representativeness of a pre-acceptance sample, when it is accepted by the authorities.

8.5.2 Incineration equipment

The incineration vessels of OCS contain the following sections: 1: liquid tanks; 2: pumping facilities and 3: incinerators. Both vessels, which have a double hull and double bottom, contain 8 liquid tanks with a total capacity of 3,176 m^3 for the Vulcanus I and of 3,161 m^3 for the Vulcanus II. Each of these liquid tanks is equipped with a high and low suction pipe to the pumping section. This double piping system is used for recirculation of the waste during incineration.
The pumping facility consists of a set of Gorator pumps (a sort of mincing pump), which are used to reduce the particle size of the solids in the waste, a recirculation pump and, for each incinerator, a set of three burner feed pumps.

The Vulcanus I is equipped with two incinerators, and the Vulcanus II is equipped with three incinerators, each of these incinerators has three rotating cup burners. Each incinerator consists of two main sections, a combustion chamber and a stack, through which the combustion gases sequentially pass. This dual chamber configuration uses the first chamber for internal mixing and the second for adequate residence time. Table OCS 2 gives the characteristics of the furnaces. The furnace wall is covered with heavy duty fire clay bricks which have to be replaced after handling about for 50,000 tons of waste (approximately once per two years).
The burners are asymmetrically placed on the periphery of the furnace in order to achieve a high turbulence, and are all at the same level (Fig. OCS 1 + OCS 2).

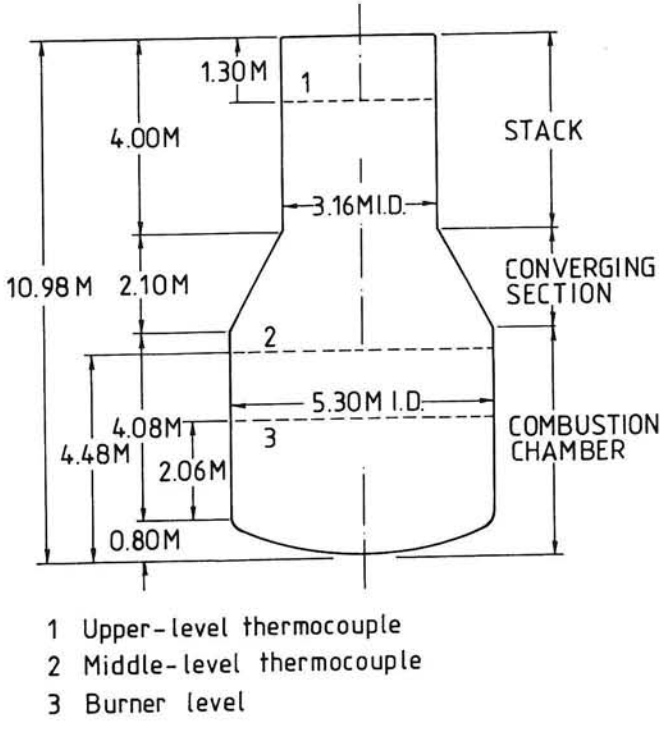

Figure OCS1. Schematic diagram of an incinerator used onboard the Vulcanus II.
Source: Ref. 99.

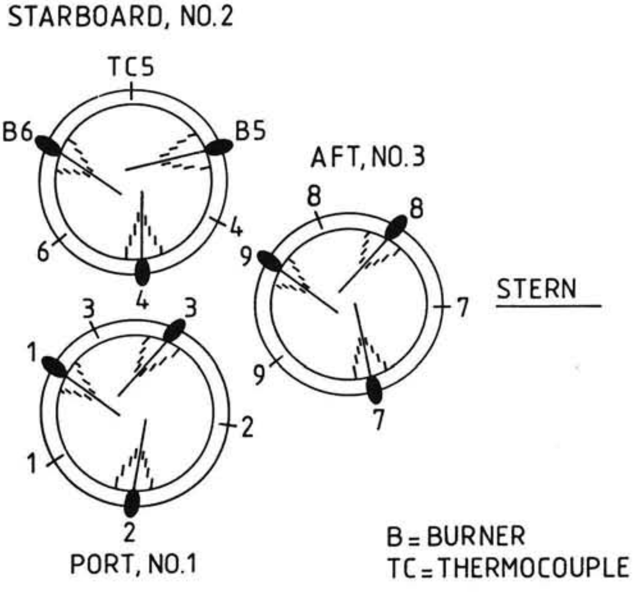

Figure OCS2. Locations of burners and thermocouples.
Source: Ref. 99

During operation, the rotary cups are rotated rapidly at a fixed speed (appr. 6500 rpm) by electric motors. Waste or fuel oil is delivered through a central tube to nozzles near the periphery of the cup. Rotational velocity spreads the fuel into a thin film, which at the rim of the cup becomes unstable and breaks up into tiny droplets. The primary combustion air is introduced through an annulus surrounding the rotary cup, accomplishing thorough mixing of fuel droplets with combustion air and shaping the flame. The combustion air, primary and secondary, is supplied by large fixed-speed fans, one per burner, each having a rated maximal capacity of 30,000 m^3/hr. The air flow rate is controlled by an adjustable damper in each airduct.

Each incinerator is equipped with seven thermocouples, one besides each burner mouth, three at middle-level and one at upper-level. The thermocouples besides the burner mouths are used to prevent overheating of the wall. The middle-level thermocouples are used to check the flame temperature. Next to each burner an optical flame sensor is installed to check the flame status. Every incinerator is equipped with two gas probes, one as backup, to sample the stackgas.

The stackgas concentration of O_2, CO and CO_2 is determined continuously for each incinerator. These data, together with the furnace temperatures and other relevant information, are recorded by a data logger system, which is owned by the Dutch Government Water Authorities ("Rijkswaterstaat").
This system is used by the Dutch authorities to retrospectively check the at-sea performance of the vessel. Two similar computer systems are present to record vital process information for the operators. One of these systems is a backup unit.

Neither of the Vulcanus vessels are equipped with effluent cleaning equipment, a factor which strongly reduces the price of the total incineration process.

8.5.3 Operating conditions

According to the London Dumping Convention the minimal operating conditions for at-sea incinceration are: a wall temperature higher than 1100 °C, a flame temperature higher than 1250 °C, combustion and destruction efficiency higher than 99.9% and a residence time higher than 1 second.
During her certification voyage in 1983 the Vulcanus II operated at an average wall temperature of 1160 °C, a residence time between 1.1 to 1.3 seconds and a CE higher than 99.99%. The DE for four test-compounds were higher than 99.99%. Normally the flame temperature of the OCS-vessels lies between 1300 °C and 1500 °C, which gives a wall temperature from 1100 to 1300 °C. The DE and CE always exceed 99.9%; usually 99.99% is exceeded. The residence time varies between 1.1 and 1.5 seconds, depending on the temperature in the incinerator. Average stack gas concentrations are 10.1% O_2, 9.1% CO_2 and 8 ppm CO.

The Vulcanus I was used for test incineration of PCB waste in the Gulf of Mexico in 1982. During these tests the Vulcanus I operated at a wall temperature between 1270 and 1320 °C, which means that the flame temperature varied from about 1470 to 1520 °C. The calculated average residence times varied from 0.91 to 1.46 seconds. A shutdown minimal wall temperature of 1200 °C was prescribed by the EPA.

When during normal operation the temperature of two of the three middle-level thermocouples of one incinerator drop below 1180 °C, the waste feed is automaticly stopped and the burners are fed with fuel oil. When the temperature again exceeds 1230 °C, the waste feed can be continued. Other alarm levels are: 10 ppm for CO, 99.9% for CE and 3% for O_2, the oxygen level alarm being rather low to function as a safety alarm.

Periodically during the incineration process, the burners require cleaning because of coke deposition on the cups. When a burner becomes noisy, indicating excessive deposition, it is switched to an oil feed, then switched off and removed from the oven and then manually cleaned. During each voyage in total about 1 kg of coke deposits, which roughly consists of 40% salts, 40% carbon and 20% unburned hydrocarbons, are removed from the burners.

8.5.4 Test results

The OCS incineration vessels have often been tested on their incineration performance. The results of some of these tests on the Vulcanus I are given in Table OCS 3. During two PCB tests on the Vulcanus I the destruction efficiency of PCBs and chlorobenzenes were determined. Table OCS 4 gives the results of these tests. During one of these tests the destruction efficiency of TCDFs was shown to be higher than 99.93%, which formed the under detection limit of the analysis apparatus. The destruction efficiency of TCDDs was not calculated because no TCDDs were detected during these tests.
Recent test incineration results on the Vulcanus II, which were obtained in 1983, are given in Table OCS 5. At the moment OCS is planning a test to sample the plumes behind the vessel during incineration. This test is meant to give information on whether or not PCDDs and PCDFs are formed in the plumes during cooling.

When reporting on OCS, it is impossible not to mention the discussion concerning at-sea incineration. This discussion concerns the risks to human health and to the environment from at-sea incineration, compared with land-based incinerators. Because of bad experiences in the past with other at-sea incineration firms, at-sea incineration, and therefore OCS, has the disadvantage of the doubt. Reports have been published stating that at-sea incineration is less safe than land incineration; however these reports are all contradicted by other reports (see references). Kleppinger and Bond have been questioning the adequacy of the incineration tests performed on the Vulcanus. However, most of these allegations are denied by EPA officials and an independent consultancy firm.

In the US this discussion resulted in an assessment study by the EPA office of Policy, Planning and Evaluation for hazardous waste incineration. This study concluded that at-sea incineration is an environmentally sound treatment option for destroying liquid hazardous wastes.
In the Netherlands a policy study on at-sea incineration is presently being performed. As a part of this study a hazard and operability study for hazardous waste incinerators was carried out. It concluded that the hazard and operability sensitivity of the Vulcanus II is limited, and in the same order of that of land based incinerators.
A recent technology assessment performed by the American Office of Technology Assessment (OTA) concluded that ocean incineration, carried out under a sufficiently rigorous and comprehensive regulatory framework, could be one of several options to fill an interim need in hazardous waste management. Under such a scenario, ocean incineration would focus on highly chlorinated wastes that can be advantageously burned at sea because of the absence of a requirement for scrubbers. With regard to incineration of special wastes, such as PCBs, OTA suggests further evaluation concerning the impact of ocean transport and incineration on the marine environment. In this evaluation special attention has to be paid to the potentially catastrophic consequences of a major marine spill and the acknowledged difficulty or impossibility of cleanup of such a spill.
These three publications may contribute to the definite political acceptance of at-sea incineration as an environmentally sound solution for destruction of certain classes of hazardous wastes.

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Table OCS 1 General acceptance criteria for chemical waste to be incinerated by OCS

Water content	≤ 5 mass %	(1)
Calorific value	≥ 3200 kcal/kg	(1)
F content	≤ 0.5 mass %	(1)
pH-value	between 6 to 8	(1)
Alkalimetal-content	≤ 0.5 mass%	(1)
Ash content	≤ 1 mass%	
Viscosity	≤ 50 cP	
Melting point	≤ -10°C	
Sediment	≤ 4 volume% ≤ 2 mass%	
Particle size	≤ 2 mm	
Vapour pressure (20°C)	≤ 1.1 bar	
Peroxide content	≤ 0.001 mass%	
Diethylether content	≤ 5 mass%	
Carbon disulfide content	≤ 0.5 mass%	
Heavy metal content:		
Hg, Cd, As, Be	≤ 1 ppm per metal	
Pb, Cu, Zn, Cr, Ni, Se, Th, Ag	≤ 50 ppm per metal	
PCB and PCT content	≤ 5 ppm	
HCH content	≤ 5 ppm	
Dichlorodiphenyltrichloroethane and related compounds	≤ 5 ppm	
PCDF content	≤ 5 ppm	
PCDD content	none (i.e. present detection limit)	

(1) higher values are accepted at a higher incineration price

Table OCS 2 Characteristics of the furnaces of the OCS vessels

	Vulcanus I	Vulcanus II
diameter bottom, m	4.8	5.3
height bottom, m	0.75	0.84
diameter chamber, m	4.8	5.3
height chamber, m	3.5	4.04
height stack cone, m	1.6	2.1
diameter stack straight, m	3.4	3.1
height stack straight, m	4.6	4
volume chamber, m^3	72	89
volume total, m^3	135	160

Diameters mentioned are inner diameters

Source: Bartelds,H.; "Submission to permitting authorities of data in lieu of trial burn results for future incinerator ships", TNO report 83-09409, 1983.

Table OCS3. Results of testburns on the incimerator ships "Vulcanus I" and "Vulacanus II"
Source: TNO/CL 82/122 and TNO/R 83/53

a.Date	Oct.1974-Jan.1975	March 1977
b.Place	Gulf of Mexico	Gulf of Mexico
c.Investigators	EPA, Shell	EPA
d.Typ of waste(s)	volatile chlorinated hydrocarbons	organochlorine wastes EDC-tar
e.waste feed	max.12.5 ton/hr/oven	11 ton/hr/oven
f.Wt.% chlorine in waste	ca.68	ca.68
g.Combustion temp (°C)	min.1200;average 1350	average 1535
h.Residence time (s)	not available	0.8-1.14
i.Combustion efficiency (%)	99.92-99.98	99.92.-99.99
j.Destruction efficiency (%)	99.98-99.998	trichloropropane: > 99.92

a.Late summer 1977	March 1981	December 1981
b.Pacific	North Sea, Zone B	Gulf of Mexico
c.EPA, TRW, USAF	TNO	TNO
d.Herbicide Orange	organochlorine and organofluorine wastes	PCB Waste
e.7.3 metric tons/hr/oven	ca.12 ton/hr/oven	5 - 9,5 ton/hr/oven
f.ca. 29	OCl: 50; OF: 6.9	29 to 66
g.average 1500	1300-1500	1470-1520
h.1	ca.1	0.91-1.46
i.99.983-99.992	99.987-99.995	99.940-99.999
j.Herbicide Orange: 99.999 TCDD:>99.88->99.99	OCl:>99.99 OF:99.4	some PCBs:≥99.946

a.January 1983
b.North Sea
c.TNO
d.EDC-tar

e.12.6 ton/hr/oven
f.ca.61
g.1360
h.1.1 to 1.3
i.>99.99
j.1,1,2-trichloroethane:
>99.9995
1,1,2,2-tertachloroethane:
>99.9983

Table OCS 4 Destruction efficiencies determined during two PCB test burns on the Vulcanus I

Substances	TNO report DE, %	TRW report DE, %
trichlorobenzenes	> 99.992	> 99.99994
tetrachlorobenzenes	> 99.967	> 99.99993
pentachlorobenzenes	> 99.995	> 99.99985
hexachlorobenzenes	> 99.996	> 99.99988
tetrachloro PCBs	> 99.993	> 99.99978
pentachloro PCBs	> 99.946	> 99.99988
hexachloro PCBs	> 99.956	> 99.99992
heptachloro PCBs	> 99.960	> 99.99992
octachloro PCBs	N.A	> 99.99975

Note: N.A. means not analysed

Sources:
- H.Compaan; "Monitoring of combustion efficiency, destruction efficiency and safety during the test incineration of PCB waste, part I",
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  EPA-600/7-83-024 1983.

Table OCS 5 Incineration test results of the Vulcanus II

Substances	TRW report DE, %	TNO report DE, %
1, 1, 2-trichloroethane	> 99.99994	> 99.9995
tetrachloroethane	n.a.	> 99.9934
1, 1, 1, 2-tetrachloroethane	n.a.	> 99.9990
1, 1, 2, 2-tetrachloroethane	n.a.	> 99.9983
1, 1-dichloroethane	> 99.99988	n.a.
1, 2-dichloroethane	> 99.99993	n.a.
trichloromethane	> 99.9996	n.a.
carbon tetrachloride	> 99.998	n.a.

Note: n.a. means not analyzed

Sources:
- D.G.Ackerman, R.G.Beimer and J.F.McGaughey; "Incineration of volatile organic compounds on the M/T Vulcanus II", TRW report for CWM, 1983.
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9 CRITICAL EVALUATION OF INCINERATION PRACTICE

In this chapter the main issues concerning the incineration of chlorinated hydrocarbon waste will be briefly addressed. This is done to give an idea of the gaps in knowledge and to assess the value of knowledge. The subjects are considered in the same order as in chapter 1 to 8.

9.1 General background

The incineration of chlorine containing organic waste is a source of PCDDs and PCDFs. However, the importance of these sources to environmental pollution is as yet unknown. Based on the knowledge of the chemical reactions involved, it can be stated that incineration of chlorinated hazardous waste is an important potential source of PCDD and PCDF emission. This fact makes it necessary to continue the research efforts in this field in order to ascertain how large the risk is from incineration of chlorinated organics. Such research will center around determining toxicity (in particular exposition--effect relations) and the degree to which the public and the environment are exposed.Since the potential risk may well be very large, it is deemed prudent to simultaneously do research to optimize the control and efficiency of the incineration process.
Because of the public concern much research has been performed in the field of PCDD and PCDF formation. However, that such research is being carried out should not lead to the assumption that no other emissions can arise from CHC incineration. Various studies have reported on polyaromatic hydrocarbon emissions and on the formation of products of incomplete combustion during and after CHC incineration. More research, also concerning the toxic effects of these emissions, is necessary to obtain a full picture of the environmental impact of CHC incineration.

9.2 Social background and legislative aspects

An aspect, which, however, is not specific for CHC incineration, is the lack of clarity concerning criteria on the basis of which legislation is enacted. Also a clear meaning of some commonly used principles, such as the "best practical means" and the "best technical means" is lacking. Due to this uncertainty, the practical meaning of these principles is continually being re-interpreted. Those who do the interpreting therefore have an important responsibility, since their decisions can have an important effect on human health and the state of the environment. Awareness of this responsibility, which obviously lies with the officials of the various environmental protection agencies, is not always manifested clearly to the public. For example, most of the regulating criteria which are used by the US EPA became international standards. EPA's criterium for testburns, the POHC system, however, has been widely critisized because of its weak scientific base. Nevertheless EPA refuses to use an alternative interim system arguing that more research is necessary. While this standpoint may be understandable from a scientific point of view, the use of a system with such clear insufficiencies does not re-assure the public.

Another example of a not carefully thought out environmental policy concerns the Waste Act permit ("Afvalstoffenwet vergunning") of the AVR installation. In an aim to prevent the formation of PCDDs and PCDFs, a definition for compounds which have to be destroyed at stricter conditions is given (see section 8.2.3). This definition, however, is far from perfect. Firstly, the definition only concerns chlorine and/or fluorine containing polycyclic compounds (CFPCs), even though chlorinated monocyclic compounds such as pentachlorophenol are proven precursors to the formation of PCDDs and PCDFs (see Fig.3 and section 4.2). Secondly, the definition of CFPCs does not contain a concentration level for CFPCs in solid waste, which, because of the prohibition of incinerating CFPCs in the old incinerator, can lead to a complete ban on the incineration of solid waste in the old incinerator, since compounds like PCDDs and PCBs can be found almost everywhere at trace levels. This ban can hardly be the objective of the environmental authorities.

9.3 Theory of thermal destruction of CHC by combustion

One of the facts derived from thermodynamics is that the conditions under which an incinerator is operated are always a compromise between complete destruction of the CHC and minimalisation of Cl_2 formation. Another, even more important conclusion from thermodynamics, is that it is possible to have a destruction efficiency of 2,3,7,8-TCDD of, for all practical purposes, 100% (> 99.999999%). However, whether this efficiency is reached in practice cannot be predicted. This uncertainty is due to the fact that the rate at which destruction occurs is dictated by chemical kinetics, and the kinetics of the chemical reactions involved are very inadequately known.

The current level of knowledge concerning the thermal destruction of CHC can be described as being at the "blackbox" stage: the possible border values are known (by thermodynamic calculations) and every needle which is pushed into the box gives new information about its internal structure (the various reaction schemes which are reported). Still one is not able to describe the full contents of the box. An answer to the questions concerning which compounds are formed during and after combustion, and their concentrations, is, however, necessary in order to be able to prevent harmful emissions.

Fortunately there are still some basic rules which can be applied to thermal destruction, but these rules are based on chemical principles which must be understood well. For instance a higher temperature gives a higher reaction rate. The higher rate, however, works for both desired and undesired reactions. In the case of a manifestly too short residence time, an increase in reaction temperature could, in principle, lead to an increase in emission of toxic compounds.

9.4 Equipment

The process of designing incineration equipment is not completely scientific. This is so because not all the aspects of the functioning of the equipment are fully understood. Temperature, turbulence and recidence time in the incinerator are, together with the fuel/air ratio, the most important operating parameters. Unfortunately, however, there is no model which quantitatively links these three parameters with the DE of a waste stream. This makes it clear that the design of an incinerator is partly a trial-and-error procedure. Planned changes in the main parameters of an existing incinerator have to be studied carefully, before being carried out continuously in practice. For instance, an increase of the combustion air will change not only the fuel/air ratio, but also the temperature; furthermore the residence time will decrease. Therefore it cannot be easily predicted whether this change will improve the destruction efficiency of the incinerator or not.

One of the general practices in operating incineration equipment is the use of a continuous waste feed installation to prevent sudden changes in the thermal load of the incinerator. Continuous feeding of solid and semi-solid waste is still difficult and needs improvement to prevent the phenomenon of "puffing" in rotary kiln incinerators.

Operating at underpressure in the oven is also a widely accepted and generally effective way of preventing fugitive emission from an incinerator. For rotary kilns which are operated at underpressure, the air tightness of the kiln seals is of critical importance. If the air inflow through the seals is too high, cold spots will arise at the end of the kiln, resulting in a lower incineration performance.

Apart from the special materials which are required because of the high operating temperatures and aggressive gases, the equipment which is used for hazardous waste incineration is not very different from the "normal" process units used in the chemical industry. None of the equipment is exclusively designed for hazardous waste incineration, which makes it clear that the incineration market is still a new and small branch of the chemical industry.

Some of the emerging technologies, however, are specifically designed for hazardous waste incineration, which indicates that this branch is expanding. The extreme conditions at which some of the installations are supposed to work can have unforeseen effects on the equipment materials, especially after long periods of operation. Therefore most of the emerging technologies still have to be tested on plant scale for a longer period to demonstrate their technical applicability and economic viability.

9.5 Process control

Most of the monitoring systems which are used give reliable information about the status of the process. One exception is the optical pyrometer for temperature monitoring, which can give unacceptable measurement error because of spectral bias factors in the combustion area. Other difficulties in process parameter monitoring occur with the waste/air ratio of solid waste, which cannot be monitored, and gas flow and liquid flow monitoring, which are not reliable.

The combustion efficiency can be regarded as the most important directly measurable parameter concerning the incineration efficiency, even though no correlation with the DE exists. It is very useful as an early warning system to prevent emission of PICs. Notwithstanding the fact that the CE is a very imperfect method of establishing the DE for CHC, this value (CE) is not even measured in many existing installations.

A monitoring system which might become important in the future is the total hydrocarbon (THC) monitoring. THC monitoring can be used to obtain information about organic emissions, although for an incinerator burning CHC waste the total halogenated hydrocarbon emission would be even more useful, especially with regard to the toxic character of some halogenated hydrocarbons. A drawback on THC and total organic chlorine monitors is the fact that these monitors only detect volatile components.

9.6 Process evalation

In the last decade much effort has been put into the improvement of analysis methods and procedures. Much progess has been made in designing sampling procedures and lowering detection limits. All these improvements can only be exploited, however, when sufficient attention is paid to effective quality control and quality assurance. Standard quality control procedures have to be developed and implemented to guarantee correct results of analyses.

The use of environmental modeling should be reviewed carefully because of the complexity of the subject. One of the key knowledge gaps is the absence of reliable exposition-effect relationships concerning the human and environmental toxicity of CHCs. It would be a counter-productive development indeed if these models would be used without understanding their limits.

With regard to the POHC problem it might be useful to create an interim policy for certification tests, as long as a sound scientific base for the POHC ranking is lacking. The use of surrogate compounds for monitoring the DE during regular waste burns should be investigated. As far as the formation of PICs is concerned, more research is necessary in order to be able to prevent unwanted emissions.

9.7 Industrial practice

Most of the companies visited have plans for future expansion. However, most of these expansion plans have been delayed because of public opposition. Expansion is necessary because of a higher volume of waste offered and also because of changes in the waste composition. Another factor is that the caloric value of the waste is decreasing; furthermore the percentage of waste offered in the form of solids is increasing rapidly. All the visited companies are aware of the importance of waste characterization. However, the analytical programs, and their degree of rigour, are different. This is partly due to differences in waste streams and environmental regulations. Furthermore it should be realized that the complexity of the waste presented (in terms of number of samples and number of substances involved) and the technical difficulty of the required analysis techniques makes a thorough analysis well nigh impossible, certainly from the point of view of costs.

All of the installations use alarm levels for certain concentrations. However, some of the levels are so high that their use might, instead of "alarm", be characterized almost as a "disaster" level.

On the basis of all the uncertainties concerning toxicity and quantitative analysis one might logically argue that the best solution would be combustion reaching a 100% destruction efficiency.

10 CONCLUSIONS

The incineration of chlorinated hydrocarbon waste is increasingly becoming an important disposal method. This fact, together with the large potential risk of CHC-emission from waste disposal units, makes it necessary to evaluate the current level of knowledge concerning incineration.

It is concluded that:

1 The technology on which the equipment is based is not new, so experience with most of the different equipment types is present. It should be pointed out, however, that most of this experience is in the field of normal incineration, not in the area of incinerating chlorine containing chemical wastes.

2 On the basis of thermodynamics it can be concluded that the complete destruction of CHC-compounds by means of incineration (i.e. combustion) is possible. The products of complete oxidative destruction (carbon dioxide, water vapour, hydrogen chloride) will not re-combine to form CHC-compounds upon cooling.
Whether complete destruction of CHC-compounds through combustion does indeed occur in an incinerator, or even whether CHC-compounds are themselves formed during the combustion process, is a matter of the chemical reactions occuring (the reaction mechanisms) and the rate at which these chemical reactions occur (the kinetics). The reaction mechanism and the kinetics involved are determined by the waste feed composition and the incinerator conditions (temperature, turbulence, residence time, degree of mixing, amount of air present, etc.). Knowledge of the reaction mechanism and reaction kinetics, as related to the waste stream composition and incinerator conditions, is rather limited and usually not sufficient to quantitatively predict which minimum incinerator conditions (in term of temperature, residence time, etc.) are necessary in order to result in a given emission level. More research in this field is necessary. The ultimate goal of this research should be knowledge that will be useful in rationally designing incinerators with a given minimal emission of CHC-compounds at minimal costs. It should be realized, however, that because of the great complexity of the waste streams which have to be destroyed and complicated nature of reaction mechanisms and kinetics involved, such research will be quite difficult and time consuming

3 As long as a rational base for the POHC-system is lacking, a dual approach in certification is needed. Instead of only demonstrating destruction efficiencies of some compounds, it will be also necessary to demonstrate the total organic emission during the certification tests.

4 A number of key parameters now being used to characterize incinerator performance do not have a scientific basis sufficiently broad for this purpose. Indeed, their use can even sometimes lead to conflicts in interpretation. In order to come to an unambiguous method of characterizing incinerator performance it will be necessary to define better parameters; in particular, the kinetic aspects of incineration (the usual bottleneck) must be taken into consideration. It will also be obvious that these better parameters must achieve a good degree of international acceptance, since destruction of CHC-wastes is a problem which does not cease at national borders.

5 Finally, and very importantly, the fact that the environmental impact of CHC incineration is still not fully understood, especially with regard to the formation and impact of PIC emissions, must be emphasized. This area must be investigated with more effort than before in order to ascertain the risks, in the form of toxic exposition-effect relations of exposure to CHCs. The most rational criteria for designing and operating CHC-incineration plants will be based on the concept of reducing risk to an "acceptable level".

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List of abbreviations

AIT	autoignition temperature
CE	combustion efficiency
CFPC	chlorine- and/or fluorine-containing polycyclic compound
CHC	chlorinated hydrocarbon, chlorinated organic waste
DE	destruction efficiency
DRE	destruction and removal efficiency
EPA	environmental protection agency
FID	flame ionization detector
GC-MS	gaschromatography-massspectrometry
HC	hydrocarbon
HpCDD	heptachlorodibenzo-p-dioxin
HpCDF	heptachlorodibenzofuran
HPLC	high pressure liquid chromatography
HxCDD	hexachlorodibenzo-o-dioxin
HxCDF	hexachlorodibenzofuran
LDC	London Dumping Convention
MM5	modified method 5
MPRSA	marine protection, research and sanctuaries act
NDIR	non-dispersive infrared
OCDD	octachlorodibenzo-p-dioxin
OCDF	octachlorodibenzofuran
PCB	polychlorinated biphenyl
PCDD	polychlorinated dibenzo-p-dioxin
PCDF	polychlorinated dibenzofuran
PCDPE	polychlorinated diphenylether
PCP	pentachlorophenol
PeCDD	pentachlorodibenzo-p-dioxin
PeCDF	pentachlorodibenzofuran
PIC	product of incomplete combustion
POHC	principal organic hazardous constituent
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
RCRA	resource conservation and recovery act
SASS	source assessment sampling system
SIM	single ion monitoring
TCDD	tetrachlorodibenzo-p-dioxin
TCDF	tetrachlorodibenzofuran
TDU	thermal decomposition unit
THC	total hydrocarbon
TSCA	toxic substances control act
VOST	volatile organic sampling train

Chlorinated hydrocarbons, in the form of chemical waste, represent a threat to the environment and public health of the world. Their proper handling, removal and destruction is critical to long term safety.

Increasingly strict government legislation is leading to an increase in the quantity of chlorinated chemical waste requiring responsible disposal. Incineration has received special attention. However, concern as to the production of toxic by-products, such as dioxin, during incineration, and other effects of the process, has led to extensive scientific research on the overall impact on the environment.

The authors describe the state-of-the-art technology for environmentally acceptable incineration of chlorinated chemical waste. Information presented is based upon a detailed review of extensive subject literature and meticulous interviews with major European companies in the field, appropriate government authorities concerned and other experts.

The equipment, waste acceptance and disposal procedures of firms involved, and the parameters and techniques used by control authorities, are critically reviewed. Findings vary widely.

Control procedures vary from strict to lax, and the control parameters used often lack a sufficiently scientific basis, which can lead to contradictory results. Additionally there is little consensus between authorities on the proper judgement criteria for the actual operations, and further research at high temperature is needed.

This book contributes to the logical ordering and structuring of the issues involved. It also clearly shows the need to reach consensus and presents ideas to reach this goal.