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## Final Report of the Committee of Experts

7 May 1986

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- To render the report more readable, technical and scientific details are summarized in appendixes at the end of each chapter.
- *2,3,7,8-tetrachlorodibenzo-p-dioxin* is abbreviated in this report to *TCDD*. If it is necessary to distinguish this substance from other tetrachlorinated TCDDs, the abbreviation 2,3,7,8-TCDD is used.
- An arrow (→) after a term refers to the 'abbreviations and explanatory notes' (14.3 and 14.4) at the end of the report.
- For details of temperature in the special-refuse incinerator, the reader is referred to explanations in Chapter 4, in particular A4.3.
- Chapter 14 also contains a bibliography, chemical structural formulae and the units of measurement used.
- Other scientific publications on the incineration of dioxin-containing residues from Seveso, together with basic scientific investigations and specific detailed information which are not explained at length in this final report, appear in the technical literature.

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# Summary

## 1 Introduction

### 1.1 Initial situation and organization

With the authorization of the Government of the Canton of Basle-City and of the Federal Council the 41 drums holding approximately 2.5 t of dioxin-containing material from ICMESA (Seveso) were transported on 4 June 1983 to Hoffmann-La Roche Ltd. for interim storage.

With a view to carrying out an operation of an exceptional nature, agreement was reached between the competent authorities of the Federal Government and of the Canton of Basle-City on the one hand, and F. Hoffmann-La Roche & Co., Ltd. and Ciba-Geigy Ltd. on the other, to study the possibility of incinerating the wastes containing 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD) in the hazardous waste incinerator (HWI) of Ciba-Geigy without hazard to the personnel or environment.

To carry out this project an organization was established under the supervision of the Federal Government in which authority for the project was vested in the Government of the Canton of Basle-City.

A committee of experts representing science and the authorities was appointed for the project. It was responsible for investigating all questions pertaining to the safety of the environment and the personnel.

### 1.2 Analysis of the problem

The problem awaiting solution can be broken down into the following topics:

- What conditions must be fulfilled during the incineration to reduce the emissions of dangerous substances – particularly of TCDD – to the point where any possibility of hazard to the environment can be eliminated? Can these conditions be fulfilled in the HWI of Ciba-Geigy?
- The methods of *sampling, sample processing and analysis* had to be tested and tried out to ensure that they were appropriate and reliable and of sufficient sensitivity to detect residual emissions with acceptable accuracy.
- The TCDD-containing wastes had to be repackaged for incineration. Here again the proposed plant and procedures had to be studied to rule out any possibility of hazard to the personnel and the environment.
- The process of *testing the HWI* prior to the main incineration had to be carried out in stages so as to preclude any hazard to the population.

## 2 The dioxin-containing wastes

### 2.1 Type and characteristics

The reaction residues from the ICMESA plant at Seveso consisted of inhomogeneous asphalt-like material, part of which was in the form of lumps. Its approximate composition was 70% common salt and 30% organic material.

The first analyses showed that the reaction residues contained an average of 100 ppm TCDD, and a total content of approximately 215 g TCDD was predicted in the interim reports.

Further analyses performed during the repackaging operation showed that the reaction residues contained between 5 and 1700 ppm TCDD, on an average between 140 and 480 ppm. After weighting all the analytical results, it was reasonable to conclude that a total of approximately 0.6 kg TCDD was incinerated. A more accurate assay was impossible because of the inhomogeneous nature of the reaction residues.

The 41 drums[1]) each consisted of an inner and an outer drum, the intermediate space being filled with packing material. Since these drums could not be incinerated as they were, the TCDD-containing material had to be removed and repackaged in a form suitable for feeding to the furnace.

**2.2 Identification**

The inner drums were removed from the outer during a special operation carried out in April and July 1984. This was done with the first six drums for purposes of identification and the results were recorded under the supervision of a notary public.

With test incinerations of TCDD-containing material in view, 6 inner drums were opened for the first time on 16 October 1984 in the presence of representatives of the authorities of the Federal Government and of the Canton of Basel-City. As the next step in the process of identification, material was taken from these drums and analysed by the Swiss Federal Research Station Wädenswil (FAW).

The other drums were opened in the presence of a representative of the Canton of Basle-City and the weight and type of the contents was examined.

In the light of the results of these examinations it may be taken as certain that the residues were in fact the reaction residues from ICMESA.

## 3 Making the wastes ready for incineration

The material was repackaged in a unit specially designed and constructed by Hoffmann-La Roche for this purpose. The repackaging plant, which operated under reduced pressure, and the detailed working instructions were assessed by the committee of experts. Permission to proceed was granted by the competent Cantonal and Federal authorities.

The plant was provided with a system of air locks for the protection of the work force. Full protective suits with external air supply were worn. The personnel selected underwent extensive aptitude tests. All the time the work was in progress they were given regular medical check-ups.

No problems were encountered in carrying out the repackaging operation.

## 4 The hazardous waste incinerator of Ciba-Geigy

The hazardous waste incinerator K 224 of Ciba-Geigy, Basle works, consists of a rotary furnace, a hold-up chamber, a waste-heat boiler and a multistage flue-gas scrubber.

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1) During the main incineration in the summer of 1985 a 42nd drum was added containing contaminated material which had accumulated during the dismantling of the reaction vessels at ICMESA.

The plant is suitable for the incineration of special and hazardous waste and is officially licensed.

Additional knowledge was required before the suitability of the furnace for incinerating TCDD-containing wastes could be assessed.

- On the one hand thermokinetic data on the decomposition behaviour of TCDD at high temperature had to be obtained in laboratory tests (see number 5).
- On the other hand the *temperature characteristics of the furnace* and the *optimal incineration conditions* had to be studied.

Proof had to be obtained that the incineration temperatures in the HWI furnace are above 1200 °C and that a residence time of more than one second is guaranteed. Tests made by specialists from Von Roll company showed that average temperatures of about 1500 °C in the rotary kiln and approximately 1200 °C in the downstream hold-up chamber can be maintained. Residence times of 1.4 seconds in the rotary furnace and in the hold-up chamber were calculated, giving a total of 2.8 seconds.

The requisite decomposition conditions could be maintained in the hazardous waste incinerator of Ciba-Geigy.

## 5 Model and laboratory investigations

Detailed knowledge of the decomposition behaviour of TCDD was essential if the TCDD-containing wastes were to be burned without hazard under the combustion conditions typically prevailing in the furnace of the HWI.

Before the test incineration could proceed in the HWI furnace, it was therefore necessary to obtain *thermokinetic data* giving information on the rate of decomposition as a variable depending on the temperature and oxygen content of the combustion air. Some of the data could be obtained from the literature. To confirm these data, and to supply others that were missing, extensive investigations were carried out on a laboratory scale with very small quantities of TCDD and chemically allied substances.

It was clear from the outset that the first test in the HWI furnace should be made without TCDD but with a test substance comparable to it in decomposition behaviour, and consequently substances allied to TCDD had to be investigated in the laboratory.

*2,4,8-trichlorodibenzofuran* (tri-CDF) was recognized to be a suitable test substance and was therefore used. Compared with TCDD, tri-CDF is of low toxicity so that test incinerations with this substance did not constitute a hazard to the environment.

Laboratory tests with tri-CDF and TCDD showed that both substances are very largely decomposed and combusted within a second at temperatures of 1200 °C.

## 6 Analytical chemistry

Suitable sampling and analytical methods were a prerequisite for

- thermokinetic studies of the decomposition of TCDD and tri-CDF at high temperature on a laboratory scale,
- studies of combustion efficiency in the HWI furnace,
- monitoring of the emissions during the incineration of the wastes.

Sampling and analytical techniques are very complex. Cooperation between the analytical laboratories of the Swiss Federal Materials Testing and Experimental Station (EMPA), Dübendorf, the Swiss Federal Research Institute for Fruit-Growing, Viticulture and Horticulture (FAW), Wädenswil, and Ciba-Geigy Ltd., Basle, allowed the methods of analysis to be tested and harmonized to the point where reliable statements could be made concerning combustion efficiency, the contamination of flue-gas, slag residues and waste-water from the flue-gas scrubber and on any recombination products formed during incineration.

Comparative studies of combustion efficiency were made during test incinerations with tri-CDF by means of sampling and sample-processing techniques performed independently of each other. Analysis was done with the aid of gas chromatography and mass spectrometry. The results of the analyses performed by EMPA and Ciba-Geigy were in the same order of magnitude.

The conventional standard analytical method was used for all assays serving to check the efficiency of the operation. However, this is a complex and time-consuming method. Ciba-Geigy therefore developed a process for short-interval trace analysis (KISA$^{\rightarrow}$) which is highly sensitive and supplies information on the TCDD content of the flue-gas within two hours. Although the KISA supplies less information than the conventional method (only the 2,3,7,8-TCDD content is assayed), the results are available comparatively quickly. The KISA was therefore used to monitor the incineration since it afforded an opportunity for rapid intervention in the event of malfunction or unexpected irregularities in the incineration.

In addition to the mandatory measurement of emissions in the flue gas by the standard analytical method, extra precautionary measures were taken to sample suspended particles and dust in the immediate and more remote vicinity of the HWI so as to detect any contamination of the environment. However, it was decided not to process and analyse the samples obtained since neither TCDD nor allied compounds were detected in the flue gas from any of the incinerations of dioxin-containing material.

Reliable analytical methods of sufficient sensitivity were devised.

A special analytical method with rapidly available results was developed for direct monitoring of the incineration.

## 7 Preparatory test incinerations with model substances

The results of studies of thermokinetics and furnace characteristics made it possible to proceed with test incinerations in the HWI.

The first incineration tests in the HWI were made with a mixture of 70% common salt, 25% p-cresol and 5% activated charcoal. These tests served to throw light on the most favourable conditions for charging the furnace (physical form of the material for incineration, batch size, packaging and throughput) and the behaviour of the furnace at high temperature over a long period.

Further test incinerations were carried out with tri-CDF. Tests with mixtures of tri-CDF, common salt and polyethylene glycol provided a basis on which decisions could be taken. The proportion of common salt was selected to reflect the composition of the reaction residues from ICMESA.

These tests showed that favourable results could be obtained by feeding the furnace with batches weighing 2.5 kilograms and adding sand for maintaining the slag layer inside the rotary kiln.

Flue-gas analyses showed that 99.9999% of the tri-CDF was eliminated in the furnace and 99.99999% after passage through the flue-gas scrubber. The committee of experts rated this combustion efficiency as good, disregarding any traces of undecomposed material in the scrubber water and in the slag. Recombination products, such as were found during the first test incineration with tri-CDF, could be avoided by improved conditions of combustion.

These tests showed that the HWI can be charged and operated without trouble, that high temperatures can be maintained over a long period, and high combustion efficiency can be attained.

## 8 First test incineration with dioxin-containing wastes

### 8.1 Risk assessment

For the first test incineration with small quantities of TCDD-containing material, any risk assessment could be confined to pollutants in the flue gas since only these could have escaped directly into the environment.

Slag and waste-water from flue-gas purification were retained so that they could not constitute any immediate and uncontrolled hazard.

The following facts were also deemed to be relevant:

- In the test incineration at the end of June 1984 99.9999% of the tri-CDF (based on the flue gas) was destroyed in the HWI furnace, i.e. it left a residue of less than one millionth of the quantity entering the process. A further 90% of the residual quantity was retained in the flue-gas scrubber. Ultimately, then, only 0.1 of a millionth of the tri-CDF entering the furnace escaped to the atmosphere.
- It was reasonable to assume in the light of the thermokinetic data that, during combustion, a similarly high decomposition efficiency would be attained with TCDD as with tri-CDF.
- A close study was also made of possible health hazards due to emissions of polychlorinated dioxins and furans in connection with municipal refuse incinerators

(MRI). In the case of the MRI studied it could be stated that these emissions did not constitute any health hazard[1]). The evaluation made on that occasion still holds good. It served as a basis for an assessment of the hazards involved by test incinerations with TCDD.

For the incineration of 1 kg of TCDD-containing residues from the reactor vessel of ICMESA, the following estimates could be made of the TCDD emissions in the air:

| | |
|---|---|
| Quantity of residue | 1 kg |
| assumed 2, 3, 7, 8-TCDD concentration | 0.5 g/kg ( = 500 ppm) |
| decomposition efficiency (based on the flue gas upstream from the scrubber) | 0.999999% |
| undecomposed residual amount | 0.5 µg |
| elimination efficiency (based on the flue gas downstream from the scrubber) | 0.9999999% |
| emission downstream from the scrubber (scrubber efficiency 90%) | 0.05 µg |

(1 microgram [µg] = $10^{-6}$ g = 1 millionth of a gram)

In the light of the risk assessment the committee of experts came to the conclusion that a test incineration with initially small quantities of dioxin-containing material was justified and without hazard for the population.

### 8.2 Objective and execution

Only a test incineration with the material itself could show whether the decomposition efficiency of 0.999999 based on the flue gas, which had been calculated for tri-CDF and was expected for TCDD, could actually be achieved during the combustion of TCDD-containing material in the HWI and to what extent accompanying materials also have a role to play.

The committee of experts proposed a test incineration with 10 kg of material in batches of 1 kg with a total TCDD content of 2 to 5 grams.

The first test incineration of TCDD-containing material was carried out without incident.

### 8.3 Results

*No* TCDD could be detected in the flue gas up- and downstream from the scrubber, in the scrubber water, or in the slag.

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[1]) According to a report of the Federal Office for Environmental Protection ('Umweltbelastung durch Dioxine und Furane aus kommunalen Kehrichtverbrennungsanlagen', Schriftenreihe Umweltschutz Nr. 5, Berne, June 1982) the emission of 2, 3, 7, 8-TCDD from a municipal refuse incinerator is approximately 15 micrograms per hour. Account must also be taken of the emissions of other polychlorinated dioxins and furans which, according to the same report, amount to approximately 20,000 micrograms per hour. However, not all dioxins and furans are equally toxic. The total emission, evaluated in terms of the differing levels of toxicity, is equivalent in an MRI to an emission of 1,000 micrograms 2, 3, 7, 8-TCDD per hour.

*Detection limits* were at the following levels:

| | |
|---|---|
| Flue gas upstream from scrubber | 1 ng/m$^3$ |
| Flue gas downstream from scrubber | 2 ng/m$^3$ |
| Waste-water | 1 ng/litre |
| Slag | 10 ng/kg |

(1 nanogram [ng] = $10^{-9}$ g = 1 thousand millionth of a gram).

These results showed that TCDD was decomposed with high efficiency and that no dioxins were formed from the other chlorine-containing organic substances.

## 9 Second test incineration with dioxin-containing wastes

### 9.1 Risk assessment

On the well-founded assumption that a similar combustion efficiency would be attained with batches of 2.5 kg material as with batches of 1 kg and that the TCDD concentration in the flue gas downstream from the scrubber was less than 1 nanogram/m$^3$, the following emission values were estimated for a test continuing for 12 hours:

| | |
|---|---|
| Duration of test | 12 hours |
| Total flue-gas volume | 120,000 m$^3$ |
| Total TCDD emission | less than 120 µg |

The worst-case assumptions of estimated emissions of 2,3,7,8-TCDD were, at 10 micrograms per hour, less than those of a municipal refuse incinerator.

### 9.2 Objective and execution

The first test incineration lasted 1 hour. It was therefore impossible to test flue-gas sampling for functional efficiency over a longer period. For this reason a second test incineration with 360 kg of dioxin-containing material was carried out for a period of 12 hours.

At the same time it was deemed expedient to increase batch weight (as in the case of tri-CDF) from 1 kg to 2.5 kg, resulting in a substantial reduction of the time taken for the main incineration.

The second test incineration with TCDD-containing material also proceeded without incident.

### 9.3 Results

*No* TCDD was detected in the flue gas up- and downstream from the scrubber, in the scrubber water, or in the slag.

The method of analysis was improved and the detection limits were at lower levels than during the first test incineration, namely:

| | |
|---|---|
| Flue gas upstream from the scrubber | 0.1 ng/m$^3$ |
| Flue gas downstream from the scrubber | 0.1 ng/m$^3$ |
| Waste-water | 1 ng/litre |
| Slag | 5 ng/kg |

Thus, even though the batch weight was increased, the second test incineration showed a higher combustion efficiency.

## 10 Main incineration

### 10.1 Risk assessment

It could be assumed on the basis of the results of the second test incineration that, given the same decomposition efficiency, the TCDD concentration in the flue gas downstream from the scrubber would be less than 0.1 ng/m$^3$.

The following values were estimated for the total duration of the main incineration:

| | |
|---|---|
| Duration | 100 hours |
| Total flue-gas volume | 1,000,000 m$^3$ |
| Total TCDD emission | less than 10 µg |

According to this estimate the TCDD emissions should, even on worst-case assumptions, be less than 1 microgram per hour. The tenfold reduction compared with the assessed risk for the 2nd incineration is attributable to the results of this test incineration.

In view of these facts the main incineration of the remaining reaction residues was deemed justified and without hazard for the population.

### 10.2 Objective and execution

It was planned that the total amount of contaminated reaction residues remaining should be burned during the main incineration.

As in the second incineration, the remaining amount of approximately 2000 kg was fed into the furnace in batches of 2.5 kg. The net incineration time was about 100 hours.

The main incineration could be carried out without incident.

### 10.3 Results and disposal

*No* TCDD was detected in the *flue gas* downstream from the scrubber (at detection limits between 0.05 and 0.2 ng/m$^3$).

The *water from the scrubber system* contained *no* TCDD and could be discharged into the industrial water treatment plant.

The *water from the slag basin* contained particles on which traces of TCDD were adsorbed. The water was filtered, discharged into the industrial water treatment plant, and the filter residue was burned in the HWI.

The 25 t forming the bulk of the total of 30 t *slag* contained about 30 mg TCDD (concentration approximately 1 mg/t). This slag was deposited at the Elbisgraben landfill (Canton Basel-Landschaft).

Some 5 t of slag with a slightly elevated TCDD concentration of approximately 30 micrograms/kg, contained about 160 mg TCDD and was sent through the HWI a second time. After this treatment the slag contained a total of only 0.08 mg TCDD (concentration 0.016 mg/t). It was also deposited at the Elbisgraben site.

No TCDD was detected in the flue gas downstream from the scrubber.

The material remaining after the incineration contained either no TCDD or only very small amounts. It could be disposed of without hazard.

## 11 Dismantling of the repackaging plant

For the planning and execution of the dismantling work all the materials that had to be handled were divided into the following categories, which determined the method of their disposal:

- certainly uncontaminated
- actually or potentially contaminated.

During the dismantling operation work was carried out, as long as possible in full protective clothing with air-supply. The movable equipment was dismantled, broken up into pieces and made ready for disposal. The protective linings of the repackaging rooms were first cleaned, then taken down and prepared for burning.

Subsequent measurements showed that the rooms of the repackaging plant were not contaminated and could be released for use again.

## 12 Disposal of auxiliary material

All auxiliary material which was actually or potentially contaminated had to be burned in the Ciba-Geigy HWI. The non-contaminated auxiliary equipment and wastes were also burned where possible, otherwise they were dumped or salvaged as scrap metal.

The approximately 10 tonnes of auxiliary material for burning contained at the most 0.02 g ( = 20 mg) of TCDD. As no TCDD could be detected in the flue gas during the main incineration of the dioxin-containing wastes, which contained approximately 600 g TCDD in 2.2 t of reaction residues, TCDD analysis could be dispensed with during the incineration of auxiliary material.

With the expected decomposition efficiency of 0.999 999 related to the flue gas, a maximum emission of only 0.000 000 02 g ( = 20 ng) TCDD would have been expected.

The auxiliary material was burned without trouble in the Ciba-Geigy HWI.

The waste-water was discharged into the industrial water purification system, whereas the approximately 11 tonnes of slag was dumped at the Elbisgraben disposal site together with the slag from the main incineration.

The incineration of auxiliary materials as well as the disposal of the residues produced were carried out without incident.

## 13 Conclusions

- Organic problematic wastes, particularly those with a substantial content of polychlorinated dioxins and furans and their precursors, can be incinerated without hazard for man and his environment.
- The following conditions must be fulfilled if problematic materials of this kind are to be incinerated without hazard:
  - Knowledge of the composition of the wastes
  - Suitability of the plant attested by trial incinerations
  - Control of all emissions and continuous monitoring of the plant by suitable measuring and regulating techniques and appropriate analytical methods
  - The employment of qualified personnel and a high level of technical know-how.

# 1 Introduction

## 1.1 Initial situation

On 10 July 1976 an uncontrolled exothermic→ reaction occurred in the chemical plant of ICMESA S.p.A.→ at Meda near Milan (Italy) during the production of the intermediate 2,4,5-trichlorophenol→ (TCP), which was used for the manufacture of hexachlorophene. During the accident an aerosol→ cloud containing, among other constituents, the highly toxic 2,3,7,8-tetrachlorodibenzo-p-dioxin→ (TCDD) was discharged from the reaction vessel into the environment. Parts of the municipality of Seveso as well as some adjoining municipalities were contaminated.

After extensive safety precautions had been taken, the dioxin-containing residues remaining in the plant were removed from the reaction vessels in the summer of 1982 and packed, together with contaminated auxiliary agents, into 41 drums. With the agreement of the Italian Government the contaminated waste was to be removed by a recognized waste-disposal firm to a licensed and officially controlled refuse disposal site. In view of governmental attitudes, public opinion and possible emotional reactions related to environmental matters, the waste-disposal firm had stipulated the strictest discretion: the site of ultimate disposal should be known only to the waste-disposal firm. However, the act of final disposal in conformity with technical and legal requirements was to be certified by a notary public.

The waste-disposal operation, which began on 10 September 1982 with the removal of the 41 drums from Italy, went wrong. The drums were stored illegally and a wide search operation was instituted.

After discovery of the 41 drums of dioxin-containing wastes in France, the Government of the Canton of Basle-City and the Federal Council granted permission on 1 June 1983 for them to be transferred to a safe interim storage site at F. Hoffmann-La Roche & Co., Ltd. in Basle. Transportation took place on 4 June. From this time onwards the drums were under the control of the Confederation and the Canton of Basle-City.

The decision of 1982 to allow the dioxin-containing wastes to be transferred to a controlled disposal site also specified the type of container: the waste was heat-sealed in plastic bags and inserted in steel drums. These drums were in turn placed inside larger drums and the space between the inner and the outer drum was filled with the insulating and binding agent 'Leca'→. The wastes were taken over by Hoffmann-La Roche in this form for interim storage.

The problem again arose of how to arrange for the safe and ultimate disposal of the toxic residues. In principle there were various ways open:

- deposition at a controlled site,
- destruction by wet chemical methods and
- incineration.

Deposition in one of the two Swiss special refuse disposal sites (Kölliken, Teuftal) was precluded from the outset by the prevailing authorization procedure. Storage in the underground site at Herfa-Neurode→ (Hessen/FRG) – intrinsically a suitable site – was not permitted by the competent authorities of the Land of Hessen.

Although laboratory methods were in fact known for destroying the material by wet chemical methods, none of the procedures had been tried out technically and no suitable plants were available. Moreover, the use of a wet chemical method seemed unpromising because of the physical properties of the dioxin-containing wastes, for it would have been exceedingly difficult to elute the dioxins from the lumps of reaction material to which they were very strongly bound by adsorption→, or to achieve an efficient reaction (matrix→ problems).

Incineration, on the other hand, is essentially a recognized process. Organic materials, including dioxins, can be decomposed at high temperatures and converted into materials which are by-and-large harmless. Suitable incinerators with efficient downstream flue-gas purification systems have been operating in Europe for some time. Inquiries addressed at a European level to the operators of such incinerators, which would in principle have been technically suitable for the incineration of dioxin-containing refuse, did not meet with an affirmative response.

Under these circumstances Ciba-Geigy indicated its willingness to destroy the wastes in its hazardous waste incinerator (HWI) on the condition that the requisite preliminary investigations yielded favourable results. It therefore seemed logical and appropriate to follow up this method of disposal.

## 1.2 Organization

An agreement was reached between the competent authorities of the Confederation and the Canton of Basle-City, on the one hand, and the firms of Hoffmann-La Roche and Ciba-Geigy, on the other, to ascertain whether the dioxin-containing residues could be combusted in the HWI of Ciba-Geigy without hazard to the population, the work force involved, and the environment. To this end, measures to set up an organization and assign responsibilities for the destruction of the residues were completed by mid-June 1983, and an agreement was concluded between Ciba-Geigy and Hoffmann-La Roche. At the same time an organization was established to superintend the whole destruction process in an advisory and supervisory capacity.

This organization (cf. Appendixes A1.1 and A1.2), comprising the project authority, supervisory and executive body, steering committee, project coordination, committee of experts and various project teams, started its work in the summer of 1983.

The Government of the Canton of Basle-City was designated as the project authority and assumed overall responsibility for the destruction operation. The supervisory and executive body, representing the project authority, sanctioned the performance of all operations. To it were seconded, as representatives of the Federal authorities, the Federal Office for Environmental Protection and the Environmental Protection Commission of Basle-City. At the operational level the steering committee was responsible for the coordination and performance of all operations.

The project authority appointed a committee of experts which was to be responsible for the technical examination and assessment of all proposals for the destruction of the residues and for ensuring operational safety and the protection of health and the environment and to report to the supervisory and executive body or the steering committee. The committee of experts comprised eight members representing science and the authorities. It worked in close conjunction with the various project teams via project coordination.

## 1.3 The problem

The crux of the whole operation was to answer the central question whether the dioxin-containing residues could be destroyed in the Ciba-Geigy HWI in a practicable manner and without hazard to the population, work force and environment. This involved in particular the extrapolation of available know-how and existing experience with similar chemical substances to the specific conditions of the incinerator, taking into account the special characteristics of the wastes to be combusted. These questions arise whenever a problem of this kind has to be solved for any special-refuse incinerator.

The tasks set can be placed essentially under the following headings:

What conditions had to be observed during incineration to keep the emissions→ of hazardous substances – particularly dioxins – sufficiently low to exclude any possible danger. Accordingly optimal conditions had to be determined for a very high combustion efficiency.

Solutions had to be found to several very disparate sets of problems involving mechanical and physical aspects relating to the charging, heating and evaporation of the residues to be introduced into the incinerator. Furthermore, the behaviour of the furnace had to be studied and the boundary conditions of important parameters of the HWI determined.

The characteristics of the HWI had to be determined in various subprojects. These characteristics included:

- the temperature characteristic in the rotary kiln and the hold-up chamber;
- the estimate of the residence time of the flue gases in the incinerator;
- the behaviour of the furnace in continuous operation at maximum capacity and in the light of the composition of the combustion material.

To remain within the permitted emission limits the following items had to be ascertained:

- conditioning→ of the combustion material;
- type of packaging and size of batch;
- charging interval;
- physical behaviour of the slag lining in the rotary kiln at the requisite temperature and the given matrix of the combustion material;
- the residual oxygen and carbon monoxide contents in the flue gas as a function of the furnace temperature, the air supply, the charging interval and the matrix.

Before trial incinerations could be made in the HWI furnace a suitable test substance had to be found which fulfilled the following conditions:

- the closest possible similarity to TCDD in physico-chemical behaviour;
- availability in large quantities;
- low toxicity compared with TCDD.

Physical and chemical data were assembled from the literature and, if necessary, supplemented by laboratory experiments and theoretical studies.

Additionally, it had to be ascertained whether the data determined for the test substance could, in the light of thermokinetic findings in the laboratory, be used to estimate the decomposition efficiency→ for TCDD in the HWI.

Complete safety could be guaranteed only if the residual emissions could be detected with sufficient accuracy. The proposed methods of sampling, sample preparation and analysis had therefore to be tested and tried out to ensure that they were reliable and sufficiently sensitive.

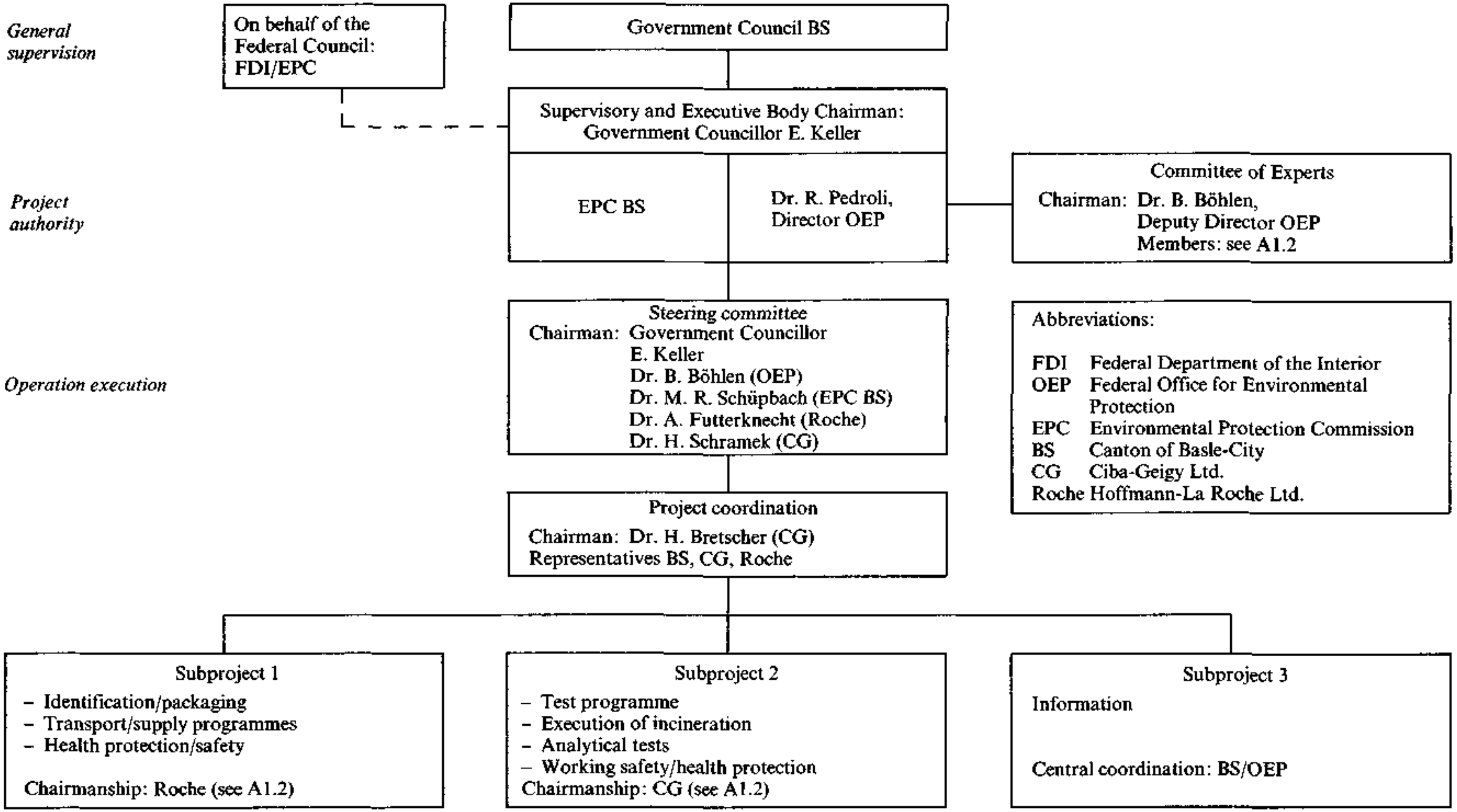
It had to be ascertained whether the existing methods for analysing flue gas, waste-water and slag were adequate for a comprehensive assessment of the emissions. Specific and quantitative methods had therefore to be elaborated so that flue gas, slag and waste-water could be analysed for TCDD and the test substance.

The dioxin-containing residues had to be repackaged for incineration. Here again tests had to be made to ascertain whether all hazards to personnel and environment could be eliminated with the equipment and operational methods available.

## 1.4 Planning

During the summer of 1983 the project teams of Ciba-Geigy and Hoffmann-La Roche worked out proposals for the destruction of the dioxin-containing residues, and in September 1983 a report was presented to the panel of experts and to the authorities and bodies involved. The projects submitted (subproject 1: Roche, subproject 2: Ciba-Geigy) deal with the following items: storage of 41 drums, repackaging operation to make the dioxin-containing residues ready for incineration, transport, thermodynamics and kinetics, test programme, incineration, environmental protection, analytical methods, emission control and safety. The solutions proposed were approved by the committee of experts and the steering committee and accepted as the basis for additional detailed investigations and the staged execution of the operation.

## Appendix A1.1 Organization for the Destruction of Dioxin-containing Material



Abbreviations:

| | |
|---|---|
| FDI | Federal Department of the Interior |
| OEP | Federal Office for Environmental Protection |
| EPC | Environmental Protection Commission |
| BS | Canton of Basle-City |
| CG | Ciba-Geigy Ltd. |
| Roche | Hoffmann-La Roche Ltd. |

## Appendix A1.2: Committee of Experts 'Incineration of dioxin-containing wastes'

Dr. Bruno Böhlen, Deputy Director (from 1.9.85 Director)
Federal Office for Environmental Protection, Berne (Chairman)

Dr. Roger Ammann
Head of Department, AC-Laboratory, Spiez

Dr. Kurt Banholzer
Dept. of Organic Chemistry, Lubricants, Waste Gases, EMPA, Dübendorf

Dr. Hans Rudolf Buser
Federal Research Institute for Fruit Growing, Viticulture and Horticulture, Wädenswil

Dr. Ruedi Müller
Dept. of Air Pollutants and Furnace Technology, EMPA, Dübendorf

Prof. Werner Richarz
Laboratory for Technical Chemistry, ETH, Zurich

Prof. Christian Schlatter
Institute of Toxicology, Schwerzenbach

Dr. Martin R. Schüpbach, Cantonal Chemist,
Cantonal Laboratories Basle-City, Basle

Hans-Heinrich Wymann, Cert. Eng., Scientific Adviser,
Federal Office for Environmental Protection, Berne (till 26.11.84) (Secretary)

Max A. Suter, Cert. Eng., Scientific Adviser,
Federal Office for Environmental Protection, Berne (from 27.11.84) (Secretary)

### Project team Ciba-Geigy

| | |
|---|---|
| Dr. Toni Baerlocher (Production) | Project management |
| Jost Hartwig (HWI) | Incineration |
| Dr. Fritz Maritz (Environmental analysis) | Analysis |
| Dr. Erwin Marti (Central function research) | Thermokinetics and KISA |
| Anton Schaerli (Works manager, Basle works) | Project management |

### Project team Hoffmann-La Roche

| | |
|---|---|
| Dr. Bruno Bachmann (Works medical officer) | Medical supervision |
| Dr. Bruno Seiffert (Works medical officer) | Medical supervision |
| Dr. Daniel Bauer (Safety and environmental protection) | Industrial hygiene |
| Heinz Holliger (Environmental engineering) | Repackaging operation |
| Dr. Hans Künzi (Safety and environmental protection) | Project management |
| Dr. Norbert Neuner (Analysis) | Analytical methods |
| Ernst Uhlmann (Environmental engineering) | Project management, repackaging operation |

Abbreviations:
EMPA = Federal Materials Testing and Experimental Station
ETH = Swiss Federal Institute of Technology

# 2 The dioxin-containing wastes

## 2.1 Type and characteristics of the wastes

During the clean-up operations at the firm ICMESA→ various wastes contaminated with TCDD→ accumulated. It was planned to burn the following items in the HWI of Ciba-Geigy:

- contaminated reaction residues1), contaminated protective clothing, tools and auxiliary material from ICMESA and slightly contaminated laboratory material, soil and material samples, protective clothing and auxiliary material which accumulated during the waste-removal, repackaging, test and control operations in Switzerland;
- the samples and analysis residues from Seveso accumulating at Givaudan and EMPA→ in Dübendorf during the years of investigations authorized by the Federal Council;
- non-polluted or in the worst case potentially polluted Leca→ which had been used for filling and protective purposes in packing the drums.

The reaction residues from the ICMESA plant proved to be exceptionally inhomogeneous in composition. This lack of homogeneity is due to the fact that the exothermic reaction was an uncontrolled process occurring in an unstirred reactor vessel, the stirrer having been switched off at the end of the shift. This caused a multiplicity of reaction centres and hence a variety of decomposition products depending – especially in their proportions – on the local temperature.

The asphalt-like, amorphous grey-black reaction residues, partly in the form of hard lumps, consisted of about 70% common salt and about 30% organic material. This organic material is composed essentially of ethylene glycol, polyethylene glycols and water-insoluble polymeric materials consisting of various polyethers with a partly chlorinated benzene nucleus as well as phenols and chlorphenols.

It was these chlorinated compounds in particular and the high common salt content which gave rise to fears that new chlorinated dioxins and dibenzofurans→ might be formed during combustion.

The TCDD content of the reaction residues proved to be very unevenly distributed and, on the basis of the preceding analyses, was stated to average about 100 ppm→ in relation to the total reaction residues. In the light of analytical studies and extrapolations made at the Joint Research Centre of the European Community in Ispra, Italy, and by Givaudan, Dübendorf, a total quantity of about 215 g TCDD in the reaction residues was *predicted.*

Various analyses made during repackaging (cf. chapter 3) showed that the TCDD content of the reaction residues lay between 5 and 1700 ppm. It may be deduced from these analyses that the average TCDD content lies with high probability (95% confidence interval→) in a range from 140 to 480 ppm which, in terms of the total amount of reaction residues, is equivalent to a range of 0.4 to 1.2 kg TCDD. After all the analytical results have been weighted, it is reasonable to conclude that altogether about 0.6 kg TCDD, along with other PCDDs→ of relatively secondary toxicological importance, was incinerated. The inhomogeneity of the reaction residues made it impossible to determine the content with greater accuracy.

The protective clothing, laboratory materials, soil and material samples, and tool parts were sometimes heavily contaminated. Since, however, the contamination was confined mainly to the surface, the total quantity of TCDD was small.

---

1) A 42nd drum containing contaminated reaction material obtained during dismantling of the reaction vessels at ICMESA was added during the main incineration operation in the summer of 1985.

## 2.2 Identification of the wastes

After the drums have been found in France the French authorities requested that the contents of the 41 drums be accurately identified. On 26 April 1984 the first phase of the prescribed identification programme was executed. In the presence of representatives of the authorities, representatives of the committee of experts and under the supervision of a notary public, 6 drums were selected at random, the outer drums were opened and the following items placed on record:

- the intact condition of the drums and closures;
- the conformity of the type and size of the inner drums and the outer drums going with them and of the closures with the data supplied prior to the opening;
- the presence of the Leca filling between the inner and the outer drums;
- the gross weight of the inner drums with reaction residues.

This act was recorded in a notarially certified deed. These random samples left no doubt as to the identity of the drums.

After the opening of the other 35 outer drums had been authorized at the meeting of experts held on 18 June 1984 and the procedure for sampling had been finalized with a view to the disposal of the outer drums, Hoffmann-La Roche executed this intermediate operation during the period from 2 to 10 July 1984.

As expected, an inner drum was found in each of the remaining 35 outer drums, and their various characteristic features showed them to be identical with the drums packed at ICMESA in 1982. This was confirmed in particular by comparison with the weights entered in the drum dossier compiled when the drums were filled and those obtained during check-weighing in the repackaging plant. The divergence of 0.58% lay within the weighing accuracy of the scales used.

After the outer drums had been thoroughly cleaned, wipe tests→ were made and the outer drums stored temporarily in the outer room of the repackaging plant. The residual contamination of the outer drums was less than 2 ng TCDD/$m^2$→. In comparison the limit for continually occupied rooms in Lombardy is 10 ng/$m^2$. Permission for disposal of the cleaned drums was granted by the Cantonal Laboratory Basle on application of the committee of experts and the steering committee.

After both committees had resolved that an initial test incineration of the reaction residues should be performed, a further phase of the identification procedure was carried out. In this phase six inner drums, selected at random, were opened, the contents were identified by reference to the drum dossier and the reaction material was sampled. Also of this operation a notarially certified deed was drawn up.

Microanalysis of the samples taken showed that the carbon, hydrogen and chlorine contents were identical with those of a sample set aside on an earlier occasion (1981).

Furthermore, analyses performed by the Federal Research Institute for Fruit Growing, Viticulture and Horticulture, Wädenswil (FAW→) yielded the following results and observations:

- 2,3,7,8-TCDD was found in all the samples analysed;
- additional polychlorinated dibenzo-p-dioxins (mono-, di-, tri- and 1,3,7,8-tetra-CDD) were found, in conformity with a specimen of the reactor content set aside in 1981; the proportions were generally identical;
- presence of the same polychlorinated dioxins in samples (soil, grass) from the environs of Seveso;
- absence of significant quantities of polychlorinated dibenzofurans→ in the residues, as also in the sample set aside in 1981 and the samples from the environs of Seveso;
- demonstration of trichlorophenol and polymeric products in the residues such as are typical of a process of the type carried out at ICMESA.

It may be taken as certain, in the light of all these identifications, that the wastes were in fact the reaction residues from ICMESA.

All the other inner drums were opened in the presence of a representative of the Cantonal Laboratory of Basle; the date, weight and type of content were systematically recorded. Samples were taken from all the drums containing reaction residues and these were also analysed by the FAW. These results were also in conformity with expectations.

During the identification and repackaging operations a total of 2,602.9 kg of reaction residues was weighed and made ready for incineration. The increase in quantity as compared with the quantity of 2,350 kg stated in the interim reports was due, on the one hand, to the 42nd drum that arrived late, and, on the other hand, to the fact that kieselguhr had to be added to two drums with greasy, semi-liquid components for purposes of solidification.

# 3 Making the wastes ready for incineration

## 3.1 General conditions

In view of the technical characteristics of the HWI→ it was clear from the outset that the drums with the dioxin-containing wastes could not be burned as integral units. Moreover, it was known that both the conditioning→ of the residues and the type of packaging and batch size would have a significant effect on the combustion process. These parameters could be predicted to a large extent in the light of experience with the HWI but they nevertheless had to be verified in test incinerations (cf. chapter 7).

In addition to these technical requirements to be met by convenient packages suitable for furnace combustion, the outside of the package – with which personnel might come into contact – also had to be free from contamination with toxic residues. In the light of all these conditions the following type of packaging was chosen: the dioxin-containing residues were packaged in double-walled polythene bags and heat-sealed. After thorough cleaning, these packages were in turn packed in two further polythene bags. The use of several protective coverings (dilution principle) and the cleaning stage ensured that the surface of the outermost package was clean. This type of container met all the technical conditions for charging the HWI and optimal combustion while leaving sufficient leeway for any modifications as regards the conditioning and quantity of the residues.

While the dioxin-containing residues were being transferred from the drums to packages suitable for combustion in the furnace, the possibility of any contact between the personnel and the material or contamination of the vicinity or environment had to be excluded. A special isolated plant had therefore to be erected and all the necessary precautionary measures instituted for protecting both personnel and environment.

The work of preparing furnace-ready packages under conditions ensuring safety, health and environmental protection as well as hazard-free transportation of the packages to the HWI was, in accordance with subproject 1 (cf. 1.4), assigned to Hoffmann-La Roche. Work commenced in autumn 1983.

## 3.2 Plant and measures for repackaging

The plant and installations for the hazard-free management of dioxin-containing residues were set up on the premises of the works civil-defence organization in the second basement of a warehouse in the factory precincts of Hoffmann-La Roche. To facilitate repackaging, the plant had to be subdivided into various functional areas such as air locks, operations room, showers, store rooms etc. (cf. Fig. 1). This subdivision, which was based more particularly on the experience acquired during the emptying and dismantling of the installation at ICMESA, made it possible, on the one-way principle, for personnel to enter the operations zone (room E) in safety and for personnel and material to be decontaminated. On completion of the plant it was inspected by the panel of experts on 4 April 1984, on 16 May the competent cantonal and federal authorities carried out the acceptance inspection, and on 20 July 1984 the plant was declared ready for operation.

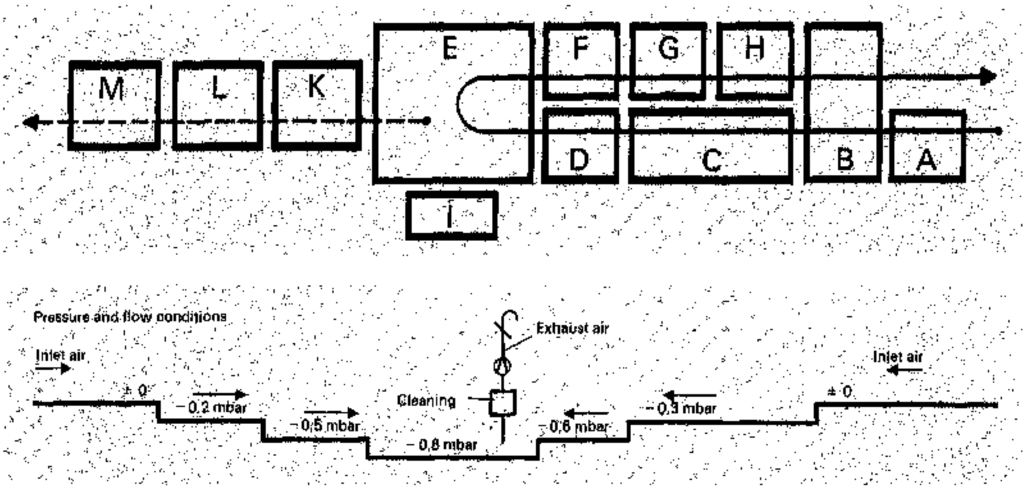
The whole plant had to be designed in such a way that, on termination of the repackaging operation, its individual parts could be decontaminated by means that were simple and consistent with environmental safety. Moreover, after the dismantling of the plant, a residual contamination not greater than 10 ng TCDD/m$^2$ (the limit for continuously occupied rooms in Lombardy) had to be guaranteed, since it was intended to restore the premises to their original use. On the one hand, materials and parts were used which could – after size-reduction where necessary – be burned in the HWI and, on the other, in all rooms exposed to potential or actual contamination the ceilings, walls and floors were lined with protective sheeting or flooring so as to produce a jointless cover.

During the repackaging operation traces of TCDD or dioxin-containing material could, in principle, escape into the environment only via exhaust air or waste-water. These emissions had to be reduced by extensive technical measures to the point where residual emissions would not constitute any hazard to the environment.

### *3.2.1 Exhaust air filtering plant*

All the areas of the repackaging plant were artificially ventilated; areas where there was contamination or potential contamination were kept constantly under reduced pressure. In this way noxious substances could be prevented from being carried by uncontrolled air currents to adjacent premises where there were unprotected personnel. The pressure and flow conditions are shown in Fig. 1.

*Figure 1: Schematic of repackaging plant*



*Key:*

A : Issue of materials
B : Cloakroom
C : Stand-by and emergency room
D : Entrance lock
E : Repackaging room
F : Protective clothing shower
G : Changing room
H : Personnel shower
I : Control station
K : Materials lock 1
L : Materials lock 2
M: Final packaging
- - - → : Flow of personnel
——→ : Flow of materials

The air was extracted from the most severely contaminated room E. Before being exhausted, it was cleaned by means of the following combination of filters:

| | |
|---|---|
| – Prefilter | Type F 3 |
| – High-efficiency particulate air filter | Type S 3 |
| – High-efficiency particulate air filter | Type S 3 |
| – Activated carbon filter | Type FAKB (carbon quality: Pittsburgh BPL 6 × 16) |

As a safety precaution a sealing air sheath under slight excess pressure was installed round the filter plant so that, in the event of a leak in the filter housing, no contaminated exhaust air would penetrate to the clean air side of the exhaust-air plant and thus escape outside (cf. Appendix A3.1).

The functional efficiency and effectiveness of the air-filter plant was tested in several steps in collaboration with the AC-Laboratorium Spiez, Gruppe für Rüstungsdienste (War Material Group). It was found that exhaust air, after passing through the two high-efficiency particulate air filters, met the requirements of the strictest VDI→ clean room class (VDI guideline 2083, Ref. [3]) which permits per cubic metre a maximum of 4,000 particles with a diameter above 0.5 micrometers.

During the repackaging operation dust particles were measured and the TCDD content in the contaminated and the cleaned exhaust air was determined at regular intervals. These measurements showed that – with the detection limits attainable by the analytical methods employed – the efficiency of the air-filter plant was certainly at least 99.999%. With this air-filter efficiency and the concentrations of 125–260 ng TCDD/$m^3$ measured in the uncleaned air during the repackaging process as a basis, it was possible to calculate the total emission into the environment via the air-filter system as follows:

| | |
|---|---|
| – Volume of air exhausted | 1,500 $m^3$/h |
| – TCDD concentration | 125–260 ng/$m^3$ |
| – Duration of repackaging operation | 14 days |
| – Air-filter efficiency | at least 99.999% |
| – Total emission via exhaust air | maximum 0.5–1.5 µg |

This total emission of 0.5 to 1.5 microgram can be compared with the emission of approx. 15 micrograms 2,3,7,8-TCDD per hour calculated in flue-gas studies of Zurich-Josefstrasse municipal refuse incinerator (Ref. [1]).

This calculation was confirmed by regular measurements made in the filtered exhaust air, for with a detection limit of 0.005 ng/$m^3$ TCDD could never be detected.

### *3.2.2 Waste-water purification plant*

Contaminated waste-water accumulated in rooms F and K from the cleaning of the personnel's protective clothing and of the innermost furnace-ready packages filled with dioxin-containing wastes. The water was collected in a pump well, cleaned in batches via a combined microfilter/active charcoal/ion exchanger and stored temporarily in a tank. The waste-water could be cycled as required and treated several times (cf. Appendix A3.2).

During the operations directed to separation of the outer and inner drums and identification of the residues as well as the repackaging operations for test incinerations a total of 5510 litres of waste-water was collected. After treatment in the waste-water purification plant no TCDD could be detected in the treated waste-water at a detection limit of 0.5 ng per litre. On the application of the committee of experts and with the authorization of the Cantonal Laboratory these waste-waters were discharged via the chemical sewerage system to the industrial waste-water treatment plant of Pro Rheno AG.

During the main operation for preparing the furnace-ready packages a total of 4480 litres of contaminated waste-water was collected, equivalent to an average daily fresh-water requirement of something over 300 litres. After treatment in the purification plant the waste-water had an average concentration of 1 to 3 ng TCDD per litre. As such levels are designated absolutely safe for waste-water treatment plants (Ref. [2]), these waste-waters were also discharged via the chemical sewerage system to the industrial waste-water plant. The measurements made showed an efficiency of 99.9% for the waste-water treatment plant.

The TCDD emission via waste-water was, according to the measurements made, 5 to 15 micrograms for the total repackaging operation. Thus, the total TCDD emission for the whole repackaging operation was of the order of maximum 15 micrograms, the major portion being contained in the waste-water and only a very small portion in the exhaust air (cf. 3.2.1). From these figures a 'loss factor' of about $2.5 \times 10^{-8}$ can be calculated compared with the total quantity of dioxin-containing material with a TCDD content of about 0.6 kg. This means that, during the entire operation of repackaging the dioxin-containing material, the loss to the environment could be kept far below one millionth part of the total quantity of TCDD.

#### *3.2.3 Respiratory air supply*

During the actual repackaging work in room E, where the dioxin-containing wastes were removed from the drums and placed in furnace-ready packages, and during the cleaning of the packages in material lock 1 (room K) there was a risk of the personnel coming into direct contact with the dioxin-containing material. To exclude the possibility of such a contact, the personnel wore protective suits with external air-supply. The respiratory air for these suits was obtained from the factory air-distribution network, conditioned and fed via a special line system to the various connections in the plant (cf. Appendix A3.3). To ensure an uninterrupted supply of respiratory air, monitoring and warning instruments were installed and an additional emergency supply from pressure cylinders was provided.

#### *3.2.4 Additional technical measures*

To ensure that the repackaging operation should proceed as smoothly as possible and to avoid time-consuming downtimes various other technical measures were instituted. Thus, apart from a reserve stock of various essential plant components, the power supply to the entire repackaging plant was safeguarded by additional independent current feed-ins. Furthermore, an automatic fire alarm and an unauthorized-entry alarm-system were installed in the repackaging plant.

### 3.3 Repackaging

The actual repackaging operations consisted essentially in removing the dioxin-containing material from the drums, comminuting it where necessary, weighing it and pouring it into plastic bags, polyethylene glycol being added to the reaction residues as an anti-dusting measure (cf. 5.2.1). Additionally, 5 samples had to be taken from each drum of reaction residues and combined to form a collective sample per drum for determination of the TCDD content. The packages then had to be cleaned externally, first with water and then with solvent-moistened cloths, and finally placed in the protective bags. For these essentially simple jobs, which were performed in rooms E and K, protective suits with external air-supply had to be worn to prevent any personal contamination. These protective suits of PVC had proved their worth in more than 2,000 hours of operations during clearing and dismantling work at ICMESA. They are completely closed, the air is supplied via a hose and there is a constant excess pressure in the suit compared with the environment. A short interruption of air supply can be made good by a permanent air reserve in the suit. For work with weakly or only potentially contaminated material (room L), and for maintenance work, light protective suits with dust-respirators but no independent air supply were used. To ensure the highest possible degree of personal protection it was a strictly observed principle that protective gear (including underwear) was used only once and to be discarded for incineration after use.

Work in protective suits was performed in shifts of two hours each. Medical and industrial hygiene studies showed that this work period posed no problems and also fitted conveniently into the operational schedule. Operational sequence and work plan were organized round this 2-hour cycle and such activities as supervision, maintenance of infrastructure, stand-by duty, etc. which were not carried out in protective clothing. The following posts were always manned at the same time:

- 2–4 men: repackaging and decontamination work
- 2 men: stand-by service
- 1–2 men: operation and maintenance of infrastructure
- 1 man: supervision

Detailed working instructions were drawn up for all functions and, during the training phase, the instruction the personnel received was intended to enable all concerned to discharge the same functions in rotation.

It was the task of the stand-by unit in the event of an incident to recover the person concerned as speedily as possible from the contaminated zone, observing all protective and decontamination measures, and to hand him over to the works medical officer. This precaution was taken because, although there was a medical check-up before every turn of duty in air-supply protective suits, the possibility of sudden indisposition, circulatory trouble or other acute health disorders could never be completely eliminated. The personnel was suitably prepared for this eventuality during training by means of simple lessons and emergency exercises. However, throughout the whole repackaging operation the stand-by unit never had to intervene.

It was the task of the maintenance service to keep the individual premises clean and to supervise and maintain the technical equipment. Special importance was attached to continuous cleaning operations since this minimized the carry-over of dioxin-containing material by the movements of personnel and material (cf. Fig. 1) and prevented contamination of non-contaminated rooms. These efforts were constantly monitored by numerous wipe tests$^{\rightarrow}$ and also by measurements of dust concentrations at selected points. The analytical results obtained during the repackaging operation confirmed the efficiency of the cleaning work, for in rooms C, G and L, which were of particular importance (transition zone from the contaminated area with protected personnel to the clean areas with unprotected personnel) only tolerable residual contaminations in the range of 0.3 to 117 ng TCDD/m$^2$ were found.

The repackaging team's work was continually monitored from control point I by the supervisory personnel and recorded on tape by a video camera. Communication was by radio and intercom. Throughout the operation a working diary was kept in which details of shift-work, activities and special incidents were recorded by the supervisor. One important point was the supervision of the inventory taken of contents of each individual drum and the labelling of the furnace-ready packages. This labelling of the individual packages in combination with the inventory list enabled a complete check to be kept of all the packaged residues. A member of the staff of the Cantonal Chemist of Basle-City supervised the inventory; all the cardboard boxes in which the furnace-ready packages were packed were stamped and initialled by him by way of certification and were checked for intactness immediately prior to incineration.

During the entire repackaging operation a total of 2,736 man hours was worked, 70% of which were devoted to infrastructural and industrial hygiene support operations and only about 30% to the main activity of repackaging the dioxin-containing residues.

The following were made ready for incineration:

| | |
|---|---:|
| 1053 packages with contaminated reaction residues | 2602.9 kg |
| 165 packages with protective suits and underwear | 274.7 kg |
| 105 packages with ancillary, test and analytical materials | 211.2 kg |
| 553 packages with Leca | 2613.7 kg |
| *A total of 1876 packages with an overall weight of* | *5702.5 kg* |

The results of the wipe tests regularly performed on the surfaces of the furnace-ready packages confirmed that the packages or the outermost protective bags were clean and could be relied upon not to cause contamination of the personnel or environment at any time.

## 3.4 Health protection and industrial hygiene

As far as possible, the repackaging operation was carried out by personnel who had already been present during the emptying and dismantling work at ICMESA in 1982 and 1983. Before the repackaging operation they underwent an extensive medical fitness test comprising previous history, condition of skin, liver, kidneys and spleen, cardiovascular and respiratory efficiency, neurological status and extensive laboratory tests. During the repackaging operation the personnel were constantly supervised by the works medical officer. At no time were there any medical findings that could be connected with contamination by dioxin-containing material. An extensive follow-up is at present in progress. Any changes as compared with the fitness test made prior to repackaging will be recorded and assessed. To date there are no indications of any changes in the parameters studied.

From the outset the type of repackaging plant – with an air-lock system and constant, specific low pressure – and the use of protective suits and packages with two protective envelopes ensured that important hygienic conditions for the safe handling of the dioxin-containing residues were fulfilled. Additional hygienic measures relating to the actual repackaging work comprised personnel training, supervision of working conditions and physical stresses during operations in protective suits, monitoring of the quality of the respiratory air and, in particular, checking for contamination by dioxin-containing material in the various rooms and on the packages (cf. 3.3). These contamination checks were performed regularly as part of a comprehensive hygienic measuring programme by means of various tests to determine the contamination of the air and of the surfaces. It was thus possible, on the one hand, to check the efficiency of the technical installations and cleaning operations and, on the other, to obtain specific indications as to how the operations might be modified and improved. During the hygienic measuring programme 317 samples were obtained and analysed.

## 3.5 Transport of the wastes

Transport of the dioxin-containing material to the special-refuse incinerating plant was by vehicles authorized to carry chemicals in accordance with the relevant road transport regulations (ADR→/SDR→) under police escort. Supplies were matched to the incinerator capacity and consequently no interim storage at Ciba-Geigy was required.

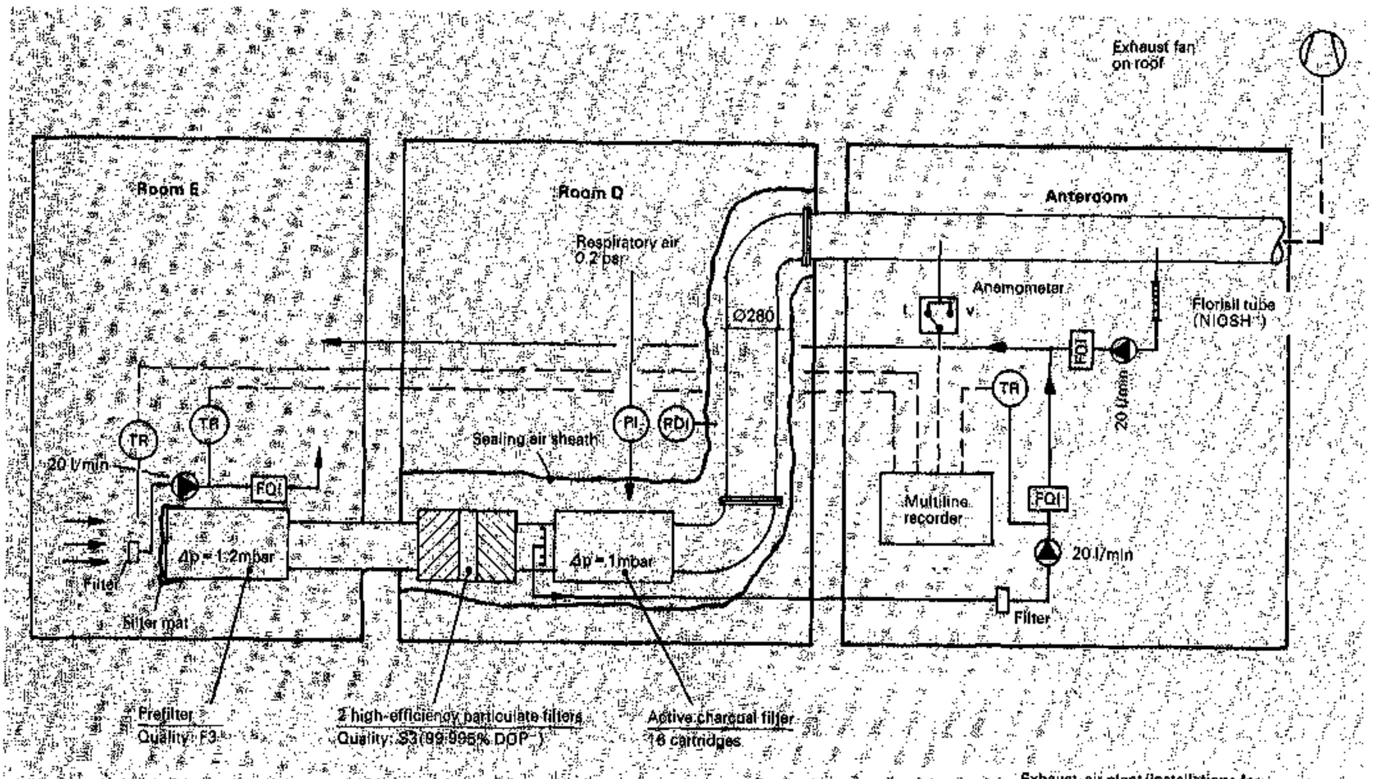
To avoid mechanical damage to the plastic bags packed with dioxin-containing residues and to ensure that, in the event of any transport or road accident, no contaminated material could leak into the environment, a special transport pack was devised. Two furnace-ready packages at a time were packed in a strong cardboard box (bursting strength: 900 kg); eight of these cardboard boxes were loaded in a leakproof palletizable transport container of wood (wall thickness 25 mm). Each load was checked before and after transport by the poisons inspector of the Cantonal Laboratory of Basle-City, likewise all accompanying papers, delivery lists, labels and the accident instruction sheet (class 6.1, No. 23/ADR→).

Transport was carried out under the direction of the Basle police, who detailed a small escort for each consignment. To ensure that the alarm should be given and initial measures promptly instituted in the event of a transport accident, each consignment was also accompanied by representatives of the Hoffmann-La Roche safety service and fire brigade, who were equipped with material for immediate measures (cordon and blanketing material, fire extinguishers, personal protective equipment etc.). In view of the plan of action prepared, the existing emergency programme for chemical accidents and the very low assessment of the accident risk no further arrangements were made.

During the main incineration operation 5 consignments (load per consignment between 10 and 20 containers) were dealt with without any incident.

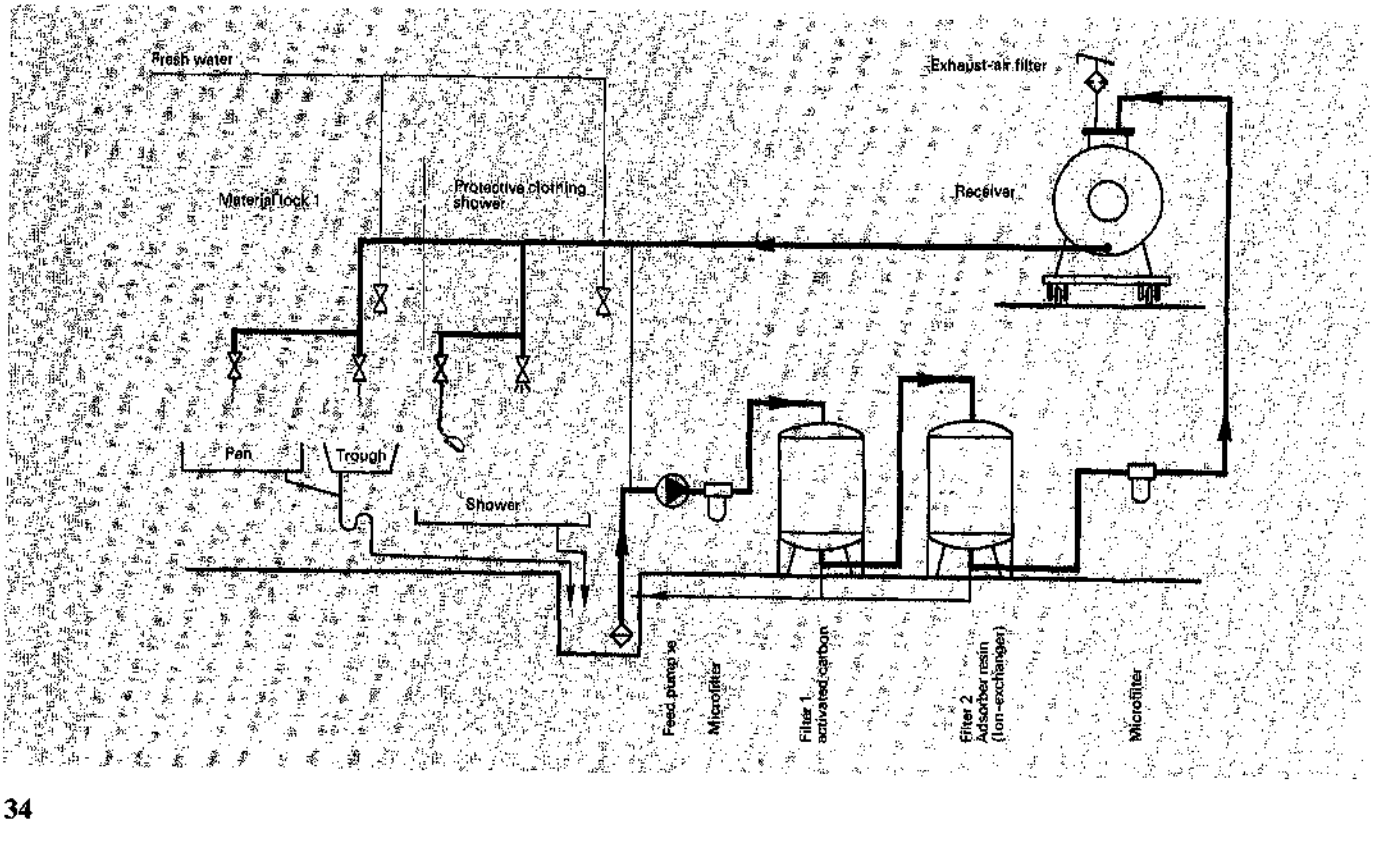
# 3 Appendixes to Chapter 3

## Appendix A3.1: Exhaust-air plant

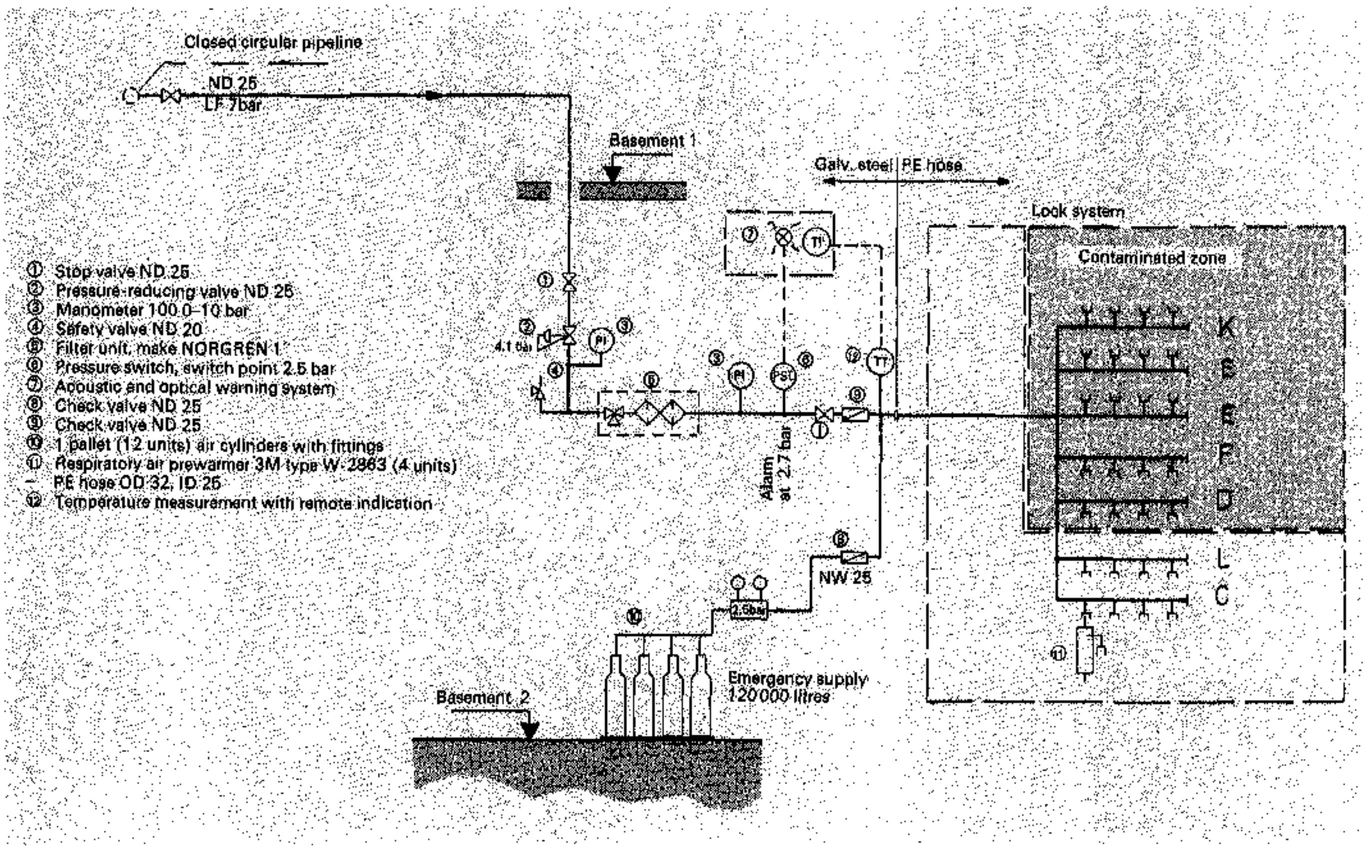


Exhaust-air plant/installations for occupational medicine measuring programme

## Appendix A3.2: Waste-water purification plant



## Appendix A3.3: Respiratory air supply



*Key to the schematics* (A3.1, A3.2, A3.3)

PDI = Pressure difference indicator
FQI = Flow quantity indicator (summation)
PI = Pressure indicator
PSL = Pressure sensor low
TI = Temperature indicator
TR = Temperature recorder
TT = Temperature transmitter
ΔP = Pressure difference

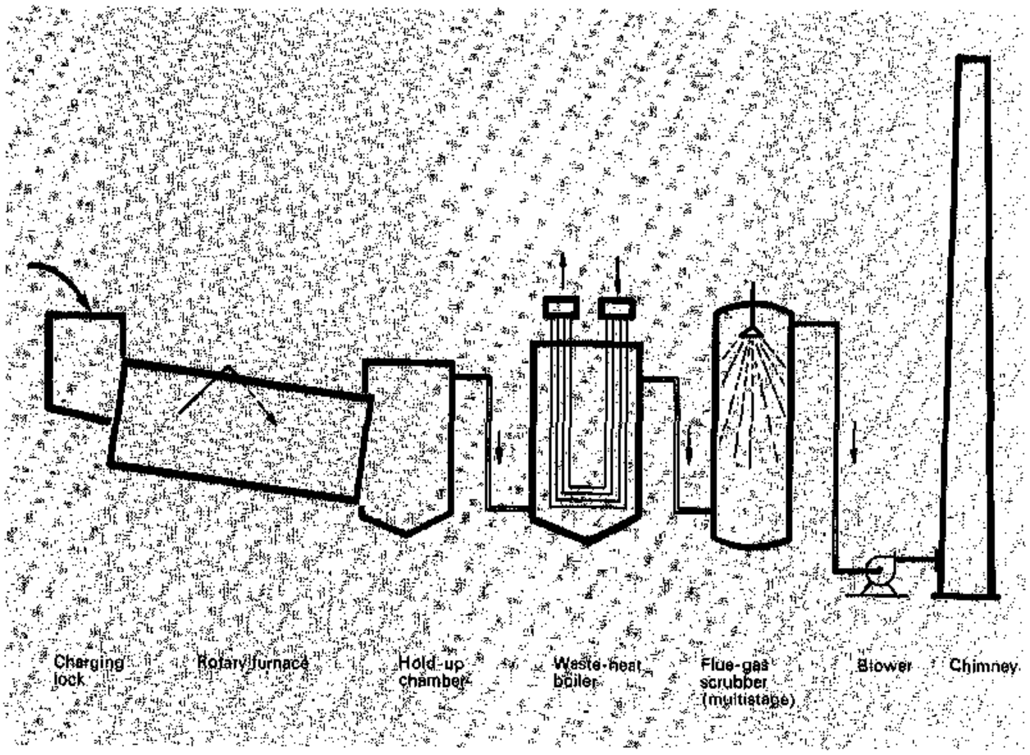
● = Pump
⊖ = Fan
⋈ = Valve
◇ = Filter

# 4

# The hazardous waste incinerator of Ciba-Geigy

The hazardous waste incinerator (HWI) K224 of Ciba-Geigy, Basle works, comprises a tubular rotary furnace, a hold-up chamber, a waste-heat boiler and a multistage flue-gas scrubber system.

*Fig. 2: Schematic of HWI (cf. Appendix A4)*



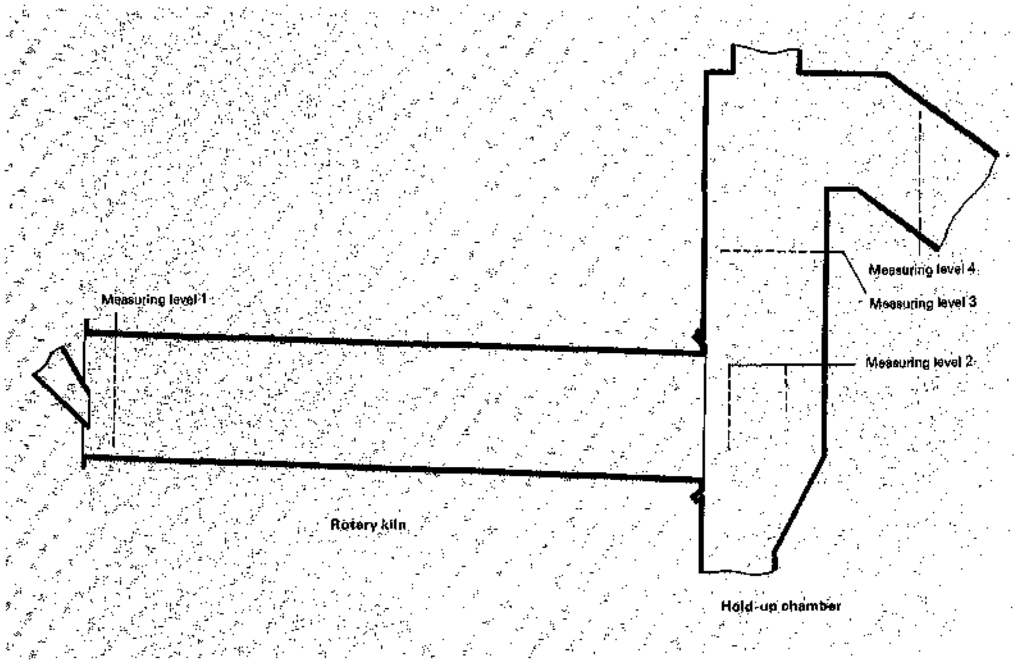
The plant is suitable and officially licensed for incinerating solid, semi-solid and liquid organic compounds of every type and a wide range of toxicities (hazardous and special waste).

The furnace is charged via an automatic hoisting device and lock.

The furnace consists of a slightly inclined rotary steel tube, lined with a 25 cm thick layer of fireclay and is heated to the requisite temperatures with heavy oil. The oil feed to the burner is controlled by thermocouples in the hold-up chamber.

Before the dioxin-containing residues were burnt, proof had to be obtained that combustion temperatures of more than 1200 °C in the HWI were guaranteed as well as a residence time of more than one second for the flue gases. Measurements made by specialists from the firm of Von Roll showed that *average temperatures of about 1500 °C can be maintained in the rotary furnace* and temperatures of *about 1300 °C in the downstream hold-up chamber.* Lower temperatures (at least 920 °C) were measured only at the lower end of the rotary furnace and were due to the entry of fresh air through the segment seal. The average temperatures stated are attained with an oil consumption of 462 l/h and a flue-gas flow rate of 6500 m$^3$/h upstream from the scrubber. With reference to the operational data (air flow, oil consumption, oxygen excess) and the characteristic data of the plant it was also possible to calculate the profile of the flue-gas temperature. There was good conformity between the calculated and the measured values.

*Fig. 3: Temperature measuring points in the HWI*



Flue-gas residence times in the HWI are difficult to determine experimentally. Because of the conditions prevailing during the temperature measurements made by Von Roll, the flue-gas residence times in the rotary furnace and in the hold-up chamber were calculated. To this end geometric dimensions and furnace conditions such as flue-gas temperature and flue-gas flow rate were used. These calculations showed that the average *residence time of the flue gases* in the rotary furnace and in the hold-up chamber was 1.4 seconds in each case, giving a total of *2.8 seconds*.

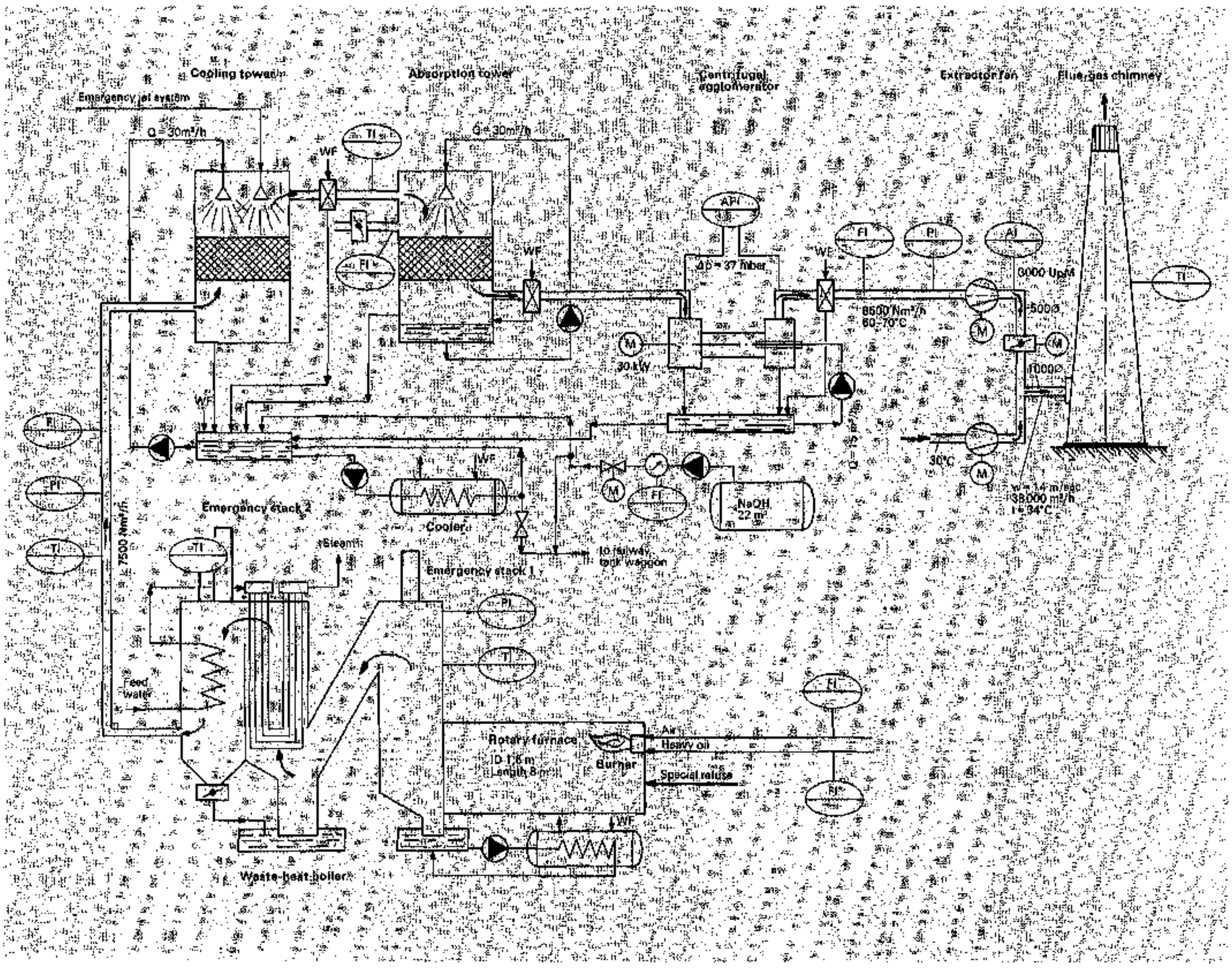
The flue gases are cleaned in the multistage scrubber system. Special attention had to be given to the fact that, in addition to the usual components, the gases contained a high proportion of common salt aerosol$^{\rightarrow}$ originating from the material combusted.

During every incineration of dioxin-containing material the wash water was cycled through a heat exchanger. Excess water was collected in a prepared tank. After each incineration the water from all the basins was pumped to the tank and stored there until a decision had been made about its disposal.

The slag obtained from the incineration of dioxin-containing material was placed in containers and stored separately until disposal had been decided upon.

# 4 Appendixes to Chapter 4

## Appendix A4.1: Schematic of HWI

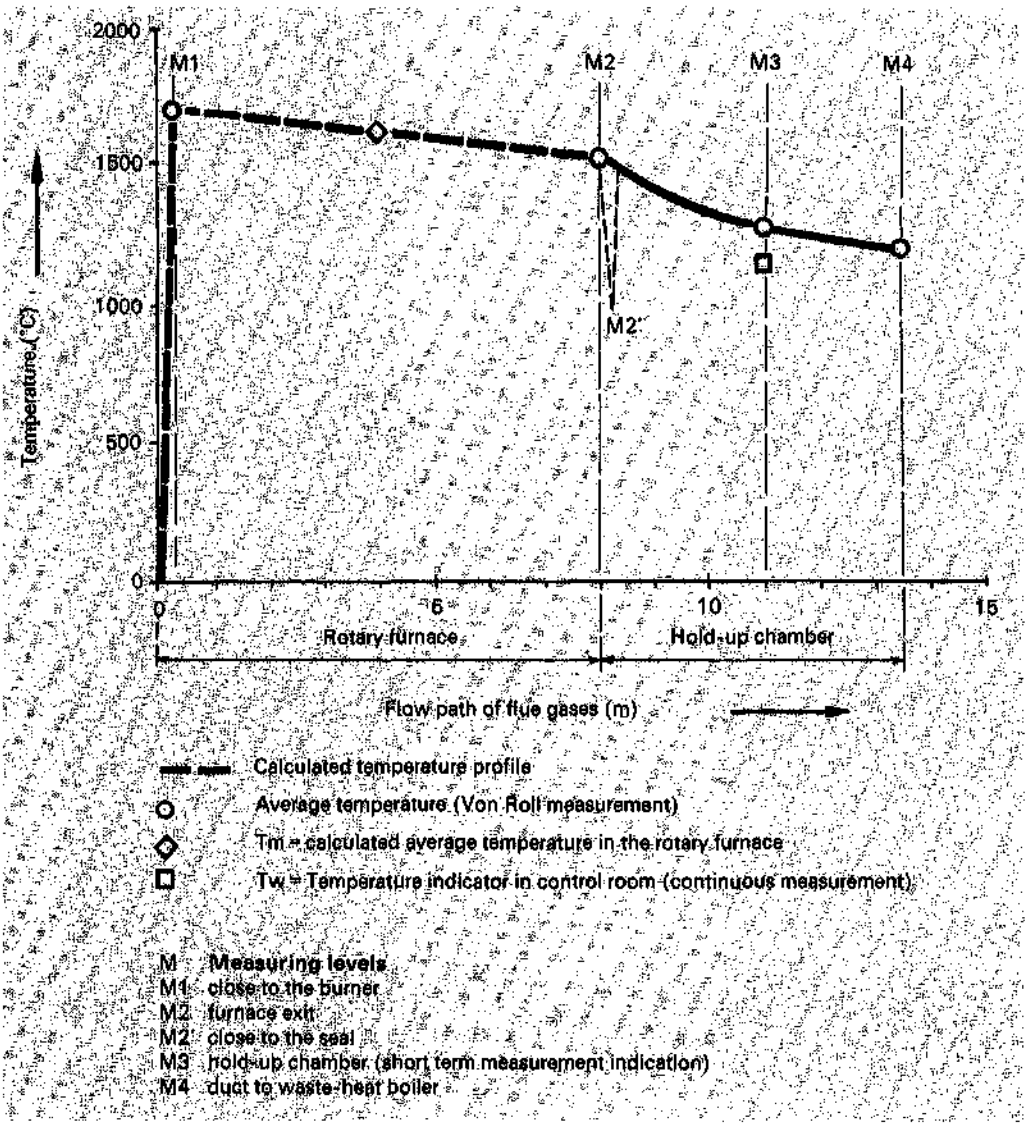


*Key*

AI = Analytical instrument
PDI = Pressure difference indicator
FI = Flow indicator
PI = Pressure indicator
TI = Temperature indicator
M = Motor
w = Flow velocity
t = Temperature
ΔP = Pressure difference
WF = Factory water
Q = Throughput

▶ = Pump
⧄ = Butterfly damper
☒ = Mist collector
⊖ = Fan
⋈ = Valve
⊜ = Compressor

## Appendix A4.2: Temperature profile in rotary furnace and hold-up chamber



The PtRh-Pt thermocouple with radiation shield and draw-off device used by Von Roll for measurements is suitable for long-term temperature measurements up to 1300 °C. In the short term temperatures up to 1500 °C can be measured. No measurements could be made in the middle and rear portion of the rotary furnace because of inaccessibility.

However, in order to obtain some notion of the temperatures in the incinerator as a whole the temperature profile in the rotary furnace and hold-up chamber was calculated on the basis of the quantities of oil and air (see Fig. Temperature profile). As the reliable measured values (measuring levels 1, 2 and 4) fitted well into the calculated temperature profile, it may consequently be assumed that this also applies to the hottest part of the rotary furnace where no measurements are possible.

Special conditions prevail at the entrance to the hold-up chamber. Air leaking through the seal causes non-localized zones of turbulence and mixing where the temperature is below the mean value or calculated value (lowest measured temperature: 920 °C).

An unprotected PtRh-Pt thermocouple without a draw-off device, located in the area of measuring level 3, serves for continuous monitoring of furnace operation. Because of the way it is designed the indicator at the measuring station supplies values which are too low (see Fig.). Thus a mean flue-gas temperature (Tw) of 1152 °C was measured at the measuring station whereas a temperature of 1250 °C was recorded at measuring level 3 in the Von Roll measurements. With this temperature reading as a starting point, a correction factor was used to calculate the temperature during the incineration operations with an accuracy of ± 25 °C on the basis of the Von Roll measurements (without combustion material). The stated values (Tm in Tables 1 + 2 and in Chap. 7ff) are the corresponding mean temperatures in the rotary furnace. However, they are not intended to simulate a spurious precision but rather to show that the requisite temperature of 1200 °C is attained and substantially exceeded in the rotary furnace.

# 5 Model and laboratory investigations

The extremely hazardous nature of 2,3,7,8-TCDD→ was deemed to preclude combustion tests involving direct charging of the HWI→ with TCDD-containing material. It was therefore decided initially to conduct trials with a test substance having similar chemical and physical properties but of lower toxicity. Thus, prior to actual combustion tests with TCDD, a substance of this type had to be found and investigated on a laboratory scale. Only in this way was it possible to carry out model and pilot trials without hazard.

## 5.1 Selection of test substance

The selection of the test substance on the basis of thermodynamic and thermokinetic considerations was of crucial importance for the design of the test incinerations and planning the laboratory investigations because predictions about the behaviour of TCDD in the combustion process were to be made on the basis of this substance. Aromatic hydrocarbons and chlorinated aromatic substances were included in this preliminary study. Non-chlorinated aromatic hydrocarbons could not be considered as test substances because of their thermal instability. Chlorinated phenols and dibenzofurans were also tested for suitability. Chlorinated phenols were rejected because the possibility of TCDD forming at an elevated temperature could not be ruled out.

An ideal substance was eventually found in the form of 2,4,8-trichlorodibenzofuran (Tri-CDF). It belongs to the category of polychlorinated dibenzofurans (PCDFs) and is therefore allied to the PCDDs and TCDD. Compared with TCDD the toxicity of tri-CDF is negligible. However, because of the close structural affinity of tri-CDF and TCDD, a very similar thermal decomposition behaviour could be safely assumed.

## 5.2 Physicochemical investigations

### *5.2.1 Basic considerations*

To enable the processes in the HWI to be assessed during the heating, vaporization, oxidative and thermal decomposition of the materials in it, it was imperative to examine their physical and thermochemical properties more closely. This was done in the light of data in the literature and more particularly on the basis of physicochemical laboratory tests at Ciba-Geigy.

Thermodynamic calculations could be used to show that tri-CDF and TCDD decompose completely into carbon dioxide, hydrochloric acid, and water in the temperature range from 800 to 1500 °C. No objection can therefore be raised to the incineration of TCDD from the thermodynamic viewpoint. However, these data do not suffice for an assessment of the time taken for thermodynamic equilibrium to be attained; in other words, the residence time of the substance in its vapor phase is of crucial importance. Kinetic calculations and experiments were therefore indispensable.

The critical parameter in practice is the decomposition efficiency of a substance in the flue gas of an HWI. It indicates how much of a substance can be decomposed thermally or by oxidation, i.e. burned, under specific conditions. Elimination efficiency comprises combustion followed by flue-gas purification. These efficiencies are calculated by the following equations:

$$\alpha' = \left(1 - \frac{m'}{m_0}\right); \quad \alpha'' = \left(1 - \frac{m''}{m_0}\right)$$

$\alpha'$ = decomposition efficiency of a substance related to the flue gas upstream from the scrubber

$\alpha''$ = elimination efficiency of a substance, related to the flue gas downstream from the scrubber

$m_0$ = quantity of substance charged

$m'$ = residual quantity of unburned substance in the flue gas upstream from the scrubber

$m''$ = residual quantity of substance emitted in the flue gas downstream from the scrubber

$m_0$, $m'$ and $m''$ are calculated during the whole combustion time.

However, the bench-scale calculation of the decomposition efficiency of a substance (based on kinetic data) cannot be extrapolated directly to calculate decomposition efficiency in the HWI. The volume of the furnace tube, for example, is as much as 100 million times greater than the volume of the laboratory vessels. Moreover, parameters such as flue-gas composition, temperature distribution, and residence time spectrum in the HWI do not reflect the ideal conditions of laboratory experiments.

To describe these differences the thermokinetic scale-up factor was introduced. It describes possible changes in the decomposition kinetics of a substance on scale-up from laboratory conditions to conditions during industrial incineration in an HWI.

The following steps were taken to resolve all this complex of questions:

- Thermokinetic measurements in the laboratory to determine the mean life of tri-CDF as a function of temperature.
- Combustion of tri-CDF in the HWI to determine the decomposition efficiency and mean life.
- Calculation of the thermokinetic scale-up factor for tri-CDF as a function of the mean furnace temperature of the HWI.
- Measurements of thermokinetic data for TCDD under the same laboratory conditions as for tri-CDF.
- Estimate of the decomposition efficiency in the HWI for tri-CDF and TCDD on the basis of laboratory results.

A factor to be considered in these investigations was that combustion involves two important physicochemical processes: vaporization and decomposition of the substance present in the vapor phase. Two sets of dynamic conditions control vaporization, depending on particle size. In the case of relatively large particles – such as particles of the dioxin-containing reaction residues – the controlling is the time required to heat the innermost zones to above the boiling point of TCDD. Relatively small particles entrained in the flue gas can be heated only during their residence time in the rotary furnace and the hold-up chamber. To prevent dust formation, therefore, the dioxin-containing reaction residues are mixed with a binding agent (polyethylene glycol) before combustion so as to ensure the longest possible evaporation time.

On the basis of all these investigations it was possible to predict with acceptable accuracy the decomposition efficiency of TCDD in the HWI and to make a reliable assessment of the hazards during combustion.

### *5.2.2 Literature*

In the literature up to the end of 1983 only five references could be found giving quantitative and thermokinetic data on TCDD. Moreover, some of this information is still incompletely documented or contains estimates based on relatively simple physicochemical models. Similarly, few physicochemical data are available for the selected test substance tri-CDF.

However, if research in the literature is extended to chlorinated dioxins that differ in structure from TCDD, to chlorinated furans and biphenyls⁻, or even to any substances with high thermal stability, the literature provides a substantially larger range of data. These publications discuss the following sets of problems: laboratory experiments, theoretical computations and combustions on a pilot or industrial scale. The most important data were incorporated in the planning and execution of the laboratory experiments.

### *5.2.3 Thermokinetic investigations*

To determine the thermokinetic behaviour of TCDD and the test substance tri-CDF use was made of laboratory microgram-range methods which had to fulfil the following conditions:

- Clearly defined and reproducible conditions relating to the thermal or oxidative stress on the substance (temperature, time, and atmosphere).
- Measured temperature in the zones permitting reasonable extrapolation to the relevant furnace temperatures.
- Experiments in vessels of different materials and with different surface-to-volume ratios.
- Possibility of assay and tracing of the substances used by means of a highly specific GC/MS$^{-}$ method.

The methods employed

- two batch methods, namely thermokinetics in gold-plated vessels and microkinetics in quartz vessels,
- a continuous method, dynamic-gas phase reaction analysis,

showed good conformity for tri-CDF in the whole temperature range of 330 to 1100 °C covered in the experiment.

On the basis of these results, a mean life of about 1 millisecond could be calculated for tri-CDF at a temperature around 1400 °C. A virtually identical mean life at the same temperature was extrapolated from the laboratory data on TCDD decomposition. Thus, it was possible to show in the laboratory that tri-CDF is a suitable model substance for the problem to be solved, and that this applies to both the physical and the chemical processes relating to tri-CDF and TCDD.

### *5.2.4 Scale-up of the laboratory results to conditions in the HWI*

On the basis of the laboratory results test incinerations with tri-CDF could be carried out in the HWI. The specific aim of these incinerations was to determine the decomposition efficiency of tri-CDF in flue gas. The relevant data and the results of the test incinerations made with tri-CDF are summarized in Table 1 (see also Appendixes A7 and A8).

Corresponding test incinerations with dioxin-containing reaction residues yielded the results summarized in Table 2.

The mean life of tri-CDF in the HWI was found to be around 100 milliseconds. Compared with the mean life in the millisecond range determined in the laboratory test there is therefore a scale-up factor of about 100.

The absolute magnitude of the scale-up factors shows that, in the HWI, as compared with laboratory decomposition, factors must be operative which prolong the life of the molecule. Factors responsible for these deviations are: size differences, temperature, residence time, localized non-homogeneities, and the concentration of all particles (aerosol particles, molecules, atoms, radicals) in the flue gas.

The residual concentrations of tri-CDF in the flue gas upstream from the scrubber (see Table 1) show that the temperatures in the rotary furnace and hold-up chamber are the crucial parameters determining decomposition efficiency. In the test incinerations at the highest temperatures (approximately 1500 °C in the rotary kiln and

*Table 1: Test incinerations with tri-CDF in the HWI*

| Test incineration | 28.03.84 | 12.04.84 | 26.06.84 1st incineration | 26.06.84 2nd incineration |
|---|---|---|---|---|
| Number of batches | 6 | 16 | 16 | 16 |
| Tri-CDF per batch (kg) | 5 | 0.625 | 0.625 | 0.625 |
| Duration of test incineration (min) | 60 | 40 | 40 | 40 |
| Flue-gas flow rate[1] | | | | |
| – upstream from scrubber ($m^3/h$) | 6600 | 7400 | 7400 | 7400 |
| – downstream from scrubber ($m^3/h$) | 7300 | 8200 | 8300 | 8300 |
| Temperature[2] | | | | |
| – Tm rotary furnace (°C) | 1530 | 1330 | 1520 | 1530 |
| – Tw hold-up chamber (°C) | 1140 | 940 | 1130 | 1140 |
| Total residence time in rotary furnace in hold-up chamber (s) | 2.8 | 2.5 | 2.5 | 2.5 |
| Tri-CDF concentration: in flue gas | | | | |
| – upstream from scrubber ($ng/m^3$) | 96[3][4] | 17000[4] | 360[3][4][5] | 320[3][4] |
| – downstream from scrubber ($ng/m^3$) | 10[6] | 190[4] | 35[3][4][5] | 24[3][4][5] |
| Quantity of tri-CDF charged – $m_0$ (kg) | 30 | 10 | 10 | 10 |
| Quantity of tri-CDF in flue gas | | | | |
| – $m'$ upstream from scrubber (mg) | 0.63 | 84 | 1.8 | 1.6 |
| – $m''$ downstream from scrubber (mg), emitted | 0.07 | 1.0 | 0.19 | 0.13 |
| Decomposition efficiency $\alpha'$[7] for tri-CDF, flue gas upstream from scrubber | 0.99999998 | 0.999992 | 0.9999998 | 0.9999998 |
| Elimination efficiency $\alpha''$[7] for tri-CDF, flue gas downstream from scrubber | 0.999999998 | 0.9999999 | 0.99999998 | 0.99999999 |

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1) Data from measurement station HWI (flue gas, humid)
2) For explanations re temperature measurement see p. 37
3) Determination by EMPA, in accordance with standard analytical method
4) Determination by Ciba-Geigy, in accordance with standard analytical method
5) Determination by Ciba-Geigy, with KISA
6) Assumption: 90% separating efficiency* of the scrubber
7) Calculation according to equations Chapter 5.2.1

*Table 2: Test incineration with dioxin-containing wastes in the HWI*

| Test incineration | 27.11.84 1st incineration | 27.11.84 2nd incineration | 19.03.85 2nd phase |
|---|---|---|---|
| Number of batches | 5 | 5 | 132 |
| TCDD per batch[8] (g) | 0.26 | 0.26 | 0.65 |
| Duration of test incineration (min) | 30 | 30 | 660 |
| Flue gas flow rate[1] | | | |
| – upstream from scrubber ($m^3/h$) | 9 600 | 9 600 | 9 100 |
| – downstream from scrubber ($m^3/h$) | 10 800 | 10 800 | 10 300 |
| Temperature[2] | | | |
| – Tm rotary furnace (°C) | 1 520 | 1 520 | 1 540 |
| – Tw hold-up chamber (°C) | 1 130 | 1 130 | 1 150 |
| Total residence time in rotary furnace and hold-up chamber (s) | 1.9 | 1.9 | 2.0 |
| TCDD concentration in flue gas[9] | | | |
| – upstream from scrubber ($ng/m^3$) | < 1[3][4] | < 1[3][4] | < 0.1[3][4] |
| – downstream from scrubber ($ng/m^3$) | < 2[3][4][5] | < 2[3][4][5] | < 0.1[3][4][5] |
| Quantity of TCDD fed | | | |
| – $m_0$[8] (g) | 1.3 | 1.3 | 86 |
| Quantity of TCDD in flue gas | | | |
| – $m'$ upstream from scrubber upper limit[10] (µg) | 5 | 5 | 10 |
| – $m''$ downstream from scrubber, emitted, upper limt[6][11] (µg) | 0,5 | 0,5 | 1 |
| Decomposition efficiency $\alpha'$[7] for TCDD, flue gas upstream from scrubber lower limit (%) | 0.999996 | 0.999996 | 0.9999999 |
| Elimination efficiency $\alpha''$[7] for TCDD, flue gas downstream from scrubber, lower limit (%) | 0.999999 | 0.999999 | 0.99999999 |

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1) Data from measurement station SRI (flue gas, humid)
2) For explanations re temperature measurement see p. 37
3) Determination by EMPA, in accordance with standard analytical method
4) Determination by Ciba-Geigy, in accordance with standard analytical method
5) Determination by Ciba-Geigy, with KISA
6) Assumption: 90% separating efficiency* of the scrubber
7) Calculation according to equations Chapter 5.2.1
8) Values correspond to 600 g TCDD in 2350 kg waste (cf. Chap. 2.2)
9) Statement of detection limit, no TCDD was detected
10) Calculation on basis of detection limit (max poss. quantity TCDD)
11) Calculation on basis of empirical values with tri-CDF, see also[6]

approximately 1200°C in the hold-up chamber) there was a mean decomposition efficiency of the tri-CDF upstream from the scrubber of at least 0.999999 (in relation to the flue gas).

The mean life of TCDD was also found to be about 120 milliseconds in the HWI. The scale-up factor was therefore about 100 in comparison with the mean life obtained in the laboratory tests.

The essential point is that the scale-up factors for tri-CDF and TCDD are in close agreement. These values also show that TCDD is decomposed in the HWI at the same rate as tri-CDF.

## 5.3 Conclusions

To summarize, the results obtained in the microkinetic investigations and the test incinerations in the HWI may be assessed as follows:

The thermal stabilities of the tri-CDF and TCDD molecules are, both theoretically and empirically, very similar in the relevant temperature range for incinerations in the HWI over 1000°C.

The test incinerations performed on 28 March and 26 June 1984 with tri-CDF at the highest temperature technically attainable in the HWI (mean temperature in the rotary furnace 1520°C) yielded decomposition efficiencies in the flue gas upstream from the scrubber better than 0.999999. In the flue gas downstream from the scrubber a total elimination efficiency at least 10 times higher, that is, over 0.9999999, was determined.

The incinerations with TCDD-containing residues also yielded an elimination efficiency in the flue gas downstream from the scrubber better than 0.999999. These findings formed the basis for estimating the hazards involved in burning TCDD-containing material in the HWI.

# 6 Analytical chemistry

All the streams of materials issuing from the HWI were assayed to ascertain, among other characteristics, their PCDD and PCDF content. Methods of sampling and analysing the flue gases, the waste-water from the scrubber and slag bath, and the slag and the ash from the waste-heat boiler are complicated and elaborate. Procedures of proven efficacy were available only for a few stages of the investigation. The analytical laboratories of EMPA$^{\rightarrow}$, Dübendorf, FAW$^{\rightarrow}$, Wädenswil, and Ciba-Geigy Ltd. Basle collaborated in the selection, testing and optimization of suitable methods for this project so as to enable reliable statements to be made on the contamination of exhaust gases, waste-waters and slag and hence on the effectiveness of the incineration. Assays of the TCDD in the reaction residues (cf. Chap. 2) and that obtained in the wipe tests (cf. Chaps. 3 and 11) were performed using recognized methods published in the technical literature.

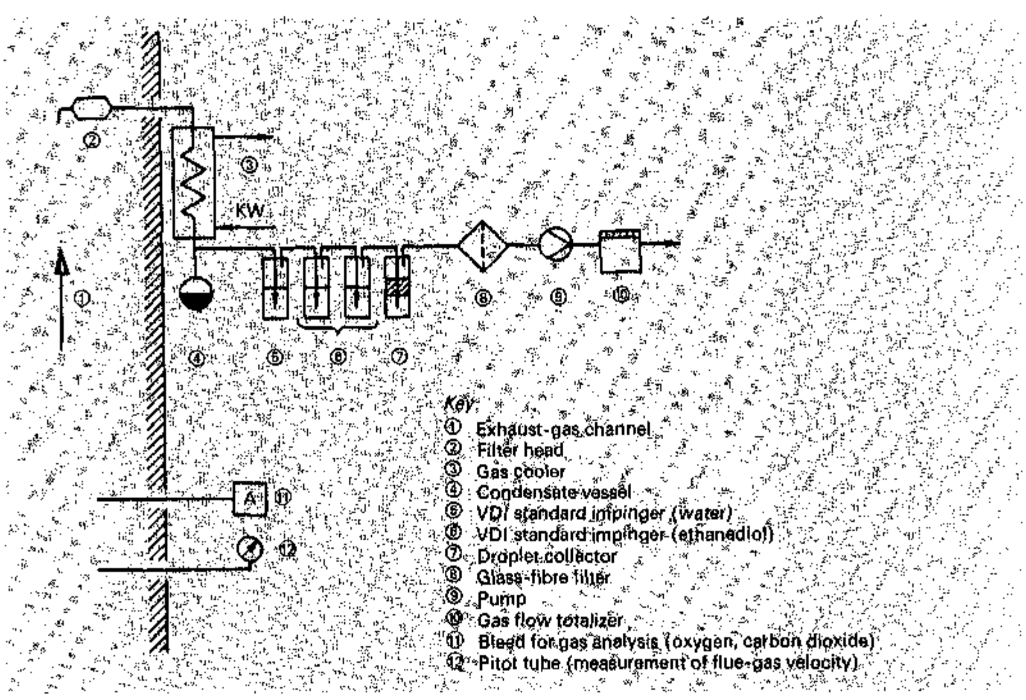
## 6.1 Flue gases

Two different methods of investigation were used: the standard analytical method (EMPA together with Ciba-Geigy) and KISA (Kurzintervall-Spurenanalyse = short-interval trace analysis) devised by Ciba-Geigy.

*6.1.1 Standard analytical method* (see Appendix A6.2)
In the standard analytical method the flue gas was sampled in repeated determinations by measuring teams from EMPA and Ciba-Geigy using identical equipment. All the samples were processed and analysed in the respective laboratories by jointly formulated procedures.

A representative portion of the volumetric flow is taken from the flue-gas channel with a glass sampler (see Fig. 4). Sampling is done at the same velocity (isokinetically) at a flow rate of about 2 m$^3$ flue gas per hour. In sampling upstream from the scrubber, dust is removed from the portion of the flow sampled by the filter head (2), which is packed with fine quartz wool and located in the flue-gas duct (1); gas downstream from the scrubber is sampled without a filter head.

*Fig. 4: Sampling apparatus for the standard analytical method*



The gas sample is cooled outside the flue-gas channel (3), and the condensate thus formed, mainly water, is collected (4). The gas sample then passes through three wash bottles (5, 6) where fine droplets and volatile components are removed from the gas sample by intimate contact with the liquids in them. Entrained droplets are then removed from the gas sample in the droplet collector (7) before it proceeds through a high-efficiency glass-fibre filter (8) to the pump (9), which has a gas flow totalizer on its output side.

To test the efficiency of the sampler system, it is spiked$^{\rightarrow}$ immediately before sampling at point (2) (for sampling upstream from the scrubber) or at point (3) of the system (for sampling downstream from the scrubber) with a known quantity of labelled TCDDs ($^{13}C^{\rightarrow}$). To check the processing of the samples taken these are likewise spiked with a known quantity of differently labelled TCDDs ($^{37}Cl^{\rightarrow}$). Recovery of these labelled substances shows whether any loss of substance has occurred during sampling or processing. Trace analyses presuppose the use of the purest possible reagents and other materials. Any contamination with PCDD and PCDF is virtually ruled out by the choice of appropriate qualities and constant analytical checks. This rechecking also extends to the apparatus used, especially the sampler.

This structurally complex sampling system is capable of detecting a broad spectrum of substances even in extremely difficult flue-gas analyses. However, sample processing takes a long time because of the large volume of the sampling apparatus with its filters, absorbents and impingers.

For assaying the various PCDDs and PCDFs in the samples under examination (flue gas upstream and downstream from the scrubber, slag, waste-waters), these are extracted with various organic solvents, after pre-treatment with hydrochloric acid where necessary. The extracts thus obtained are purified by column chromatography. The individual stages of purification are summarized in Appendix A6.2. The PCDDs and PCDFs are separated by high-resolution gas chromatography (GC). A mass spectrometer (MS) is used to identify the individual compounds.

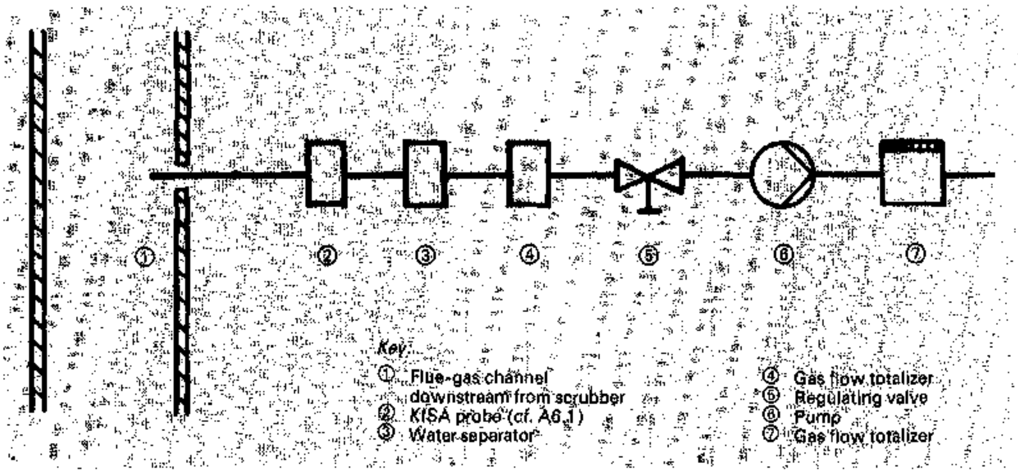
Constant improvements led to a steady increase in the sensitivity of the analytical methods. During the main incineration a detection limit of 0.2 ng TCDD/m$^3$ was attained in the flue gas downstream from the scrubber for sampling times of between 16 and 21 hours.

### *6.1.2 Short-interval trace analysis (KISA)*

For monitoring the flue gas during the incineration of dioxin-containing residues an analytical method was required which would ensure continuous surveillance of the combustion process. The time-consuming standard analytical method is not suitable for this purpose, and Ciba-Geigy therefore developed for monitoring purpose a short-interval trace analysis (KISA) with which information on the TCDD content in the flue gas can be obtained rapidly (within 1–2 hours).

The sampling principle is based on a procedure that is widely used for trace analysis in aqueous systems. KISA sampling is represented schematically in Fig. 5. A partial flow of about 1 litre per minute of the water-saturated flue gas at a temperature of about 50 °C is drawn in at the entrance of the probe via a glass-wool filter. In the front portion of the probe (2) the flue gas is heated to 75 °C and passed through an activated carbon filter heated to 100 °C. Thus, the organic components of the flue gas which volatilise under these conditions are concentrated in the system. To test the system for separating power and substance losses during sample processing and analysis a specific quantity of labelled TCDD ($^{13}C^{\rightarrow}$) is placed on a wad of glass wool at the orifice of the probe. The volume of the sampling probe (5 ml) is small. Prior to rinsing the probe

*Fig. 5: Sampling apparatus for KISA*



with only 5 ml carbon disulphide as a solvent a second internal standard $^{37}\mathrm{Cl}^{\rightarrow}$-TCDD is placed on the glass wool at the orifice. In this way any extraction losses can be detected quantitatively. The extract so obtained, which can be concentrated rapidly, is put through a GC-MS analysis without after-purification.

With a collected volume of 50 litres the detection sensitivity is approximately 0.1 ng TCDD/$m^3$ flue gas. Specificity and detection sensitivity are comparable with those of the standard analysis method.

Because of its relative simplicity, the KISA allows TCDD analyses to be performed in cycles of about 1 hour.

## 6.2 Slag

The slag was removed in containers. Throughout the combustion period the slag was sampled every 15 minutes with a special sampler and ground down to a size of 4 mm in a hammer mill. Milled samples from each container were mixed for 5 minutes in a mixer (Loedige type) to produce a mixed sample.

From each mixed sample 1000 g was given to EMPA and 1000 g to Ciba-Geigy for analysis for unburned TCDD. Processing and analysis were carried out as described in Appendix A6.3. The detection limit was 5 ng/kg.

## 6.3 Waste-water

All waste-waters, made alkaline with caustic soda as an anti-corrosion measure, were collected separately in railway tank waggons and homogenized by agitation with compressed air before sampling. Samples taken from these tank waggons were filtered in case undissolved suspended matter was present. The filtrate and the solids were examined separately. The solids were processed like slag and the clear aqueous solution according to the 'waste-water' schematic (Appendix A6.3). Both part samples were then united and analysed. The detection limit for TCDD stood at 1 ng per litre.

## 6.4 Environmental monitoring

As a precautionary measure an environmental monitoring network was set up and operated to test outside air. The network was so designed that any pollution of the outside air by unexpected noxious emissions from the HWI could have been detected. The period during which monitoring was continued and the sampling intervals were selected so that environmental pollution from other sources could have been recognized. However, where there are no emissions, no pollution can be expected. In view of this it was decided that sampling should be carried out in every case but that the samples should not be examined if the emissions were undetectable or negligible. It was finally decided to abstain from processing and analysing the samples since neither TCDD nor any allied compounds had been found in the flue gas in any of the incinerations of dioxin-containing material.

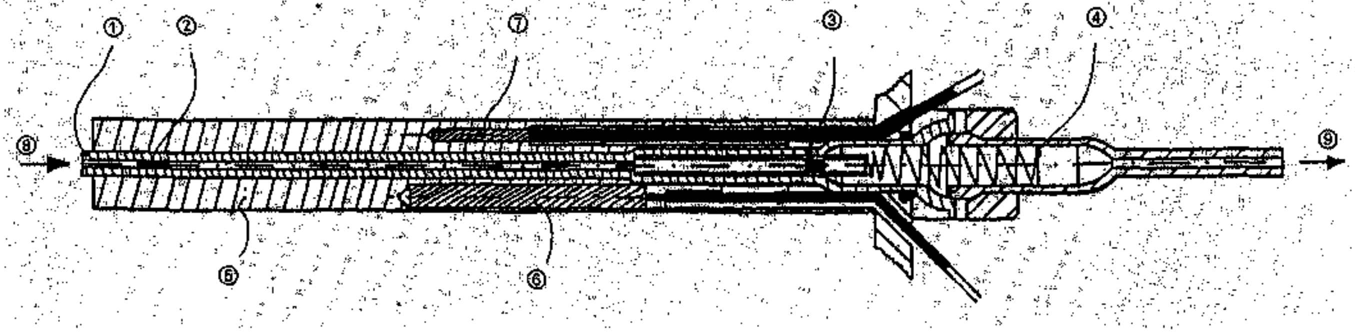
The location of the sampling points can be seen in the plan (Appendix A6.4). The main criteria for the selection of these sites were the expected dispersal of the flue gases as well as local characteristics (built-up areas, main traffic axes, risk of disturbance by passersby). The sampling programme began in February 1984 and continued until the end of June 1985.

At all nine sampling sites the coarser, sedimentable dust was measured with the Bergerhoff→ apparatus (Ref. [3]). At each sampling site 6 collecting vessels were set up and exchanged after 2 weeks' exposure. At two of these sites (Nos. 4 and 8) finer suspended dust was also filtered from the outside air with a high-volume sampler→. Every two weeks 30 filters at each site accumulated the suspended dust in about 15000 $m^3$ of outside air. The apparatus was serviced and the samples taken by the EMPA with the aid of the Cantonal Laboratory, Basle City.

# 6 Appendixes to Chapter 6

**Appendix A6.1:** **KISA probe**

Device for adsorbing TCDD on activated carbon



*Key:*

① Glass tube

② Glass wool with standard ($^{13}$C-TCDD)

③ Activated carbon filter

④ Spring-mounted holder for filter

⑤ Heating cylinder

⑥ Cartridge-type heater

⑦ Temperature sensor Pt 100

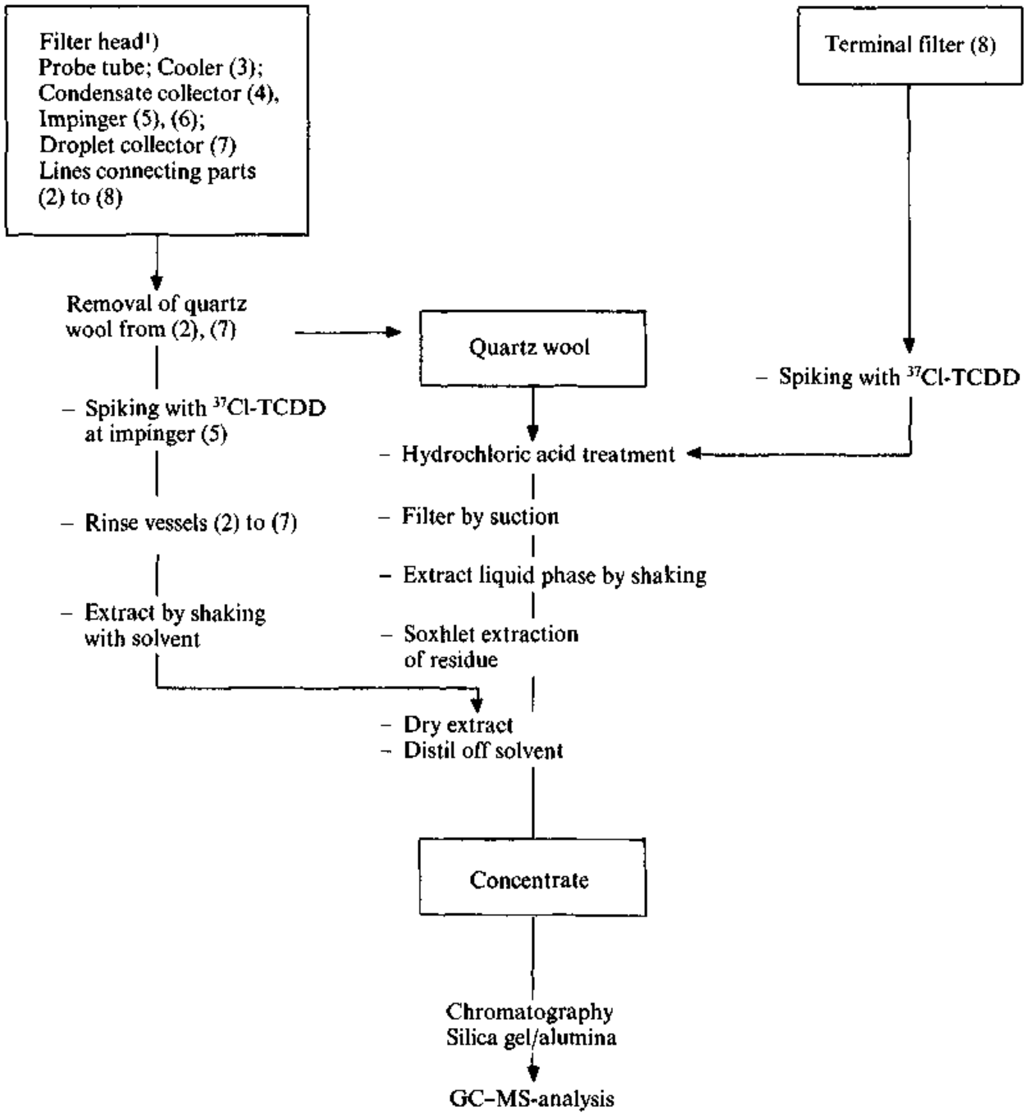
⑧ Flue gas

⑨ To vacuum pump

## Appendix A6.2: Flue gas (standard method for processing and analysing of samples)

All samples are individually processed an analysed. Grouping together in the schematic indicates only that the same operations are performed.

(The numbers in brackets refer to Fig. 4, 6.1.1)

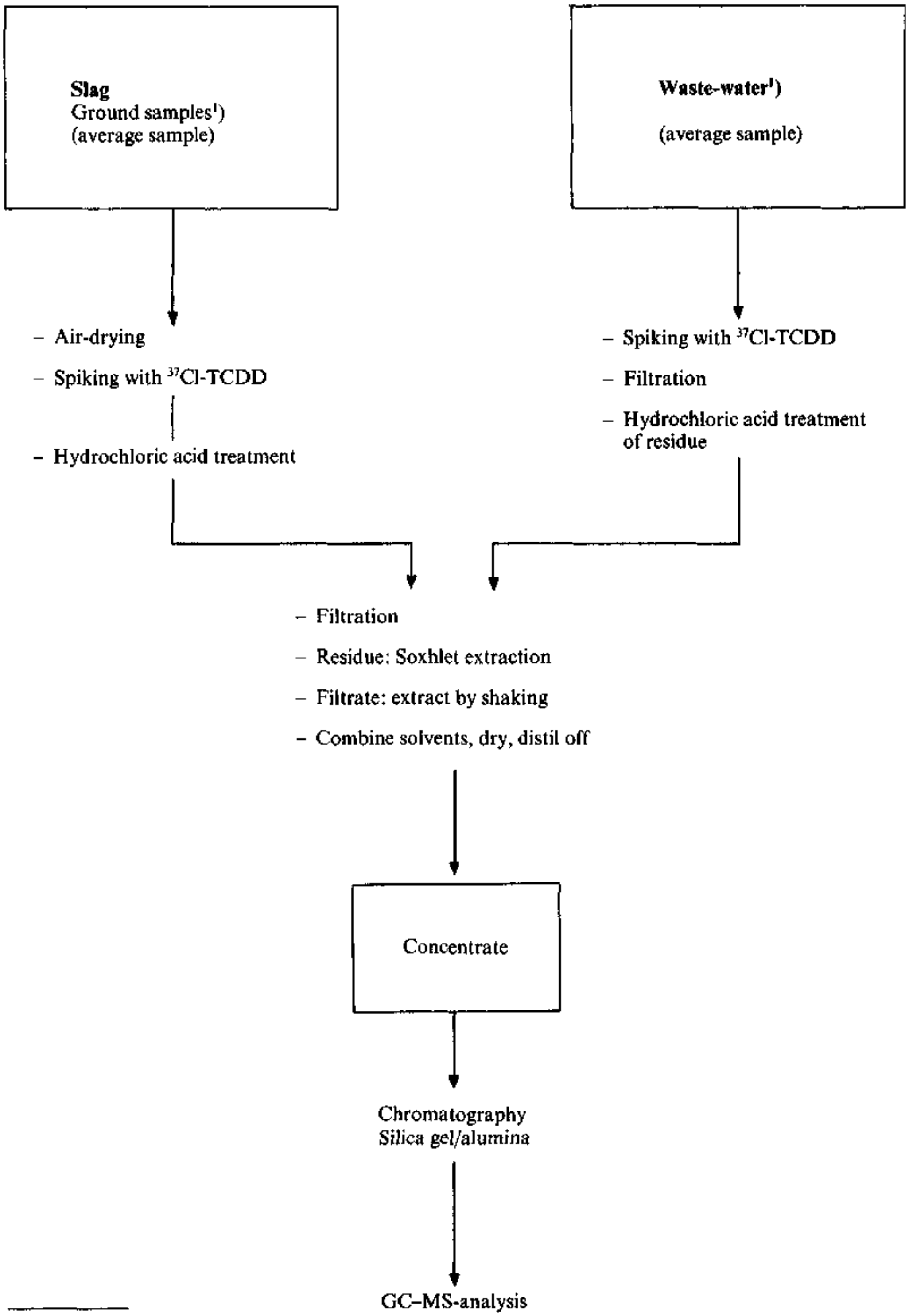


---

GC: high resolution gas chromatography (25 m SE 54)
MS: Finnigan 4600 mass spectrometer
1) filter head only when sampling upstream from the scrubber

## Appendix A6.3: Slag and waste-water (standard method for processing and analysis of samples)

All samples are individually processed and analysed. Grouping together in the diagram indicates only that the same operations are performed.



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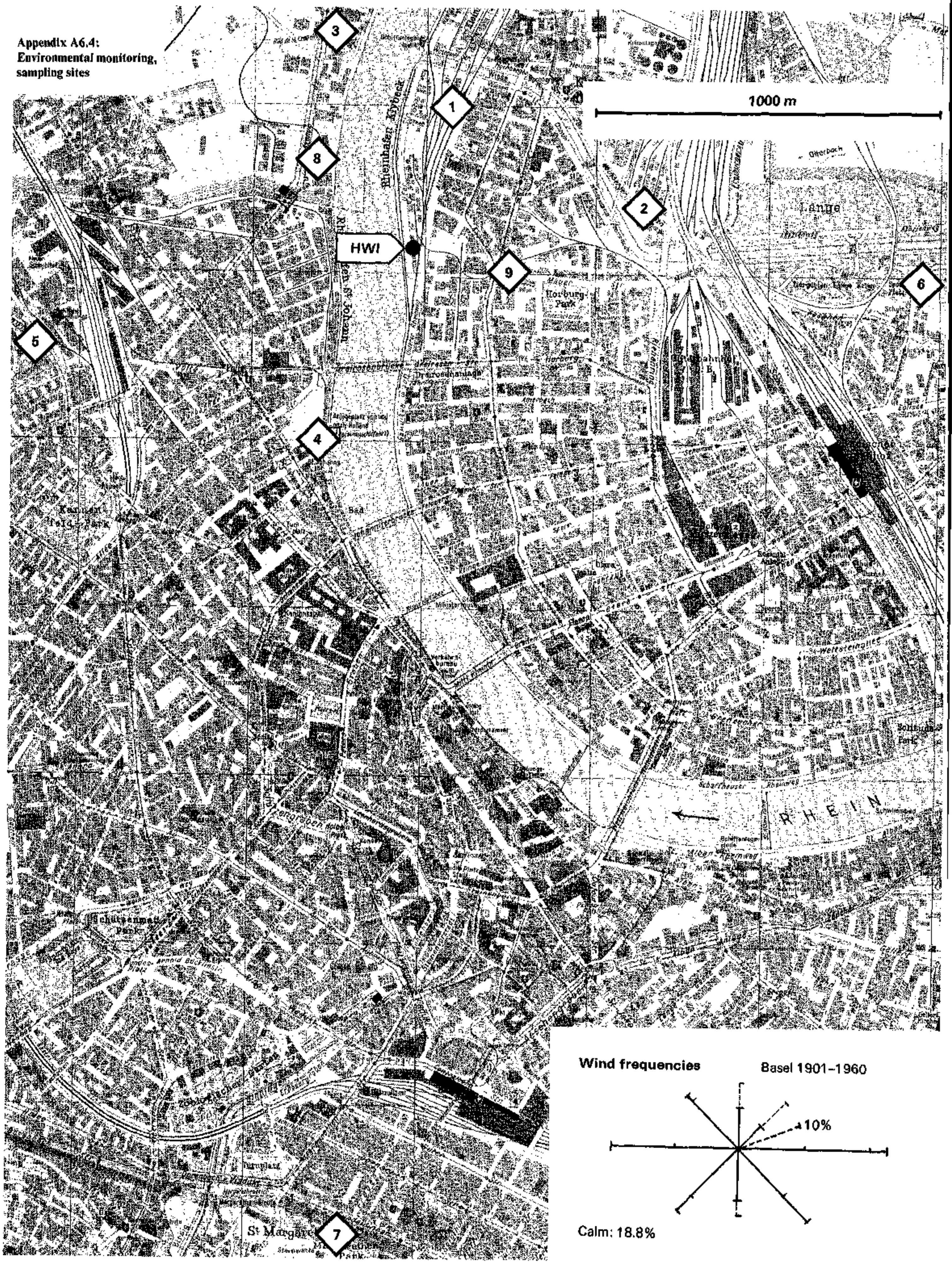
1) Sampling and processing by Ciba-Geigy

**Appendix A6.4: Environmental monitoring, sampling sites**



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# 7 Preparatory test incinerations with model substances

## 7.1 Objective

In the light of the results obtained from the thermokinetic studies and the determination of furnace characteristics it was possible to proceed to test incinerations in the rotary furnace (cf. Appendix A7).

The first two test incinerations with a mixture of 70% common salt, 25% p-cresol and 5% activated charcoal served to shed light on

- the influence of the high salt content on combustion behaviour at high temperatures, slag behaviour, the measuring devices and the entire HWI system, and
- on the batch size, the type of packaging and the behaviour of the batches in the furnace.

The following test incinerations with mixtures of 2,4,8-trichlorodibenzofuran (tri-CDF) with common salt and polyethylene glycol (PEG), with the proportion of salt corresponding to the composition of the reaction residues from ICMESA, served to

- confirm the results obtained from the thermokinetic laboratory investigations,
- test pollutant control together with the requisite installations,
- ascertain the combustion and scrubber efficiency of the HWI,
- ascertain whether additional oxygen must be supplied to the combustion to ensure an adequate final oxygen concentration, and
- to determine and fix the batch size, the type of packaging and the throughput.

The preparatory test incineration created no hazards, for it is common practice to use the HWI to incinerate organic and inorganic wastes similar to those envisaged in the test incinerations of salt-cresol mixtures without any pollution of the environment. There is no evidence of the formation of prohibited toxic pollutants during the incineration of such mixtures. In view of its low toxicity and the preceding laboratory tests it was also considered safe to incinerate tri-CDF (see 5.3).

## 7.2 Execution

The preparatory test incinerations were carried out in close collaboration with the committee of experts during the period from February to June 1984. Appendix A7 summarizes the most important details.

## 7.3 Results

The preparatory test incinerations served to *demonstrate:*

- that the HWI can be fed and operated without trouble,
- that high temperatures can be maintained even for long periods and
- that high combustion efficiency and good scrubber efficiency can be attained (cf. Chapter 5).

Feeding the furnace with batches weighing 2.5 kilograms was found to give good results. To encourage uniform combustion the powdery material was bound by the admixture of PEG$^{-}$. The batches were packaged in plastic bags which were always fed into the furnace with a portion of sand in order to maintain an adequate slag lining of the rotary furnace.

The *analytical results* show that in the furnace and hold-up chamber the tri-CDF is eliminated in relation to the flue gas with an efficiency of 0.999 999 and, together with the flue-gas scrubber, an efficiency of 0.999 9999 (cf. Table 1, Chapter 5). Recombination products of the type found during the first test incineration with tri-CDF could be avoided by improved combustion conditions.

# 7 Appendix to Chapter 7

## Appendix A7: Details concerning the preparatory test incinerations

### Incineration on 15.02.84

| | |
|---|---|
| Objective | Acquisition of initial experience with residues containing an extremely high proportion of common salt |
| Quantity | 50 kg of material for incineration, subdivided into 10 batches of 5 kg |
| Composition | 70% NaCl$^{\to}$, 25% p-cresol, 5% activated charcoal Norit SX-1; jute bag as outermost cover to prevent slipping in the furnace. |
| Charging interval | 2.5 minutes |
| Duration | 25 minutes |
| Temperature | Hold-up chamber: 1190°C (Tw) |
| Result | Experience obtained with incineration of materials with a high salt content was favourable |

### Incineration on 27.02.84

| | |
|---|---|
| Objective | Test of analytical method, determination of relocation rate$^{\to}$ |
| Quantity | No furnace charge (blank test) |
| Result | No TCDD could be detected in the flue gas in a blank trial to test the analytical method before incinerating the test substance tri-CDF. A 97% relocation rate was obtained for $^{13}$C-TCDD. |

### Incinerations on 28.03.84

*First incineration* (with cresol)

| | |
|---|---|
| Objective | 1. To test furnace behaviour at high temperatures<br>2. To check slag behaviour<br>3. To check batch size and behaviour of batches |
| Quantity | 720 kg of material for incineration, subdivided into 144 batches of 5 kg |
| Composition | 70% NaCl, 25% p-cresol, 5% activated charcoal Norit SX-1; packaging with and without jute bag. |
| Charging interval | 3 minutes |
| Duration | 6.75 hours |
| Temperature | Hold-up chamber: 1140°C (Tw) |

*Second incineration* (with tri-CDF)

| | |
|---|---|
| Objective | 1. To check flue gas analysis<br>2. To check batch size and behaviour of batches |

| | |
|---|---|
| Quantity | 30 kg of material for incineration |
| Composition | tri-CDF→ dry, powdered; packaging without jute bag;<br>6 batches of 5 kg |
| Charging interval | 10 minutes |
| Duration | 1 hour |
| Temperature | Rotary furnace 1530 °C (Tm), hold-up chamber 1140 °C (Tw) |
| Analytical method | Analysis of flue gases upstream from scrubber for tri-CDF and other compounds, analysis of slag |

*Results of the two incinerations*

Combustion was partly incomplete (soot formation, some escape of carbon monoxide).

More than 200 different organochlorine compounds in quantities from 10 to 1,000 ng/$m^3$ (per component) were detected in unpurified flue gas. PCDDs and PCDFs, both tetra- to octachlorinated, were found in quantities of 400 to 1,000 ng/$m^3$. These groups of substances are presumably formed by recombination reactions.

2, 3, 7, 8-substituted PCDDs could not be found among the principal components. The decomposition efficiency of the tri-CDFs used was very high (more than 0.999 999 9) based on the flue gas.

The medium to difficultly volatile compounds from the flue gas were mainly adsorbed on particulate matter and collected as dust in the quartz-wool filter.

The isomer distribution of the PCDDs approximated to that in the values found in municipal refuse incinerator (MRI) emissions.

The use of jute bags did not result in any improvement in furnace charging behaviour and subsequent incinerations were carried out without jute bags.

### Incineration on 12.04.84

| | |
|---|---|
| Objective | 1. To ascertain suitable conditioning→<br>2. To ascertain combustion and scrubber efficiency |
| Quantity | 40 kg of material for incineration,<br>subdivided into 16 batches of 2.5 kg plus 20 kg sand per batch |
| Composition | 10 kg tri-CDF dry, powdered; 23.2 kg NaCl; 6.8 kg PEG→ 1500. |
| Charging interval | 2.5 minutes |
| Duration | 40 minutes |
| Temperature | Rotary furnace 1330 °C (Tm), hold-up chamber 940 °C (Tw) |
| Analytical method | Analysis of flue gas upstream and downstream from scrubber for tri-CDF and other compounds |
| Result | Because of the low temperature chosen the decomposition efficiency of tri-CDF in relation to flue gas was only 0.999 99. No recombination products could be detected. |

## Incinerations on 26.06.84

| | |
|---|---|
| Objective | 1. To determine the residual oxygen concentration<br>2. To determine the combustion and scrubber efficiency<br>3. To test the analytical methods |
| Quantity | 2 × 40 kg material for incineration subdivided into 2 × 16 batches of 2.5 kg plus 20 kg of sand per batch |
| Composition | 20 kg tri-CDF dry, powdered; 46.4 kg NaCl; 13.6 kg PEG 1500. |
| Charging interval | 2.5 minutes |
| Duration | 2 × 40 minutes |
| Extra oxygen | *1st incineration:* with extra oxygen in the combustion air (about 70 litres/sec)<br>*2nd incineration* without extra oxygen |
| Temperature | *1st incineration:* hold-up chamber 1130 °C (Tw)<br>*2nd incineration:* hold-up chamber 1140 °C (Tw) |
| Analytical method | Analysis of flue gases upstream and downstream from the scrubber for tri-CDF and other compounds, analysis of scrubber water and slag for tri-CDF. |
| Result | The results of flue-gas analysis showed that tri-CDF was eliminated with an efficiency of 0.999999 in the furnace and hold-up chamber and of 0.9999999 after passing through the flue gas scrubber.<br>No recombination products were detected.<br>In the slag (about 400 kg) 6 to 10 micrograms of tri-CDF per kg were found in the test incineration with oxygen and 2 to 3 micrograms in the test without extra oxygen.<br>In the waste-water (approx. 8 $m^3$) 6.2 and 9.5 ng TCDD per litre were found. |

| | |
|---|---|
| *Residue disposal* | In all tests the *waste-waters* accumulating were discharged via the chemical sewerage system to the water treatment plant and the *slag* was transported in containers to a controlled Swiss landfill site. |

# 8 First test incineration with dioxin-containing wastes

## 8.1 Risk assessment

In the first test incineration on 27 November 1984 involving small quantities of TCDD-containing material the risk assessment could be confined to the noxious materials in the flue gas since only these could have escaped directly into the environment.

The slag and wash-water from the flue-gas purification were retained so that they could not be the source of any immediate and uncontrolled hazards.

The preparatory test incineration on 26 June 1984 showed that only 0.1 millionth of the tri-CDF fed to the furnace escaped into the atmosphere. It was expected that the combustion of TCDD would produce a decomposition efficiency similar to that of tri-CDF. On the basis of these findings the following emissions were estimated:

| | | |
|---|---|---|
| The 2,3,7,8-TCDD concentration[1]) assumed for the purposes of calculation | 0.5 | g/kg ( = 500 ppm) |
| Decomposition efficiency (based on the flue gas upstream from the scrubber) | 0.999999 | % |
| which is equivalent to an undecomposed residual quantity of | 0.5 | µg/kg |
| Elimination efficiency (related to flue gas downstream from the scrubber) | 0.9999999% | |
| Emission downstream from the scrubber (scrubber efficiency 90%) | 0.05 | µg/kg |

That is to say, an emission totalling 0.5 microgram TCDD is to be expected from the incineration of 10 kg. In comparison the emission of 2,3,7,8-TCDD from a municipal refuse incinerator (MRI) is about 15 micrograms per hour according to the report of the Federal Office of Environmental Protection (Ref. [1]). However, account must also be taken on the emission of other polychlorinated dioxins and furans which, according to the same report, comes to about 20,000 micrograms per hour. Not all TCDDs and TCDFs are equally toxic, however. The total emission, assessed in terms of differences in toxicity, is equivalent in the case of an MRI to an emission of about 1,000 micrograms 2,3,7,8-TCDD per hour (TCDD equivalent$^{-}$).

The question of health hazards due to emissions of polychlorinated dioxins and furans has, on the other hand, been closely studied in connection with MRIs. In the case of the MRI investigated, it could be categorically stated that these emissions did not constitute any health hazard (Ref. [1]).

This statement continues to be valid. It was taken as a basis in assessing the risk arising from test incinerations of TCDD. The committee of experts therefore reached the conclusion that the combustion of 10 kg in batches of 1 kg could be authorized without any hazard to man or the environment.

## 8.2 Objective and execution

On 27 November 1984 two lots of 5 kg of dioxin-containing reaction residues with a TCDD content totalling 2 to 5 g were burned in two tests separated in time (cf. Appendix A8). The purpose was to ascertain,

- whether the combustion efficiency determined for tri-CDF is also attained in the incineration of TCDD-containing material and
- whether certain organic substances also present in the residues have an adverse effect on combustion efficiency or generate undesirable recombination products.

---

[1] At that time (before the repackaging) no analytical results concerning the average TCDD concentration in the residues were available (see Chap. 2.1).

In the test incineration with additional oxygen it was to be ascertained whether the combustion process could be significantly improved.

The course of combustion was additionally monitored by means of the KISA. The test incineration was to be shut down if the TCDD concentration in the flue gas downstream from the scrubber should exceed 500 ng/m³.

All water that might come into contact with contaminated material or the flue gases and also the slag was collected and retained until a decision had been made as to disposal.

## 8.3 Results

No TCDD could be detected in the flue gas either upstream or downstream from the scrubber. The good results obtained using the KISA were confirmed by the standard analytical method. Negative results were also obtained for the waste-water and slag.

The detection limits were:

| | |
|---|---|
| Flue gas upstream from scrubber | 1 ng/m³ (dry) |
| Flue gas downstream from scrubber | 2 ng/m³ (dry) |
| Water | 1 ng/litre (water from scrubber and slag bath) |
| Slag | 10 ng/kg (slag homogenized and milled) |

In the light of these findings the waste-waters were discharged via the chemical sewerage system to the industrial water purification plant and the slag was dumped at a controlled Swiss disposal site.

Additional oxygen had no effect on the decomposition efficiency and consequently extra oxygen was dispensed with in subsequent incinerations.

The results confirmed that TCDD is decomposed with high efficiency and that neither dioxin nor other problematic reaction products are formed from the other chlorine-containing organic substances.

# 8 Appendix to Chapter 8

## Appendix A8: Details concerning the test incineration with dioxin-containing wastes

### 27.11.84: Two incinerations

| | |
|---|---|
| Objective | 1. To ascertain combustion behaviour<br>2. To determine the residual oxygen concentration<br>3. To test the analytical apparatus and methods |
| Quantity | 2 × 6 kg of material for incineration, subdivided into 2 × 5 batches of 1.2 kg plus 15 kg of sand per batch |
| Composition | 10 kg dioxin-containing material from Seveso plus 2 kg PEG 1500 |
| Charging interval | 6 minutes |
| Duration | 2 × 30 minutes |
| Extra oxygen | *1st incineration:* with extra oxygen in the combustion air (approx. 70 litres/second)<br>*2nd incineration:* without extra oxygen |
| Temperature | *1st incineration:* rotary kiln 1520 °C (Tm), hold-up chamber 1130 °C (Tw)<br>*2nd incineration:* rotary kiln 1520 °C (Tm), hold-up chamber 1130 °C (Tw) |
| Analytical method | Analyses of the flue gases upstream and downstream from the scrubber for TCDD and other compounds, analysis of the scrubber water and the slag for TCDD. |
| Result | No TCDD could be detected in the flue gas either upstream or downstream from the scrubber. The good results obtained with the KISA were confirmed by the standard analysis method. Results were also negative for the waste-water and slag. Decomposition efficiency was not improved by extra oxygen. |

# 9 Second test incineration with dioxin-containing wastes

## 9.1 Risk assessment

In the first test incineration of 27 November 1984 no TCDD could be detected in either the flue gas or the scrubber water.

On the well-founded assumption that a similar combustion efficiency can be obtained with 2.5 kg material (excl. PEG cf. A9/composition) as with 1 kg batches and that the TCDD concentration in the flue gas downstream from the scrubber is less than 1 ng/m$^3$, the following emission values were estimated for this test:

| | |
|---|---|
| Test duration | 12 hours |
| Total flue-gas volume | 120,000 m$^3$ |
| Total TCDD emission | less than 120 $\mu$g |

The estimated worst-case emission of 2,3,7,8-TCDD is, at less than 10 micrograms per hour, smaller than that of a municipal refuse incinerator.

A test incineration with TCDD-containing material of 12 hours' duration, equivalent to a maximum of 360 kg material, was therefore deemed to be justified and without hazard for the population.

The continual improvement in the analytical methods enabled lower detection limits for TCDD to be achieved and also stricter shut-down criteria to be fixed.

In addition, the use of KISA made a rapid intervention possible in the event of accidents. The committee of experts fixed a TCDD concentration of more than 20 ng/m$^3$ in the flue gas downstream from the scrubber as a shut-down criterion. It was not necessary to assess the risk for the other refuse since waste-water and slag were collected without residue.

## 9.2 Objective and execution

The second test incineration (cf. Appendix A9) of dioxin-containing waste performed on 19 March 1985 was intended to confirm the good results obtained during the incineration on 27 November 1984. It was also considered appropriate to increase the batch weight from 1 to 2.5 kg (not counting the PEG) as was done with the tri-CDF batches (see 7.3), since this would substantially reduce the duration of the main incineration.

At the same time it had to be shown that

- flue-gas sampling over a lengthy period of time could be carried out without trouble, and
- that a high combustion efficiency could be achieved with the increased batch weight.

The waste-water and the slag were collected and kept until a decision was made concerning disposal.

## 9.3 Results

Combustion proceeded throughout without trouble. The larger batches gave no problems.

TCDD could not be detected in the flue gases upstream and downstream from the scrubber either with the *KISA* or the *standard analytical method.* As in the first test incineration with dioxin-containing reaction material neither the waste-waters nor the slag contained detectable quantities of TCDD. Nor could any problematic recombination products be detected.

The detection limits were:

| | |
|---|---|
| Flue gas (up- and downstream from scrubber) | 0.1 ng/m$^3$ (dry) |
| Water | 1 ng/l |
| Slag | 5 ng/l |
| Ash from waste-heat boiler | 10 ng/kg |

As in the previous test incineration the waste-waters (about 35 $m^3$) were discharged via the chemical sewerage system to the industrial water treatment plant, the slag (3.75 tonnes) was deposited at a controlled Swiss landfill. In the light of these good results the incineration of the bulk of the TCDD-contaminated material from ICMESA could be considered.

# 9 Appendix to Chapter 9

| | |
|---|---|
| **Appendix A9:** | **Details concerning the second test incineration of dioxin-containing wastes** |
| | **19.03.85: Incineration in three phases** |
| *Objective* | 1. To confirm the results of the incineration on 27.11.84<br>2. To determine the combustion behaviour of the larger batches<br>3. To test the standard analytical method and the KISA |
| | *First phase* |
| Quantity | 14.4 kg subdivided into 12 batches of 1.2 kg each<br>(1 kg Seveso material; 0.2 kg PEG) plus 15 kg of sand per batch |
| Composition | 12 kg of dioxin-containing material from Seveso plus 2.4 kg PEG 1500 |
| Charging interval | 5 minutes |
| Duration | 1 hour |
| | *Second phase* |
| Quantity | 396 kg |
| Composition | 330 kg of dioxin-containing material from Seveso plus 66 kg PEG 1500 in 3 kg batches<br>132 batches of 3 kg (2.5 kg Seveso material; 0.5 PEG)<br>Quantity of sand per batch: 15 kg |
| Charging interval | 5 minutes |
| Duration | 11 hours |
| | *Third phase:* |
| Quantity | 20 kg |
| Composition | Tools contaminated with TCDD, 4 batches of 5 kg |
| Charging interval | 5 minutes |
| Duration | 20 minutes |
| *Temperature* | In all 3 phases:<br>rotary kiln 1540 °C (Tm), hold-up chamber 1150 °C (Tw). |
| *Analytical method* | In all three phases: analysis of flue gases upstream and downstream from the scrubber for TCDD and other compounds, analysis of the scrubber water and the slag for TCDD. |
| *Result* | No TCDD could be detected in the flue gases upstream or downstream from the scrubber either with the *KISA* or the *standard analytical method.* As in the first test incineration with dioxin-containing material, no TCDD could be detected in either the waste-waters or the slag. |

# 10 Main incineration

## 10.1 Risk assessment

The results of the second test incineration with dioxin-containing material warranted the assumption that, given the same decomposition efficiency, the TCDD concentration in the flue gas would be less than 0.1 ng/m$^3$.

The following values were estimated for the total duration of the main incineration operation:

| | |
|---|---|
| Duration | 100 hours |
| Total volume of flue gas | 1,000,000 m$^3$ |
| Total emission of TCDD | less than 100 µg |

This estimate held good for the remaining quantity of reaction residues from the 42 drums weighing about 2.2 tonnes and containing a total of approximately 600 grams of TCDD.

The estimated worst-case emission of TCDD should be less than 1 microgram per hour. The estimate of an emission smaller by a factor of ten than that estimated for the second test incineration is justified by precisely the results of this test incineration.

In the light of these findings it was deemed safe to proceed with the main incineration of the remaining reaction residues. There would be no hazard for the population, the personnel or the environment if the combustion conditions observed under the strictest control during the test incineration of 19 March 1985 were maintained.

## 10.2 Objective and execution

It was the purpose of the main incineration to combust all that remained of the approximately 2.2 tonnes of highly contaminated residues. This was done during the week from Monday 17 to Friday 21 June 1985, taking a total of 108 hours to complete. According to the details given in Appendix A10 the majority of the residues were made up into 2.5 kg batches. The incineration was monitored by the KISA process. It was decided that the operation should be *shut down* if any of the following conditions arose:

In the incinerator:

- technical failures in the plant;
- abnormal conditions in the furnace interior (monitored visually by TV);
- persistence of any of the three following conditions for more than 3 minutes ( = charging interval):
  - temperature below 1100 °C in the hold-up chamber (control room reading);
  - oxygen content in the flue gas under 7%;
  - carbon monoxide content in the flue gas more than 50 ppm.

With regard to the KISA:
- TCDD content in flue gas downstream from the scrubber more than 20 ng/m$^3$;
- KISA failure.

With regard to the standard analytical method:
- simultaneous failure of the sampling equipment of Ciba-Geigy and EMPA.

Slag, ash and waste-water were retained and, like the flue-gas samples downstream from the scrubber, examined for TCDD and other compounds.

## 10.3 Results

At no time during the entire incineration did any faults develop in the furnace. The operation was not shut down as a result of any of the foregoing conditions. In terms of combustion the main incineration proceeded according to plan and without problems; the temperature in the hold-up chamber averaged 1140 °C (Tw), corresponding to 1530 °C (Tm) in the rotary furnace.

No TCDD could be detected in the *flue gas downstream from the scrubber* as measured by the KISA at two-hourly intervals (detection limit 0.05 to 0.2 ng/m$^3$). This finding was subsequently confirmed by the standard analysis of the flue-gas samples downstream from the scrubber. Furthermore, no other PCDDs or PCDFs could be detected.

The *water from the scrubber system* (about 185 m$^3$) was collected in four railway tank waggons. With a detection limit of 0.5 to 0.6 ng per litre, no TCDD could be detected in four of the tank waggons. One waggon contained 5 ng TCDD per litre and 3 micrograms 2,4,5-trichlorophenol per litre as well as traces of thermally-formed substances such as occur in municipal and industrial incinerating plants.

The *water from the slag basin* (about 7 m$^3$) was collected separately. It contained 1245 ng TCDD per litre and 3.8 mg 2,4,5-trichlorophenol per litre and therefore had to be treated. The TCDD (total 9 milligrams) was entirely adsorbed on the sedimented fine particulate matter.

The slag accumulated during the main incineration (about 30 tonnes) consisted primarily of silicates. It contained portions of metal originating from the combustion of an inner drum that had been cut up into small pieces. The slag was collected in skips; it contained traces of TCDD.

Six skips filled with 25.4 tonnes of slag contained 0.01 to 3.6 mg TCDD per tonne of slag, an average of less than 1 mg/t. The total quantity of TCDD was approximately 30 mg. One skip with 4.7 tonnes of slag had a TCDD content of 32.0 to 46.0 mg/t or a total quantity of 150–220 mg.

The TCDD content in the slag of the main incineration suggests that, during the combustion of the approximately 1,200 batches, portions of the slag were contaminated by undecomposed and probably only weakly heated starting material from certain batches. However, as no TCDD was detected in the flue gas and the slag was collected in skips, a possible hazard to the population and environment was precluded at every point of time.

### 10.4 Disposal of the waste-waters

The *water from the scrubber system* (185 m$^3$) was discharged to the industrial water treatment plant via the chemical sewerage system.

The *water from the slag basin* (7 m$^3$) was filtered via a filter containing activated charcoal. After repeated analysis (TCDD content 0.17 ng/litre) the filtrate was discharged to the industrial water treatment plant. The filtration residues containing traces of TCDD were burned in the SRI (cf. A10.2) along with the auxiliary equipment.

### 10.5 Disposal of the slag

Incineration of the approximately 2 tonnes of reaction residues from Seveso and approximately 0.2 tonnes of material from Givaudan S.A. in Dübendorf produced a total of 30.15 tonnes of slag. The relatively large amount of slag compared with the quantity of residues burned was due to the sand it had been necessary to add. Of the total amount of slag accumulated, 25.4 tonnes contained about 30 mg TCDD and another 4.75 tonnes 150 to 220 mg TCDD.

The following points had to be considered in order to ensure environmental safety during disposal.

Two methods were considered in principle: depositing at a landfill or a second passage through the incinerator.

In a municipal refuse incinerator (MRI) with a throughput of about 180,000 t/year some 60,000 t of slag is produced containing about 500 mg TCDD, and 6,000 t of filter dust containing about 1,000 mg TCDD. Every year about 600,000 t of slag and

60,000 t of filter dust is dumped at refusal disposal sites or used for road-making. In comparison the approximately 30 mg TCDD in the 25.4 t of slag obtained from the main incineration is to be deemed insignificant.

Wash-out tests with comminuted slag showed that, if water was used as a solvent, the TCDD concentration lay roughly in the solubility range of TCDD. Unlike the filter dust from an MRI, the HWI slag is in lumps. A large part of the dioxin residues it contains is enclosed in vitrified material. In comparison, filter dust from an MRI contains more soluble components.

Quantitative comparisons with MRIs and the wash-out tests suggested that deposition of all slag in a Class III disposal site could be accomplished without hazard to the groundwater and environment.

The committee of experts decided:

- to release the 25.4 t of less contaminated slag from the main incineration containing approximately 30 mg TCDD for deposition at a landfill;
- to reprocess the 4.7 t of slag containing 150–220 mg TCDD in the HWI.

In the slag obtained from the second passage through the furnace (about 5 t) a total of 0.08 mg (concentration 0.016 mg/t) was still detected.

This slag was deposited at the Elbisgraben landfill (Canton Basel Landschaft). The drainage water from this site is collected and sent to a municipal sewage treatment works.

# 10 Appendixes to Chapter 10

## Appendix A10.1: Details of the main incineration from 17 to 21 June 1985

*Quantities and composition*

(total 1,205 batches)

| Sequence | Designation | Batch size (not including PEG 1500) | Number of batches |
|---|---|---|---|
| 1 | Reaction material with lumps not larger than a hen's egg | 2.5 kg[1]) | 852 |
| 2 | Content of drum No. 42 with lumps not larger than a hen's egg, insofar as reaction material is involved | 2.5 kg[2]) | 47 |
| 3 | Clothes ex Seveso | variable[3]) | 165 |
| 4 | Material from Seveso | max. 5 kg[3]) | 55 |
| 5 | Material from Givaudan with lumps not larger than a hen's egg, insofar as reaction material is involved | 2.5 kg[2]) | 51 |
| 6 | Leca¬ from drum No. 42 | 2.5 kg[4]) | 30 |
| 7 | Inner drum No. 4 cut up | approx. 8 kg[5]) | 4 |
| 8 | Absorbent paper from slag treatment | – | 1 |

1) Each batch contains in addition 0.5 kg PEG 1500
2) In the case of metallic parts, earth, and the like the weight ranged up to a maximum of 5 kg. No PEG 1500 had to be added provided no reaction material was involved. In addition, the dimensions specified in 3) were not to be exceeded.
3) The dimensions of 500 mm × 300 mm × 300 mm were not to be exceeded. No adddition of PEG 1500 was required.
4) The Leca from the other drums had already been disposed of under the supervision of the Cantonal Chemist via the HWI.
5) Tests to ascertain whether the cleaned and cut-up inner drums could be disposed of via the HWI of Ciba-Geigy were successful.

*Packaging*

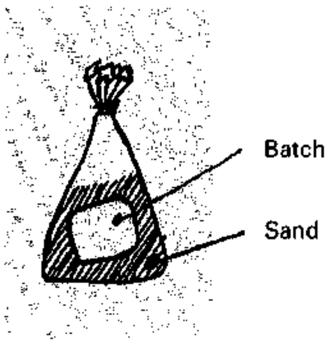
Each batch was packaged in a total of 3 bags of 0.1 mm thick polyethylene film:

- a double bag as the primary package
- 1st protective bag
- 2nd protective bag.

Before they were heat-sealed the air was removed from bags as far as possible.

*Charging interval*

Charging took place at intervals of 5 minutes. Each batch was then placed, as shown in the sketch, in another bag filled with about 15 kg of sand.



*Duration*

After the plant had been heated up for 5 hours, the incineration took 103 hours. Charging was suspended for 8 hours on one occasion to change the scrubber water. The incineration itself took 95 hours.

*Temperature*

The temperatures averaged 1140°C (Tw) in the hold-up chamber, corresponding to 1530°C (Tm) in the rotary furnace.

*Flue-gas analysis*

No TCDD was detected in any of the samples.

The KISA provided analysis values for the TCDD content in the flue gas downstream from the scrubber. Including the 3 blank tests, a total of 54 analyses was made with the KISA. In the blank tests and in most (45) of the analyses, the detection limit stood at 0.1 $ng/m^3$. On five occasions the detection limit was 0.05 and once 0.2 $ng/m^3$.

TCDD determinations using the standard analytical method were made during the main incineration only downstream from the scrubber. The detection limit at 0.2 $ng/m^3$ was rather higher than during the test incinerations because during the much longer sampling period the samples were heavily contaminated.

*Residual materials*

The incineration produced a total of:
30,150 kg slag
60 kg (approx.) ash from the waste-heat boiler
192,340 kg waste-water, comprising
    185,090 kg from the scrubber and
    7,250 kg from the slag basin.

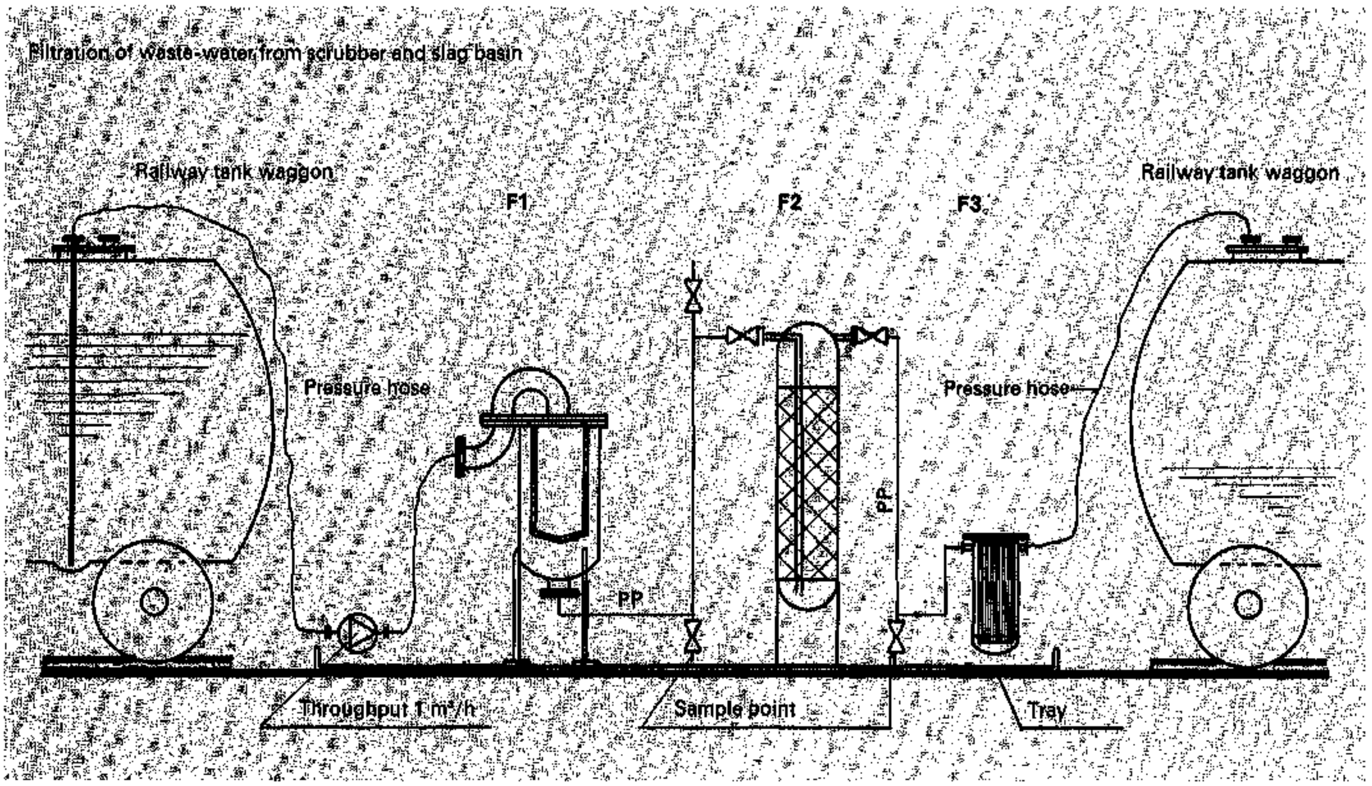
**Appendix A10.2:**

### Disposal of the waste-water from the slag basin

The water from the slag basin, totalling 7,250 l, was treated in a small-capacity filter plant. The operation had to be performed twice because, the first time, when about 45% of the supernatant water was being drawn off, too much of the sedimented fine particulate matter was taken – as a result of turbulence due to moving the tank waggon. The filtration residues, along with the auxiliary equipment, were incinerated in the HWI. On completion of filtration, the filtrate collected in a railway tank waggon was agitated by bubbling through nitrogen and two samples of 2.5 litres each were sent for analysis to the EMPA. A concentration of 0.17 ng TCDD per litre was detected, equivalent to a filtration efficiency of 99.987%. This level was well below the permitted maximum concentration (TCDD concentration max. 10 ng/l or a total content of max. 100 micrograms TCDD), and consequently, with the agreement of the Basle Office for Water Pollution Prevention, the filtrate was discharged via the chemical sewerage system into the industrial water treatment plant. The railway tank waggons were cleaned with a high-pressure water jet (Atümat). Wipe tests in the interior of the tank failed to detect any TCDD at a detection limit of 0.15 $ng/m^2$. The filter plant was subsequently disposed of in the HWI.

*Schematic: Filtration of waste-water*

| Filters: | F1<br>GAF-bag filter | F2<br>AK Filter | F3<br>liquid filter |
|---|---|---|---|
| Type: | RB-1 | AKS 1′ | FFU-Q-30 |
| Material: | PP | Polyester | PP |
| Filter medium: | PP 25 µm (10 µm, 5 µm) | Activated charcoal 0.4 to 1.5 mm (16 l) | PP roll cartridge 5 µm (3 µm, 1 µm) |



*Technical data on 1st filtration*

| Filter type | | Consumption | Number of filter changes |
|---|---|---|---|
| RB-1 (GAF) | 25 µm (pore size) | 10 units | 20 |
| RB-1 (GAF) | 10 µm (pore size) | 10 units | |
| AKS 1 | 0.4 mm to 1.5 mm (particle size) | | |
| FFU-Q-30 | 5 µm (pore size) | 10 units | 10 |

- Mean throughput: 10 litres/min.
  (between 0 and max. 25 litres/min. depending on degree of waste-water pollution and the filters)
- Filtered quantity of waste-water: approx. 4,000 l
  (of a total 7,250 l, 3,250 l was drawn off unfiltered)
- Mean filtration time between filter changes: 20 min. (≙ 200 l)
- Number of interruptions due to filter changes: 20 (each of approx. 25 min.)

*Technical data on 2nd filtration*

| Filter type | | Consumption | Number of filter changes |
|---|---|---|---|
| RB-1 (GAF) | 25 µm (pore size) | 7 units | 25 |
| RB-1 (GAF) | 10 µm (pore size) | 18 units | |
| AKS*) | 0.4 mm to 1.5 mm (particle size) | – | – |
| FFU-Q-30 | 3 µm (pore size) | 10 units | 35 |
| FFU-Q-30 | 1 µm (pore size) | 25 units | |

*) New filter unit, the filter used in the first operation was incinerated.

- Mean throughput 12 litres/min.
- Filtered quantity of waste-water 7,250 l
- Mean filtration time between filter changes 18 min. ( ≙ 210 l)
- Number of interruptions due to filter changes 35 (each of approx. 20 min.)

The used filters were packed in plastic bags as the work proceeded. A total of 107 packages was filled and incinerated in the HWI.

**Appendix A10.3:**

**Disposal of the slag**

During the main incineration operation a total of 30.15 tonnes of slag (including ash from the waste-heat boiler) was produced and collected in 7 skips. Mixed samples from each skip were tested for TCDD and TCP$^{\rightarrow}$.

Six skips holding a total of 25.4 tonnes of slag had a TCDD content of less than 0.01 to 3.6 mg of TCDD per tonne (total content approximately 30 mg TCDD) and a TCP content of less than 1 to approximately 43 mg/t. No TCDD could be found in the aqueous phase on random wash-out tests. This weakly contaminated slag could be deposited directly at the Elbisgraben landfill (Class III site) without additional treatment along with the 11.32 tonnes of slag from the incineration of the auxiliary materials (cf. 12.4).

TCDD content of the slag from the main incineration

| Skip No. | Quantity of slag t | TCDD content mg/t |
|---|---|---|
| 1 | 4.85 | 0.01– 0.8 |
| 2 | 5.0 | 0.03– 1.5 |
| 3 | 5.35 | 1.3 – 2.6 |
| 4 | 3.85 | 0.1 – 0.4 |
| 5 | 4.25 | 0.1 – 0.3 |
| 7 | 2.1 | 2.4 – 3.6 |
| 6 | 4.75 | 32.0 –46.0 |
| For comparison:<br>filter dust from a municipal refuse incinerator | | 0.1 – 5 |

Skip No. 6 with a total of 4.75 tonnes of slag, on the other hand, had a mean TCDD content of 32 to 46 mg/t. No polychlorinated PCDDs and no PCDFs could be detected in this slag, but it did contain

- 2,4,5-trichlorophenol (2 g/t),
- mono-, di- and trichlorodibenzo-p-dioxin,
- 1,3,7,8-TCDD (2.3% of the quantity of 2,3,7,8-TCDD),

which had also been detected in the original reaction residues. Their presence suggests that part of the slag had apparently been contaminated by inadequately decomposed and probably only weakly heated starting material from certain batches. In the wash-out tests 5.6 ng TCDD per litre was detected in the aqueous phase. This slag, containing a total of between 150 and 220 mg TCDD, was again treated in the HWI furnace.

The brittle, vitreous slag was broken up in the skip into pieces no bigger than fist-size. 20 to 25 kg comminuted slag at a time was placed in a double polyethylene bag. One batch was fed every 2 minutes into the furnace heated to over 1200°C (rotary furnace Tm = 1500°C, hold-up chamber Tw = 1110°C). Every 15 minutes a 1 litre sample of the newly accumulated slag was comminuted in a hammer mill to a grain size of 4 mm. All the milled samples were combined in a Loedige mixer. This mixed sample was found to contain 0.016 mg TCDD/t and no TCP (detection limit 100 mg/t). The 5 tonnes of slag accruing from this operation was deposited at the Elbisgraben landfill. The amount of slag increased because some of the protective slag lining of the furnace is inevitably removed as well. In the light of the small quantity of TCDD and the experience obtained with the main incineration neither the flue gases nor the waste-waters were sampled or analysed.

The personnel comminuting the slag and pouring it into bags was protected by a disposable overall, a light dust-mask, rubber gloves and goggles.

## Appendix A10.4 Wash-out tests

The wash-out of TCDD from the slag with water was tested in the laboratory to assess whether the main incineration slag could be disposed of at a landfill. The method based on DIN 38414 (Ref. [4]) is used by EMPA to determine the leaching behaviour of materials intended for deposition.

*Method*

100 g slag was taken from a weakly contaminated (0.4 microgram TCDD per kg) sample and 100 g from a more severely contaminated (32 micrograms per kg) sample were vigorously shaken for 24 hours with 1 litre of deionized water or toluene-saturated water, then filtered and processed in the manner indicated in schematic A6.3 and analysed. A sample of the residue (deemed fit for deposition) from the electrostatic filter of a municipal refuse incinerator was treated in precisely the same way for comparison with the samples of slag.

*Result*

No TCDD could be detected in the weakly contaminated sample or in the electrostatic filter ash either in the deionized or toluene-saturated water.

On the other hand, 5.6 ng of TCDD per litre could be detected in the deionized wash-out water from the more severely contaminated slag sample. The corresponding value for toluene-saturated water was 2.1 ng of TCDD per litre. In these samples, therefore, between 0.1 and 0.2% of the TCDD they contained was eluted in the wash-out test.

# 11 Dismantling of the repackaging plant

## 11.1 The problem

At the end of the repackaging operation all the technical equipment and aids which were actually or potentially contaminated had to be disposed of safely and without hazard to the environment. Incineration in the Ciba-Geigy HWI was again chosen as the safest method of disposal. This implied that the parts to be disposed of had – like the reaction residues – to be reduced to a form suitable for feeding into the furnace.

The specific problem raised by this operation was the order in which the dismantling was to proceed. On the one hand, plant serving to protect the personnel and environment had to be left standing long enough for the possibility of any hazard to the personnel or the environment to be eliminated. On the other hand, it was precisely this plant which, by reason of its function, had been exposed to heavy contamination with TCDD and might, on being dismantled and broken into pieces, again cause a certain amount of contamination.

Refuse categories had to be established for the preparation and disposal of the parts of the dismantled infrastructure. On grounds of safety the only distinction made was between CONTAMINATED and NON-CONTAMINATED without regard to the specific possibilities available for decontaminating only weakly contaminated parts.

The following disposal methods were chosen for these two categories:

*Contaminated refuse:*
- disposal in the HWI

*Non-contaminated refuse:*
- combustible: Roche boiler house
- non-combustible: dumping or scrap metal salvage

The cleaning operations performed while the work of dismantling was in progress did not, however, affect the mode of disposal; their sole purpose was to protect the personnel and to ensure that the premises could be restored to their original use.

## 11.2 Risk assessment

The hazards to those engaged in the demolition of the infrastructure – all of whom had been involved in the repackaging operation – were deemed to be relatively slight compared with the demolition work at ICMESA or the repackaging operation itself.

Thus, in the reactor room of the TCP plant at ICMESA a ground contamination with TCDD of 410,000 ng/m$^2$ was determined, compared with a maximum of about 20,000 ng/m$^2$ in the repackaging room in Basle. Moreover, the physical stress and risk of a defect in the protective equipment due to mechanical stress were substantially less. As long as the progress made with dismantling permitted, work was carried out in the air-supply protective suits (cf. Chap. 3.3) in order to protect the personnel. Even after the protective clothing shower had been dismantled this clothing could be taken off without difficulty and discarded for incineration.

Wipe tests were continually performed in rooms C, G, H and L (cf. Fig. 1, p. 28) so as to monitor the degree of contamination during dismantling. The upper limit set for TCDD was 10 ng/m$^2$ (limit in Lombardy for continually occupied rooms).

*Contamination measurements*

Measurements made during dismantling work yielded the following TCDD-contamination levels:

| | |
|---|---|
| Repackaging room E | 6,000 to 20,000 ng/m$^2$ |
| Protective clothing shower F | 1,500 ng/m$^2$ |
| Material lock K | 11,000 ng/m$^2$ |
| Entrance lock D | 270 ng/m$^2$ |

Accordingly the work was done in the order of diminishing TCDD concentrations.

### 11.3 Execution

One condition imposed during the construction of the repackaging plant was that, on completion of the operation, it should be possible for the premises to be restored to their original purpose. For this reason rooms D, E, F, G and K were lined throughout with protective sheeting of high-pressure polyethylene and PVC flooring material.

*Order of dismantling*

a) Dismantling and breaking up of internal equipment, tools and aids which were not fixed or no longer required;
b) First cleaning of the contaminated rooms and technical installations;
c) Dismantling of the fixed technical equipment and installations;
d) Dismantling and chopping up of wooden constructions (doors, walls etc.);
e) Cleaning with trichloroethylene and then removal of the protective sheeting from ceilings, walls and floors;
f) Other dismantling work;
g) Dismantling of other non-contaminated material.

Simply after cleaning with trichloroethylene (step e) wipe tests revealed the following residual TCDD contaminations, which are generally regarded as safe:

| | |
|---|---|
| – Repackaging room, concrete wall | 4 ng/m$^2$ |
| – Material lock K, wooden wall | 8.4 ng/m$^2$ |
| – Protective clothing shower, concrete floor | 2.4 ng/m$^2$ |
| – Changing room G, wooden wall | 1.5 ng/m$^2$ |
| – Material lock L, wooden wall | 0.6 ng/m$^2$ |

### 11.4 Release of premises

After restoration to the original condition and the final cleaning operation, the TCDD-levels in all rooms were clearly below the limit of 10 ng/m$^2$ used in Lombardy for constantly occupied rooms (below the detection limit from 0.3 ng/m$^2$ to a maximum of 5.3 ng/m$^2$).

The premises were released for normal use in agreement with the Cantonal Laboratory of Basle-City and the Civil Defence Office of the Canton of Basle-City.

# 11 Appendixes to Chapter 11

**Appendix A11.1:** **Details of the dismantling procedure** (as per chapter 11.3)

*a) Dismantling and breaking up for movable items of equipment*
To begin with, all the unneeded movable items of equipment from the contaminated rooms were broken to pieces and packaged in room E.

*b) First cleaning of the contaminated rooms*
Thereafter all the rooms were thoroughly cleaned, starting with the repackaging room. Walls, ceilings, and floors were washed down with water to which detergents had been added and then dried. The washing water was treated in the in-plant water purifying plant (cf. schematic, Appendix A3.2).

*c) Dismantling of the fixed technical installations*
The next step was to dismantle the filter elements from the exhaust air-filter plant; these were broken up and replaced by a high-efficiency particulate filter (S3 with an upstream filter mat). TCDD-emissions were thus prevented until the operation was terminated. Subsequently all energy installations (except the respiratory air and electricity supply) and the waste-water purification plant were dismantled. Activated charcoal, ion-exchange resins and all parts of the dismantled plant were reduced to a form suitable for the furnace and packaged. The packages were then heat-sealed in two other protective envelopes. These packs were then cleaned with moist paper cloths. Apparatus were then taken apart as far as possible and the individual components broken up where necessary. Compass saws and shears were mainly used to cut up equipment and the inner drums so as to avoid generating dust.

*d) Dismantling and breaking up of wooden constructions*
All wooden doors with frames giving access from the repackaging room E to the adjacent rooms were removed, cut up small and packaged.

*e) Cleaning and dismantling of the room linings*
The linings of the rooms were rubbed down with cloths moistened with trichloroethylene. In rooms D, F, G and K the PVC-floorings were removed and packaged in the repackaging rooms. Thus more or less all the contaminated parts inside the repackaging plant were either removed or cleaned twice. The linings could then also be removed from the walls, ceilings and floor of the repackaging room itself. The floor of the repackaging room was then re-covered with new plastic sheeting in view of the further cutting up and packaging operations to be done there.

*f) Additional dismantling work*
The order in which other work was performed was:

- Installation of an emergency lighting system inside the lock system;
- Dismantling, cutting up and packaging of the lighting fixtures;
- Elimination of the substitute exhaust-air plant and shut-down of air-inlet fans;
- Thorough cleaning of the repackaging room.

Up to this point all work was performed in full protective clothing. For subsequent work 'Tyvek' light protective clothing with 'Colonia' dust-mask was worn:

- Dismantling and packaging of the air distribution network;
- Removal of PVC-flooring in the material lock L and cleaning of room;
- Packaging of heat-sealing equipment and other materials ready for the furnace.

With these measures the contaminated portion of the repackaging plant was demolished and made ready for final destruction.

*g) Dismantling and disposal of the non-contaminated materials*
In conclusion the non-contaminated items such as wooden walls and doors, air-inlet plants, personnel showers etc. were dismantled and disposed of in the following manner:

| | |
|---|---|
| – Combustible refuse (approx. 9 $m^3$) | in Roche boiler house |
| – Metal parts (approx. 400 kg) | scrap-metal salvage |
| – Builder's rubbish (approx. 2 $m^3$) | to landfill |

The 42 outer drums were released by the committee of experts for melting down in a steelworks. Although they could have been melted down without any hazard, no permit could be obtained. The committee of experts therefore recommended deposition at the Elbisgraben landfill.

## Appendix A11.2: Figures relating to the disposal of the infrastructure

*Labour requirements*
It took a team of 5 men 10 working weeks to demolish the infrastructure, which is equivalent to approximately 2000 man hours.

*Protective outfits*
The equipment used consisted of:

- 185 full protective suits of the 'Mururoa' type
- 148 protective suits of the 'Tyvek' type

*Packages*
As in the case of the reaction residues, the refuse was packed in plastic bags, packages containing metal parts being placed additionally in cardboard boxes. The maximum weight per package was 5 kg.

The following number of packages was made ready for incineration or melting down:

| | |
|---|---|
| – Metal parts, inner drums | 98 |
| – Infrastructure | 573 |
| – Protective outfits | 473 |
| – Sample material | 19 |
| | 1163 |

# 12 Disposal of auxiliary material

### 12.1 Risk assessment

No TCDD could be detected in the flue gas during the main incineration of dioxin-containing material (approximately 600 g of TCDD in approximately 2.2 tonnes of reaction residues).

In the light of this result, permission could be granted for the incineration of auxiliary material (auxiliary equipment, laboratory instruments and aids, samples and packages, which contained a maximum of 0.02 g TCDD in approximately 10 tonnes of material) without any hazard to the population, personnel or environment.

Additional TCDD-analyses in the flue gas and analysis of the slag and waste-waters could be dispensed with because of the very small TCDD-content in the auxiliary material.

### 12.2 Objective and execution

During this incineration operation all the auxiliary materials accumulating in the individual firms (Ciba-Geigy, Roche and Givaudan) and laboratories (EMPA and FAW), on the one hand, and the filtration residues from the disposal of the slag-basin water (cf. item 10.4), on the other, were to be burned. The operation was carried out from Monday 18 to Thursday 21 November 1985 over a total time of 68.5 hours. The average temperature in the hold-up chamber was 1260°C.

The liquid waste was collected in a pressure vessel and fed from this into the furnace. The solid waste was packaged either in plastic containers (painters' buckets or 30-litre drums), plastic bags or cardboard boxes in lots of two to twenty kilograms (cf. Appendix A12). The suitability of the various packages for feeding into the furnace was tested in trials made in July and November 1984. During the November trial some 2.6 tonnes of non-contaminated Leca clay aggregate (cf. Chap. 2.1) was disposed of in the HWI.

The following conditions were to be observed during the burning of the auxiliary material:

- flue-gas temperature above 1100°C in the hold-up chamber (control room reading);
- oxygen concentration in flue gas above 7%;
- carbon monoxide concentration in the flue gas below 50 ppm.

### 12.3 Results

The operation was carried out according to programme. During the entire combustion period there was no disturbance requiring the incineration to be discontinued.

### 12.4 Disposal of waste-waters and slags

The waste-waters from the scrubbers and the slag basins were discharged via the chemical sewerage system to the industrial water treatment plant.

In addition to the material for incineration approximately 3.5 tonnes of sand had to be fed into the furnace in order to maintain a minimal slag lining. The 11.32 tonnes of slag from this incineration was collected in containers and disposed of along with the slag from the main incineration.

# 12

# Appendix to Chapter 12

## Appendix A12: Details of the incineration of auxiliary material on 18–21 November 1985

*Quantities and Composition*

1,799 packages weighing from 2 to 20 kg (total weight approximately 10,400 kg) were burned.

| Description | Package type | Number of packages |
|---|---|---|
| – Sample materials and laboratory utensils from Givaudan and EMPA/FAW | Painter's buckets | 407 |
| | Plastic bags | 67 |
| – Material from the Roche repackaging plant | Plastic bags | 573 |
| – Protective outfits from the repackaging operation and dismantling | Plastic bags | 473 |
| – Sample materials from Roche | Plastic bags | 19 |
| – Cut up inner drums and other metal parts from the Roche repackaging operation | Cardboard boxes | 98 |
| – Sample materials and laboratory utensils from Ciba-Geigy | 30-litre-drums | 35 |
| – Filtration residues from the disposal of water from slag basins (main incineration) | Plastic bags | 107 |

*Packaging*

Batches (without filtration residues) which were not put into drums or cardboard boxes were always packed in a total of three bags made from 0.1 mm thick polyethylene film:

- double bag as primary package
- 1st protective bag
- 2nd protective bag

Air was removed from the bags as far as possible before heat sealing.

*Charging interval*

Charging took place at intervals of 2 to 2.5 minutes, i.e. 24 to 30 packages were fed to the furnace every hour.

Particularly when 30-litre plastic drums were being burned, a total of approximately 3.5 tonnes of sand was fed into the furnace. This addition of sand also depended on the behaviour of the slag.

*Duration*

After 2 hours' heating up of the plant, incineration of the solid waste took 64 hours and that of the liquid waste 1 hour. In the night of 19 November 1985 charging had to be suspended for approximately 1.5 hours because of a build-up of slag in the hold-up chamber which first had to be removed.

*Temperature*

The temperature in the hold-up chamber (Tw) averaged 1160°C, corresponding to 1550°C in the rotary furnace (Tm).

*Residual materials*

11.32 tonnes of slag accumulated during the incineration. These were not tested for TCDD, since the quantity of TCDD originally contained in the 10.4 tonnes of auxiliary material totalled only 10 mg. It had been shown that the greater part of this TCDD was destroyed under combustion conditions and consequently any residual quantity of TCDD was insignificant compared with the 30 mg in the slag of the main incineration.

# 13 Conclusions

An ad hoc organization comprising representatives of the authorities, science and industry was formed to carry out the project 'incineration of dioxin-containing residues from Seveso'. The organization proved its value in practice, and cooperation was good between all the parties involved.

At the beginning the firms of Hoffmann-La Roche and Ciba-Geigy put forward their plans for the execution of the work in accordance with the allocation of responsibilities agreed upon (Hoffmann-La Roche: storage, repackaging and transport of the waste. Ciba-Geigy: incineration and the preliminary studies this required). These plans were examined and found in order by the committee of experts; they formed a sound basis for all subsequent operations.

The questions that were open at the beginning of the operation (cf. page S2 of the Summary) may be answered as follows:

- The *conditions* to be observed *during incineration* could be laid down in the light of laboratory trials and test incinerations.
- The *methods for sampling, sample processing and analysis* were tried out and improved; they proved their value. The low detection limits and the reproducibility that were attained fulfilled the stipulated conditions.
- A special plant had to be built for *handling and repackaging* the dioxin-containing waste and had to be disposed of at the end. The design of this plant proved to be correct; the repackaging operation proceeded smoothly in spite of the elaborate and complicated work it involved.
- The stepwise testing of the Ciba-Geigy HWI showed that it was suitable for incinerating this dioxin-containing material.

The following conclusions may be drawn from the findings made during the preparation and execution of the incineration operation:

1. It is possible to incinerate organic problematic wastes, particularly those that contain substantial proportions of dioxins and furans as well as their precursors, without hazard to man and his environment.
2. The hazard-free incineration of such problem-raising materials depends on certain preconditions being fulfilled:
   - knowledge of the composition of the wastes,
   - suitability of the plant demonstrated in test incinerations,
   - adherence to certain minimum requirements in continuous operation,
   - monitoring of all emissions and continuous supervision of the plant with adequate measurement and control techniques and the availability of analytical facilities capable of giving quick results
   - the employment of qualified personnel and a high level of technical know-how.
3. A plant equipped for the incineration of such problem-raising wastes must be capable of maintaining high temperatures in continuous operation and ensuring a sufficient residence time of the incinerated material and the flue gases at high temperatures. It must also be equipped with an efficient flue-gas scrubber.
4. The type of material, batch size, charging interval and type of packaging are items of importance for hazard-free operation. In continuously operating plants, charging should also be as continuous as possible.
5. Proof of the suitability of a plant is essential before the authorities may grant a permit for the incineration of wastes representing special hazards to the environment.

# 14 Explanatory notes

## 14.1 References

[1] Swiss Federal Office of Environmental Protection (Publ.): 'Umweltbelastung durch Dioxine und Furane aus kommunalen Kehrichtverbrennungsanlagen' (Environmental impact of dioxins and furans from municipal refuse incinerators), in the series Umweltschutz No. 5, Berne, June 1982.

[2] Verband der Chemischen Industrie e.V. (Publ.): 'Dioxin in der Umwelt' (Dioxin in the environment), in the series Chemie + Fortschritt, No. 3, p. 18/19, Frankfurt/M, 1985.

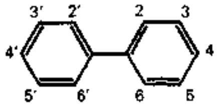
[3] Richtlinien des VDI (Verein Deutscher Ingenieure) (Guidelines of the Association of German Engineers), VDI-Verlag GmbH, Düsseldorf.
VDI 2083: Reinraumtechnik (Clean room technology)
Blatt 3 (Feb. 1982): Messtechnik (Measurement techniques)
VDI 2119: Messung partikelförmiger Niederschläge (Measurement of particulate depositions):
Bestimmung des partikelförmigen Niederschlags mit dem Bergerhoff-Gerät (Determination of particulate deposition with the Bergerhoff apparatus)
VDI 2463: Messen von Massenkonzentrationen (Immissionen)
Basisverfahren für den Vergleich von nicht fraktionierten Verfahren (Determination of mass concentrations [immissions])
Basic process for the comparison of non-fractionated processes)
Blatt 8 (Aug. 1982): Messtechnik.

[4] DIN Deutsches Institut für Normung e.V., Berlin. Beuth Verlag, Berlin, Cologne.
DIN 38414: Deutsche Einheitsverfahren zur Wasser-, Abwasser- und Schlammuntersuchung, Teil 4 (Okt. 1984): Schlamm und Sedimente (German standard method for the examination of water, waste-water and sludge, Part 4 (Oct. 1984): sludge and sediments)

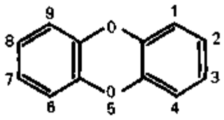
## 14.2 Chemical structural formulae

At the numbered positions chlorine atoms (Cl) can be substituted for the hydrogen atoms of the benzene rings. The number and position of chlorine atoms determine the chemical and toxic properties of each compound.

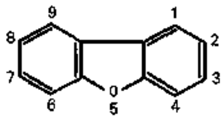
Biphenyls



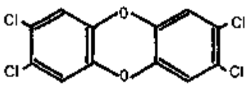
Dibenzodioxins



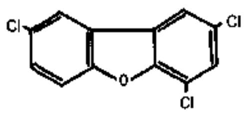
Dibenzofurans



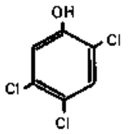
TCDD 2,3,7,8-tetrachlorobenzo-p-dioxin



Tri-CDF 2;4,8-trichlorodibenzofuran



TCP 2,4,5-trichlorophenol



## 14.3 Abbreviations and explanations

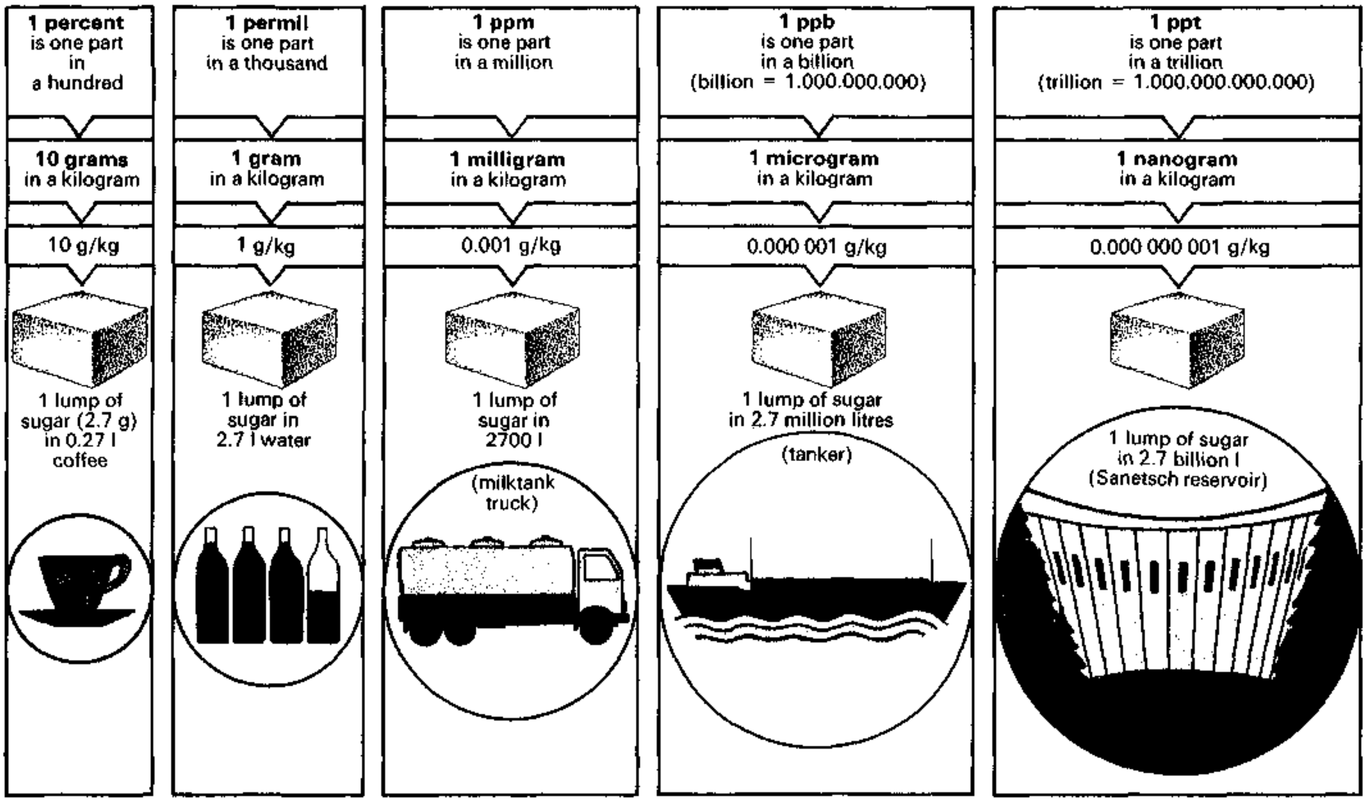
| | |
|---|---|
| *ADR* | Accord européen relatif au transport international des marchandises dangereuses par route (European agreement on the road transport of hazardous goods, 30 Sept. 1957) |
| *Adsorption* | Gases, vapours or dissolved substances which are taken up on the surface of solid particles are bound by adsorption |
| *Aerosol* | Solid (dust, smoke) or liquid (fog) particles in a suspended state |
| *Bergerhoff* | Method for determining dust deposition from the air (see Guideline VDI 2119, [3]). The collecting surface of the 6 Bergerhoff pots set up at each measuring site totals 425 $cm^2$ (see Chap. 6.4). |
| *Biphenyl* | see 14.2, chemical structural formulae |
| $^{13}C$ | Carbon isotope with the mass number 13 |
| $^{37}Cl$ | Chlorine isotope with the mass number 37 |
| *Conditioning* | Treatment intended to obtain specific behaviour in a material (e.g. in combustion) |
| *Confidence interval* | Concept from statistics: The 95% confidence interval means that a value outside the given interval is to be found at the most in 5% of all cases. |
| *Decomposition efficiency* | Ratio of the quantity of a substance burned to the total quantity entering the process |
| *Dibenzodioxin* | see 14.2, chemical structural formulae |
| *Dibenzofuran* | see 14.2, chemical structural formulae |
| *DOP* | Dioctyl phthalate |
| *Elimination efficiency* | Ratio of the quantity of a substance eliminated by combustion in the furnace and by separation in the scrubber to the total quantity of substance entering the process |
| *Emission* | The process of discharging into the atmosphere. Also applied to the material being discharged. |
| *EMPA* | Eidg. Materialprüfungs- und Versuchsanstalt (Swiss Federal Materials Testing and Experimental Station), Dübendorf |
| *Exothermic* | refers to chemical processes which are accompanied by the evolution of heat, e.g. combustion |
| *FAW* | Eidg. Forschungsanstalt für Obst-, Wein- und Gartenbau (Swiss Federal Research Institute for Fruit-Growing, Viticulture and Horticulture), Wädenswil |
| *GC* | Gas chromatograph |
| *GC-MS* | Gas chromatograph combined with mass spectrometer |
| *Herfa-Neurode* | Underground disposal site for special refuse in the caves of a salt mine at Herfa-Neurode, Hessen, FRG |
| *High-volume sampler* | Sampler with a high volumetric throughput for measuring dust suspended in the air and dust deposition according to Guideline VDI 2463, Blatt 8 (Lit. [3]) |
| *HWI* | Hazardous waste incinerator |

| | |
|---|---|
| *ICMESA* | Icmesa S.p.A., Meda, was a subsidiary of Givaudan S.A., Geneva, which is in turn a member of the Hoffmann-La Roche group |
| *KISA* | Kurz-Intervall-Spuren-Analyse (Short-interval trace analysis) (See Chap. 6.1.2) |
| *Leca* | Light expanded clay aggregate |
| *Matrix* | (in this context): base material at the surface of which substances are taken up by adsorption |
| *MS* | Mass spectrometer |
| *NaCl* | Sodium chloride = common salt |
| *NIOSH* | National Institute of Occupational Safety and Health, Cincinnati, Ohio, USA |
| *PCDDs* | Polychlorinated dibenzo-p-dioxins; 2, 3, 7, 8-TCDD is one of 75 different PCDDs |
| *PCDFs* | Polychlorinated dibenzofurans; 2, 4, 8-tri-CDF is one of 135 different PCDFs |
| *PE* | Polyethylene ( = polythene) |
| *PEG* | Polyethylene glycol (PEG 1500: a type of PEG) |
| *ppm* | parts per million (see 14.4, Units of measurement) |
| *Recovery* | Ratio of the recovered quantity to the starting quantity of a substance which was used for spiking. The recovery is a measure of the accuracy of an analysis |
| *SDR* | Verordnung über die Beförderung gefährlicher Güter auf der Strasse (Order concerning the road transport of hazardous goods) of 17 April 1985 |
| *Separation efficiency* | efficiency of pollutant separation in the scrubber or filter (ratio of the quantity separated to the total quantity of pollutant) |
| *Spike* | A small known quantity of an isotope-labelled substance (such as $^{13}C$→ or $^{37}Cl$→) is added to an analytical sample (see recovery→) |
| *Standard analytical method* | Analytical method for assaying TCDD and other PCDDs, as explained in Chapter 6 |
| *TCDD* | 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (see 14.2) |
| *TCDD equivalent* | of a mixture of different PCDDs is the quantity of 2, 3, 7, 8-TCDD which has the same toxic action as this mixture |
| *TCP* | 2, 4, 5-trichlorophenol (see 14.2) |
| *Tri-CDF* | 2, 4, 8-trichlorodibenzofuran (see 14.2) |
| *VDI* | Verein deutscher Ingenieure (Association of German Engineers) |
| *Wipe test* | Sampling method for determining the contamination of surfaces |

### 14.4 Units of measurement used

| | | | |
|---|---|---|---|
| mg | milligram | = $10^{-3}$ g | = 0.001 g |
| µg | microgram | = $10^{-6}$ g | = 0.000 001 g |
| ng | nanogram | = $10^{-9}$ g | = 0.000 000 001 g |
| µm | micrometer | = $10^{-6}$ m | = $\frac{1}{1000}$ mm |
| $m^3$ | cubic metre: in the case of gases this refers to a normal $m^3$ (volume of a gas under normal conditions: 0 °C and 1.013 bar) | | |
| $ng/m^2$ | nanogram per square metre (amount of pollutant per square metre found in the wipe test performed on surfaces) | | |

## Chemistry has different scales of measurement



| | | | | |
|---|---|---|---|---|
| **1 percent** is one part in a hundred | **1 permil** is one part in a thousand | **1 ppm** is one part in a million | **1 ppb** is one part in a billion (billion = 1.000.000.000) | **1 ppt** is one part in a trillion (trillion = 1.000.000.000.000) |
| **10 grams** in a kilogram | **1 gram** in a kilogram | **1 milligram** in a kilogram | **1 microgram** in a kilogram | **1 nanogram** in a kilogram |
| 10 g/kg | 1 g/kg | 0.001 g/kg | 0.000 001 g/kg | 0.000 000 001 g/kg |
| 1 lump of sugar (2.7 g) in 0.27 l coffee | 1 lump of sugar in 2.7 l water | 1 lump of sugar in 2700 l (milktank truck) | 1 lump of sugar in 2.7 million litres (tanker) | 1 lump of sugar in 2.7 billion l (Sanetsch reservoir) |

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